Plenary Lecture
Room Town & Country A - Session PL-MoM

Plenary Lecture
Moderator: Johanna Rosen, Linköping University, Sweden

8:00am **PL-MoM-1 Welcome and Opening Remarks***,*

8:20am **PL-MoM-2 Engineering 2D MXene Surfaces for Functional Films and Coatings***, **Yury Gogotsi (yg36@drexel.edu)**,* Drexel University, USA **INVITED**

MXenes (carbides, nitrides, oxycarbides and carbonitrides of early transition metals) are a very large family of 2D materials. They have a chemical formula of $M_{n+1}X_nT_x$, where M is a transition metal (Ti, Mo, Nb, V, Cr, etc.), X is either carbon and/or nitrogen (n=1, 2, 3 or 4), and T_x represents surface terminations (O, OH, halogens, chalcogens). The large variety of structures and compositions, availability of solid solutions on M and X sites, and control of surface terminations offer a plethora of materials to produce and investigate.[1] Combining their plasmonic properties with ease in aqueous processing, high electronic conductivity (over 20,000 S/cm), biocompatibility, and excellent mechanical properties, which exceed other solution-processable 2D materials, MXenes have the characteristics enabling numerous applications.[2]Inherent to their 2D structure, the charge carriers responsible for MXene's optical responses and electronic transport are very close to the surface that has an exceptional ability to undergo reversible chemical and electrochemical reactions to add or change surface terminations. MXenes can be applied to a variety of surfaces to provide electronic and ionic conductivity, control optical properties in a wide range of wavelengths, produce electrochromic films, and even achieve a low friction coefficient. Polymers, paper, and fabrics coated by MXenes from aqueous or organic solutions acquire unique surface properties. The properties of MXene coatings can be optically or electrochemically modulated. Many technological advances can be enabled by these chemically and optically responsive conductive coatings.[1,3,4]

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Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM1-1-MoM

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces I

Moderators: Damien Faurie, Université Sorbonne Paris Nord, France, **Barbara Putz**, Empa, Switzerland

10:00am **CM1-1-MoM-1 Exploring Nanostructure Behavior and Ordering Dynamics Through Advanced Electron Microscopy***, **Lilian Vogl (lilian.vogl@berkeley.edu)**,* University of California at Berkeley, USA*; P. Schweizer,* Lawrence Berkeley Lab, University of California at Berkeley, USA*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; A. Minor,* University of California at Berkeley, USA **INVITED**

Characterizing the structure-property relationship and unraveling mechanism on atomic level is not only key for the development of novel nanostructures but also helps to improve the performance of materials on the bulk-scale. *In situ* electron microscopy enables the direct observation of how nano-objects respond to external stimuli, such as mechanical loading or heat treatment. For instance, the significant impact of a disordered crystal structure on the mechanical properties has been widely observed in bulk-alloys. However, the investigation of ordering characteristics in semiconducting and metallic nanostructures (thin films, nanowires) has been largely unexplored. Considering the large surface area to volume ratio of nanostructures, it is expected that local variance within the crystal lattice would have an amplified effect. Therefore, studying the precise characteristics of local ordering in nanostructures becomes all the more important to better tailor their behavior.

By using our unique small-scale model systems of alloyed nanowires, we investigate the transition from the disordered state to intermetallic phases by *in situ* heating experiments. With increasing degree of ordering, microdomains are observed showing characteristic long-rang periodicity. Visualized by 4DSTEM, such local ordering induces strain at the order-disorder domain boundary. For metallic nanowires, the size effect of “smaller is stronger” has been established, showing that nanostructures have superior mechanical properties compared to their bulk counterpart. Now, alloyed nanowires offer the opportunity to further optimize the mechanical response by tuning the ordering degree. *In situ* mechanical testing (including the acquisition of stress-strain curves) of single-crystalline nanowires with different degree of ordering demonstrate the slip-to-twin transition. While solid-solution nanowires deform via twinning, ordered ones show distinct slipping mechanism.

But ordering isn't limited to its pivotal role in alloyed systems. In the case of designing semiconducting thin films, in addition to composition, short-range ordering (SRO) can be utilized to adjust the band gap. The presence of preferential neighbors in the range of 1-2 unit cells in an otherwise random lattice induces diffusive intensity distributions in the diffraction pattern which can be visualized by energy filtered 4DSTEM. In order to manipulate the short-range ordering within the thin films, they undergo heating or irradiation, inducing atoms to exchange positions and thereby altering the local ordering.

10:40am **CM1-1-MoM-3 Autonomous Health Tracking in Self-Reporting MAX and MAB Phases***, **Peter Pöllmann (poellmann@mch.rwth-aachen.de)**[1], S. Lellig, D. Bogdanovski, A. Navid Kashani, M. Hans,* Materials Chemistry RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; D. Holzapfel, C. Azina, P. Zöll,* Materials Chemistry RWTH Aachen University, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J. Schneider,* Materials Chemistry RWTH Aachen University, Germany

Materials health defining mechanisms including chemical changes induced by annealing and oxidation have been tracked via contact-based *in-situ* resistivity measurements. The resulting changes in structure and composition have been analyzed by scanning transmission electron microscopy (STEM), selected area electron diffraction (SAED), high-energy X-ray diffraction (HEXRD), as well as differential scanning calorimetry (DSC) and related to the resistivity data. From this comparison, it is evident that Cr_2AlC, MoAlB as well as $(CrB_2)_nCrAl$ (n=1,2) exhibit autonomous self-reporting behavior as it was demonstrated that structural and chemical changes, influencing materials health, can be readily tracked by contact-based *in-situ* resistivity measurements in an application-relevant temperature regime.

Furthermore, a proof of concept for contactless materials health monitoring has been demonstrated for the first time. This contactless resistance measurement was benchmarked with respect to contact-based resistivity measurements as well as the methods mentioned above to probe structure and composition. It was shown that phase changes, decomposition, and oxidation can be tracked contactless. The proposed method can hence be utilized in the future to track the remaining lifetime of complex-shaped, fast-moving components enabling efficient and therefore more sustainable component utilization.

11:00am **CM1-1-MoM-4 Correlation of Laser-Reflection and Thermionic Emission of Thermally Loaded Coatings Under UHV Conditions***, **Lukas Wimmer (lukas.wimmer@tuwien.ac.at)**,* Vienna University of Technology, Austria*; C. Bienert, R. Schiftner,* PLANSEE SE, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria

In (ultra) high vacuum conditions the evaporation of materials at high temperatures is an important issue, which may significantly reduce the lifetime of thin coatings. To analyze the behavior of film evaporation at high temperatures, the surface evolution has been monitored in-situ using thermionic remission and a laser reflection setup. The temperature during the investigations was regulated by a pyrometer on a designated spot via direct resistive sample/substrate heating. The identified correlation between these two signals showed the capabilities of the measurement system and technique to
develop new materials for high temperature applications, such as thermal barrier or thermionic emission coatings.

Within this study different oxide coatings have been analyzed, based on reactive magnetron sputtered ZrO_2 and Y_2O_3 films on tungsten substrates. Depending on the thermal stability of the respective materials, the coatings of various thickness were tested at temperatures in the range of 1200-1800°C
while keeping the total pressure below 10^{-5} Pa. Even though the thermionic emission of the oxide coatings provides information regarding the coating breakdown, the reflection signal is more decisive. The reflection signal shows a strong dependence on the thickness of the “transparent” oxide coatings,
allowing to obtain close information on the film evolution. For instance, the evaporation rate of ZrO_2 at 1700 °C was determined to be appr. 10 nm/h for pressures below 10^{-5} Pa. The combination of the reflection signal and thermionic emission on the other hand allows an observation of the chemical
stability of the film. The investigated oxide coatings thereby maintain their chemical composition throughout the high temperature process and eventually evaporate completely.

11:20am **CM1-1-MoM-5 Bill Sproul Award and Honorary ICMCTF Lecture: When Stressed Condensed Matter Reveals Its Ultimate Secrets: Thin Film Growth Dynamics Probed by Real-Time Diagnostics***, **Gregory Abadias (gregory.abadias@univ-poitiers.fr)**[2], K. Solanki,* Institut PPrime - CNRS - ENSMA - Université de Poitiers, France*; M. Kaminski,* Karlsruhe Institute of Technology (KIT), Germany*; A. Michel,* Institut PPrime - CNRS - ENSMA - Université de Poitiers, France*; A. Vlad, A. Resta, A. COATI,* Synchrotron SOLEIL, France*; B. Krause,* Karlsruhe Institute of Technology (KIT), Germany*; D. Babonneau,* Institut PPrime - CNRS - ENSMA - Université de Poitiers, France **INVITED**

Metallic thin layers grown by physical vapor deposition (PVD) are ubiquitous in many technological areas, as key components of optoelectronic devices, architectural glazing or sensors. Due to the non-equilibrium nature of PVD, the formation of a thin solid layer from condensation of a vapor flux onto a substrate is inevitably accompanied by the development of a stress build-up [1]. The accumulated stress can significantly reduce the performance, integrity and durability of the material, so that a fundamental understanding of intrinsic stress sources, being either of tensile or compressive type, is needed. In recent years, significant progress has been gained thanks to the potentiality offered by real-time and in situ diagnostics [1-4].

We will present some recent advances on stress evolution during growth of polycrystalline metal layers based on a series of real-time wafer curvature and X-ray synchrotron experiments, and physical models. In contrast to

[1] **Graduate Student Award Finalist**

[2] **Bill Sproul Awardee**

epitaxial systems, where the stress evolution is often dominated by interface-related stresses, polycrystalline layers growing on weakly-interacting substrates reveal a complex stress evolution resulting from a subtle interplay between interface formation and microstructural evolution. Through several illustrative examples covering a broad range of sputter-deposition conditions (working pressure, temperature, particle flux, bias voltage, ionization degree) and spanning different film/substrate interaction, the influence of kinetics and energetics on growth morphology and stress development will be discussed [5], with main emphasis laid on the early growth stages. The impact of energetic particle bombardment on the compressive stress build-up observed during sputter-deposition of refractory metal layers will be explored, and the results discussed in the frame of a kinetic model which includes the influence of grain size, deposition rate and adatom mobility [6].

We will also show that nanoscale phase transformation during the course of film growth can be unraveled from the combination of real-time optical/electrical and surface-sensitive X-ray methods [3,4,7]. Finally, recent findings on the impact of gas additives and wetting agents on the growth morphology of ultrathin Ag layers will be highlighted, with the ultimate goal to produce ultrathin and ultrasmooth Ag layers for use as transparent conductive electrodes [8]. On a broader context, the knowledge gained from these real-time and in situ diagnostics may provide guidelines for efficient growth manipulation strategies in order to target specific applications.

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Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Town & Country C - Session CM4-1-MoM

Simulations, Machine Learning and Data Science for Materials Design and Discovery I

Moderator: Davide G. Sangiovanni, Linköping University, Sweden

10:00am **CM4-1-MoM-1 High-Throughput Rapid Experimental Alloy Development (HT-READ)**, ***Kenneth Vecchio (kvecchio@ucsd.edu)***, University of California at San Diego, USA **INVITED**

The development of high-throughput materials development strategies in the thin-film field have moved forward more quickly than bulk material high throughput strategies, primarily due to the need in bulk materials to account for microstructure effects on properties.In addition, the current bulk materials discovery cycle has several inefficiencies from initial computational predictions through fabrication and analyses. Much of the information and knowledge generated existed in isolated data silos making integrated approaches more challenging. This was the motivation for the 2011 Materials Genome Initiative, which sparked advances in many high-throughput computational techniques related to materials development. However, computational techniques ultimately rely on experimental validation.Furthermore, bulk materials are generally evaluated in a singular fashion, relying largely on human-driven compositional choices and analysis of the volumes of generated data, thus also slowing validation of computational models. Thus, increasing the rate of materials experimentation is fundamental to improving materials research, and requires parallelizing, automating, and miniaturizing key steps in experimental materials research, including computation, synthesis, processing, characterization, and data analysis.

To overcome these limitations, we developed a High-Throughput Rapid Experimental Alloy Development (HT-READ) platform and methodology that comprises an integrated, closed-loop material screening process inspired by broad chemical assays and modern innovations in automation. Our method is a general framework unifying computational identification of ideal candidate materials, fabrication of sample libraries in a configuration amenable to multiple tests and processing routes, and analysis of the candidate materials in a high-throughput fashion. An artificial intelligence agent is used to find connections between compositions and material properties.New experimental data can be leveraged in subsequent iterations or new design objectives. The sample libraries are assigned unique identifiers and stored to make data and samples persistent, thus preventing institutional knowledge loss.This integrated approach paves the way for truly compositionally-accurate and microstructurally-informed bulk materials development in a highly accelerated manner.This overall strategy has enabled our group to achieve the ability to design, fabricate, and fully characterize more than 800 bulk alloy samples per year with a single researcher.

10:40am **CM4-1-MoM-3 Fundamental Investigation for Film Quality Prediction Based on Zone Model in Magnetron Sputtering**, ***Kohei Kuroshima (kohei-kuroshima@osakavacuum.co.jp)***, *I. Ikeda,* Osaka Vacuum, Ltd., Japan; *Y. Gotoh,* Department of Electronic Science and Engineering, Kyoto University, Japan; *M. Iguchi, S. Sugimoto,* Osaka Vacuum, Ltd., Japan

There are diagrams for film structures that are closely related to film properties, called the structure zone model. Thornton's model[1] uses a pressure for one axis, so the model may vary depending on the sputtering apparatus. Anders[2] argued the structure zone diagram (SZD) for the films deposited under presence of energetic particles. In the SZD, the axes are the normalized energy of the particles incident on the substrate, E* and the generalized temperature, T*.

Although it is said that this model cannot be used to predict film structure at points on the E*-T* plane, a trial to predict the structure on the SZD was done in this study. We focused on magnetron sputtering and calculated E* using only the kinetic energy when sputtered particles are incident on the substrate, and with measured substrate temperature, and verified whether Anders' SZD could be applied. We developed a sputter particle transport simulation software and calculated E*. This simulation includes the thermal motion effect of the process gas[3]. For validation, two common types of magnetron sputtering equipment were used to deposit film samples at several combinations of sputtering pressure (0.3-4.0 Pa), target-to-substrate distance (50-100 mm), and substrate temperature (RT-450 ℃). The input power was constant at 300W DC. We observed the surface and cross section of the samples by Scanning Electron Microscope (SEM). It was confirmed whether the structure of the film deposited with the condition which is represented by a certain point on the SZD was consistent with the structure represented by the ZONE.

As a result, under the conditions corresponding to the film structures of ZONE 1 and ZONE 2 on the SZD, the SEM images of the film had the characteristics of each ZONE. On the other hand, under conditions corresponding to the ZONE T, which is the transition region, it was found that the film structure did not show the texture of ZONE T so much, but strongly showed the structure of the adjacent ZONE, especially in the area near the boundaries of the zones.

Following SZD, we are developing a new diagram which exhibits film properties instead of film structure[4].

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11:00am **CM4-1-MoM-4 Are ML Potentials Useful to Understand Deformation and Fracture of Ceramics?***, Nikola Koutná (nikola.koutna@tuwien.ac.at),* *S. Lin,* TU Wien, Austria*; L. Hultman,* Linköping University, Sweden*; P. Mayrhofer,* TU Wien, Austria*; D. Sangiovanni,* Linköping University, Sweden **INVITED**

Theoretical understanding of atomic-scale mechanisms underlying deformation and crack growth in ceramics enables rational design of alloys, superlattices, or nanocomposites with optimized combination of hardness and toughness. Simulations represent an important counterpart to experiment, being relatively inexpensive and allowing to impose well-defined loading conditions, thus making fair comparisons within one material class. Certain comprehension of how ceramics behave subject to mechanical loads can be achieved by *ab initio* methods, however, experimentally-relevant predictions require a combination of finite-temperature effects and large-enough models to consider extended crystallographic defects. In this talk I will discuss the exciting and rapidly growing field of machine-learning interatomic potentials (MLIPs) for molecular dynamics and how these can be used to study the onset of fracture. Transition metal diborides and MAB phases (i.e. atomically-thin laminates of ceramic/metallic-like layers) will serve as model materials to showcase a possible training strategy for the MLIP development and challenges upon up-scaling beyond length scales of *ab initio* reach. Furthermore, simulations of crack initiation in TiB_2 as well as the formation of ripplocations in Ta_2AlB_2 and other MAB phases under certain loading conditions will be interpreted in the light of experimental data available via collaborators. The ML potentials will turn out to be quite useful.

11:40am **CM4-1-MoM-6 Transformation Plasticity and Fracture in MB_2 (M=Ti, Ta, W, Re) Diborides via Ab-Initio and Machine-Learning-Potential Molecular Dynamics***, Shuyao Lin (shuyao.lin@tuwien.ac.at),* TU Wien, Institute of Materials Science and Technology, Austria*; T. Leiner,* Montanuniversität Leoben, Leoben, Austria*; Z. Chen,* Austrian Academy of Sciences, Austria*; R. Janknecht,* TU Wien, Institute of Materials Science and Technology, Austria*; F. Tasnadi,* Linköping University, Sweden*; Z. Zhang,* Austrian Academy of Sciences, Austria*; L. Hultman,* Linköping University, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversitat Leoben, Austria*; D. Sangiovanni,* Linköping University, Sweden*; N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria

In this contribution we employ ab-initio molecular dynamics (AIMD) and machine learned interatomic potential molecular dynamics (ML-MD) simulations to elucidate trends and typical patterns in the mechanical response of transition metal diborides. Four representative diboride systems, MB_2, are selected, with M from the group IV (Ti), V (Ta), VI (W), and VII (Re) of the periodic table. The AIMD simulations serve to find finite-temperature equilibrium lattice parameters of the chosen diborides and to estimate their tensile and shear response at the atomic scale. The thereby produced *ab initio* dataset is used to fit and validate machine-learning interatomic potentials for ML-MD (within the moment tensor potential, MTP, formalism), providing a basis to study deformation behavior at the nanoscale. By controlling the phase structure (the AlB_2, WB_2, and ReB_2-prototype phase), supercell size (few to dozens of nm^3), and imposing well-defined loading conditions (tensile or shear deformation with various loading directions and temperatures), our ML-MD simulations allow assessing similarities as well as fundamental differences between the studied diborides. Considering a nanoscale model with a pre-indent on the surface, we go one step further and discuss ML-MD predictive power and limitations in the light of experimental results for an indented TiB_2 thin film.

12:00pm **CM4-1-MoM-7 Machine-Learning Potential for Accurate Predictions of Elastic Properties in Amorphous W-B-C***, Pavel Ondracka (ondracka@mail.muni.cz),* *J. Ženíšek,* Masaryk University, Czechia*; G. Nayak,* RWTH Aachen University, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; P. Vašina,* Masaryk University, Czechia

Amorphous tungsten boron carbide is a prospective material for protective coatings, with superior ductility and crack resistance [1], and yet the subtle details of its atomistic structure and origin of its excellent mechanical properties are still unclear. Due to the small sizes of representative models and limited timescales of *ab initio* molecular dynamics based on density functional theory, it is difficult for this standard methodology to reliably predict structural and mechanical properties of amorphous W-B-C. Such predictions lead to strongly anisotropic mechanical properties and large uncertainties in the results. We solved the issues by fitting interatomic potential in a general nonlinear atomic cluster expansion (ACE) form [2] to this material system using an active learning approach to sample the amorphous configuration space and the D-optimality criterion and MaxVol algorithm to efficiently construct the training set [3]. The potential was trained for the W content between 10 and 60 at. % and C:B ratios between 4:1 and 1:4. Subsequently, we employed a melt & quench procedure to generate amorphous structural models containing more than 10000 atoms which yielded an isotropic mechanical response and revealed trends with respect to the system composition, density and quenching rates. The thus obtained values of Young's modulus were successfully validated against experimental data.

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Protective and High-temperature Coatings
Room Town & Country D - Session MA3-1-MoM

Hard and Nanostructured Coatings I

Moderators: Marcus Günther, Robert Bosch GmbH, Germany, **Rainer Hahn**, TU Wien, Institute of Materials Science and Technology, Austria, **Stanislav Haviar**, University of West Bohemia, Czechia, **Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

10:00am **MA3-1-MoM-1 Nitride and Carbide Layers: Point Defects, Interfaces, Mechanical Properties***, Daniel Gall (galld@rpi.edu),* Rensselaer Polytechnic Institute, USA **INVITED**

We explore transition metal nitride and carbide compounds and multilayers using a combination of epitaxial layer growth, first-principles calculations, and measurements of lattice parameters and mechanical properties. Rock-salt structure nitrides are both mechanically and thermodynamically stable for group 3 transition metals. However, increasing the valence electron concentration by moving towards the right in the periodic table increases the strength of metal-metal bonds leading to a brittle-to-ductile transition and enhanced toughness, but also decreases the vacancy formation energy on both cation and anion sublattices, resulting in vacancy-stabilized compounds like cubic WN with a dramatically reduced elastic modulus, and new thermodynamically stable phases like a 5-fold coordinated base-centered monoclinic stoichiometric MoN. Epitaxial WC_x layers exhibit a cubic phase that is stabilized by carbon vacancies but phase competition involving hexagonal and orthorhombic W_2C and amorphous carbon lead to an epitaxial breakdown. Epitaxial MoC_x shows a similar phase competition between cubic δ-MoC_x(111) and hexagonal β-Mo_2C(0001) as a function of CH_4 content in the processing gas. In contrast, epitaxial TiC_x is phase pure over a large composition range as the cubic phase is stabilized by the entropy of random C-vacancies for $x < 1$. However, carbon interstitials and small clusters are energetically unfavorable leading to amorphous C segregation for $x > 1$, as detected by photoelectron and Raman spectroscopies. This causes a decrease in the elastic modulus and hardness from 462 and 31 GPa for stoichiometric TiC to 201 and 13.5 GPa for $x = 1.8$. Epitaxial $TiC_{1-x}N_x$ (001) layers show a nearly composition independent elastic modulus but a hardness that decreases approximately linearly from 31 to 21 GPa with increasing $x = 0.0$-1.0. TiN-TiC multilayers exhibit a 5-30% superlattice hardening effect, reaching 34 GPa for an epitaxial layer with a 6 nm lattice period.

10:40am **MA3-1-MoM-3 The Influence of the Carbon Source on the Mechanical and Electrical Properties of Magnetron-Sputtered Titanium Carbonitride Coatings***, Juliana Kessler (juliana.kessler@kemi.uu.se),* Uppsala University, Angstrom Laboratory, Sweden

Titanium carbonitride coatings were investigated for use in electrochemical cells. Here, contact resistance should be minimal while maintaining mechanical strength and a fairly good corrosion resistance. Similar to titanium carbides, an increased carbon content leads to the formation of an amorphous carbon (a-C) phase resulting in nanocrystalline grains of titanium carbonitride surrounded by an a-C matrix. Fine-tuning the microstructure of titanium carbonitride films contact resistance can minimise contact resistance as it is largely determined by surface properties such as hardness and formability, which in turn vary with the amount and structure of the a-C phase. Depending on the carbon source used during the sputter process, the microstructure of the deposited films changes. The aim of this work is to compare the formation of a-C during sputter deposition using two different carbon sources: graphite and methane. Films were either deposited by co-sputtering from a Ti- and a graphite target under N_2 flow or by sputtering solely from a Ti-target under N_2 and CH_4 gas flow. For each process films of different carbon content were deposited and analysed using XRD, XPS, SEM, and Raman spectroscopy. Additionally, properties such as hardness, resistivity, and contact resistance were also investigated. Results show that the carbon concentration of the films varies from 10-24 at.%. Using XPS and XRD, it was found that the films contain NaCl-type Ti(C,N) and an amorphous carbon (a-C) phase. For different carbon concentrations Ti(C,N) shows a varying lattice parameter between 4.26 to 4.32 Å. Furthermore, an increasing overall carbon content causes an increased amount of a-C phase, which has a significant effect on the properties of the films. Comparing the a-C content of films with a similar overall carbon content suggests that carbon is more effectively incorporated in Ti(C,N) grains when using methane as a carbon source. The hardness of the films varied between 12 and 35 GPa and it was found to be dependent on the carbon content, where a lower carbon content corresponded to a reduced hardness. The peak hardness of 35 GPa was found for the film with the highest carbon content deposited using methane as a carbon source. In terms of contact resistance, the lowest values (below 10mΩ) were found for titanium carbonitride coatings with small amounts of a-C, which outperformed both titanium carbide and nitride reference coatings.

11:00am **MA3-1-MoM-4 A Strategic Design Approach Controlling the B-Solubility in Transition Metal Nitride-Based Thin Films**, ***Rebecca Janknecht* *(rebecca.janknecht@tuwien.ac.at)***, *K. Weiss, N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria*; E. Ntemou,* Department of Physics and Astronomy, Uppsala University, Sweden*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Limited B-solubility in fcc-TiN poses significant challenges to the applicability of Ti-B-N-based hard coatings. In particular, excess B tends to segregate at the grain boundaries instead of being fully incorporated in the fcc lattice. Although increasing the B content enhances mechanical properties such as hardness, forming excess amorphous grain boundary phases can significantly reduce fracture toughness. Compared to TiN, we observed an increase of 10 GPa in hardness (up to 36.9±1.8 GPa) but a decrease in fracture toughness of roughly 25 % (down to 2.1±0.1 $MPa*m^{0.5}$). Assisted by ab-initio DFT calculations, we previously demonstrated that additional Ti (to deviate from the TiN–TiB tie-line) is required to fully incorporate more B (up to 8.7 at%) in the TiN lattice while minimizing B-rich amorphous phases. Here, we expand this research by adjusting the metal sub-lattice through Ti-, Cr-, Al- or Zr-addition to a Ti-B-N compound target (50 at.% Ti, 40 at.% N, and 10 at.% B). Our study highlights the key-role of kinetics in non-reactive deposition processes to overcome the thermodynamic limits of B-solubility in TiN. Through changing the stoichiometry by knowledge-based metal addition, we propose a general strategy to enhance the B solubility in transition metal nitride-based thin films.

11:20am **MA3-1-MoM-5 The Influence of Bilayer Periods and Ratios on Mechanical and Tribological Properties of TiN/MoN Superlattice Thin Films**, *Z. Gao, J. Buchinger, R. Hahn,* TU Wien, Institute of Materials Science and Technology, Austria*; Z. Chen, Z. Zhang,* Austrian Academy of Sciences, Austria*;* ***Paul Mayrhofer (paul.mayrhofer@tuwien.ac.at)***, TU Wien, Institute of Materials Science and Technology, Austria

Transition metal nitrides are commonly used in hard and protective coating industry, but still limited by low intrinsic fracture toughness. Encouraged by the previous study that superlattices (SLs) could remarkably improve strength and ductility, in this study, some TiN/MoN SL thin films are sputtered on (100) MgO substrates. These SLs are with bilayer periods ($Λ$) of 2–23 nm and a bilayer ratio ($\ell_{TiN}:\ell_{MoN}$) of 1:1, 1:0.5, 1:1, 1:2, and 1:2.7. This work is aim to explore the influence of bilayer periods and ratios, and the vacancies on TiN/MoN superlattice. All SLs – independent of bilayer period, bilayer ratio, and nitrogen content – present a rocksalt structure, with high-order satellite peaks during X-ray diffraction. But a weak tetragonal β-Mo_2N signal is also detected for the SLs with Λ = 7.3 nm ($\ell_{TiN}:\ell_{MoN}$ = 1:2). The SLs with bilayer ratios of 1:0.5 and 1:2 do not show superlattice effect and bilayer-period-dependent. The SLs with $\ell_{TiN}:\ell_{MoN}$ = 1:2.7 provide highest hardness due to a higher nitrogen supply during deposition. Contrary, the SLs with $\ell_{TiN}:\ell_{MoN}$ = 1:2 have the worst mechanical properties due to the tetragonal β-Mo_2N phase exist. Among all SLs investigated, those with $\ell_{TiN}:\ell_{MoN}$ = 1:1 provide the best blend of mechanical properties, such as H = 34.8 ± 1.6 GPa, K_{IC} = 4.1 ± 0.2 MPa√m, and μ = 0.27, when Λ = 9.9 nm. This study extends our understanding of superlattice effect in general, especially on the influence of bilayer periods and bilayer ratios, as well as nitrogen supply and heterogeneous microstructures, which is benefit to next SL design.

11:40am **MA3-1-MoM-6 TiN/CrN and TiSiN/CrN Multilayer Coatings Deposited in an Industrial–scale HiPIMS System**, ***Neus Sala (neus.sala@iqs.url.edu)***, IQS School of Engineering - Universitat Ramon Llull, Spain*; M. Abad,* IQS School of Engineering - Universitat Ramon LLull, Spain*; C. Colominas,* FLUBETECH, S.L., Spain*; R. Franz, C. Kainz, M. Rebelo de Figueiredo,* Montanuniversität Leoben, Austria*; C. Rojas, J. Sánchez-López,* CSIC-Universidad de Sevilla, Spain

TiN/CrN and TiSiN/CrN multilayer coatings of varying bilayer period (Λ) were deposited in an industrial-scale deposition system by means of reactive High Power Impulse Magnetron Sputtering (R–HIPIMS). For each composition, three different coatings were deposited with bilayer periods of approximately 85 nm, 15 nm and 5 nm by alternating the sputtering of the different metallic targets in a nitrogen-containing atmosphere.

The influence of the Λ is investigated in regard of the chemical composition, microstructure, and mechanical properties of the coatings.

All coatings present a very smooth and compact structure in SEM images. XRD showed separate crystalline phases for the samples with high bilayer periods. However, as the bilayer period decreases, the crystalline peaks overlap, which would suggest epitaxial growth of the two crystalline phases.

A superlattice structure is confirmed by satellite peaks in the X-ray diffractograms for the TiN/CrN coatings with Λ ≤ 15 nm. TEM and EELS of the TiSiN/CrN coatings show that Si is substitutionally incorporated into the TiN crystalline lattice without segregation of amorphous SiN_X phases. However, epitaxial growth is interrupted by amorphous zones, particularly in samples with smaller bilayer periods.

For the TiN/CrN system, the highest nanoindentation hardness value obtained is 32 GPa while for TiSiN/CrN coatings, it is 28 GPa. In both cases, the maximum hardness value is found for the samples with Λ 15 nm regardless of the composition.

12:00pm **MA3-1-MoM-7 Residual Stress Measurement and Effective Deformation Thickness of Metal Interlayer in Multilayer Hard Coatings - Using TiN/Ti/TiN/Ti as a Model Architecture**, ***I-Sheng Ting (gary820902@yahoo.com.tw)***, *J. Huang,* National Tsing Hua University, Taiwan

High residual stress is one of the critical problems encountered in hard coatings deposited by physical vapor deposition. In industrial applications, introducing a metal interlayer, such as Ti and Cr, is a common practice to relieve the residual stress, thereby enhancing the adhesion and life span of the hard coatings. Our previous studies [1,2] proposed an energy-balance physical model to evaluate the stress and energy relief efficiency of metal interlayers in hard coatings. The assumption of the model was that the relief of stored elastic energy (G_S) in the hard coating and the bending energy of the Si substrate are balanced by the plastic work done by the metal interlayer. The results showed that the energy relief efficiency of the metal interlayer depends on the plastic behavior of the metal, where Zr interlayer has a lower extent of stress relief in ZrN/Zr coating than Ti interlayer in ZrN/Ti coating [1], because the strength coefficient (k) of Zr is higher than that of Ti. In addition, the results indicated that the plastic deformation capability of the metal interlayers is not fully consumed, and the plastic deformation of the metal interlayer is localized within a narrow layer nearby the coating/interlayer interface, which was named as effective deformation thickness (EDT). The EDT was used to depict the energy relief extent in the bilayer coatings [2]. However, whether the energy-balance model and the concept of EDT could be applied in a multilayer structure is still unclear. In this study, the alternated four layered TiN/Ti/TiN/Ti coating was selected as a model architecture to investigate the stress relief and stress distribution of multilayer hard coatings. TiN coating with Ti interlayer was deposited on Si substrate using dc unbalanced magnetron sputtering, where the TiN film and Ti interlayer were alternately stacked to produce structure, TiN, TiN/Ti, TiN/Ti/TiN and TiN/Ti/TiN/Ti. The overall stress and the layered stress of the coatings were measured using the laser curvature method and the average X-ray strain (AXS) combined with nanoindentation methods [3-5], respectively. By using the energy-balance model and the concept of EDT [1,2], the stress and energy relief efficiency of the multilayer architecture could be estimated.

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Functional Thin Films and Surfaces
Room Town & Country A - Session MB4-MoM

2D Materials: Synthesis, Characterization, and Applications

Moderators: Chih-Yen Chen, National Sun Yat-sen University, Taiwan , **Ying-Hao Chu**, National Tsing Hua University, Taiwan

10:00am **MB4-MoM-1 Influence of Plasmonic Coupling and Size Effect on Photocatalysis of MoS_2/Au Hybrid Nanostructures for Water Splitting**, ***Yi-Hsueh Chen (t870116@gmail.com)***, *J. Ruan,* NCKU, Taiwan

Hydrogen energy is a clean andsustainable form of energy for our environment, serving as a viable alternative energy source that can be used without the production of greenhouse gases. Utilizing solar energy to split the water and generate hydrogen in the presence of photocatalysts is a promising and economic approach to address the current energy and environmental crisis. MoS_2 has been recognized as the most efficient photocatalyst for hydrogen evolution among non-noble metals. In particular, MoS_2 nanosheets exposed lots of active sites for the attachment of proton and later reduction reactions, and the efficiency is better than nanoflowers or bulk morphology. However, the absorption wavelength of MoS_2 nanosheets is almost within the UV region, in addition to the challenge of high electron/hole pairs recombination rate. Visible light accounts for 95% of sunlight and UV light occupies only 5%. It is vital for photocatalysts to efficiently harvest visible light and avoid exciton recombination. The absorption of visible light is able to cause strong localized surface plasmon resonance (LSPR) of gold nanoparticles (AuNPs), which has been widely investigated to promote light absorbance. Nevertheless, the desired dispersion patterns of AuNPs for the optimization of plasmonic resonance are less achievable. As an approach to maximize the amount of energy absorbed from the sunlight, we aim to design and fabricate hybrid particles composed of AuNPs and MoS_2 nanosheets with the control of coupling effect among AuNPs and the size of AuNPs. We have successfully grown MoS_2 nanosheets directly on the (111) planes of gold nanoparticles to form the core-shell structure with controlled thicknesses. Furthermore, the extent of enhancement of plasmonic coupling for gold nanoparticles with different diameters, i.e. 16 nm and 38 nm has been verified. Through the achieved adjustment of edge-to-edge distances among AuNPs and the size of AuNPs, the required condition for the best plasmonic resonance to absorb visible light is able to be clarified and thus optimizes the hot electron transition from AuNPs to MoS_2, which critically enhances desired hydrogen production.

10:20am **MB4-MoM-2 Sputter Deposition of Hexagonal Boron Nitride Films**, ***Minsuk Seo (seo3@llnl.gov)***, *L. Bayu Aji,* Lawrence Livermore National Laboratory, USA*; Y. Tzeng, S. Kim,* Stanford University, USA*; Y. Zhou, L. Wan, C. Kim, B. Wang, T. Heo, L. Zepeda-Ruiz,* Lawrence Livermore National Laboratory, USA*; S. Chu,* Stanford University, USA*; S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Hexagonal boron nitride (hBN) films are attractive for several emerging energy-related applications. Extensive previous research has focused on the growth and properties of either ultrathin hBN films with thicknesses up to a few monolayers or cubic BN films. The synthesis of wafer-scale hBN films with controlled thickness above ~10 nm with desired properties remains a challenge. Here, we present results of our ongoing systematic study of polycrystalline hBN films with thicknesses in a wide range of 50-6000 nm deposited by several variants of reactive magnetron sputtering with a radiofrequency (RF) driven discharge. We describe how the plasma discharge characteristics and, hence, resultant major film properties can be controlled by the magnetron source design, the confining magnetic field, and process parameters such as the working gas pressure (influencing landing neutral atom ballistics and energetics), substrate temperature (adatom mobility), and substrate bias (bombarding ion energy). Even without epitaxy, with substrates held close to room temperature, hBN films are polycrystalline, characterized by a FWHM of the major E_{2g} Raman vibrational mode (1370 cm^{-1}) in the range of 40 – 100 cm^{-1}, depending on deposition conditions. The FWHM reduces to ~30 cm^{-1} when a higher deposition temperature of 600-800 ºC is used. Interestingly, all as-grown films are polycrystalline (turbostratic, with asymmetrically stacked layers) rather than amorphous even for a high deposition pressure of 50 mTorr, characterized by low landing atom energetics. We also describe how these film growth and characterization experiments are guided by results of in-situ plasma diagnostics.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA2734.

10:40am **MB4-MoM-3 Advancing 2D Materials for Future Electronics: Selective Synthesis, Transferring Processes, and Device Integration**, ***Ching Yuan Su (cysu@ncu.edu.tw)***, National Central University, Taiwan **INVITED**

Two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMDs) have attracted significant attention due to their exceptional electrical properties, holding promise for next-generation nanoelectronics. However, integrating 2D materials into IC devices presents challenges, including precisely controlled synthesis methods, defect-free transfer processes, and back-end-of-line (BEOL) device integration.

In this talk, I will discuss advancements in selectively seeding growth of high-quality 2D materials on insulating substrates using a new precursor and advanced process. Additionally, an efficient and reliable method for the wafer-scale transfer of graphene and other 2D materials, ensuring integrity and cleanliness, will be presented. Finally, I will highlight the concept of a heterogeneously integrated 3D-IC, combining a 2D-based field-effect transistor (FET) with high-performance memory, showcasing the potential for BEOL and monolithic integration of 2D-based 3D-ICs.

11:20am **MB4-MoM-5 Reduced Electrocatalytic potential of Nitrate to Ammonia through MoS_2 Deposited Carbon Felt based Flexible Electrode**, ***Prateek Sharma (prateeksharma1688@gmail.com)***, *C. Liao, Y. Chang, D. Huang, W. Hsu, J. Huang, Y. Lai,* Ming Chi University of Technology, Taiwan

The increasing need, for environment friendly and energy efficient methods to remove nitrate from water has prompted the investigation of inventive electrocatalytic techniques. This work highlights an approach to convert nitrate into ammonia at low potential using carbon felt coated with Molybdenum disulfide (MoS_2) nanosheets as a flexible electrode. The layered structure of MoS_2, with exposed edge sites, provides active catalytic sites for the reduction reactions. This enhances the catalytic activity compared to other materials, contributing to more efficient nitrate ion degradation, making it a potential candidate for sustainable water treatment.MoS_2 can be deposited on flexible substrates, such as carbon felt, creating flexible electrodes.the flexible nature of the MoS_2-deposited carbon felt electrode enhances the catalytic activity, allows for easy integration into existing water treatment systems, providing adaptability and scalability for practical applications. This research contributes towards the formation of efficient MoS_2 nanosheets as catalyst material for the advancement of electrocatalysis for sustainable water treatment but also underscores the significance of flexible electrodes in enhancing the adaptability and efficiency of the nitrate to ammonia conversion process. The findings presented in this conference aim to foster discussions and collaborations towards the development of energy-efficient and environmentally friendly technologies for nitrogen removal from water sources.

Keywords: Nitrate ion reduction, Electrocatalysis, Flexible electrode, Electrodeposition, MoS_2 nanosheets

11:40am **MB4-MoM-6 Transport Studies on Pulsed Laser Deposited $Ti_3C_2T_x$ - MoO_3 System**, ***Shravani Kale (shravanikale90@gmail.com)***, *D. Sabale, S. Kale,* Defence Institute of Advanced Technology Pune, India

$Ti_3C_2T_x$, belonging to the MXene family, exhibits distinctive characteristics that render it highly suitable for p-n diode/Schottky diode applications, particularly in conjunction with MoO_3 compounds. $Ti_3C_2T_x$ - MoO_3 can offer exceptional thermal and mechanical stability, coupled with its elevated electrical conductivity and favorable chemical sensing ability, which makes these systems as an optimal choice for electronic device fabrication.

In this work thin films of $Ti_3C_2T_x$ -MoO_3 bilayers are deposited using Pulsed Laser Deposition (PLD) technique, specifically tailored for studying the diode characteristics. The deposition process utilized a low laser energy density strategy, allowing the exploration of various compositions. The experiments employed a krypton fluoride (248 nm) excimer laser operating at a laser energy density of 1.5 J/cm2. First layer of $Ti_3C_2T_x$ was deposited on sapphire substrate with substrate temperature 700°C, target to substrate distance as 5 cm and laser repetition rate of 10 Hz. The vacuum inside the chamber was 1.5 x 10^{-5} mTorr. The MoO_3 was deposited on to the MXene layer using same energy density and base vacuum with substrate temperature of 400°C, and pulse repetition rate of 8 Hz. Here the oxygen partial pressure was maintained at 75 mTorr during deposition.

The compositional and morphological properties of $Ti_3C_2T_x$ -MoO_3 films were investigated using X-ray diffraction, Field-emission scanning electron microscopy (FESEM), and EDAX. The transport characteristics show a systematic change from Schottky behavior to p-n junction diode characteristics as a function of varying deposition parameters. Variation in PLD energy density and substrate temperature were the main parameters which were varied. These results would be exhibited in this presentation. A novel non-Silicon based system is hence projected as a potential candidate for electronic and optoelectronic applications.

Tribology and Mechanics of Coatings and Surfaces
Room Palm 1-2 - Session MC1-1-MoM

Friction, Wear, Lubrication Effects, and Modeling I

Moderators: Giovanni Ramirez, Oxford Instruments, USA, **Michael Chandross**, Sandia National Laboratories, USA

10:00am **MC1-1-MoM-1 Modern Analytical Methods for Characterizing Wear Surfaces and Subsurfaces***, **Thomas Scharf (thomas.scharf@unt.edu)**,* The University of North Texas, USA **INVITED**

It is now common to employ focused ion beam (FIB)-SEM and subsequent TEM characterization techniques to study 'site-specific' deformation structures. In this talk, I will highlight more underutilized diffraction and imaging techniques, such as Precession Electron Diffraction (PED)-TEM, Transmission Kikuchi Diffraction (TKD)-SEM, as well as 3-D FIB serial sectioning to interrogate subsurface structural evolution during sliding wear. *First*, new insights into solid lubrication mechanisms in directed energy deposition (DED) metal matrix composites (Ni/TiC/graphite) reveal that the improved tribological behavior is due to the in-situ formation of a low interfacial shear strength amorphous carbon tribofilm that is extruded to the surface through refined Ni grain boundaries. 3-D FIB serial cross-sectioning inside the worn surfaces of these composites revealed that the tribological stresses in the subsurface extrude the graphitic, primary carbon towards the surface through intergranular separation of refined nanocrystalline Ni grains. *Second*, surface and subsurface structural evolution during sliding wear of an in situ nitrided DED titanium alloy, Ti-35Nb-7Zr-5Ta (TNZT), was studied by cross-sectional TEM coupled with PED. Corresponding precession–orientation imaging phase maps were used to determine the orientation and percentage of α and β-Ti in the worn nitrided TNZT. The maps revealed that the nanocrystalline grains of soft/compliant β are much smaller (10-100 nm) than hard/stiff α grains (>100 nm). Wear reduction is due to the combination of the above phases and increase in the alignment of {0002}-textured coarser α grains along the sliding direction with absence of texture in the highly refined β grains. *Lastly*, I will show how coupled cross-sectional TKD-SEM can interrogate the microstructural evolution in a Co-Cr alloy sliding on a Ta-W alloy.

10:40am **MC1-1-MoM-3 Wear-Protection Performance and Durability of *in-Situ*-Deposited Carbon TribofilmsDerived from Intrinsically Strained Cycloalkane Molecules as Lubricant Additives***, Z. Al Hassan, H. Wise, T. Martin, S. Liu, Q. Wang,* ***Y. W. Chung (ywchung@northwestern.edu)**,* Northwestern University, USA*; S. Berkebile,* US Army Research Laboratory, USA

Wear-protective coatings on tribo-component surfaces are usually applied *via* vapor deposition methods. Once worn, they can only be restored through component disassembly. In our study, we explored *in situ* carbon tribofilm deposition using intrinsically strained cycloalkane molecules. These molecules, when dissolved in lubricants, can induce tribopolymer formation under stress and temperature at asperities. Our previous work on cyclopropane-carboxylic acid (CPCa) as an additive in polyalphaolefin and dodecane demonstrated the successful deposition of micron-thick carbon tribofilms in 15 minutes during pin-on-disk testing with a ten-fold reduction in wear. New results show that even after the removal of CPCa from the lubricant, these tribofilms continue to provide wear protection for up to 40 hours. Detailed surface examination using Raman spectroscopy helps us unravel the underlying mechanism for such extended durability of these carbon tribofilms. This research suggests a unique approach to providing unlimited replenishment of wear-protective layers.

11:00am **MC1-1-MoM-4 Lubricant Interaction of Triboactive CrAlMoCuN Coatings in Steel Contacts***, K. Bobzin, C. Kalscheuer,* ***Max Philip Möbius (moebius@iot.rwth-aachen.de)**,* Surface Engineering Institute - RWTH Aachen University, Germany

Conventional lubricants are designed for wear and friction reduction in steel-to-steel contacts. Rising power densities require enhanced wear resistance of machine components. This can be achieved using hard CrAlN coatings, although their chemical inertness limits interaction with lubricants. Therefore, Mo and Cu are incorporated into CrAlN coatings, promoting tribo-chemical interaction with lubricants. Mo can interact with sulfur to create MoS_2 tribofilms. Cu acts catalytically for this reaction and can enhance tribofilm formation for Fe_x-P_y and a-C. In most applications like gear boxes, bearings or chain drives, it is economically and technologically challenging to coat all components. Therefore, this study focuses on coating-steel contacts. Three CrAlMoCuN coatings and one CrAlN reference were deposited using physical vapor deposition (PVD). Coating characterization includes morphology, coating thickness, chemical composition, indentation hardness, surface roughness and compound adhesion. All coatings, along with an uncoated reference, were tribologically investigated using a pin on disk (PoD) tribometer. As substrate, the chain pin steel 58CrV4 was used, quenched and tempered to H = (52±1,5) HRC. The PoD parameters were an initial contact pressure of p_{PoD} = 1,400 MPa, a relative velocity of v_{rel} = 0.1 m/s, and a temperature of T_{PoD} = 70 °C. 100Cr6 steel was used as counterpart and Polyalphaolefin (PAO) as lubricant. PAO was highly additivated with sulfur and phosphorous. Tribofilms were investigated using energy dispersive spectroscopy (EDS) and Raman spectroscopy. All CrAlMoCuN systems showed lower coefficients of friction compared to both references indicating the formation of MoS_2 containing tribofilms. This correlates with a significantly reduced total wear volume.Via EDS, Cu-enriched lubricant residues were found on the uncoated counterparts in the CrAlMoCuN system, indicating the interaction of Cu with the lubricant in the tribological contact for the first time. The results show high potential of CrAlMoCuN coatings for lubricated machine element applications.

Plasma and Vapor Deposition Processes
Room Palm 5-6 - Session PP6-MoM

Microfabrication Techniques with Lasers and Plasmas

Moderator: Carles Corbella, George Washington University, USA

10:00am **PP6-MoM-1 Laser Bioprinting: From the Breast Tumor Microenvironment to Migration in Wound Healing Assays***, **Doug Chrisey (douglasbchrisey@gmail.com)**,* Tulane University, USA **INVITED**

Laser bioprinting can be both additive (depositing cells) and subtractive (etching) and both have power to study the micro-physiological behavior of heterogeneous tissue constructs *in vitro*. The use of a UV laser in both these scenarios is shown to be very powerful and this presentation will show results over this wide range of applications. The most enriched cell types in the breast tumor microenvironment are cancer cells, cancer-associated fibroblasts, and tumor-associated macrophages. To recapitulate the cellular dynamics of the breast tumor microenvironment *in vitro*, the most abundant cell types need to be incorporated. Laser direct write bioprinting offers a precise, gentle, and reproducible method to print disparate cell types in user-defined geometries. Herein, we develop novel laser direct write cell printing protocols – first as a customizable generalized framework, which is then adapted to print homotypic and heterotypic cancer-stromal arrays, and human macrophages. We demonstrate the ability to fabricate *in vitro*heterocellular constructs for studying cell-cell signaling in healthy and diseased microenvironments, as well as the capability to print human immune cells with high fidelity to pave the way for bioprinting immunocompetent tissue models going forward. Traditional *in vitro* scratch assays lack standardization due to poor control over wound geometry and fail to account for cell proliferation. Here, we developed a novel scratch assay that enables precise control over wound geometry using CAD/CAM laser photoablation and takes cell proliferation into consideration using a simple reaction- diffusion based mathematical model. We demonstrated that diffusivity in precisely photoablated cell layers serves as a more accurate measure of cell motility than the rate of gap closure. Further, we biologically validated this assay using cells harvested from patients and patient-derived xenografts to gain insights into the influence of the presence stromal cells on metaplastic and non-metaplastic triple negative breast cancer metastasis.

10:40am **PP6-MoM-3 Plasma-Assisted Nanofabrication of Advanced Nanoplasmonic Surfaces for SERS Applications**, ***Uros Cvelbar (uros.cvelbar@ijs.si)***, Jozef Stefan Institute, Slovenia **INVITED**

In the realm of plasmonic detection, pivotal for applications such as food and water quality monitoring, theranostics, and virus and toxin analysis, Surface Enhanced Raman Scattering (SERS) stands out as a powerful technique. Employing vibrational spectroscopy and surface nanoengineering, SERS leverages metallic nanoparticles to enhance signals through the confinement effect of the electromagnetic field, creating intense 'hot spots' near nanoscale metal surfaces. The morphology and arrangement of plasmonic nanomaterials crucially influence the formation of hot spot networks. This presentation focuses on our recent research in the plasma-assisted fabrication of advanced nanoplasmonic surfaces, showcasing nanocarbon structures, metal-oxide nanotrees, and coupled nanogold. Utilizing various plasma setups, including low-pressure and atmospheric pressure, we demonstrate their versatility, reliability, and fast, one-step processing. These surfaces excel in detecting cancerogenic toxins at ppb levels, ultrafast recognition of trace chemicals, and even bacterial DNA detection with nanogram sample amounts. The talk underscores the significant potential of plasma-assisted nanofabrication in advancing nanoplasmonic surfaces for a broad spectrum of analytical applications.

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11:20am **PP6-MoM-5 Enhancing Tribological Performance of Carbon-Based Coatings Through Pulsed Lasertexturation**, ***Constant Boris Rieille (constant.rieille@bfh.ch)***, *S. LeCoultre,* Berner Fachhochschule BFH, Switzerland

This presentation aims to explore laser-textured carbon-based coatings and their improved tribological properties for different applications against various materials, including brass, titanium, aluminum and steel. The study involves a comprehensive comparative analysis with benchmark carbon coatings from the market, focusing on the performance of these coatings in diverse conditions.

Moreover, our research delves deeper into the tribolayer that forms on counterpart surfaces and employs advanced analytical techniques such as Raman spectroscopy and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis (SEM+EDX) to gain insights into the intricate mechanisms at play.The contribution of topographical variations and structural changes to the carbon coating will be discussed.

We will also introduce a novel model to elucidate why laser textured carbon layers exhibit superior tribological performance compared to their untextured coatings and compare as well different possible mechanism for carbon transformation depending on laser pulse length between nano and femtosecond.

At the end of the presentation, we aim to present an innovative method for producing a high-performance coating that can be used for tribological applications in the cutting tool, watchmaking, and micromechanics industries.

11:40am **PP6-MoM-6 Designing Chiral Micropatterns via Ion Beam Colloidal Lithography**, *S. Portal,* ***Carles Corbella (ccorberoc@gwu.edu)***, George Washington University, USA*; O. Arteaga,* University of Barcelona, Spain*; A. Martin, T. Mandal,* New York University, USA*; V. Dinca,* National Institute for Laser, Plasma, and Radiation Physics, Romania*; B. Kahr,* New York University, USA

Optically anisotropic materials were fabricated via colloidal lithography and characterized by scanning electronic microscopy (SEM), confocal microscopy, and polarimetry. First, a mask consisting of hexagonal compact arrays of silica sub-micron particles (500-600 nm in diameter) was produced via Langmuir-Blodgett self-assembly. After that, the deposited mask pattern was transferred onto the underlying substrate by means of ion beam etching using an electron-cyclotron-resonance (ECR) plasma source. Monocrystalline silicon and commercial glass were used as substrates. In the etching processes, screw-like shaped pillars were carved into the substrates by irradiating their surfaces at oblique incidence and varying stepwise the azimuthal angle. Different chiral structures were obtained depending on the rotation direction of the azimuthal angle steps. Finally, thin gold films were deposited on top of the pillars to enhance the material optical properties through plasmon resonance effect. Polarimetric measurements were realized at normal and oblique incidences to assess the anisotropy of the samples. The etching directions have an influence on the value of the linear birefringence and linear dichroism. A dependence of the birefringent parameters on the angle of incidence of the light was found: an amplification of the chiroptical response of the material was observed at increasing angle of incidence. This fast, cost-effective technique is promising for the preparation of large micropatterned surfaces aimed at photonic and biological applications.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-1-MoM

Coatings for Batteries and Hydrogen Applications I

Moderator: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany

10:00am **TS1-1-MoM-1 New Coating Methods for New Electrolyzer Technologies for PEM Electrolyzer and AEM Electrolyzer**, ***Thomas Kolbusch (tkolbusch@coatema.de)***, Coatema, Germany **INVITED**

The author describes in his talk the scale up process for PEM electrolyzers regarding coating technologies.The first part of the talk shows the need for scale up in the green hydrogen market due to the huge amount of green hydrogen which has to be produced till 2030 and 2050 to reach net zero targets. For this industrial standardization of coating processes are needed as soon as possible. Here the upscale process of reproducible and reliable roll 2 roll equipment are shown and getting over the limiting factors like dimension instability of membrane materials and multi layer coating applications of rare materials like iridium.

The second part describes the boundaries of todays coating methods describing the parameters needed to be optimized. The background on one of the standard methods today, slot die coating is described here in detail with some theoretical background on slot die coating technology and an overview on developments for intermittent slot die coatings. The third part of the talk describes a new digital fabrication method for electrolyzers and shows the opportunity for the overall green hydrogen market using digital fabrication methods, reducing the carbon footprint of coating equipment for PEM electrolyzer.

10:40am **TS1-1-MoM-3 Dual Doped Two-dimensional Carbon Supported Single Atomic Iron for Oxygen Reduction Reaction in Alkaline-Exchange Membrane Fuel Cells**, ***Afandi Yusuf (afandi2102@gmail.com)***, *F. T. D. Wijaya, H. Hsin-Chih, C. Wang,* National Taiwan University of Science and Technology, Taiwan

Single atom catalysts (SAC) represent an intriguing option due to their ability to unlock the latent catalytic potential in oxygen reduction reaction (ORR). Nevertheless, the endurance of individual atomic entities is confronted by numerous impediments, encompassing the dissolution of metallic species, metal agglomeration, and the deactivation of catalytically active sites. A crucial factor in enhancing stability lies in the judicious selection of a compatible support catalyst capable of fostering strong metal-support interaction (SMSI).

Carbon is widely utilized as a catalyst support material owing to its favorable electron conductivity and the ability assume diverse dimensional configurations, ranging from 0D to 3D. Additionally, the carbon support facilitates additional customization, such as the introduction of Chalcogen or Pnictogen atom groups through doping, leading to enhanced catalytic activity.

In this work, we successfully fabricated a two-dimensional porous nanosheet electrocatalyst designed to enhance the Oxygen Reduction Reaction (ORR) in Anion-Exchange Membrane Fuel Cells (AEMFCs). This catalyst featured single atomic active sites of Iron supported by a Nitrogen-Phosporus co-doped Carbon material, aimed at reducing catalyst cost and thereby increasing the accessibility of the fuel cell for commercial applications. The electrochemical performance of the material was exemplified by the MDP-4-Fe-800 sample, demonstrating an onset potential of 0.97 V, an $E_{1/2}$ of 0.86 V, and a $J_{limiting}$ of 5.5 mA/cm^2 under alkaline conditions, surpassing that of commercial Pt/C under the same conditions. Moreover, the material exhibited notable stability after 30,000 cycles, experiencing only a marginal 0.39 mA/cm^2 in $J_{limiting}$ and 30 mV decrease in both onset and $E_{1/2}$. While MDP-4-Fe-800 did not outperform the single-cell performance of commercial Pt/C, it displayed commendable activity, generating a power density of 244.8 mW/cm^2.

11:00am **TS1-1-MoM-4 CO_2 Laser Processed Nickel Catalyzed Graphene Coating for Electrocatalytic Water Splitting and Energy Storage Applications***, **Suparna Saha (suparna.saha@tcgcrest.org),*** TCG CREST (RISE), India*; S. Hiwase,* IISER PUNE, India*; S. Ogale,* IISER PUNE, TCG-CREST(RISE), India

Development of efficient, cost-effective, and environmentally friendly processes for the realization of high-quality graphene on metallic substrates is highly desirable for multiple energy applications as well as next-generation graphene-based green electronics. Several polymers including those derived from natural sources represent a rich source of carbons that can be converted into graphitic carbons by energy inputs in different forms. Lasers represent a form of energy input that is direct-write type and does not need the whole substrate to be heated at high temperatures for carbonization. Herein, we examine carbonization of natural product-derived polymer(s) into graphitic (few layers graphene) carbon using CO_2 laser-assisted direct-write process. Such a process is generally termed as Laser-Induced Graphene (LIG). In particular, we demonstrate the key and interesting role played by nickel in enhancing the degree of graphitization (Ni-LIG). Indeed, the unique advantage of this nickel-catalyzed scanning laser-induced transient pyrolysis process implemented under ambient conditions is that we are able to uniformly graphitize the thermoset polymer coating that would otherwise yield hard carbons or a mixture of ordered/disordered carbon in a furnace-based pyrolysis process. It was observed that upon optimized laser processing condition, the Ni-$(CH_3COO)_2$. $4H_2O$ salt added to the polymer gets reduced to Ni (111), which in turn catalyzes the nucleation process. We note the appearance of disordered carbon chains initially, which upon interacting precisely with the nickel surface lowers the activation barrier for graphene formation by annealing the defects. Moreover, due to the very low lattice mismatch between Ni (111) and graphene, a strong interphase is formed, facilitating efficient contact and charge transfer. As the surface coating is decorated with a mixture of Ni/NiO (as confirmed by XRD and XPS), water dissociation as well as adsorption of water oxidation intermediates is promoted, leading to an impressive value of overpotential for oxygen evolution reaction (OER) at 10 mA/cm^2 of only 330 mV in 1M KOH. We also examined the case of urea-incorporated material to induce N-doping so as to enhance the conductivity via the incorporation of the Π-conjugated system. However, the incorporated pyrrolic N defects in the carbon layer were noted to hinder the nucleation of graphitization at the Ni atom, resulting in a low I_G/I_D ratio. This material was therefore studied for charge storage property by cyclic voltammetry and galvanostatic charge-discharge (GC) measurement. It was found that N-doped N-Ni-LIG has a higher specific capacitance compared to Ni-LIG.

11:20am **TS1-1-MoM-5 Bimetal Phosphide (NiCoP)/Graphitic Carbon Nitride(g-C_3N_4) Composites for Hydrogen Evolution Reaction in Alkaline Electrolyte***, **Yu-Hsuan Kao (hsuan890411@gmail.com),*** National Cheng Kung University, Taiwan*; S. Wang,* Southern Taiwan University of Science and Technology, Taiwan*; J. Huang,* National Cheng Kung University, Taiwan*; Y. Shen,* Hierarchical Green-Energy Material (Hi-GEM) Research Center, Taiwan

In order to address the growing energy crisis and environmental concerns, the development of hydrogen energy through electrochemical water splitting into hydrogen represents a viable solution. The hydrogen evolution reaction (HER) during water splitting is multi-electron transfer process that requires catalysts to proceed at appreciable rates. Noble metals have been widely used for water splitting due to their low Gibbs free energy; however, their high cost limits their availability and hinders commercialization. To address this challenge, we conducted a study on HER in alkaline electrolytes with the aim of developing highly efficient and durable electrocatalysts. The efficiency of HER in an alkaline environment is determined by a delicate balance among three crucial factors: the energy required to dissociate water molecules, hydrogen adsorption (H_{ad}) on the catalyst's surface, and the prevention of hydroxyl adsorption (OH_{ad}), often referred to as the poisoning of active sites.

Graphitic carbon nitride (g-C_3N_4) has been extensively studied due to its two-dimensional layered structure and high nitrogen content. However, its poor conductivity limits its application in the field of HER. Therefore, we modified transition metal phosphide on g-C_3N_4 to enhance its conductivity and increase the number of active sites. Additionally, it has been mentioned in previous studies that nickel and cobalt atoms can promote the reaction kinetics of HER in the first and second steps, respectively, thus improving the efficiency of HER in an alkaline electrolyte. Therefore, we synthesized NiCoP/g-C_3N_4 composites in different weight percent to replace the platinum electrode in a 1.0 M KOH electrolyte.

We used Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM) to determine the structure of NiCoP/g-C_3N_4. In addition, Linear Sweep Voltammetry (LSV) and Tafel slope were employed to confirm the electrochemical performance of NiCoP/g-C_3N_4 in HER. The results demostrate that we successfully synthesized g-C_3N_4 and NiCoP/g-C_3N_4 electrocatalysts using a wet chemical method and calcination. Furthermore, the electrochemical results indicate that the addition of 10 wt% NiCoP to g-C_3N_4 significantly improves and exhibits excellent performance in HER in an alkaline electrolyte, reducing the overpotential from 560.7 mV to 338.9 mV and decreasing the Tafel slope from 197.2 mV/dec to 89.6 mV/dec. Then we will use in-situ TEM and in-situ Raman analysis to confirm the contribution and role of the NiCoP alloy on g-C_3N_4 in the hydrogen evolution reaction.

11:40am **TS1-1-MoM-6 Hybrid Inorganic-Organic Nanolayered Thin Films Based on Zns-Ethylenediamine for the Photocatalytic Production of Hydrogen***, L. Cerezo,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; K. Valencia,* Instituto de Ingenieria, Universidad Nacional Autónoma de México*; M. Bizarro, **Sandra E. Rodil (srodil@unam.mx)**, A. Hernández-Gordillo,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

Hybrid ZnS-ethylenediamine nanomaterials ($ZnS(en)_{0.5}$) were produced in a mixed solvent of water, butanol, and ethylenediamine by solvothermal and precipitation methods. The effect of different molar ratios H_2O/Zn^{2+} between 15 and 91 have been investigated by diverse techniques; TG-DSC analysis, X-ray Diffraction, Scanning Electron Microscopy, Infrared, and Diffuse Reflectance spectroscopy. The material was then exfoliated using a combined sonication-illumination process to obtain stacked 2D ZnS nanolayers intercalated with the organic material. After optimization, the as-prepared and exfoliated $ZnS(en)_{0.5}$ nanosheets were prepared as films by spin coating to evaluate the photocatalytic H_2 production reaction. The H_2 evolution reaction was performed in a homemade glass photoreactor containing 30 mL of ethanol-water solution (50:50 vol. %). Eight films were fixed around the internal walls of the glass reactor. The solution was magnetically stirred (at 600 rpm), irradiated with UV light provided by a Hg lamp Pen-ray (of λ=254 nm and I_0 = 4.4 mWcm^{-2}), and placed in the center of the solution into the quartz tube. The system was bubbled with N_2 (to reduce the O_2 pressure), then it was sealed, and the lamp was turned on. The quantity of H_2 was measured using a Shimadzu GC-2014 gas chromatograph and N_2 as the carrier gas. The photocatalytic activity of all the as-prepared and sonicated-irradiated $ZnS(en)_{0.5}$ samples was evaluated by 6 h and 6 cycles. The results showed an enhancement of 7 to 22 times in the H_2 production rate as a function of the synthesis and exfoliation conditions. Intrinsic hydrogen evolution rates up to 76 mmolg^{-1}h^{-1} were achieved using the optimized exfoliated $ZnS(en)_{0.5}$ hybrid material. This value constitutes a record in the community, which is more significant when the lamp's low power is considered. The increased photoactivity was correlated to the degree of exfoliation and the number of stacked ZnS layers in the structure.

12:00pm **TS1-1-MoM-7 One-pot Synthesis of $NiFeCo(OH)_x$@FeOOH@$(NiFeCo)S_x$ Electrocatalyst for Urea Oxidation Reaction***, **Thi Xuyen Nguyen (nguyenxuyen1511@gmail.com)**, Z. Wei, J. Ting,* National Cheng Kung University, Taiwan

Urea oxidation reaction (UOR) is a promising energy-saving avenue for sustainable hydrogen production. However, the 6-electron transfer reaction lead the sluggish kinetic. In this work, an ultrafast, one-step method has been used to synthesize novel $NiFeCo(OH)_x$@FeOOH@$(NiFeCo)S_x$ heterostructure supported on Ni foam as electrocatalyst toward UOR. We demonstrate that the $NiFeCo(OH)_x$@FeOOH@$(NiFeCo)S_x$ exhibits outstanding UOR performance with a low potential of 1.36 V versus reversible hydrogen electrode at a current density of 100 mA cm^{-2}. The catalyst also shows great durability for 50 hours at 10 mA cm^{-2}. The outstanding electrochemical performance is attributed to the high surface area, the faster electron transfer, free of binder, and the synergistic effects of among metallic components.

Monday Afternoon, May 20, 2024

Keynote Lectures
Room Town & Country A - Session KYL1-MoA

Keynote Lecture
Moderator: Johanna Rosen, Linköping University, Sweden

1:00pm **KYL1-MoA-1 Engineered Functional Coatings for Clean Energy and Sustainability Applications***, **Satishchandra Ogale (satishogale@gmail.com)**,* Research Institute for Sustainable Energy, TCG-CREST, Indian Institute of Science Education and Research, India **INVITED**

Functional coatings are key to all clean energy applications including energy harvesting, storage and conservation, and by implication to the emergent issues in the domain of sustainability. Coatings enable intelligent decoupling and independent manipulation of surface and bulk properties; as such, they can allow synergistic integration of various phenomena operating in energy devices on different length scales. This includes management and control of electrical, mechanical, optical, thermal and other properties of interest to realize a desired optimum performance. In this talk, I will outline this scenario by taking examples of recent research in the fields of Batteries, photo/electro-catalysis for clean fuels, hybrid perovskite solar cells, and triboelectric nanogenerators. I will also briefly discuss the scaling up issues of the employed experimental coating methods of interest to industry.

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM2-1-MoA

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes I

Moderators: Thomas Edwards, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, **Olivier Pierron**, Georgia Institute of Technology, USA

1:40pm **CM2-1-MoA-1 Micromechanics During Hydrogen Charging and the Study of Hydrogen Barrier Coatings***, **Maria Jazmin Duarte (j.duarte@mpie.de)**, H. Gopalan, J. Rao, C. Scheu, G. Dehm,* Max-Planck Institut für Eisenforschung GmbH, Germany **INVITED**

Understanding the effects of hydrogen in materials became a pressing topic with the imminent shift towards green technologies, and the use of hydrogen as energy carrier. It is expected that the use of hydrogen will increase in all industries, together with the need for safe transport and storage and consequently the development of new materials and technologies to cope with it. A critical challenge is hydrogen-induced damage, or hydrogen embrittlement, that can cause the sudden failure materials. Hydrogen barrier coatings represent, in this regard, an appealing option to prevent and/or slow down the hydrogen ingress into structural alloys that are susceptible to embrittlement.

To characterize hydrogen and its effects in materials, at the relevant small-scale dimensions where embrittlement initiates, is a substantial yet demanding task. Current studies on hydrogen effects are in their majority limited to post-mortem probes and ex-situ charging, which neglect diffusible hydrogen, its migration and desorption at the analysis time. To rise above these constraints, we designed a novel “back-side” charging approach, to perform micromechanical testing during hydrogen charging [1]. Hydrogen is generated electrochemically at the back-side and diffuses towards the testing (front-side) surface. This unique method allows differentiating between the effects of trapped and mobile hydrogen, and performing well controlled measurements with different hydrogen levels monitored over time to consider hydrogen absorption, diffusion and release.

Using this new method, we unraveled dynamic effects of hydrogen on the mechanical properties of bulk alloys [2], and recently, we successfully applied it to study of hydrogen barrier coatings [3,4]. In this talk, I will present an overview of the technique, together with the case study of an Al_2O_3 hydrogen barrier coating. The hydrogen diffusion on Al_2O_3, ~9 orders of magnitude slower with respect to the used substrate, was measured by Kelvin probe. The mechanical stability of the coating was tested by nanoindentation and nanoscratching during hydrogen loading. The accumulation of hydrogen at the substrate-coating interface reduces the critical load required for cracking and leads to local delamination. Mechanical tests were complemented by atom probe tomography, confirming the presence of hydrogen close to the substrate/coating interface, and transmission electron microscopy, revealing the underlying microstructural changes.

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2:20pm **CM2-1-MoA-3 The Micromechanical Behavior of Magnetron Sputtered TiN/Nb Multilayers***, S. Kagerer, N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria*; L. Zauner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wójcik,* Institute of Materials Science and Technology, TU Wien, Austria*; G. Habler,* Department of Lithospheric Research, University of Vienna, Austria*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; O. Hunold,* Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; **Rainer Hahn (rainer.hahn@tuwien.ac.at)**,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Damage tolerance is a prerequisite for using protective coatings in components subject to long-term stress. Physical Vapor Deposition offers possibilities in coating architectures using combinations of ductile and hard materials, even on the nm scale. However, ductility through dislocation motion is often suppressed on the micro-scale due to geometric limitations, resulting in unusually brittle behavior. In this work, we show a linear dependence between the necessary shear stress for dislocation motion in Nb layers and the overall plastic behavior of micropillar samples.

Computational pre-screening identifies fcc-TiN/bcc-Nb as a promising system providing stable, sharp, and strong interfaces with essentially different elastic moduli. Using a TiN compound target enables a sharp interface without nitrogen cross-contamination. Layer variation and changing the TiN to Nb ratio offer insights into the small-scale plastic behavior using the micropillar compression test. These show a fluent transition from ductile deformation for thick Nb layers to a brittle behavior similar to monolithic TiN upon decreasing the Nb layer thickness.

Combining micromechanical data with TEM analysis of fractured micropillars, we correlate these observations with increased stresses necessary for dislocation motion within the confined layer slip model. Furthermore, we will show the results of unique experiments combining micromechanics with synchrotron nanodiffraction to understand the stress situation in a pillar and describe deformation mechanisms.

2:40pm **CM2-1-MoA-4 Deformation Behaviour and Plasticity in FCC-BCC High Entropy Alloy Nanolaminate Structures***, S. Tsianikas,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; C. Tian,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; C. Guerra-Nuñez,* Swiss Cluster AG, Thun, Switzerland*; J. Michler, X. Maeder, **Amit Sharma (amit.sharma@empa.ch)**,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

In recent years, metal multilayer composites have been the focus of research due to their exceptional mechanical properties. Recent experimental [1-3], theoretical, and modeling [4]studies on multilayers have indicated that the enhancement of both strength and ductility is related both to the structure and properties of the interfaces between the layers, as well as the thicknesses and properties of the individual layers [5]. In spite of the ample literature available on pure metallic nanolaminate structures, the experimental data on compositionally complex alloy multilayers is rather missing.

In this context, here we present recent experimental data on the fabrication and mechanical behavior of nanolaminate FCC-BCC high entropy alloy thin films with interlayer thicknesses 50 nm. The alternating FCC-BCC layers are separated by atomic layer deposition of 2 nm amorphous Al2O3 layer without breaking the vacuumin a new Cluster System combining both ALD and PVD in the same equipment (Swiss Cluster AG). As a model system, FCC-NiCoCrFe and BCC- NiCoCrFe-Al (with Al ~10 at. %) layers with a total thickness of 3 microns is deposited on Si (100) substrate by magnetron sputtering and subsequently tested by micro compression and nanoindentation experiments. The mechanical response of the multi-layered structures is also compared with FCC-BCC multilayer without ALD and single-layer FCC and BCC counterparts. The uniformity in composition and microstructure of interlayers is confirmed by performing S/TEM imaging along the cross-section samples prepared by FIB using a standard liftout procedure. The microcompression experimental results on micro-pillars show a clear effect of interfaces and interlayer size effect on the mechanical response of nanolaminates at different strain rates. The post-mortem electron microscopy investigation provides insight into deformation mechanisms and deformation-induced phase transformations in the individual layers. This first study on multilayer film of two HEA’s will help fundamental studies on high entropy alloys and transformative to other complex systems.

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3:00pm **CM2-1-MoA-5 Characterisation of Hydrogen in Coatings and Thin Films Using Atom Probe and TDMS**, ***Peter Felfer (peter.felfer@fau.de)***, Friedrich-Alexander University, Germany **INVITED**

In the transition to hydrogen as a future energy vector, thin films and coatings play a crucial role. Prominent current applications are coatings for bipolar plates in fuel cells and electrolyzers. In the future, many more applications are likely, such as diffusion barrier and hard coatings on high-strength or wear exposed components such as valves and hydrogen injectors. This is because many base materials of hard coatings have very low hydrogen diffusion coefficients. However, real hard coatings are not single crystals and thus a much better understanding of the interaction of hydrogen with real hard coatings is required. Especially interactions between hydrogen and crystal defects are important as they carry permeation and trigger failures.

To understand these interactions, we are developing new nanoscale characterisation methods. These include the development of an special atom probe with ultra-low hydrogen background for nanoscale imaging and a similar thermal desorption system for analysis of mobile and trapped hydrogen. Both of these systems are based on titanium ultra-high vacuum chambers, drastically reducing the amount of background hydrogen in the vacuum. As a result, very little to no spurious hydrogen appears in the analyses. For the titanium atom probe, this has been demonstrated in voltage pulsing already. This method of analysis is however not suitable for coatings. A laser for the analysis of non-conductive materials such as thin films and coatings is currently being fitted. This unlocks the ability to quantitatively image hydrogen in thin films at the nanoscale and thus shed light on the prermeation mechanisms and interactions with crystal defects. First results will be shown in the talk. In parallel, we are testing the titanium thermal desorption system on thin films, to complement the nanoscale imaging of the atom probe with qualitative and eventually quantitative results on the amounts of mobile and trapped hydrogen in thin films.

4:00pm **CM2-1-MoA-8 Analysis of Stress Field in Nickel Borides Layer Produced by Vickers Indentation Tests in Cross Section: Finite Element Method**, ***T. N. Cabrera-Yacuta (tcabreray1800@alumno.ipn.mx)***, *G. Rodríguez-Castro, A. Meneses-Amador, I. Arzate-Vázquez,* Instituto Politécnico Nacional, Mexico; *O. Morales-Contreras,* Universidad Autónoma de Baja California, Mexico; *I. Campos-Silva, M. Melo-Pérez,* Instituto Politécnico Nacional, Mexico

This research studies numerically the stress fields formed in layers of nickel borides generated by Vickers indentations in cross section at different distances from the layer/substrate interface. Three powder-pack boriding conditions at 850, 900 and 950 °C for 2, 4 and 6 h, respectively, were applied to Inconel 718 for the formation of nickel borides. By means of X-ray diffraction, the Ni_4B_3, Ni_2B, Ni_3B phases were identified. In addition, a hardness range between 23.8 and 26 GPa was determined by Berkovich instrumented indentation, while 280 to 380 GPa for Young's modulus. The stress fields were analyzed by the finite element method using an explicit dynamic analysis. The numerical model is constituted by a Vickers indenter as a discrete and rigid body and by a 3D deformable solid defined through sections. As the layer thickness increases, the system is less sensitive to applied loads and the magnitude of stress fields decreases. Simulation results show that the maximum principal stresses cause cracking in the layer and that the shear stresses are not high enough to cause its delamination. The thicker layer/substrate system offers a higher resistance to cracking formed at 950 °C for 6h.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country C - Session IA1-MoA

Advances in Application Driven Research and Hybrid Systems, Processes and Coatings

Moderators: Ladislav Bardos, Uppsala University, Sweden, **Vikram Bedekar**, Timken Company, USA, **Hana Barankova**, Uppsala University, Sweden

1:40pm **IA1-MoA-1 PVD Thin Film Coating Materials in Semiconductors and Impact of CHIPS Act**, ***Shlok Sundaresh (sshlok91@gmail.com)***, Tosoh SMD, Inc., USA **INVITED**

The CHIPS and Science Act in the United States has led to significant investments in domestic semiconductor manufacturing recently. It details the importance of building a resilient domestic supply chain with funding emphasis on construction, expansion, or modernization of commercial facilities. Semiconductor manufacturing involves numerous processing steps and one of those critical steps is thin film deposition of materials on wafers to form various patterns using PVD technology. Continued pursuit of Moore's law warrants advances in technology, and materials innovation plays a key role for achieving this. PVD sputtering target material developments are extremely critical for the performance of semiconductors as these are used as consumable sources for building them. The CHIPS Act has recognized this providing specific examples of PVD sputtering targets. The talk will thus focus on advances in manufacturing of key materials for sputtering these thin films in semiconductors along with the potential boost from the CHIPS Act towards this technology.

2:20pm **IA1-MoA-3 Production and Characterization of Coating-Substrate Combinations for Ceramic Data Storage Media**, ***Erwin Peck (erwin.peck@tuwien.ac.at)***, TU Wien, Institute of Materials Science and Technology, Austria; *B. Hajas,* TU Wien, Austria; *A. Kirnbauer, L. Kreuziger,* TU Wien, Institute of Materials Science and Technology, Austria; *C. Pflaum,* Ceramic data solutions holding GmbH, Germany; *G. Liedl,* TU Wien, Austria; *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Nowadays data storage and its sustainability is a topic of great importance, not only for cloud providers but also for other companies and even for people in their personal lives. Most of the data stored is referred to as cold data, meaning it is very rarely changed and accessed (e.g. photos, research results). That cold data must be stored, in order to do that, cloud providers run server farms utilizing hard drive discs (HDD). In that way they make the data available on the users' demand. Those server farms need a lot of energy, and the storage capacity is limited. To overcome the issue of needed energy and limited capacity, a new form of storage media is in the focus of our research. By utilizing a certain coating-substrate combination, it is possible to write data into ceramic data carriers using a femtosecond laser. By applying this method, it is possible to write a large amount (1.25 Gigabyte) of data onto a relatively small area (100 cm^2) of the ceramic data carrier. Within our research we analyzed different coating-substrate combinations regarding their mechanical properties and laser ablation characteristics. The coatings investigated were synthesized by magnetron sputtering and argon nitrogen gas mixture using different composite targets e.g. Ti, Cr, TiAlCr, and AlCrNbTaTi. The coatings were deposited on different substrates including sapphire, silicon, glass, and austenitic steel. All the coatings were investigated by XRD showing a single-phase fcc-structure and hardness values ranging from 21 to 33 GPa. After investigating structure and mechanical properties, laser ablation tests were conducted to determine the laser ablation threshold and to find suitable coating-substrate combinations for the aimed application. Furthermore, after writing data into the samples, the samples were tested for their thermal stability, oxidation resistance, and corrosion resistance. These studies prove the exceptional stability and durability of such ceramic data storage media. Once written, storing the data is almost without any energy consumption and such ceramic data carriers would allow to save 99% of the currently used energy for storing such data.

2:40pm **IA1-MoA-4 Microstructure Tuning of MXene ($Ti_3C_2T_x$) Systems for Device Applications**, ***Sangeeta Kale (sangeetakale2004@gmail.com)***, *S. Kale, D. Sable,* Defence Institute of Advanced Technology, India **INVITED**

Titanium Carbide (Ti_3C_2Tx, MXene)materials, which are obtained via systematic removal of Aluminium (Al) layers from Ti_3AlC_2 (MAXene) system, have caught extreme due to their interesting structure of alternating two-edge shared octahedral layers of Ti_6C and highly porous accordion-like structure [1-2]. MXene shows work-function tuneability, porosity variations and varied surface-chemistry interplay, as a function of different synthesis processes [3]. Sensors, Schottky diodes, energy harvesters, and storage devices are envisaged from these materials [4].

Removal of Al layers using hydrofluoric acid (HF) is one common approach to convert MAXene to MXene and create porous structures and active surface states between the inter-digited octahedra structures. On the other hand, along with various other physical processes, pulsed laser deposition (PLD) system yield a range of thin films from stoichiometric high-quality thin films to defect-engineered films.

This talk will explore three different studies: i) bulk studies on the HF-etched-Ti_3AlC_2, yielding a tuneable work-function system, as a function of acid concentration [3] ii) thin films of Carbon-deficient Ti_3AlC_2 using PLD showing semiconducting behaviour on n-Si substrate [4]; and iii) bulk chemical treatment of MXene- molybdenum oxide (MoO_3) [5]

nanocomposites to form a mutually synergistic system for gas (NH_3) sensing at room temperature. Ti_3AlC_2 material show p-type behavior; when deposited on n-Si or Alumina substrate, with strained growth depending upon the substrate; with different termination groups and morphological differences. Chemically synthesized MoO_3-MXenenanocomposites evolve as a synergistic system with improved room-temperature sensing sensitivity of MoO_3 along with a stable, yet highly reactive -O, -OH and -F sites of MXene surface. These studies are further explored for wide range of device applications.

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3:20pm **IA1-MoA-6 Decorative Coatings in Watch Making Industry: From Laboratory to Industry**, ***Joël Matthey (joel.matthey@positivecoating.ch)***, Positive Coating SA, Switzerland; *O. Banakh,* Haute Ecole Arc Ingénierie, Switzerland; *L. Steinmann,* Positive Coating SA, Switzerland

Discovered in the late 1960's, the atomic layer deposition (ALD) is nowadays an established and widespread technology implemented in the industry. Despite being still predominantly applied to semiconductor devices, ALD has recently found its path into new sectors. One of them is the watchmaking niche market where design and reliability play a major role in luxury products. Due to its unique features, ALD offers attractive decorative coatings on complex components and brings innovation in terms of corrosion barrier. It is especially valid when combining the benefits of ALD with other technologies such as magnetron sputtering or electroplating. The aim of this presentation is recounting the extremely fast technology transfer of ALD from laboratory experiments to industrial scale processes. Through results and achievements, the fruitful collaboration between the University of Applied Sciences (HE-ARC) and Positive Coating SA is presented. Throughout the manufacturing sequence, the demanding requirements to obtain high-quality decorative coatings are discussed. When operating ALD technology to color tridimensional parts, simulated and experimental results show that fluidics regularly prevails over ALD process parameters. Furthermore, innovative processes using ALD as a substitute for obsolete technologies are addressed: namely red-gold anti-tarnishing, brass corrosion protection, and two-colored process without masking. Despite successful accomplishments, the technical and industrial challenges to tackle in the coming years are listed to evolve the ALD technology from the semiconductor to the decorative world. The conclusion is illustrated by specimens of luxury watches where decorative coatings highlight superb designs.

4:00pm **IA1-MoA-8 Real-Time Particle Detection for Enhanced Coating Deposition Processes**, ***Sylvain LeCoultre (sylvain.lecoultre@bfh.ch)***, *C. Rieille,* Berner Fachhochschule ALPS, Switzerland **INVITED**

Coatings and the associated vacuum deposition processes will play an increasingly significant role in upcoming technological trends, particularly in the fields of photonics, optics, and Industry 4.0. However, the demands for these applications are imposing increasingly stringent requirements in terms of defect size and particle inclusions within functional layers. This is primarily attributed to the ongoing reduction in the size of device structures. Particles ranging in size from a few hundred nanometers to a few microns have proven to be a major challenge during various deposition processes. These minuscule particles often lead to component failures, resulting in unacceptably high rejection rates. Therefore, the development of deposition technologies capable of monitoring and significantly reducing the incorporation of particles into coatings is essential to access and succeed in these emerging markets.

As part of a multi-partner research project, we are focusing on the development of methods for the detection and real-time monitoring of particles generated in physical vapor deposition (PVD) processes, with particular emphasis on electron beam deposition and sputtering systems. Our research objectives include understanding the different sources of particle generation, whether related to the process, mechanical movements or the cleanliness of the deposition reactor during a production campaign. It also involves determining their size distribution and tracking their velocity in the vacuum environment with spatial and temporal resolution. In addition, we aim to contribute to the development of applicable strategies for eliminating particle sources during the vacuum deposition process, thereby increasing production yields.

To achieve these goals, we are engaged in the research and development of an in situ particle detector solution based on the fundamental principles of visible light beam scattering by particles. The chosen method will be compared with other possible particle detection methods suitable for high vacuum environment. First results on particle detection during different phases of a deposition batch will be presented. In addition, a first insight into the development of a data analysis algorithm that could enable informed decisions to be made for the maintenance of parts to be changed will be discussed.

4:40pm **IA1-MoA-10 Microscopic Characterization of Optical Properties and Film Thickness Using Imaging Spectroscopic Ellipsometry**, ***Hanaul Noh (hanaul@parksystems.com)***, Park Systems, USA

Ellipsometry is a well-known, non-destructive optical method to measure a thin film's thickness and optical properties. It has been widely used to characterize the complex refractive indices of materials or to control the quality of a film's thickness in manufacturing processes. Demands on microscopic characterizations of optical properties have been greatly increased for new materials and structures such as 2D materials, photonic devices, to name a few. Conventional ellipsometry, however, has been restricted to a spatial resolution of several tens of microns due to the spot size limitation. Here, we introduce imaging spectroscopic ellipsometry (ISE), which enables 1-micron lateral resolution, and its application to novel materials and structures. The ISE technique can be extensively used for new materials research and quality control of industrial applications.

5:00pm **IA1-MoA-11 Plasma PVD by Small Spiral Ta Hollow Cathode**, *H. Baránková, N. Suntornwipat,* ***Ladislav Bardos (ladislav.bardos@angstrom.uu.se)***, Uppsala University, Angstrom Laboratory, Sweden

Small spiral hollow cathodes represent interesting options for local plasma processing applications. The radio frequency powered small diameter spiral hollow cathodes made from 0.45 mm diameter Ta wire rolled around 0.5 mm diameter rod have been tested in coatings by physical vapor deposition (PVD) on silicon substrates at gas pressure of 3 Ttorr. Both the reactive PVD of TaN in pure nitrogen and Ta in pure argon resulted in similar rates of about 0.1 µm/min with maximum thickness in the centre of the coating spots. However, central parts of the spots can often contain large amounts of droplets from the melted spiral outlet. At higher RF powers the droplets from the melted sharp tip of the spiral can damage the coating and even melt the Si substrate. The heating of the spiral outlet was more intense in nitrogen than in argon. After 20 min also temperature of the sample table reached 500 °C in nitrogen plasma and up to 400 °C in argon. The sharp cut of the wire at the outlet of spiral can increase the local electric field and intensify eroding of the sample. Similar effect was confirmed by sharp ended stainless-steel medical needle with 1 mm outer diameter used as the hollow cathode.

5:20pm **IA1-MoA-12 Improvement of Surface Adhesion of Fluoropolymer Using Linear Ion Beam Source**, ***Sunghoon Jung (hypess@kims.re.kr)***, *J. Yang, E. Byeon, D. Kim, S. Lee, J. Park,* Korea Institute of Materials Science, Republic of Korea

Fluoropolymers, known for their excellent chemical and thermal resistances and low dielectric constants, play a pivotal role across diverse sectors. The inherent low surface energy of fluoropolymers, however, presents a notable challenge in terms of compatibility with other materials. Traditional methods to integrate fluoropolymers with different substances have largely relied on sodium-based chemical etching. These methods, while effective, often compromise the surface smoothness and are not environmentally sustainable.

In this study, we propose an innovative technique for the surface enhancement of fluoropolymers utilizing a linear ion beam source. By meticulously adjusting the ion beam process parameters, we have developed fluoropolymer bases with significantly improved hydrophilic characteristics. Additionally, this advanced technology has successfully increased the adhesive strength between fluoropolymer surfaces and the copper layers in flexible copper-clad laminates. The adoption of this novel surface modification method holds immense potential, especially in fabricating components for next-generation 6G mobile communication technologies, where strong and reliable adhesion is critically important.

Protective and High-temperature Coatings
Room Palm 5-6 - Session MA2-1-MoA

Thermal and Environmental Barrier Coatings

Moderators: Sabine Faulhaber, University of California, San Diego, USA, **Pantcho Stoyanov**, Concordia University, Canada

1:40pm **MA2-1-MoA-1 Oxygen Permeability, Degradation and Failure Analysis Formulated by Artificial Intelligence of Environmental Barrier Coatings under Adverse Environments Environments**, ***Kuiying Chen (kuiying_chen@hotmail.ca)***, National Research Council of Canada; *K. Lee,* NASA Glenn Research Center, USA **INVITED**

Environmental barrier coatings (EBCs) are typically used to protect ceramic matrix composites (CMCs) under harsh environmental attack such as water vapor-induced recession in aero-engines. Under adverse operations, the oxygen permeability of ytterbium disilicate (YbDS) topcoat and thermally grown oxide (TGO) silicon dioxide in EBCs plays a key role in determining EBCs durability and lifespan. Using physics-based model and thermodynamics along with defect reaction formulae, oxygen permeabilities under both dry oxygen and water vapor conditions, as well as different temperatures, partial pressures and topcoat modifiers, are investigated. Results show that oxygen permeability of YbDS is an order of magnitude larger than that for TGO, indicating TGO hinders the oxidant diffusion stronger, proving to be diffusion rate controlling layer while water vapor strongly increases oxidant permeation.

Solid particle erosion of EBCs was numerically evaluated using mechanics-based formulae where the model parameters are fitted to the test data. The cutting wear, the deformation wear and their relationship with erosion rate are elaborated, while possible mechanisms of erosion rate correlated with EBCs microstructures are explored. The failure mechanisms of EBCs under solid particle erosion processes are discussed combining microstructures, internal cracking within topcoat and external erosion on the topcoat surface. The kinetic behavior of erosion and its effect on life span in EBC are calculated based on the erosion rate obtained from the mechanics-based model.

A non-destructive technique based on convolution neural network (CNN) in deep learning is used to evaluate crack evolution in EBCs. The candidate crack region of interest (ROI) was identified by using Visual Geometry Group Network (VGG) as baseline network, and CNN detector was then used to refine the candidate regions which provide a comprehensive feature for better crack detection. With the information on crack evolution, a fusion lifetime prediction model was used to estimate the remaining lifetime of EBCs system. The performance of the used model on remaining life span was examined.

2:20pm **MA2-1-MoA-3 Effect of Thermal Barrier Coatings on the Thermal Management of a Jet Engine Combustion Chamber**, ***Rodrigue Beaini (rodrigue.beaini@polymtl.ca)***, Polytechnique Montréal, Canada

The aircraft engine industry depends extensively on the advancement of high-performance materials and protective coating systems to enable a continuous ascent in engine performance requirements. In this context, thermal barrier coatings (TBCs) play a key role by providing a protective layer between the hot gases generated by combustion and the underlying metallic components. This allows higher operating temperatures and pressures which results in higher engine efficiency, lower fuel consumption and reduced environmental impact.

TBCs have significant effects on the three primary heat transfer mechanisms, namely convection, conduction and radiation. Considerable efforts have been deployed over the past years to ensure that TBCs possess low thermal conductivity, however, the radiative component has been comparatively largely ignored mainly due to the complexity of the assessment techniques.

This research aims to understand and quantify the impact of high-performance TBCs on the heat management in engine combustion chamber. To accomplish this, a laboratory-scale combustion chamber rig, equipped with a kerosene burner, has been designed and built to mimic aircraft engine conditions. The burner has a tunable power level and can be operated under various flame equivalence ratios, ranging from fuel-lean to rich conditions. Multiple diagnostic tools have been integrated such as thermocouples, heat flux gardon gauges and a multispectral IR camera. A novel approach to solve for emissivity and temperature at high temperatures (> 900°C) using IR imaging was developed, accounting for the multiple reflections inside the combustion chamber and apparent emissivity of a surface in an enclosed cavity. TBCs with different porosities were compared under 5 flame conditions, and an evaluation of the CMAS (calcium-magnesium-alumina-silicate) infiltration inside the pores and its impact on the performance of the TBCs in the combustion chamber was studied. We show and quantify how higher porosity in a TBC leads to a lower temperature on the substrate and how CMAS infiltration increases the temperature locally on the contaminated surface.

Key words:

Thermal barrier coatings (TBC), high temperature, IR imaging, heat transfer, kerosene burner, CMAS

2:40pm **MA2-1-MoA-4 Elevated Temperature Micro-Scale Impact Testing of Thermal Barrier Coatings for Erosion Simulation**, ***Ben Beake (ben@micromaterials.co.uk)***, *J. Roberts,* Micro Materials Ltd, UK; *L. Isern, C. Chalk, J. Nicholls,* Cranfield University, UK

Higher engine operating temperatures will increase the efficiency of gas turbines, saving fuel and reducing CO_2 emissions. However, it is challenging to develop TBC systems with required low thermal conductivity and high resistance to CMAS attack while maintaining or improving their resistance to high temperature impact and erosion. To speed up TBC development a high efficiency impact / erosion test method providing rapid data with small volumes of material is needed.

A novel nano-/micro-mechanical test technique has been developed to experimentally simulate the stochastic nature of the repetitive particulate impacts that occur in high temperature erosion by performing multiple impacts at different locations on the TBC surface [1]. In the randomised impact test, a specified number of individual impacts occur with defined energy and chosen statistical distribution within a set area. Analysis of instantaneous depth vs. time data from every impact shows how residual depth, coefficient of restitution and kinetic energy loss all vary throughout the test to provide evidence of changing damage mechanisms.

Single impacts, repetitive impact and randomised impact tests have been performed at room temperature on EB-PVD 7YSZ and Gadolinium Zirconate coating systems deposited on aluminised Nimonic 75 alloy coupons. Differences in erosion rate and some erosion mechanisms were well replicated in the shorter impact tests compared with erosion test data [2].

The experimental capability has recently been extended to higher temperatures. Tests were performed at 500 °C and 825 °C on the 7YSZ coating with a ~25 µm radius diamond indenter so that each impact only affected a few columns. The depth on initial impact increased with temperature due to the softening of the TBC. Although the final impact depths were greater at higher temperatures, the increase with continued impact was smaller than at room temperature. 7YSZ impact behaviour at 825 °C is compared to previously reported erosion data obtained with a high temperature erosion rig at Cranfield and in the literature [3].

For comparison repetitive impact tests were also performed on a bulk glass (fused silica) at 25, 250, 400, 650 and 825 °C. At higher temperature there was reduced cracking in the multiple impact tests. This was balanced by a gradual softening over the temperature range with the result that the maximum impact depths were found at intermediate temperatures.

[1]UK Patent Application #2217939.4. [2] BD Beake et al, ICMCTF, 2023. [3] RG Wellman, JR Nicholls, J Phys D: Appl Phys. 40 (2007) R293-R305 and Tribol. Int. 41 (2008) 657-662.

3:00pm **MA2-1-MoA-5 Influence of Coating Variables on the Steam Oxidation of Modified Si / $Yb_2Si_2O_7$ Environmental Barrier Coatings**, ***Kang Lee (ken.k.lee@nasa.gov)***, *R. Webster, J. Stuckner, A. Garg, L. Wilson,* NASA Glenn Research Center, USA

Environmental barrier coatings (EBCs) have enabled the implementation of SiC/SiC ceramic matrix composites (CMCs) in gas turbines by protecting CMCs from H_2O. Improving the reliability of CMC components requires long-life EBCs and accurate EBC lifing. Steam oxidation-induced failure is one of the most critical EBC failure modes. NASA has developed modified Si / $Yb_2Si_2O_7$ EBCs by adding dopants such as Al_2O_3, mullite, and/or YAG ($Y_3Al_5O_{12}$) in the $Yb_2Si_2O_7$ topcoat, which reduce the parabolic oxidation rates by more than ten folds in steam. Modified EBCs have shown that oxidation kinetics are highly sensitive to the chemistry of SiO_2 oxide scale, which in turn is influenced by the chemistry of EBC and CMC. Plasma-sprayed silicate coatings contain a large amount of amorphous phase due the rapid quenching of molten droplets during the coating formation. Annealing is often employed to stabilize the EBC phase by crystalizing the amorphous phase prior to oxidation testing. Our study has shown that the effects of annealing on oxidation kinetics are influenced by the EBC chemistry. The current understanding of the complex relationship between selected EBC variables (EBC chemistry, CMC chemistry and annealing condition) and the EBC oxidation behavior will be discussed. Various analytical techniques such as scanning electron microscopy, x-ray diffractometry and transmission electron microscopy are used to help understand the relationship.

3:20pm **MA2-1-MoA-6 Effect of Pre-Oxidation on the Growth of Thermally Grown Oxide and High Temperature Durability of Thermal Barrier Coatings***, **Do Hyun Kim (dohyunkim@kims.re.kr)**, Y. Kang, H. Kwon, Y. Yoo, Y. Park, S. Lee,* Korea Institute of Materials Science, Republic of Korea

Thermal barrier coatings(TBCs) are widely applied in turbine components of modern jet engines and land base gas turbine to reduces the surface temperature of superalloy substrate. Typically, TBCs consist of a ceramic top coat with low thermal conductivity and an Al-rich and oxidation-resistant metallic bond coat. Upon exposure at high temperature over 1,000℃, a protective thermally grown oxide(TGO) layer, predominately α-Al_2O_3, is formed between the top coat and the bond coat, which is considered to be the most crucial factor that determine the durability and life of TBCs system. Therefore, to enhance the durability and reliability of turbine component in high temperature, the formation of a slow growing TGO is substantial.In this study, we performed the pre-oxidation of bond coat to improve the oxidation resistance of bond coat in TBCs. As coated bond coats were pre-oxidized with different heat treatment conditions of atmosphere, low oxygen, and vacuum for the initial formation of TGO, and then TBC samples were exposed to high temperature during isothermal oxidation. The results showed that the growth behavior of the TGO layer on the bond coat surface during isothermal oxidation was significantly changed by the pre-oxidation heat treatments. In order to explore the mechanism of the improved oxidation resistance of pre-oxidized bond coats, the chemical composition, phase constitutes and thickness of TGO(α-Al_2O_3 and spinel oxide), and microstructural changes of bond coat were characterized. Finally, furnace cycle test(FCT) were performed to evaluate the TBC lifetime.

4:00pm **MA2-1-MoA-8 Correlative Microscopy and AI-assisted Image Analysis Synergetic Approach on High Temperature Applications Coatings***, **Hugues Francois-Saint-Cyr (hugues.fsc@thermofisher.com)**,* Thermo Fisher Scientific, USA*; A. Scarpellini,* Thermo Fisher Scientific, Netherlands*; B. Winiarski,* Thermo Fisher Scientific, Czechia*; J. Yorston, R. Pelapur,* Thermo Fisher Scientific, USA

High-temperature applications coatings require the validation of a thorough checklist regarding their chemical and mechanical properties, as-deposited and within the environments they are designed for.

In order to gain a solid understanding of those complex structures, the use of correlative microscopy (CM) workflows provide a structured approach to integrating microscopy and analytical techniques, delivering a multi-dimensional and multi-modal view of the analyzed samples.

Beside the traditional CM approach where X-ray, Electron-beam, and Ion beam techniques complement each other, today engineers and scientists expect additional help from the image analysis (IA) linking those techniques. Namely, Artificial Intelligence (AI)-assisted IA has become a must-have, allowing specialists, and non-specialists alike, to quickly produce results.

Yet, the use of Deep-Learning (DL) as part of this process still requires setting up a meaningful ground truth, using a “human-in-the-loop” AI-assisted training steps to speed up time-to-results.

We illustrate the synergy between CM and AI-assisted IA by treating the example of a Thermal Barrier Coating (TBC) designed as an afterburner liner of a turboramjet engine.

This example was chosen because of its complexity where several ceramic layers (top coats, bond coats) together with metallic substrates were designed to maintain their efficiency at high temperatures and extremely oxidizing environments. Since their performance and durability are intimately linked to their microstructure and composition, the CM workflow encompasses broad ion beam (BIB) milling, Scanning electron microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS), as well as a cross-section using a Focused-Ion Beam (FIB) system.

A clean and easy to characterize cross-section has been automatically prepared by the CleanMill BIB, without user intervention. Combined and always-on SEM/EDS information, automatically delivered by ChemiSEM, has highlighted cracks, oxidation, interfaces, interphases and chemical variations within the various layers. With AI-assisted IA, as long as the specimen preparation is respectful of the sample integrity, researchers can now boost their CM efficiency level.

4:20pm **MA2-1-MoA-9 Characterization of SiO_2 Thermally Grown Oxide Kinetics and Stress Evolution of EBCs with Al-Containing Dopants***, **Michael Lance (lancem@ornl.gov)**, M. Ridley, B. Pint,* Oak Ridge National Laboratory, USA

SiC ceramic matrix composites (CMCs) are desirable for use in combustion environments to achieve higher turbine operating temperatures, although CMCs require environmental barrier coatings (EBCs) for protection from the gas environment. EBC systems are known to primarily fail through coating delamination via growth of a thermally grown oxide (TGO) at the EBC – silicon bond coat interface especially when exposed to steam, which accelerates the TGO growth rate. The TGO undergoes a phase transformation during thermal cycling, which results in stresses that may encourage EBC spallation. Yb-silicate EBCs with mullite and yttrium aluminum garnet (YAG) dopant additions were deposited on SiC substrates with a Si intermediate bond coating and exposed to thermal cycling in flowing steam.The impact of Al dopant additions on the TGO growth rate and the impact of the SiO_2 phase transformation were assessed. Photo-stimulated luminescence spectroscopy (PSLS) was used to characterize the Al-containing phases and to measure stress evolution in the EBC following exposure using the stress-induced peak shift of the R-lines of mullite and YAG. Raman microscopy was used to map the Yb-silicate phases in the EBC and the SiO_2 phases in the TGO following exposure. Wavelength dispersive x-ray spectroscopy (WDS) tracked the concentration of Al in the EBC and the TGO with exposure time. This research was funded by the Advanced Turbine Program, Office of Fossil Energy and Carbon Management, U.S. Department of Energy.

4:40pm **MA2-1-MoA-10 Deposition and Characterization of Si–B–C–N Coatings by HiPIMS/RFMS Co-sputtering***, L. Chang,* Department of Materials Engineering, Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan*; **Yun-Rui Zhang (M12188037@mail2.mcut.edu.tw)**,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan*; Y. Chiang,* International PhD Program in Plasma and Thin Film Technology Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan*; P. Huang, Y. Zhang, B. Jiang,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan*; W. Chen,* Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan

The effect of the B content on the structure, chemical bond character and hardness of Si–B–C–N coatings was systematically studied. The coatings fabrication process included the deposition of an Ti interlayer at a temperature of 400 °C to promote adhesion. Subsequently, Si–B–C–N coatings were prepared by high-power pulsed magnetron and rf magnetron co-sputtering from SiC and B_4C targets in Ar + N_2 gas mixtures. Specifically, we studied the oxidation behavior of the coatings and the evolution of the microstructure, composition, and mechanical properties upon an isothermal oxidation test performed in 15 ppm O_2/Ar at 650°C. We found that an optimized $Si_{26}B_5C_{26}N_{43}$ (at.%) coatings protected the 6wt% Co-WC substrate against oxidation. Stable amorphous structure of Si–B–C–N coatings hindered inward oxidation of O.

5:00pm **MA2-1-MoA-11 Influence of Gas Composition on the Growth Behavior of CVD Processed HfC Coatings for Ultra-high Temperature Application***, **Byung-Hyuk Jun (bhjun@kaeri.re.kr)**, J. Lee, D. Kim, H. Lee,* Korea Atomic Energy Research Institute, Republic of Korea

Refractory metal carbides for thermal protection under ultra-high temperature condition have attracted much attention due to their potential applications in field of advanced aerospace hypersonic vehicles, such as rocket and scramjet components. Hafnium carbide (HfC) has high melting point of 4163 K, low thermal conductivity, high mechanical properties, excellent resistance to oxidation and thermal corrosion, which make it very attractive for coating applications in improving the ablation resistance of carbon/carbon composites in extremely combustion environment. The deposition of coatings was performed in a hot-wall type low pressure CVD furnace under the working pressure of 50 Torr. $HfCl_4$-C_3H_6-H_2-Ar system was applied to deposit HfC coatings on graphite substrate. $HfCl_4$ powder (99.9%) was used as the hafnium source and C_3H_6 instead of CH_4 as the carbon source was used to lower the deposition temperature. H_2 and Ar were used as reducing gas and diluting gas, respectively. In this work, a special powder feeder was designed to supply $HfCl_4$ powder into the reaction zone constantly. The delivery rate of $HfCl_4$ powder was fixed to be about 1 g/min.

The gas composition of $HfCl_4$-C_3H_6-H_2-Ar and deposition temperature were mainly varied to optimize the HfC deposition condition for the purpose of obtaining dense and superior oxidation resistant HfC coatings with high deposition rate. Phase, crystal structure and crystallinity of the HfC coating layers were investigated by X-ray diffraction, and the results showed good crystalline phase with different preferred orientations depending on the deposition condition. Surface morphology and microstructure for the plane and cross-section were observed by a scanning electron microscopy. Raman spectroscopy analysis was performed to find out the C-deficit/-excess of HfC coatings. Quantitative analysis of the HfC composition including impurities inside coating layer was performed using Rutherford backscattering spectrometry (RBS) and elastic recoil detection-time of flight (ERD-TOF) methods. Mechanical properties of the HfC coatings including hardness and Young's modulus were examined with nanoindentor. These results of the growth behavior depending on the deposition parameters including gas composition are described.

5:20pm **MA2-1-MoA-12 Promising SiOxNyCz Coatings for Glass Protection in Aggressive Chemical Media***, **Farah Inoubli (farah.inoubli@cnrs-orleans.fr)**, B. Diallo,* CNRS/Université D'Orleans, France*; K. Topka,* Air Liquide Laboratories, Japan*; T. Sauvage,* CNRS/Université D'Orleans, France*; R. Laloo, V. Turq,* CNRS-CIRIMAT, France*; B. Caussat,* CNRS, France*; N. Pellerin,* CNRS/Université D'Orleans, France

Despite of its high chemical inertia, Glass still interacts when exposed to aqueous solution. This reactivity could be problematic when it concerns particularly food and medicines containers. Thus, one of the biggest challenges that pharmaceutics and food industries are facing consist of limiting this interaction. But how?

In this work, we expose very promoting results on chemical vapour deposited silicon oxycarbonitride coatings in terms of chemical resistance in front of extremely aggressive aqueous solutions.

Different precursors were used leading to various film compositions with tunable properties. Pure silica films were obtained from tetraethylorthosilicate (TEOS) precursor. However, tris(dimethylsilyl)amine (TDMSA) and a novel proprietary trisilylamine-derivative precursor (TSAR) developed and provided by Air Liquide led to silicon oxycarbonitride films with different oxygen, nitrogen and carbon contents, depending on the deposition parameters (precursor, gas flow rates ratios and deposition temperatures td).

Films deposited on the two sides of a flat silicon monocrystalline substrate were subjected to moderately long alteration of one month in a citric acid aqueous solution with pH adjusted to 8 and under thermal conditions of 80°C. Their chemical resistance was assessed by tracking the structural evolution, the changes in the elemental composition and the calculation of the dissolved thickness if it exists. A wide range of characterization techniques were used for this purpose, namely ion beam analysis such as ERDA, RBS and NRA techniques, FTIR spectroscopy, XPS. SEM and AFM imaging techniques were also used to explore the changes occurring to surface state of our layers after exposure to the aqueous solution. Finally, nanoindentation tests have been done to verify any alteration happening to the hardness and the elasticity of the films. Very promising results were found especially for films both concentrated in N and C with a very high corrosion resistance even in such extreme chemical and thermal conditions.

To be closer to reality, pharmaceutical type I glass vials that have been successfully coated with SiOxNyCz thin layer, were tested according to the severe screening conditions of the United States Pharmacopeia USP<1660> chapter. They withstood to the test by preventing the degradation of the glass matrix with an average improvement factor of about 95% compared to a bare vial.

This excellent performance can make these materials a real key for the future of the pharmaceutical industry and can be transferable to multiple applications of surface coating by adaptation of the deposition conditions.

Protective and High-temperature Coatings
Room Town & Country D - Session MA3-2-MoA

Hard and Nanostructured Coatings II

Moderators: Marcus Günther, Robert Bosch GmbH, Germany, **Rainer Hahn**, TU Wien, Institute of Materials Science and Technology, Austria, **Stanislav Haviar**, University of West Bohemia, Czechia, **Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

1:40pm **MA3-2-MoA-1 In Operando Studies of Hard Coatings Using High-Energy X-Ray Diffraction***, **Lina Rogström (lina.rogstrom@liu.se)**,* Linköping University, IFM, Sweden **INVITED**

Wear resistant coatings covering tools used for metal machining experiences tough conditions during application, such as high temperatures and stresses. The detailed nature of tool wear is still largely unknown. One limitation to access the material behavior in the contact zone between the tool and the workpiece is the lack of line-of-sight to this area. The contact zone is in the order of 1 mm^2 and characterized by steep gradients in temperature and stress. The material behavior is thus expected to vary significantly within the contact zone, why local analysis is crucial to understand the relation between material properties and wear behavior. Due to the complex situation, model studies at high temperature and/or pressure do not provide a full understanding of the material behavior, instead, real-time methods to access the contact area are needed.

High-energy x-rays are highly suitable for studies of the hidden contact area between tool and workpiece since they can penetrate several mm of coating and workpiece, and in some case also the substrate material. TiAlN is one of the most common materials for wear resistant coatings. It's favorable mechanical properties at high temperatures are related to the spinodal decomposition of the fcc-TiAlN phase, the details of which successfully have been characterized by high-energy x-ray scattering techniques [1].

To study the tool in real time during metal machining, we have designed a small-scale lathe that can be placed at the high-energy materials science x-ray beamline P07 at Petra III [2]. The lathe allows for longitudinal and orthogonal turning using industrial tooling systems and is built for industrial cutting parameters such as cutting speed and feed. Its design enable access to the tool-chip interface with an x-ray beam during turning. In this presentation, results will be presented from in operando experiments performed (i) with the x-ray beam parallel to the tool flank side and (ii) with the x-ray beam parallel to the tool rake face. The results will be discussed in terms of possibilities and limitations of in operando high-energy x-ray diffraction techniques to access the material behavior in real time during metal machining.

[1] M. Odén, L. Rogström et al., Appl. Phys. Lett. 94, 053114 (2009); L. Rogström et al., Thin Solid Films 520, 5542 (2012); A. Knutsson, L. Rogström et al., J. Appl. Phys. 113, 213518 (2013); N. Norrby, L. Rogström et el., Acta Mater. 73, 205 (2014).

[2] L. Rogström et al., Rev. Sci. Instr., 90, 103901 (2019); L. Rogström et al., Submitted for publication (2023).

2:20pm **MA3-2-MoA-3 Exploring High Temperature Decomposition and Age Hardening in Wurtzite $Ti_{1-X}Al_XN_Y$ (X=0.75 to 0.98, Y=0.82 to 1) Thin Films***, **Janella Mae Rosario Salamania (janella.salamania@secotools.com)**,* Seco Tools AB, Sweden*; F. Bock,* Linköping University, Sweden*; L. Johnson, K. Calamba Kwick, I. Schramm,* Sandvik Coromant, Sweden*; A. Farhadizadeh,* Linköping University, Sweden*; T. Hsu,* Sandvik Coromant, Sweden*; F. Tasnadi, I. Abrikosov, L. Rogström, M. Odén,* Linköping University, Sweden

Wurtzite TiAlN is an intriguing material. It forms in high Al-content industrial grade tool coatings and has potential as a semiconductor with adjustable band gap and can serve as an insulating motif for superconductors and piezoelectric crystals. The characterization of wurtzite TiAlN poses challenges due to the difficulty in synthesizing them as single-phase solid solutions. As a consequence, its thermodynamic and elastic properties are not determined, and the influence of high-temperature and crystallographic defects are unknown.

The research presented here explores the properties and behaviors of wurtzite TiAlN alloys. It covers the challenges associated with synthesizing single-phase solid solutions of wurtzite TiAlN and the unknown thermodynamic, elastic properties, and high-temperature behavior of wurtzite $Ti_{1-x}Al_xN$. First-principles calculations were used to predict a phase diagram encompassing miscibility gaps and spinodals for both cubic and wurtzite $Ti_{1-x}Al_xN$ and the full elasticity tensor. Metastable stoichiometric wurtzite $Ti_{1-x}Al_xN$ films with varying Al content were grown by arc deposition using pulsed bias voltage at a low-duty cycle. High-temperature annealing induced spinodal decomposition in the wurtzite $Ti_{1-x}Al_xN$, resulting in nanoscale compositional modulations and age hardening of 1-2 GPa.

The high-temperature behavior of wurtzite TiAlN is affected by the presence of nitrogen vacancies. To study this in HRSTEM we grew nitrogen-deficient epitaxial wurtzite $Ti_{1-x}Al_xN_yy$ films, which revealed decomposition into intermediary MAX-phases, segregating into c-TiN, w-AlN phases, and TiAl nanoprecipitates after high-temperature annealing. The semi-coherent interfaces between the wurtzite phase and precipitates contribute to age hardening of approximately 4-6 GPa, persisting even after annealing at 1200°C. This study sheds light on how nitrogen vacancies impact the decomposition and mechanical properties of wurtzite TiAlN, offering valuable insights into the behavior of these materials under extreme conditions.

2:40pm **MA3-2-MoA-4 Enhancing the Thermal Stability of $V_{0.25}Al_{0.25}N_{0.50}$ by Oxygen Incorporation**, ***Matej Fekete (fekete@physics.muni.cz)**, D. Neuß, M. Hans, G. Nayak,* RWTH Aachen University, Germany*; Z. Czigány,* Center for Energy Research, Hungary*; S. Karimi Aghda,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; J. Sälker, J. Schneider,* RWTH Aachen University, Germany

Thermal stability and mechanical behavior are key criteria for the design of the next generation of protective coatings. Today, transition metal aluminum nitrides are benchmark coatings on tools and components because of their combined thermal, chemical, and mechanical stability.

To enhance the thermal stability of metastable fcc NaCl-type $V_{0.25}Al_{0.25}N_{0.50}$ coatings, oxygen is integrated into the material system. High power pulsed magnetron sputtering at 450°C is utilized to synthesize metastable fcc $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ coating and reference $V_{0.25}Al_{0.25}N_{0.50}$. Coatings are annealed in a vacuum for 30 minutes to up to 950 °C and 1300 °C for $V_{0.25}Al_{0.25}N_{0.50}$ and $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$, respectively.

Decomposition of V and Al within the nitride phase is observed to start at 800 and 900 °C in $V_{0.25}Al_{0.25}N_{0.50}$ and $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$, respectively, although a formation of a few nm scale aluminum-rich regions in as deposited $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ is detected by atom probe tomography. Selected area electron diffraction data reveal the presence of wurtzite phase in the $V_{0.25}Al_{0.25}N_{0.50}$ annealed at 950 °C, while in $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ annealed at 1300 °C no secondary phase is detected. The thermal stability enhancement by oxygen incorporation can be understood based on the magnitude of the relevant migration barriers as well as the formation energies for vacancies.

3:00pm **MA3-2-MoA-5 Interplay of Substrate Template Effects and Bias Voltage Regarding the Microstructure of Cathodic Arc Evaporated fcc-$Ti_{0.5}Al_{0.5}$N Coatings**, ***Michael Tkadletz (michael.tkadletz@unileoben.ac.at)**, N. Schalk, H. Waldl,* Montanuniversität Leoben, Austria*; B. Sartory, J. Wosik,* Materials Center Leoben Forschung GmbH, Austria*; J. Keckes, J. Todt,* Montanuniversität Leoben, Austria*; M. Burghammer,* European Synchrotron Radiation Facility, France*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; M. Pohler,* Ceratizit Austria GmbH, Austria

Ever since the implementation of hard coatings as wear protection for cutting tools, their microstructural design has been of major interest. While the effect that deposition parameters such as the applied bias voltage or the substrate temperature have on the microstructure are frequently investigated and rather well understood, commonly less attention is paid to the used cemented carbide substrates. Yet properties like their phase composition and carbide grain size significantly influence the resulting coating microstructure. Thus, within this work, substrate template effects are studied on fcc-$Ti_{0.5}Al_{0.5}$N coatings grown by cathodic arc evaporation onto cemented carbide substrates with different WC grain sizes. A systematic variation of the bias voltage resulted in coarse, intermediate and fine grained coating microstructures, which revealed substrate template-based coating growth at low bias voltages and bias dominated coating growth at high bias voltages. In addition, a strong influence of the applied bias voltage on the resulting preferred orientation of the deposited coatings was observed, providing the basis to tailor their fiber texture to <100>, <110> or <111>. Elaborate X-ray diffraction and electron microscopy studies contributed to gain further understanding of the substrate template effects and revealed that implementation of a suitable base layer offers the possibility to effectively prevent any influence of the used substrate on the microstructural evolution of the coating. The obtained results set the fundament to implement tailored microstructures with designed gradients of crystallite size, preferred orientation and consequently mechanical properties, which, as required, either utilize substrate template effects or avoid them.

3:20pm **MA3-2-MoA-6 Decomposition of Single Crystal $Hf_{1-x}Al_xN$ Films Grown at High Temperatures and the Effect on Mechanical Properties**, ***Marcus Lorentzon (marcus.lorentzon@liu.se)**,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; T. Zhu,* Nagoya University, Japan, China*; N. Takata,* Nagoya University, Japan*; S. Nayak, J. Palisaitis, G. Greczynski,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; J. Rosen,* Linköping University, IFM, Sweden*; J. Birch, N. Ghafoor,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

TM-Al-N is an important class of ceramic coating materials that exhibit excellent functional properties. The well-studied TiAlN material system has a high hardness and elastic modulus, good thermal stability, low electrical resistivity, and can also work as diffusion barriers. A similar material, but much less studied, HfAlN offers potential for high-temperature applications thanks to the extreme temperature stability of HfN with a melting point of ~3300°C. In this study we have grown single crystal cubic $Hf_{1-x}Al_xN_y$ on MgO(001) substrates at 800°C using reactive magnetron co-sputtering from elemental Hf and Al targets. A high flux (J_{ion}/J_{metal}>9.2) of low energy (20 eV < E_{ion} <26 eV) ion assistance was employed with -30V substrate bias. An improved crystalline quality of HfAlN films was obtained on adding up to 30 at.% Al. Similar to the case of annealed TiAlN [1], characteristic spinodal decomposition (in this case surface initiated during growth), with striking check-patterned lattice of AlN-rich and HfN-rich domains is observed in lattice-resolved STEM imaging and confirmed by characteristic satellite reflections in synchrotron wide-angle x-ray scattering and in selected area electron diffraction. Thanks to the nanosized compositional modulations, the nanoindentation hardness of the films showed a substantial increase from 26 GPa to 40 GPa on adding 6 to 30 at.% Al in the HfAlN film which is lower concentrations than previously reported [2]. The fracture mechanics of $HfN_{1.22}$ and $Hf_{0.93}Al_{0.07}N_{1.15}$ films studied by micropillar compression testing showed unusual ductile behavior with uniform deformation and substantial strain hardening in the HfN film, contrary to the characteristic catastrophic brittle failure common for ceramics. When alloying with Al the pillars attain catastrophic failure on activation of a single slip system {111}<011>, although a substantially higher stress is required for the shear failure. We will uncover the microscopic origin of the non-characteristic (but beneficial) ductile behavior of $HfN_{1.22}$ in relation to the stoichiometry of the film and point defect formation, in particular anti-site point defects which affect the physical properties of HfN_y[3]. We will highlight the impact of increasing Al content on the size of the check-patterned modulation in the cubic phase films and preliminary results of spinodal decomposition in high Al-content wurtzite $Hf_{0.59}Al_{0.41}N_{1.23}$.

[1] P. H. Mayrhofer *et al.*, *Appl. Phys. Lett.*, vol. 83, no. 10, Sep. 2003

[2]B. Howe *et al.*, *Surface and Coatings Technology*, vol. 202, no. 4, Dec. 2007

[3]H.-S. Seo *et al.*, *Journal of Applied Physics*, vol. 97, no. 8, Apr. 2005

4:00pm **MA3-2-MoA-8 Influence of the Thickness of TiAlSiN on the Thermal Properties as Input Parameter for FEM–Simulation**, *K. Bobzin, C. Kalscheuer, **Nina Stachowski (stachowski@iot.rwth-aachen.de)**,* Surface Engineering Institute (IOT) - RWTH Aachen University, Germany*; B. Breidenstein, B. Bergmann, F. Grzeschik,* Institute of Production Engineering and Machine Tools (IFW) - Leibniz Universität Hannover, Germany

Hard coatings like TiAlN deposited by physical vapor deposition are state of the art for wear and oxidation protection of cutting tools. The cutting performance depends on coating material and process as well as cutting edge microgeometries. Both have an influence on the thermomechanical tool loads resulting in tool wear. Therefore, for a process adapted design, the consideration of the entire system is necessary. One approach to substitute costly machining investigations and save material resources is the use of Finite Elemente (FE)-based chip formation simulations. However, in order to perform these simulations, information about chemical, thermal and physical coating behavior in the temperature range relevant for machining is necessary. In the present study, nanocomposite TiAlSiN coatings with varying coating thicknesses were deposited on cemented carbide tools by HPPMS /dcMS processes. The effect of coating thickness on coating morphology, chemical composition, thermal diffusivity as well as indentation hardness and indentation modulus at θ = 20 °C, θ = 200 °C,θ = 400 °C and θ = 600 °C was analyzed. Additionally, the distribution of the heat, generated during turning 42CrMo4+A was simulated for the coated cutting tool as preliminary step for the chip formation simulation. A columnar morphology with constant chemical composition was determined for all coating variants. While the arithmetic mean value of the coating roughness increased with increasing coating thickness, there was no influence of coating thickness on thermal diffusivity and high temperature coating hardness measurable. Nevertheless, an influence on the tool temperature can be observed in the application behavior in turning tests as well as in the simulation. As a possible cause, the contact conditions change due to a larger cutting edge microgeometry caused by a higher coating thickness, which leads to a higher temperature. The present results show that by dimensioning the tested TiAlSiN hard coating, no influence of the selected coating thickness on properties such as thermal diffusivity and the indentation hardness of the coating has to be considered. An individual adaptation of the coating thickness within a range of 2 µm $\leq d_s \leq$ 6 µm to the tool geometry is therefore easily possible for the investigated TiAlSiN coatings without further modification of the coating.

4:20pm **MA3-2-MoA-9 Non-Reactive Magnetron Sputtering of Ti-Al-N Coatings***, Balint Hajas (balint.hajas@tuwien.ac.at), S. Bermanschläger, T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S. Kolozsvari,* Plansee SE, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Hard protective coatings allow for increased lifetime of machining tools and more versatile applications. Although (Ti,Al)N coatings have a rich history in material science with various improvements for their production, little is known about their non-reactive deposition using Ti-Al-N compound targets.

Reactive deposition of such (Ti,Al)N coatings is studied in-depth, showing that especially for sputtering the resulting microstructure and consequently properties (next to deposition rate) hugely depend on the N_2-partial pressure used. Alternatively, such nitrides can also be prepared non-reactively using nitride compound targets. Here, we use powder metallurgically prepared TiN–AlN compound targets with either 50, 66, or 80 mol% AlN to prepare (Ti,Al)N coatings with various chemical composition through non-reactive DC as well as pulsed DC magnetron sputtering.

The primary investigations focused on how the mechanical properties such as hardness and indentation modulus depend on various deposition conditions, such as sputtering power density, pulse frequency, substrate temperature, substrate-to-target distance, and magnetron condition. Detailed investigations by X-ray diffraction showed that while all (Ti,Al)N coatings obtained from the $(TiN)_{0.5}(AlN)_{0.5}$ target were single-phase face centered cubic (fcc) structured those obtained from the $(TiN)_{0.2}(AlN)_{0.8}$ target were single-phase hexagonal close packed (hcp) wurtzite-type structured. The hcp-phase fraction within the (Ti,Al)N coatings prepared with the $(TiN)_{0.34}(AlN)_{0.66}$ target strongly depends on the deposition conditions. The maximum hardness of the fcc-(Ti,Al)N coatings was ~38.2 GPa, and that of the hcp-(Ti,Al)N coatings was 29.3 GPa. When compared with the reactive deposition of fcc-(Ti,Al)N using similar deposition conditions, the non-reactive route allows for a doubled deposition rate, thus contributing to reducing energy consumption for their preparation.

4:40pm **MA3-2-MoA-10 nc-Sic/a-C Coating for Industrial Applications***, Mojmir Jilek (jilek.jr@shm-cz.cz), O. Zindulka,* SHM sro, Czechia*; Z. Studeny,* University of Defence, Czech Republic

Silicon carbide is one of the hardest materials. In the form of thin layers, it is prepared primarily using CVD technology.

Presented PVD deposition technology (rotary sputtering of segmented targets with high power) allows deposition of SiC based coatings with hardness higher than 60GPa more than 10um thick. This coating shows nanocrystalline composite structure of nc-SiC/a-C.

In cutting test, our coating achieved 60% lifetime compared to thick diamond layer. In contrast to diamond layer, the SiC coating deposition is simpler and coated tools can also be easily reground, or chemically decoated.

5:00pm **MA3-2-MoA-11 Synthesis and Investigation of Crystalline (Ta,Al)B_2 and AlB_2 Thin Films***, Chun Hu (chun.hu@tuwien.ac.at)*[1]*, S. Lin,* Institute of Materials Science and Technology, TU Wien, Austria*; P. Pöllmann, S. Mráz,* RWTH Aachen University, Germany*; T. Wojcik,* Institute of Materials Science and Technology, TU Wien, Austria*; J. Schneider,* RWTH Aachen University, Germany*; N. Koutná, P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Transition metal diboride thin films are promising functional materials with outstanding mechanical properties and thermal stability. However, development of magnetron-sputtered TMB_2 thin films is challenging, since their composition typically deviates from 1:2 metal-to-boron stoichiometry. We developed $(Ta_{1-x}Al_x)B_y$ (x=0–0.48, y=1.23–2.29) thin films and use Ta-Al-B as a model system to study the correlation of microstructure, boron stoichiometry, and mechanical properties implementing experimental and computational materials science. The proposed reasons for off-stoichiometry include angular distribution of the sputtered species, their scattering in the gas phase, re-sputtering and potential evaporation from the grown films for the complex evolution of film compositions, as well as energetic preference for vacancy formation and competing phases as factors for governing the phase constitution. The changes in stoichiometry correlate with the evolution of microstructure, hardness, and elastic modulus. Increasing y from 1.23 to 1.64 leads to the highest hardness (38.8 GPa) among $(Ta_{1-x}Al_x)B_y$ studied here due to promoted formation of the AlB_2-prototype phase. $(Ta_{1-x}Al_x)B_y$ with y=1.97-2.29, corresponding to x up to 0.48, reveal gradually decreasing hardness (down to 31.3 GPa) due to the increased AlB_2-fraction. Complementing the studies for $Ta_{1-x}Al_xB_y$ solid solutions, we also synthesized crystalline AlB_x (x = 1.99, 1.97, 2.27) thin films and studied mechanical properties, thermal stability, and oxidation resistance. This is the first report about AlB_2 thin films with an AlB_2-prototype crystal structure, which is difficult to crystallize due to the close-to-zero formation energy. The $AlB_{2.27}$ thin film shows an exceptional oxidation resistance with an onset temperature of ~1000 °C.

5:20pm **MA3-2-MoA-12 Tribocorrosion and Biocompatibility Analysis of Carbide-derived Carbon (CDC) Surface Modification for Hip Implants***, Yani Sun (ysun98@uic.edu)*[2]*, H. Kanniyappan, M. Karunanidhi, M. Daly, M. McNallan, M. Mathew,* University of Illinois at Chicago, USA

Total hip replacement (THR) suffers from inferior tribocorrosion damage, which may lead to the premature failure of hip implants. Carbide-derived carbon (CDC) is a carbon material derived from carbide precursors. Previously, we have proved that CDC can effectively protect Ti6Al4V from tribocorrosivedamages under open-circuit potential (OCP). Nonetheless, some fundamental properties and biological analysis of CDC are still lacking. Therefore, this study aims to characterize CDC's thickness and biological responses before and after tribocorrosion tests to evaluate CDC as a biomaterial.

CDC was synthesized on the Ti6Al4V disk (11 mm dia x 7 mm) by electrolysis method and confirmed by Raman spectroscopy. Prior to the experiments, the control group Ti6Al4V disks were polished with a mirror finish (Ra<50 nm). The tribocorrosion testing was conducted on a customized reciprocal sliding (±2 mm) tribocorrosion system at 1 Hz for 3600 cycles, which was connected to a Gamry potentiostat. Bovine calf serum (BCS) with 30 g/L proteins was selected as the electrolyte to simulate human body fluid. Three electrodes were used where the working electrode is the sample, the counter electrode is a graphite rod, and the reference electrode is a standard calomel electrode (SCE). The electrochemical protocol was followed with three stages, which are (i) initial stabilization with OCP, (ii) tribocorrosion stage with OCP and potentiostatic (PS), and (iii) final stabilization with OCP. To measure thickness, a diamond saw sectioned the disk, and the ion-milled section was examined under SEM with EDS. MG-63 human osteoblast-like cells were employed to test the cytocompatibility of CDC, and the cell viability was quantified using the Alamar blue assay. Also, the bioactivity of CDC was studied with 4',6-diamidino-2phenylindole (DAPI) staining assay live/dead assay.

As a result, the produced CDC shows an excellent tribocorrosion performance, presenting around 30-fold lower potential variation than Ti6Al4V. Also, the CDC was detected by Raman spectroscopy and found under SEM at the wear scar even after the tribocorrosion test. Interestingly, a carburized layer of approximately 5 um was observed; however, a distinct layer of CDC was not showing under SEM. Regarding the biocompatibility

[1] **Graduate Student Award Finalist**

[2] **Graduate Student Award Finalist**

analysis, no significant difference was found in CDC's cell proliferation compared to the control group Ti6Al4V, and living cells were shown on the sample. According to the amount and the cell shapes, no noticeable difference was found between CDC and the Ti6Al4V, verifying CDC's biocompatibility on the Ti6Al4V substrate.

Functional Thin Films and Surfaces
Room Town & Country A - Session MB1-MoA

Thin Films and Surfaces for Optical Applications

Moderators: Jörg Patscheider, Evatec AG, Switzerland, **Juan Antonio Zapien**, City University of Hong Kong

1:40pm **MB1-MoA-1 Improvements to Multilayer Dielectric Coatings to Enable Internal Confinement Fusion at the National Ignition Facility (NIF)**, ***Colin Harthcock (harthcock1@llnl.gov)***, Lawrence Livermore Laboratory, USA **INVITED**

Since the advent of the laser, it has been theorized that high power lasers could be used as drivers for inertial confinement fusion (ICF), which has the possibility of revolutionizing our energy generation and dependance.As such, the US Department of Energy (DOE) has invested in this technology since the early 1970s, culminating in the building of the National Ignition Facility (NIF) from 1997 - 2009. However, it was quickly understood that the damage to the multilayer dielectric (MLD) interference coatings in the laser system may be key fluence and power limiting components. As such there was a huge, interdisciplinary effort to understand laser matter interactions leading to damage and the associated laser-damage prone precursors and mitigations. In this talk, we will discuss the basic layout of the NIF laser system and the associated coatings. Notable were the issues with the coating of high quality, meter-sized optics with good uniformity and high damage performance – this necessitated the use of electron beam evaporation for many of the high fluence, large aperture mirrors. For each of these MLD coating types, we will discuss the typical issues, typical damage-prone precursors and the associated mitigations. For many of the mirrors, nodular-type defects have been shown to increase the local electric field, absorption and greatly decrease the damage resistance of the coating. Furthermore, we will discuss other defects, such as stoichiometric issues, crystallinity, and nanobubbles.

2:20pm **MB1-MoA-3 Investigating Thin Ito Films for Light Detectors at Cryogenic Temperatures**, ***Giorgio Keppel (giorgio.keppel@lnl.infn.it)***, *O. Azzolini, C. Pira, A. Kotliarenko, M. El Idrissi, D. Ford,* Legnaro National Laboratories, Italian National Institute for Nuclear Physics, Italy

Indium tin oxide (ITO) is a widely used transparent conductive oxide thin film. ITO shows promising behaviours in various applications, such as biosensors, flat panels, and photovoltaics, due to its excellent electrical conductivity and optical transparency [1]. However, there has been limited recent research on its performance and characterisations at low temperatures [2].

In our study, we propose using ITO thin coatings for bolometric light detectors, which are currently used in cryogenic experiments for detecting rare events. It includes the direct detection of dark matter and the search for neutrinoless double-beta decay. Calorimetric detectors provide a straightforward solution for photon detection at cryogenic temperatures (mK) [3]. According to the authors' knowledge, there are preliminary measurements of ITO films below 12 K [2].

In our work, ITO thin films were deposited onto silicon wafers and quartz samples by magnetron sputtering technique using ITO target at room temperature on DC mode. The 90 to 900 nm deposited samples were characterized using X-ray diffractometry (XRD) to study their crystallinity and stoichiometry and scanning electron microscopy (SEM) to analyze their morphology and growth behaviour. The electrical characteristics of the ITO films were evaluated at both room temperature and cryogenic temperature (77 K and 4.2 K) using an upgraded resistive measurement system [4].

As a result, we present a study on the electrical properties of thin ITO coatings at cryogenic temperatures below 12 K in correlation with their optical properties. Additionally, we demonstrate the initial findings on developing silicon-based light detectors that incorporate ITO films and utilize the Neganov-Luke effect.

[1] Aydın, Elif Burcu et al. TrAC Trends in Analytical Chemistry, 97(2017): 309-315.

[2]Pawlak, et al., P. Sensors,17(2017),51.

[3] Novati, V., et al. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 940, (2019) 320-327.

[4]D. Ford et al.. LNL Annual Report (2022),162.

2:40pm **MB1-MoA-4 Key Success Factor of Solid-Phase Crystallization Through Postannealing Under Atmospheric Conditions on Amorphous Conductive W-Doped In_2O_3 Ultra-Thin Films with Thicknesses of Less Than 10 Nm**, ***Rajasekaran Palani (palani.rajasekaran@kochi-tech.ac.jp)***, *T. Yamamoto,* Kochi University of Technology, Research Institute, Japan; *M. Maehara, Y. Okada, K. Kinoshita,* Sumitomo Heavy Industries, Ltd., Industrial Equipment Division, Japan

In this work, for wide applications of W-doped In_2O_3 (IWO) films, we investigate the structural, electrical, and optical properties of amorphous and polycrystalline W-doped In_2O_3 (WO_3: W content of 1 wt. % (=0.6 at.%)) ultra-thin films. First, amorphous (*a*-IWO) films with thicknesses (*t*) ranging from 5 to 50 nm were deposited on glass substrates without intentionally heating of the substrates by reactive plasma deposition with dc arc discharge. Then, under atmosphere-condition for 30 min, we carried out the solid-phase crystallization (SPC) of *a*-IWO films at different temperatures of 200 and 250ºC. Experimental results yield that the postannealing temperature is a key factor to improve the properties of polycrystalline IWO (*p*-IWO) films. Concerning the effects of the SPC on structural properties of ultra-thin IWO films, we used in-plane X-ray diffraction (XRD: Rigaku SmartLab) which is very effective to study the microstructure characterization of the thin films. Electrical and optical properties were determined by Hall-effect (Nanometrics HL5500PC) and UV-Vis-NIR spectrophotometer measurements (Hitachi U-4100), respectively. We observed not sharp diffraction peaks but just broad ones in case of as-deposited IWO films with *t* of a 10 nm or less. As a result of the SPC concerning IWO films with *t* of 7 and 10 nm, we found the polycrystallized IWO films, regardless of the postannealing temperature (T_p); those films have a cubic bixbyite crystal structure (space group of *Ia*-3). In-plane XRD measurement results showed as follows: for 10-nm-thick *p*-IWO films at different T_p, we found that an increase in T_p promoted (111) directed orientation, whereas we observed no above effect of T_p for 7-nm-thick *p*-IWO films. Hall-effect-measurement results showed that the transformation from *a*- to *p*-IWO films reduces carrier concentration (n_e) together with enhanced Hall mobility (μ_H) at any given *t*. This implies that SPC decreased the density of *n*-type donor defects, oxygen vacancies. The analysis of the data of optical absorption coefficients indicated the distinct difference in the effects of T_p on the electrical and structural properties between 7- and 10-nm thick *p*-IWO films. For 10-nm-thick IWO films, an increase in T_p enhanced the crystallographic (111) orientation between grains. On the other hand, for 7-nm-thick IWO films, the above increase remarkably improved the lattice order in the grains: We, thereby, have achieved μ_H of 60.5 $cm^2/(Vs)$ and n_e of 0.81×10^{20} cm^{-3} higher than those of 10-nm IWO films. In order to tailor electrical properties combined with optical properties of IWO films, the optimization of postannealing is essential.

4:00pm **MB1-MoA-8 Multifunctional Bragg-Reflector-Enhanced Electrochromic Devices with Adjustable Optical Performance**, *M. Crouan, B. Baloukas, O. Zabeida, J. Klemberg-Sapieha,* ***Ludvik Martinu (ludvik.martinu@polymtl.ca)***, Polytechnique Montréal, Canada

Electrochromic (EC) all-solid-state devices (ASSDs) are of great interest in various industrial applications, such as smart glass for buildings, airplane windows, lenses, and mirrors. These devices possess allow one to dynamically change their optical properties, transitioning from a bleached state to a colored state through a redox reaction following the application of a low voltage. Due to the inherent properties of EC materials, ASSDs exhibit significant absorption and transmission modulation and, as a result, a limited capacity for reflection modulation. Yet, achieving a reflection increase upon coloration can offer new functionalities in terms of aesthetics and the development of innovative optical filters.

The implementation of EC Bragg mirrors (ECBM) using WO_3 and ITO bilayers in an ASSD hence holds significant promise as a means of reaching a substantial increase in reflection at specific wavelengths during coloration. In this work, we compared a conventional ASSDs with various ECBM configurations incorporated into an ASSD. Specifically, via a comprehensive optical modeling study, we designed an ASSD which changes from a transparent anti-reflective state to a mirror-like opaque state within the visible spectrum. The fabricated antireflective ASSD with 2-bilayers of WO_3/ITO displayed an increase in R_{lum} from 1.4% in the bleached state to 8.9% in the colored state. By minimizing the constraints on the antireflective properties, we achieved a reflection increase of 19.8% upon coloration, opening new possibilities for dynamic optical interference filters.

4:20pm **MB1-MoA-9 Quantitative Strong Optical Nearfield Enhancement by Coupling Bloch Surface Wave Packet and Localized Surface Plasmon of Aunp for Surface-Enhanced Raman Spectroscopy**, *M. Phoo,* ***Juan Antonio Zapien (apjazs@cityu.edu.hk),*** City University of Hong Kong

We present the ultra-high near-field enhancement (EF~10^8) that results from exciting Localized Surface Plasmon in gold nanoparticles (AuNP) using the high-Q photonic resonance from a Bloch Surface Wave (BSW) stack. The BSW stack is composed of a16 dielectric SiO_2 and Ta_2O_5 layers with total thickness ~2 um. Optical characterization is performed by spectroscopic ellipsometry (SE) in the spectral range (400-1200 nm). Excellent agreement between the SE data and modelling from i) standard Fresnel equations and matrix transfer formalism (FE- model) and ii) Finite-Difference Time-Domain (FDTD) method demonstrate efficient coupling between the photonic (BSW) and plasmonic (LSP) modes. Furthermore, the BSW stack enables high photonic confinement acting as an energy reservoir inside the multilayer stack; the high Q, ~5000, BSW photonic mode efficiently pumps the AuNP LSP, resulting in total near-field enhancement ~10^8. Our experimental results and modelling demonstrate dual sensing with chemical identification, from Surface-Enhanced Raman Scattering (SERS), with simultaneous quantification, via BSW sensing.

4:40pm **MB1-MoA-10 Strongly Thermochromic VO_2-Based Smart Coatings for Room-Temperature Applications Prepared on Glass**, ***Michal Kaufman (mkaufman@kfy.zcu.cz)****, J. Vlček, J. Houška, S. Farrukh,* University of West Bohemia, Czechia

Vanadium dioxide (VO_2) exhibits a reversible phase transition from a low-temperature monoclinic VO_2 (M1) semiconducting phase to a high-temperature tetragonal VO_2 (R) metallic phase at a transition temperature of approximately 68 °C for the bulk material. The automatic response to temperature and the abrupt decrease of infrared transmittance without attenuation of luminous transmittance in the metallic state make VO_2-based coatings a promising candidate for thermochromic smart windows reducing the energy consumption of buildings.

To meet the requirements for large-scale implementation on building glass, VO_2-based coatings should satisfy the following strict criteria simultaneously: a deposition temperature close to 300 °C, a transition temperature close to 25 °C, an integral luminous transmittance T_{lum} > 60%, a modulation of the solar energy transmittance ΔT_{sol} > 10%, long-term environmental stability, and a more appealing color than yellowish or brownish colors in transmission.

The paper deals with a scalable sputter deposition technique for the preparation of strongly thermochromic YSZ/W and Sr co-doped VO_2/SiO_2 coatings on standard soda-lime glass at a relatively low substrate surface temperature (320 °C) and without any substrate bias voltage. The W and Sr co-doped VO_2 layers were deposited using a controlled high-power impulse magnetron sputtering of a V-W target combined with a simultaneous pulsed DC magnetron sputtering of a Sr target in argon-oxygen gas mixtures. The bottom antireflection Y-stabilized ZrO_2 (YSZ) layers were deposited using a controlled reactive high-power impulse magnetron sputtering of a Zr-Y target, while the top antireflection SiO_2 layers were deposited using a reactive mid-frequency bipolar dual magnetron sputtering of two Si targets.

The fundamental principles of this technique, and the design, structure and optical properties of the thermochromic coatings are presented. The coatings exhibit a transition temperature of 22-25 °C with an integral luminous transmittance T_{lum} up to 64% (at almost the same luminous transmittance above the transition temperature) and ΔT_{sol} =11%. Such a combination of properties, together with the relatively low deposition temperature (320 °C), has not yet been published by other teams for thermochromic VO_2-based coatings prepared by a scalable deposition technique compatible with the existing magnetron sputter systems in glass production lines and in large-scale roll-to-roll deposition devices.

5:00pm **MB1-MoA-11 Nanostructured Metal Thin Films with Enhanced Mechano-Optical Properties for Solar Radiation Isolation***, A. Xomalis,* NTNU Trondheim, Norway*;* ***Barbara Putz (barbara.putz@empa.ch)****,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; X. Zheng,* KU Leuven, Belgium*; A. Groetsch,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; G. Vandenbosch,* KU Leuven, Belgium*; J. Michler, J. Schwiedrzik,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Thin metal films on flexible polymer substrates are used widely in satellite missions as they show extreme thermal isolation and high interface strength at a minimum specific weight. Here, we show how nano-structuring of Al thin films on polyimide can create plasmon resonances, allowing interplay with visible radiation while reflecting the unwanted infrared responsible for device heating. Focused ion beam milling was used to create areas of a repetitive ring pattern in Al thin films (100 nm thickness), with variations of the ring diameter (1.9 and 2.2 µm), periodicity (2.4 and 3.1 µm) and trench thickness (partially or fully perforation the Al films). Uniaxial tensile tests with *in situ* optical measurements reveal that the nano-patterning of the thin films results in crack-free domains, leading to resilient optical resonances withstanding applied strains up to ∼20%. We also perform nanoscale electromagnetic and mechanical simulations to evaluate the thin films' mechano-optical behaviour. Our simulations well fit the experimental positions of strain localization, resulting in crack formation and thin film damage. The central parts of the ring pattern in the structured thin films remain crack-free at applied strains exceeding the crack onset strain of unpatterned, continuous coatings by >84%. Fragmentation analysis shows how, in contrast to unpatterned films, the developing crack pattern and spacing can be tailored by choosing appropriate structural parameters. Such small-footprint, resilient, and lightweight devices are highly desirable for heat rejection, communications, and spectroscopies in harsh environments.

Tribology and Mechanics of Coatings and Surfaces
Room Palm 1-2 - Session MC1-2-MoA

Friction, Wear, Lubrication Effects, and Modeling II

Moderators: Michael Chandross, Sandia National Laboratories, USA, **Giovanni Ramirez**, Oxford Instruments, USA

1:40pm **MC1-2-MoA-1 Thermally Sprayed Hardmetal Coatings - Strategies for Replacement of WC-Co(Cr)**, ***Lutz-Michael Berger (Lutz-Michael.Berger@ikts.fraunhofer.de)****, J. Pötschke, S. Conze,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany **INVITED**

In 2023 the 100th anniversary of the invention of WC-Co was celebrated. It is one of the most successful composite materials ever and is applied as a sintered tool and wear protection, as well as a coating material. The reason for this success, are the extraordinary properties of WC, but also the nearly perfect interaction with Co as the binder metal. However, there are significant differences between sintered bodies and thermally sprayed WC-Co. These differences are the reason why nowadays WC-10Co4Cr is the standard material composition for highly wear-resistant coatings for service. As thermally sprayed coatings are serving more often at high temperatures and in corrosive environments, Cr_3C_2-NiCr is established as a second successful composite. The standard compositions have been developed on an empirical base, and have changed only little for decades, while there were significant changes in the feedstock powder production technologies.

However, there are currently several challenges which require to create alternatives with respect to environmental and health safety, supply, and of course technical performance. Reasons are the need to replace Co as the binder due to health and environmental issues but also the classification of both Co and W as critical raw materials.

Different possible strategies for partial (the binder only) and full WC-Co(Cr) replacement are currently investigated and will be discussed in detail. Thus, different complex binder alloys for WC-based thermal spray coatings are explored and compared with other alternative binder materials such as Ni or Fe-based alloys.

With respect to the full replacement of WC-Co(Cr) alternative hard materials are investigated:

- Cr_3C_2 with additions of WC in order to improve the low-temperature wear properties of Cr_3C_2-NiCr

- TiC/TiCN or NbC/NbCN as cubic hard materials with Ni- or Fe-based alloy binders
- High-entropy carbides as the most recent development in this field.

One of the advantages of these alternative hard materials is their better compatibility with Co-free binder materials.

In order to develop effective coating material compositions, it is necessary to have a reliable approach for their selection. By using sintering bodies for this purpose, the interactions of the hard and the binder phase can be studied, and the potential of individual novel compositions can be evaluated.

2:20pm **MC1-2-MoA-3 Tribological Properties of Metallic Surfaces Obtained by 3D Additive Manufacturing (Laser Metal Deposition Process), for Repairing Applications***, T. ZURCHER, E. CHARKALUK,* Ecole Polytechnique, France*; **Vincent FRIDRICI (vincent.fridrici@ec-lyon.fr)**,* Ecole Centrale de Lyon - LTDS, France

The repair of worn metal parts represents a significant strategic challenge for industries. These repairs must be both economically and environmentally advantageous. Many ”conventional” repair processes are still used today to meet this need. However, most of these processes are not well-suited for performing fine repairs with complex geometries. An additive manufacturing (AM) process belonging to the Direct Energy Deposition family, called Laser Metal Deposition (LMD), addresses this specific need. This involves putting next to each other and stacking small weld joints called ”beads”, melting metal powder by projecting it under the focal point of a laser. The small diameter of the laser beam and the guidance of the nozzle’s movement by numerical control enable high-resolution repairs. The study of the mechanical properties of parts/repairs from this AM process has already been extensively addressed in the literature. However, very few studies have focused on their wear resistance property. This work thus focuses on the experimental study of the wear resistance of parts repaired by the LMD process, with the ultimate goal of providing methodological recommendations leading to repairs with good wear resistance. Inconel 718 and 316L stainless steel are studied in the case of a dry sliding flat-on-flat contact with reciprocating motion, under different conditions.

Through a detailed analysis of the wear of these repairs, a better understanding of their tribological behavior was acquired. Various wear modes based on tribological parameters, materials properties and LMD process parameters were highlighted. Furthermore, these studies have shown that the repair strategy and sliding direction do not significantly impact their wear resistance. Studies of residual stresses before and after wear tests have demonstrated that the inherent residual stresses of this process have a non-significant impact on wear. These studies have also shown that wear results are highly dependent on the repair material used and the tribological conditions applied on the repairs. Notably, it has been observed that 316L steel exhibits better wear resistance under similar tribological conditions. However, it has been demonstrated that IN718 repairs have a more competitive wear resistance compared to conventionally manufactured parts composed of the same alloy.

2:40pm **MC1-2-MoA-4 Improved Anti-Friction of Diamond-Like Carbon Incorporating Titanium***, **Jae-Il Kim (jaeil@kims.re.kr)**, Y. Jang, J. Kim,* Korea Institute of Materials Science (KIMS), Republic of Korea*; N. Umehara,* Nagoya University, Japan

Diamond-like carbon (DLC) is commonly introduced as a solid lubricant and anti-wear coating. On the other hand, the tribological performance of DLC is highly dependent on the intercontact with the mating material, which may result in high friction. The lubricity of DLCs is believed to be due to the carbonaceous transition layer formed on the mating materials. Industrially, steel- or copper-based alloys have been used as counterparts against DLCs to date, however, it is hard to achieve low friction in tribopairs with them due to the difficulty in forming a carbonaceous transfer layer.

We attempted to solve this problem by doping highly reactive titanium into DLC. Among many transition metals, titanium in particular has a large number of *d*-orbital vacancies, which can easily interact with the 2*p*-orbital of carbon. Therefore, we introduced the idea that this chemical property can promote the formation of a carbonaceous transfer layer, which we aimed to form a low-friction C/C contact interface to enhance the lubricity of the DLC/steel tribopair.

Ti-doped DLC was fabricated by co-depositing DLC with a filter cathode vacuum arc method and Ti with an unbalanced magnetron sputter. The tribological performance as a function of Ti concentration was investigated, and the tribofilms formed on the counterparts were chemically characterized. In conclusion, we report that the Ti-doped DLC exhibited enhanced long-term low-friction characteristic and superlubricity in various environments.

3:00pm **MC1-2-MoA-5 Tribological Study of Magnetron Spurrered W-S-(C) Thin Films Sliding Against Aluminium at High Temperatures***, **Todor Vuchkov (todor.vuchkov@ipn.pt)**, S. Jahan Sunny, A. Cavaleiro,* University of Coimbra, Portugal

Forming of Aluminium is often performed at elevated temperatures due to its poor formability and springback at room temperature. Forming of aluminium at elevated temperatures causes significant tribological issues like adhesive wear and galling, i.e. there can be significant material transfer from the workpiece to the tool/die. Due to the harsh conditions (temperatures up to 500°C), liquid lubricants cannot be utilized and solid lubricants can be an alternative. Self-lubricating thin films deposited by magnetron sputtering are good candidates for alleviating this issue, especially the ones containing transition metal dichalcogenides since they provide good lubrication in environments that lack humidity. In this study we deposited three types of films containing transition metal dichalcogenides (TMDs), of which one consisted only of WS_x and two films were alloyed with carbon (~27 and 35 at. % of carbon). We utilized various techniques for characterizing the physico-chemical properties of the deposited films like scanning electron microscopy, X-ray diffraction at elevated temperature and thermo-gravimetric analysis. The mechanical properties were assessed using scratch testing and nanoindenation. Tribological testing was performed against aluminium (1000 series) balls at room temperature, 200° and 400°C. The unalloyed WS coating had more porous columnar morphology while the carbon-alloyed ones showed increase compactness with reduced intercolumnar porosity. The thermal analysis indicated that the maximum operating temperature should be ~400-430 °C, for the pure WS coating, and a higher value of ~480-490°C for the carbon alloyed films. The thin films had good adherence to the tool steel substrates with an Lc2 critical load of 20-30 N and no gross delamination up to 70 N of load. The tribological results indicate that the unalloyed WS coating is the best solution for friction reduction against aluminium at the examined testing temperatures (up to 400°C). The carbon alloyed coatings also provided friction reduction but friction instabilities were observed and the film with the highest carbon content suffered excessive galling at 400°C. In terms of wear, the unalloyed WS coating generally suffered more wear compared to the other coatings. The results of the study present a high potential of the TMD-based sputtered coatings for applications involving sliding against aluminium at elevated temperatures.

4:00pm **MC1-2-MoA-8 Understanding the Tribological Mechanisms of TiO_2 Thin Layers: The Role of Composition and Structure of the Oxide Layer on Wear in Relation to Color Variation***, **Sarah Marion (sarah.marion@emse.fr)**, M. LENCI,* Mines Saint-Etienne, Université de Lyon, CNRS, France*; C. MINFRAY, V. FRIDRICI,* Laboratoire de Tribologie et Dynamique des Systèmes, Université de Lyon, Ecole Centrale de Lyon, France*; L. DUBOST,* IREIS, HEF group, France*; J. FAUCHEU, R. CHARRIERE,* Mines Saint-Etienne, Université de Lyon, CNRS, France

Although titanium is not a noble material, it is attracting more and more attention in the luxury industry (jewelry, watches, packaging) because of its lightness, hypoallergenic properties and, above all, the many colors it can produce when coated with a thin layer of TiO_2. However, its use in luxury goods is currently limited because its colors do not last very long. The wear resistance of thin colored layers of TiO_2, and especially the preservation of the original color, is an important issue for luxury jewelry.

The degradation of the color of anodized titanium is well studied in the field of architecture [1,2] and in this case, is mainly linked to a change of the thickness of the TiO_2 layer in the presence of acid rain. In addition, Diamanti et al [3] have shown that prolonged rubbing in an artificial sweat solution causes partial discoloration of the anodized titanium surface. However, the origin of the color degradation in this case has not been identified. The interferential origin of the color makes it particularly sensitive to a variation in thickness, but also to a variation in the chemical composition and internal structure of the oxide layer through a change of the refractive index.

The aim of this study is therefore to compare the wear resistance of thin TiO_2 layers produced by different processes. One is to anodize a Ti-6Al-4V substrate and the other is to deposit a TiO_2 layer by magnetron sputtering on a Ti-6Al-4V substrate. The influence of the chemical composition, crystallinity, internal morphology and thickness of the oxide layer on tribological behavior is studied and correlated with the change in color observed during dry rubbing and rubbing in the presence of artificial sweat.

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[2] M. Kaneko, M. Kimura, K. Tokuno, Corros. Sci. 52 (2010) 1889-1896.
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4:20pm **MC1-2-MoA-9 Tribocorrosion Behaviours of TiZrNbTaFeC High Entropy Carbide Coatings by Superimposed HiPIMS and MF System**, ***Ismail Rahmadtulloh (ismailrahmadtulloh2@gmail.com)**, C. Wang,* National Taiwan University of Science and Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan

Recently, the tribocorrosion issue has become crucial in various industry applications due to its impact on the failure and degradation of materials. In this study, TiZrNbTaFeC high entropy alloy carbide coatings (HEACCs) were deposited on the surface of AISI 52100 using a superimposed high power impulse magnetron sputtering (HiPIMS) and medium-frequency (MF) sputtering system. We observed an amorphous-like phase in coatings containing carbon within the range of 0 to 16.53 at.%. However, a transition to an FCC structure occurred when the carbon content increased to 32.4 and 35.8 at.%. The highest average hardness of 22.1 GPa was observed for HEAC#14 with a carbon content of 32.4 at.%. The coatings were immersed in a 0.5 H2SO4 solution at room temperature. At static corrosion, the carbon-free TiZrNbTaFe coating has a higher polarization ratio of 6.53×10^4 Ωcm^2 followed by HEAC#18 (35.8 at.% C) of 3.71×10^4 Ωcm^2, indicating excellent corrosion resistance. For the tribocorrosion tests, the coatings were subjected to 1 N load using a pin-on-disk tribometer at a sliding speed of 50 rpm. The wear rate and details of tribocorrosion studies on TiZrNbTaFeC high entropy alloy carbide coatings will be explored.

4:40pm **MC1-2-MoA-10 Friction and Wear of a-C:H and a-C:H:Si Coatings Sliding Against Different Counterpart Materials Under Dry and Moist Environments**, ***Francisco A. Delfin (delfinf@frcu.utn.edu.ar)**,* National University of Technology, Regional Faculty of Concepción del Uruguay (UTN – FRCU), Argentina*; J. Jeoffrey,* Universiti Teknologi Petronas, Malaysia*; M. Schachinger, C. Forsich,* University of Applied Sciences Upper Austria*; S. Brühl,* National University of Technology, Regional Faculty of Concepción del Uruguay (UTN – FRCU), Argentina*; D. Heim,* University of Applied Sciences Upper Austria

The self-lubricating effect of DLC coatings is a very well-known feature, although they have yet to occupy a substantially influential position in mainstream tribological applications. This objective is increasingly critical due to the escalating worldwide focus on achieving energy efficiency, lowering fuel consumption and cutting environmentally harmful emissions. To reach these milestones, a deeper understanding of DLC coatings is required, namely regarding the intricate relationship of friction and wear rates within diverse tribosystems, where parameters such as relative humidity and the material of the counter body show decisive influence. In this work, DLC coatings were deposited using a modified commercially available PA-CVD system on AISI 4140 steel. Two kind of coatings were produced, a-C:H and a-C:H:Si, at temperatures of 450 °C and 550 °C. Process gas consisted of a mixture of argon, acetylene, and HMDSO as silicon precursor. Characterization was carried out by means of nanoindentation, Raman spectroscopy, as well as GDOES and EDX. Tribological behavior was evaluated by means of Pin-on-Disk, using the coated sample as the disk, a 12 N normal load, a speed of 0.4 m/s and a total sliding distance of 2000 m. Counterparts were 6 mm balls, of which three different materials were used: AISI 52100 bearing steel, Al_2O_3 and Si_3N_4. Test chamber was conditioned using forced air recirculation and beakers containing either water or regenerated silica gel to create a humid or a dry environment, respectively. Friction coefficient was registered during the entire test. The wear track was evaluated with optical and confocal microscopy, as well as SEM/EDX and Raman spectroscopy. Hardness and elastic modulus increased with deposition temperature, and the values were doubled with silicon doping. However, a lower friction coefficient and wear volume loss were found in Si-free samples. In general, the coatings showed varied responses to the different environments and counterparts: a-C:H showed oxidation with higher humidity, whereas a-C:H:Si exhibited high wear in the drier ambient, producing several peaks in the friction coefficient during the test. The steel counterpart exhibited a lubricious oxide layer that helped reduce the friction coefficient, thus performing better in the humid environment. The Si_3N_4 counterpart showed the highest adhesion when sliding against a-C:H:Si, although a rather low friction coefficient and wear was shown when testing the Si-free samples.

5:00pm **MC1-2-MoA-11 Evaluation of the Sliding Wear Performance of Binary CrN and Nanocomposite CrSiCN Coatings in Arctic Environments**, *N. D'Attilio, **Forest Thompson (forest.thompson@sdsmt.edu)**, N. Madden,* South Dakota School of Mines and Technology, USA*; E. Asenath-Smith,* US Army Corps of Engineers Cold Regions Research and Engineering Laboratory, USA*; G. Crawford,* South Dakota School of Mines and Technology, USA

The efficiency, service lifetime, and durability of engineering components operating in the severe cold and dry environments found in Earth's polar regions can potentially be improved using protective coatings based on transition metal nitrides. However, the tribochemical wear behavior of these ceramic materials is particularly sensitive to operating conditions. Thus, there is a need to understand the influence of arctic environments on the sliding wear performance of these coatings. In this work, binary CrN, columnar CrSiCN, and glassy CrSiCN coatings were produced using filament-assisted reactive magnetron sputter deposition. The coatings were characterized using energy dispersive X-ray spectroscopy, X-ray diffraction, transmission electron microscopy, and atomic force microscopy. The mechanical properties of the coatings were tested using nanoindentation and the wettability of the coatings was determined using tilting-base contact angle goniometry. A ball-on-flat tribometer equipped with an active cooling stage and dry air source was used to assess the tribological performance of the coatings under various combinations of coating surface temperatures and environmental dewpoints. Ultimately, the microstructure and amorphous phase content was found to play a major role in the performance of CrN-based coatings in these environments. The wear resistance of all coating types was found to suffer under a combination of low surface temperature (-20 °C) and low dewpoint (-33 °C), while their frictional behavior under frosting conditions (-20 °C surface temperature, -10 °C dewpoint) was primarily controlled by the presence of ice at the contact zone.

5:20pm **MC1-2-MoA-12 Designing Hydrogen-Free Thick Diamond Like Multilayer Carbon Coatings for Load Bearing Applications**, ***Muhammad Usman (muusman2-c@my.cityu.edu.hk)**,* City University of Hong Kong

Diamond like carbon (DLC) coatings are in focus from a last few decades due to its exceptional mechanical and tribological properties. High hardness, low coefficient of friction and wear rate are some of the intrinsic characteristics. Due to this unique combination, it is widely used in microelectromechanical systems (MEMS), automotive sector, tools and dies, laser barcodes scanners etc. However, industrial bearings, load bearing implants and machine elements are high load applications. Single layer DLC can be divided into two (1) hard (2) soft. Both (hard, soft) types have their own limitations: hard DLC possesses high compressive residual stresses and experiences buckling induce adhesion failure under high load whereas soft DLC lacks wear resistance and better mechanical properties [1]. Researchers shifted from single layer to multilayer architecture in DLC to achieve high hardness and toughness simultaneously as these are inversely correlated [2-4]. This was made possible by stacking alternate hard and soft layers which not only reduce compressive residual stresses in the coating but also increase toughness compared to hard monolayer [3]. Thus, load bearing capacity of the coating increases. The current research aims to evaluate the impact of overall thickness of multilayer DLC (found to be excellent in our previous research) on atomic bonding, mechanical properties, residual stresses, scratch adhesion and wear resistance particularly at high contact stress which are missing previously. Therefore, new multilayer DLC coatings are designed with alternate hard and soft layers using closed field unbalanced magnetron sputtering system. Discrete sharp interfaces are produced by selecting two different bias voltages. Hard to soft layer ratio (1:1) and layer thickness (50nm) are kept constant for all specimens. 0.5µm, 1µm, 2µm, 3µm, 4µm thick coatings (fig. 1) are deposited onto steel substrate having Cr/CrC_x interlayer. Scanning electron microscope (SEM), Raman spectroscopy, nanoindenter, scratch adhesion tester and tribometer are employed for characterization of specimens. Raman analysis depicts decreasing I_D/I_G ratio and increasing full width at half maximum (FWHM) trend by increase in overall coating thickness. Hardness and residual stress are in inverse and direct relation to thickness respectively. Interestingly, scratch adhesion resistance is found to be within same range for all specimens. Moreover, this multilayer DLC design exhibited excellent wear resistance under high loading conditions. Wear rate values are within one order of magnitude for all samples.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-2-MoA

Coatings for Batteries and Hydrogen Applications II

Moderator: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany

2:00pm **TS1-2-MoA-2 Effect of Atomic Layer Deposited Films on Three-Dimensional Electrodes for Lithium-Ion Batteries***, P. Lin,* National Chung Hsing University, Taiwan*; **Chih-Liang Wang (wangcl@mx.nthu.edu.tw),*** National Tsing Hua University, Taiwan

The great capability of atomic layer deposition (ALD) in precisely controlling the film quality, such as thickness, composition and comformality has been paid much attention. Herein, we presented a study of coating nanocomposite metal oxides via ALD on three-dimensional electrodes for lithium-ion batteries. The three-dimensional electrodes were prepared by the hydrothermal synthesis of TiO_2 nanorods on carbon cloths. The nanocomposite metal oxides of TiO_2 and ZnO were deposited on TiO_2 nanorods by ALD. The effect of metal oxides on electrochemical performance was systemically investigated by using different ALD cycles of TiO_2 and ZnO. The results indicated that the reversible capacity and rate performance of three-dimensional electrodes can be improved after ALD nanocomposite metal oxides. The improved performance can be attributed to the function of ALD TiO_2 to not only alleviate the volume change and the growth of solid electrolyte interphase but also improve electronic conductivity. More details related to battery performances and film properties, influenced by the ALD cycle of individual metal oxide, will be reported in the presentation.

2:20pm **TS1-2-MoA-3 Effects of Additives on Electrochemical Performance of Sodium Ion Batteries***, **Ting Ching Lin (tim881231@gmail.com)**, J. Huang,* National Cheng Kung University (NCKU), Taiwan*; C. Chang,* National University of Tainan, Taiwan

In recent years, the surge in electric vehicle popularity and the push for renewable energy development by various governments globally have enhanced energy security, mitigated the risk of fuel leaks, and lessened the dependence on imported fuels. This has been achieved by ensuring a steady supply of electricity and diversifying fuel sources. As the demand for lithium continues to rise with the increased adoption of lithium-ion batteries, attention is turning towards sodium ion batteries due to the limited availability of lithium resources. Sodium ion batteries are gaining traction, particularly in the electrical and electronic sectors. Their operational principle closely mirrors that of lithium-ion batteries, encompassing positive and negative electrodes, isolation membranes, and electrolytes. Notably, sodium ion batteries offer cost advantages over lithium batteries, with more readily available precursor materials for the negative electrode and a lower carbonization temperature during graphite negative electrode production. Despite these merits, sodium ion batteries currently encounter challenges, such as lower energy density and storage capacity compared to lithium batteries. The cycle life of existing sodium ion batteries also falls short of that seen in commercial lithium batteries. The primary hurdles stem from the lower energy density and suboptimal cycling performance, which heavily rely on the formation of solid electrolyte interface (SEI) films on the electrode surface.

To address these challenges, the research proposes a novel approach: the combination of different kinds of new ion additives to form a composite additive. The aim is to create a stable and dense SEI that exhibits thinness, electronic insulation, and ion conductivity. This approach seeks to overcome the limitations of sodium ion batteries, particularly their low energy density and poor cycling performance, by fostering the development of an enhanced SEI.

In this research, we used electrochemical impedance spectroscopy (EIS) to measure interface resistance, and used X-ray photoelectron spectroscopy (XPS), Scanning Electron Microscope (SEM), Fourier-transform infrared spectroscopy (FTIR) to observe the electrode surface and analyze the SEI film. The results indicate that the addition of the NaDFP ionic additive effectively improves the retention of battery capacity and establishes a durable SEI film.

Keywords: sodium ion batteries, new ion additives

2:40pm **TS1-2-MoA-4 Effect of SiOx/RGO via Phosphorus Doping as Anode Materials for Lithium-Ion Batteries***, **Wen-Feng Lin (chanes40417@gmail.com)**, J. Huang, S. Brahma,* National Cheng Kung University (NCKU), Taiwan*; Y. Shen,* Hierarchical Green-Energy Materials Research Center (Hi-GEM), Taiwan

Lithium-ion batteries has been one of the promising energy storage devices due to its high energy density, high capacity, and non-memory effect. Anode is one of the important component of the batteries. To meet the demand of electronic devices, scientists are dedicated to develop novel anode materials since the traditional graphite has the drawback of low theoretical capacity (approximately 372 $mAhg^{-1}$), which cannot achieve the requirement of the high-energy devices. There are different types of materials during lithiation/delithiation process, such as alloys, transition metals, and insertion/desertion materials. Among them, we choose non-stoichiometric silicon oxide (SiO_x, $0 < x < 2$) because it has relatively low volume expansion as compared to pure silicon. However, the ratio of volume expansion is still a non-negligible phenomenon since it indirectly affects the capacity. Therefore, we utilize the characteristics of reduced graphene oxide (rGO) and phosphorus (P) to improve the disadvantages of SiO_x. The character of rGO is the carrier of lithium ions and electrons owing to the 2D-layered structure. Besides, rGO is a carbonaceous material which can enhance the conductivity of anode materials. For the purpose of improving initial coulombic efficiency (ICE), P acts as dopant that can create extra space for lithium-ion storage and transport because the chemical and physical structures of rGO may be changed. We first synthesize SiO_x/rGO, then modify the composite with P by using phosphoric acid as P source in the second step followed by post annealing as the last step. The final product is named as P-SiO_x/rGO (1P, 2P represent different concentration of phosphoric acid). From the results of XPS, P bond with O and EDS mapping shows the uniform distribution of P. Hence, the analyzed results ensure the doping of P. Further, the electric properties are verified through the testing of battery performance, charge/discharge, cycling and C-rate are included. Compared to the un-doped and doped samples, ICE of the latter (42.5 % for 1P-SiO_x/rGO and 56.2 % for 2P-SiO_x/rGO) are higher than the former (39.7 % for un-doped SiO_x/rGO), which means the effect of P is achieved. On the other hand, P-doping also stabilized the structure of electrode, the lithiation capacity of 1P-SiO_x/rGO and 2P-SiO_x/rGO retain a value of 340 and 424 $mAhg^{-1}$, respectively at 0.1 Ag^{-1} after C-rate testing, while 291 $mAhg^{-1}$ for the un-doped electrode, indicating an enhancement of the cyclability and rate performance of the composite.

3:00pm **TS1-2-MoA-5 The Research of Different Pre-Lithiation Methods to Enhance Coulombic Efficiency of SnO_2 Modified TiO_2 as Anode Material in Lithium-Ion Battery***, **Cheng-Hsun Ho (n56124032@gs.ncku.edu.tw)**, J. Huang,* National Cheng Kung University (NCKU), Taiwan*; Y. Shen,* Hierarchical Green-Energy Materials Research Center (Hi-GEM), Taiwan

Lithium-ion batteries have been widely applied in our daily lives and there is an ongoing demand for LIB with higher energy density, lower self-discharge, longer cycling life and better safety. Titanium dioxide (TiO_2) has emerged as a highly promising anode material for lithium-ion batteries due to its remarkable cycling stability, impressive rate performance, cost-effectiveness, and environmental friendliness. Nevertheless, the main obstacles associated with this material include its limited electronic/ionic conductivity and lower theoretical capacity. In order to overcome this issue, our research has been modifying high-capacity material (e.g., SnO_2) into TiO_2 with an eye to promoting its theoretical capacity. Modifying SnO_2 into TiO_2 reduces the impedance and increases the Li-ion diffusion rate. The SnO_2/TiO_2 composite is synthesized by the chemical bath with $Sn(BF_4)_2$, HBF_4, $Na_2S_2O_3$ and TiO_2 (rutile and anatase mixed phase) followed by annealing at different temperature. From the TEM and XRD results, the SnO_2/TiO_2 composite had been successfully synthesized. It can be inferred from the figure that the structure of the composite might be the shell of the SnO_2 & TiO_2 solid solution while the core remains TiO_2 structure. However, the table below shows the serious fading problem of SnO_2/TiO_2 composite with different annealing temperature during the first and second cycle. Active lithium loss (ALL) in the initial lithiation process causes irreversible capacity of LIBs due to the formation of unstable solid electrolyte interface (SEI) layer on the electrode surface. To resolve the problem, pre-lithiation has been widely accepted as one of the most promising strategies to compensate for active lithium loss. Our group have been dedicated to trying various pre-lithiation techniques, such as electrochemical and thermal evaporation of lithium. Electrochemical pre-lithiation aims to generate stable SEI layers by applying constant voltage while lithium evaporation deposition involves depositing various thickness of lithium to achieve different levels of pre-lithiation. The ultimate goal would be giving out advantages and challenges of each one then finding out the optimal approach to improve cycling performance of tin-based anodes in lithium-ion batteries.

3:20pm **TS1-2-MoA-6 Study on the Characteristics of Garnet-Type Solid Electrolytes in Lithium Metal Solid-State Batteries with Multilayer Interfaces**, ***Hung-Ju Chen (m46111060@gs.ncku.edu.tw)***, *J. Hung, S. Lin,* National Cheng Kung University (NCKU), Taiwan

Lithium-ion batteries (LIB), which is a rechargeable battery, mainly used in related electronics industries, such as transportation vehicles, medium to large uninterruptible power systems (UPS), solar systems, energy storage systems, electric hand tools, aerospace equipment, power battery market and aviation battery. The LIB life would decrease with increasing in the number of charge and discharge cycles. Besides, the risk of LIB electrolyte is a liquid organic solvent, which is easy to burn and explode in case of fire. Recently, solid-state electrolytes have attracted attentions and show the many advantages including high safety, high energy density, and greater temperature tolerance. Among different types of solid-state electrolytes, garnet-type LLZTO ($Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$) electrolyte has high ionic conductivity (10^{-3}to10^{-4}S / cm) and chemical stability towards lithium metal. However, lithium dendrites will be generated during the charge and discharge process of solid electrolyte batteries. The dendrites could lead to short circuit and failure of battery. Moreover, poor contact in the interface between solid electrolyte and lithium metal could cause the increased impedance and decreased conductivity. The aim in this study is to use different types and proportions of metal fluorides to modify the interface; meanwhile, the interface forms an electronically insulating and lithium-friendly lithium fluoride layer to promote the chemical diffusion of lithium in lithium metal alloys and reduce interface impedance. After the project, we expect that a new generation of lithium metal solid-state batteries will be developed.

4:00pm **TS1-2-MoA-8 Characterization Study of Sustainable Lithium Ion Battery with Cathode of Recycled $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC)**, ***Yi-Chieh Tseng (e54101161@gs.ncku.edu.tw),*** National Cheng Kung University (NCKU), Taiwan*; Y. Shen,* Hierarchical Green-Energy Materials Research Center, Taiwan*; J. Huang,* National Cheng Kung University (NCKU), Taiwan

Nowadays, to meet the requirements of applying on portable electronic devices and electronic vehicles, energy storage system need to have high energy density and high power density. $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) as the cathode for lithium-ion batteries (LIBs) could fulfil the demands. However, NMC is considered not friendly to the environment and harmful to man. To reduce the mining of poisonous, we had recycled the 622 and 811 NMC powder from the used battery of the electrical racing cars. By ultrasonic washing the electrodes in sodium chloride (NaCl) solution, the powder containing lithium (Li), nickel (Ni), magnesium (Mn), cobalt (Co), iron (Fe), aluminum (Al) and copper (Cu) is obtained. To remove the undesirable elements (Fe, Al and Cu), we washed the powder with various acids and used the Cyanex 272 to extract the target elements. From the X-ray diffraction (XRD) pattern, the recycled 622 and 811 NMC powder showed the characteristic peak of Ni, Mn and Co, proving the effectiveness of the extraction method. It was then assembled into coin cell (CR2032), still showing stable and relatively high capacity performance. In situ techniques are also used to examine the stability of the battery by recycled material, to be commercialized in the future. As the sustainability is the key requirement to be commercialized, the recycled battery with NMC as the cathode would have strong competitiveness.

4:20pm **TS1-2-MoA-9 Investigation of Y-doped $Li_7La_3Zr_2O_{12}$(Y-LLZO) Coatings by Colloidal Coating Process for the Electrolyte of all Solid-state Battery**, ***Yen-Yu Chen (yychen@mail.npust.edu.tw)***, *G. Yao,* National Pingtung University of Science and Technology, Taiwan*; X. Yan,* Chinese Culture University, Taiwan

Lithium ion batteries (LIBs) were widely applied on computer, communications, and consumer electronics for decades, as well as on the electric vehicles in recent years. Due to the risks of liquid electrolytes for current LIBs, solid state electrolytes for LIBs were investigated. In this study, Y-doped $Li_7La_3Zr_2O_{12}$ (Y-LLZO) materials were prepared by a solid-state reaction method. After well-dispersed, Y-LLZO coatings were deposited on the $LiCoO_2$/Y-LLZO composite anode from the Y-LLZO suspensions by a spin-coating method. The crystal phase analysis by the X-ray diffraction (XRD) method shows, the cubic perovskite phase of Y-LLZO can be obtained after calcined at 900ºC for 12 h. The grain size of the Y-LLZO powders observed by the scanning Electron Microscopy are most within several μm. The crystal phase of the Y-LLZO samples after sintered at 950ºC for 1 h is still mainly perovskite phase but become the tetragonal structure. A few of minor $La_2Zr_2O_7$ phase can be found in the sample, that may due to the generation of the volatile lithium species during sintering. The Y-LLZO sample with Al_2O_3 sintering aid shows higher density and larger grain size after sintering. The thickness of the Y-LLZO coatings are around several μm. The detail electrical properties will be shown in the following report.

Keywords: All solid-state lithium ion battery, LLZO, coatings, colloidal process, solid electrolyte

4:40pm **TS1-2-MoA-10 Higher Power Density NVPF-CNT@Ni//CNF@Ni Configuration via Hydrothermal Route for Flexible Na-ion Capattery**, ***Gagan Kumar Sharma (gkumarsharma@ph.iitr.ac.in)***, *A. Pramanik,* Rice University, USA*; D. Kaur,* Indian Institute of Technology (IIT) Roorkee, India*; P. Ajayan,* Rice University, USA

Considering the electrochemical performance and structural stability of nanohybrids, $Na_3V_2(PO_4)_2F_3$ (NVPF), multi-walled carbon nanotubes (MWCNTs), and carbon nanofibers (CNF) are emerging materials to promote the flexible sodium-ion capattery (FNIC) as a hybrid energy storage system. Direct incorporation of hydrothermally synthesized NVPF into MWCNT nanoarrays has been achieved on foldable nickel (Ni) foil via the slurry casting approach. We report an efficient utilization of the synergistic effect of ball-milled nanocomposites to design the FNIC cell from NVPF-MWCNT@Ni (battery-type) and CNF@Ni (capacitor-type) electrodes. The as-obtained FNIC device exhibits a remarkable specific capacitance of 136.17 F g^{-1} with a corresponding specific capacity of 26.48 mAh g^{-1}at a potential scan rate of 1 mV s^{-1}. The charge storage ability is mainly viewed as the synergism stimulated across unique interfacial surface construction provided by NVPF and carbon-derived conductive host materials. Subsequently, the constructed asymmetric NVPF-MWCNT@Ni//CNF@Ni architecture exhibits a maximum working voltage of 0.70 V and a noticeable power density of 15.84 kW kg^{-1} at 2.50 Wh kg^{-1}. The abundance of conducting pathways in hybrid nanoarrays facilitates intercalation/deintercalation of Na^+/SO_4^{-2} ions into the electroactive sites, further endorsing pseudocapacitance. Besides, the flexibility test outcomes illustrate practically unperturbed electrochemical properties at a 160º bending angle, indicatingexcellent mechanical robustness. The FNIC cell retains90% of initial capacitance over 2,000 charge-discharge cycles, revealing a longer service lifespan attributed to advanced rate capability. The current study offers new avenues to develop energy storage systems for next-generation portable and wearable electronics at large-scale applications.

5:00pm **TS1-2-MoA-11 Technological and Economical Aspects of Precious Metal Sputtering on Full-Size PEM Electrolyzer Components**, ***Alexander Wemme (wemme.alexander@vonardenne.com)***, *R. Stock,* VON ARDENNE GmbH, Germany*; C. Simons,* Materion Advanced Materials, Germany*; D. Fuller,* Materion Corporation, USA

Sputter coating is a well-established process to produce thin layers with excellent properties, which can be used to replace electroplating of electrolyzer components with far less material consumption, hence minimizing cost of coating and thus the overall cost of the electrolyzer stack.

With precious metal material prices constituting up to 98% of the operating cost of a sputter coating equipment, the focus of production control shifts from minimizing downtimes and maximizing output to mitigate material losses as well as possible. Coating operations and the sputter target supply chain have to be evaluated under completely different aspects.

MATERION and VON ARDENNE have cooperated in implementing processes and technologies to drive this paradigm shift in cost structure by developing full-scale rotatable precious metal sputter targets.

The development of precious metal rotary targets will play a dominant role to achieve high utilization of target material thus keeping precious metal input and finance at low level in comparison to planar targets. The focus was to establish a target manufacturing process specifically designed for precious metals offering high homogeneity of target material, perfect sputtering behavior and layer formation. An additional objective was to maximize precious metal utilization by implementing an efficient recycling process.

In this presentation, the results of this recent work to make sputtering of precious metals economically advantageous will be discussed. Additionally, the practical implementation of such sputter targets in coating tools with hardware specifically designed to complement the precious metal life cycle from target fabrication over coatings at industrial scale to recycling is presented.

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM2-2-TuM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes II: Fracture and Fatigue
Moderator: Matteo Ghidelli, CNRS, France

8:00am **CM2-2-TuM-1 Minimizing FIB Artifacts in Microcantilever Fracture: A Case Study on the Role of Grain Boundaries in Microfracture***, **Subin Lee (subin.lee@kit.edu)**, Y. Zhang,* Karlsruhe Institute of Technology (KIT), Germany*; S. Brinckmann,* Forschungszentrum Jülich GmbH, Germany*; M. Bartosik,* Montanuniversität Leoben, Austria*; C. Kirchlechner,* Karlsruhe Institute of Technology (KIT), Germany **INVITED**

In recent years, the application of Focused Ion Beam (FIB) for small-scale fracture testing has gained significant prominence. While simple cantilever-based geometries are commonly used for micro-fracture studies, concerns persist regarding FIB-induced artifacts, specifically those caused by a Ga ion beam, affecting the accurate measurement of fracture toughness at the micron scale. These concerns include issues such as residual stresses resulting from ion implantation, chemical interactions of gallium ions leading to segregation at the notch front, and the limited size of the notch root radius.

In this presentation, we demonstrate bridge-notch micro cantilever fracture which can minimize FIB artifacts by using atomically sharp natural cracks. Departing from the conventional through-thickness notch, we employ a well-defined bridge-notch for a single cantilever fracture test [1]. Through *in situ* SEM fracture tests, direct observations reveal that extremely thin bridges fail first, generating sharp natural cracks which is free of FIB artifacts. Consequently, this enables a more precise measurement of fracture toughness with reduced scatter. This phenomenon is observed across four different nitride hard coating systems.

Utilizing the bridge notch approach, which enhances statistical analysis, we study the impact of grain boundaries in microfracture. Testing columnar-grained nitride coatings with two loading directions parallel and perpendicular to the film's growth direction, we find that longer crack path results in higher fracture toughness. Furthermore, using a multi-layered coating with an epitaxially-grown structure near the coating-substrate interface and a nano-grained structure in the upper coating region, it is revealed that the epitaxially grown part without grain boundaries exhibits a 30% higher fracture toughness compared to the nano-grained coating. This documents that the fracture toughness of hard coatings is controlled by grain boundary fracture.

[1] Y. Zhang, M. Bartosik, S. Brinckmann, S. Lee, C. Kirchlechner, Direct observation of crack arrest after bridge notch failure: A strategy to increase statistics and reduce FIB-artifacts in micro-cantilever testing, Materials & Design 233 (2023) 112188.

8:40am **CM2-2-TuM-3 Bending Fatigue Testing of 3D-printed PETG and ABS to Investigate Feasibility for Tidal Turbine Blades***, H. Myers,* Oxford University, UK*; Y. Chen,* ***Steve Bull (steve.bull@ncl.ac.uk)****,* Newcastle University, UK

Three-point fatigue bending tests (1Hz) of 3D-printed ABS and PETG specimens conducted in air or seawater are reported in the current study. These are used to produce S-N curves for ABS and PETG. The results indicate no significant effect of seawater on fatigue life by comparing the lifetimes of samples tested in seawater with the S-N curves produced. The S-N curves for the two materials are similar, indicating a common feature controlling fatigue life which is hypothesised to be defects introduced in 3D printing. Preliminary examination with 3D optical microscopy corroborates this as a plausible explanation. Finally, approximate calculations are used to demonstrate that these materials may feasibly be used for tidal turbine blades, but any design must especially consider blade strength and stiffness, possibly at the expense of hydrodynamic efficiency.

9:00am **CM2-2-TuM-4 Influence of Annealing-Induced Substrate Element Diffusion on the Microstructure and Mechanical Properties of TiN/TiCN Coatings Synthesized using Chemical Vapor Deposition***, **Fabian Konstantiniuk (fabian.konstantiniuk@unileoben.ac.at)**, M. Schiester,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

TiN/TiCN deposited by chemical vapor deposition (CVD) is widely used as hard coating system for cemented carbide cutting tools, typically under an Al_2O_3 top layer. During the deposition of the Al_2O_3 top layer, the underlying TiN and TiCN layers are exposed to high temperatures. Therefore, the present study focuses on the influence of this Al_2O_3 deposition step, which is mimicked by a vacuum-annealing treatment, on the microstructure and mechanical properties of the TiN/TiCN coating. By applying advanced characterization techniques such as scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), atom probe tomography (APT), and micro-mechanical bending tests on both, as-deposited and annealed coatings, changes in the microstructure and mechanical properties were studied. It was found that W and Co diffusion takes place along the TiN and TiCN grain boundaries from the substrate into the coating. While the hardness, Young's modulus, and fracture toughness remained unaffected by the annealing treatment, a significant decrease of the fracture stress with increasing annealing time was observed.

9:20am **CM2-2-TuM-5 Mechanical Properties of Thin Films Deposited by HiPIMS onto Flexible Substrates***, **Tereza Kosutova (tereza.kosutova@angstrom.uu.se)**,* Uppsala University, Department of Electrical Engineering, Sweden*; M. Tavares da Costa,* Karlstad University, Sweden*; K. Gamstedt,* Uppsala University, Department of Materials Science and Engineering, Sweden*; D. Drozdenko,* Charles University, Czechia*; T. Kubart,* Uppsala University, Department of Electrical Engineering, Sweden

Our study focuses on the strength and ductility of thin films deposited by magnetron sputtering on flexible substrates. Although thin films are widely used in surface engineering, their application on foils brings new requirements on the mechanical properties of the coating material as well as the substrate-coating interface. Here, we aim on the determination of mechanical properties of thin films deposited by dc and high power impulse magnetron sputtering (HiPIMS). The main goal is to identify deposition conditions that ensure good adhesion and ductility of the layers and therefore facilitate applications of coated metal foils.

In-situ testing in an SEM is used to quantify the film cracking during tensile loading and thus analyse the distribution of fracture strain and interfacial shear strength of the coating material. This technique is complemented by the strain field analysis of the substrate foils determined by digital image correlation to identify defects that could induce stress concentration and premature failure. Thin films of copper, titanium and amorphous carbon are evaluated as examples with different intrinsic ductility. Furthermore, the effect of interlayers was investigated. The behaviour of the films deposited on two different foils of aluminium and PET is compared.

To identify the impact of different deposition parameters, we analysed a series of samples deposited using different values of the duty cycle and the substrate bias. The results are correlated to the morphology, microstructure and chemical composition analysed mainly by SEM, XRD and EDX techniques. Whereas the copper exhibits high ductility and a good adhesion can be achieved with an ion assistance, the fracture behaviour of the titanium is dependent on the growth conditions.

9:40am **CM2-2-TuM-6 Fatigue-Induced Abnormal Grain Growth in Metallic Thin Films***, Q. Li,* Georgia Institute of Technology, USA*; A. Barrios,* Colorado School of Mines, USA*; Y. Yang,* Georgia Institute of Technology, USA*; M. Jain,* Sandia National Laboratories, USA*; Y. Liu,* Georgia Institute of Technology, USA*; B. Boyce,* Sandia National Laboratories, USA*; T. Zhu,* ***Olivier Pierron (olivier.pierron@me.gatech.edu)****,* Georgia Institute of Technology, USA

This presentation describes a microelectromechanical system (MEMS) based setup to investigate grain growth in ultrafine grained and nanocrystalline metallic thin films under high/very high cycle loading conditions (i.e., up to 10^9 cycles). The advantage of the technique is that it can test different metals (fcc, bcc, different textures) under identical loading conditions. The governing hypothesis is that abnormal grain growth occurs under this loading regime, and that the family of growing grains is mainly dictated by elastic anisotropy. Our preliminary results on Au and Al thin films are compared to our previous work on ultrafine grained Ni. Abnormal grain growth in Au is observed, as in Ni, however, the orientation of the growing grains is different for Au and Ni, given the difference in initial texture. The experimental results can be compared to micromechanics analyses and phase-field modeling, in order to better understand the origins of the thermodynamic driving force.

10:00am **CM2-2-TuM-7 Nanoscale Fatigue Measurements on Diamond-Like Carbon Coatings***, **Joshua Vetter (joshua.vetter@de.bosch.com)**, M. Günther, P. Hofmann, S. Grosse,* Robert Bosch GmbH, Germany*; S. Schmauder,* University of Stuttgart, Germany

Diamond-like carbon (DLC) coatings are frequently used to improve wear performance of technical components in tribological systems. Appropriate fatigue properties of the coating system are fundamental to ensure the functionality. The mechanical failure of the coating can lead to spallation and delamination processes already through further low external stresses and hence to total component failure. Therefore, precise measurements are mandatory. Established analysis like the Rockwell test according to DIN 4856 as well as scratch tests are performed with a single overload above the critical strength of the DLC coating disregarding real operating conditions and failure mechanisms e.g. fatigue through cyclic loads. In our study, we performed cyclic nanoscale fatigue measurements of DLC coatings to consider application-related stresses. The coating systems were deposited by PVD and PACVD techniques varying e.g. the thicknesses of the functional and support layer systems. Cyclic nanoindentation measurements with spherical diamond indenters were performed to evaluate the fatigue behaviour. We have shown that promising results can be obtained from this type of measurements. Suitable test parameters were defined to investigate a wide range of different coating systems within a few hours by adjusting static force and force amplitude. Effects of different coating designs, layer thicknesses and mechanical properties (e.g. indentation hardness, indentation modulus, residual stress and yield strength) of the DLC layer could be evaluated. The critical stress for various DLC layer thickness was evaluated with a FEM simulation and compared to the results obtained from the fatigue measurements. With this, essential adjustments of the mechanical properties of the DLC layer were found to increase the fatigue limit. Furthermore, the effect of an additional pre-treatment by annealing under elevated temperatures from 250 °C up to 450 °C was investigated. The results of the nanoscale fatigue test provide information on previously unknown effects that could not be detected with nanoindentation hardness tests. For various DLC systems the thermal degradation under application related stresses could be shown. Our new measurement technique reveals that previous measurements e.g. adhesion measurement results from typical single overload or hardness measurements tests are not conclusive enough to consider application-related load spectra and that cyclic loads are necessary to guarantee the requested operation condition testing environment. Hence the developed fatigue test allows us to adapt the coating systems to the requirements of the real components.

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 5-6 - Session CM4-2-TuM

Simulations, Machine Learning and Data Science for Materials Design and Discovery II

Moderators: Po-Liang Liu, National Chung Hsing University, Taiwan , **Ferenc Tasnadi**, Linköping University, Sweden

8:00am **CM4-2-TuM-1 DFT + ML + Calphad: From Qualitative to Quantitative Phase Stability Predictions***, **Moritz to Baben (mtb@gtt-technologies.de)**, P. Keuter, C. Früh, B. Reis, F. Tang,* GTT-Technologies, Germany **INVITED**

Today, phase stability predictions using quantum mechanical calculations can be considered state-of-the-art for metallurgical coatings and thin films. However, these predictions are usually qualitative in nature, partly because of missing data and partly because the processes are complex and not in thermodynamic equilibrium.

Here, it is shown how

(I) data gaps concerning phase stability can be closed by a the combination of 0 K DFT calculations, machine learning to cheaply extend the data validity to relevant temperatures and Calphad methodology to describe phase stability of solid solutions and thus solid-gas equilibria.

(II) phase stability data can then be used to make quantitative predictions for magnetron sputtering, i.e. a process that is usually considered to be far from equilibrium, using the para-equilibrium approach (nitrogen stoichiometry of TiAlN, to Baben et al., MRL 5 (2017) 158) or using a small process model based on the Hertz-Knudsen equation (stoichiometry of Mg-Ca Thin Films, Keuter et al, Materials 16 (2023) 2417).

8:40am **CM4-2-TuM-3 Cu-Zr-Al Thin Film Metallic Glasses in a Wide Range of Compositions and Growth Conditions***, **Jiri Houska (jhouska@kfy.zcu.cz)**, P. Zeman,* University of West Bohemia, Czechia

Cu-Zr-Al thin film metallic glasses are investigated by a combination of simulations of their atom–by-atom growth with magnetron sputtering. We fulfill all requirements which maximize the usefulness of the results: mutual support of calculated and experimental data, simulation algorithm which exactly reproduces what is happening in the experiment, wide compositional range (from pure Cu to pure Zr and from [Al] = 0% to 20%), wide range of growth conditions (energy of arriving atoms, temperature, growth template). We focus on the homogeneity, densification, short-range order (bonding preferences and coordination numbers), medium-range order (common neighbor and network ring statistics) and functional properties. Special attention is paid to the key building blocks of Cu-Zr-Al: not only icosahedral clusters (12 vertices) but also newly identified supraicosahedral clusters (16 vertices).

First, we identify crystalline Zr-rich compositions (on any growth template) and Cu-rich compositions (with a strong effect of growth template), and glasses (as homogeneous as what result from a random distribution of atoms) at [Cu] = 20% to 80-85%. Increasing [Cu] in the glassy compositions leads to increasing coordination of both Cu and Zr, packing factor and icosahedron-like medium-range order. Second, increasing [Al] in glassy $Cu_{0.46}Zr_{0.54-x}Al_x$ preserves the homogeneity (at a very low preference to form Al-Al bonds) and once again leads to increasing coordination of all elements, packing factor and concentration of icosahedral clusters (around smaller Cu and Al) and supraicosahedral clusters (around larger Zr). All of that is achievable at low energy delivered into the growing films, while delivering too much energy (by energetic bombardment or by ohmic heating) may be even harmful.

While the atomic-scale simulations provide a lot of information not accessible experimentally, they are correlated with and explain experimental data including increasing hardness, Young's modulus, glass transition temperature and crystallization temperature with increasing [Cu]/[Zr] and [Al]/[Zr]. Collectively, the results [1,2] are important for understanding the structures and properties of this class of metallic glasses, and for optimizing their compositions and pathways for their preparation.

[1] J. Houska, P. Machanova, M. Zitek, P. Zeman, J. Alloys Compd. 828, 154433 (2020)

[2] J. Houska, P. Zeman, Comp. Mater. Sci. 222, 112104 (2023)

9:00am **CM4-2-TuM-4 Impact of TM Elements on Structural, Thermodynamic and Mechanical Properties of CrN***, **David Holec (david.holec@unileoben.ac.at)**,* Montanuniversität Leoben, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

CrN belongs to a family of transition metal nitrides used as protective coatings in automotive, aerospace, tooling and other applications. It poses a specific challenge for *ab initio* modelling due to its genuine magnetic properties: it has an antiferromagnetic (AFM) orthorhombic structure below the Néel temperature (T_N~room temperature) and adopts paramagnetic (PM) cubic B1 above T_N.

In this contribution, we use *ab initio* calculations to study the alloying impact of TM elements (Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Mo, W) on CrN in its application-relevant PM-B1 phase. Apart from V, all other elements increase the lattice parameter of CrN consistently with the corresponding binary TMNs. The enthalpy of isostructural mixing is the largest for Y due to large internal strains, followed by the group IVB elements. Interestingly, $H_{mix}$is negligible in the whole compositional range for Sc and V and becomes even negative (stable solid solutions) for $Cr_{1-x}Ta_xN$. Nb, W and Mo exhibit more complicated, composition-dependent behaviour. As quantified by the *B/G* ratio and the Cauchy pressure (C_{12}-C_{44}), the mechanical properties strongly correlate with the valence electron concentration of the ternary $Cr_{0.89}TM_{0.11}N$ solid solutions. While Mo and W are the most potent ductility enhancers, Sc and Y are predicted to embrittle CrN.

9:20am **CM4-2-TuM-5 Fracture Toughness: Atomistic Understanding of Directional and Temperature Dependence for the case of $Ti_{1-x}Al_xN_y$**, ***Davide Sangiovanni (davide.sangiovanni@liu.se)***, Linköping University, Sweden

The fracture toughness (K_{Ic}) of single-crystal lattices and interface structures is a physical property that depends on temperature and crystallographic orientation. For ceramic thin films, experimental characterization of K_{Ic} is complicated by the presence of grain boundaries or structural inhomogeneities. Narrow scatter among measured K_{Ic} values (1-to-5 MPa $\sqrt{m}$), combined to relatively large statistical uncertainties (±1 MPa $\sqrt{m}$), vanifies attempts to rank different hard ceramics according to their effective fracture resistance.

Taking B1-structure $Ti_{1-x}Al_xN_y$ as representative ceramic systems, I present results of atomistic fracture-mechanics simulations carried out at different temperatures (*T*) and for diverse crystallographic orientations of the fracture plane (hkl) / crack front [h'k'l']. The approach — based on K-controlled *nanoscale* loading, implemented with anisotropic *T*-dependent elastic responses **[1]** — can reliably forecast *observable* mechanical responses.

Direct atomistic observations of localized transformation-induced or slip-induced plasticity in flawed $Ti_{1-x}Al_xN_y$ lattices allow understanding and quantifying the impact of small-scale yielding on K_{Ic} and fracture strength values calculated as a function of *T* and (hkl)[h'k'l']. Moreover, the simulation results evidence limits of Griffith (^{G}) and Rice (^{R}) criteria for predictions of stress intensities that lead to brittle-fracture (K_{Ic}^G) and dislocation emission (K_{Ie}^R). Alternative descriptors — based on properties evaluated by homogeneous deformation of defect-free crystals **[1,2]** — are proposed as convenient means to rapidly screen mechanical strength, tendency to undergo plastic deformation, and fracture resistance at any temperature of interest.

The talk will also briefly cover our recent developments in machine-learning interatomic potentials for cutting-edge description of materials subject to deformation at realistic conditions **[3]** and *ab initio* database of ceramic properties computed from 0 K to elevated temperatures **[4]**.

[1] Physical Review Materials (2023) https://doi.org/10.1103/PhysRevMaterials.7.103601

[2] Science Advances (2023) https://doi.org./10.1126/sciadv.adi2960

[3] Preprint (2023) https://doi.org/10.48550/arXiv.2309.00996

[4] npj Computational Materials (2022) https://doi.org/10.1038/s41524-022-00698-7

9:40am **CM4-2-TuM-6 Exploring Surface Energy and Work Function Changes in ZnGa2O4(111) via Ab Initio Studies**, ***Po-Liang Liu (pliu@dragon.nchu.edu.tw)***, *Y. Lin,* National Chung Hsing University, Taiwan

The metal oxide semiconductor gas sensor holds promise as the primary component for environmental monitoring within artificial intelligence-based systems designed for household and industrial gas detection. The fabrication of ZnGa2O4 thin films has been advanced due to their capacity to operate within sensor temperature ranges and discern the composition and concentration of mixed gases. The n-type semiconductor nature of ZnGa2O4 enables the detection of NO2 and H2S molecules. This semiconductor exhibits rapid and robust sensing responses along with high signal intensity towards NO2 and H2S, thereby anticipating an enhancement in sensor operational efficiency, particularly in terms of elevated temperature utilization. Hence, this study employs ab initio calculations based on the density functional theory to determine the surface energy of ZnGa2O4(111). The analysis reveals that the ZnGa2O4(111) surface comprises Ga, Zn, and O elements. Findings indicate that the surface energy for Zn-Ga-O-, O-, and Ga-terminated ZnGa2O4(111) range between 0.0516 to 0.2335 eV/Å2, 0.0516 to 0.7789 eV/Å2, and 0.0464 to 0.5918 eV/Å2, respectively. The Ga-terminated ZnGa2O4 has the lowest surface energy of 0.0464 eV/Å2 in a Ga-rich environment, showing the Ga-terminated ZnGa2O4(111) is the most favorable surface. The work function change of Zn-Ga-O-, O-, and Ga-terminated ZnGa2O4(111) are 3.70 eV, 0.48 eV, and 6.35 eV, respectively. This highlights that the Ga surface atoms demonstrate a maximum work function change, consistent with previously experimental observations

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country C - Session IA2-1-TuM
Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications I
Moderator: Jan-Ole Achenbach, KCS Europe GmbH, Germany

8:00am **IA2-1-TuM-1 Influence of Plasma Carburizing on Corrosion Behavior and Interfacial Contact Resistance of Austenitic Stainless Steels**, ***Phillip Marvin Reinders (p.reinders@tu-braunschweig.de)***, *P. Kaestner, G. Bräuer,* Technische Universität Braunschweig, Germany

Austenitic steels are known for their high corrosion resistance but at the same time have low wear resistance and high interfacial contact resistance (ICR), which limits their application e. g. as bipolar plates in Proton Exchange Membrane Fuel Cells (PEMFC). Plasma diffusion treatment, specially the well-known plasma nitriding, improves the hardness and interfacial contact resistance but mostly worse the corrosion behavior in PEMFC environment.

Aim of this study is to evaluate the less known plasma carburizing as a suitable process for functionalization austenitic stainless steels. For this purpose, a number of processes were executed under specific variation of temperature ranging from 360 °C to 450 °C and duration of 10 to 16 h. The samples were analyzed using x-ray diffractometer, x-ray photoelectron spectroscopy, SEM, Vickers microindentation, potentiodynamic polarization and ICR measurements.

It could be shown that the corrosion current density (1.78 $\mu A \cdot cm^{-2}$) of the treated samples are an order of magnitude lower than those of the reference (17.38 $\mu A \cdot cm^{-2}$). The ICR was also reduced from > 1000 $m\Omega \cdot cm^{-2}$ down to 31 $m\Omega \cdot cm^{-2}$. After corrosion, even lower values around 15 $m\Omega \cdot cm^{-2}$ were achieved. The targets according to DOE (< 1 $\mu A \cdot cm^{-2}$ and < 10 $m\Omega \cdot cm^{-2}$) were almost achieved. A comparison to the plasma nitrided samples was also performed and shows the high potential of plasma carburizing.

Keywords: plasma carburizing, s-phase, austenitic stainless steel, corrosion behavior, interfacial contact resistance, bipolar plate

8:20am **IA2-1-TuM-2 Laser-Induced Diffusion of an Aluminum Clad in an Aerospace Aluminum Alloy: Microstructure and Corrosion Behavior**, ***Milton Lima (miltonsflima@gmail.com)***, *E. Morais, S. Silva, R. Siqueira,* Institute for Advanced Studies, Brazil

The AA2024-T3 AlClad alloy is an aluminum alloy widely used in the aerospace industry. The AlClad designation refers to the application of a pure aluminum coating on the alloy surface to improve corrosion protection. Although this alloy has satisfactory mechanical behavior and corrosion resistance for use in aerospace applications, the aluminum coating often wears or peels during service, exposing the substrate to the corrosive environment. The objective of this work was to improve the adhesion of the coating to the alloy substrate through fiber laser glazing, where different current values of the pumping diode were used. This treatment aimed to improve the anchorage between the aluminum layer and the alloy substrate, making the structures more reliable and secure. The laser used was a continuous wave ytterbium-doped fiber laser with a wavelength of 1.07 µm, beam quality (M2) equal to 9, minimum beam diameter of 0.1 mm and displacement speed of 50 mm/s. Argon gas was also used to protect the specimens and the lens with a flow rate of 7 l/min. The analyses were performed using methods such as profilometry, pin-on-plate slip wear, nano-indentation, light optical microscopy, scanning electron microscopy, energy dispersive spectroscopy and electrochemical corrosion tests. Based on the results obtained, it was found that the objective of the study was achieved for all glazed specimens when the pumping current exceeded 50%. There was an increase in the metallurgical bonding between coating and substrate and a decreasing surface roughness with increasing diode pump current. In conditions where the laser pump current was between 50% and 70% the corrosion current densities values are similar to the material, without laser glazing, which indicates that the corrosion resistance was not affected in these cases. In this way, specimens with better coating adhesion, surfaces with lower average roughness and greater hardness were obtained. Consequently, less wear was observed while keeping corrosion resistance similar to that provided by the pure aluminum layer.

8:40am **IA2-1-TuM-3 Tribological and Corrosion Behaviour of Crn and AlCrn Coatings over Nitrided Medium Alloy Steel***, J. Maskavizan, E. Dalibon,* National University of Technology (UTN), Argentina*; **Sonia Brühl (sonia@frcu.utn.edu.ar)**,* National UNiversity of Technology (UTN), Argentina

Different Cr based coatings were deposited over medium alloy AISI 4140 steel in industrial facilities (Oerlikon Balzers Argentina), to improve wear and corrosion resistance in aggressive environments, like the plastic forming industry, and other applications in the aluminum industry. As AISI 4140 is a soft substrate, tests were carried out in two conditions: i) quenched and tempered (Q&T), ii) Q&T plus ion nitriding.

Friction and adhesive wear test were in a carried out in a rotational pin on disk machine using an alumina ball 6 mm in diameter as counterpart. The coatings were characterized by SEM and XRD. The corrosion test consisted in anodic polarization in a chloride solution. Finally, the film adhesion was tested by Rockwell C indentation and Scratch test at constant loads.

Both coatings resulted about 2.7-3 microns width. They presented good adhesion tested with Rockwell C indentation over nitrided substrates but not so good (HF3) for unnitrided ones. In the scratch test the critical load was over 50 N for the CrN but the AlCrN presented some spallation at the same load.

The CrN coatings presented the lower coefficient of friction in the Pin on Disk test at 5 N load. To measure wear loss, 12 N was used in the duplex case, meaning nitrided plus coating. The wear volume was less in the CrN too. In the corrosion test, only the CrN film showed a quasi-passive zone in NaCl solution, meanwhile the AlCrN presented active dissolution.

The observation of the wear tracks and the film microstructure, so as the surface after corrosion, allowed to explain the difference between nitrided and non nitrided substrates primarily, having this last combination a low load bearing capacity. Between both films, some slightly differences between mechanical properties explain the best behavior of CrN.

9:00am **IA2-1-TuM-4 Influence of the Cathodic Bias Parameters on Corrosion Resistance in the Micro-Arc Oxidation Coating of AZ31B Magnesium Alloy***, **Shih-Yen Huang (f08525129@g.ntu.edu.tw)**, Y. Lee, Y. Chu,* National Taiwan University, Taiwan

Micro-arc oxidation (MAO) is a surface treatment applied to valve material to form a multifunctional ceramic coating based on the principle of anodizing. By regulating electrical parameters and adjusting electrolyte composition, the MAO coating has the capability to meet diverse specifications across numerous domains. Among the various MAO process equipment, the bipolar pulse power supply stands out for its flexible process parameters and fast coating growth rate, which is attributed to the introduction of cathodic bias. The incorporation of cathodic bias has been proven to benefit the properties of the MAO coating by reducing the discharging energy and promoting the crystalline transition within the oxide phase of aluminum. However, the impact of cathodic bias in the MAO process is seldom discussed in magnesium alloy applications.

In this research, AZ31B magnesium alloy was used as the substrate to produce MAO coating, with the objective of clarifying the mechanism of cathodic biason the growth mechanism of MAO.Under controlled anodic bias parameters and cathodic duty ratio,the best corrosion resistance, as observed in the electrochemical impedance spectroscopy (EIS) result, was achieved with an impedance value of $2.55x10^6\ \Omega\cdot cm^2$ when the total charge quantity input through cathodic bias equaled that through anodic bias.Under the same condition, the corrosion resistance decreases regardless of whether the cathodic charge quantity is higher or lower than the anodic charge quantity, and a significant decrease in impedance value by two orders of magnitude was found when the ratio of cathodic charge quantity to anodic charge quantity exceeded 1.33. Moreover, under controlled cathodic charge quantity, MAO coatings were found to exhibit an impedance value of $10^6\ \Omega\cdot cm^2$ while the ratio of cathodic current density to anodic current density remained below 1. However, there was a notable decline in impedance value when the ratio exceeded 1.33.These results suggest that the influence of both the total charge quantity and the instantaneous input current density of the cathodic bias on the corrosion resistance of MAO coatings might be attributed to the limiting current density in the cathodic bias period.

9:20am **IA2-1-TuM-5 Nanolubricants: Pioneering Sustainable Solutions for the Lubrication Industry***, **Anirudha Sumant (sumant@anl.gov)**,* Argonne National Laboratory, USA **INVITED**

Over the past decade, the forefront of tribological studies has been illuminated by the exceptional properties of graphene, along with other 2D materials and their synergies with various nanomaterials. These cutting-edge nanolubricants have demonstrated unparalleled wear and friction performance across diverse systems. Their remarkable ability to achieve near-zero levels of friction and wear (known as superlubricity), extends even to macroscopic scales in different environments and under moderate to high contact pressures. This positions them as a promising alternative to traditional oil-based lubricants. Despite their impressive performance, the sustained and long-term reliability of these solid nanolubricants under more intricate tribological conditions remains a subject of ongoing investigation. Establishing their credibility as a potential replacement for oil-based lubricants necessitates a deeper understanding of their behavior in complex scenarios.

At Argonne National Laboratory, we have made significant strides in developing various nanolubricants. Our research showcases the attainment of superlubricity on rough steel contacts, even under high contact pressures (~1GPa), in both linear and sliding-rolling contacts as well as at high temperatures in an ambient environment. Furthermore, these nanolubricants exhibit stability over extended periods, enduring 70 kilometers of linear sliding without failure.

Our investigation delves into the role of tribochemistry at the micro/nanoscale and its profound impact on tribological performance at the macroscale. We present compelling examples resulting from collaborations with industry partners, particularly within the automotive sector, focusing on applications such as metal stamping. This progress not only sets the stage for future breakthroughs but also marks a significant stride toward realizing oil-free superlubricity in real-world applications. By doing so, these research efforts make a substantial contribution to the broader mission of decarbonization and offer sustainable solutions for the evolving lubrication industry

10:00am **IA2-1-TuM-7 Structural – Tribological Performance Evaluation of Ti-6Al-4V ELI Alloy after Sequential Surface Treatments***, **Daniel Toboła (daniel.tobola@kit.lukasiewicz.gov.pl)**, P. Chandran,* Łukasiewicz Research Network – Krakow Institute of Technology, Poland*; J. Morgiel,* Institute of Metallurgy and Materials Science of Polish Academy of Sciences, Poland

Titanium alloys are characterized by high specific strength, formability and corrosion resistance, but poor wear. The high cost of both metallurgical processing of its ore as well as later mechanical working, machining and the need to improve surface hardness by a proper treatment generally limits its wider application to aviation or military industry. The durability of the mechanically or physico-chemically upgraded surface layer depends to the largest extent on its: (i) geometrical irregularities and (ii) microstructure changes in the sub-surface area, which decide on the surface integrity of the material. Optimizing the latter is critical for components being employed in sliding or rolling contact with other parts and are subject to rapid wear resulting in significantly reduced life-times [1]. Hence, this study focuses on the influence of plastic deformation of near surface areas induced by slide burnishing/shot peening followed by sequential gas and plasma nitriding processes on the tribo-mechanical properties of the Ti-6Al-4V ELI alloy.

The Ti-6Al-4V ELI alloy substrates were subjected to heat treatment followed by a sequence of surface treatments like: turning (T), turning + burnishing (T+B), turning + burnishing + gas/plasma nitriding (T+B+GN/PN), turning + shot peening (T+SP), turning + shot peening + gas/plasma nitriding (T+B+GN/PN). Details of the mechanical treatments and gas nitriding parameters were described in our previous work [2,3]. Subsequently, all the substrates modified in this way were subjected to a detailed investigation involving both their phase composition and microstructure characterization as well as assessment of friction coefficient, hardness and sliding wear properties. Preliminary investigations revealed the in-situ formation of a very thin amorphous ‘tribo-layer’ which could prove to be beneficial during tribological contact. The effect of surface mechanical working applied as pre-treatment for the gas and plasma nitriding on the enhancement of tribo-mechanical properties of Ti-6Al-4V ELI alloy will be discussed in detail in the presentation.

1. Philip JT. et al., Friction, 7(6), (2019) 497–536
2. Toboła D. et al., Appl. Surf. Sci., 515 (2020) 145942
3. Toboła D. et al., Appl. Surf. Sci., 602 (2022) 154327

10:20am **IA2-1-TuM-8 Wear Particle Emission Influenced by Surface Conditions of an Alumina-Coated Cast Iron Disc**, ***Ran Cai (cai12r@uwindsor.ca)***, *X. Nie,* University of Windsor, Canada; *Y. Lyu,* Lund University, Sweden

Hard coatings can be applied to a traditional cast iron brake disc to increase wear resistance and thus reduce brake particle emission. An alumina coating prepared through a modified plasma electrolytic oxidation (PEO) process also shows a promise in wear reduction for the automotive brake disc. This work was to study effect of the alumina coating on the wear particle emission of the cast iron brake disc using a dedicated pin-on-disc (PoD) tribotester combined with an airborne particle emission measurement system. The testing samples included uncoated and alumina-coated cast iron discs with different surface roughness finish. Two different commercially available brake pad materials—non-asbestos organic (NAO) and low-metallic (LM)—were used as tribotesting counterparts. To simulate surface roughening effect by de-iced salt corrosion, salty water was sprayed on the sample surface and let it dry between the interval of subsequent tribotests. The data evaluation covered coefficients of friction (COF), specific wear rates, particle number concentrations, and particle size distribution. The friction tribolayers and emitted particles were analysed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) for better understanding of morphology and elemental compositions of the particulates. More discussions were given to the PEO coating process in terms of its role played in coating surface texturing, tribolayer formation, and wear particle emission at the disc surface.

10:40am **IA2-1-TuM-9 Metal Coated Carbon Fiber EMI Shielding Material**, *Y. Li,* National United University, Taiwan; *H. Chen,* Michigan State University, USA; *S. Chen,* National Yang Ming Chiao Tung University, Taiwan; *S. Chen, Z. Hsieh,* ***Chien-Chon Chen (ccchen@nuu.edu.tw)***, National United University, Taiwan

An electroplating method was used to modify the surface morphology of carbon fiber bundles. It deposits a layer of nickel film on the surface of carbon fiber bundles. The process can further apply to the subsequent applications of carbon fiber in electromagnetic wave shielding materials and metallurgical bonding at the interface of metal-based composites. In this study, the carbon fiber bundles' surface was first treated with hot nitric acid (80 °C, 30 min) to remove the polymer and activate the carbon fiber surface. Subsequently, a direct current electroplating method (3.5 V, 30 min) was used to deposit a 2 μm thick nickel film on the surface of carbon fiber bundles and carbon fiber fabric with a diameter of 7 μm. The weight of the carbon fiber increased by 1.9 times after nickel electroplating on the carbon fiber surface. To reduce the weight of the final product, efforts can be made in the future to decrease the thickness of the nickel layer. However, it is important to consider that as the nickel layer thickness decreases, the coverage of the nickel layer on the carbon fiber surface will also decrease.This research paper also provides detailed research and discussion on the relevant processes of metallization treatment on carbon fiber surfaces, including the design of electroplating fixtures, surface pre-treatment, electroplating treatment, and post-treatment.In this paper, hot nitric acid is used to replace high-temperature decomposition of polymer on the carbon fiber surface. Electroplating is employed to deposit nickel metal on the surface of carbon fiber bundles, with control over the voltage and duration of the electroplating process. The obtained nickel film thickness is observed, measured, and analyzed. Furthermore, the electromagnetic wave shielding properties of the carbon fiber with nickel electroplating are measured.

Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-1-TuM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderator: Francisco Javier Pérez Trujillo, Universidad Complutense de Madrid, Spain

8:20am **MA1-1-TuM-2 Tunable Aluminide Coatings for Surface Finish and Improved Oxidation and Hot Corrosion Behaviour of Additive Manufactured Ni-Based Superalloys**, ***Fernando Pedraza (fpedraza@univ-lr.fr)***, *D. PIEL, T. KEPA,* La Rochelle University, France **INVITED**

The widespread use of additive manufactured (AM) components has become a hot topic over the past 10 years. Many of the mechanical properties are surface-dependent because of the derived roughness due to e.g. semi-molten powders. The reactivity of the AM materials also increases because of the greater active surface. In addition, AM materials contain many metallurgical defects including e.g. dislocations, twins, various grain sizes, etc. which make the materials more susceptible to attack in particular under high temperature conditions where the harsh gas and molten reagents can go through. While different alternatives including e.g. chemical and electrochemical polishing, laser remelting, etc. have been proposed to lower the roughness and densify the surface, the AM materials still degrade fast.

The alternative that will be presented in this paper is based on the use of aluminium-based coatings made by slurry. As opposed to electrolytic or gas phase processes where the coating follows the surface roughness, the slurry process partly melts the surface, blends the uppermost layers of the AM alloy with the coating material and results in a diffused gradient layer that can be tailored to tune the chemical composition and microstructure. The examples will be given for different additive manufactured nickel-based alloy systems including the popular equiaxed or single crystalline nickel-based superalloys.

Simple nickel aluminide coatings will be shown to dramatically improve the oxidation resistance of IN-718 at temperatures as high as 800°C and of Alloy 699XA at 950°C through the development of a thin and adherent Al_2O_3 scale. The application of Al/Si slurry coatings improves dramatically the hot corrosion resistance under Na_2SO_4 against conventional vapour phase and simple Al slurries due to the layered segregation of Si_xW_y. The incorporation of microreservoirs made of MCrAlY in the aluminium diffusion coating matrix can in contrast improve both the oxidation and the hot corrosion resistance.

9:00am **MA1-1-TuM-4 Application of Machine Learning Algorithms to Characterize Aluminide Diffusion Coatings and to Predict their Ageing Behavior**, ***Vladislav Kolarik (vladislav.kolarik@ict.fraunhofer.de)***, *M. Juez Lorenzo,* Fraunhofer Institute for Chemical Technology ICT, Germany; *P. Praks,* IT4Innovations National Supercomputing Center, VSB - Technical University of Ostrava, Czechia; *R. Praksova,* IT4Innovation National Supercomputing Center, VSB - Technical University of Ostrava, Czechia

Aluminide diffusion coatings are an efficient and economic technique to protect steels against corrosion at high temperatures in harsh environments. They can be deposited as aluminum slurry through various deposition methods, such as spraying or brushing, followed by a heat treatment to form the diffusion coating. Machine learning algorithms offer a significant potential for optimizing and customizing the coatings for a specific application with desired coating characteristics and for predicting the ageing behavior during operation. The experimental effort can be minimized reducing the costs significantly and accelerating the development. Symbolic Regression was chosen to investigate the potential of machine learning to determine the slurry deposition parameters that lead to the targeted coating characteristics and to predict the ageing behavior.

Output parameters characterizing the diffusion coating were defined as well as input parameters on which they depend. Experimental data from former projects were used to train the algorithm applying a train/cross-validation split of 50/50. To assess the robustness of the coating system the thickness of the deposited slurry was calculated top-down from the experimental data after different ageing times and plotted versus the values adjusted during the slurry deposition process. The result reveals the deviation to the adjusted values and separates the sample sets, where the deposition process was under control from those with high fluctuation of the slurry thickness deviation. Output parameter characterizing the ageing progress, such as coating thickness, number of layers and their thicknesses, pores concentrations and FeAl precipitations in the Fe_2Al_5 layer were calculated as a function of time inferring predictions. The results show that machine learning is highly useful for complex systems influenced by numerous parameters, whose interrelation and meaningfulness is difficult to be described by classical physical modelling.

9:20am **MA1-1-TuM-5 Pack-Aluminizing Mechanisms in Stainless Steel Additively Manufactured**, *E. B. Varela,* PGMEC-Universidade Federal do Paraná, Brazil; *H. Abreu-Castillo,* PIPE - Universidade Federal do Paraná, Brazil; *G. Prass, J. Pacheco,* Instituto SENAI de Inovação em processamento a laser,, Brazil; ***Ana Sofia C. M. D'Oliveira (sofmat@ufpr.br)***, Universidade Federal do Paraná, Brazil

Sustainable development of high temperature parts typically requires surface treatment to enhance performance, including metallic parts processed by additive manufacturing (AM). Challenges of diffusion processed surfaces depend on the microstructure of AM parts being protected and are being addressed in this investigation. This research contributes to the discussion of the impact of additive microstructure on the diffusion mechanisms and characteristics of aluminide coatings. Pack-aluminization was applied to AM AISI316L stainless steel processed by PTA-DED, L-DED and L-PBF. Pack-aluminizing was carried out at 850°C for 1h and with a pack-mixture composition of 10%Al-3%NH_4Cl-87%Al_2O_3. Results show that, regardless of the substrate condition, aluminized coatings are composed of an external Fe_2Al_5 intermetallic layer and an interdiffusion region exhibiting two sub-layers, an intermediate layer of the intermetallic FeAl and an internal layer of α-Fe(Al) close to the substrate. The first evidences of the impact of additive multilayer structures is the non uniform interface with the substrate associated with the interlayer regions. Changes in the microstructure in these regions regions are a consequence of solidification mechanisms of each deposited layer creating local fluctuations in the atomic diffusion rate. The substrate microstructure also impacts the thicknesses of each layer, external and interdiffusion regions of the aluminized coatings. With the thicker external layer exhibited by the roller substrate (21,5±1,3 µm) and the thicker interdiffusion layer for the Stainless steel processed by PTA-DED (3,6± 0,4 µm): It is interesting to point out that inspite of the differences in microstructure L-DED and L-PBF AM materials exhibit very similar features that differ from PTA-DED that has a thinner external, 15,7±0,9 µm of the set of materials processed. The observed differences between coatings can be accounted for by the non-uniform characteristics of microstructure of the multilayer additive materials as opposed to the more uniform grain structure of the rolled substrate. Between additive materials, the finer microstructure of L-AM materials induced a larger density of diffusion paths forming a thicker external layer ±19 µm. Results allow to conclude that thicker external layers are accompanied by a thinner interdiffusion region behavior associated with an earlier formation of two compositional gradients in the coarser PTA-DED microstructure, at the surface and at the interface between the Fe_2Al_5 /substrate, accounting for the thicker sublayers in the interdiffusion region.

9:40am **MA1-1-TuM-6 Synthesis of Novel Multi-Element TM-Aluminides by Multilayer Magnetron Sputtering***,* ***Vincent Ott (vincent.ott@kit.edu)****, M. Duerrschnabel, U. Jaentsch, M. Klimenkov, S. Ulrich, M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal Aluminides in the B2 structure like NiAl and FeAl are well known for their combination of mechanical properties and oxidation resistance which make them suitable materials for high temperature applications. However, these materials often suffer from brittle material behavior at room temperature, hampering their machinability and utilization. The RuAl phase shows improved RT ductility due to its greater number of available slip systems compared to other binary aluminides in the B2 structure. To investigate and potentially further improve the mechanical and protective behavior of transition metal aluminide thin films, a multi-layer approach was used to synthesize novel multi-elemental solid-solution aluminides of the type (Ru_x, Me_{1-x})Al. The deposition of nanoscale multilayer films thereby allows to circumvent thermodynamic restrictions in equilibrium bulk conditions to generate supersaturated aluminide phases in thin films outside the phase boundaries. The correlation between the thin films microstructure and the mechanical properties is discussed. The phase formation is observed by HT-in-situ-XRD, while the mechanical properties as well as the microstructure are examined by microindentation and TEM analysis respectively.

10:00am **MA1-1-TuM-7 Structural Evolution and Oxidation Resistance of Al/Si Alloyed Transition Metal Carbide Thin Films***,* ***Sophie Richter (sophie.richter@tuwien.ac.at)****,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; E. Ntemou, D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria

Transition metal carbides (TMCs) are known for their mechanical properties, high-temperature stability and melting points exceeding 3000 °C. However, their exceptional high-temperature properties are offset by their sensitivity to oxidation. This study focuses on an alloying strategy incorporating Al and Si as strong oxide-forming elements to extend their oxidation resistance in demanding environments. Using a combinatorial physical vapor deposition (PVD) approach, group IV to VI transition metal carbides were systematically investigated by co-sputtering Al and Si next to TMCs. This comprehensive study covers a wide range of structural and chemical compositions, which are thoroughly characterized by X-ray diffraction (XRD), nanoindentation, and elastic recoil detection analysis (ERDA) calibrated X-ray fluorescence (XRF) to achieve precise chemical quantification. Subsequently, a subset of selected compositions based on structural and mechanical criteria is analyzed concerning their oxidization resistance. In-situ XRD monitors the formation of oxide scales in synthetic air environments up to 1200 °C. In addition, conventional oxidation experiments in a box furnace contribute to a comprehensive understanding of the oxidation behavior of these TMCs. The formed scales are thoroughly described by transmission electron microscopy unraveling details on the diffusion kinetics of the oxide formers. This research not only explores the fundamental mechanisms that determine the scale formation of TMCs, but also provides valuable insights into the growth mechanism of ternary face-centered cubic (fcc) TM-Al/Si-C solid solutions synthesized by PVD techniques.

10:20am **MA1-1-TuM-8 Hot Corrosion of Arc Evaporated $Ti_{1-x}Al_xN$ on Ni-Cr-Co Based Superalloys***,* *O. Hudak, A. Scheiber, P. Kutrowatz, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*;* ***Helmut Riedl (helmut.riedl@tuwien.ac.at)****,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Hot corrosion is an accelerated oxidation process that occurs in high-temperature environments (650-950 °C) in the presence of sulfur-rich exhaust gases and salt-impurities. The subsequent formation of high-melting sulfate salts and their deposition on machine components induces accelerated degradation of operating parts through the formation of a porous and non-protective corrosion scale. Notably, Ni-, Co-, and Fe-base superalloys used in aerospace and power generation industry are particularly susceptible to hot-corrosion attacks.

This research explores arc-evaporated $Ti_{1-x}Al_xN$ as a promising protective coating material mitigating hot-corrosion effects on superalloys. $Ti_{1-x}Al_xN$ coatings with varying metal ratios were arc evaporated onto a NiCoCr-based superalloy and subjected to hot-corrosion testing in a specially designed hot corrosion rig. Utilizing a Na_2SO_4-$MgSO_4$ salt mixture, both coated and uncoated samples were thermally treated in an SO_x-rich atmospheres for a duration of up to 30 h. The primary objective was to enhance the understanding of the corrosion mechanisms of $Ti_{1-x}Al_xN$ coatings under low-temperature hot corrosion (LTHC, at 700°C), as well as high-temperature hot corrosion (HTHC, at 850°C) conditions. The scale formation was analyzed through a variety of high-resolution characterization techniques ranging form XRD, SEM, to HR-TEM.

Results revealed that arc evaporated Ti_{1-x}AlxN exhibits superior corrosion resistance compared to the bare NiCoCr-based alloy in both temperature regimes. Under LTHC conditions, a localized and accelerated attack was observed, driven by an initial nitride-to-sulfate transformation and followed by a synergistic fluxing mechanism. This mechanism involved the formation of layered oxide domains rich in TiO_2 and Al_2O_3, due to the acidic nature of the liquid salt interface. The obtained scale was dominated by Al_2O_3, known for its enhanced stability under acidic conditions. In contrast, under HTHC conditions, a more uniform development of the corrosion scale was noted. Similar to LTHC, a sequential fluxing produced Ti-rich and Al-rich oxide domains that over time formed a layered corrosion scale. The stability of TiO_2 under basic conditions resulted in the primary formation of a porous TiO_2 scale at the scale-salt interface, followed by a substantial band of Al-rich oxide.

This research contributes valuable insights into the hot corrosion behavior of arc evaporated $Ti_{1-x}Al_xN$ coatings, and highlights their potential as protective coatings for components exposed to aggressive high-temperature environments.

10:40am **MA1-1-TuM-9 Characterization of Li-rich Corrosion Products Formed onto Aluminized and Uncoated Steels after Molten Carbonates Exposure***,* *P. Audigié, S. Rodríguez,* ***Alina Agüero (agueroba@inta.es)****,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Public authorities are strongly encouraging the adoption of new thermal energy storage (TES) systems in order to meet the requirements for clean energy worldwide. However, installation, maintenance and materials for such TES imply rather high costs which can hinder their implementation. To remedy this, various corrosion resistance slurry aluminide coatings have been developed at INTA onto ferritic and austenitic steels as low-cost alternative materials for structural components in contact with molten salt. Emphasis has been placed on Li-rich molten carbonate exposure at high temperature of such coated and uncoated materials and expressly on the identification and characterization by advanced techniques (GDOES, TEM) of Li-rich corrosion products as Li cannot be detected by conventional techniques. Microstructural features of $LiFeO_2$, $LiFe_5O_8$, $LiAlO_2$ both alpha- and gamma- phases among others and Li effect will be discussed. Presence of two distinct peaks of Li were detected in the $LiAlO_2$ oxide formed onto the slurry aluminide coated T92 heat treated at low temperature and exposed 2000h at 650ºC with Li, Na and K carbonates. Similar behavior was observed with the aluminized 310H austenitic steel after 1000h of exposure in the same environment at 700ºC. Li penetration into the different studied materials will thus be described.

Protective and High-temperature Coatings
Room Town & Country D - Session MA3-3-TuM

Hard and Nanostructured Coatings III

Moderators: Marcus Günther, Robert Bosch GmbH, Germany, **Rainer Hahn**, TU Wien, Institute of Materials Science and Technology, Austria, **Stanislav Haviar**, University of West Bohemia, Czechia, **Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

8:00am **MA3-3-TuM-1 Physical Properties of Pure Tantalum Nitrides Thin Films***, **Angeline Poulon-Quintin (angeline.poulon@icmcb.cnrs.fr)**,* Univ. Bordeaux, CNRS, ICMCB, France*; A. Achille,* ICMCB, CNRS, France*; D. Michau,* CNRS, ICMCB, France*; M. Cavarroc,* SAFRAN, France

Transition metal nitrides coatings are widely studied because of their good optical, mechanical, thermal... properties. Depending on the microstructure, coatings present different properties. For tantalum nitride (TaN), stable (hexagonal) and metastable (cubic) phases can be deposited as coatings. In this study, their physical and adherence properties on 316L stainless steel and AlN substrates depending on the microstructure and the thin film PVD technique used, are compared. Both Reactive High Power Impulse Magnetron Sputtering (R-HiPIMS) and Reactive RadioFrequency Magnetron Sputtering (RF-MS) were selected. Characterisations of structures and films microstructures were realised by *Grazing* Incidence X-Ray diffraction and Electron Microscopies (SEM and TEM). Scratch tests and nanohardness measurements were used to compare adherence and mechanical properties. Electrical properties were explored with a four-point probe.

The correlation between microstructure, process and physical properties is discussed. The aim of this study is to show the interest for specific applications of the hexagonal TaN thanks to the quantification of its physical properties and/or tuning its microstructures.

8:20am **MA3-3-TuM-2 Magnetron Sputtered $Cr_{1-x}Ta_x$ Coatings***, **Jan-Ove Söhngen (jan-ove.soehngen@kit.edu)**, V. Ott, S. Ulrich, M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Refractory alloy thin films can exhibit unique properties which make them suitable candidates in high temperature applications. The model system chosen for our study is Cr-Ta. $Cr_{1-x}Ta_x$ coatings with various Ta contents weresynthesized by magnetron sputtering utilizing acombinatorial experiment in thin film deposition. We used a segmented circular target consisting of two half plates of pure Cr and Ta for the deposition at 250 W DC target power, 0.4 Pa Argon pressure, 0 V substrate bias and ≈ 150°C substrate temperature. Polished steel substrate samples of 10x10x1 mm^3 were placed in a horizontal line opposite to the target. Thus, we obtained different $Cr_{1-x}Ta_x$ coatings with various Ta content in a single deposition experiment.

The amount of Cr and Ta determined by electron micro analyses was used to classify the XRD (X-Ray diffraction) results:

1. All coatings are crystalline.
2. The XRD reflections of the coatings with Ta content between 15.3 at.% and 39.7 at.% exhibit similar shape and suggest these coatings are polycrystalline and grow in a single-phase bcc (body centered cubic) solid solution structure.
3. In contrast to the coatings with a lower amount of Ta, the XRD reflections of coatings with 68.5 at.% Ta content show a broader (110)-signal, indicating a much smaller crystal size and the (110) reflection of the coating with 80 at.% Ta exhibits a sharp reflection near the position of the (110)–reflection of the bcc structure and a broader shoulder, suggesting an overlap of different reflections.

This indicates a transition in the microstructure of the coatings with increasing Ta content. No intermetallic phase $TaCr_2$ was found in any of these coatings. Pure crystalline Ta coatings were not bcc structured. Transmission electron microscopy analyses will resolve the microstructure further.

Mechanical properties of the coatings were studied by micro-indentation. The hardness and Young`s modulus of the $Cr_{1-x}Ta_x$ coatings in dependence of their Ta content and as well of the pure Cr and Ta coatings will be discussed. Due to solid solution strengthening, the Vickers hardness of the $Cr_{1-x}Ta_x$ coatings exhibits a local maximum in relation with the Ta content.

8:40am **MA3-3-TuM-3 Overview and Trends in Application Driven Developments of Wear Resistant Coatings***, **Denis Kurapov (denis.kurapov@oerlikon.com)**,* Oerlikon Surface Solutions AG Pfäffikon, Zweigniederlassung Balzers, Liechtenstein **INVITED**

The long history of the wear protective coating deposited by physical vapour deposition (PVD) technology starts more than 40 year ago from the coatings applied on cutting and forming tools. During the last years the requirements on the wear resistance in tooling industry getting more and more demanding giving strong impulses for development of new surface solutions and deposition technologies.

With significantly increased level of requirements on the performance of the wear protective coatings the development of new solutions goes more and more into direction of tailored solutions. Development of such solutions based on understanding of the wear mechanisms and correlation between coating properties and its performance. Deposition technologies need to be developed in the way to enable deposition of the coatings with desired properties.

In this paper we present an overview of the latest developments of surface solutions and PVD technologies. The main focus put on history and resent advances in development of wear protective coatings as well as on progress in arc evaporation and magnetron sputtering deposition technologies.

9:20am **MA3-3-TuM-5 Enhancing the Thermal Stability and Cutting Performance of fcc-AlCrN by Oxygen Incorporation***, A. Michau,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; **Tomasz Wojcik (tomasz.wojcik@tuwien.ac.at)**, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; D. Kurapov,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria

Protective coatings applied in advanced machining processes typically encounter extreme thermo-mechanical loads easily exceeding temperatures above 1000 °C. In this context, the thermal stability and, hence, the decomposition behaviour of the applied coatings is still the key-parameter for enhanced durability. Recent studies on oxygen incorporation in (Ti,Al)(O,N) highlighted the potential of defect-engineered meta-stable structures, as for the formation of wurtzite AlN domains, the non-metal mobility is decisive in the shared oxygen/nitrogen sublattice. Here, relatively small amounts of oxygen are efficient to double the required energy to form w-AlN out of $(Ti,Al)(O_xN_{1-x})$ compared to (Ti,Al)N.

Based on these results, we thoroughly investigated the decomposition behaviour of oxygen-doped $Al_{0.70}Cr_{0.30}(O_{1-x}N_x)$ coatings grown by arc evaporation. During the reactive growth, the oxygen was incorporated by varying the flow rates between 15 to 70 sccm compared to 940 to 990 sccm nitrogen (p_{dep} around 4 Pa). All coatings were grown using an Oerlikon Balzers INNOVENTA kila equipped with AlCr 70/30 targets. These variations lead to purely fcc structured $Al_{0.70}Cr_{0.30}(O_{1-x}N_x)$ coatings obtaining as-deposited hardness values of 40 ± 2 GPa. The decomposition behaviour was investigated in tailormade vacuum annealing treatments (T_{an} = 700 to 1200 °C) as well as cutting tests, clearly indicating enhanced stability for the oxygen-containing coatings. The detailed phase decomposition process was investigated by transmission electron microscopy (TEM) using selected area electron diffraction, energy-dispersive x-ray spectroscopy, and high resolution TEM. The incorporation of oxygen delays the fcc to w-AlN transition from at least 800 to 1000 °C, which correlates with the results observed in the cutting tests. In more detail, crater and flank wear formation and progression are clearly delayed during wet and dry milling operations. In summary, this study highlights the potential of defect engineering via oxygen incorporation, enhancing the thermal stability of metastable fcc-structured AlCrN based coatings. In contrast to metal alloying approaches, the non-metal sublattice adaption is a simple but highly effective way to tune the properties of well-established nitrides.

9:40am **MA3-3-TuM-6 Enhancing Toughness in Nanocomposite AlCrSiN Thin Films by Crack Deflection at Sublayers: Correlating Microstructure and Micromechanical Properties***, **Kevin Kutlesa (kevin.kutlesa@unileoben.ac.at)**, M. Meindlhumer,* Montanuniversität Leoben, Austria*; A. Lassnig,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; R. Daniel,* Montanuniversität Leoben, Austria*; A. Medjahed,* ESRF, France*; J. Keckes,* Montanuniversität Leoben, Austria

Wear-resistant transition metal nitride (TMN) thin films are recognized for their exceptional hardness, high Young's modulus, superior thermal stability and oxidation resistance. However, their application is often limited by their brittleness leading to a low fracture toughness. This contribution presents a design approach encompassing (i) a nanocomposite AlCrSiN microstructure, (ii) a multilayer architecture reinforced with (iii) precisely controlled precipitation within targeted sublayers. The objective is to enhance the toughness of TMN thin films while preserving high hardness and other functional properties.

Cathodic arc evaporation was used to deposit two reference monolithic thin films, namely $Al_{0.63}Cr_{0.27}Si_{0.1}N$ and $Al_{0.675}Cr_{0.075}Si_{0.25}N$, along with a multilayer thin film consisting of alternating sublayers of these two materials. A carefully adjusted vacuum heat-treatment at 1050°C for 5 min was applied to tailor the microstructure through precipitation. Qualitative analysis of the heat-treatment's impact on thin film microstructure was conducted using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Additionally, insights into the assembly and elemental distribution in the nanocomposite microstructure were obtained through energy-dispersive X-ray spectroscopy in TEM. Cross-sectional synchrotron X-ray nanodiffraction (CSnanoXRD) at the ID13 beamline of ESRF in Grenoble facilitated the correlation of cross-sectional variations in phases, texture, microstructure, and residual stresses with the architecture and thermal history of the thin films. The nanoscale characterization revealed a nanocomposite microstructure composed of cubic Cr(Al)N and wurtzite Al(Cr)N nanocrystals with sizes of ~5 nm. In the material with lower Si content the heat-treatment induced the precipitation of cubic Cr(Al)N, while in the higher Si content material precipitation was effectively suppressed. Consequently, in the heat-treated multilayer a cross-sectional alternation of sublayers with significant precipitation and sublayers devoid of any precipitation was observed. Mechanical properties were assessed through *in situ* bending tests on freestanding microcantilevers prepared by focussed ion beam milling. The Young's modulus, fracture stress and fracture toughness were determined by loading up to fracture unnotched and notched cantilevers, respectively. A stepwise crack-propagation was observed in the heat-treated multilayer, revealing an unprecedented extrinsic toughening mechanism that significantly improved the fracture response.

10:00am **MA3-3-TuM-7 Mechanical Properties and Tribological Performance of AlCrMoN/TiSiN Nanostructured Multilayer Coatings***, **Ming-Xun Yang (u6au6vmp711@gmail.com)**, Y. Chang,* National Formosa University, Taiwan

A TiSiN coating with a nanocomposite structure where TiN grains are surrounded by a SiN_x matrix possesses excellent mechanical properties and make it a promising selection for wear protection of cutting tools in machining applications. However, TiSiN coatings suffer from high residual stresses and thus limit the tribological performance and hinder high temperature applications of monolithic TiSiN coatings. Recently, Mo-containing AlCrMoN coatings have received widespread attention because of improved tribological performance and toughness. In this study, the mechanical and tribological properties of AlCrMoN/TiSiN coatings with different modulation geometries, namely modulation period and modulation ratio were elaborated. During the coating process of AlCrMoN/TiSiN, CrMoN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. An impact fatigue test using a cyclic loading device and ball-on-disc wear tests at room temperature and 500 °C were conducted to evaluate the correlation between tribological properties and coating structures of the deposited coatings. X-ray diffraction (XRD) was used to characterize the microstructure, phase identification and residual stress. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM). A Rockwell indentation tester and a scratch tester were used to evaluate the adhesion strength between the coating and the substrate. The coating hardness and the elastic modulus were measured by nanoindentation. The addition of AlCrMoN into TiSiN to form a multilayer architecture provides an alternative for a hard-and-lubricious coating. The design of gradient-and-multilayered AlCrMoN/TiSiN coatings is anticipated to be advantageous in applications to enhance the mechanical properties and wear performance of mechanical parts and cutting tools.

10:20am **MA3-3-TuM-8 Influence of Deposition Pressure and Gas Mixture on the Microstructure and Phase Composition of Arc Evaporated TiSiN Coatings***, **Nina Schalk (nina.schalk@unileoben.ac.at)**, Y. Moritz, G. Nayak, D. Holec,* Montanuniversität Leoben, Austria*; C. Hugenschmidt,* Technical University of Munich, Germany*; V. Burwitz,* Technical University Munich, Germany*; L. Mathes,* Technical University of Munich, Germany*; C. Saringer,* Montanuniversitat Leoben, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; M. Tkadletz,* Montanuniversitat Leoben, Austria

Owing to their advantageous properties including excellent hardness and high oxidation stability, arc evaporated TiSiN coatings are frequently used as protective hard coatings for various machining applications in the metal cutting industry. Within this work, the influence of a varying N_2 deposition pressure and the addition of Ar to the deposition atmosphere on the microstructure and phase composition of TiSiN coatings was studied in detail. All coatings exhibited a feather-like and fine-grained structure and showed an amorphous SiN_x phase fraction. Further investigation of powdered TiSiN coatings revealed a significant decrease of the lattice parameter with increasing N_2 deposition pressure, while the elemental composition was identical for all coatings. Consequently, the changes of the lattice parameter can either be attributed to the formation of a TiSiN solid solution and/or to the formation of vacancies during the deposition process. Neither atom probe tomography nor Doppler position annihilation broadening could unambiguously clarify the presence of either a TiSiN solid solution or vacancies. Thus, the powdered TiSiN coatings were studied by *in-situ* XRD in vacuum up to 1200 °C in order to gain insight into the evolution of the lattice parameter at elevated temperatures, which suggests that at lower temperatures vacancies are annihilated and then at higher temperatures Si diffuses out of the TiSiN solid solution. The coating synthesized at the lowest pressure and the one grown in a mixed N_2 and Ar atmosphere already reached the lattice parameter of pure TiN after the high temperature XRD experiment, while for the coatings grown at higher pressures an additional annealing treatment was necessary to reach this value, which might indicate that more Si is incorporated into the TiSiN solid solution at higher deposition pressures and that the additional kinetic activation stemming from the Ar ions results in less Si incorporation. The assumption that at lower annealing temperatures defects are annihilated and at higher temperatures Si diffuses out of the solid solution could be corroborated by differential scanning calorimetry and complimentary investigations of annealed coatings on substrates using energy dispersive X-ray spectroscopy and atom probe tomography. Density Functional Theory (DFT) calculations indicate that defects only play a subordinate role for the low observed lattice parameters in as-deposited state and that the addition of Ar to the deposition atmosphere results in a different incorporation of Si into the TiSiN solid solution.

10:40am **MA3-3-TuM-9 Enhanced Mechanical Properties and Thermal Stability of Novel Nanocrystalline AlNi / Al_2O_3 Multi-layered Coatings Deposited by a Combined Physical Vapour Deposition and Atomic Layer Deposition Approach***, **Hendrik Constantin Jansen (hendrik.jansen@empa.ch)**, B. Putz, A. Sharma,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; M. Hans,* RWTH Aachen University, Germany*; S. Lellig,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, RWTH Aachen University, Germany*; J. Schneider,* RWTH Aachen University, Germany*; J. Schwiedrzik, J. Michler,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; T. Edwards,* NIMS (National Institute for Materials Science), Japan

A one-chamber-design combining physical vapour deposition (PVD) and atomic layer deposition (ALD) without breaking vacuum allows deposition of Al coatings with Al_2O_3 interlayers. These novel Al coatings possess enhanced thermal stability and mechanical properties compared to their pure PVD nanocrystalline counter-parts.
Further recent advances involve multi-layered $Al_{98}Ni_2$ / Al_2O_3 and $Al_{95}Ni_5$ / Al_2O3 (25 / 1 nm) coatings as well as their respective pure $Al_{98}Ni_2$ and $Al_{95}Ni_5$ PVD counterparts, which were deposited to evaluate the influence of grain boundary complexion engineering and the unique crystalline / amorphous interface on mechanical properties and thermal stability. The coatings were annealed at 160°C and 210°C to allow not only grain growth but also segregation enrichment at grain boundaries and triple junctions. Subsequently, microstructural stability was investigated based on lateral grain growth by X-Ray Diffraction χ-scanning and GIWAXS – out-of-plane Al grain size being limited by the 1 nm Al_2O_3 interlayers. Mechanical testing by

both nanoindentation and micropillar compression at multiple strain rates allowed mechanical property analysis of the high-strength AlNi / Al_2O_3 multilayer coatings, which reached a yield strength of more than 1.3 GPa, outperforming a previously reported Al / Al_2O_3 (25 / 1 nm) coating achieving 1 GPa. Ultimately, high-resolution analyses by trans-mission electron microscopy and atom probe tomography allowed the enhanced properties to be linked to both grain boundary decoration and secondary phases that hinder dislocation and grain boundary movement.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP1-1-TuM

PVD Coating Technologies I

Moderators: Christian Kalscheuer, RWTH Aachen University, Germany, **Vladimir Pankov**, National Research Council of Canada

8:00am **PP1-1-TuM-1 Discharges Modes Relevant to Plasma-Based Coatings: an Analysis of Their Physics and Economics**, ***Andre Anders (andre.anders@iom-leipzig.de)***, Leibniz Inst. of Surface Eng. (IOM), Germany **INVITED**

Physical Vapor deposition (PVD) has matured over the last decades, where plasma processes have been added to control the microstructure of thin films and coatings. The different processes make use of different discharge modes, such as magnetically enhanced glow (magnetron discharge) and arc discharges, where the latter has the most prominent and very different sub-modes of thermionic and cathodic arcs.However, these are not the only ones.The overview connects the discharge physics of the different modes – resulting in plasmas of quite different properties – to the film microstructure, control options, but also considers the economics (especially energy considerations) associated with the different approaches.

8:40am **PP1-1-TuM-3 Design of an Innovative Cathodic Arc Source with High Deposition Rate and Low Macroparticles Generation**, ***Raül Bonet (raul.bonet@eurecat.org)***, Eurecat Technological Center of Catalonia, Spain; *L. Carreras,* Tratamientos Térmicos Carreras S.A, Spain; *J. Orrit-Prat, J. Caro,* Eurecat Technological Center of Catalonia, Spain

Within the group of PVD techniques, the cathodic arc evaporation technique stands out for its performance, which is characterized by a nearly 100% ionized, high energy plasma. Its versatility, lower economic cost compared to other deposition techniques and easy industrial scaling has led to a massive industrial implementation for the preparation of coatings and thin layers of different nature. One of the disadvantages of the cathodic arc technique is the generation of macroparticles because of the electric arc discharge on the cathode surface. This fact can be an important technological limitation for those cases where a good surface finish, low friction coefficient or good wear and corrosion resistance is required. Traditionally, this problem has been solved by applying magnetic filters that separate the macroparticles from the plasma ions. However, this solution involves a considerable reduction in the deposition rate, which makes its industrial implementation difficult. On the other hand, in order to reduce the coating process costs, cathodic arc sources that allow a high deposition rate are required.

In this work, an innovative cathodic arc source has been designed to achieve a deposition rate of up to 20 microns/hour, with a reduction of 80 % of macroparticles. In order to increase the deposition rate, a high-current pulsed source (100-500 A, 10-20000 Hz) has been used to generate the arc discharge between the anode and cathode. On the other hand, to reduce the generation of macroparticles, an optimized magnetic field configuration around the cathode has been obtained by means of Finite Elements Method (FEM) simulation, which allows to induce a fast and homogeneous movement of the electric arc on the cathode surface. Standard transition metal nitride (CrN, AlTiN) hard coatings obtained using this source exhibit excellent surface finish and improved mechanical properties in terms of adhesion and hardness.

9:00am **PP1-1-TuM-4 TaB_X Thin Film Synthesis from an Industrial-Sized DC Vacuum Arc Source**, ***Igor Zhirkov (igor.zhirkov@liu.se)***, *A. Petruhins, A. Shamshirgar,* Materials Design Division, IFM, Linköping University, Sweden; *S. Kolozsvári, P. Polcik,* PLANSEE Composite Materials GmbH, Germany; *J. Rosen,* Materials Design Division, IFM, Linköping University, Sweden

Thin films of transition metal borides are gaining increasing attention due to their physical and chemical characteristics. Most publications in this area focus on TiB_2, synthesized through various sputtering techniques, targeting applications as protective hard layers. Tantalum diboride, TaB_2, is another system with interesting properties, especially for high temperatures, but is much less explored. The elastic modulus of TaB_2 is ~ 2 times lower than that of TiB_2, but displays similar high hardness, combining high strength with high resistance to elastic and plastic deformation. Deposition of TaB_2 coatings with the industrially relevant physical vapor deposition (PVD) process DC vacuum arc is virtually absent in the literature. Still, DC arc deposition allows synthesis of coatings with a deposition rate unreachable for any other PVD technique. This motivates development and investigation of arc processes for TaB_2 synthesis. In the present work, we investigate DC arc plasma generation and deposition of TaB_x, and compare to previously investigated TiB_x. We use an industrial scale arc plasma source, Hauzer CARC+, which utilizes plane cathodes of 100 mm in diameter. Process stability and cathode dependent features of arcing is evaluated, and plasma analysis with respect to charge-state resolved ion energy is performed, showing a high ionization degree, and ion energies extending well above 100 eV. It is well known that plasma generation from compound cathodes gives a mass-dependent angular distribution for the elements of the compound, which is confirmed for the here investigated borides. This, in turn, is one of the factors contributing to a resulting film composition diverging from the cathode composition. The plasma characterization and macroparticle generation is correlated to deposited thin films; their composition, structure and properties. Altogether, the results show that DC vacuum arc is an industrially relevant technique for deposition of metal diborides.

9:20am **PP1-1-TuM-5 Plasma Enhanced Magnetron Sputtering and Its Applications in Industry**, ***Jianliang Lin (jlin@swri.org)***, Southwest Research Institute, USA **INVITED**

Plasma enhanced magnetron sputtering (PEMS) technology is an advanced version of the conventional magnetron sputtering technique. The PEMS technique draws electrons off of hot filaments installed in a sputtering system when electrons have gained enough energy to exceed the work function of the filaments. The electrons collide with neutral atoms and generate a large number of ions through impact ionization. As a result, a global hot filament assisted plasma is formed in the entire chamber which is independent of the magnetron discharge plasma.The hot filaments also provide additional thermal energy without using external heating elements. Plasma diagnostics showed that the majority of the ions in the PEMS plasma exhibited low energies of less than 5 eV. However, a significant increase in the ion flux can be achieved by increasing the hot filament discharge current. The extra ion fluxes provide enhanced ion bombardment on the substrates, which is beneficial for improving the structure and properties of coatings. The PEMS plasma can be utilized to perform different surface engineering tasks, e.g. plasma cleaning/etching, plasma nitriding, and coating depositions. It can be easily combined with other magnetron sputtering techniques, e.g. DC, RF, pulsed DC, and high power impulse magnetron sputtering (HiPIMS) to enhance ion fluxes and thermal energies. In this presentation, the principle and characteristics of the PEMS technology will be introduced. Technical examples of PEMS coatings for different industry applications will be reviewed, for example, solid particle erosion resistant coatings for aerospace and Oil&Gas, duplex coatings for die casting dies, low friction nanocomposite coatings for combustion engine piston rings, protective coatings for high temperature sCO_2 environment, etc.

10:00am **PP1-1-TuM-7 Sustainable and Economical Production of High-Quality HIPIMS Coatings**, ***Stephan Bolz (stephan.bolz@cemecon.de)***, *B. Mesic, O. Lemmer, C. Schiffers,* CemeCon AG, Germany

Constant improvement of ceramic coatings for cutting tools aiming at best wear resistance under conventional and extreme conditions is driven by the development of new workpiece materials with improved properties. Economical machining of such materials requires ever denser and harder coatings with better adhesion to the tool substrate. In addition to the required coating properties, however, the economical production of these coatings plays a more important role since some time. Shorter coating processes, reduced handling and lower energy consumption are the right keywords to well describe the current situation.

Considering these aspects, high-performance coating technologies, such as HiPIMS, are becoming more and more interesting for the market. Thanks to HiPIMS dense, hard, adhesive, and droplet-free layers can be deposited in highest quality with high energy efficiency at high deposition rates. Furthermore, well-chosen HiPIMS pulse parameters combined with an appropriate bias synchronization can avoid high residual stress of coatings for sharp edged cutting tools.

In our presentation we show that optimization of HiPIMS pulse parameters leads to a significant increase in metal ionization, accompanied by improved coating properties of an (Al,Ti,Si)N layer. The improved coating properties include above all a denser microstructure and a smoother surface, which allows to skip time consuming and energy-intensive post-treatment steps. Brilliant shine and best optical appearance are related with low friction and perfect chip removal during use. This combination of layer properties is a guarantee for a perfect surface finish of the workpiece.

10:20am **PP1-1-TuM-8 Increasing the Metal Ion Flux Fraction in Industrial Conditions***, **Peter Klein (pklein@mail.muni.cz)**, J. Hnilica,* Masaryk University, Czechia*; V. Sochora,* SHM s.r.o., Czechia*; P. Vašina,* Masaryk University, Czechia

The field of coating technologies progressively changes. Before, PVD technologies were utilized to produce a coating with a single superior quality such as very high hardness, high ductility, or very low roughness. Nowadays, due to increasingly sophisticated applications, a combination of superior properties is required. Generally, high-quality coatings require high ion flux to be formed, which is easily achievable by arc–based techniques, but those are prone to have high roughness of produced films. This work reports on high ionized metal flux fraction (IMFF) in industrial DC magnetron conditions.

A biased QCM was employed in the industrial magnetron deposition system to quantify the metal ion contribution to the forming film. The used deposition system can utilize up to four cylindrical rotating electrodes, each measuring 50 cm in length and 10 cm in diameter. For the titanium magnetron cathode, up to 40 kW DC power can be supplied over the 90 cm^2 racetrack, providing a current density of around 0.8 $A.cm^{-2}$. Such a high current density is rather similar to pulsed power techniques and unsurprisingly, up to 30% of IMFF can be obtained purely in the DC operation. A striking difference from laboratory DC magnetron discharges, where the literature states the IMFF can reach only up to 2%.

The IMFF can be further enhanced in the described system through the utilization of a lateral glow discharge (LGD). Lateral glow discharge uses one of the arc electrodes as an electron source. Produced electrons from the arc cathode are drawn to the opposite arc electrode, forming an area over the magnetron cathode where the collision with the sputtered metal occurs. This increases IMFF by a further 10%, which makes this a comparable system to HiPIMS. Unlike HiPIMS, the introduction of LGD into the DC magnetron sputtering process does not affect the deposition rate. Despite LGD being arc-based technology, it does not create macroparticles, but It has to be noted that the LGD requires multi-electrode configuration to run.

10:40am **PP1-1-TuM-9 Unraveling the Dynamics of Reactive Magnetron Sputtering: Insights into Feedback Control, Metastable Conditions, and Long-term Stability***, **Josja Van Bever (Josja.VanBever@UGent.be)**, K. Strijckmans, D. Depla,* Ghent University, Belgium

High-quality coatings with optimized stoichiometry in reactive magnetron sputtering are essential for numerous industrial applications. This demands meticulous control of process conditions within the transition region between metallic and poisoned modes, achieved through feedback control or high pumping speeds [1]. Despite advancements, a comprehensive understanding of the convergence and steady-state conditions in feedback control for this context is still elusive.

In this study, we present *precise feedback* measurements, focusing on the intricate dynamics within the aluminum-oxygen system. Our investigations unveil two distinct metastable states dependent on the system's history. We establish a clear connection between these states and the *double hysteresis* phenomenon, as predicted by the Reactive Sputtering Deposition (RSD) model [2-4] and substantiated by prior research on IV-characteristic data analysis [5]. This linkage is achieved through careful manipulation of discharge current density and process parameters associated with target poisoning mechanisms.

Delving into the *long-term stability* of the double hysteresis in feedback control, we compare it with stable transition conditions achieved through high-pumping speeds. Our discussion encompasses various factors influencing *long-term stability, including target erosion effects [6], chamber wall gettering, anode effects [7]*, and fluctuations induced by the chosen process control. *A new type of feedback input signal is introduced* to compensate for plasma and chamber wall effects.

Furthermore, we explore diverse feedback convergence strategies, shedding light on the path toward an optimal approach that considers the stability of each set of transition conditions. This understanding provides a valuable guideline for industry professionals seeking to employ feedback control reproducibly and efficiently.

Our research significantly contributes to the body of knowledge in reactive magnetron sputtering, providing insights into the intricate interplay between feedback control, metastable conditions, and long-term stability. These findings promise to elevate the precision and reliability of thin film deposition processes, with implications for a wide range of technological applications.

References are found in the supplementary material.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-3-TuM

Coatings for Batteries and Hydrogen Applications III

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Chen-Hao Wang**, National Taiwan University of Science and Technology, Taiwan

8:00am **TS1-3-TuM-1 Oxygen Vacancy in Atomic Metal Oxide Clusters Demonstrate Outstanding Electrochemical Activity***, **Tsan-Yao Chen (chencaeser@gmail.com)**,* National Tsing Hua University, Taiwan*; K. Wang,* National Central University, Taiwan **INVITED**

Hierarchical structured heterogeneous catalyst comprising atomic metal oxide clusters with high contents of oxygen vacancy (O^V) and the carbon or Co oxide supported metal / oxide nanoparticle (NPs) is developed for electrocatalytic application. Such a catalyst processes a collaboration between O^Vs and the neighboring atoms in the electrochemical reaction. With this characteristic, the reaction kinetics of all steps are simultaneously operated consequent leading to a quantum leap on the current density and stability of the redox reaction. Apart from using noble metals, atomic scaled Co oxide clusters (CoO_x^a) were employed. Those clusters are decorated in surface defect regions of Co oxide supported Pd nanoparticles (CoOx-Pd) by using self-aligned nanocrystal growth followed by ultra-high-speed quench reaction with strong reduction agent. The decorated CoO_x^a localize electrons from the neighboring atoms and thus boost the activity of CoOx-Pd in ORR. With a proper reaction time and loading control, the CoOx-Pd enhance its mass activity by 340 times as compared to that of commercial Pt catalysts in an alkaline electrolyte of 1.0M KOH.

8:40am **TS1-3-TuM-3 Enabling Lightweight PEMFCs Based on PVD-Coated Aluminium Bipolar Plates for Aviation Applications***, **Parnia Navabpour (parnia.navabpour@teercoatings.co.uk)**, G. Sanzone, S. Field,* Teer Coatings Limited, UK*; K. Zhang,* University of Birmingham, UK*; H. Sun,* Teer Coatings Limited, UK

The aviation sector is a significant player in the global energy crisis and toward climate change. It currently accounts for 12% of transport-related CO_2 emissions and 2-3% of all anthropogenic emissions. To tackle this, targets have been set by various governments and organisations on aviation CO_2 emissions and fuel efficiency. One tenable way to achieve these targets is through the use of hydrogen fuel cells for propulsion and/or auxiliary power units (APUs) in aircraft. The specific power of the fuel cell stack is a critical key performance indicator in the aviation industry, with bipolar plates being one of the most important components in a fuel cell stack, in terms of volume, weight and cost. Conventional PEMFCs utilise bipolar plates which are made from graphite or stainless steel. Hundreds of cells are needed within a multi-kW stack, hence a relatively small weight saving per plate will result in a large weight saving in the stack. The use of aluminium bipolar plates will enable the delivery of power densities double those of stainless steel bipolar plates. Challenges remain, however, with the corrosion of aluminium bipolar plates. This work focuses on the development of highly conducting and corrosion resistant coatings, aimed for PEMFC aluminium bipolar plates. The coatings were deposited using closed-field unbalanced magnetron sputtering technology and were evaluated for their adhesion and mechanical properties, as well as interfacial contact resistance and corrosion performance. Aluminium bipolar plates were coated and used in single cell fuel cells and tested under accelerated stress test conditions. The coated aluminium plates were compared with graphite plates and show the potential for using coated aluminium bipolar plates within PEMFCs.

9:00am **TS1-3-TuM-4 Grazing Magnetron Sputtering of Cu_xO-MoS_2 Electrodes for Hydrogen Production***, J. Castro, D. Cavaleiro,* University of Coimbra, Portugal*; M. Lima,* University of Minho, Portugal*; **Albano Cavaleiro (albano.cavaleiro@dem.uc.pt)**, S. Carvalho,* University of Coimbra, Portugal

The world energy grid faces a big issue in transit forward clean energy. Enlarging the possibilities to advance in cleaning the energy grid, humanity has made bids in several technologies, contemplating using Hydrogen as a sustainable and clean fuel. However, their production has important issues to overcome, such as the employment of expensive materials, which are non-abundant and challenging to obtain and process. Decreasing the manufacturing cost of electrodes used for producing Hydrogen could be a determinant to scale up this technology with competitive prices and, simultaneously, reduce the carbon footprint through affordable and environmentally friendly processes.

Copper is well known for its electrical properties; compared to other metals, it is cheaper and abundant. Recently, MoS2 has been demonstrated to favour the Hydrogen Evolution Reaction (HER). The present work presents the first insight into mixing these two materials using the grazing magnetron sputtering technique in a reactive atmosphere. C sheets and copper (sheets and foam) were used as substrates. SEM and EDS were used to determine the sample's morphologies and their chemical composition. Besides, several electrochemical techniques were employed to determine the electrochemically active surface area – ECSA, via linear sweep (LSV) and cyclic voltammetry (CV) and its electrochemical behaviour via electrochemical impedance spectroscopy (EIS). The results showed that including oxidised copper species together with MoS2 decreased the overpotential to start the HER at 10 mA/cm2 current density (~12% vs. the MoS2 overpotential). On the other hand, the sample with copper oxidised in a zig-zag configuration showed the highest double-layer capacitance and, hence, the highest ECSA, meaning that the obtained morphology during the deposition, influenced the electrochemical activity significantly.

Exhibitors Keynote Lecture
Room Town & Country A - Session EX-TuM

Exhibition Keynote Lecture
Moderator: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

11:00am **EX-TuM-1 Material Innovations and Challenges of Thin Films and Plasma Applications for 3 nm Node and Beyond***, Samuel Chiu (Samuel_Chiu@amat.com),* Applied Materials, Taiwan **INVITED**

The inventions of integrated circuits (1958) and the prediction of Moore's Law (1965) will celebrate its 66^{th} and 59^{th} anniversary in 2024, respectively. The foundation of semiconductor industry and its amazing achievement has dramatically changed the way we lived.

With the advents of Artificial Intelligence (AI), Machine Learning and AR/VR (Artificial Reality, Virtual Reality) applications enabled by advanced semiconductor technology, there are high hopes we will see significant breakthrough in many areas such as vaccine research, auto-pilot, astro-physics and super computing, etc.

Taiwan plays a critical role as a hub of semiconductor R&D and manufacturing for the past several decades. In this presentation, the latest innovation of thin film materials and plasma-related process to drive the success of advanced technology nodes will be described. Furthermore, the future challenges and opportunities beyond 3nm nodes in order to keep Moore's Law alive will also be presented.

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM1-2-TuA

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **CM1-2-TuA-1 Structural Evolution of Nanoparticles Under Realistic ConditionsObserved with Bragg Coherent X-Ray Imaging**, ***Marie-Ingrid Richard (marie-ingrid.richard@cea.fr)***, CEA Grenoble, France **INVITED**

The advent of the new 4th generation x-ray light sources represents an unprecedented opportunity to conduct *in situ* and *operando* studies on the structure of nanoparticles in reactive liquid or gas environments. In this talk, I will illustrate how Bragg coherent x-ray imaging [1] allows to image in three dimensions (3D) and at the nanoscale the strain and defect dynamics inside nanoparticles as well as their refaceting during catalytic reactions [2–4]. As an example, we successfully mapped the lattice displacement and strain of a Pt nanoparticle in electrochemical environment (see Figure 1). Our results reveal that the strain is heterogeneously distributed between highly- and weakly-coordinated surface atoms, and propagates from the surface to the bulk of the Pt nanoparticle as (bi)sulphates anions adsorb on the surface [5].

We will also discuss the possibility to measure particles as small as 20 nm [6] and to enable high-resolution and high-energy imaging with Bragg coherent x-ray diffraction at 4th generation x-ray light sources [7]. Finally, I will highlight the potential of machine learning to predict characteristic structural features in nanocrystals just from their 3D Bragg coherent diffraction patterns [7].

We acknowledge funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 818823).

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2:20pm **CM1-2-TuA-3 Grain Boundary Segregation/Complexions in MT-CVD Ti(C,N) Thin Hard Coatings Analyzed by Nano-SIMS and Atom Probe Tomography**, ***Idriss El Azhari (idriss.elazhari@uni-saarland.de)***, *J. Barrirero,* Saarland University, Germany*; N. Valle,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; J. García,* Sandvik Coromant, Sweden*; C. Pauly, F. Soldera,* Saarland University, Germany*; L. Llanes,* Universitat Politècnica de Catalunya, Spain*; F. Mücklich,* Saarland University, Germany

Ti(C,N) is one of the most utilized thin hard coatings in metal-cutting industry in the last twenty years. In prior works, the authors carried out multi-scale testing and characterization experiments in which industrial cutting inserts coated with Ti(C,N) wear resistant hard coatings are contrasted to Zr(C,N) coated counterparts. The purpose was to comprehend the influence of the coating's microstructural features **on the deformation behavior of each coating and the corresponding impact on the entire coated cutting tool system**. The investigation showcased that the more compatible coefficient of thermal expansion of Zr(C,N) with the substrate, the better cohesive strength at the grain boundaries and the plastic deformation were found to assign to the Zr(C,N) coated hardmetal improved structural integrity and fracture toughness in comparison to Ti(C,N) [1,2].

In this work, the focus is shifted toward Ti(C,N) to understand the correlation between deposition temperature and its impact on the microstructural features and segregation/complexions at the grain boundaries. For this purpose Ti(C,N) was deposited on a WC-Co substrate at two different temperatures (885°C and 930°C) using a moderate temperature CVD process (MT-CVD). Electron Backscatter Diffraction (EBSD) is used to examine microstructures. High-resolution secondary ion mass spectrometry imaging (nano-SIMS) and atom probe tomography (APT) were combined to investigate compositional variations inside single crystals and segregation at the grain boundaries. It is shown that segregation of chlorine at the grain boundaries is affecting not only the grain size of the columnar crystals, but texture and crystal shapes are indeed affected and modified as the chlorine concentration is decreasing with increasing temperature deposition. Methods to tailor the microstructure of these compounds are discussed and suggested.

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4:00pm **CM1-2-TuA-8 *In situ* Studies of Nucleation and Growth by High Energy X-Ray Scattering**, ***Jens Birch (jens.birch@liu.se)***, *N. Ghafoor, F. Eriksson,* Linköping University, Sweden*; S. Stendahl,* Uppsala University, Sweden*; S. Dorri, S. Nayak,* Linköping University, Sweden*; L. Rogström,* Uppsala University, Sweden **INVITED**

The understanding of the formation of nanoscale structures and their properties, requires time-resolved analytical tools able to probe into the nano realm. High energy (HE) X-rays, with wavelengths in the 0.01-10 nm range, provided by state-of-the-art synchrotrons feature four synergetic properties: High penetration depth, small scattering angles, very low beam divergence, and high intensity. This makes it easy to design in situ sample environments for experiments providing a large amount data using a sub-µm probe size, at a high rate data acquisition. Thus, HE X-rays lend themselves well for *in situ* and *operando* time-resolved experiments to shed light onto elusive nanoscale phenomena. A purposefully designed UHV-based deposition system for time-resolved *in situ* studies of thin film nucleation and growth processes is presented with examples ranging from high precision nm-period multilayer neutron mirrors to wear-resistant coatings, grown by magnetron sputtering and cathodic arc deposition at the High Energy Materials Science beamline P07 at PETRA III in Hamburg.

In situ time-resolved HE XRD,was used to study microstructural evolution of Ni/Ti:B_4C multilayer neutron mirrors in real time. Combining incorporation of $^{11}B_4C$ with temporally modulated ion-assistance during deposition, it was possible to achieve amorphous layers with interface widths s=4 Å (a reduction from 7 Å for state-of-the-art). The neutron reflectivity was observed to increase by 43%, implying up to 10x higher neutron throughput and a significantly increased neutron wavelength range for future neutron guides.

Another example is *in situ* characterization of epilayer strain evolution during magnetron sputter epitaxy of single crystal 6 nm-bilayer periodic superlattices of$CrB_{1.7}/TiB_{3.3}(0001)/Al_2O_3(0001)$. XRD revealed a rapid initial relaxation of superlattice-substrate misfit strain, from -0.067%, in the first bilayer period to -0.0013 % during growth of the 2nd bilayer. This observation precludes substrate misfit strain as driving force for an observed B segregation to tissue phases extending transversely through several bilayer periods.

Phase stability during cathodic arc as well as magnetron syntheses of polycrystalline TiAlN tool coatings were studied. The precipitation sequence and size evolutions of metastable cubic Ti-rich TiAlN nanocrystallites (responsible for hardening) and Al-rich wurtzite phase (causing over-hardening) could be followed in detail.

The improved prospects for future availability of the *in situ* deposition system upon installation of a large 1500 kg capability hexapod at the Swedish Materials Science beamline P21 will be presented.

4:40pm **CM1-2-TuA-10 Multidimensional Elemental and Molecular Analysis for Surface & Interface Studies**, ***Kayvon Savadkouei (kayvon.savadkouei@horiba.com)***, HORIBA, USA; *P. Chapon, A. Stankova,* HORIBA, France

Surface and Interface corrosion studies require the use of complementary analytical techniques as each instrumentation provides results based on the interaction of the investigated material with a probing medium [1].

Obtaining elemental and molecular information for different probing size and depth are especially crucial.

HORIBA offers a Platform with multiple instruments able to tackle these complex analytical challenges.

Glow Discharge relies on plasma to sputter a representative area of a material and provides fast elemental depth profile with nanometer resolution [2].

Coupling GD and Raman microscopy allows us to obtain molecular information at various depths with micrometer lateral resolution [3,4].

Applying the GD software ideal to follow transient signals to a simultaneous ICP instrument coupled with an electrochemical cell (AESEC technique) offers deep insight on dissolution mechanisms and metallic surfaces performances [5].

We will illustrate the benefit of this Surface Platform for Elemental and Molecular Analysis with selected results on metallic parts for high temperature fuel cells, hard facing materials in Na fast reactors, perovskite solar cells, hydratation of anodic films and DCL coatings on bipolar plates.

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Surface Engineering - Applied Research and Industrial Applications
Room Town & Country C - Session IA2-2-TuA
Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications II

Moderators: Vikram Bedekar, The Timken Company, USA, **Satish Dixit**, Plasma Technology Inc., USA

2:00pm **IA2-2-TuA-2 Impact of Novel Thermal Spray Material Solutions for Future Aerospace Applications and the Impact on Sustainability for the Environment and Business**, ***Matthew Gold (matthew.gold@Liberty.Rolls-Royce.com)***, Rolls-Royce North America **INVITED**

This presentation discusses the sustainability of materials and processes as applied to surface solutions in gas turbine engines.With the Aerospace industry under increasing pressure to improve the environmental performance of gas turbines, there is a growing need to reduce emissions and improve efficiency.This paper will outline the challenges associated with conventional materials and processes as well as the future materials that are being considered.

With an increase in turbine temperatures industry is moving towards more advanced materials systems for survivability.Over the last decade, industry has increased its use of rare earth oxides in thermal barrier coatings to help overcome the challenge of survivability in this harsh environment.This advance in materials comes with an impact on sustainability for the environment and business.

This presentation discusses these advanced materials for future applications and the challenges that will be encountered for sustainability.This will include raw materials, abundance, availability, and the need to understand the impact of process efficiency on their usage.

2:40pm **IA2-2-TuA-4 Evaluation of Thick Erosion-Resistant TiCrN Coating Deposited on Engine Impellers**, *Q. Wang,* The University of British Columbia; Aurora Scientific Corp, Canada; *L. Hsu,* Aurora Scientific Corp, Canada; ***Da-Yung Wang (dayung.wang@ubc.ca)***, The University of British Columbia, Canada; Aurora Scientific Corp, Canada; SurfTech Corp, Taiwan;, Canada

Metal-nitride hard coatings deposited through physical-vapor-deposition (PVD) techniques are increasingly being utilized in aircraft engines to protect compressor components against erosion caused by sand particles. Among these coatings, TiCrN, a ternary nitride coating with nano-layered configuration, exhibits promising results for application on turbine engine impellers to enhance erosion resistance. However, the deposition of TiCrN on impeller blades poses a unique challenge due to the sharp leading and trailing edges with curved airfoils, causing a shadowing effect during coating deposition. This can lead to non-uniform coating at sharp edges, resulting in spallation caused by high residual stress. To address this challenge, we employed various strategies, including a specially designed fixture providing two-axial rotation to the impeller, the incorporation of masking fingers to mitigate high coating deposition rates at sharp edges, modification of the ion cleaning process to enhance coating adhesion, and adjustments to chamber conditions such as increased working pressure using a mixture of N_2 and Ar gases while reducing the substrate bias voltage to reduce coating residual stress.

The TiCrN coating, applied to a stainless-steel impeller and flat coupons by using cathodic arc deposition, underwent comprehensive characterization and testing. The coated impeller exhibited excellent surface coverage without spallation or cracking. The TiCrN-coated blades displayed consistent chemical compositions, and the surface roughness values (Ra) were maintained below 0.7 µm. The average hardness value of the coating was 2204 HV. The coating had excellent coating/substrate adhesion strength with critical loads higher than 40 N. Compared to the uncoated 1Cr11Ni2W2MoV substrate alloy, the TiCrN-coated blades demonstrated more than two times improvement in erosion resistance at 30°, 60° and 90° impingement angles. Furthermore, the TiCrN-coated samples exhibited no signs of corrosion damage after exposure to salt fog for 60 hours. In conclusion, the TiCrN coating applied to the stainless-steel substrate demonstrated exceptional performance in terms of erosion resistance, highlighting its potential for use in protecting turbine engineer impellers in aircraft engines.

3:00pm **IA2-2-TuA-5 Enhancing Aeronautical Ice Protection Systems through Innovative Porous Ceramic Coatings**, ***Alessandro Corozzi (alessandro.corozzi@issmc.cnr.it)***, ISSMC-CNR, Italy; *J. Mora Nogues,* INTA (National Institute of Aerospace Technology) - Spain; *M. Caruso, M. Raimondo,* ISSMC-CNR, Italy

The formation and following accretion of different forms of ice poses serious safety and operational challenges in wind farms and airplanes, high voltage power lines, telecommunication systems, condenser surfaces, offshore platforms, locks, and dams. Intense efforts are therefore dedicated to developing passive ice protection systems (IPS) that can control or prevent ice formation. Anti-wetting materials applied on the target surface have been explored as potential ice-phobic surfaces [1], with the Slippery, Liquid-Infused Porous Surfaces approach (SLIPS) being one of the most innovative and intriguing possible solutions to inhibit ice accretion or weaken the ice adhesion strength without any power supply [2].

This study presents the design of anti-wetting hybrid SLIPS coatings for cold environments that comprise an inorganic, porous ceramic scaffold with grafted fluoroalkyl silane molecules infused with a lubricant polymer. The reduction of ice adhesion was determined with the Double Lap Shear Test, while the dynamic behavior of droplets was evaluated via goniometric contact angle hysteresis calculation, at both room and sub-zero temperatures [3, 4].

For the modeling of the different icing phenomena that happen on the proposed air intake, dedicated testing methodologies have been developed: i) direct impingement of supercooled droplets through an icing wind tunnel located in a cold climate chamber, and ii) running wet icing in which there is a water flow coming from an upstream heated area.

The coatings, validated through laboratory experiments and tests in icing wind tunnels, will undergo further testing in real-world icing conditions using a flight test aircraft as part of NATO's AVT-332 activity "In-Flight Demonstration (CDT) of Icephobic Coating and Ice Detection Sensor Technologies".

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4:00pm **IA2-2-TuA-8 Next Generation of Compositions & Coatings for Netzero & Sustainable Aviation***, **Tanvir Hussain (tanvir.hussain@nottingham.ac.uk)**,* University of Nottingham, UK **INVITED**

Thermal spray has proven to be a versatile coating deposition technique for many materials for wear, corrosion and thermal barrier applications; however, it is still challenging to spray oxygen-sensitive nano materials or carbides which sublimate in thermal spray.

Here we present a summary of various new approaches to deposit graphene nanoplatelet coatings and carbon nanotubes on their own from suspension and powder, as well as pre-mixed powders and composite suspension thermal spray. The new hardware modification and feedstock development allow direct incorporation of carbon-based nanomaterials into the thermal sprayed coatings that allow improvement in performance (for example, over two orders of magnitude in wear). Similarly, SiC is a cheap, abundant material for many engineering applications, including wear, but their lack of melting in a plasma or combustion flame in a desirable manner makes it very challenging to turn these into coatings. Here, we have developed a suspension and solution precursor process, a one-step route to produce composite coatings where SiC comes from suspension and the precursor salts (yttrium aluminium garnet here) transform into a protective matrix in the coating. This one-step process of suspension and solution precursor thermal spray has the potential to transform the materials portfolio of thermal sprayable materials.

Finally, axial injection suspension plasma sprayed coatings with columnar microstructures from ‘non-flammable’ organic solvent-based Yttria Stabilized Zirconia (YSZ) suspension will be introduced. The talk will cover the consequences of CMAS infiltration into these new coatings. The degradation of the coating mechanical properties due to CMAS ingression will be reported along with residual stresses using Raman spectroscopy. The common thread through all these examples will be reducing our CO2 footprint and improving component lifetime to achieve towards a netzero aviation.

4:40pm **IA2-2-TuA-10 Improved High Temperature Tribology for Aero-Engine Components by PVD Coatings***, **A.O. M. Eriksson (anders.o.eriksson@oerlikon.com)**,* Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein*; T. Middlemiss,* Oerlikon Balzers Coating UK Ltd., UK*; C. Jerg, E. Vaziri Beiraghdar, P. Kaller,* Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein*; T. Stelzig,* Oerlikon Balzers Coating Germany GmbH, Germany*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein

Aero engines operate under aggressive environments in which some of their components are exposed to temperatures well above 600°C. Under these conditions fretting and sliding wear is a major concern. For thermal management, dedicated materials like single crystal superalloys or Titanium aluminides are used in combination with protective coatings such as thermal barrier coatings and environmental barrier coatings. Besides thermal management, tribological behavior is important for engine components, such as shrouds, mechanical seals, rings, or joints, which are in contact with counterparts. Relative motion caused by vibrations is a common reason for fretting or sliding wear of the surfaces in contact. Pits and grooves on the contacting surfaces, as well as debris of removed material, may result in crack initiation and in failure of the component. Because the service temperatures are well above the application area for standard carbon-based tribological coatings, we have explored PVD coatings of oxides and nitrides. Coatings have been applied on superalloy specimens and tested in reciprocal sliding motion against superalloy counterparts at temperature of about 700 °C. The PVD coatings significantly reduced wear of the coated specimens, in contrast to extensive wear in the pairing of uncoated superalloy specimen with uncoated superalloy counterpart. Moreover, the evolution of the friction coefficient through the reciprocal sliding test was evaluated, where the coated specimen quickly stabilized at a constant value as opposed to the uncoated test conditions. The stable wear conditions are attributed to a tribologically transformed layer which was observed on the surface of the coatings, comprising components of the coating and superalloy material of the counterpart. The coatings can thus help to enhance lifetime and performance of tribologically loaded high-temperature components.

5:00pm **IA2-2-TuA-11 Development of Environmentally Friendly Solid Carburizing for Improving Fatigue Properties of AISI 4118 Steel***, **Tomofumi Aoki (ao.tomofumi@keio.jp)**, D. Kasai,* Graduate School of Science and Technology, Keio University, Japan*; M. Hayama,* Keio University, Japan*; S. Takesue,* Kyoto Institute of Technology, Japan*; M. Tsukahara, Y. Misaka,* Neturen Co., Ltd., Japan*; J. Komotori,* Keio University, Japan

Gas carburizing is used extensively in the industry to improve the fatigue properties and the wear resistance of steel. However, the process is time-consuming and emits large amounts of gases, such as CO_2. Thus, we focused on atmospheric-controlled induction heating fine-particle peening (AIH-FPP) to resolve these challenges.

AIH-FPP combines induction heating and fine-particle peening. Shot media was projected onto a specimen heated with an IH coil. In AIH-FPP, when carbon is used as the projection media and steel is used as the base material, carbon can diffuse into the steel, and carburizing can be achieved rapidly. We named this process environmentally friendly solid carburizing, as it controls CO_2 emission and lessens the environmental burden. Accordingly, the aim of this study is to improve the fatigue properties of steel in a reduced time using this process.

The material used in this study was SCM 420H (AISI 4118 or equivalent) and the steel was machined into hourglass-shaped specimens. The air in the chamber was replaced with N_2 gas. The specimens were heated to 1273K for 30 s and then held at the temperature for 60 s. While heating and maintaining the temperature, steel particles coated with carbon were projected. The specimens were then cooled with N_2 gas. Afterward, these were requenched. We also prepared conventional gas carburized specimens.

An electron probe micro analyzer (EPMA) was employed to analyze the distribution of carbon concentration. The microhardness of each specimen was examined on their longitudinal section using a micro Vickers hardness tester. The fatigue test was conducted under axial loading with the stress ratio of -1 at room temperature, and test frequency of 10 Hz.

Environmentally friendly solid carburizing process diffused carbon up to 300 µm from the specimen surface and increased the carbon content on the specimen surface to approximately 0.5 mass%. No significant decrease in hardness was observed in the vicinity of the specimen surface. This result suggests that grain-boundary oxidation did not occur. This is because of the extremely low O_2 present in the treatment chamber, indicating that no CO was produced during the treatment. In addition, we consider that C_2H_2 is not produced during the treatment due to the displacement of the air with N_2 gas in the chamber. These results strongly suggest that the carbon diffused in this process by a mechanism different from the conventional gas carburization.

The fatigue life at the stress amplitude of 700 MPa was approximately 10 times longer than that of a conventional gas carburized specimen. This is because of the higher hardness on the specimen surface.

Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-2-TuA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Germany, **Francisco Javier Pérez Trujillo**, Universidad Complutense de Madrid, Spain

1:40pm **MA1-2-TuA-1 Fabrication, Characterisation and Fretting Wear Testing of Magnetron Sputtered Cr and CrN Coated Zr Alloy Cladding for Enhanced Accident Tolerance in Light Water Reactors***, T. Rachid Netto,* Manchester Metropolitan University, Brazil*; A. Evans,* ***Peter Kelly (peter.kelly@mmu.ac.uk),*** Manchester Metropolitan University, UK*; D. Goddard, J. Cooper,* National Nuclear Laboratory, UK

Research into accident-tolerant fuels (ATFs) for light water reactors (LWRs) has focused on improving the safety of zirconium alloy fuel rod claddings and one of the more developed approaches is the use of chromium coatings deposited onto the claddings. In addition to performing in oxidising conditions, normal operation also causes fretting wear on the fuel rod surface, which requires tribological improvements.

The aim of this work, therefore, is to produce Cr and CrN coatings using the magnetron sputtering technique for Zr alloy nuclear fuel rod cladding material to enhance oxidation and mechanical resistance. This research is examining how the integrity and microstructure of the coating is affected by deposition conditions and coating thickness. The coatings were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), optical profilometry and contact angle goniometry. A linear reciprocating wear tester was used to mimic fretting. Our results demonstrate that fretting resistance can be related to the different densities and thickness of coating produced and, in turn, related to the deposition parameters.

2:00pm **MA1-2-TuA-2 Fuel-cladding Thermochemical Interaction Study of Cr_2O_3 Coating Deposited by DLI-MOCVD on Zircaloy-2 Substrate***,* ***Kenza Zougagh (kenza.zougagh@cea.fr),*** Université Paris-Saclay, CEA, Service de Recherche en Matériaux et procédés Avancés, France*; R. Chanson, A. Quaini, F. Rouillard, S. Gossé,* Université Paris-Saclay, CEA, Service de recherche en Corrosion et Comportement des Matériaux, France

In a nuclear reactor, the fuel cladding is the subject of particular attention since it constitutes the first safety barrier. Its mechanical integrity must therefore be guaranteed in a wide range of conditions from nominal operation to hypothetical incidental conditions.

The idea of improving the behavior of the zirconium-based claddings with the addition of external coatings in the frame of ATF (Accident Tolerant Fuels) is now widespread. However, internal thin films coatings can also be an effective solution to increase the resilience of fuel claddings under undesirable situations. There are many fewer developments proposing the addition of these internal coatings, probably due to the difficulties encountered in developing proper homogenous layers along the full-length.

In this work, chromium oxide is studied as a candidate material for an internal layer of the nuclear fuel cladding for the mitigation of pellet-cladding thermochemical interaction. This coating is deposited by the DLI-MOCVD process on a Zircaloy-2 substrate. This process has been already demonstrated relevant for coating the internal surface of nuclear fuel claddings [1]. This study highlights the influence of the process parameters on the coating properties. After satisfactory film deposition, physico-chemical and microstructural properties of the coating are characterized. The performance of the chromia layer against Zircaloy – UO_2 interaction is investigated at high temperature between 400 and 800°C using diffusion couple testing with natural UO_2 pellets. Moreover, the interaction between the chromia layer and Zircaloy is studied at temperatures up to 1200°C. All experimental results are compared to thermodynamic predictions using the Calphad method.

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2:20pm **MA1-2-TuA-3 Evaluation of Wear and Corrosion Resistance in Acidic and Chloride Solutions of Pvd-Crn Coatings on Untreated and Plasma Nitrided Aisi 4140 Steel***, A. Maskavizan, E. Dalibon,* National University of Technology (UTN), Faculty of Concepción del Uruguay, Argentina*; S. Farina,* CNEA and CONICET, Buenos Aires, Argentina*; J. Quintana,* CNEA (CAC), Buenos Aires, Argentina*;* ***Sonia P. Brühl (sbruhl@gmail.com),*** National University of Technology (UTN), Faculty of Concepción del Uruguay, Argentina

CrN coatings deposited by Physical Vapor Deposition (PVD) are widely used due to their high hardness and high wear resistance, low friction coefficient and superior corrosion resistance. The latter makes this coating appropriate for protecting forming tools, moulds and components used in chemical processing.

In this work, single layer CrN coatings were deposited on plasma nitrided and non treated AISI 4140 steel. The influence of nitriding on the wear resistance, coefficient of friction and corrosion resistance in acidic solutions and chloride solutions was studied.

Thickness of the coatings was measured using optical microscopy, and surface hardness was assessed with a Vickers microindenter. Adhesion was determined using Rockwell indentation applying 150 kg and Scratch test at different constant loads. Sliding wear resistance was studied with Pin-on-Disk tests under different normal loads and sliding distances, the coefficient of friction was registered during the tests and volume loss was calculated. Corrosion tests were carried out using a 3.5 % NaCl solution and a 0.5 M H_2SO_4 solution as electrolytes. Nitrided steel without any coating was used also as comparison.

Coating thickness was approximately (2.6 ± 0.4) µm and surface hardness reached a value of (1960 ± 160) $HV_{0.05,}$ being this a composed hardness because of the low film thickness. Adhesion was good for both substrates, non nitrided and nitrided steel, in both cases, it could be classified as HF1 according to VDI 3198 standard. In the case of the Scratch test, in the only coated samples, without nitriding as pre treatment the film cracking was observed at 50 N in the track, whereas in the duplex sample the coating had a better load bearing capacity and reached 70 N without damage. No delamination was detected around the scratch track in all cases. Wear volume loss was undetectable in the pin-on-disk test for the coated systems, whereas it was approximately 30 x 10^{-3} mm^3 for the nitrided steel and 150 x 10^{-3} mm^3 for the untreated steel. In the corrosion tests, the coating showed a passive behaviour as tested in NaCl solution and the corrosion current density was significantly lower for coated samples in the H_2SO_4 solution, proving that the CrN coating is suitable for protecting the steel substrate in both chloride and acidic media.

2:40pm **MA1-2-TuA-4 Deposition using CHC-PVD Method and High Temperature Oxidation of TiAlCrYSi Coatings on TiAl***,* ***Radoslaw Swadzba (radoslaw.swadzba@git.lukasiewicz.gov.pl),*** Lukasiewicz Research Network – Uppersilesian Institute of Technology, Poland*; B. Mendala, L. Swadzba,* Silesian University of Technology, Poland*; U. Schulz, N. Laska, P. Bauer,* German Aerospace Center (DLR), Germany

This work concerns the application of Closed Hollow Cathode - Physical Vapor Deposition (CHC-PVD) method for the deposition of TiAlCrYSi on a 48-2-2 TiAl alloy. During the deposition process the samples were placed within the hollow cathode with diameter of 80 mm and length of 160 mm and nominal composition Ti-54Al-14Cr-0.5Si-0.5Y (at. %). The study involved the detailed analysis of the coating's growth mechanism, initial microstructure as well as phase transformations using high resolution Transmission and Scanning Transmission Electron Microscopy (HRTEM and STEM) as well as Scanning Electron Microscopy (SEM) and high temperature X-ray diffraction (HT-XRD). In the as-deposited state the obtained CHC-PVD TiAlCrYSi bond coating was found to be characterized by a columnar microstructure that contained both amorphous and crystalline regions. It has been found that the latter were composed of a strongly textured, hexagonal C14 $Ti(Al,Cr)_2$ Laves phase. It was shown that upon high temperature exposure the coating forms a dual phase microstructure composed of the $Ti(Al,Cr)_2$ Laves and TiAl phases. The coatings were pre-oxidized in pure oxygen atmosphere at 900 °C for 2 hours to form an adherent and stable Thermally Grown Oxide (TGO) and were then coated with Thermal Barrier Coatings (TBCs) using EB-PVD. The obtained coatings were tested under isothermal (50 hours) and cyclic oxidation (1000 1h cycles) conditions at 900 °C. Detailed microstructural investigations using STEM allowed to characterize the thermally grown oxide (TGO) scale. These investigations provided microstructural evidence for the Cr effect on the formation of Al_2O_3 during pre-oxidation treatment. Yttrium was found to segregate to the grain boundaries of alumina oxide scale during high temperature oxidation, indicating the occurrence of the reactive element (RE) effect.

3:00pm **MA1-2-TuA-5 The Influence of Molten Pool Behaviour on the Microstructure and Characteristics of Additive Manufactured Ti-6Al-4V Alloy Composite Coatings***, Olawale Samuel Fatoba (proffatobasameni@gmail.com), T. Jen,* University of Johannesburg, South Africa

Numerous varied engineering applications make use of titanium and its alloys. Its low density, strong specific strength, and excellent resistance to corrosion make it one of the best materials for industrial use. Its low hardness and weak tribological qualities, however, limit its applications and shorten its life service. Surface modification can increase the surface's integrity and increase its availability for a wider range of industry applications. Additive manufacturing efficiently produces and repairs intricate geometrical components in the aerospace, biomedical, and automotive industries. The ultimate quality and structure of the manufactured coatings are influenced by a multitude of powder particle factors and properties; the powder flow rate is also dependent upon the powder morphology, distribution, porosity, angularity, motional interaction of the particles, and their hardness property. The microstructural morphology of the α- and β-phases of titanium alloys is determined by the arrangement of lamellar and equiaxed structures, as well as the fine and coarse texture of the structures. The lamellar structures become fine or coarse depending on the pace of cooling.

The coated specimens were created using direct laser metal deposition (DLMD), and X-ray diffraction (XRD), optical microscopy (OPM), electron dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) were used to characterize the microstructure of the as-received samples. The Vickers hardness tester and the DY2300 Series potentiostat were used to measure the microhardness and corrosion behavior, respectively. The findings demonstrated that Ti-6Al-4V's ultimate tensile strength can advance significantly in terms of surface integrity. The micrographs demonstrate how the α-phase's unique characteristics, which set it apart from earlier beta phases, caused anisotropy in the mechanical characteristics and the coarsened structures made of a high concentration of Ti, Al, and Si. The titanium-aluminide intermetallic compounds are the most prevalent crystallographic phases, and this is what is responsible for the materials' increased hardness. The right proportion of Si and Cu weight percentage in the reinforcing powder, along with an ideal laser intensity and scanning speed, results in a coating with enhanced corrosion resistance; the material corrodes more slowly than a Ti-6Al-4V substrate.

Keywords: Ti-6Al-4V alloy, microhardness, microstructure, additive manufacturing, molten-pool, mechanical properties.

4:00pm **MA1-2-TuA-8 Investigations of Water Vapor Enhanced Oxidation on TiAl-Based Alloys: Evaluation of Protective Coating Systems***, Ronja Anton (ronja.anton@dlr.de), N. Laska,* German Aerospace Center (DLR), Germany

Currently, intermetallic γ-TiAl alloys are being used as material for turbine blades in the low-pressure turbine to replace the heavier Ni-based superalloys due to their due to their comparatively half the density. Their limitation to service temperatures below 800 °C is due to strength and creep resistance at elevated temperatures, as well as a reduced oxidation resistance. The latter can be surpassed with the aid of remarkably effective oxidation-protective coatings. These coatings result in the formation of a dense thermally grown oxide (TGO) scale, Al_2O_3. However, new turbine engine concepts, such as the Water Enhanced Turbofan (WET) engine concept or the use of hydrogen-based fuels in jet engines, introduce higher amounts of water vapor. Now, not only the γ-TiAl alloys need to be evaluated under more severe conditions, but also the highly studied protective coatings need to be tested in this harsher environment. The mechanism by which water vapor content and temperature may be affecting uncoated and coated γ-TiAl alloys needs to be understood.

For a further enhancement of the protection, a coating system with a ceramic top coat should be considered. Protective coating systems on SiC/SiC CMCs forming SiO_2 as an TGO layer, mostly contain Yb- or Y-silicates as a top coat due to their low oxygen diffusion and matching coefficient of thermal expansion (CTE). A protective coating system for γ-TiAl alloys with Al_2O_3-forming bond coats could be completed by Yb-aluminates, which also show low oxygen diffusion and CTE comparable to the alloys.

In the present work, γ-TiAl alloys were tested isothermally under water vapor enhanced oxidation up to 30 wt.% water in a tube furnace. The growth of a thick Al_2O_3/TiO_2 mixed oxide scale was analyzed on uncoated γ-TiAl alloys. Different coating concepts such as Ti-Al-Cr, Al-Si and Ti-Al-C deposited by DC magnetron sputtering could already improve the resistance of γ-TiAl alloys in dry oxidation conditions. In water vapor enhanced oxidation processes, the growth of the protective Al_2O_3 oxide scale is increased. In order to assess the need for ann ceramic top coat, the oxide growth as a function of temperature and different water contents was evaluated. Therefore, different analyses like SEM, EDX, XRD and thermogravimetric analyses were performed. Finally, first concepts of Yb-aluminates as a protective ceramic top layer by using the previously established layers as bond coating are introduced in terms of reactive sputter deposition, phase stability and improvement of the coating system.

4:20pm **MA1-2-TuA-9 Effect of Duty Cycle and N_2 Flow Rate on Structure and Oxidation Behavior of VN Coatings Deposited by High Power Impulse Magnetron Sputtering***, Ruo-Syuan Chen (pamela.chan34@gmail.com), J. Huang,* National Tsing Hua University, Taiwan

Unlike traditional nitride metal protective coatings, VN coatings possess not only superior mechanical properties and corrosion resistance but also self-lubrication characteristics. The formation of Magnéli oxide phases at high temperature can enhance wear resistance [1]. Previous literature indicated that the duty cycle and N_2 flow rate have significant influence on the quality and properties of VN thin films [2-4]. Although there have been numerous studies on the oxidation behavior of VN coatings, the influence of nitrogen flow rate and duty cycle on their structure and oxidation behavior remains unclear. Therefore, this study aims to investigate the oxidation behavior of VN coatings deposited at different duty cycles and N_2 flow rates. VN coatings with a thickness of 1 mm were deposited on Si substrate by high power impulse magnetron sputtering (HiPIMS).The duty cycles were controlled to be 3% and 10%. The N_2 flow rates were set at 2 and 4 sccm. After deposition, the N/V ratios of the coatings were determined using X-ray photoelectron spectroscopy and the microstructure was observed by scanning electron microscopy (SEM). X-ray diffraction was used to characterize the crystal structure and the preferred orientation of the coatings. The residual stress of the specimens was measured by laser curvature measurement and average X-ray strain combined with nanoindentation methods [5,6]. The oxidation behavior of the coatings was investigated using thermo-gravimetric analysis at temperature ranging from 400 to 700°C in dry air atmosphere. From the experimental results, the oxidation behavior of the VN coatings was discussed.

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4:40pm **MA1-2-TuA-10 Surface Modification of Copper by Electrical Discharge Coating using 3D-Printed SUS -420 Steel Electrodes***, Siddanna Awarasang (siddanna.awarasang@gmail.com),* National Central University,Taiwan*; J. Hung,* National Central University, Taiwan

This study presents a novel approach to surface science by exploring the integration of 3D-printed SUS-420-steel coatings onto copper substrates through Electric Discharge Coating (EDC) processes. Unlike conventional methods, this approach utilizes 3D Printed electrodes (3DPE) for coating, offering a compact and efficient process. Through systematic optimization of process parameters, including discharge energy levels and coating processes, the study achieves significant improvements in coating thickness from 15.40 to 141.16 µm, microstructure, and composition. Surface analyses and Energy Dispersive X-ray Spectroscopy (EDS) scans reveal steel-rich areas, microcracks, and uniform distribution across the substrate. The resulting coatings exhibit enhanced mechanical properties, including increased hardness and improved resistance to corrosion and thermal degradation. This breakthrough not only opens new avenues in coating industries for complex surfaces but also underscores the potential for further innovation in material deposition technologies.

Tribology and Mechanics of Coatings and Surfaces
Room Town & Country B - Session MC2-1-TuA

Mechanical Properties and Adhesion I

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, **Bo-Shiuan Li**, National Sun-Yat Sen University, Taiwan

1:40pm **MC2-1-TuA-1 Boosting Mechanical Properties of Metallic Thin Films Through Advanced Nanoengineered Design Strategies***, B. Francesco,* LSPM-CNRS, France*; A. Brognara,* Max-Planck-Institut für Eisenforschung, Germany*; P. Djemia, D. Faurie,* LSPM-CNRS, France*; A. Li Bassi,* Politecnico di Milano, Italy*; G. Dehm,* Max-Planck-Institut für Eisenforschung, Germany*; **Matteo Ghidelli (matteo.ghidelli@lspm.cnrs.fr),*** Laboratoire des Sciences des Procédés et des Matériaux (LSPM), CNRS, France **INVITED**

The current trend toward miniaturization in devices components in key technologies such as micro-/nanoelectronics, energy production, sensors and wear protection requires the development of high-performance nanostructured films with superior mechanical properties. Especially, mutually excluding structural properties such as high yield strength and ductility need to be combined, but also high adhesion with the substrate and large fatigue resistance. In order to trigger microstructure-induced material properties, control of the micro-scale structure, atomic composition, average grain size, and layer/film thickness must be optimized based on nanoengineering design concepts.

Here, I will present recent results for several class of advanced thin film materials including nanostructured metallic glasses (ZrCu/O, ZrCuAl/O...)[1-3] high entropy alloys (CoCuCrFeNi, Al/CoCuCrFeNi) and nanolaminates (fully amorphous, amorphous/crystalline)[4], showing how the control of micro-structure affect the and micro-scale mechanical behavior and enable ultimate mechanical properties.

Among the main results, I will show the potential of Pulsed Laser Deposition (PLD)[1, 2] as a novel technique to synthetize nanostructured cluster-assembled ZrCu, ZrCuAl/O, and CoCuCrFeNi films, reaching ultimate yield strength (>4 GPa) and ductility (>15 %) for ZrCuAl/O films. I will show how the control of the sublayer thickness (from 100 down to 5 nm) in fully amorphous nanolaminates influences the deformation behavior suppressing the shear bands formation, while tuning the mechanical properties with mutual combination of large ductility (> 10%) and yields strength (>2.5 GPa). Finally, I will show how alternating CrCoNi (crystalline)/TiZrNbHf (amorphous) nanolayers results in an high compressive yield strength (3.6 GPa) and large homogeneous deformation (~15%)[4].

Overall, our results pave the way to the development of nanostructured thin films with boosted mechanical properties and wide application range.

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2:20pm **MC2-1-TuA-3 The Evolution of Residual Stress in the Immiscible Cr-W Alloy System***, **Tong Su (tong_su@brown.edu)**,* Brown University, USA*; J. Robinson, G. Thompson,* University of Alabama, USA*; E. Chason,* Brown University, USA

Metal alloy films are used in numerous technical applications such as magnetic storage, catalysis and hard coatings. As with any coating, residual stress is critical to their adhesion and physical properties. While there have been numerous studies of residual stress evolution in elemental metal systems under different processing conditions with corresponding mechanisms, there are far fewer in alloys.Such studies have been indispensable to understand adatoms evolution and residual stress development. In this work we study the stress in Cr-W which is a continuation of work performed in the Mo-V and W-V systems. These alloys are BCC elements that exhibit a miscibility gap which thermodynamically drive the elements to partition from the other. The measurements were performed at several deposition rates from 0.8 nm/s to 6.0 nm/s and pressures of 0.27 Pa and 0.47 Pa with the stress measured by an in-situ wafer curvature measurement technique. While thermodynamically driven to partition, the results indicate that alloy stress can be explained with similar mechanisms invoked for elemental systems. Nevertheless, the kinetic parameters that control the stress are a complicated superposition of the effects of the single elemental components.

2:40pm **MC2-1-TuA-4 Adhesion and Friction-wear Characterization of W-doped Hydrogenated Diamond-like Carbon (a-C:H) Coatings***, **Ihsan Efeoglu (iefeoglu@atauni.edu.tr)**, Y. Totik, G. Gulten, B. Yaylali, M. Yesilyurt,* Atatürk University, Turkey*; R. Gunay, G. Kara, B. Altintas,* TUSAS ENGINE INDUSTRIES (TEI), Turkey

AISI 4130 alloy steel, a significant material type for the majority of engineering applications in the industry, is used extensively in the aerospace, automotive, and defense industries due to its crucial characteristics, including high strength, durability, machinability, and corrosion resistance. Enhancing this material's surfaces mechanical and tribological characteristics with Tungsten (W)-doped diamond-like carbon (DLC) coatings stands out as a way to improve its performance in this investigation. Amorphous hydrogenated diamond-like carbon (a-C:H) coating has great mechanical and tribological properties. In this study, W-doped DLC coatings have been deposited on AISI 4130 via closed-field unbalanced magnetron sputtering. A L9 orthogonal array of the Taguchi method was utilized to optimize the variable coating parameters applied in the magnetron sputtering process. The microstructure, thickness, and composition of the a-C:H:W coatings were examined using scanning electron microscopy. The crystallographic characteristics of coatings were evaluated using X-ray diffraction in order to provide an extensive understanding of the coating structure. The specific measurements of the hardness and elasticities of the coatings were obtained using the nanoindentation test. The scratch test method was used to examine the adhesion properties of the coatings by determining their critical load values at which film delamination occurred. The tribological behavior of uncoated AISI 4130 substrate and a-C:H:W coating was determined with a pin-on-disc tribometer against an Al_2O_3 ball under dry sliding conditions. Delamination and gradual failures occurring in the wear test of the uncoated specimen increased the friction coefficient. On the contrary, the a-C:H:W coating exhibits such superior tribological properties that the friction coefficient decreased due to the prevention of delamination and gradual failures to a certain extent. It was observed that the scratch-adhesion properties of the coated specimens significantly contributed to the improvement of tribological performance.

3:00pm **MC2-1-TuA-5 Numerical and Experimental Evaluation of Cyclic Contact Loads on Titanium Borides***, A. MENESES AMADOR, G. RODRIGUEZ CASTRO, **Hugo Alberto Pérez Terán (hap_ter@hotmail.com)**, M. Melo-Pérez,* Instituto Politécnico Nacional, Mexico

In this work, an experimental and numerical study of the contact fatigue test on titanium boride (TiB_2/TiB) coatings is presented. The boride layers were formed at the surface of Ti6Al4V alloy using the powder-pack boriding process at temperatures of 1050 °C for10, 15 and 20 h of exposure times in order to obtain three different thicknesses. Optical microscopy was used to characterize the boride layer, the results showed an outer TiB_2 layer and an inner TiB layer (whiskers). The mechanical characterization (hardness and Young's modulus) was carried out using Berkovich instrumented indentation technique. From the set of experimental conditions of the boriding process, cyclic contact loads were applied with a MTS Acumen equipment by repetitive impact of a sphere on the layer-substrate system. The experimental methodology consisted first determining the critical static load (load magnitude where cracks are observed) afterward cyclic sub-critical loads are applied with a frequency of 6 Hz for the three coatings. The test results indicate that the thinner coating exhibited better behavior under cyclic contact loads while thicker thickness showed greater damage under similar conditions. In order to evaluate the stress field generated in the boride layer during the application of static and dynamic loads, numerical simulations based in the finite element method were developed. The results showed good approximations with regard to contact diameters and residual depths obtained experimentally.

4:00pm **MC2-1-TuA-8 Mechanical Characterization of Nb-doped MoS_2 Coatings Deposited on H13 Tool Steel using Nb-based Interlayers**, ***Miguel Rubira Danelon (miguel.danelon@usp.br)**, N. Kyioshi Fukumasu,* University of São Paulo, Brazil*; A. Alves Carvalho,* Aeronautic Institute of Technology, Brazil*; R. Rodrigo Rego,* Aeronautics Institute of Technology, Brazil*; I. Fernanda Machado, R. Martins de Souza, A. Paulo Tschiptschin,* University of São Paulo, Brazil

Molybdenum disulfide is a 2D material with excellent lubricant properties, attributed to a low coefficient of friction (COF) resulting from weak Van der Waals forces between lattice layers and shear-induced crystal orientation. However, film oxidation harms its efficacy in humid atmospheres, leading to an increased COF and poor surface adhesion, making its use preferable in dry or vacuum conditions. To overcome these challenges, doping MoS_2 with elements, such as Nb, Ti, C, and N, emerges as a promising solution. Doping alters the reactions between the film and environmental oxygen atoms, reducing the environmental sensitivity of the film. Literature reports that doping MoS_2 with Nb promotes the formation of NbS_2 phases, which exhibit superior oxygen-trapping capabilities compared to conventional MoS_2 films, increasing its performance in humid conditions. Nevertheless, the adhesion of these coatings to a steel substrate present challenges and strategies involve the reduction of residual stresses and increase chemical affinity to the substrate by using of niobium-based materials as interlayer. Different interlayer characteristics, such as hardness, thickness and composition, can influence adhesion. A metallic niobium interlayer enhances film adhesion but, alternatively, a NbN interlayer, with ceramic characteristics, such as higher hardness, further improves adhesion. In this study, Nb-doped MoS_2 films were deposited on H13 steel using the pulsed direct current balanced magnetron sputtering technique. Different niobium-based interlayers were deposited to evaluate tribological behavior and adhesion properties of Nb-doped MoS_2 coatings. Scratch tests, conducted at room temperature and humidity, without lubrication, and under a progressive load, were performed to analyze the COF and adhesion of the coating, while instrumented indentation tests were conducted to assess the hardness and elastic modulus of the coatings. The Nb concentration of the films and interlayer was evaluated using scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDS). Results indicated that a thicker interlayer optimally promoted the adhesion of the film, together with a high concentration of Nb on the interface between the Nb-doped MoS_2 film and the niobium-based interlayer. This result is justified by the increase of hardness led by higher Nb concentrations. Furthermore, better adhesion of the film promoted a low COF at greater load during tests. In summary, niobium-based materials can be used to enhance the adhesion properties of Nb-doped MoS_2 films and consequently improve their performance.

4:20pm **MC2-1-TuA-9 Mechanical Properties and Adhesion of Al Thin Films with Al_2O_3 Interlayers on Flexible Substrates**, ***Johanna Byloff (johanna.byloff@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P. Renault,* University of Poitiers, France*; D. Faurie,* Université Paris-Saclay, France*; S. Husain,* University of Poitiers, France*; D. Casari, T. Edwards, B. Putz,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Metal thin films on polymers serve a variety of applications in the packaging, flexible electronics, and space sector. Challenges include mechanical failure during use, material restrictions, and non-recyclability. In the Aluminium (Al)-Polyimide (PI) system, favorable adhesive properties are attributed to an amorphous Al-O-C interlayer [1-3] (IL, 5 nm thick) between the metal film and the PI substrate. Through a combined atomic layer (ALD) and physical vapor deposition (PVD) setup, we are uniquely able to mimic interlayers artificially over a wide thickness range to study their mechanical and interfacial benefits. Using this setup, Al thin films (150 nm) with different Al_2O_3 interlayer thicknesses (0, 0.12, 1, 5, and 25 nm) were deposited on a polyimide substrate. These bi-layer samples were subjected to equi-biaxial tensile loading [4] with in-situ X-ray diffraction and electrical resistivity measurements at Synchrotron SOLEIL. The evolution of Al film stress, width of the Al diffraction peak and electrical resistivity could be determined as a function of IL thickness and applied strain. The Al and oxide layer thickness and microstructure as well as crack density and spacing after testing were investigated using scanning and transmission electron microcopy. Our results reveal a positive influence of the preceding ALD step on the mechanical properties of the Al thin films. All films with artificial ALD interlayers show reduced roughness and grain width in their PVD sputtered Al layers, resulting in a higher 0.2% yield stress, while overall maintaining ductile electro-mechanical behavior. This is possibly due to modifications of the PI substrate surface through ALD. Significant embrittlement was observed only in the Al film with 25 nm interlayer thickness. Most notably, comparison of a 5 nm artificial and natural interlayer shows a similar resistivity but a two-fold increase in yield strength in the artificial case. Adhesion between metal film and polymer substrate was evaluated with the tensile induced delamination method, indicating better adhesion (lower buckle density) with artificial Al_2O_3 interlayers.

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4:40pm **MC2-1-TuA-10 Buckling Structures, a Relevant Signature of the Mechanical Properties of Film/Substrate Systems**, ***Christophe COUPEAU (christophe.coupeau@univ-poitiers.fr)**,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; G. PARRY,* SIMAP, Grenoble-INP, CNRS, France*; J. DURINCK,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Thin films and coatings are used in a wide range of technological applications, such as microelectronics, packaging or optics. They often develop high residual stresses during the deposition process, sometimes about few GPa in compression. Such large compressive stresses may cause the nucleation and growth of buckling structures that generally result in the loss of functional properties that were initially conferred to such film/substrate composites. The aim of our studies is consequently to have a better understanding of the buckling phenomenon, by identifying the relevant parameters to prevent, to limit, or to control its occurrence.

From an experimental point of view, the fine investigation by optical and atomic force microscopies of the morphology of elementary buckling structures is consequently of great interest in order to qualitatively, or even quantitatively, extract some mechanical parameters of the film/substrate systems. Our studies concern for instance the effect of both elasticity [1-3] and plasticity [4] of the substrates on the maximum deflection of the buckles, the question of vacuum below the buckling structures [5], the effect of a pressure mismatch between the buckled film and its substrate on the occurrence of specific structures (such as donut-like or flower-like buckles) [6,7], the limit of the elastic theory framework to understand the buckling when plasticity is taking place in the film [8].

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5:00pm **MC2-1-TuA-11 Elastic-Plastic Buckling of Gold Thin Films Into Straight-Sided Blisters and Bubbles**, ***Kimheng Meng (kimheng.meng@grenoble-inp.fr)**, G. Parry,* INP Grenoble, France*; M. Hurier, N. Dahmane, C. Coupeau,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Thin films and coatings, used in a wide range of technological applications, are often industrially produced by physical vapor sputtering techniques which may lead to very high levels of internal stresses [1]. These high stresses trigger damage mechanisms, such as buckling delamination. Preventing buckling is hence a major issue for industrial applications of coatings. Various buckling morphologies have been commonly observed such as straight-sided buckles (SSB) [2,3] and circular blisters [4]. Those buckles morphologies often evolve into more complex buckles by a combined effect of secondary buckling and crack front propagation, giving rise to structures known as telephone cords or varicose structures [5,6].

In this work, we report on SSB and circular blisters experimentally observed by optical and atomic force microscopy on gold ductile thin films deposited by physical vapor deposition on silicon wafers. It is shown that, whatever the buckle dimensions, their maximum deflections are higher than those expected by the elastic theory (based on Föppl-Von Karman plate equations). By using finite elements method (FEM) simulations, it is showed that taking into account plastic deformations in the film well explains the experimentally observed shapes (see Figs 1 and 2). The Young's modulus of the thin film, as well as the full set of parameters of the plasticity hardening law have been identified using nano-indentation tests coupled with finite elements solution. The numerical results are presented, discussed and compared to the experimental observations, shedding some light on the genesis of those structures, highlighting in particular the importance of taking the film loading history (buildup of stress inside the film during deposition) into account.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP1-2-TuA

PVD Coating Technologies II

Moderators: Christian Kalscheuer, RWTH Aachen University, Germany, **Vladimir Pankov**, National Research Council of Canada

1:40pm **PP1-2-TuA-1 Use of van der Waals Layers and Ultrahigh Vacuum Environment to Control Composition and Crystallinity in Sputter-Deposited Thin Films**, ***Suneel Kodambaka (kodambaka@vt.edu)***, Virginia Tech, USA; *K. Tanaka, A. Deshpande, P. Arias, A. Aleman, H. Zaid, M. Liao,* University of California at Los Angeles, USA; *C. Ciobanu,* Colorado School of Mines, US; *M. Goorsky,* University of California at Los Angeles, USA **INVITED**

Compositional control in sputter-deposited thin films is typically achieved via changing the deposition parameters, such as partial pressure of the reactive gases, substrate temperature, deposition fluxes, and the target composition. Common approaches to improve crystallinity, to increase grain size and the grain orientation in thin solid films typically involve the use of single-crystalline substrates, high substrate temperatures combined with low deposition fluxes, and energetic ion beams.

In this talk, I will present approaches involving the use of ultra-low (e.g., 0.002%) partial pressures of the reactive gases and van der Waals (vdW) layers as buffer layers to grow thin films of desired composition and enhanced crystallinity. Using Ta-C and Mo-S as model materials systems, we demonstrate compositional tunability and improved crystallinity. We also shown that Ta_2C thin films grown on $Ta_2C(0001)$ covered with hexagonal boron nitride (hBN), a vdW-bonded material, are more highly oriented than those films grown directly on bare $Ta_2C(0001)$ under identical deposition conditions. That is, heteroepitaxial growth across a vdW layer seemingly yields better crystalline quality than homoepitaxy. We observe similar highly-oriented growth of face-centered cubic Pd, body centered cubic Mo, and hexagonal MoS_2 thin films on hBN-covered substrates. Our results provide new insights into the factors underlying the growth of highly-oriented thin films.

2:20pm **PP1-2-TuA-3 Methods for Rapid Modeling of PVD Processes to Establish a Digital Twin of a Coater**, ***Stephane Lucas (slu@incosol4u.com)***, Laboratoire d’Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, Belgium; *G. Atanasoff,* AccuStrata, USA; *P. Moskovkin, J. Muller,* Laboratoire d’Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, Belgium; *E. Haye,* Innovative Coating Solutions - ICS., Belgium

Thin film materials are key components in a variety of applications including automotive and mechanical engineering, optics, nanotechnology, medical applications, photovoltaics and displays. Their performance and reliability depend to a high degree on the precision, reproducibility and intrinsic performance of the coatings involved. Besides empirically derived know-how, fundamental insights of the mechanisms underlying the synthesis process and intrinsic material properties can be easier acquired through a coupled process and material modelling approach. Therefore, with increasing size, throughput, functional integration of coated products as well as market specific regulatory requirements, a simulation-driven development of deposition processes and advanced thin film materials becomes a necessary tool.

The Virtual Coater™ project aims to realize an easy-to-operate and computer-low-resources computational material-modelling platform that serves as a translation environment to accelerate the development of thin film materials and the related deposition processes. Making use of existing and validated simulation tools, it provides a multi-physics approach for the prediction of deposition process features as well as intrinsic film properties.

Process features from a 3D description of industrial coater includes the prediction of film uniformity and deposition rate, whereas intrinsic film properties are linked to the composition, microstructure and morphology (e.g. density, surface roughness and defects), optical, mechanical and electrical properties. Besides detailed models of process dynamics and film material models, this simulation framework is capable of real-time capable process simulation.

These developments together will lead to a much efficient approach and tool to support the co-design of coating materials and substrate systems, optimization of PVD processes, and reduced overall new coating system development cycle time by 50-100%, and material savings and waste reductions for developing the new coating systems by at least by 4-5 folds, comparing to traditional experimental trials and error approaches.

We will present the latest developments in the field (ours and from others), and we will demonstrate how a modeling platform built on optimized fast multi-scale algorithms can depict a “digital twin” of an industrial magnetron sputtering system, and how it can be used to tune the deposition process to achieve desirable coating properties. Extension toward coating properties optimization with Genetic Algorithms will also be presented together with 2D and 3D examples.

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2:40pm **PP1-2-TuA-4 Generating Spokes in Direct Current Magnetron Sputtering Discharges by an Azimuthal Strong-to-Weak Magnetic Field Strength Transition**, ***Martin Rudolph (martin.rudolph@iom-leipzig.de)***, *W. Diyatmika,* Leibniz Institute of Surface Engineering (IOM), Germany; *O. Rattunde, E. Schuengel,* Evatec AG, Switzerland; *D. Kalanov,* Leibniz Institute of Surface Engineering (IOM), Germany; *J. Patscheider,* Evatec AG, Switzerland; *A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany

Spokes in magnetron discharges are zones of enhanced excitation and ionization that can be suspected to influence the ion ejection from the plasma toward a substrate and by that influence a deposited thin film morphology. Here, we show that spokes can be generated at a desired location by introducing a step in the magnetic field strength along the racetrack. For the experiments we use a magnetron with a 300 mm Al target operated in direct current mode. Two magnetic field strength transitions are obtained when splitting the racetrack into a section with a weak parallel magnetic field strength above the racetrack of ≈ 40 mT, and a strong magnetic field strength section with ≈ 90 mT. Using a gated intensified charge-coupled device (ICCD) camera, we observe the generation of spokes where drifting electrons transit from the strong to the weak magnetic field. The generated spokes move against the electron Hall drift into the strong magnetic field section, thereby creating a region of high spoke activity. The observation can be explained by an accelerating electron drift velocity as the magnetic field strength weakens. At the transition from the weak to the strong magnetic field, we observe a region of enhanced light emission that we attribute to the accumulation of electrons due to a lower drift velocity in a strong magnetic field. The observed effect is similar to a cross-corner effect known from rectangular magnetrons and we confirm here that this effect is primarily due to the change in the magnetic field strength and not caused by the geometry of the racetrack.

3:00pm **PP1-2-TuA-5 the Surface Temperature of a 2” Water-Cooled Ti Target Measured During DC Magnetron Sputtering**, ***Stephen Muhl (muhl@unam.mx)***, *J. Cruz, A. Garzon,* Universidad Nacional Autonoma de Mexico

The lateral temperature of a 2” diameter water-cooled titanium target was measured using an electrically floating fine, 0.005” wire, type K chromel-alumel thermocouple. The temperature measurements were performed as a function of the DC plasma power (power densities of 1.0, 2.2 and 4.1 W/cm2) and Ar gas pressures of 10 to 60 sccm. Typically, the temperature difference between the centre of the target and inside the racetrack was more than 200 oC, the racetrack temperature increased almost linearly with the applied power to a maximum value of ~840 oC.

The target temperature was also investigated as a function of the N_2 gas concentration in the Ar gas mixture (1 to 20%), and these measurements are compared with the elemental composition of the deposits produced.

4:00pm **PP1-2-TuA-8 Black Metal Thin Films Deposited on Cooled Substrates by Sputtering**, ***Midori Kawamura (kawamumd@mail.kitami-it.ac.jp)***, *H. Iino, H. Mori, Y. Otomo, T. Kiba, Y. Abe,* Kitami Institute of Technology, Japan; *M. Ueda,* Hokkaido University, Japan; *M. Micusik,* Slovak Academy of Sciences, Slovakia; *M. Hruska, M. Novotny, P. Fitl,* University of Chemistry and Technology, Czechia

Black metal thin films with a porous structure being broadband light absorber are attractive for various applications such as photothermic conversion and photodetection. Recently, they are expected to be applied to gas sensors, due to their large surface area. In addition to vacuum evaporation, sputtering has also been reported as a method for preparation of black metal thin films[1)]. It has been well known that porous films can be obtained at low substrate temperature and high Ar gas pressure based on the structure zone model by Thornton. We have attempted to prepare black Al, Ag and Au thin films by sputtering on the substrate cooled with liquid nitrogen to suppress surface diffusion of atoms. The sputtering power and Ar gas pressure were also changed to obtain the films with porous structure. An RF magnetron sputtering system, in which the substrate can be cooled by liquid nitrogen, was mainly used for the deposition. The films were deposited on glass and Si substrates at room temperature, -80°C, and -170°C with Ar gas pressure of 6.5 - 33.3 Pa and sputtering power of 100 - 150 W at background pressure below 3.3×10^{-5} Pa. The deposited films were characterized by four point probe, SEM, AFM, XRD, XPS, and spectrophotometer.The Al films obtained at low temperature were black in color. However, metallic luster was observed from the backside of glass substrate. It means that a porous layer was formed after a thin dense layer was formed on the substrate. It was also found that black films formed by deposition at high Ar gas pressures and high RF powers. The light absorption of the films obtained was as high as 80% for the black Al films. The samples had a columnar structure and (100) crystal orientation.In conclusion, our results show that black metal films can be obtained by sputtering at low temperatures, high gas pressures and high RF powers. As shown in the figure, conditions which we explored for Al deposition are beyond the SZM. We are currently engaged in experiments with new deposition conditions, such as sputtering in Kr gas and DC power discharge, and results of these experiments will be presented as well.

Acknowledgement This work was supported by JST SICORP Grant Number JPMJSC2108, Japan, the Ministry of Education, Youth and Sports of the Czech Republic project No. 8F21008, and project No. JP22420 from the International Visegrad Fund.

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4:20pm **PP1-2-TuA-9 Intelligent Lubricating Coatings Based on the Oblique Angle Deposition Technology**, *J. Liang, K. li, K. Le,* ***Shusheng Xu (ssxu@licp.cas.cn)***, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

This research introduces an innovative approach to construct intelligent lubricating coatings by filling lubricants into the oblique angle deposited hard porous film. Oblique angle deposition as an attractive technique in physical vapor deposition is utilized to synthesize nanostructured thin films with controlled modification of morphology, such as porosity and column inclination. Under the influence of the shadowing effect, the oblique angle deposited TiN-based films often display porous morphology. Thus, the process begins with the oblique angle deposited porous TiN-based films. The hard porous films cannot only conduct as a load-bearing layer to improve the wear resistance, but also serves as storage space for the lubricant. In this research, carbon filled porous TiN coatings have been constructed, which exhibits lower friction than TiN film while yet having similar mechanical properties to the latter. Furthermore, humidity-adaptive "chameleon" coating was designed by filling the MoS_2 on oblique angle deposited porous TiCN film. Under low humidity condition, the filled MoS_2 lubricant release to the contact surface to form a low friction tribofilm. While this MoS_2-based tribofilm would fail and be removed by the friction force under high humidity condition, but the carbon phase in TiCN films would immediately release to contact surface to form a new low friction tribofilm. Therefore, the constructed MoS_2 filled TiCN coatings can respond to changing humidity conditions by self-adjustment of contacted surface properties to maintain good tribological performance in fluctuating humidity conditions. In conclusion, the research indicates that oblique angel deposition of hard porous film to store the lubricants offers a novel strategy to design the intelligent lubricating coatings. By reasonable design of the structure and composition of porous film and filled lubricants, various intelligent coatings are expected to be constructed, marking a significant advance on the field of surface engineering, especially for the applications under fluctuating environmental conditions.

4:40pm **PP1-2-TuA-10 Advanced Process Control for PVD Coating Technologies in Production Lines**, ***Thomas Schütte (schuette@plasus.de)***, *J. Urbach, P. Neiß, M. Radloff,* PLASUS GmbH, Germany

As specifications in the thin film industry become more and more demanding, high production yields and cost effective production becomes a major factor in this competitive market. Increasing demands for better specifications and lower scrap rates drive the demand for efficient process control systems which gather comprehensive in-situ data of the process conditions as well as product properties.

Spectroscopic plasma process monitoring is a standard measurement technique to acquire data from the actual coating process in real-time. Also, time-resolved electrical measurements of generator power, voltage and current provide valuable process information especially in pulsed plasma applications. In addition, in-situ broadband photometric measurements can reveal important properties of the growing coating such as film thickness or color values.

This presentation will introduce the combined in-situ data acquisition from spectroscopic plasma monitoring, electrical measurements and photometric thin film measurements in demanding coating processes like metallic and reactive sputtering, HIPIMS, PECVD and microwave driven processes. By combining information from the different measurement techniques in a single system and evaluating the comprehensive data in real-time process control becomes more accurate and reliable and in turn enhances production stability and improves product quality.

Examples from various coating applications in industry and R&D are presented, including tribological, optical and architectural glass coating processes.

Topical Symposium on Sustainable Surface Engineering
Room Palm 5-6 - Session TS2-TuA

Sustainable Processing and Materials Selection for Surface Solutions

Moderators: Jörg Vetter, J.Vetter-S3-consulting, Germany, **Fan-Bean Wu**, National United University, Taiwan

1:40pm **TS2-TuA-1 Microplasma-Enabled Upcycling for Nanomaterials Synthesis and Applications**, ***Wei-Hung Chiang (whchiang0102@gmail.com)***, National Taiwan University of Science and Technology, Taiwan **INVITED**

Microplasmas are a special class of electrical discharges formed in geometries where at least one dimension is less than 1 mm. As a result of their unique scaling, microplasmas operate stably at atmospheric pressure and contain large concentrations of energetic electrons (1-10 eV). These properties are attractive for a range of nanomaterials synthesis and nanostructure engineering such as metal nanostructures and semiconductor nanomaterials [1]. Recently, we found that the energetic species including radicals, ions and electrons generated in the microplasmas were capable of initiating electrochemical-assisted reactions for the nucleation and growth of graphene quantum dots (GQDs), silicon quantum dots (SiQDs), and metal nanoclusters (MNCs). Moreover, we discover a simple and controlled synthesis of metal/metal, metal/QD heterostructures using our unique microplasma engineering. In this presentation, I will discuss these topics in detail, highlighting the advantages of microplasma-based system for the synthesis of well-defined nanomaterials for emearging appplications including detections of SARS-CoV-2 proteins [2], cancer and neurotransmitter biomarkers [3, 4], drug delivery [5] and environmental applications such as clean water production [6] and CO_2 adsorption [7]. These experiments will aid in the rational design and fabrication of nanomaterials for nanotechnology-enhanced biosensors and may also have significant impact in emerging applications for next generation biomedical applications.

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2:20pm **TS2-TuA-3 Enhancing Hydrogen Production in 2D Materials via Surface Modifications: An Atomistic Study***, N. Khossossi, S. Sagar,* ***Poulumi Dey (p.dey@tudelft.nl)****,* TU Delft, Netherlands

Hydrogen (H2) is one of the most potential candidates of sustainable energy produced in an eco-friendly manner. However, there are several challenges to be met before realization of H2 as an energy source. Known bottlenecks are slow kinetics and high overpotential associated with Hydrogen Evolution Reaction (HER), inefficient storage and H2 induced mechanical degradation of structural materials e.g., steels. To establish a viable 'H2-based economy', such bottlenecks could be addressed by designing materials with enhanced properties. To this end, the development of strategies for surface modification e.g., single-atom catalysts (SACs) supported on two-dimensional (2D) materials, are highly desirable. In this study, we perform Machine Learning (ML) assisted high-throughput screening of SACs supported on a 2D Ga-based system to expedite the prediction of HER overpotential. Firstly, Density Functional Theory (DFT) calculations are performed to investigate the catalytic properties of the system for HER. Our results reveal that, akin to many other 2D materials, the pristine Ga-based system is inert for HER due to its weak affinity towards hydrogen. However, the defective Ga-based system with surface sulfur-vacancy, exhibits highly desirable HER catalytic activity. Subsequently, we demonstrate the ML-accelerated prediction of HER overpotential for all transition metals on the system. By leveraging DFT calculations performed on 14 distinct SACs, we put forward a ML based model that maps the HER overpotentials to the atomic properties of the corresponding SACs. The trained ML model exhibits exceptional prediction accuracy and significantly reduces the prediction time compared to DFT calculations. Moreover, we identify an intrinsic descriptor that elucidates the relationship between the atomic properties of SACs and the overpotential. Our study thus provides valuable insights and a robust methodology for screening SACs on 2D materials, facilitating the design of high-performance catalysts for HER.

2:40pm **TS2-TuA-4 Surface Wettability Modification of Polymers for Use in Electrocaloric Heat Pumps***,* ***Maria Barrera (maria.isabel.barrera.marin@fep.fraunhofer.de)****,* Fraunhofer FEP, Germany*; D. Pinkal, M. Wegener,* Fraunhofer IAP, Germany*; F. Fietzke,* Fraunhofer FEP, Germany

Electrocaloric (EC) materials show a reversible temperature change in response to an external electric field, under adiabatic conditions [1]. In Germany, six Fraunhofer Institutes are working on the development of a refrigerant-free, energy-efficient electrocaloric heat pump, in which the heat transfer is done through latent heat when a fluid evaporates or condenses on the EC material. Due to their relatively high electrocaloric activity and mechanical flexibility, relaxor ferroelectric terpolymers such as P(VDF-TrFE-CFE) are being used as single thin films of a few micrometers thickness as well as multi-layer components to increase the thermal mass of the system [2].

In general, polymers have an intrinsic hydrophobic surface, which might have drawbacks for some applications. As an approach to overcome the poor surface wettability of the polymer components, there is a motivation to use superhydrophilic polyimide (PI) films for encapsulating the EC components, producing a complete wetting of the surface by the working fluid and hence improving the latent heat transfer for optimal performance of the electrocaloric heat pump. Additionally, PI also exhibits outstanding heat resistance and excellent chemical resistance [3], which makes it suitable as insulating material when the application of relatively high electric fields is required for inducing electrocaloric activity on the terpolymers.

For this purpose, the wettability of 12.5 µm thick PI films (Upilex-S, Ube Industries) has been modified by pulsed magnetron sputtering under O_2 atmosphere, combining surface roughening and deposition of metal oxide layers. It has been found that the hydrophilic nature of the coatings together with the appropriate surface topography ensure a durable superhydrophilic performance of the flexible PI foils for (up to now) more than 290 days after treatment.

Results about the influence of composition variation, treatment time, material deposited, and surface roughening on the wetting properties of the PI foils will be presented. Finally, the integration of the encapsulating PI film with the EC polymer components is discussed.

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3:00pm **TS2-TuA-5 High Volume Coating of Metallic Plates for Hydrogen Applications–A Challenge for Coating Machine Builders***,* ***Philipp Immich (pimmich@hauzer.nl)****, R. Bosch, K. Fuchigami, R. Jacobs, T. Karla, P. Broekx,* IHI Hauzer Techno Coating B.V., Netherlands*; T. Hurkmans, J. Ummels, F. Schuivens,* IHI Ionbond AG, Netherlands

The hydrogen market is growing rapidly. The industry is developing for technical solutions for hydrogen generation and hydrogen-based electricity generation for mobile and stationary applications, and universities and institutes are investigating solutions for the long term. Today's challenge is to bridge the gap between current low to medium technology maturity level and market demand: how to be able to produce hydrogen on large scale and how to scale fuel cell production to high volumes? IHI Hauzer and IHI Ionbond are working on this challenge for many years, developing low cost coatings to supply to the market either by machine solutions and coating services. Key components of electrolyzers and fuel cell stacks like bipolar plates, PTL sheets and CCM's need high quality coatings to enable good catalyst performance, good electrical conductivity and good corrosion properties. For bipolar plates and PTL sheets, Hauzer and Ionbond have developed coatings based on PVD and DOT technology. In the presentation, both technologies will be addressed, including the current status of market introduction and our expected further roll-out within the next years. For PVD, the current main challenges related to machine and process solutions for high speed inline coating will also be addressed. For DOT technology the current main challenges are related to upscaling production capacity in the near future and optimizing precious metal use further.We will further address the requests from the market especially the electrolyzer business and give an outlook about possible solutions to serve these demands.

4:00pm **TS2-TuA-8 Iron Aluminide-Based Coatings as Sustainable Alternative for High Temperature Wear Protection***, H. Rojacz, K. Pichelbauer, M. Rodriguez Ripoll,* AC2T Research GmbH, Austria*; G. Piringer,* University of Applied Sciences Burgenland, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*;* ***Carsten Gachot (carsten.gachot@tuwien.ac.at)****,* Vienna University of Technology, Austria

Strengthened iron aluminides show excellent mechanical properties up to 600°C. Therefore, coatings based on the intermetallic phase Fe_3Al are promising candidates to replace Co-, Cr- and Ni- rich coatings; critical raw materials with a high ecological impact. Different strengthening mechanisms can be used in order to increase the hardness of such coatings. Silicon can be used to for solid solution strengthening, whereas carbon as well as the combination Ti and B can be used to precipitate hardphases, intended to result in increased wear resistance. In this study, the influence of different amounts of alloying on the processing and moreover the wear resistance was evaluated. A thorough analysis of the materials and the present phases was conducted, using scanning electron microscopy, electron backscatter diffraction, hot hardness testing, nanoindentation as well as high temperature abrasion testing. Results show that the hardness can be significantly increased from ~260 HV10 to ~ 350 HV10 via solid solution strengthening with silicon or TiB_2 precipitations. Over 405 HV10 can be achieved by precipitating perovskite-type carbides $Fe_3AlC_{0.6}$. Hot hardness results show a good stability of the coatings >500°C. The wear results show a significant reduction of abrasive wear at high temperatures when strengthened, leading to lower wear rates at elevated temperatures due the increased formation of mechanically mixed layer. The obtained wear rates were used to estimate a lifetime utilised for ecological impact calculations from cradle to gate to compare the developed coatings with other wear protection coatings. Here, a reduction of the ecological impact of ~80% compared to cobalt based coatings can be assessed, showing the high potential of iron aluminide-based claddings as high temperature wear protection.

Surface Engineering - Applied Research and Industrial Applications
Room Palm 5-6 - Session IA3-WeM

Innovative Surface Engineering for Advanced Cutting and Forming Applications

Moderators: Denis Kurapov, Oerlikon Surface Solutions AG Pfäffikon, Liechtenstein, **Christoph Schiffers**, CemeCon AG, Germany

8:00am **IA3-WeM-1 How to Design a Coating for Metal Sheet Deformation Starting from Cutting Tools***, **Alessandro Bertè (berte@lafer.eu)**, P. Colombi,* Lafer Spa, Italy **INVITED**

Metal sheet transformation processes still represent a fundamental sector of activity for the mechanical industry and for PVD coatings as well, as the latest have a primary role in reduction of production costs, thanks to the increase of the life of the mold and the reduction of friction during the molding phase.

Lafer has always invested in research for innovative surface treatments including coatings, aimed to improve the state of the art, in order to increase wear resistance of the moulds.

This research focuses on the mold throughout its entire life cycle, starting from its machining process and ending to its application on the field.

For this reason, the goal is twofold: namely to develop a coating for cutting tools used during mold construction while creating a high-performance coating for ferrous metal sheet deformation.

The starting point concerned the cutting tool: once the geometry and the material to be machined were defined (1.2379 steel hardened to 62 HRC), the influence of cutting edges preparation, coating and post-finishing techniques were investigated with the aim of minimizing tool wear.

Various coatings formulations on the market, specific for this application, were tested (AlTiN, AlCrN, AlTiSiN) and subsequently an AlTiSiN-based coating was developed using HiPIMS technology: the study allowed the improvement of the thickness uniformity, increasing the coating adhesion while optimizing its hardness and elastic modulus.

All the tested solutions were compared in terms of the wear of the cutting edges, finding that the HiPIMS AlTiSiN coating reached the best performances.

The second part of the project concerned the mold: a demanding geometry for ferritic metal sheet molding was identified and the cutting tools for the machining of the mold were prepared with the method defined above.

Field tests were carried out by comparing the uncoated mold against the current Lafer solution on the market (TiAlCN), based on the number of compliant produced parts.

Subsequently, a new TiCN-based coating deposited with arc technology was developed: the various tests led to a reduction of the friction coefficient and coating wear rate and increase of its fatigue resistance, measured through multiple impacts technique.

A molding comparison between the new and the actual solutions was carried out: the new coating led to a reduction in lubricant consumption and a significant increase in the number of produced parts.

Future developments will investigate the joint effect of a surface hardening process underneath the newly developed PVD coating and its performances with different types of metal sheet materials.

8:40am **IA3-WeM-3 Effect of Current Density on the Pulsed-DC Powder-Pack Boriding Process (PDCPB)***, I. Campos-Silva,* ***J.L. Rosales-Lopez (jrosales96@hotmail.com)****, M. Olivares-Luna, K. Chaparro-Pérez, E. Hernández-Ramírez,* Instituto Politécnico Nacional, Mexico*; A. Contreras-Hernández,* Tecnológico Nacional de México/Instituto Tecnológico de Tuxtepec, Mexico

In this study a novel method denominated pulsed-DC powder-pack boriding process (PDCPB) was used to develop FeB/Fe_2B layers on the surface of an AISI 316 L steel. The layers were obtained at 1123 - 1223 K, exposure times of 1800 – 7200 s for each temperature, employing current densities around of 230 and 460 $mA\cdot cm^{-2}$ with polarity inversion changes of the electric field of 10 s over the material's surface. A boriding agent composed by 70% B_4C, 20% SiC and 10% KBF_4 was used for the entire set of experimental conditions. The diffusion/electromigration-controlled growth of the FeB/Fe_2B layers on the AISI 316 L steel was validated by the "Mean Diffusion Coefficient" model. A positive effect of the current density on the boron activation energies of FeB and Fe_2B (~157 and ~165 $kJ\cdot mol^{-1}$ for the results obtained on 230 $mA\cdot cm^{-2}$, and ~150 and ~147 $kJ\cdot mol^{-1}$ at 460 $mA\cdot cm^{-2}$, respectively) were obtained; these results were lower (20% for the current intensity of 230 $mA\cdot cm^{-2}$ set and 26% for the current intensity of 460 $mA\cdot cm^{-2}$, respectively) than those reported for conventional powder-pack boriding process.

Furthermore, during the heating and electric field induction periods of the PDCPB, the temperature between the electrodes (T_E) and the electrical resistivity of the boriding agent (E_R) were sampled. In the same way, the induction of the electric field during PDCPB was possible due to KBF_4 percolation in the boriding agent and the transformation of part of the electron flux kinetic energy into heat (Joule effect), reducing drastically the E_R.

9:00am **IA3-WeM-4 Challenges Dealing with Industrial Coating Development and Tailor-Made Production***, **Klaus Pagh Almtoft (kpa@dti.dk)**, B. Christensen,* Danish Technological Institute, Denmark **INVITED**

The materials requirements of manufacturing industries encourage job coating companies to develop and adapt improved coatings or customize existing ones for emerging markets. The combination of coating research and development (R&D) for industrial applications, tailor-made coating solutions and job coating presents several practical challenges and opportunities.

One of the primary challenges in practice is translating R&D outcomes into scalable production processes. While the laboratory environment enables precise coating control and optimization, replicating these conditions on an industrial scale often proves difficult. Factors such as process variability, equipment limitations, the influence of complex geometries of real parts, and time and cost constraints can significantly impact the feasibility of implementing new coating technologies and processes. Different time scales between R&D and production may further complicate the process. In the pursuit of a solution, understanding every detail of the underlying science is not always feasible. A pragmatic approach can expedite the development process but requires a high expertise to avoid pitfalls.

Tailor-made solutions, while offering a high degree of customization, come with their own set of challenges. In daily PVD job coating operations, low volume production of certain parts demands flexibility and often non-standardized batches – frequently with mixed types of parts. This increases the need for skilled and highly experienced people to ensure consistent coating quality and performance. Additionally, coating processes developed for such applications need to be sufficiently robust to ensure the desired functionality, even when the geometrical setup of the coating system varies. In some cases, the use of simulation tools aids in optimizing batch setups to ensure sufficient coating homogeneity or thickness on the critical surfaces of components.

Despite these challenges, the potential benefits of customized coating solutions are substantial and serve many customers having a limited number of parts. By aligning R&D efforts more closely with production realities, it is often possible to accelerate the development of tailor-made PVD coatings and improve their production adoption.

This talk discusses some of the complexities encountered in bridging the gaps between R&D and production, focusing on applied customized sputter coating solutions and regular job coating. Practical examples of R&D using industrial scale DCMS and HiPIMS coatings for machine components and tools will be used as cases.

9:40am **IA3-WeM-6 a Comprehensive Study of HiPIMS Coated Tool and Microtool Performance: From Edge Preparation to Micro-Machining Tests***, **Pablo Díaz Rodríguez (pablo.diazr@nano4energy.eu)**, J. Santiago,* Nano4Energy, Spain*; A. García,* Nano4Energy, Colombia*; I. Fernández, A. Wennberg,* Nano4Energy, Spain*; P. Collignon,* PD2i, France*; Á. Guzmán, D. Sanmartín, J. Molina-Aldeguia,* Universidad Politécnica de Madrid, Spain*; M. Monclus,* IMDEA Materiales, Spain

The high standards and requirements demanded in high-speed machining (HSM) applications – some examples are the precise manufacturing of IC Molds or biomedical devices - comprise a delicate control of the tool preparation as well as coatings design and finish, especially in the case of microtools with a diameter below the millimeter.

The work developed covers not only the coating step, but also the preparation of the tool, focusing on:

a) Microtool cutting edge preparation.

b) HiPIMS deposition, as the use of this technology allows the preparation of hard coatings with high smoothness, low density of defects, and good homogeneous coverage of 3D intricate parts (thus able to match the low tolerances required for micromachining) makes this technology ideal for these applications. The tested coatings are based on Si- and B- containing AlTiN and were deposited in different sets of tools, according to their specific requirements, attaining hardness values of 35 GPa and good adhesion. Moreover, oxidation studies were performed to determine the stability of these coatings, analysing, and comparing the results in terms of SEM, TEM, and XRD, observing a greater oxidation resistance for the Al containing coatings.

c) Machining tests, which, in addition to mechanical properties analysis, provide information regarding the performance of the coatings under operation conditions. The materials selected for machining are Hardened Steel (HRC60) and Ti6AlV4 alloy, and the finishing of the machined parts, as well as the wear suffered by the tool is analyzed.

11:00am **IA3-WeM-10 Effect of Phase Separation in the Anticorrosion Performance of AlCrFeNi High-Entropy Alloy***, **Chih-Chen Lee (janislee0123.en12@nycu.edu.tw)**, I. Tasi,* National Yang-Ming Chiao Tung University, Taiwan*; H. Chen,* Michigan State University, Taiwan*; C. Chen,* National United University, Taiwan*; S. Chen,* National Yang-Ming Chiao Tung University, Taiwan

Due to reaching net-zero emissions, offshore wind power is one of the methods to get clean energy. To improve the anti-corrosion performance of wind turbine towers, researchers are always seeking the candidates to enhance or replace the stainless steel 316 base material. In our study, we found that AlCrFeNi HEA exhibited a better anti-corrosion performance than SS 316 in both the salt spray and acid immersion test. Especially, its corrosion resistance could be significantly improved by controlling the phase ratio. Gas-atomized HEAs can retain the ideal high-entropy state owing to the sluggish effect and rapid cooling process. The as-atomized AlCrFeNi powders presented a superior resistance to acid solutions, but weakened after experiencing high temperature environment. Through careful investigations, it was found that Al and Ni elements have the lowest mixing enthalpy, promoting the preferential formation of AlNi phase from the uniformly distributed matrix. As a result, ordered AlNi and FeCr phases are formed within the BCC structure. It has a chemical composition closely matching the designated component ratios, composed of a BCC/B2 phase composed of AlNi and a BCC/A2 phase composed of FeCr. From the acid immersion test, we found that the rich AlNi phases were preferentially corroded, decreasing corrosion resistance. Furthermore, argon gas was commonly used to atomize the melt and has a lower specific heat capacity, which allows sufficient time for melted droplets to form spherical shapes with better flowability due to cohesive forces. The AlCrFeNi HEA powder produced by gas atomization exhibits a good anti-corrosion performance because it maintains the initial high randomness phase and prevents the segregation of elements. It also shows a spherical shape and excellent flowability, making it suitable for coating applications in harsh environment.

Keywords: High-entropy alloys, Gas atomization, AlCrFeNi, Annealing, Phase transition, anti-corrosion performance

11:20am **IA3-WeM-11 Surface Conditioning and New Applications Using Advanced Plasma Etching Technology***, **Dominic Stangier (dominic.stangier@oerlikon.com)**,* Am Boettcherberg 30-38, Germany

Plasma etching plays an essential role for the vacuum-based cleaning of tools and components to remove native oxide films and small contaminations. This inherent treatment of the substrate material prior to every PVD process directly influences the adhesion and consequently the overall performance of the substrate coating compound. Therefore, different processes such as glow discharges and metal ion etching methods are commonly conducted, which are however on the one side strongly limited in their etching rate as well as performance and on the other side lead to macro defects on the surface of the substrate significantly reducing the performance of the coated tools. To overcome these challenges an improved etching process, which combines the high plasma density of cathodic arc evaporation with a noble gas-based glow discharge called advanced Arc Enhanced Glow Discharge (AEGD) is used. In this context, the unique possibility to independently control the bias potential and freely modulate the pulse pattern with a simultaneous scalable plasma density for the etching process open up a broad field of new pre-treatment options for PVD coated tools.

Fundamental investigations for the limits and correlations of the aforementioned etching parameters on the surface condition, near subsurface region and the coating adhesion of nitrides are conducted using cemented carbide substrates. The etching rate is directly linked to the applied bias level as well as to the current used on the cathode and anode. As a result of the high etching rates, a new approach for a targeted cutting edge preparation for micro tools is presented, showing the possibility of generating asymmetric cutting edge shapes (form factors up to $K = 2.7$). The performance is evaluated in milling tests, proving a reduction of the process forces for milling HSS (62 HRC). Furthermore, for tool steels an adjusted composition of the plasma allows the nitriding of the surface near region, which also leads to improved performance of coating systems for dies and molds. Thus, the presented investigations prove the extended possibilities and application fields offered by the advanced AEGD technology.

11:40am **IA3-WeM-12 Advances in Microhard Machining: From Etching-based Asymmetrical Cutting Edge Preparation to Cutting Performance of TiAlN-based Thin Films***, **Nelson Filipe Lopes Dias (filipe.dias@tu-dortmund.de)**, A. Meijer, C. Jäckel, D. Biermann, W. Tillmann,* TU Dortmund University, Germany

Micromilling of hardened and tempered tool steels offers significant potential for die and mold manufacturing due to the high precision in dimension and shape of filigree geometries combined with high surface integrity. Nevertheless, the high hardness of these steels impose considerable thermo-mechanical loads on the cutting edge of micromilling tools. Hence, it becomes essential to employ an adapted combination of cutting edge preparation alongside the application of wear-protective PVD thin films with improved properties. This integrated approach is crucial for enhancing cutting performance and prolonging the service life of tools when machining hard materials. Arc-enhanced glow discharge (AEGD) ion etching emerges as a promising pretreatment, serving not only to enhance thin film adhesion, but also to produce asymmetrical cutting edge geometries in small scale for micromilling tools of ultrafine-grained WC-Co cemented carbide. Already 15 min of AEGD ion etching yields in considerable cutting edge rounding and the formation of asymmetrical shapes with form-factors $K \geq 2$. The obtained cutting edge geometries promote favorable cutting behavior in terms of process forces and wear development in machining tests of a hardened and tempered powder metallurgical high-speed steel (AISI M3:2). In addition to the AEGD ion etching pretreatment, the effectiveness of micromilling tools substantially relies on the application of a protective PVD thin film with enhanced tribo-mechanical properties. Both the selection of the TiAlN-based thin film system and the employed sputtering technology play pivotal roles in determining the cutting performance of the coated tools. In comparison to the traditional TiAlN, quaternary TiAlSiN and TiAlTaN thin films exhibit superior wear resistance for micromilling tool steels with high hardness and carbide content. The use of high power impulse magnetron sputtering (HiPIMS) further enhances cutting performance and wear resistance, particularly for TiAlSiN. To overcome the low deposition rates of pure HiPIMS processes, a hybrid approach combining direct current magnetron sputtering (dcMS) with HiPIMS is a viable alternative, taking advantage of the benefits of both processes. This hybrid dcMS/HiPIMS technique also proves beneficial in producing TiAlN-based thin films that exhibit improved cutting performance and wear resistance compared to pure dcMS thin films. These findings emphasize the importance of a coordinated approach involving ion etching and PVD deposition for effectively reducing wear and process forces in micromilling difficult-to-machine materials.

12:00pm **IA3-WeM-13 Natural Rock Star: PVD-Functionalizing of Nature-Derived Materials for Cutting Applications***, **Wolfgang Tillmann (wolfgang.tillmann@tu-dortmund.de)**, N. Lopes Dias,* TU Dortmund University, Germany*; B. Breidenstein, B. Denkena, H. Petersen,* Leibniz University Hannover, Germany

The manufacturing process of traditional cutting materials such as cemented carbide involves significant energy consumption and costly raw materials that are often linked to environmental harm during extraction. To address these concerns, there is a growing demand for developing sustainable cutting materials. In this context, natural materials stand out as both environmentally friendly and abundant. Natural rocks, in particular, are promising due to their hardness, which typically ranges from 8 to 16 GPa depending on the rock type. The suitability of these natural materials for cutting applications can be enhanced by functionalization the surface properties through the application of a protective thin film using physical vapor deposition (PVD) technology.

In preliminary investigations, the suitability of various rock types, such as Alta quartzite, flint, lamellar obsidian, quartz, and Silver quartzite as cutting material is analyzed. Cutting inserts are crafted from these natural rocks and subsequently ground. A TiN thin film is deposited onto the various natural rock inserts using a magnetron sputtering process. The resulting TiN thin films crystallize in a cubic structure on all rock types and reveal hardness values comparable to TiN thin films grown on tool steel. A ground surface of the natural rocks promote good adhesion of the TiN thin films. To assess the cutting performance and wear characteristics of PVD-coated natural rocks, turning tests are conducted using the aluminum alloy Al7075. The TiN thin film significantly enhances wear resistance, thus extending the service life of the cutting inserts. Additionally, it is observed that the distinct material properties of the natural rocks significantly affect the wear behavior. Rock types with a more homogeneous structure demonstrate improved wear resistance over extended cutting lengths.

The utilization of a PVD-coated natural rock emerges as a promising concept for broadening the spectrum of cutting materials and promoting sustainability in their manufacturing. A tailored adjustment of the grinding process for cutting inserts with an adapted thin film design is anticipated to further elevate the cutting performance of natural rock inserts.

Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-3-WeM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling III

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Germany, **Francisco Javier Pérez Trujillo**, Universidad Complutense de Madrid, Spain

8:00am **MA1-3-WeM-1 Characterization and Evaluation of Physical-Chemical Properties of Novel Ternary and Quaternary Molten Salts and Their Economic and Environmental Impact in Parabolic Trough Technology: Corrosion Effects**, *M. Lambrecht, D. Maria Teresa, L. Maria Isabel, G. Garcia Martin, J. Chaves,* ***Francisco Pérez Trujillo (fjperez@ucm.es)****,* Universidad Complutense de Madrid, Spain*; P. Audigie, A. Aguero,* INTA, Spain

Only molten salt combinations are used as a heat storage medium in CSP to date. Alkaline nitrates and nitrites have been successfully utilized as heat transfer fluids (HTF) and heat storage medium (HSM) in concentrated solar power (CSP) plants. Particularly, the binary mixture combination 60%$NaNO_3$ - 40%KNO_3, well known as Solar Salt with a freezing point around 220ºC and thermal decomposition at 560ºC [1]. Separately, there is a synthetic thermal oil that comprises the commercial parabolic trough (PT) technology to capture the heat of solar radiation. This costly HTF with a melting point about 12ºC and high environmental impact yields the heat to Solar Salt by means of exchangers. The maximum thermal energy storage temperature reached is about 390ºC, their energy power is thus limited by the organic heat carrier fluid. There are investigations aiming to increase the working temperature range a long with a unique molten salt (MS) as heat capture and storage medium. Ternary and quaternary low melting point mixtures with addition of $LiNO_3$ and $Ca(NO_3)_2$ have been presented as direct systems candidates according to their better physic - chemical properties than Solar Salt but, nonetheless, these previous investigations have deemed a full properties study with additional environmental and economic aspects to weigh the best selection criterion to envisage alternative fluids.

This investigation evaluates the important properties (melting point, degradation temperature, specific heat capacity, density and energy density) of the novel mixtures46% wt.$NaNO_3$-19%wt.$Ca(NO_3)_2$- - 35%wt.$LiNO_3$ (T1) and 33%wt.$NaNO_3$-22%wt.KNO_3-29%wtCawt.$(NO_3)_2$-16% wt.$LiNO_3$ (Q-1). Life Cycle Assessment (LCA) has been used to calculate the environmental impact of the mixtures through the software tool Simapro7 in comparison with the Solar Salt. Likewise, an economic simulation of their usage in a direct and indirect parabolic through (PT) configuration has also been estimated by means of Levelised Cost of Energy (LCOE) parameter, which was customized for the TES facility, ($LCOE_{TES}$).

The effects of molten salts chemical composition in the high temperature corrosion of metalic materials and coatings will be analized.

In this study, a 50 MW and 6 hours heat storage capacity PT plant has been considered for $LCOE_{TES}$ estimation . This parameter was assessed by means of an in-house method from articles references and data extrapolation to simulate price variations by replacing novel multicomponent fluids by Solar Salt as HSM.

8:20am **MA1-3-WeM-2 Influence of the BN Content on the Microstructure and the Mechanical Properties of Cr_3C_2-NiCr-BN Composite Coatings Prepared by a Novel HVOF Process Using Ethanol as a Fuel**, *S. Liu,* UTBM, France*; M. Arab Pour Yazdi,* ***Pavel Sedmak (pavel.sedmak@anton-paar.com)****, J. Nohava,* Anton Paar, Switzerland*; M. Moliere, H. Liao,* UTBM, France

Cr_3C_2-NiCr-BN composite coatings were thermal sprayed on 304 stainless steel substrates using an ethanol-fueled High-Velocity Oxygen Fuel (HVOF) process. We examined the impact of varying Boron Nitride (BN) contents (ranging from 0 wt% to 15 wt%) in the feedstock on the microstructure and mechanical properties of the resulting coatings. Our findings reveal that the different BN contents significantly influence the microstructure, interlayer porosity, nanohardness, scratch resistance, and sliding wear resistance of the composite coatings. As the BN content increased, the interlayer porosity of the coatings increased and the BN content also contributed to an increase in the nanohardness of the films.In addition, a higher BN content resulted in a reduction in the coefficient of friction, but at the expense of an increase in the wear rate and a decrease in the scratch resistance.

Notably, when the BN content reached 15%, the composite coating exhibited its lowest coefficient of friction. However, the wear rate was simultaneously increased due to the higher interlayer porosity of this particular coating. These results provide valuable insight into the optimization of BN content to achieve the desired balance of mechanical properties in Cr_3C_2-NiCr-BN composite coatings.

8:40am **MA1-3-WeM-3 Oxidation Behavior of Si-Based Coatings on Refractory Multi-Principal Element Alloys**, ***Brady Bresnahan (bresn047@umn.edu)****, D. Poerschke,* University of Minnesota, USA

The large design space for refractory multi-principal element alloys (MPEAs) provides opportunities to tune alloy chemistry to simultaneously optimize the bulk and surface properties. This investigation studied Si-based coatings to improve the oxidation resistance of refractory alloys. A set of MPEAs systematically exploring composition variables related to silicide formation were produced by arc melting and coated by pack cementation and slurry processing. The effects of alloy and coating compositions on coating microstructure were studied to understand refractory metal partitioning between silicide phases. The phase evolution after oxidation was similarly explored where the tendency to form protective oxides and mass change were used to evaluate the composite material performance and understand alloy and coating composition effects. These insights will enable coupled alloy and process design to improve oxidation resistance while taking advantage of the superior high temperature yield strengths of refractory MPEAs for aerospace applications.

9:00am **MA1-3-WeM-4 Multifunctional Nanostructured ZrN-Cu Coating for Maritime Applications**, ***José D. Castro (jodcastroca@unal.edu.co)****,* University of Coimbra, Portugal*; M. Lima, I. Carvalho,* University of Minho, Portugal*; J. Sánchez-López,* Instituto de Ciencia de Materiales de Sevilla (ICMS), Spain*; R. Escobar-Galindo,* University of Sevilla, Spain*; C. Rojas,* Instituto de Ciencia de Materiales de Sevilla (ICMS), Spain*; S. Carvalho,* University of Coimbra, Portugal

Ships are essential to globalisation since they are the primary mode of transportation for goods worldwide. Any potential ship issue could affect the global economy. Corrosion and biofouling are prevalent problems linked to maritime elements. From this angle, the most widely used product was paint made of tributyltin (TBT), which was outlawed in 2008. Given this requirement, multifunctional coatings appear to be a great alternative to TBT. Magnetron sputtering technology can obtain nanoarchitectures to gather different materials and enhance characteristics. The present work presents an insight into a nanostructured film with ZrN and Cu (obtained via Deep Oscillation and DC magnetron sputtering, respectively). SS316L was used as the substrate, widely used in the naval industry. ZrN coating without copper was employed as a control sample. SEM, EDS, XRD, TEM, Nano-indentation, scratch tests, and tribology measurements assessed the characteristics of the films. Electrochemical impedance spectroscopy (EIS) until 30 days and potentiodynamic polarisation measurements were conducted in a 3.5 wt. % NaCl solution to replicate the work regime. The halo test evaluated the inhibition of microorganisms. The results demonstrate that Cu migration towards the surface (with chemical activation using NaOCl solution) reduces bacterial growth. Besides, inductively coupled plasma optical emission spectrometry (ICP-OES) and transmission electron microscopy (TEM) show that the ZrN nanolayers (~ 6nm thick) control the embedded copper nanoparticles (~ 12 nm thick) release. On the other hand, the chemical activation decreases the film corrosion resistance, the mechanical properties and the tribological performance regardless of the testing conditions (wet or dry). The findings indicate that the obtained films may be used instead of TBT paint in components used in ships as a potential way to prevent biofouling and corrosion when exposed to seawater.

9:20am **MA1-3-WeM-5 New Black Ceramic Coating on LZ91 Magnesium Alloys by Micro-Arc Oxidation***, Hung-Chi Chen* ***(mouyuan75@yahoo.com.tw)****, S. Jian,* Ming Chi University of Technology, Taiwan

LZ91 Magnesium alloy has improved mechanical properties and a low density but their limited resistance to corrosion limits their application. Therefore, it is a great challenge to increase the stability of LZ91 alloys under corrosive factors and environments. The anodized oxide film of magnesium alloy has many defects (poor bonding strength, low wear and corrosion resistance,) in traditional surface coloring technology. These defects have largely limited the applications of magnesium alloy. Micro-arc oxidation (MAO) is a new electrochemical surface treatment technology, suitable for treating the aluminum, magnesium and titanium and other light metal alloys. In electrolyte by the arc discharge plasma generated of the substrate oxidation and high temperature melting, the film was formed with high hardness and corrosion resistance.

This study uses MAO treatment to increase the corrosion resistance of LZ91 alloy, used copper oxide and $KMnO_4$ to change MAO film color. Then, black ceramic film with uniform color, smooth surface, compact structure and excellent corrosion on LZ91 alloys was successfully obtained by MAO treatment. The aim of this study is to added with various chemical element in MAO electrolyte to change the film color to black and has excellent corrosion resistance.The morphology, structure, adhesion and corrosion behavior of the bi-layered composite coating has been investigated by scanning electron microscopy (SEM), 3D white light interferometry. In this study, MAO coatings were prepared, and the effects of adding $KMnO_4$ and copper oxide to the electrolyte on the corrosion resistance and color of the coating LZ91 magnesium alloy were evaluated.

11:00am **MA1-3-WeM-10 Study on the Characterization of Adding CeO_2 Particles on Micro-arc Oxidation Coated AZ91D Magnesium Alloys***, Po-Wei Lien* ***(lanbow888@gmail.com)****,* MING Chi University of Technology, Taiwan

AZ91D magnesium alloy has the advantages of low density, high tensile strength, high elongation, and easy processing. Compared with other light metals, magnesium alloys are lighter. And it has been widely used in our daily life. Unfortunately, aluminum-magnesium alloys are prone to corrosion, which may cause serious consequences, so a simple and environmentally friendly surface treatment technology must be developed.

Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation, is one of the most effective and emerging methods for forming inorganic ceramic layers on various light metals. Compared to the traditional anodizing process, MAO coatings exhibit higher mechanical properties, enhanced corrosion resistance, and are also more environmentally friendly. During the MAO treatment, due to the deposition effect, the coating solidifies and contracts, resulting in surface structural defects such as microcracks. Hence, the addition of CeO_2 particles in the electrolyte aims to seal micro-pores and introduce self-healing capabilities.

This study uses AZ91Dwas utilized as the research substrate, and CeO_2 was introduced into the electrolyte. The investigation aimed to observe the presence of CeO_2 particles within the micro-pores on the MAO surface and evaluate the self-healing functionality during salt spray experiments. Surface corrosion resistance of AZ91D was examined through scanning electron microscopy (SEM) to assess its microstructure. Corrosion identification was conducted via electrochemical impedance spectroscopy (EIS) and salt spray testing. Surface roughness was measured using atomic force microscopy (AFM).

Keywords: AZ91D alloy; Ceramic oxide layer ; Micro-arc oxidation; CeO_2 particles ; self healing

11:20am **MA1-3-WeM-11 Characteristics Of High-temperature Resistant Coating Prepared By the Liquid Spray Technique***, Yan-Rui Chen* ***(eric19990329@gmail.com)****,* National Taipei University of Technology, Taiwan*; T. Wu,* Researcher of National Chung-Shan Institute of Science & Technology, Taoyuan city, Taiwan*; Y. Yang,* Distinguished professor of National Taipei University of Technology, Taiwan*; Y. Wu,* Professor of National Taipei University of Technology, Taiwan

In the coating technology, liquid spray (LS) is different from the traditional thermal spraying technology. The liquid spray coating is made by using compressed air. The spray liquid sprayed from the nozzle is subjected to high pressure and collides with the still air at high speed. The liquid spray splits and slows down due to air resistance, and turns into mist to form a coating,which can keep the original characteristics of the material during the spraying process and have a denser coating. Refractory metals, boride (XB_2), has good performance at high temperature, used in the electronics industry, aviation and defense. This study used liquid spray to prepare refractory metals boride (XB_2),high temperature resistant coating, discusses the liquid spray under different process parameters (working distance, solidification conditions) affected the microstructure changes of the coating and its mechanical properties, such as porosity, hardness, tensile strength, etc.

11:40am **MA1-3-WeM-12 Development of Tantalum Bond Coating for Thermal Barrier Coating by the Cold Spray***, Wei-Che Hung* ***(xauxdy111@gmail.com)****,* National Taipei University of Technology, Taiwan*; W. Li, Y. Chung,* Researcher of National Chung-Shan Institute of Science & Technology, Taiwan*; Y. Yang, Y. Wu,* National Taipei University of Technology, Taiwan

In the coating technology, cold spray(CS) is different from the traditional thermal spraying technology. The cold spray coating is formed by plastic deformation without high temperature melting, which can keep the original characteristics of the material during the spraying process and have a denser coating. This study we focus on depositing tantalum(Ta) as the protective coating and also the bond coat for the thermal barrier coatingon differentcurvature shape to simulate curved shell of an actual aircraft by using cold spray process.The results show that the cold spray coating can cause the powder to have good plastic deformation as the chamber pressure, temperature and closer working distance increase, so it has lower porosity and forms a dense coating. The Ta bond coat is well bonded with the substrate and atmospheric plasma spraying is used to prepare the YSZ top coat.

12:00pm **MA1-3-WeM-13 Protection Against Heavy Oil Fouling and Sulfidation: Comparison of PVD and Thermal Sprayed Coatings***, Fellipy Rocha* ***(fellipy.rocha@polymtl.ca)****,* Polytechnique Montréal, Canada*; L. Vernhes, F. Khelfaoui,* Velan, Canada*; G. Patience, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Valve malfunctions pose a significant and expensive threat to the gas and oil industry, leading to valve position switch failure,poor reactor pressure control, and shutdown. Safety and environmental adverse phenomena are related to worn valve maintenance. The valves are subjected to severe service at high temperature (300 – 450 °C), high pressure drop (20 – 250 bar), and erosive reactor effluents. Heavy crude oil and bitumen hydrocracking require materials that simultaneously withstand wear, oxidation, sulfidation, and coke deposition. In this work, we evaluate the protective efficacy between thin magnetron sputtered films and thermally sprayed Co-based coatings. The samples were submerged in sour crude oil at 450 °C and 110 bar for 2 h to assess their fouling resistance.

In the first part, we evaluated three thermal sprayed Co-based coatings, Co-1, Co-2, and Co-3, varying mostly in Ni, Mo, Si, W, and C contents. The as-sprayed samples exhibited typical lamellae structure, and after fusing they presented an enhanced crystallinity with a Co-Cr-Mo-Si microstructure. Surface image analysis allowed us to quantify the level of surface fouling; specifically, the worst-performing Co-1 coating showed 100% intensity, followed by 89%, and 75% for Co-2 and Co-3. After heat treatment, the same samples exhibited 95%, 15%, and 3% intensity, respectively. SEM-EDS/WDS images confirmed sulfur infiltration into the defects of the as-deposited coatings, as well as a better performance against sulfidation after fusing.

In the second part, we studied room temperature sputtered Al_2O_3 that was initially amorphous with a hardness of 11.1 GPa. Annealing at 1000 °C formed different metastable alumina polymorphs, predominantly γ-Al_2O_3 and α-Al_2O_3. Heat treatment improved alumina adhesion and increased hardness to 20.6 GPa. FIB-SEM-EDS cross-section analyses revealed an interaction between the substrate and the annealed coating. No fouling was observed on the amorphous Al_2O_3, but it was noted on the annealed samples. For comparison, HiPIMS-deposited nitride coatings fabricated with a cylindrical magnetron exhibited a very good adhesion and higher hardness, as well as good fouling protection.

In conclusion, we developed and successfully applied an optical technique to assess fouling on different surfaces. In general, amorphous materials tend to perform better, and especially coatings possessing high hardness are adequate for the heavy oil erosive environment.

Protective and High-temperature Coatings
Room Town & Country C - Session MA4-1-WeM

High Entropy and Other Multi-principal-element Materials I

Moderators: Erik Lewin, Uppsala University, Sweden, **Jean-François Pierson**, IJL - Université de Lorraine, France

8:40am **MA4-1-WeM-3 Growth and Properties of Epitaxial High-Entropy Alloy Thin Films**, ***Thomas Seyller (thomas.seyller@physik.tu-chemnitz.de)***, Chemnitz University of Technology, Germany **INVITED**

High-entropy alloys (HEAs) are discussed for applications in the fields of corrosion and wear protection as well as electrocatalysis. Although the surface properties of HEAs play a central role in these applications, they are still largely unexplored. This is - at least to a certain extend - caused by the unavailability of single-crystalline samples. In this presentation, recent progress is reported on the growth and subsequent characterization of epitaxial CoCrFeNi films [1]. The films were deposited by DC magnetron sputtering from spark-plasma sintered targets [2] using single-crystalline oxide substrates. A characterization of structural, chemical and electronic properties of the films was performed by different techniques including X-ray diffraction (XRD), scanning electron and transmission electron microscopy (SEM, TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), angle-resolved photoelectron spectroscopy (ARPES), low-energy electron diffraction (LEED) and, more recently, by scanning tunnelling microscopy (STM). It is demonstrated that epitaxially grown HEA films have the potential to fill the sample gap, allowing for fundamental studies of properties of and processes on well-defined HEA surfaces over the full compositional space.

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9:20am **MA4-1-WeM-5 Effect of Elemental Additions (X: Pt, Al, Ti, and Ag) on the Microstructure and Electrical Properties of CrMnFeCoNiX-Based High-Entropy Alloy Thin Films**, ***Salah-eddine Benrazzouq (salah-eddine.benrazzouq@univ-lorraine.fr)***, *J. Ghanbaja, S. Migot, A. Nominé, J. Pierson, V. Milichko,* Institut Jean Lamour - Université de Lorraine, France

High-entropy alloys (HEAs) have garnered significant attention across various research and industrial fields owing to their exceptional properties, which originate from their complex multiprincipal element composition. This study delves into the phase evolution, microstructure, and electrical properties of the Cantor alloy (CrMnFeCoNi) enhanced by the incorporation of additional elements such as Pt, Ti, Al, and Ag. The deployment of DC magnetron co-sputtering has been crucial in achieving homogeneous films with precise stoichiometric and morphological control. This technique has enabled the systematic investigation of the structural evolution between crystalline phases (FCC, BCC) and amorphous states and their subsequent impact on the properties of the films. We carried out comprehensive characterization using X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), resistivity measurements, and optical reflection measurements to assess the films' structural, microstructural, electrical, and optical attributes.

Abundant nanotwins were observed in the CrMnFeCoNi and CrMnFeCoNiPt films, both of which possessed a single FCC crystalline structure. The CrMnFeCoNiAl films transitioned from a single FCC phase to a duplex FCC + BCC phase structure, eventually stabilizing as a single BCC structure. The duplex FCC+BCC phase exhibited a low degree of nanotwins with larger grains of each phase. The CrMnFeCoNiTi films displayed an amorphous structure at various percentages, whereas the CrMnFeCoNiAg films exhibited a multiphase structure comprising single Ag and CrMnFeCoNiAg phases. Notably, Ag formed precipitates zone within the Cantor matrix. The observed phases were consistent with predictions made using thermodynamic criteria, despite the far-from-equilibrium conditions.

The study reveals that altering the concentration of elements such as Al and Pt significantly impacts the films' crystallographic structure and microstructure. Specifically, the electrical resistivity increased with the addition of elements in the single-phase regions. Notably, values of electrical resistivity were even higher in the duplex phase for the Al-doped samples due to the additional scattering effects of FCC/BCC phase boundaries in the alloys. The incorporation of silver was found to decrease the material's resistivity, likely because of the increased precipitation of silver within the Cantor matrix. Furthermore, optical reflectance and temperature-dependent electrical resistivity measurements confirm the metallic behavior of our alloys.

9:40am **MA4-1-WeM-6 Property Evaluation of Nd Doped NiCoFeAlTi Non-equiatomic High Entropy Alloy Films and the Influence of Post-annealing Treatment**, ***Chia-Lin Li (chialinli@mail.mcut.edu.tw)***, Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan

The effects of Nd addition on the microstructures and mechanical properties of non-equiatomic NiCoFeAlTi high entropy alloy films (HEAFs) were studied in this work. A series of NiCoFeAlTi HEAFs doped with Nd, ranging from 0 to 8.7 at.% Nd, was prepared by magnetron co-sputtering. Subsequently, a post-annealing treatment at 700°C was executed to investigate the changes in microstructure and mechanical properties exhibited by all films. The mechanical properties, phases and microstructures of Nd doped HEAFs and annealed films were characterized by the nanoindentation, X-ray diffractometer (XRD) and transmission electron microscopy (TEM), respectively. Based on XRD results, amorphous structures were identified in all Nd doped NiCoFeAlTi HEAFs. After annealing, the films exhibit a mixture of HEA FCC, NdNi HCP and L12 phases due to annealing-induced crystallization. For the mechanical properties of Nd doped HEAFs, both the hardness and elastic modulus showed an initial increase, reaching the maxima of ~9.3 GPa and ~158 GPa at 0.61 at.% Nd addition, respectively,and then decreased with the increasing Nd content. The influence of post-annealing treatment of Nd doped NiCoFeAlTi HEAFs on the microstructures and mechanical properties will be given further in this study.

11:20am **MA4-1-WeM-11 Effect of Substrate Temperature on Properties and Microstructure of High Entropy Alloy Thin Films Deposited by Magnetron Sputtering Systems**, ***Yi-Jun Yan (yjyan@gapp.nthu.edu.tw)***, *F. Ouyang,* National Tsing Hua University, Taiwan

In recent years, high-entropy alloy thin films have attracted much attention because of their higher strength and lower cost than bulk materials. This study used magnetron sputtering to prepare $Ni_{30}Co_{30}Fe_{13}Cr_{15}Al_6Ti_6$ high-entropy alloy (HEA) thin film on a Si substrate. We investigated the effect of substrate temperature on the properties and microstructure of HEA thin films, including nanotwin formation, grain growth, hardness, and roughness. The composition of the film is uniformly distributed, and different substrate temperatures did not cause significant changes in the concentration of film elements. The thin film fabricated at low substrate temperature has a highly (111)-oriented columnar grain structure, and the nanotwin boundaries are parallel to the substrate surface with average twin spacing of 1.4 nm. As the substrate temperature increased, the columnar grain structure gradually disappeared and transformed into a BCC+FCC dual-phase polycrystalline structure. The hardness of thin film possesses a maximum hardness of 1.92 GPa at the substrate temperature of 100 ^{o}C, but as the substrate temperature rises, the grain growth and detwinning cause the hardness to decrease. The resistivity of HEAs is about 105 uΩ-cm, and there is no obvious correlation with the substrate temperature. The HEA thin films also exhibit a flat surface morphology with a root mean square roughness value of 0.5 nm at low substrate temperature. But the root mean square roughness value increased to 1.5 nm as substrate temperature increased, which is due to the grain growth inside the films. The residual stress of the film changed from compressive stress to tensile stress as the substrate temperature increases. The results of this study show that the substrate temperature greatly influences the microstructure, twin crystal growth, hardness, and residual stress, and corresponding mechanism will be discussed in the talk.

11:40am **MA4-1-WeM-12 A Combinatorial Approach to Developing Sputter-Deposited AuBiTaW High-Entropy Alloy Films for Inertial Confinement Fusion Applications**, ***Daniel Goodelman (goodelman1@llnl.gov)***, *D. Strozzi, S. Kucheyev, L. Bayu Aji,* Lawrence Livermore National Laboratory, USA

After achieving inertial confinement fusion (ICF) ignition in December 2022, further optimization of material properties and experimental protocols are required to increase the fusion energy gain. To accomplish this goal, we are designing a new generation of hohlraums. Typically fabricated via magnetron sputtering, hohlraums are centimeter-scale sphero-cylindrical cans made from Au or depleted U with a wall thickness of >10 µm, serving as the outer housing for fusion fuel capsules. They must balance design constraints including high laser light-to-x-ray conversion efficiency, mechanical and corrosion stability, and electrical resistivity for magnetically assisted implosion. Here, we present results of a combinatorial magnetron co-sputtering study, aimed at developing a family of AuBiTaW films to address these outstanding challenges. Effects of the alloy composition and deposition process parameters on the microstructure, residual stress, mechanical properties, and electrical transport will be considered, as well as implications for ICF applications.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344 and was supported by the LLNL-LDRD Program under Project No. 23-ERD-005.

12:00pm **MA4-1-WeM-13 Tungsten-Based Complex Concentrated Alloys for Fusion Applications***, M. Vigil,* University of Wisconsin–Madison, USA*; **Sabine Faulhaber (sfaulhaber@ucsd.edu)**, M. Patino, D. Nishijima, A. Zaloznik, M. Simmonds, T. Lynch, M. Baldwin, K. Vecchio, G. Tynan,* University of California San Diego, USA

A complex concentrated alloy (CCA) has been identified as a promising candidate material for use in nuclear fusion applications. Previously, tungsten-based complex concentrated alloy thin films have been found to exhibit high radiation resistance [1].

This work represents the first study of fuel retention in bulk W-based complex concentrated alloys as plasma-facing components. A bulk W-based CCA was synthesized by spark-plasma sintering (SPS) and characterized by x-ray diffraction (XRD), scanning electron microscopy / electron dispersive x-ray spectroscopy / electron backscatter diffraction (SEM/EDS/EBSD) and Auger electron spectroscopy (AES) before and after exposure to fusion-relevant plasma at deuterium-ion fluences of $2 \cdot 10^{26}$ m^{-2}.

During plasma exposure optical emission spectroscopy (OES) was used to measure elemental sputtering; transient grating spectroscopy (TGS) was employed to measure the changes in thermal diffusivity and thermal desorption spectroscopy (TDS) allowed measurement of deuterium retention.

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Functional Thin Films and Surfaces
Room Town & Country D - Session MB2-1-WeM
Thin Films for Electronic Devices I

Moderators: Claudiu Falub, Evatec AG, Switzerland, **Julien Keraudy**, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, **Panos Patsalas**, Aristotle University of Thessaloniki, Greece, **Jörg Patscheider**, Evatec AG, Switzerland

8:00am **MB2-1-WeM-1 N-Doped Ba(Ti,Zr,Ta,Hf,Mo)O_3 Films Based Thin Film Transistors for UV Sensing***, **Van Dung Nguyen (dungk57v@gmail.com)**,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; K. Chang,* National Cheng Kung University (NCKU), Taiwan

In this research, N-doped Ba(Ti,Zr,Ta,Hf,Mo)O_3 dielectric films were integrated into ZnSnO-channel thin film transistor for a UV detector. The combinatorial sputtering was developed to fabricate the N-doped Ba(Ti,Zr,Ta,Hf,Mo)O_3 film. N-doped Ba(Ti,Zr,Ta,Hf,Mo)O_3 film exhibited a high dielectric constant (k ≈ 322), low leakage current density ($J_L \approx 10^{-11}$), and low dielectric loss of approximately 0.1, which is promising for gate dielectric layer in TFT applications. The resulting TFTs exhibited a high on/off current ratio of 10^8, high saturation mobility (μsat) of 196.36 $cm^2V^{-1}s^{-1}$, low threshold voltage (V_T) of 0.02 V, and low subthreshold swing of 0.072 $Vdec^{-1}$. Moreover, the devices exhibited stable performance with small V_T shifts and negligible changes in the maximum drain current under gate bias stress (GBS). Furthermore, the N-doped Ba(Ti,Zr,Ta,Hf,Mo) O_3-based phototransistor exhibited high sensitivity (S) up to 10^6 and high responsibility (R) of 1171.85 A/W.

8:20am **MB2-1-WeM-2 Electrical Properties Based on 2D GaSe Nanobelts on the Metal-Semiconductor-Metal Photodetector***, **Bo-Lin He (money332482587@gmail.com)**, C. Wang,* National Taiwan University of Science and Technology, Taiwan

Gallium Selenide (GaSe) nanobelts grows in the furnace through gold catalysis methods. Scanning electron microscopy (SEM) image can observe that on the top of GaSe nanobelts have an Au particle. It shows the growth mechanism is vapor liquid solid (VLS) on the substrate. Firstly, the X-ray diffraction pattern (XRD) shows that GaSe exhibits a hexagonal crystal structure, where gallium and selenium atoms are arranged in alternating layers, forming a layered structure. Secondly, the Raman spectrum shows the different vibration modes at different four peaks. Lastly, GaSe demonstrates a direct bandgap of approximately 2.12 eV, in the ultraviolet-visible (UV) analysis shows the direct bandgap of approximately 2.33 eV.

In this work, GaSe nanobelts device with Ni electrodes are used the rapid temperature annealing (RTA) to control it and the results of SEM, EDS and line scan show the Ni is diffusing into the GaSe nanobelt, thus, forming the NiGaSe/GaSe heterojunction structure, the electrical characteristic results also imply the structural transformation of nanobelt. The varied temperature measurement results that determined the value of Schottky barrier is ~ 0.2 eV and the band alignment structure also proves the contact type is Schottky barrier. The electrical measurement results prove that the electrical property is improving and the performance of photodetector exhibits different to the device without annealing. The electrical results of MOSFETs of GaSe nanobelts by increasing drain currents with higher minus gate voltage means the electron-holes are the mainly charge carriers in the GaSe nanobelts, the results also show the electron-holes are leading the drain currents and it indicates that the GaSe is a p-type semiconductor. The gm (Transconductance) which defined as the ratio of changing out-put current at changing in-put voltage is about 3×10^{-13} S, and the mobility reveals how easy of charge carriers flow into the semiconductor and the value is about 1.5×10^{-3} $cm^2/V{\cdot}S$.

Keywords: nanobelts, hexagonal, vapor liquid solid (VLS), direct bandgap, rapid temperature annealing (RTA), heterojunction structure, electrical characteristic, Schottky barrier, photodetector, MOSFETs

8:40am **MB2-1-WeM-3 Strain-Induced Self-Rolled-Up Thin Films for Extreme Miniaturization and Integration of Passive Electronic Components***, **Xiuling Li (xiuling.li@utexas.edu)**,* The University of Texas at Austin, USA **INVITED**

The fundamental physical principle underlying self-rolled-up membrane (S-RuM) nanotechnology is the strain-driven spontaneous deformation of 2D membranes into 3D architectures. S-RuM technology offers a unique solution for achieving 3D functional hierarchical architectures without the challenges associated with processing in three dimensions. Through strain engineering, it opens up new possibilities by facilitating the creation of practically unlimited complexity in L-C circuits, integrated photonics, and lab-on-a-chip integration of soft and hard materials. Importantly, these advancements are achieved through the utilization of well-established CMOS-compatible planar processing techniques.

In this talk, I will present examples of S-RuM based passive electronic components, including on-chip inductors, transformers, L-C networks.I will discuss how S-RuM technology can potentially to break the constraints of size, weight, and performance of RFICs and power electronics.

9:20am **MB2-1-WeM-5 Enhanced Synaptic Characteristics Under Applied Magnetic Field in V_2O_5/Ni-Mn-In Based Switching Device for Neuromorphic Computing***, **Kumar Kaushlendra (kumar_k@ph.iitr.ac.in)**, D. Kaur,* Indian Institute of Technology Roorkee, India

The present study reports a memory structure Al/V_2O_5/Ni-Mn-In on a flexible stainless-steel (SS) substrate for neuromorphic applications. The fabricated device exhibits gradual SET and RESET switching characteristics with an OFF/ON resistance ratio of ~100, good consistency of 4500, and excellent data retention capability up to 3000 s. The current-voltage (I-V) study supports an Ohmic conduction mechanism in the low resistance state (LRS). In contrast, the trap-controlled modified space charge conduction mechanism demonstrated the high resistance state (HRS). The resistance versus temperature measurement (R-T) in the LRS and HRS of the device signifies that oxygen vacancies form the conduction filament. We further analyze the synaptic functioning by applying identical consecutive voltage pulses, and the device's conductance change has been observed. These characteristics show a good representation of the biological memory synapse in terms of the artificial memory device. Long-term potentiation (LTP) and long-term depression (LTD) show nonlinear and asymmetry behavior, which is substantial for neuromorphic applications. A considerable shift in LTP and LTD was detected by applying external temperature and magnetic field. This is explained via temperature and magnetic field strain in the functional Ni-Mn-In bottom electrode of the fabricated device. The mechanical flexibility of the memory structure was tested by exploring the switching characteristics with various bending angles and bending cycles. Therefore, the present study offers new avenues for flexible devices with high data storage capability for futuristic neuromorphic applications.

9:40am **MB2-1-WeM-6 Electrolyte Gated Transistors for Neuromorphic Signal Processing and Biosensing***, **Luke Sylvander (luke.sylvander@rmit.edu.au)**, P. Le, C. Tan, H. Tran,* RMIT University, Australia*; D. McKenzie,* University of Sydney, Australia*; D. McCulloch, J. Partridge,* RMIT University, Australia

An Ar plasma immersion ion implantation (PIII) process has been employed to introduce free-radical covalent binding sites in spin-on polymer layers. These layers have been incorporated as dielectric layers into lateral electrolyte-gated transistors (EGTs) with characteristics resembling those of biological synapses. Specifically, if the gate electrode of the EGT is taken to be the pre-synapse and voltage pulses are applied, the resulting source-drain output mimics aspects of postsynaptic signals. Notably, this postsynaptic output is sensitive to the dynamics of the double layers (DLs) that are formed at the two polymer/electrolyte interfaces when the presynaptic voltage is applied. If biomolecules are covalently immobilised on the PIII-treated polymer dielectric layer, the dynamics of the DL formation/decay are altered, as are the postsynaptic signals. This provides a neuromorphic detection signal and enables the EGTs to be used as artificial sensory synapses. This talk will cover the PIII treatment of the polymer layers, device fabrication/characterisation and biosensing measurements from the EGTs.

11:20am **MB2-1-WeM-11 Tracking the Metal-Insulator Transition at $YTiO_3/LaTiO_3$ Interfaces Grown by the Soft Chemical Method***, **Alexandre Simoes (zirpoli.simoes@unesp.br)***, UNESP, Brazil

In the last couple of years, perovskites and transition metal oxides have demonstrated high potential for energy storage/processing applications. Materials usually used in random access memory devices, such as perovskites and transition metal oxides (TMO), have shown potential to be applied in the fabrication of other types of nonvolatile memories. Correlated electron random access memories (CeRAMs) were recently developed for exhibiting partially filled *3d* bands in addition to showing resistive switching as a result of strong electronic correlations. It is worth mentioning that the band structure of related electronic materials depends not only on the d-orbitals of the transition metals, but also on the p-orbitals of neighboring oxygen atoms. In this work, oxide interfaces with piezoelectric, magnetic and metal-insulator transition based on $YTiO_3/LaTiO_3$heterostructured films were investigated. The Mott insulator, $YTiO_3$, was deposited onto a Mott insulator, $LaTiO_3$,via polymeric precursor method. Spin coating was performed to obtain a $YTiO_3/LaTiO_3$ heterostructured thin films deposited onto $Pt/TiO_2/SiO_2/Si$ substrates. Structure, morphology, and electrical properties of the films were assessed. The $YTiO_3/LaTiO_3$heterostructures exhibit ferromagnetic and piezoelectric behavior ($d_{33máx}$≈8.11 pm/V), which may be attributed to smaller grain (average grain size≈20.00 nm) and, thus, a higher grain boundary density, and stress in the film plane due to the different properties of the interface. The dielectric permittivity and dielectric loss at 1 KHz were found to be 70 and 0.41, respectively. *I-V* measurements on different electrode areas confirmed a metal-to-insulator transition, indicating a potential application in correlated electron random access memory (CeRAM).

11:40am **MB2-1-WeM-12 Adsorbing Chiral Molecules on High Entropy Iron Vanadate ($FeVO_3$) for Biomolecule Detection and Photoelectrochemical Cell Applications***, **Amit Kumar Sharma (z11212022@ncku.edu.tw)**, Y. Su,* National Cheng Kung University (NCKU), Taiwan

Chiral-induced spin selectivity (CISS) is at the forefront of photoelectrochemical water splitting and energy storage applications. CISS addresses the inhibition of hydrogen peroxide production by polarizing the spin of the ˙OH radical, thereby reducing the overpotential required by the photocatalyst to achieve high current density. This is achieved by conjugating chiral molecules with photocatalysts via self-assembly to induce electron spin selectivity from the electrolyte. Concurrently, numerous investigations have demonstrated the manipulation of spin polarization in metal oxides to foster spin selectivity and charge separation. However, such modifications are largely governed by the coordination structure and valence states of the transition metal. Additionally, the conjugation of chiral molecules onto metal oxides encounters obstacles such as sensitivity to light exposure, high conductivity barrier, and inadequate active sites.

To address these challenges, we have fabricated high entropy iron vanadate metal oxide to serve a dual purpose as a biomolecular sensor and photoelectrochemical cell-based energy generator. High entropy oxides (HEO) have established their photocatalytic prowess in the UV regime of the light spectrum. To expand their applicability in visible light photocatalysis, HEOs should exhibit narrow bandgap, high electron-hole separation rate, low electron-hole recombination rate and an electronic band structure conducive to water splitting reaction.

In light of these studies, we investigate $FeVO_3$ nanosheets synthesized through solid-state reaction for enhanced near-infrared (NIR) absorption capability, magnetic property, and chromic response upon oxidation under prolonged exposure to visible light during photocatalysis. Furthermore, three enantiomers, viz. L- and D-arginine, L- and D-cysteine, L- and D-tryptophan, will be conjugated on the surface of the nanosheets to create a composite structure. The dual oxidation state of vanadium in $FeVO_3$, i.e. VO^{2+} and VO_2^{+}, assists in NIR absorption and provides interaction sites for chiral molecules through surface defects. The chemical adsorption and CISS for ˙OH radical will be assessed using circular dichroism (CD) and absorption spectroscopy. At the same time, the altered magnetic properties of the composite will be examined via magnetic force microscopy (MFM) and superconducting quantum interference device (SQUID). The selective binding affinity of the chiral amino acid towards the nanosheet will be assessed by optical and electrochemical measurements to differentiate between the L- and D- enantiomers. Appropriate composites will be selected rationally based on the visible to NIR absorption, reduced sensitivity to visible light, and photocurrent density in electrolytes.

Tribology and Mechanics of Coatings and Surfaces
Room Town & Country B - Session MC2-2-WeM

Mechanical Properties and Adhesion II

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, **Bo-Shiuan Li**, National Sun-Yat Sen University, Taiwan

8:00am **MC2-2-WeM-1 *In Situ* Micromechanical Characterization of Thin Films: Strain Rate, Size and Microstructure Related Experiments in the SEM***, **Szilvia Kalacska (szilvia.kalacska@cnrs.fr)***, CNRS LGF, Mines St. Etienne, France*; L. Petho,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; G. Kermouche,* Mines St. Etienne, France*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P. Ispanovity,* Eötvös Loránd University, Hungary **INVITED**

Creating multi-layered thin films with alternating dissimilar sublayers is proposing unusual (electric, thermal, optical, etc.) properties to be experimentally investigated. In such a system where grain size and texture can be controlled by the deposition/annealing process represents a unique opportunity to focus on some aspects of the deformation processes driven by the collective behaviour of dislocation. Our aim was to create a system with large enough grains (500-800 nm in diameter) and engineer flat grain boundaries to study plastic deformation modified by the presence of barriers.

A hybrid thin film deposition system (Swiss Cluster) was used to create the samples by combining atomic layer deposition (ALD) and physical vapour deposition (PVD) [1]. Sequential deposition of approx. 1 μm thick multilayers were separated by 10 nm thick Al_2O_3 interlayers. The initial 100-250 nm grain size was increased by extensive heat treatment (@800°C for 4h under Ar atmosphere, Fig. 1a). Such final specimen was quite challenging to create without porosities or major delamination from the substrate after heat treatment.

Afterwards, micropillars were fabricated using focused ion beam (FIB) milling close to the edge of the bulk sample (Fig.1b). These micropillars were then compressed at various strain rates (0.1-1000/s) using a nanodeformation setup (Alemnis AG). High (angular) resolution electron backscatter diffraction (HR-EBSD) was applied to study the geometrically necessary dislocation (GND) density distribution after low and high strain rate deformations. Sequential FIB-slicing [2] was applied to create 3D reconstructions of the deformed volumes.

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8:40am **MC2-2-WeM-3 Assessing Brittleness of Indium Tin Oxide Layers on Glass Substrates with Nanoindentation**, *Kurt Johanns (kurt.johanns@kla.com), S. Varma, J. Hay, B. Crawford,* KLA-Tencor, USA

Many of the materials used in manufacturing semiconductors are susceptible to cracking, i.e., exhibit brittle failure during processing and in application.While the definition of brittle is well understood, assigning a “brittleness” value to a given material or system of materials is not easy as “brittleness” is not a material property.Here, we define a simple set of nanoindentation experiments in an effort to assess the brittleness of Indium Tin Oxide (ITO) layers and provide feedback to semiconductor manufacturers looking to mitigate latent defects that may initiate and propagate during processing. Multiple ITO film thicknesses in different residual stress states of ITO are tested. Results show that indentation testing is capable of assessing the brittleness of ITO on glass when experimental and material system artifacts are taken into account. Multiple examples of nanoindentation and nanoscratch testing are provided with a focus on advantages and improved sensitivity over related techniques.

9:00am **MC2-2-WeM-4 The Effect of Nitrogen Flow Rate and Deposition Power on the Mechanical Properties and Microstructure of TiN Thin Film Deposited by HCD-IP Method**, *Ching-Cheng Chen (moricechen@gmail.com), K. Lan,* National Tsing Hua University, Taiwan

Due to the high strength-to-weight ratio, aluminum alloys are widely used in various industries. However, relatively low surface hardness limits the development of aluminum alloys. Various coatings deposited by PVD method have been proposed to enhance the surface hardness and corrosion resistance. Due to the excellent hardness, TiN coating is commonly used as a protective film. In addition, its dense structure effectively inhibits the corrosion of metal substrate. It was reported that substrate bias significantly affects the ZrN film structure deposited on AISI stainless steel 304, resulting in improved corrosion resistance [1]. Elevated deposition temperature helps the growth of ZrN thin film with a high quality. However, aluminum alloys might loss its hardness after high temperature depositions, and there are few articles discussing the effect of bias on the mechanical properties and corrosion resistance of TiN thin film when depositing under low-temperature by hallow cathode deposition ion-plating method (HCD-IP) on an aluminum alloy substrate.

Therefore, the purpose of this study was to investigate the effect of substrate bias on the mechanical and corrosion properties of TiN thin films coating on the aluminum alloy 6061. The TiN thin films were deposited by HCD-IP system under low temperature (<200℃). After deposition, the structure and texture of TiN thin films were confirmed by scanning electron microscope (SEM) and X-ray diffraction (XRD). Scratch test and nanoindentation were carried out to measure the adhesion strength and surface hardness. Salt spray test and polarization curve were used to evaluate the corrosion resistance of the TiN coated samples.

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9:20am **MC2-2-WeM-5 Effect of Metal Interlayers on Stress Relief of Mo_2N/Mo and Mo_2N/Ti Bilayer Coatings on Si Substrate by High Power Impulse Magnetron Sputtering**, *Yun-Yang Sun (yysunk@gapp.nthu.edu.tw), J. Huang,* National Tsing Hua University, Taiwan

The purpose of this study is to investigate the effect of different metal interlayers and interlayer thickness on the relief of residual stress in g-Mo_2N/metal bilayer coatings. Previous studies [1,2] have indicated that the metal interlayers such as Ti and Zr in transitional metal nitride/metal bilayer systems can significantly relieve stress, where the interlayer with a sufficient thickness can act as a buffer layer and relieve stress through plastic deformation, and the interlayer is usually under tensile stress state. However, when the thickness of interlayer is insufficient, the metal interlayer will act as a transitional layer to transfer the stress to the substrate. Mo is one of the metals that is commonly used in metal interlayer. However, from our previous study [1], the plastic properties of the metal interlayer, such as strength coefficient and strain hardening coefficient, may strongly affect the behavior of plastic deformation and change the capability of stress relief. Therefore, this study aimed to investigate the elastic and plastic properties of Mo and Ti interlayers on stress relief of Mo_2N coating on Si substrate. Mo_2N coatings were deposited on Si substrate by high power impulse magnetron sputtering (HiPIMS). The thickness of the coatings was controlled at about 1000 nm and Ti and Mo interlayers were set at 100, 150, 200, and 250 nm deposited by dc-UBMS. After deposition, the Mo/(Mo+N) ratio was determined by electron probe microanalysis, and the thickness of specimens was measured by the cross-sectional images from scanning electron microscopy and confirmed by the compositional depth profiles using Auger electron spectroscopy. X-ray diffraction were used to characterize the crystal structure and texture. The residual stress was measured by laser curvature measurement and average X-ray strain methods. Hardness and elastic constant were assessed by nanoindentation, and the atomic force microscopy was used to measure the surface roughness.

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9:40am **MC2-2-WeM-6 Microstructure and Mechanical Behavior of Magnetron Co-Sputtering Mo-Ta-N Coatings**, *JIA-YI HSU (u0978750703@gmail.com), F. Wu,* Department of Materials Science and Engineering, National United University, Miaoli , Taiwan

The binary refractory metal nitride, Mo-Ta-N, coatings were fabricated and characterized in this study. The relationship between its microstructure and mechanical properties of the magnetron sputtering Mo-Ta-N coatings were investigated. The coatings were deposited using radio frequency reactive magnetron co-sputtering technique with input power control. The Mo-Ta-N thin films were prepared under a fixed inlet gas Ar/N_2 ratio and input power of 12/8 sccm/sccm and 150 W on Mo, respectively. The input power of Ta was tuned from 50 to 150 W to adjust the microstructure and composition. The addition amount of Ta and the deposition rate increased monotonically from 3.7 to 16.8 at.% and from 5.4 to 6.7 nm/min, respectively, as a function of Ta input power, while the (Mo+Ta)/N ratio kept a steady value around 1.0. The Mo-N film showed well-defined Mo_2N (111) and (200) facets with minor MoN (111) and (220) reflections. The Mo-Ta-N coatings exhibited a polycrystalline microstructure with MoN(111), Mo_2N(111), Mo_2N(200), TaN(111), TaN(200) and TaN(220) multiple phases and showed the nano-crystalline structure according to the broadened diffraction peaks. A maximum hardness of 18 GPa was found for the Mo-Ta-N coating deposited at an input power of 150/100 W/W. A sufficient adhesion was revealed and a better wear resistance was realized for Mo-Ta-N coatings with 6.8 and 10.4 at.% Ta and nanocrystalline multiple phase feature.

Keywords: refractory metal nitride, Mo-Ta-N, co-sputtering, multiple phase, nanocrystalline.

11:00am **MC2-2-WeM-10 Function of Mo Metal Interlayer in γ-Mo_2N/Mo Bilayer Coatings on D2 Steel Deposited by High Power Pulsed Magnetron Sputtering**, *Y. Fang, Jia-Hong Huang (jhhuang@mx.nthu.edu.tw),* National Tsing Hua University, Taiwan

The purpose of this study was to investigate the function of Mo metal interlayer in the γ-Mo_2N/Mo bilayer coatings deposited by high power pulsed magnetron sputtering (HPPMS) on D2 steel substrate. The interlayer thickness was designed from 50 to 150 nm, and the thickness of γ-Mo_2N was controlled at 1000 nm. The results indicated no significant change in chemical compositions, microstructure, and mechanical properties of the Mo_2N coatings by adding a Mo interlayer. The residual stress of the bilayer coatings was measured by two methods. Laser curvature method was applied to measure the overall stress of the bilayer samples on Si substrate. The stress in individual layers was measured by the average X-ray strain method. For samples on Si substrate, the compressive stress in Mo interlayer was higher than that of the Mo_2N coating, which was also much higher than the yield strength of Mo ($σ_{y,Mo}$). This is quite different from the expected function that the interlayer can relieve stress by plastic deformation. The stress measurements on samples on D2 steel substrate showed that the Mo interlayer is under a very high compressive stress (> 6$σ_{y,Mo}$), indicating that the interlayer cannot relieve stress by plastic deformation. Instead, the interlayer serves as a transitional layer that transfers the stress in Mo_2N to D2 steel substrate, where the D2 steel near the interface relieve the stress by plastic deformation, and the extent of stress relief is related to the interlayer thickness. The high strength coefficient and strain hardening exponent may be the reason that Mo cannot serve as a buffer layer but become a transitional layer. All samples show quite low wear rate, where the formation of the self-lubricating Magnéli oxides may be the major factor. Although the Mo interlayer can increase the adhesion strength of Mo_2N coating on D2 steel substrate, it is not necessary to add a Mo interlayer because the adhesion strength of Mo_2N on D2 steel substrate is sufficient for the wear test. Moreover, adding a Mo interlayer withinadequate thickness (50 nm) may not be beneficial to the stress relief of the Mo_2N coatings.

11:20am **MC2-2-WeM-11 Micro-Arc Oxidation of Commercially Pure Titanium Subjected to Hydrostatic Extrusion***, Lukasz Maj (l.maj@imim.pl),*
Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Poland*; F. Muhaffel,* Istanbul Technical University, Turkey*; A. Jarzebska, A. Trelka, D. Wojtas, K. Trembecka,* Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Poland*; J. Kawalko,* AGH University of Science and Technology, Poland*; M. Kulczyk,* Unipress Extrusion, Poland*; M. Bieda,* Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Poland*; H. Cimenoglu,* Istanbul Technical University, Turkey

Micro-arc oxidation (MAO) proved itself as very efficient method of the surface modification of so-called “valve metals” like titanium, aimed at improving their properties like wear resistance, bioactivity, antibacterial performance, etc. Enhancement of above-mentioned properties is connected with formation of well adhering oxide coating on the top of the substrate material thanks to the electrochemical reactions driven by the ions exchange between the substrate and electrolyte. Thus, not only the selection of proper electrolyte and MAO process conditions is important, but also microstructure of the substrate material. The plastic deformation of the substrate material may also affect the mechanisms of the oxide formation.Grain refinement and formation of higher density of low angle (LAGB) and high angle grain boundaries (HAGB) allows many more sites for the oxides nucleation to be formed what accelerates the coating formation. Application of severe plastic deformation techniques such as hydrostatic extrusion provided amazing results in terms of strengthening of metallic materials such as titanium, allowing for its widespread application, especially as future dental implants. Owing to the hydrostatic extrusion characteristics microstructure refinement down to the nanometric scale may be achieved, increasing strongly the density of LAGB and HAGBs, also having a huge impact on eventual surface modification with the methods like MAO.However, there is a lack of information about microstructure and tribological properties of the MAO coatings deposited on the surface of hydrostatically extruded titanium. In this work, titanium grade 4 substrates was subjected to 3-pass hydrostatic extrusion and subsequent rotary swaging reducing the initial diameter from 50 mm down to 5 mm.The rods were cut into diameter and subjected to MAO process in phosphate-based electrolyte with the help of the bipolar pulsed power supply.Such power supply allows for far better control of the electrochemical reactions during the deposition process than direct current or unipolar pulsed ones.Before the MAO coatings deposition, the cp-Ti substrates were thoroughly investigated in terms of determination of the HAGB and LAGB density with the SEM/EBSD method in order to determine their influence on the properties of the forming oxide surface layer. The microstructure observations (SEM/TEM) supported by phase and chemical analysis (XRD, SAED, EDS) allowed us discuss the mechanisms of oxide coating formation and correspond to their tribological behavior.

Acknowledgement: This research was funded by the National Science Centre of Poland, grant number UMO-2020/39/D/ST8/01783.

11:40am **MC2-2-WeM-12 Effect of Ultrasonic-Assisted Machining for Surface Functionalization of Innovative Work-Hardening Multi-Principal-Element Alloys***, **Marcel Giese (marcel.giese@bam.de)**, D. Schroepfer, M. Rhode,*
Bundesanstalt für Materialforschung und -prüfung, Germany*; B. Preuss, T. Lindner, N. Hanisch, T. Lampke,* Institute of Materials Science and Engineering (IWW), Chemnitz University of Technology, Germany

Multi-principal-element alloys (MPEAs) are an alloying concept consisting of at least two main alloying elements resulting in unique microstructures and potentially superior physical, mechanical and chemical properties, for instance a high work hardening capacity. These characteristics are determined by four core effects: sluggish diffusion, severe lattice distortion, high-entropy and cocktail effect. The development of MPEAs is a promising approach to extend the range of applications of conventional alloys by exploiting these core effects. In the present study, as reference to the conventional high-manganese steel X120Mn12 (ASTM A128), characterized by particularly high work hardening capacity generating exceptional mechanical properties, work-hardening MPEAs based on the equimolar composition CoFeNi in combination with Mn and C were developed. Specimens were produced as bulk material by melting via an electric arc furnace. In a second step the specimens undergo a surface finishing via milling process. Therefore, a hybrid milling process was used which, in addition to producing defined surfaces, also has the potential to reduce tool wear and increase surface integrity by introducing compressive stresses and increasing hardness through pronounced work hardening in comparison to conventional machining. The so-called ultrasonic-assisted milling (USAM) is characterized by an axial oscillation of the tool during the milling process. The machining parameters were varied to analyze the effect on work hardening together with process forces during milling and resulting surface integrity. Subsequently, microstructure evolution, hardness as well as resulting wear resisting capacity were investigated and correlated with the composition and the USAM parameters. For the MPEA CoFeNi-Mn12C1.2 a pronounced lattice strain and grain refinement due to the plastic deformation during the USAM was recorded, especially at high USAM amplitude and lower cutting speed due to the greater number of tool oscillations per cutting engagement. Consequently, a hardness increase of up to 380 HV0.025 was induced for the aforementioned MPEA exhibiting a higher wear resistance compared to the X120Mn12. This shows the promising approach for the development of work-hardening materials based on new alloy concepts such as MPEAs allowing also coatings required for applications in tribological systems. As conventional hard and wear-resistant coatings are challenging in machining due to massive tool wear this approach of functional coating materials with high hardening capacity during USAM have the potential to reduce tool wear and ensure a adequate surface integrity and wear resistance.

12:00pm **MC2-2-WeM-13 Metal/Oxide Nanolaminates of Al/Al2O3 by PVD-ALD: Understanding & Maximising Strength-Ductility***, **Thomas Edwards (thomas.edwards@empa.ch)**,*
NIMS (National Institute for Materials Science), Japan*; B. Putz, T. Xie, L. Vogl, H. Jansen, A. Groetsch, M. Watroba, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

The extent of the embrittlement in ductile-brittle multilayers often depends on the modulation period ($t_{brittle}$ + $t_{ductile}$) as well as on the modulation ratio ($t_{brittle}$/$t_{ductile}$) [1]. In this work, ductile-brittle multilayers of Al / Al_2O_3 / Al... were produced on Si substrates by a unique combination of atomic layer (ALD, Al_2O_3) and physical vapour deposition (PVD, Al) within a single deposition system. Using this ALD/PVD combination, neighbouring layer thicknesses can easily differ by one order of magnitude or more. In particular, the ability to deposit continuous sub-nm layers with ALD opens up a wide range of otherwise unachievable modulation and thickness ratios. The thicknesses and structures of the ALD layers were verified by HR-TEM imaging of lift-outs. The amorphous oxide layer thickness was previously optimised in the 0.1 nm – 10 nm range by microcompression, considering crack onset and propagation as a function of oxide layer thickness in tensile tested multilayer films. Here, the crystalline metal layer thickness is varied (10 nm – 250 nm) to optimise strength. The multilayer structure has good adhesion between individual layers and the oxide layers show increasing stretchability with decreasing film thickness. *In situ* TEM tensile loading was performed to evaluate the role of the amorphous-crystalline interfaces on dislocation motion in metallic layers, whilst microcompression at variable temperature and strain rate was used to quantify the activation parameters; this is compared with molecular dynamics simulations. The thermal stability of such multilayer films was also studied up to 0.9 T/T_m.

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Plasma and Vapor Deposition Processes
Room Palm 3-4 - Session PP3-WeM

CVD Coating Technologies

Moderators: Hiroki Kondo, Kyushu University, Japan, **Frederic Mercier**, University of Grenoble Alpes, France

8:00am **PP3-WeM-1 Area-Selective Deposition of DLC Using Optoelectronic-Controlled Plasma CVD Method***, **Susumu Takabayashi (stak@ariake-nct.ac.jp)**,*
National Institue of Technology, Ariake College, Japan **INVITED**

Diamond-like carbon (DLC) is an amorphous carbonaceous material composed of sp^2 carbon, sp^3 carbon and hydrogen. We propose a controlled DLC film synthesis by photoemission-assisted plasma-enhanced chemical vapor deposition (PA-PECVD). PA-PECVD is a DC discharge plasma with the aid of photoelectrons from the substrate on which a deep UV light irradiates. The current flows only in the UV-irradiated area and the starting voltage of the glow discharge, called photoemission-asssietd glow discharge (PAGD), becomes stable owing to plenty of photoelectrons as initial electrons. The discharge before starting PAGD occurs is photoemission-assisted Townsend discharge (PATD). The current in PATD is around 10,000 time larger than that in conventional Townsend discharge. The substrate is not subject to the sheath electric field, so minute and precise synthesis with a rate of nm/min. is realized in PATD. With PATD, we actually succeeded to fabricate a graphene field effect transistor (GFET) with a DLC top-gate dielectric and synthesize oxygen and nitrogen-doped DLC films on the order of nm thickness. With PA-PECVD, we are developing and exploring application of DLC in nano-electronics and science.

8:40am **PP3-WeM-3 Advanced and Economical Hot-Filament CVD Diamond Coating Technology for Deposition of High-Performance Diamond Coatings on Tungsten Carbide Tools***, Frank-R. Weber (frw@webertechnologies.de),* Weber Technologies GmbH, Germany

Diamond coating systems at Weber Technologies utilize a unique activation mechanism in hot-wire CVD diamond coating technology for the deposition of high-performance diamond coatings. The area of application of this coating technology ranges from wear protection to electronic and medical applications as well as semiconductor technology. High growth rates with low energy consumption have increased the cost-effectiveness of the diamond coating process. The crystallite size and the coating morphology of the diamond layers can be specifically adapted by varying the process parameters. This enables the deposition of 10 to 20 nm ultra-nanocrystalline monolayers as well as microcrystalline layers with crystallite sizes between 1 to 10 µm. Due to our innovative CVD diamond coating process for deposition of high-performance diamond coatings, we can adjust optimal coating structure and scalable crystallite sizes in relation to the respective machining application, e.g., specific application-optimized gradient diamond coatings. The ultra-nanocrystalline diamond coatings are dense and tight from layer thicknesses of 1 to 2 µm. Diamond coating solutions with outstanding coating performance have been optimized for the respective machining application in various materials (CFRP, CFC, graphite, ZrO2 ceramics and Al alloys). Various examples of increased performance when machining with diamond-coated tools in different materials will be presented.

9:00am **PP3-WeM-4 Microstructure and Mechanical Properties of TiZrN and TiZrCN Coatings Grown by Chemical Vapor Deposition***, Akihiro Murakami (amurakam@mmc.co.jp), M. Okude,* Mitsubishi Materials Corporation, Japan

Chemical Vapor Deposition (CVD) method has been used for the industrial production of wear resistant coatings on cutting tools and TiCN coatingshave been widely used for several decades because of its excellent hardness, good thermal and chemical stability. New CVD coatings that is superior to TiCN are continuously explored, and it is reported that ZrN and ZrCN has advantageous properties as wear resistant coatings. However, there are few reports on TiZrN and TiZrCN coatings.

In this work, TiZrN coatings were deposited from $TiCl_4$-$ZrCl_4$-N_2-H_2 precursors at 1050°C (HT-TiZrN). And TiZrCN coatings were produced from two precursor systems: TiCl-$_{-4}$-$ZrCl_4$-N_2-CH_4-H_2 precursors at 1050°C (HT-TiZrCN) and $TiCl_4$-$ZrCl_4$-CH_3CN-N_2-H_2 precursors at 900°C (MT-TiZrCN). All coatings were deposited on TiCN coated cemented carbide.

We investigated microstructure, crystal orientation and hardness. HT-TiZrN has granular structure and lower hardness than conventional TiCN. HT-TiZrCN has columnar-like-structure, and its hardness is close to conventional TiCN. On the other hand, MT-TiZrCN has columnar structure, (211) crystal orientation and higher hardness than TiCN. In addition, Electron Back Scattered Diffraction (EBSD) analysis revealed partial epitaxial growth of TiZrCN on TiCN.

These coatings were evaluated by turning tests of alloy steel (AISI:4140). As a result, cutting performance of MT-TiZrCN coatings was superior to conventional TiCN. It seems that higher hardness of MT-TiZrCN enhances the cutting performance.

11:00am **PP3-WeM-10 New Perspectives of Atmospheric Pressure Dielectric Barrier Discharges for the Deposition of Thin Films : From Uncontrolled Amorphous Plasma-Polymer Layers to Chemically Patterned and Crystalline (in)Organic Coatings***, François Reniers (freniers@ulb.ac.be),* Université libre de Bruxelles, Belgium **INVITED**

For more than a century, atmospheric pressure dielectric barrier discharges (DBDs) have been used industrially for gas conversion, the Siemens ozone process dates from 1857 [1], and for surface treatment. Deposition of coatings remained confidential, due to the poor control of the quality of the films. Indeed, the very small mean free path at atmospheric pressure leads to species with very low energies, and random processes due to moving filaments often occur.

We show that, nowadays, starting with organic precursors, DBD can lead to chemically well controlled and tunable thin films, with a variety of properties (hydrophobic/hydrophilic). We establish correlations between the gas phase chemistry (analyzed by mass spectrometry) and the coating chemistry (characterized by XPS and IR spectrometry)[2]. The effect of the nature of the carrier gas (Ar or He) on the roughness and chemistry of the deposited coating is evidenced and explained[3]. With the improvement of the understanding of the plasma chemistry, amorphous inorganic coatings (SiOx, TiO_2) can now be easily deposited. By controlling the substrate temperature and the plasma parameters, pure and dense crystalline TiO_2 can now be deposited by APDBDs [4]. By modifying the gas composition, introducing ammonia into the plasma, N-doped TiO2, photocatalytic (and antiviral) under visible light can now be synthesized in one single step [[].

Very recently, one could immobilize streamers in a DBD and use them to deposit, in one simple step, locally chemically patterned organic films. The local chemistry (analyzed by µXPS) is depending on the gap between the electrodes, the power impulsion mode (continuous vs pulsed), the precursor flow. A physico-chemical interpretation is proposed [6,7].

Finally, injecting a precursor for inorganic coating in such discharges with immobilized filaments, in appropriate substrate and plasma streamer conditions, crystalline spots, with multi-micron length crystal needles were for the first time synthesized.

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11:40am **PP3-WeM-12 Novel Metal Boride Coatings in the System Zr-Hf-Ti-B by LPCVD***, Mandy Höhn (mandy.hoehn@ikts.fraunhofer.de), M. Krug, S. Höhn, B. Matthey,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

The synthesis of metal diboride thin films is recently attracting large interest. Boron forms binary compounds with most metals. These materials in general are high-melting, extremely hard solids with high degrees of thermal stability and chemical inertness.

In this work the preparation of mixed metal boride coatings with Me = Zr, Hf, Ti by chemical vapor deposition (CVD) is described. A low-pressure CVD (LPCVD) process using the metal tetrachlorides $MeCl_4$ (Me = Zr, Hf or/and Ti) as precursors as well as BCl_3, H_2 and Ar is applied. At a deposition temperature of 850°C and a deposition pressure of 6 kPa boride layers were prepared. The coatings were characterized with respect to phase composition, crystal structure, hardness and wear behaviour.

Layers were deposited in the binary systems $HfTiB_2$, $ZrTiB_2$ and $HfZrB_2$ as well as in the ternary system $HfZrTiB_2$. The deposited diboride layers show crystalline structures with a high hardness of up to 38 GPa. Depending on the precursor ratio layers with single phase diboride composition or a mixture of different metal diborides were obtained. Phase composition and structure were examined using SEM, EDX and EBSD-analysis. The measured tensile stress in the obtained coatings depends on the deposition conditions and varies between 300 MPa and 800 MPa.

A strong adherence on hardmetal inserts is achieved by using a thin TiN bonding layer prior the diboride deposition. Scratch test measurements showed critical loads of about 90 N. In cutting tests a high performance of the CVD diboride coatings was observed. $HfZrTiB_2$ coated inserts showed a higher lifetime in comparison with state-of-the-art CVD-TiB_2 coatings in face-milling of TiAl6V4.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP4-1-WeM

Deposition Technologies for Carbon-based Coatings I

Moderators: Ivan Kolev, IHI Hauzer Techno Coating B.V., Netherlands, **Biplab Paul**, PLATIT AG, Switzerland

8:00am **PP4-1-WeM-1 Molecular Dynamics Study of Interfacial Phenomena in Diamond-Like Carbon Films***, Kwang-Ryeol Lee (krlee@kist.re.kr),* Korea Institute of Science and Technology (KIST), Republic of Korea*; X. Li,* Chinese University of Mining and Technology, China **INVITED**

Due to the experimental limitations in precisely characterizing the complicated evolution of a-C film deposition and their physical and chemical properties, molecular dynamics simulation has been widely employed for atomistic understanding of the structural evolution and investigating structure-property relationship. Especially, much attention has been drawn to reactive molecular dynamics simulation technology that can include the chemical reaction during the atomic scale structure evolution. We compared various reactive force field (ReaxFF) models in terms of the structural properties of the simulated a-C films prepared by atom-by-atom deposition approach. By linking the structural properties of the film with the difference in the parameter sets of the ReaxFF models, we reveal that the carbon triple bond stabilization energy in the ReaxFF model, v_{trip}, significantly affects the growth dynamics and structural evolution of the simulate a-C films. Tribological behavior of amorphous carbon surface was extensively investigated in atomic or molecular scale by the reactive molecular dynamics simulation. Simulational study of friction in hydrogenated surface of a-C revealed that hydrogenating the a-C surface only improved the friction property drastically while not deteriorating the intrinsic properties of a-C films. The analysis of interfacial structure demonstrated that being different with a-C:H cases, the competitive relationship between the stress state of H atoms and interfacial passivation caused by H and C-C structural transformation accounted for the evolution of friction coefficient with surface H content. This disclosed the friction mechanism of a-C with surface hydrogenated modification and provides an approach to functionalize the carbon-based films with combined tribological and mechanical properties for specific applications. The reactive molecular dynamics simulation resulted in fundamental understanding of low-friction mechanism. We comparatively investigated the friction property and structural information of contacting interface under different passivated or graphitized states. For the passivation mechanism, the low friction behavior attributes to the reduction of both the real contact area and shearing strength of graphitized sliding interface due to the passivation of a-C dangling bonds. However, the graphitization mechanism strongly depends on the size and layer number of graphitized structure, causing the transition of sliding interface from a-C/a-C, a-C/G to G/G, which is followed by the low-friction mechanism evolved from passivation synergistic effect between graphitization and passivation to graphitization mechanism.

8:40am **PP4-1-WeM-3 Study of ta-C Thick Film Deposition Using FCVA-Based Hybrid Coating System***, Jongkuk Kim (kjongk@kims.re.kr), J. Kim, J. Jang, Y. Jang,* Korea Institute of Materials Science, Republic of Korea

Tetrahedral amorphous carbon (ta-C) coating film has a high sp^3 content and excellent wear resistance and heat resistance even without hydrogen, so it is used in various industrial fields such as cutting tools, automobiles and molds.

In the vacuum arc process using a carbon target, coating is difficult for a long time due to the unstable movement of the arc spot inside the carbon target, resulting in poor thickness and an enlarged coating area. In addition, the Ta-C coating film deposited by this method has high internal stress, making it difficult to increase its thickness.

We controlled the electric and magnetic fields to stabilize the arc spot movement of the carbon cathode for a long period of time, allowing the carbon arc target to be used stably for up to 24 hours at a discharge current of 160 A.

The designed hybrid coating system consists of 1) anode-layer ion source (ALIS) for the etching processes, 2) an unbalanced magnetron sputter (UBM) for the interlayer deposition, 3) a filtered cathodic vacuum arc (FCVA) source for the ta-C film deposition, and 4) pulsed bias power. To apply the designed hybrid coating process, a system consisting of a single ALIS, two UBMs, and eight FCVAs with a maximum deposition area of 900 mm in diameter and 500 mm in height was built to deposit a 7 µm coating film on a piston ring used in an automobile engine.

We have also built a smaller machine with similar capabilities that can deposit rainbow coatings (up to 0.7 um) and black coatings (0.7-3 um) on non-ferrous cutting tools for a variety of applications, depending on their thickness.

9:00am **PP4-1-WeM-4 Diamond-Like Films of Tetrahedral Amorphous Carbon Deposited by Anodic Arc Evaporation of Graphite***, Bert Scheffel (bert.scheffel@fep.fraunhofer.de), O. Zywitzki,* Fraunhofer FEP, Germany

A physical vapor deposition process using anodic arc evaporation in combination with a hollow cathode arc discharge was applied to the evaporation of graphite for deposition of hydrogen-free carbon layers. The diamond-like carbon (DLC) films deposited on 100Cr6 steel substrates were investigated by nanoindentation, Raman spectrometry, FE-SEM, AFM and spectroscopic ellipsometry. The relationships between the process parameters and the coating properties are discussed. Coatings deposited without bias voltage at substrate temperatures < 200°C are very hard (61-75 GPa) with also very high Young's modulus (588-685 GPa). The evaluation of the Raman spectra indicated a high proportion of tetrahedral sp3 bonds in the range of 70-88 %. The coatings proved to be completely droplet-free and have a very low surface roughness as confirmed by FE-SEM and AFM. The deposition rates in the range of 4-18 nm/s are exceptionally high for such ta-C coatings, which is a good prerequisite for industrial applications.

9:20am **PP4-1-WeM-5 Constitution and Properties of TiC1-x:H/a-C:H Nanocomposite Thin Films Prepared by HiPIMS Processes at Low and Elevated Temperature***, Sven Ulrich (sven.ulrich@kit.edu), C. Poltorak,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; H. Sternschulte, J. Grau,* Technical University of Applied Sciences Augsburg, Germany*; J. Julin, T. Sajavaara,* RADIATE, University of Jyväskylä, Finland*; A. Bergmaier,* University of the Bundeswehr Munich, Germany*; K. Seemann, M. Dürrschnabel, M. Stüber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Carbon-based nanocomposites with tunable multifunctional properties are suitable candidates for diverse fields of applications like tribology or biological, medical and energy technologies. Reactive HiPIMS is selected as a coating process with a Ti-target, an average target power of 5 kW, 50 µs pulse length, 550 µs cycle duration, working gas pressure of 0.3 Pa, 300 sccm Ar working gas flow and up to 40 sccm CH_4 reactive gas flow as well as 200°C and 400°C substrate temperatures. HiPIMS show a high ion fraction of the film-forming particles and the deposited energy by ion bombardment during film growth can be adjusted precisely. The constitution and microstructure war determined by a combination of several analytical techniques: EPMA, ERDA, Raman spectroscopy, XRD, TEM and HRTEM. It is shown that by varying the methane reactive gas flow, the following structures can be adjusted: Ti, TiC_{1-x}:H and TiC:H single layer coatings as well as TiC:H/a-C:H nanocomposites. A clear correlation is identified between the constitution and microstructure with the mechanical properties.

9:40am **PP4-1-WeM-6 Effect of Deposition Temperature and Nitrogen Concentration on Highly Conductive a-C:H:N Films Obtained by Means of DC PACVD***, Manuel Schachinger (manuel.schachinger@fh-wels.at),* University of Applied Sciences Upper Austria*; F. Delfin,* University of Applied Sciences Upper Austria, Argentina*; C. Forsich, D. Heim,* University of Applied Sciences Upper Austria*; B. Rübig, T. Müller, C. Dipolt,* Rubig GmbH & Co KG, Austria

a-C:H films are known for their distinct properties such as excellent wear resistance, chemical inertness and a low coefficient of friction. However, these films are typically highly electrically insulating materials. In view of the constantly increasing demands on technical components, it is critical to further expand the areas of application of a-C:H coatings by combining their desired and well-established material properties with low electrical resistivity. One way to decrease the specific electrical resistance of DLC films substantially is via the utilization of high-temperature DC PACVD. For further optimization of the electrical properties, nitrogen doping may be applied. In this work, a-C:H:N films were deposited at 450°C and 550 °C via DC PACVD on steel and titanium substrates, employing C_2H_2 and an additional N_2 flow. This resulted in an N_2 concentration of 0-63 vol. -% in the gas mixture. Subsequently, film characterization was carried out via nanoindentation, density measurement, calotest, the van der Pauw method, GDOES and Raman spectroscopy. Nanoindentation showed that hardness was increased at higher deposition temperatures and continued to increase with nitrogen gas concentrations up to a certain point. Thereafter, at trend inversion was observed. Density was higher for 550°C deposition compared to the 450°C process and increased for both temperatures with higher N_2 gas concentrations up to 31 vol. -%. Thereafter, a trend reversal was observed, pointing towards an increased fraction of terminating structures such as C-H or CN triple bonds and a lower fraction of C-C sp^3 bonding in the material. Coating thickness decreased from 40 µm to 14 µm at 450°C and from 32 µm to 12 µm at 550°C with increasing nitrogen flow following an exponential function. Specific resistivity reached an average minimum of 1688 µΩ cm at 31 vol. -% N_2 for 550°C, which approximates the conductivity of compressed graphite powders. In addition, it decreased by several decades at 450°C, reaching an average minimum of 45 000 µΩ cm. GDOES analysis showed that nitrogen concentrations in the films were markedly low ranging from 0,08 to 1,3 at. -% on average. Raman analysis indicates that nitrogen incorporation induces disordering effects in the film structure, combined with a rise in the number and size of aromatic clusters. In summary, the addition of nitrogen as a process gas successfully enhanced the properties of the film, resulting in materials that exhibited higher hardness than martensitic steels with an electrical resistivity equivalent to that of compressed graphite powders.

Protective and High-temperature Coatings
Room Town & Country C - Session MA4-2-WeA

High Entropy and Other Multi-principal-element Materials II

Moderators: Erik Lewin, Uppsala University, Sweden, **Jean-François Pierson**, IJL - Université de Lorraine, France

2:00pm **MA4-2-WeA-1 Effect of Bilayer Periodic Thickness Ratios on the Mechanical Properties and Corrosion Resistance of TiZrNbTaFeN/TiN High Entropy Alloy Nitride Multilayer Thin Films***, **Sheng-Yuan Hung (jjj881029253@gmail.com)**,* Ming Chi University of Technology, New Taipei, Taiwan*; B. Lou,* Chang Gung University, Taoyuan, Taiwan*; J. Lee,* Ming Chi University of Technology, New Taipei, Taiwan

Due to the excellent mechanical and physical properties of high entropy alloy thin films, they have attracted extensive attention and research from the global industry, academia, and research institutions in recent years. In this study, an equimolar TiZrNbTaFe high entropy alloy target and Ti target were used to deposit TiZrNbTaFeN/TiN multilayer films on AISI304 stainless steel, AISI420 stainless steel, and silicon wafers substrates by a high power impulse magnetron sputtering (HiPIMS) system. The bilayer period thickness ratios of TiZrNbTaFeN and TiN layers were adjusted from 1:1 to 1:2 and 2:1. The cross-sectional morphology of each thin film was observed with a field emission scanning electron microscope. The crystal structure of the multilayered film was analyzed with an X-ray diffractometry. A nanoindenter, scratch tester, and pin-on-disk wear tester were used to measure the hardness, elastic modulus, adhesion, and wear resistance. The corrosion resistance of multilayered thin films in 0.1 M sulfuric acid aqueous solution was tested by the electrochemical workstation. Effect of bilayer periodic thickness ratios on the microstructure, mechanical properties, and corrosion resistance of TiZrNbTaFeN/TiN multilayer films will be explored

2:20pm **MA4-2-WeA-2 Enhanced Mechanical Properties of Nitrogen-Supersaturated High-Entropy Alloys via Phase Manipulation***, **Yujie Chen (yujie.chen@adelaide.edu.au)**,* University of Adelaide, Australia

N-supersaturated $Fe_{50}Mn_{30}Co_{10}Cr_{10}$ high-entropy alloys (HEAs) were prepared via magnetron sputtering at various N_2 flow rates (R_N) of 4, 8, 10, 15 and 20 sccm, denoted hereafter as N4, N8, N10, N15 and N20, respectively. It was found that the N content rose up from 6.5 to 28.9 at.% when R_N increased from 4 to 20 sccm. Both N4 and N8 exhibit a face-centred cubic (FCC) structure. An increase inR_N to 10 sccm and 15 sccm resulted in the formation of an FCC and hexagonal closed-packed (HCP) dual-phase structure. The volume fraction of the FCC phase increased with a further increase in R_N, leading to a predominant FCC structure in N20. Despite their unusually high N concentration of up to 28.9 at.%, the HEAs comprises solid solution phases without nitride formation. Notably, the N15 HEA with 21.8 at.% N shows an impressive hardness of 20 GPa, comparable to ceramics, while demonstrating exceptional damage-tolerance with considerable plasticity. The excellent combination of high hardness and damage-tolerance is believed to stem from 1) massive solid solution strengthening caused by a high level of N intake, 2) a dual-phase FCC and HCP structure supposedly due to the low stacking fault energy, and 3) stress-induced FCC to HCP phase transformation. These findings demonstrate that, in contrast to the high brittleness as seen in nitrides, N-supersaturated HEAs can undergo large plastic deformation like pure metallic materials, thus opening up a new avenue for enhancing the mechanical properties of advanced alloys for applications under extreme loading conditions.

2:40pm **MA4-2-WeA-3 Mechanical and Anticorrosive Properties of Laminated (NbTaMoW)N_x Films***, **Yan-Zhi Liao (11289034@mail.ntou.edu.tw)**, Y. Chen,* National Taiwan Ocean University, Taiwan

(NbTaMoW)N_x films were prepared through cosputtering with four element targets. The distinction in characterization between the laminated nitride films fabricated at substrate holder rotation speed R_H of 2 and 10 rpm and homogeneous high-entropy alloy nitride films prepared at R_H of 30 rpm were evaluated. The nitrogen flow rate (f_{N2} = [N_2/(N_2+Ar)]) during the sputtering process was set at 0.1, 0.2, and 0.4, respectively. The deposition rate decreased from 43.8 to 33.7 nm/min with increasing f_{N2} from 0.1 to 0.4 at R_H of 2 rpm due to the target poisoning effect, whereas the deposition rate decreased from 46.4 to 34.8 nm/min at R_H of 10 rpm. The phase structures and mechanical and anticorrosive properties of the (NbTaMoW)N_x films were studied. The results indicated that a metallic phase dominated structure was observed for the films prepared at f_{N2} of 0.1, whereas nanocrystalline and face-centered cubic nitride phases were obtained for films fabricated at f_{N2} of 0.2 and 0.4, respectively. The films deposited at f_{N2} of 0.4 exhibited hardness values of 25.2 and 26.1 GPa for the films prepared at R_H of 2 and 10 rpm, respectively, which were lower than 29.9 GPa for the films prepared at R_H of 30 rpm. Potentiodynamic polarization tests were conducted out for evaluating the anticorrosive properties of the films on SUS420 substrate.

3:00pm **MA4-2-WeA-4 Structure and Mechanical Properties of (Al,B,Cr,Si,Ti)-based Thin Films***, **Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at)**, P. Konecny,* TU Wien, Institute of Materials Science and Technology, Austria*; R. Hahn,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Ceramics based on the high-entropy concept mostly consist of refractory metals such as Ta, Hf, Zr, W, V etc. These metals are good nitride and carbide formers which is why they are mainly used especially for PVD coatings. Nevertheless, the production of these elements needs a lot of energy input due to their very high melting points. Furthermore, these elements are very heavy which in consequence makes them hard to process and rather expensive. In this study we want to focus on a material system consisting of Al, B, Cr, Si, and Ti which are comparably light and cheap elements and the production of a corresponding compound target consumes less energy. To get an idea of the properties of coatings based on this material system we investigated “metallic” coatings as well as nitrides and oxides. The coatings were synthesised by magnetron sputtering using a single composite target with an equiatomic composition and different gas mixtures. All the coatings produced show XRD amorphous diffraction patterns without any indication of crystalline phases. Also, SEM images of fracture cross-sections do not show the, usually characteristic, columnar growth which further underpins the results obtained by XRD measurements. The hardness and indentation modulus of the coatings range from ~10 to 22 GPa and from ~170 to 260 GPa, respectively, depending on the character of the coating. To get information of the bonding state, XPS measurements were carried out. Furthermore, in-situ cantilever bending tests were done to investigate the fracture toughness of the coating depending on their either “metallic”, nitride, or oxide character.

3:20pm **MA4-2-WeA-5 Synthesis and Characterization of High Entropy Ceramic Coatings from Cr-Hf-Mo-Ta-W Refractory Metal System***, S. Debnárová, T. Stasiak, V. Buršíková,* Masaryk University, Czechia*; Z. Czigány, K. Balázsi,* HUN-REN Centre for Energy Research, Hungary*; S. Lin, N. Koutná,* Technische Universität Wien, Austria*; **Pavel Souček (soucek@physics.muni.cz)**,* Masaryk University, Czechia

High entropy alloys (HEAs) are multicomponent materials containing at least five principal elements with contents ranging between 5 and 35 at.%. The high entropy concept also extends to ceramics, such as oxides, nitrides, borides and carbides. High entropy materials can exhibit high strength and hardness at low as well as high temperatures, outstanding structural stability, wear, corrosion and oxidation resistance. This makes them promising candidates for next-generation replacements of traditional materials in many areas of the industry.

In this contribution, we are examining the formation of single-phase high entropy nitrides and high entropy carbides NaCl-type fcc structure from the Cr-Hf-Mo-Ta-W system. Magnetron sputtering was used for all depositions. An ambient temperature was used for the first deposition set, while an elevated temperature of 700°C was used for the second to observe the influence of the temperature on the crystallization. Argon/nitrogen gas admixture was used in nitrides, while argon/acetylene was used in carbides. This led to the first difference in reaching different nitrogen/carbon content in the coatings. While sputtering in nitrogen is a typical representative of reactive magnetron sputtering and nitrogen content never exceeded 50 at.%, sputtering in acetylene belongs to the hybrid PVD-PECVD deposition processes, also known as unsaturated reactive sputtering, and much higher carbon content in the coatings is reached. The deposition rate did not significantly decrease for all reactive gas flows. The structure and mechanical properties of the coatings were heavily influenced by the reactive gas flow for both systems. In films deposited without acetylene flow, a bcc metallic phase was observed.

Increasing reactive gas flow first showed an amorphous structure and then an fcc multielement carbide structure. Therefore, the ability of the system to form either metallic or ceramic nitride and carbide single phases was confirmed. Amorphous coatings exhibited a dense microstructure, while crystalline films were more columnar with multilayered structure at the nanoscale given by the deposition process geometry. The mechanical properties of the deposited films were good, exhibiting a hardness of up to 25 GPa, while the majority of the coatings were around 20 GPa. There was no great difference between the hardness of the corresponding nitrides and carbides.

This research was supported by project LM2018097, funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA23-05947S financed by the Grant Agency of the Czech Republic.

3:40pm **MA4-2-WeA-6 Mechanical and Oxidation Properties Evaluation of Equimolar and Non-Equimolar High Entropy Alloy Boron Carbonitride Coatings***, **Igamcha Moirangthem (igamcha@gmail.com)**,* National Taiwan University of Science and Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*; C. Wang,* National Taiwan University of Science and Technology, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan

In recent studies, high entropy alloy (HEA) nitride and carbide coatings have shown improved chemical and mechanical properties as compared to conventional alloy nitride and carbide coatings. Various combinations of transition metals in equimolar ratio as well as non-equimolar ratio carbide and nitride coatings have been explored recently for excellent mechanical and chemical properties using physical vapor depositions. In this study, an equimolar TiZrNbTaFe alloy target and a non-equimolar $Al_4Cr_2NbSiTi_2$ alloy target were used to fabricate their boron carbonitride phases using superimposed high power impulse magnetron sputtering. A radio frequency (RF) power source was used for the boron target. The coatings were deposited on p-type Si (100), AISI 304, and AISI 420 stainless steel substrates. The nitrogen flow was maintained at a constant rate, and the acetylene flow rate was varied. The microstructures, phases, and surface roughness of the HEA boron carbonitride coatings were investigated by a field emission scanning electron microscope, X-ray diffractometer, and atomic force microscope, respectively. The nanohardness was measured using nanoindentation. A pin-on-disk tribometer was used to study the wear characteristics of these coatings. The effects of heat treatment, oxidation, and potentiodynamic polarization of these coatings were also examined. The mechanical, chemical, and oxidation properties of TiZrNbTaFeBCN and AlCrNbSiTiBCN boron carbonitride coatings were explored in this work.

4:00pm **MA4-2-WeA-7 Research on the Effects of Various Acetylene Contents on the Mechanical Properties of TiZrNbTaFeBCN High Entropy Alloy Films***, **Meng-Hsueh Chuang (norman12lin@gmail.com)**,* National Taiwan University of Science and Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan*; C. Wang,* National Taiwan University of Science and Technology, Taiwan

The conventional alloys are made of one primary element with the addition of small or moderate amounts of alloying elements to yield an alloy with specific properties. However, in 2004, Professor Jien-Wei Yeh from National Tsing Hua University, Taiwan, and Professor Brain Cantor from the University of Oxford, UK, independently introduced innovative material systems known as multicomponent alloys and high entropy alloys (HEAs). These breakthroughs garnered significant attention and research interest from the global academic, industrial, and scientific communities and led to a new distinct branch in materials research. The effects of various acetylene gas flow rates on the chemical composition, microstructure, phase structure, hardness, and wear resistance of TiZrNbTaFeBCN high entropy alloy films were investigated. The HEA thin films were prepared by co-sputtering an equimolar TiZrNbTaFe high entropy target and a TiB_2 target onto the surfaces of AISI420 stainless steel, AISI304 stainless steel, and P-type (100) silicon wafer substrates using fixed nitrogen gas flow rate and different acetylene flow rates. The structures of thin films were determined by an X-ray diffractometer. The cross-sectional morphologies of thin films were examined by field emission scanning electron microscopy (FE-SEM). A nanoindenter and scratch test were used to evaluate the hardness and adhesion properties of thin films, respectively. Effects of carbon contents on the mechanical properties of TiZrNbTaFeBCN HEA thin films will be discussed.

Functional Thin Films and Surfaces
Room Town & Country D - Session MB2-2-WeA

Thin Films for Electronic Devices II

Moderators: Claudiu Falub, Evatec AG, Switzerland, **Julien Keraudy**, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, **Panos Patsalas**, Aristotle University of Thessaloniki, Greece

2:00pm **MB2-2-WeA-1 Electro-optic Thin Film Switch for Silicon Photonics Quantum Computer***, **Vimal Kamineni (vimal@psiquantum.com)**,* PsiQuantum Ltd., USA **INVITED**

A general-purpose quantum computer has a broad range of applications from finance, healthcare, climate, security, computing, materials, to other industry verticals as companies continue to explore the possibilities. PsiQuantum is on a mission to build and deploy the world's first useful quantum computer utilizing integrated silicon photonics. Photonic qubits uniquely overcome the scaling challenges associated with error correction for implementing a large-scale fault tolerant quantum computer. These photonic qubits are implemented in an integrated custom process stack, co-developed with our semiconductor foundry partners. The talk will cover our development towards building a scalable integrated silicon photonics platform with focus on a high performance electro-optic thin film switch. Our linear optics operations are probabilistic, and efficiency of successful events is boosted by multiplexing using an electro-optic switch. The electro-optic material induces an optical phase shift when voltage is applied, and it is fabricated using barium titanate (BTO). Thin film BTO was downselected for our application as it offers the highest Pockels coefficient at room temperature when grown epitaxially as a thin film on silicon substrates. BTO enables high speed phase shifters with low loss and power consumption which are critical metrics for a quantum computer.

KEYWORDS

Silicon photonics, quantum computing, qubit, electro-optic switch, barium titanate

2:40pm **MB2-2-WeA-3 The Path to Deterministic Chaos in Resistively Switching $Hf_{0.5}Zr_{0.5}O_2$ Thin Films via Period-Doubling Bifurcations***, **Sebastian Obernberger (sebastian.obernberger@inrs.ca)**, K. Kohlmann,* Institut national de la recherche scientifique - Centre Énergie Matériaux Télécommunications, Canada*; A. Sarkissian,* Plasmionique Inc., Canada*; P. Antici,* Institut national de la recherche scientifique - Centre Énergie Matériaux Télécommunications, Canada*; C. Schindler,* Munich University of Applied Sciences, Germany*; A. Ruediger,* Institut national de la recherche scientifique - Centre Énergie Matériaux Télécommunications, Canada

The burgeoning interest from industry, research, and policymakers in cutting-edge domains of information technology, such as artificial intelligence, quantum computing, and quantum cryptography, underscores the pressing need for advanced electronic infrastructure. One promising development lies in the creation of novel "neuromorphic" memory cells designed to function as artificial synapses within neural networks, leveraging their intrinsic "spike-timing-dependent plasticity." While the simulation of such behavior has historically proven inefficient on conventional von-Neumann-architecture computers, our study unveils an intriguing opportunity: the observation of period-doubling bifurcations in ReRAM (Resistive Random-Access Memory) based neuromorphic cells.

Herein, we detail the fabrication and analysis of RF-magnetron sputtered TiN/$Hf_{0.5}Zr_{0.5}O_2$ (HZO)/Au capacitors, elucidating their switching behavior. Our investigation delves into the resistive switching mechanisms within the HZO layer, encompassing the formation and dissolution of conductive filaments and the modulation of tunneling barriers via the tunneling electroresistance effect (TER). Through this analysis, we discern energy dissipative phenomena culminating in a negative feedback loop in the "spike-timing-dependent plasticity." Crucially, this negative feedback loop engenders bifurcations within the cell's switching dynamics, serving as a conduit to deterministic chaos. Harnessing and controlling these bifurcations not only enhances the efficacy of neuromorphic cells as artificial synapses but also facilitates their deployment as rapid-switching, easily managed random number generators.

3:00pm **MB2-2-WeA-4 Stoichiometric Engineering of Rotary Metal Oxide Targets for Thin Film Applications: A Focus on Zinc Oxide Based Alternatives***, Jing Yang (jyang@sciengineeredmaterials.com),* SCI Engineered Materials, Inc., USA

Indium Tin Oxide (ITO) is the most widely used transparent conductive oxide (TCO) for flexible electronics. With its demand increasing for applications such as liquid crystal displays, smart windows, thin film photovoltaics,architectural windows, and polymer-based electronics, the historically volatile pricing of Indium presents a concern for manufacturers. Zinc Oxide based materials, given Zn's abundance in Earth's crust, emerge as a cost-effective alternative for thin film applications.

Zinc Tin Oxide (ZTO), a potential candidate as the TCO layer in OLED, the channel layer in Thin Film Transistor (TFT), and the interlayer for low-E glass, faces challenges in DC-sputtering due to the spinel structure of Zinc Stannate. One solution is to employ reactive sputtering of Zinc and Tin metal targets. This approach introduces difficulty in terms of precise stoichiometric control and overall quality of finished film. Alternatively, RF sputtering of a ZTO target may be employed, but the film growth rate is very slow.

In this study, we explore the use of a conductive, sintered oxide target as the solution that offers controlled DC sputtering and high-quality film production. We demonstrate compounding various ratios of Zinc and Tin oxides into single targets to create conductive targets in both planar and rotary geometries for DC sputtering. The study assesses the stoichiometric impact on target manufacturing and the subsequent thin film properties, comparing the electrical and optical properties of ZnO-based films with traditional TCOs like ITO. We also present a conductive rotary target designed for high power density, crucial for high-throughput industrial applications.

3:20pm **MB2-2-WeA-5 Flexible FSMA Based Magnetoelectric Sensor***, Davinder Kaur (davinder.kaur@ph.iitr.ac.in),* Indian Institute of Technology Roorkee, India

The present study reports the fabrication of highly flexible, cost-effective, nano-structured magnetic field sensor comprising AlN/Ni-Mn-In ME heterostructure fabricated over magnetostrictive Ni foil. The magnetodielectric and magnetoelectric characteristics of the ME heterostructure based flexible magnetic sensor has been thoroughly investigated. The ultra-low magnetic field up to or less than ~1 μT has been easily detected from the fabricated sensor. Hence, the present lead-free ME heterostructure integrated over flexible substrate can enhance the multifunctionality in futuristic flexible magnetic field sensors for room temperature applications. Moreover,the surface acoustic wave (SAW) delay line-based piezo resonator was fabricated over highly flexible AlN/Ni-Mn-In/Kapton for flexible MEMS application. The fabricated device resonates at ~1.40 GHz. The effect of the external magnetic field on the resonance frequency (f_R) of the device has also been investigated and tunability ($\Delta f_R/f_R$) ~9% was observed. The device displays high sensitivity of ~0.94 Hz/nT at room temperature. The flexibility of the fabricated magnetic field sensors has been investigated in terms of the bending cycles and bending angle. The sensor characteristics remain unchanged up to ~ 2500 bending cycles. Hence, the device consisting ME heterostructure fabricated over flexible substrates shows its full potential towards the flexible and wearable electronics.

Keywords: Ferromagnetic shape memory alloys, flexible magnetic sensor, lead-free piezoelectric, magnetostrictive effect, surface acoustic waves (SAW), Bulk acoustic waves (BAW)

3:40pm **MB2-2-WeA-6 Growth of Nanostructured Molybdenum Disulfide (Mos_2) Thin Film for the Application of Electronic Materials***, I. Giwa, K. Qian, F. Sanchez, E. Mawire, S. Dong, E. Smith, Q. Yuan, **Zhigang Xiao (zhigang.xiao@aamu.edu)**,* Alabama A&M University, USA

We report the fabrication of molybdenum disulfide (MoS_2) thin films–based electronic devices. Nanostructured molybdenum disulfide (MoS_2) thin films are grown as the active semiconducting channel material for the fabrication of MoS_2-based field-effect transistors using plasma-enhanced atomic layer deposition (ALD). MoS_2–based electronic devices such as MoS_2 field-effect transistors, inverters, and ring-oscillators are fabricated with the ALD-grown MoS_2 film using the clean room-based micro- and nano-fabrication techniques. Hydrogen sulfide (H_2S) gas is used as the S source in the growth of molybdenum disulfide (MoS_2) while molybdenum (V) chloride ($MoCl_5$) powder is used as the Mo source. The MoS_2 film will be analyzed by the high-resolution tunnel electron micrograph (HRTEM), scanning electron micrograph (SEM), X-ray photoelectron spectroscopy (XPS) analysis and Raman spectrum analysis. The fabricated MoS_2 device wafer will be annealed at high-temperatures (800 – 900 °C), and the electrical property of the MoS_2–based electronic devices will be measured before and after the high-temperature annealing and will be compared. The characterization results of the nanostructured molybdenum disulfide (MoS_2) thin films and the measurement results on the fabricated MoS_2–based electronic devices will be reported in the ICMCTF 2024 Conference.

Acknowledgements: The research is supported by National Science Foundation under Grant No. ECCS-2100748

4:00pm **MB2-2-WeA-7 High Voltage on-Chip Micro Supercapacitor as a Miniaturized Energy Storage Device for Microelectronic Applications***, **Sheetal Issar (sheetal.pd@ic.iitr.ac.in)**,* Indian Institute of Technology Roorkee, India*; D. Jhajhria,* Indian Institute of Technology Kanpur, India*; R. Chandra,* Indian Institute of Technology Roorkee, India

High voltage microsupercapacitors (MSCs) along with energy harvesters can be used to integrate miniaturized self-powered system in many microelectronic devices. On-chip MSCs are considered as one of the promising energy storage devices due to their high energy density, long cycle life, and fast charging-discharging rate. In this regard, transition metal nitrides (TMNs) based nanostructured are considered as an effective electrode material for fabrication of high performance on-chip MSCs due to their high electrical conductivity. We report fabrication of highly stable interdigitated micro patterns of titanium vanadium nitride (TiVN) and titanium chromium nitride (TiCrN) over a SiO_2-coated Si substrate by using single-step reactive DC magnetron sputtering technique. Generally, the low voltage window of on-chip MSCs is a bottleneck in designing miniature power source in microelectronic devices. One of the most technical challenges with the on-chip MSCs is to enhance cell voltage without compromising its tiny size. The electrochemical voltage window of the MSCs is greatly dependent over the electrolyte itself. In the present work, different electrolytes such as aqueous, water-in-salt, and ionic liquid incorporated polymer gel electrolyte are utilized to check the electrochemical performance of TMN-based MSCs. An exceptionally high voltage window of more than 3 V is achieved in TiVN and TiCrN-based MSCs with $TEABF_4$/ethylene carbonate/propylene carbonate ionic liquid entrapped in the polyvinylidene fluoride (PVDF) polymergel electrolyte. The on-chip MSC exhibits an optimum capacitance of ~500 $\mu F.cm^{-2}$ at a current density of 0.07 $mA.cm^{-2}$ with an energy density of ~ 0.7 $\mu Wh.cm^{-2}$ and a power density of 169.02 $\mu W.cm^{-2}$. This study provides new opportunities to integrate nanocomposite-based microelectrodes directly for on-chip MSCs for utilization as high voltage miniaturized power sources.

4:20pm **MB2-2-WeA-8 Few-layered Multi-transition Metal Dichalcogenide Alloy Absorber for High-performance Photodetector***, **I-Hsi Chen (telescope50311@gmail.com)**, T. Nguyen, J. Ting,* National Cheng Kung University (NCKU), Taiwan

Low-dimensional materials including quantum dots, nanowires, and two-dimensional materials have attracted increasing research interest in the fields of electronics and optoelectronics. Photodetector is no exception as the use of monolayer two-dimensional (2D) material in photodetector has attracted a great deal of attentions. Among them, 2D transition metal dichalcogenide (TMDC) offers unique semiconductor properties, including quantum spin Hall effect, valley polarization, and two-dimensional superconductivity.

We report the growth of few-layered multi-metallic TMDC alloys with salt-assistance on SiO2/Si substrates with controllable composition using a chemical vapor deposition (CVD) technique. Composition control has been investigated by varying the concentration of individual precursors. Various analyses were carried out to understand the material properties, including structural, physical, chemical properties, and the performance of TMDCs in photodetectors.

4:40pm **MB2-2-WeA-9 $BaTiO_3$ Epitaxial Thin Films Integrated on Si by Pulsed Laser Deposition for Electro-Optic Modulators***, **Heungsoo Kim (heungsoo.kim.civ@us.navy.mil)**, S. Mathews,* Naval Research Laboratory, USA*; A. Posadas, A. Demkov,* The University of Texas at Austin, USA*; A. Piqué,* Naval Research Laboratory, USA

$BaTiO_3$ (BTO) is a ferroelectric material that has large Pockels coefficient. Recently, there has been an increasing interest on epitaxial BTO films integrated on Si as a promising material platform for building electro-optic (EO) modulators.The Pockels, or linear-electro-optic effect is the first order change in the index of refraction under applied electric field and has an advantage over other optical modulation methods because it can operate at very low power and very high frequencies. Depending on lattice matching and thermal expansion difference with the substrate, BTO films can be grown either c-oriented BTO (elongated axis normal to the substrate surface) or a-oriented BTO (elongated axis parallel to the substrate surface). The electro-optic response in BTO films is highly dependent on their crystallinity and domain structures. For $BaTiO_3$ integration on Si, a $SrTiO_3$ (STO) buffer layer was first deposited on Si (001) substrate by molecular beam epitaxy. BTO films were then grown on STO-buffered Si template via pulsed laser deposition (PLD) at various oxygen pressures (10 – 50 mTorr) and substrate temperatures (600 – 760 °C). By optimizing the oxygen deposition pressure and substrate temperature, we were able to grow *a*-oriented domain structures of BTO films, which is a preferred domain structure for EO modulators due to a large Pockels effect in this configuration. We will present details of optimization processes to achieve *a*-oriented domain structures of BTO films along with their electro-optic responses.

This work was supported by the Office of Naval Research (ONR) through the Naval Research Laboratory basic research program.

5:00pm **MB2-2-WeA-10 Self-Powered Bi-Directional Photocurrent Switching Effect in Epitaxial GaN and 2D Materials Heterostructures***, **PARGAM VASHISHTHA (S3914033@STUDENT.RMIT.EDU.AU)**,* RMIT University, Australia*; G. Gupta,* CSIR-National Physical Laboratory, India*; S. Walia,* RMIT University, Australia

Conventional broadband optoelectronic devices face limitations when serving as a single detector for broadband and narrow-band applications due to their one-way photocurrent, restricting their potential uses in photodetection. However, a promising solution is emerging: bi-directional photocurrent switching. This advancement opens doors to unique functions like optical logic operations. We have developed optoelectronic devices using epitaxial 3D-GaN and 2D materials heterojunction, incorporating engineered bi-directional photocurrent. By harnessing a self-powered photocurrent switching effect, we can change the photocurrent's direction based on the incident light's wavelength, even at 0V bias. Our devices cover a broad spectrum, detecting light from ultraviolet-C to Infrared-B. For instance, our Bi_2Se_3/GaN device reaches a peak photoresponsivity of 584 mAW^{-1} at 355nm and -297 mAW^{-1} at 1405 nm, while our MoS_2/GaN device shows bidirectional photocurrent under very low applied bias. Moreover, we have developed special logic gates using a single bipolar photodetector, responding to different dual radiation inputs. These findings pave the way for future multifunctional photonic integrated devices and systems.

Tribology and Mechanics of Coatings and Surfaces
Room Town & Country B - Session MC3-1-WeA

Tribology of Coatings and Surfaces for Industrial Applications I

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Rainer Cremer**, KCS Europe GmbH, Germany, **Stephan Tremmel**, University of Bayreuth, Germany

2:00pm **MC3-1-WeA-1 Tribological Coatings to meet Future Requirements for Green Mobility***, **Steffen Hoppe (steffen.hoppe@tenneco.com)**,* Tenneco Powertrain, Product & Technology, Germany **INVITED**

The global transportation industry is taking on the challenge of decarbonizing propulsion with the goal of achieving climate-neutral mobility. Hydrogen-powered internal combustion engines (H_2-ICEs) are the mix of applicable and complementary technology solutions. This technology can drive decarbonization on a broad scale, especially in commercial truck, off-highway and industrial applications. Non-fossil fuels like ammonia, methanol or e-fuels are required to achieve net-zero-CO2 emissions in marine and aviation markets.

The introduction of non-fossil fuels has a significant impact on the tribology systems in ICEs. Due to the significant differences in physical and chemical properties of hydrogen, ammonia, and methanol compared to gasoline and diesel fuel, the combustion strategies need to be adapted to these fuels. Advanced coating solutions are required for ICEs components to address the impact on the tribological systems caused by higher combustion temperatures, oil dilution or deterioration, and water entrapment.

This paper will show how the critical tribological system of piston rings can be optimized by developing high performance coatings. Hydrogen free DLC coatings, advanced thermal spray coatings and new electrochemical coatings are applied to achieve robust tribological systems in decarbonized propulsion systems.

2:40pm **MC3-1-WeA-3 Current-Induced Friction and Graphitization Effects in Amorphous and Tetrahedral Amorphous Carbon Coatings on M2 Steel: An Electro-Tribological Investigation***, **Amir Masoud Khodadadi Behtash (khodada1@uwindsor.ca)**, A. Alpas,* University of Windsor, Canada

In electric vehicles, protecting bearings from shaft voltages and bearing currents is key to avoiding premature wear and failure. Diamond-like carbon (DLC) coatings, with their low friction and insulating properties, could extend bearing life and reliability. This study assesses how electrical current affects the frictional behaviour of M2 steel coated with non-hydrogenated diamond-like carbon (a-C) and tetrahedral amorphous carbon (ta-C), by comparing their coefficients of friction (COF) against an AISI 52100 steel counterface under varying currents but the same loading conditions using a ball-on-disk tribometer. The uncoated M2 steel exhibited COF values ranging from 0.55 to 0.62, suggesting frictional instability and a tendency towards oxidation with sliding under electrical currents (Figure 1). The a-C coatings maintained a stable coefficient of friction under 0.15 up to currents of 1200 mA. In contrast, the ta-C coatings showed variable COFs, starting at 0.20 and rising above 0.60, indicating less stability under electrical currents. Micro-Raman analyses revealed graphene formation within the wear tracks of a-C samples upon exposure to induced current (Figure 2a). This current-induced graphitization within the wear tracks correlates with the a-C coating's low and stable COF. In contrast, ta-C coatings, with a higher sp^3 content, underwent less graphitization and more oxidation (Figure 2b) at the steel interface when subjected to the same electrical current. The increase in D peak intensity within wear tracks of a-C samples at higher currents suggested a rise in defect density in graphene layers formed. The mechanisms underlying these observations, including the interplay between graphitization and electrical current, as well as their implications for electro-tribological systems, will be discussed in the presentation.

3:00pm **MC3-1-WeA-4 Compositionally Graded MoS_2-WC Spray Coatings for Robust Tribological Protection in Low Viscosity Fuels***, **Euan Cairns (euancairns@my.unt.edu)**, J. Decker,* University of North Texas, USA*; S. Dixit,* Plasma Technology Inc., USA*; S. Berkebile,* Army Research Laboratory, USA*; D. Berman, S. Aouadi, A. Voevodin,* University of North Texas, USA

Increased usage of low carbon emission fuels, such as ethanol and dodecane, are driving a critical need for advanced lubricious materials to extend the wear life of fuel pump components. Solid lubricants are traditionally employed in applications where liquid lubrication is insufficient if not impossible. We demonstrated that molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) films spray-coated onto 52100 steel and WC-17Co surfaces decreased friction and wear during sliding in hydrocarbon fuels. Solid lubricant coatings were substantially more robust while sliding in non-polar dodecane fuel, where friction coefficients of less than 0.1 were maintained for thousands of sliding cycles. Meanwhile, in polar ethanol fuel, low friction was only kept for a few hundred cycles before sharp failure of the coatings, due to oxidation and removal of the lubricant from the wear track.

In this study, we propose to further enhance the wear resistance of crucial components in fuel pumps via designing compositionally graded MoS_2-WC coatings. The microstructure and wear data were evaluated using scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). Analysis of worn surfaces was performed using optical profilometry and Raman spectroscopy to analyze the chemical evolution inside the wear track across multiple fuel chemistries. Insights gained from this study offer valuable information for the development of robust lubrication solutions in the realm of low carbon emission fuel applications.

3:20pm **MC3-1-WeA-5 Tribological Behavior of DLC Coatings: Wear Map of Oil Lubricated Contacts in a Three-Pins-on-Disc Test Configuration***, **Julien Keraudy (julien.keraudy@oerlikon.com)**, N. Manninen, F. Rovere,* Oerlikon Surface Solutions AG, Liechtenstein

Diamond-like carbon (DLC) coatings have emerged as a promising coating solution able to combine high wear resistance and low friction coefficient. In fact DLC coatings comprise a family of different carbon based coatings which can show a broad range of properties based on the fraction of sp3/sp2 bonds and also on the amount of incorporated hydrogen or metal dopants.

In the present study different DLC coating variants were tested regarding their tribological performance.The coatings were tested in three pin-on-disc configuration under additive oil (ZDDP) lubricated conditions. Different pressure x velocity (P.V) conditions were tested during endurance tests in order to identify the coatings performance over a broad range of P.V conditions. The lubrication regimes were identified by Stribeck curves in order to determine the lubrication regimes for the different test parameters. The coatings were analyzed by scanning electron microscopy (SEM), profilometry and optical microscopy after the tribological tests, in order to evaluate the wear mechanisms. The coatings were characterized regarding their topography and morphology (by means of SEM analysis), roughness (by profilometry analysis) and hardness (by nanoindentation). The coatings chemical properties, roughness and hardness are strongly correlated with the tribological performance.

3:40pm **MC3-1-WeA-6 Structural and Tribo-mechanical Properties of AlCrVYON Thin Films with Varying O Contents Sputtered from Either AlCrVY or AlCrY and V Targets**, *W. Tillmann, **Finn Ontrup (finn.ontrup@tu-dortmund.de)**, D. Aubry,* TU Dortmund University, Germany*; E. Schneider, M. Paulus, C. Sternemann,* Fakultät Physik/DELTA, TU Dortmund University, Germany*; N. Lopes Dias,* TU Dortmund University, Germany

The incorporation of Y and V into AlCrN has previously proven effective in enhancing oxidation resistance and tribological properties at elevated temperatures. As this improvement stems from the oxide formation of these elements, depositing O-containing AlCrVYN presents a promising approach for directly synthesizing thin films with enhanced tribo-mechanical properties for high-temperature applications. Therefore, AlCrVYON with varying O contents were deposited using a hybrid dcMS/HiPIMS process in two distinct approaches. In a reactive process, AlCrVYON was either sputtered from two AlCrVY targets or co-sputtered from AlCrY and V targets. For both configurations, the O_2 flow rate was varied from 0 to 20 sccm.

Sputtering from AlCrY+V targets results in higher O contents from 1.4 to 31.3 at.–% compared to the other target setup which achieves up to 20.7 at.–%. High-resolution x-ray diffraction using synchrotron radiation reveals a cubic CrN phase for all thin films, independent of the O content and target configuration. Nanoindentation tests show that the hardness stays at a high level above 40 GPa for an O content of up to 6.5 at.–% for AlCrVYON sputtered from AlCrVY targets and up to 14.7 at.–% for those sputtered from AlCrY+V targets. However, for higher O concentrations the hardness for both AlCrVYON variants decreases. Due to a constant decrease in the elastic modulus with an increasing amount of O, a maximum in the H/E ratio is observed for the aforementioned O contents. Furthermore, the tribological properties were analyzed using a high-temperature tribometer. No significant reduction of the coefficient of friction is noted at room temperature and only a slight improvement is visible in the higher temperature range for all AlCrVYON thin films, except the ones with the maximum H/E ratio. Annealing the thin films deposited from two AlCrVY targets for 2 h at 500, 600 and 700 °C demonstrates a high oxidation resistance for all AlCrVYON of at least 6.5 at.-% O, as no decrease in hardness, nor an increase in O content could be identified post-annealing. However, the thin films sputtered from AlCrY+V targets perform different in this regard, as the hardness decreases for all thin films after annealing at 600 °C.

In summary, the AlCrY+V target configuration produces AlCrVYON with higher O contents, resulting in a significantly different oxidation resistance. Other than that, both configurations show similar trends, demonstrating the advantage of adding small amounts of O into AlCrVYN. Thus resulting in a maximum of the H/E ratio for explicit O contents, depending on the target configuration.

4:00pm **MC3-1-WeA-7 Development and Process Optimization of Suspension Plasma Spray Coating to Enhance the Frictional Properties and Wear Resistance**, ***Yong-Jin Kang (free83@kims.re.kr)**, Y. Yoo, S. Lee, D. Kim,* Korea Institute of Materials Science, Republic of Korea

Chromium oxide (Cr_2O_3) coating produced by the atmospheric plasma spray (APS) process is widely used in industrial fields such as anilox rolls, doctor blades in the paper-making industry, pump sleeves, and break discs that require resistance to sliding wear and corrosion. However, due to its low mechanical properties and high surface roughness and porosity, the development of alternative coating processes such as suspension plasma processes(SPS) is required. Accordingly, in this study, we developed a chromium oxide coating with low surface roughness, high hardness, and excellent wear resistance through a suspension plasma spray (SPS) process. By optimizing the stand-off distance, feedstock powder size, and power during SPS process, dense Cr_2O_3 coating with a porosity less than 2% was achievable. Microstructures and mechanical properties of as coated samples were characterized by SEM, XRD, surface profiler. Then, tribological properties, such as friction coefficient and wear rate, were evaluated by ball on disk test. The wear resistance of Cr_2O_3 coatings via SPS and APS processes was compared with their intrinsic microstructure and mechanical properties.

4:20pm **MC3-1-WeA-8 Excellent Mechanical, Tribological and Anticorrosive Properties of Nanocomposite Coating Based on Polyvinyl Alcohol/MXene/Tannic Acid**, ***Dieter Rahmadiawan (n18127046@gs.ncku.edu.tw)**,* National Cheng Kung University (NCKU), Taiwan, Indonesia*; S. Chen Shi,* National Cheng Kung University (NCKU), Taiwan

This study investigates the effects of incorporating tannic acid into a polyvinyl alcohol (PVA)/MXene film. The composite was characterized for its mechanical, corrosion resistance, and tribological properties. The addition of tannic acid was found to enhance the mechanical strength of the composite, attributed to its crosslinking capabilities and interactions with the MXene nanosheets. Corrosion resistance was significantly improved, as tannic acid acted as a corrosion inhibitor, forming a protective layer on the composite surface. Tribological tests revealed reduced wear rates and improved frictional behavior, indicating the effectiveness of tannic acid in enhancing the lubricating properties of the PVA/MXene system. The comprehensive analysis presented in this study underscores the potential of PVA/MXene/Tannic Acid composites for applications demanding superior mechanical performance, corrosion resistance, and tribological efficiency.

4:40pm **MC3-1-WeA-9 Effects of Various Al/Cr Composition and Deposition Conditions on Surface Properties, Mechanical and Tribological Properties of AlCrN Coatings**, ***SHINICHI TANIFUJI (tanifuji.shinichi@kobelco.com)**, M. NAKAMURA, R. TAKEI, S. KUJIME, T. TAKAHASHI,* Kobe Steel, Ltd., Japan

The environment in which tools and molds are used in production is becoming harder and harder year by year. Therefore, coatings applied by physical vapor deposition are required to have high hardness and oxidation resistance in order to extend the lifetime of tools and dies. Typical examples of coatings with such properties are AlTiN and AlCrN coatings. The oxidation resistance of coatings is attributed to the Al content of the coating, and it is known that the higher the Al content, the higher the oxidation resistance. On the other hand, the hardness of the coatings differs, with AlTiN and AlCrN coatings showing maximum hardness at 67 at% and 77 at% Al content, respectively. It is known that when the Al content in both coatings exceeds these levels, a decrease in hardness occurs due to the precipitation of soft AlN in the coating.

At last year's conference, KOBELCO introduced its new Cathodic arc evaporation system, AIP-iX. Using the new μ-Arc evaporation source installed in the system, KOBELCO reported on the surface properties of AlCrN coating with 75% Al content as observed by scanning electron microscopy, the coating hardness as measured by nanoindentation test, and the crystal structure of the coating by X-ray diffraction method. The results of the crystal structure of the coatings were also reported by the X-ray diffraction method. The results of the nanoindentation test and the crystal structure of the coating by X-ray diffraction are also reported. The surface smoothness of the coating is superior to that of the conventional cathodic arc deposition coating, and the cubic crystal structure is confirmed, indicating that a hard coating can be formed.

On the other hand, one of the main characteristics of μ-Arc is that it has fewer surface macro-particles than conventional coatings, but the effect of the surface properties of the coating on the tribological properties of the coating has not yet been clarified. In order to meet the needs of industrial applications, it is important to clarify the relationship between tool and die performance and the properties of the coatings. In this report, we describe the results of our studies of AlCrN coatings prepared under various compositions and deposition conditions, and the effects of these conditions on surface properties, mechanical and tribological properties, as well as the relationship of these coatings to tool and die performance.

5:00pm **MC3-1-WeA-10 Effect of Multilayer Architecture on Mechanical Properties and Cutting Performance of AlTiBN/AlCrBN Coatings**, ***Chung-En Chang (abcd0214milk@gmail.com)**, Y. Chang,* National Formosa University, Taiwan

Ti-6Al-4V alloy is a currently popular material known for its high fracture toughness and hardness, making it a preferred choice for industries like aerospace and automotive due to its excellent processing properties.

However, during the machining of Ti-6Al-4V, substantial heat is generated due to its relatively low elastic modulus and thermal conductivity. This excess heat accelerates tool wear and can lead to tool failure. In recent years, AlTiN and AlCrN hard coatings have become widely used for cutting tools. Machining difficult-to-cut materials has become a trend, and to enhance the properties of the coatings for processing these materials. Appropriate amounts of Boron (B) elements can be added to improve hardness, toughness, thermal stability, and wear resistance of the AlTiN and AlCrN coatings. The addition of Boron (B) atoms promotes the formation of a nano-composite structure, which includes AlTiBN and AlCrBN solid solutions, surrounded by an amorphous BN phase. In this study, the influence of AlTiBN/AlCrBN coatings with different multilayer architectures on the wear behavior and cutting performance of the carbide cutting tools was investigated in machining of Ti alloys. The multilayer thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of the films. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM) equipped with energy-dispersive X-ray spectroscopy (EDS). A Rockwell indentation tester and a scratch tester were used to evaluate the adhesion strength between the coating and the substrate. The coating hardness and the elastic modulus were measured by nanoindentation. The design of multilayered AlTiBN/AlCrBN coatings is anticipated to inhibit the grain growth, and leads to grain refinement effect, which expected to increase the mechanical properties and cutting performance of coatings.

Coatings for Biomedical and Healthcare Applications
Room Palm 3-4 - Session MD1-1-WeA

Surface Coatings and Surface Modifications in Biological Environments I

Moderator: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

2:00pm **MD1-1-WeA-1 Synergistic Antibacterial Activity and Ion Release of Ag-Cu and Ag-Cu-Mg Coatings**, ***Serdar Sonay Ozbay (sozbay@deakin.edu.au)***, *G. Rajmohan,* Deakin University, Australia*; A. Cobley,* Coventry University, UK*; J. Sharp,* Deakin University, Australia*; G. Azar,* Coventry University, UK

Silver (Ag) and Copper (Cu) thin films have been widely studied as antibacterial coatings to functionalise textile surfaces to fight antibiotic-resistant bacteria and healthcare-acquired infections (HAI) in hospitals. The release of metallic ions is considered to be the main antibacterial mechanism for both metals. Therefore, maintaining a steady ion release from the metallic coatings is necessary to achieve a sustained antibacterial activity. Despite the high effectiveness of Ag ions as antibacterial agents, Ag coatings suffer from a limited antibacterial activity due to the decreasing Ag ionisation rate caused by surface passivation. In contrast, Cu coatings exhibit rapid but brief antibacterial action due to the fast release of Cu ions. Recently, studies on combined Ag-Cu systems have reported an enhanced Ag ionisation and a synergistic antibacterial activity between Ag and Cu.

This study investigates how different compositions of Ag-Cu alloy thin film coatings can improve the limitations of pure metals to achieve a steady and long-term antibacterial efficacy. The Ag-Cu ($Ag_{75}Cu_{25}$-$Ag_{50}Cu_{50}$-$Ag_{25}Cu_{75}$) alloys were deposited on PET textiles using magnetron sputtering technique. The growth process and microstructures of the thin films were characterised by XRD and TEM/EDS. Additionally, the galvanic relationship and antibacterial synergy between the Ag and Cu components in different alloys were investigated through the ion release studies and antibacterial tests. Finally, the effects of a more electrochemically active metal on the properties of Ag-Cu alloys were studied by co-sputtering Mg into Ag-Cu thin films.

The results showed that both $Ag_{75}Cu_{25}$ and $Ag_{50}Cu_{50}$ coatings improved the plateauing of Ag ion release and provided a steady Cu ion release. Antibacterial efficacy of Ag-Cu thin films followed the order: $Ag_{50}Cu_{50}$ > $Ag_{25}Cu_{75}$ > $Ag_{75}Cu_{25}$ > Ag ≈ Cu. Due to the sufficient release of both Ag and Cu ions in the $Ag_{50}Cu_{50}$ coating, this sample demonstrated superior antibacterial performance compared to both other alloys and pure metal coatings. Moreover, this coating maintained a >90% bacterial reduction rate after two antibacterial test cycles, outperforming the other coatings. The ion release studies of Ag-Cu-Mg ternary alloys showed a further reduction in both Cu and Ag ion release, with the effect of less noble Mg on the Cu ion release being more significant compared to that on the Ag ion release. Overall, our results suggest that Ag-Cu and Ag-Cu-Mg thin films are promising candidates for hospital textiles that require a steady and prolonged antibacterial activity.

2:20pm **MD1-1-WeA-2 Iridium Oxide Based Electrodes for Bio-Interface Applications**, ***Po-Chun Chen (cpc@mail.ntut.edu.tw)***, National Taipei University of Technology, Taiwan **INVITED**

Iridium oxide has attracted extensive attention due to its unique advantages including excellent chemical stability and sensitivity, impressive electrochemical catalytic activity, sufficient electric conductivity, and desirable biocompatibility. To date, iridium oxide has been widely explored in applications such as anodes for water electrolysis, electrochromic layers for smart windows, and pH sensors. In addition, iridium oxide is known for its superb charge storage capacity and long-term stability renders it a desirable candidate as a bio-interface electrode for implantable bio-medical electronic devices. In this study, we developed solution processes to prepare iridium oxide film for bio-interface applications. We also characterized the electrochemical properties of the iridium oxide films and examined its stability. The iridium oxide film was found to be robust and revealed excellent charge storage capacity and charge injection capability. Additionally, the solution process allows the synthesis of iridium oxide hybrid film by combining plasma protein with enhanced electroactivity, improved cytocompatibility, and controllable electrically responsive protein release to enhance neuronal activity. Therefore, the iridium oxide film plays a multifunctional role as an electrode for bio-interface applications.

3:00pm **MD1-1-WeA-4 Improvement of Corrosion Resistance of Biodegradable Mg-Ca Alloy by Atomic Layer Deposition Technique**, ***Hsin-Chih Lin (hclinntu@ntu.edu.tw)***, *P. Lin, H. Chen, K. Lin,* National Taiwan University, Taiwan

Biodegradable Mg-Ca alloy has high application potential in the fields of cardiovascular stent, wound healing device and orthopedic implant. However, the degradation rate of Mg-Ca alloy is too fast to provide enough support for a long time, and it may also cause pH rise and excessive hydrogen production in vivo, which may lead to cell inflammation, vascular blockage, and other negative problems. Hence, how to precisely control the degradation rate and effectively reduce the corrosion rate is an important issue for Mg-Ca implants. Recently, we have conductive extensive studies on improving the corrosion resistance of Mg-Ca alloy by atomic layer deposition (ALD) technique. It is found that the atomic layer plasma treatment (ALPT) enhances the corrosion protection of the ZrO_2 film grown by thermal-driven ALD mode (TALD-ZrO_2), further reducing the corrosion rate of Mg-Ca alloy. The ALPT effect significantly increases the crystallinity and reduces oxygen defects of the TALD-ZrO_2 film, effectively improving the corrosion resistance of the TALD-ZrO_2 film, and the maximum enhancement is observed by using 30s-ALPT time. The corrosion rate of Mg-Ca alloy is highly reduced by more than one order of magnitude, which is reflected in the reinforcement of diffusion suppression of TALD-ZrO_2 film processed by the ALPT treatment. ALPT technique is suggested as a potential and feasible method to prepare TALD-ZrO_2 films with high film quality and corrosion protection.

3:20pm **MD1-1-WeA-5 Nanospectroscopy and Nanochemical Imaging Using Photothermal AFM-IR on Biomolecular Sensors and Hydrated Self-Assembled-Monolayers**, ***Nafiseh Samiseresht (nasajobjo@gmail.com)***, Max-Planck Institut für Eisenforschung, Germany*; G. Figueroa-Miranda, D. Mayer,* Forschungszentrum Juelich GmbH, Germany*; M. Rabe,* MPI für Eisenforschung GMBH, Germany

Nanostructured self-assembled-monolayers (SAMs) on solids are common platforms for functionalizing and controlling chemical and physical properties of surfaces with applications in diverse fields such as corrosion, catalysis and bio-sensors. Here Resonance enhanced AFM-IR is used to obtain nanoscale topographic information and spectroscopic, i.e. chemical information on such systems [1], in order to better understand the interplay between nanostructure and function. A tunable pulsed quantum cascade including four chips and a fast optical parametric lasers provides the IR source in the ranges of 910-1900 cm^{-1} and 2700-3900 cm^{-1}. Using a gold coated silicon cantilever on gold substrate provided high sensitivity to detect monolayer and single molecule.

First, results on aptamer SAMs on gold used as SARS-CoV-2 biosensors will be presented. Tapping mode AFM-IR was employed to characterize the surface after each fabrication step and after analyte binding to the receptor layer to provide insight to molecular conformational and structural variation as well as chemical composition of this system. Binding of single molecule proteins was detected (figure 1 in supplemental document).

Second, biomolecule-repellent oligoethylene glycol (OEG)-based SAMs on gold were studied. In such systems the molecular conformation of OEG and the structure of interfacial water are thought to strongly influence the repellent character [3]. Tapping mode AFM-IR investigation of water films adsorbed on nano-domains of OEG SAMs were performed under elevated relative humidity and provided structural details of the OEG moieties and adsorbed H_2O.

[1] G. Figueroa-Miranda, C. Wu, Y. Zhang, L. Nörbel, Y. Lo, J. A. Tanner, L. Elling, A. Offenhäusser, D. Mayer, Bioelectrochemistry, **136**, 107589, 2020.[2] P. Harder, M. Grunze, R. Dahint, G. M. Whitesides, P. E. Laibinis, J. Phys. Chem. B **102**, 426-436, 1998

3:40pm **MD1-1-WeA-6 An Electrochromic IrOx Nanofibrous Film for Multifunctional Bio-Interface Sensing Applications***, **Yu-Jen Tao (stephanie881111@gmail.com)**, P. Chen,* National Taipei University of Technology, Taiwan

Bio-interface sensing has attracted a lot of attention in recent years. For example, hydrogen peroxide (H_2O_2) and pH variation are essential detection targets in various fields, including clinical control and environmental protection. This present work reports a design of a non-enzymatic H_2O_2 electrochemical sensor and an electrochromic pH sensor with IrOx nanofibrous film. Additionally, the electrochemical performance of the IrOx nanofibrous film can be manipulated by the annealing parameters. The resultant materials are characterized through field emission scanning electron microscopy, X-ray diffraction analysis, and X-ray absorption spectroscopy. Furthermore, the electrochemical sensing performance of the IrOx nanofibrous film is evaluated by cyclic voltammetry, electrochemical impedance spectroscopy, and chronoamperometric (i-t) techniques. The sensitivity of the IrOx nanofibrous film is checked to investigate the effect of annealing parameters on the H_2O_2 sensing. The performance of the nanofibers in the electro-reduction of H_2O_2 is programmable by controlling the metallic Ir contents. The IrOx nanofibrous film annealed at 550°C with a ramping rate of 2.5 °C exhibits better electrocatalytic activity towards the electro-reduction of H_2O_2. Further, the broad linear range (0.1 to 1000 μM), low detection limit (LOD) of 0.16 μM with an excellent sensitivity is successfully achieved. The IrOx nanofibrous film can electrochromically detect the pH variation with a super-Nernst sensitivity of 80 mV/pH. Additionally, the IrOx nanofibrous film has appreciable selectivity in the presence of potentially interfering biological molecules, and its practical applicability is demonstrated in MCF-7 human breast cancer cells.

4:00pm **MD1-1-WeA-7 Bespoke Atmospheric Pressure Plasma Polymerization Process with an Acrylic Acid-Based Hybrid Precursor on Polylactic Acid Nonwoven for Antibacterial Scaffolds***, **Wei-Yu Chen (wychen@mail.mcut.edu.tw)**, Y. Chiang, T. Chu, L. Chang, J. Lee,* Ming Chi University of Technology, Taiwan

There is presently considerable interest in applying polylactic acid (PLA) nonwoven as a scaffold material in biomaterials due to its porous structure, biodegradability, favourable mechanical properties and renewable nature. However, the chemically-inert and hydrophobic surface of PLA limits its biocompatibility and poses challenges to improve its antibacterial ability through modification for inhibiting postoperative infection. In addition, PLA nonwoven is sensitive to most chemical methods for both functionalization and sterilisation. To tackle these issues without impairing the PLA nonwoven, a tailored atmospheric pressure plasma (APP) system along with a hybrid precursor of acrylic acid and silver nitrate was designed and employed for surface functionalization. In this system, electrons and reactive species created during the APP process were utilised for reducing silver nanoparticles from the hybrid precursor. By performing APP polymerization and reduction simultaneously, a silver nanoparticle-embedded and carboxyl-rich polymerized film was prepared and deposited on the PLA nonwoven surface. This study presents a comprehensive analysis of the wettability, hydrophilicity stability, surface elemental composition, biocompatibility and antibacterial efficacy of the PLA nonwoven surface functionalized using the proposed APP method. Compared with conventional methods, this process is capable of immobilising a higher percentage of carboxyl functional groups with improved efficiency on enhancing antibacterial properties.

Keywords: atmospheric pressure plasma, textile functionalization, biodegradable polymers, polylactic acid, scaffolds, acrylic acid, silver nitrate, antibacterial property

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP4-2-WeA

Deposition Technologies for Carbon-based Coatings II

Moderators: Ivan Kolev, IHI Hauzer Techno Coating B.V., Netherlands, **Biplab Paul**, PLATIT AG, Switzerland

2:00pm **PP4-2-WeA-1 DLC-Coating Against the Backdrop of High Economic Requirements***, **Jens Emmerlich (jens.emmerlich@de.bosch.com)**, D. Tiedemann,* Robert Bosch Manufacturing Solutions GmbH, Germany*; V. Gupta,* Robert Bosch Manufacturing Solutions GmbH, India*; K. Boebel,* Robert Bosch Manufacturing Solutions GmbH, Germany **INVITED**

In the pursuit of economic viability, this study delves into the strategic utilization of Diamond-Like Carbon (DLC) coatings, emphasizing the distinctive advantages offered by diverse deposition sources. Microwave and cathodic arc deposition, magnetron sputtering as well as High-Power Impulse Magnetron Sputtering (HiPIMS) emerge as pivotal techniques, each contributing unique attributes to the economic landscape. Microwave and cathodic arc deposition showcase efficiency in scalability and uniformity, optimizing the cost-effectiveness of large-scale applications. Sputtering, on the other hand, proves adept at achieving precision and controlled film properties, catering to industries with specific coating requirements. The innovative approach of HiPIMS introduces enhanced adhesion and superior film density, paving the way for extended component lifespan and reduced maintenance costs. Beyond these, the infusion of artificial intelligence (AI) emerges as a pivotal factor in predicting coating parameters and thus orchestrating cost reduction and minimizing scrap rates. By leveraging AI algorithms, the deposition process is optimized with unprecedented precision, ensuring an ideal balance between coating thickness, quality, and resource utilization. This study delves into the economic benefits derived from the application of DLC coatings in combination with AI, shedding light on their potential to enhance durability, reduce maintenance costs, and contribute to overall operational efficiency. As industries strive to navigate the intricacies of a competitive economic environment, the integration of DLC coatings emerges as a strategic imperative for achieving both performance excellence and economic viability.

2:40pm **PP4-2-WeA-3 Comparison of Performance Parameters of Carbon Coatings by Different PVD Methods***, **Martin Kopte (Kopte.Martin@vonardenne.com)**, J. Walther, B. Gebhardt, H. Proehl,* VON ARDENNE GmbH, Germany

PVD based carbon coatings show superior electrochemical resistance enabling durable coatings for metallic bipolar plates in PEM fuel cells etc. High durability and high conductivity (low interfacial contact resistance – ICR) of bipolar plates are essential, nevertheless only a cost-efficient coating method will have the chance for industrialization. Therefore, we only investigated PVD methods which allow scaling of the bipolar plate coating volume to MW and GW powers per year, which are electron-beam based PVD, as the method for highest productivity and deposition rate, and plasma based PVD which is high power magnetron sputtering and (pulsed) cathodic laser arc in our case. The electrical conductivity or ICR and corrosion performance of all those carbon coatings have been optimized to compete with gold coatings at fuel cell operation voltage. Anyway, the limits of the electrochemical corrosion performance of different carbon coatings at high electrochemical potentials occurring for split seconds on the cathode side of the bipolar plate during start/stop of a fuel cell can be crucial for the overall layer stack performance and durability. Depending on the deposition method and parameters, the properties of the carbon layer stack can highly differ from each other which leads to a different corrosion performance at such a high electrochemical potential.

3:00pm **PP4-2-WeA-4 Carbon-Based Coatings with Tailorable Properties as a Function of sp^3:sp^2 Hybridization***, **Biplab Paul (b.paul@platit.com)**, G. Wahli, J. Kluson, H. Bolvardi, A. Lümkemann,* PLATIT AG, Switzerland

Carbon-based coatings offer a variety of exceptional properties, including mechanical (hardness, elastic modulus, friction coefficient), physical (optical, electrical), chemical (chemical inertness), and biomedical (biocompatibility) properties. However, to exploit the entire range of functionalities from this class of coatings we need appropriate technologies to make the coatings preferentially engineered. For example, carbon-based coatings can be engineered to be graphite like or diamond like by preferentially tuning the ratio of sp^3/sp^2 hybridization in the coatings. The monolithic tetrahedrally-bonded coatings (ta-C), with 100% sp^3 content, provide the highest hardness, while amorphous carbon (a-C) coatings with $sp^3/sp^2 < 1$ provide softer coatings with low coefficient of friction (COF), useful for many frictionless mechanical applications. PLATIT's advanced coating units, integrating sputtering, arc and PECVD techniques, provides the unique scope to grow a plethora of diamond like coatings (DLC) with varying functionalities, categorized as DLC1 (metal doped a-C:H with sp^2 > 50%, i.e., sp^3/sp^2< 1), DLC2 (Si doped a-C:H), and DLC3 (hydrogen free ta-C with sp^3 > 50%, i.e., sp^3/sp^2> 1). The DLC1 coatings are grown by sputtering from metal targets (e.g. Ti, Cr, etc.) in acetylene atmosphere, offering the scratch proof aesthetic black coatings, useful for decorative and biomedical applications. The DLC2 coatings are grown by PECVD technique, offering the hard coatings (Hardness = 30-35 GPa, Lc2 = 30 N), useful for cutting tools and for various mechanical and electronic components. The DLC2 coatings being grown by PECVD technique, they offer the coating possibilities on difficult parts with complex geometries and miniaturized dimension (e.g., microtools). The DLC3 coatings are done by sputtering from carbon target at low temperature, providing hardness (H) > 40 GPa, and scratch resistance with Lc2 > 30 N, while COF < 0.2. With such high hardness and low COF values the DLC3 coatings offer the best coating solution for machining nonferrous materials. The physical properties of carbon-based coatings can be directly corelated to their color, which is defined by L*a*b* values. Figure 1 shows the L* values of carbon-based coatings as a function of hardness. The high L* values for DLC3 coatings indicate their higher transparency than other DLC coatings. This is attributed to the higher degree of sp^3 hybridization in DLC3 coatings as compared to that of DLC1 and DLC2 coatings.

3:20pm **PP4-2-WeA-5 Atmospheric Pressure Plasma Functionalization of Diamond Particles for Use as Quantum Sensors***, G. McGuire,* Rivis, Inc., USA*; M. Torelli,* ***Nickolas Nunn (nnunn@adamasnano.com)****, O. Shenderova,* Adámas Nanotechnologies, Inc., USA **INVITED**

Negatively charged nitrogen vacancy centers (NV^-) in diamond have unique properties making them excellent candidates for nanoscale magnetic and electric field sensors, as quantum bits as well as other applications. As quantum sensors they promise comparable sensitivity at room temperature to commonly used magnetic field sensors that must be cooled to liquid helium temperature, for example. NV centers may occur as neutral NV^0 or negatively charged NV^-, however, it is only NV^- that exhibits this magnetic sensitivity. With growing interest in the use of quantum sensor it is necessary to ensure predictable and reliable performance which requires uniform NV^- formation. However, the stability of NV^- centers is strongly influenced by the surface functionalization of diamond particles. Both nitridation and fluorination have been shown to help stabilize NV^- centers especially for shallow NV centers which provide greater sensitivity. Uniform functionalization of particles in batches is necessary for cost effective production. This has been investigated using an atmospheric pressure plasma system. Results of treatment in fluorine and nitrogen-based plasmas will be reviewed. Fluorescence spectroscopy was used as a means to determine the presence of NV^0 and NV^- following treatment and the impact of the treatment will be discussed.

4:00pm **PP4-2-WeA-7 Quantification of the sp^3 Content in DLC Films Deposited by HiPIMS Using EELS and NEXAFS***,* ***João Carlos Oliveira (joao.oliveira@dem.uc.pt)****,* University of Coimbra, Portugal*; A. Vahidi,* University of Coimbra, Pakistan*; R. Serra,* University of Coimbra, Portugal

Diamond-like carbon (DLC) films are a class of amorphous carbon materials with unique properties, including high hardness, low coefficient of friction (CoF), high wear resistance and chemical inertness, biocompatibility, and excellent electrical insulation. Therefore, these films have been commonly used in various industries, such as aerospace, automotive, biomedical, and microelectronics.

The advent of High-Power Impulse Magnetron Sputtering (HiPIMS) in the last two decades opened a new route for magnetron-sputtered coating. In HiPIMS, a large fraction of the sputtered atoms is ionized due to the several orders of magnitude higher plasma densities than in DCMS. Although HiPIMS has been successfully implemented for many metals, it is much less effective for DLC coatings deposition since C has significantly higher ionization energy and lower ionization cross-section than typical metals.

In previous works, the authors have shown that adding Ne to the plasma significantly improves the properties of DLC films deposited by Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS. Replacing half of the Ar process gas by Ne allowed for the deposition of denser films, with hardness up to 25 GPa, while still retaining a low CoF. Furthermore, the specific wear rate (SWR) of the DLC films decreased by close to 50 %, both in linearand reciprocating slidingagainst steel counterparts, being comparable with state-of-the-art hard DLC deposited by CAD and PLD.

The main objectives of the present work were to quantitively evaluate the sp^3 content in DLC films deposited by DOMS, to identify the relevant film formation mechanisms and to better understand process-properties relationships resulting from the addition of Ne to the plasma. DLC films were deposited by DOMS both in pure Ar and in mixed Ar + Ne plasmas. Quantitative evaluation of the sp^3 content in the films was performed by Electron Energy Loss Spectroscopy (EELS) and Near Edge X-ray Absorption Fine Structure (NEXAFS). Additionally, for comparison purposes, Raman spectroscopy was also used for qualitative assessments of the film's sp^3 content. Although hydrogen was not purposefully incorporated in the DLC films deposited in this work, the hydrogen content was measured by Elastic Recoil Detection Analysis (ERDA) in combination with Rutherford Backscattering Analysis (RBS). T. The surface morphology of the DLC films was characterized by Scanning Electron Microscopy (SEM) while their microstructure was investigated by High-Resolution Transmission Electron Microscopy (HRTEM).

Topical Symposium on Sustainable Surface Engineering
Room Palm 5-6 - Session TS5-WeA

Circular Strategies for Surface Engineering

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Nina Schalk**, Montanuniversität Leoben, Austria

2:00pm **TS5-WeA-1 Coated Cemented Carbides – Tooling a Sustainable Future***,* ***Uwe Schleinkofer (uwe.schleinkofer@ceratizit.com)****, C. Czettl,* CERATIZIT Austria GmbH, Austria **INVITED**

The demand for high performance manufacturing process in industries like aerospace, automotive and general engineering led to very productive and rapidly developing chip removal processes. Thuss coated cemented carbide cutting tools were developed during the last decades significantly to reduce costs and increase productivity. In addition to these needs, the sustainability aspects of such tools in terms of manufacturing and application got more and more in focus. One of the biggest contributors here is the raw material, mainly the element Tungsten for the Tungsten Carbide used in the cemented carbide. Examples of recycling technologies and closed loop scenarios to get back the worn-out tools will be summarized to show the state of the art. The influence of tailored microstructures and properties of coatings play a decisive role for the durability and performance of the tool. Furthermore, the metal cutting applications will be discussed to discuss the main factors influencing the sustainability in the chip removal process. The energy consumption of the machine is related to that of cooling pumps and additional aggregates. Examples are shown how innovative machining strategies can contribute to a more sustainable future.

2:40pm **TS5-WeA-3 Designing Selective Stripping Processes for Al-Cr-N Hard Coatings on WC-Co Cemented Carbides***, A. Kretschmer, V. Jaszfi, V. Dalbauer,* TU Wien, Institute of Materials Science and Technology, Austria*; V. Schott, S. Benedikt, A. Eriksson,* Oerlikon Balzers, Liechtenstein*; A. Limbeck,* TU Wien, Austria*;* ***Paul Heinz Mayrhofer (paul.mayrhofer@tuwien.ac.at)****,* TU Wien, Institute of Materials Science and Technology, Austria

Hard coatings like (Al,Cr)N are commonly used to protect cemented carbide cuttings tools from wear and corrosion. While such coatings increase the tool-lifetime, they also hinder the recycling effort of damaged tools. We report a new recycling strategy for coated cemented carbide tools by applying an interlayer between an arc evaporated $Al_{0.7}Cr_{0.3}N$ coating and the WC-Co substrate. By selectively dissolving this interlayer in a concentrated basic solution, the coating spalls off the substrate, which is left intact. Four bases have been tested as saturated solutions: LiOH, NaOH, KOH, and CsOH, of which NaOH showed the highest reactivity. It was therefore used for subsequent investigations. Three different methods have been tested: (1) a metallic Al-doped interlayer region between substrate and coating can be removed in 3 h at 140 °C. Depositing an (2) $Al_{0.7}Cr_{0.3}$ or (3) $Al_{0.9}Cr_{0.1}N$ interlayer leads to a significantly faster removal compared to the first method. Hereby a substrate could be fully de-coated in 4 h at only 110 °C. The reaction time was also decreased by pre-treating the samples in concentrated HCl, HNO_3, or H_2SO_4 solutions at 90 °C for 10 min before subjecting the samples to the NaOH bath. Such treated substrates were fully de-coated in 3 h at only 90 °C. While HNO_3 oxidized the substrates significantly, HCl and H_2SO_4 caused only negligible substrate damage.

3:00pm **TS5-WeA-4 Perspectives on Sustainability of Coated Metal Cutting Tools***, **Lars Johnson (lars.johnson@sandvik.com)**,* Sandvik Coromant R&D Materials and Processes, Sweden **INVITED**

Effects of climate change due to the emissions of greenhouse gases (GHG) from human activity is increasingly apparent, as predicted by climate science. Therefore, there is urgency in reducing the emission of GHG globally to meet the Paris Agreement goals of limiting the level of global warming. For the manufacturing industry, the last couple of years have been focused on the setting of targets in agreement with these goals, using frameworks as the Science Based Targets Initiative [1]. For example, Sandvik group has set targets of reduction of scope 1 and 2 GHG emissions to 50 % by 2030, 90 % by 2040, and net zero for scopes 1, 2, and 3 by 2050. To meet these ambitious yet necessary targets, improvements must be made across the full value chain; from suppliers and production, to customers' use of and the recycling of our products. Coated metal cutting tools are an interesting example to consider for the coating field, as the coating of tools have greatly enhanced their performance and service lifetime over the last half-century. Here, perspectives of the improvement in energy efficiency and reduction of GHG emissions will be discussed. Starting from the deposition process itself, where recent reports on low-temperature deposition indicates that significant reductions in energy usage are possible [2]. Yet, as further improvements are needed, implications of how the coating equipment field needs to develop will also be considered. Another perspective is the impact of performance of the total GHG emissions over the lifetime of the tool at the user, where its performance and stability determine the total contribution to the emission when manufacturing a component. Finally, the need for reuse and recycling of used tools is also considered, which also greatly affects their sustainability. In closing the need for holistic approaches will be emphasized, to avoid sub-optimizations, as it is our collective need and our collective improvements that will determine to what level we can mitigate climate change.

1. https://sciencebasedtargets.org/

2. Li, Xiao, *Toward Energy-efficient Physical Vapor Deposition: Routes for Replacing Substrate Heating during Magnetron Sputtering by Employing Metal Ion Irradiation*, Linköping University 2023, https://doi.org/10.3384/9789180752428

3:40pm **TS5-WeA-6 Towards Responsible Surface Engineering***, **Marcus Hans (hans@mch.rwth-aachen.de)**, J. Schneider,* RWTH Aachen University, Germany*; A. Matthews,* University of Manchester, UK*; C. Mitterer,* Montanuniversität Leoben, Austria

Surface engineering comprises technologies, which enable improved structural and functional surface properties. Plasma-assisted physical vapour deposition (PVD) covers a set of advanced plasma-assisted surface engineering technologies, increasingly employed to address global challenges, such as reduction of CO_2 emissions. Despite the smaller volume and mass of thin films and coatings compared to bulk materials as well as the relatively low synthesis temperatures of PVD compared to other surface engineering technologies, PVD processes are often resource-intensive. In this review we critically evaluate two important questions in this context:

1. How sustainable are PVD processes and materials?
2. Which pathways are needed for responsible surface engineering?

The consideration of energy and mass balances demonstrates that state-of-the-art PVD processes and materials are not necessarily sustainable. Responsible surface engineering comprises pathways to enhance the sustainability of processes as well as materials and involves a change in mindset of materials scientists and process engineers.

4:00pm **TS5-WeA-7 Reprocessing High Performance Cutting Tools – Performance Plus with Dedicated Coating Solutions***, **Dominik Blösch (d.bloesch@platit.com)**, C. Krieg,* PLATIT AG, Switzerland*; J. Kluson,* PLATIT a.s., Czechia*; H. Bolvardi, A. Lümkemann,* PLATIT AG, Switzerland*; B. Torp,* PLATIT Inc., Switzerland **INVITED**

In the last decades, the research and development within surface engineering has focused mainly on the enhancement of surface properties by the design of multifunctional coatings and surfaces, while the sustainability of such processes and products was typically neglected. The approach of a circular economy for surface engineering requires innovative rethinking along the lines of reducing, reusing, repairing, and recycling. In this contribution we would like to introduce circular economy strategies for surface engineering as follows:

1. Sustainability with in-house PVD production: By integrating the coating process into the tool production plant, shipping between job coating centers and production places becomes superfluous, effectively reducing CO_2 production through optimized logistics. Furthermore, one major benefit of an vertically integrated coating center is having the PVD process including all aspects of the process chain on site. This permits functional coatings to be developed for specific applications, bringing us to the next point...
2. Extend usage by "Dedicated development": Using flexible in-house PVD technology including pre- and post-treatment de-coating and washing, the life of the coated part is maximized. Each step in the process chain is optimized individually. The lifetime of the coated parts for each specific application can thereby be extended rather than applying the typical job-coating business strategy where "one size fits all". The full potential of even the best PVD coatings cannot be exploited when making compromises in terms of coating type, coating thickness and plasma treatment.
3. Resource conservation by reprocessing to restore original production quality: Worn tools are refurbished several times by resharpening just prior to reaching end-of-life, effectively preventing scrap. One challenge of reprocessing (de-coating, resharpening, cutting edge preparation, washing, coating, post-polishing) is removal of the worn and often partially oxidized PVD coating without damaging the base material below. Leveraging know-how for each individual process step, we achieve the original manufacturing quality in tools to enable multiple service lives.

Using this threefold approach of vertical integration, dedicated development, and reprocessing, substantial improvement to the sustainability of PVD-coatings is achieved without necessitating any compromise on quality.

Awards Ceremony and Honorary Lecture
Room Town & Country A - Session HL-WeHL

Bunshah Award Honorary Lecture

6:05pm **HL-WeHL-2 R.F. Bunshah Award and ICMCTF Lecture Invited Talk: Making More Wear-Resistant Surfaces via Tribochemistry – from Cutting Tools to Flying Things**, ***Yip-Wah Chung (ywchung@northwestern.edu)***[1], Northwestern University, USA **INVITED**

To most of us in the metallurgical coating community, making a component more durable against wear means providing a wear-protective coating appropriate to the substrate of that application. Given that wear is a system parameter, it is prudent to consider other components in the tribological system that can be exploited to provide enhancements of its wear resistance, particularly within lubricated systems. Remarkably, some materials, even under modest contact conditions, can interact with lubricants to produce lubricious, wear-protective carbon-based films. These tribochemical reactions offer a route to apply a renewable, protective coating precisely when and where it is needed. In other instances, having the appropriate surface chemistry may increase residence time of lubricant molecules, thus amplifying their wear protection. Exploring tribochemistry as a means to making more durable surfaces across a broad range of systems is a promising avenue of enquiry. Whether through designing specialized coatings, selecting alloy substrates with optimum compositions and microstructures, or refining lubricant formulations, we will delve into the scientific basis of this approach. We will discuss examples of coatings used for cutting tools and protective overcoats in computer disk drives to components in vehicle power systems and speculate on potential directions for future explorations.

[1] **R.F. Bunshah Awardee**

Protective and High-temperature Coatings
Room Town & Country C - Session MA5-1-ThM

Boron-containing Coatings I

Moderators: Martin Dahlqvist, Linköping University, Sweden, **Anna Hirle**, TU Wien, Austria

8:20am **MA5-1-ThM-2 Study of W and Zr Interdiffusion in the WB_2 – ZrB_2 System***, Yue Zhou (yznwb@mst.edu), S. Filipovic, D. Lipke, W. Fahrenholtz, G. Hilmas,* Missouri University of Science and Technology, USA **INVITED**

Bulk $WB_2$and ZrB_2 ceramics were fabricated by combining powder synthesis and densification methods. Powder synthesis was executed in a graphite furnace, and SPS was employed for powder densification. The raw powders used for WB_2 synthesis were commercial WO_3, B_4C, and carbon black. WB_2 was synthesized at 1600℃ in vacuum for 2.5 hours. The synthesized powder was densified at 1700℃ in vacuum under a pressure of 50 MPa for 10 minutes. For ZrB_2, the raw powders were ZrO_2, B_4C, and carbon black. Synthesis was performed at 1650℃ in vacuum for 1 hour, and the densification was accomplished at 2050℃ in vacuum under a pressure of 50 MPa for 10 minutes. The fabricated WB_2 and ZrB_2 ceramics were contacted and annealed at 2000 – 2200℃ for different periods for the W and Zr element diffusion study. The morphologies and elements concentrations of the WB_2 - ZrB_2 interfaces were characterized by TEM-EDS. Interdiffusion flux profiles were constructed based on the EDS line scans, and the interdiffusion coefficients were calculated.Finally, Arrhenius plots of the diffusions for each element were established and the corresponding activation energies were calculated.

9:00am **MA5-1-ThM-4 W-Based Thin Film Metallic Glasses Doped with Ni, Zr and B for Industrial Applications***, Antonin Kubicek (kubicek@shm-cz.cz), V. Sochora,* SHM, s.r.o., Czechia*; Z. Studeny,* University of Defence, Czech Republic*; P. Soucek,* Masaryk University, Czechia*; Z. Pokorny,* University of Defence, Czech Republic*; T. Schmidtova, J. Zenisek,* Masaryk University, Czechia

Thin film metallic glasses (TFMGs) have recently become the target of intensive research with a focus on potential applications in many sectors, where their properties can surpass their crystalline counterparts. However, their use in industry can be limited by their low hardness and Young modulus, which does not allow them to effectively withstand certain types of wear (e.g. abrasive).

As a material in the family of TFMGs, tungsten-based coatings stand out thanks to their relatively high hardness and Young modulus, and their high temperatures of glass transition and crystallization. In combination with low coefficients of friction and other outstanding properties, generally attributed to the metallic glasses, it makes them a promising candidate for potential industrial applications.

Therefore, W-Ni-B and W-Zr-B coatings were deposited using direct current magnetron sputtering. Several industrially relevant physical properties of these coatings were compared. Among others their response to Vickers indentation, surface roughness, mechanical properties, surface free energy and tribological performance in contact with industrially relevant types of materials such as Al2O3 ceramics and AISI 440C stainless steel.

9:20am **MA5-1-ThM-5 Effect of Ti and Zr Contents on the Microstructure, Mechanical Properties, and Corrosion Resistance of WZrTiB Boride Thin Films***, Wei-Xiang Fang (wayneisboy14@gmail.com),* Ming Chi University of Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan

Transition metal borides (TMBs) are known for their high melting point, wear resistance, corrosion resistance, high-temperature resistance, and high hardness. In this study, the pure Ti, Zr, and W_2B_5 targets were connected with the high power impulse magnetron sputtering (HiPIMS) power and radio frequency power, respectively, to prepare five WZrTiB boride thin films with different Ti and Zr contents. The coatings were deposited on p-type Si (100), AISI 304, and AISI 420 stainless steel substrates. The cross-sectional morphologies and crystalline structures of thin films were investigated by field emission scanning electron microscopy (FE-SEM) and X-ray diffractometry. The transmission electron microscopy was also employed to explore the microstructure and phase of each thin film. The hardness and elastic modulus of each film were further measured by a nanoindenter. A pin-on-disk tribometer was used to study the wear characteristics of these coatings. An electrochemical workstation to analyze the corrosion resistance of WZrTiB boride thin films. Effects of Ti and Zr contents on the microstructure, mechanical properties, and corrosion resistance of WZrTiB boride thin films will be explored in this work.

9:40am **MA5-1-ThM-6 Influence of Spatial Heterogeneity on Mechanical Properties in Multilayered Coatings***, Marek Gocník (marek.gocnik@unileoben.ac.at),* Montanuniversität Leoben, Austria*; M. Vidiš, T. Fiantok,* Comenius University Bratislava, Slovakia*; P. Švec, Jr.,* Institute of Physics, Slovak Academy of Sciences, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Slovakia*; M. Truchlý, V. Izai, T. Roch, L. Satrapinskyy, V. Šroba,* Comenius University, Bratislava, Slovakia*; M. Meindlhumer,* Montanuniversität Leoben, Austria*; B. Grančič, P. Kúš,* Comenius University, Bratislava, Slovakia*; J. Kečkéš,* Montanuniversität Leoben, Austria*; M. Mikula,* Comenius University, Slovak Academy of Sciences, Slovakia

Excellent mechanical properties of hard coatings based on transition metals diborides are accompanied by typical problems of these ceramic materials – affinity to crack formation and weak plastic response to deformation. In this work we focused on preparation and investigation of the structure, mechanical properties and fracture toughness of hard coatings based on superlattices (SL) and multilayers (ML) TiB_2/TaB_2 with different thicknesses of the bi-period λ in the interval of 4 to 40 nanometers, prepared by magnetron sputtering. In the work, series of analytical methods are used for the complex characterization of the coatings, and the results of the mechanical behavior are supported by the results of theoretical modelling based on density functional theory (DFT). The basic binary coatings differ in their structure and mechanical properties, where $TiB_{2.8}$ is typically overstoichiometric, has a nanocomposite character and hardness (H) exceeds 40 GPa. In the case of $TaB_{1.4}$, it is a understoichiometric coating with an amorphous structure and a lower hardness H ≈36 GPa. Their combination in the form of periodically repeating very thin layers leads to the typical behavior of nanostructured materials according to the Hall-Petch relationship when the hardness increases above 42 GPa at λ= 6 nm. Gradually increasing λ results in a subsequent decrease in H. This character of the change in mechanical behavior is hidden in the nanostructur. At a very fine modulation λ < 12 nm, local epitaxial growth occurs when lattice matching was observed at the interface of the layers. At the same time, the TiB_2/TaB_2coatings had a crystalline character across the entire thickness, and the presence of the hexagonal TiB_2 phase and TaB_2 as well was identified in the individual layers. These layers showed higher resistance to deformation during hardness measurements and therefore higher hardness values were measured. At coarser modulation periods λ > 20 nm, the crystalline character of the TiB_2 layer is preserved but the TaB_2layer again forms a disordered structure after growing a few nanometers. This softer TaB_2 phase affects the overall hardness values which are lower. Nevertheless, hardness values atthe level of ≈33 GPa still classify these coatings as extremely hard. Fracture-mechanicalbehavior, i.e., resistance to crack propagation is dependent on the thickness of the bi-period when an increase in the value of the critical stress intensity factor K was observed by approximately 16% (K_{IC}= 3.45 MPa $m^{1/2}$) in the TiB_2/TaB_2coating with λ= 8 nm compared to binary $TiB_{2.8}$, where K_{IC}= 2.974 MPa $m^{1/2}$

10:20am **MA5-1-ThM-8 Self-Formation of Dual-Phase Nanocomposite Coatings Within Ternary Zr-Cu-B System***, D. Thakur, M. Cervena, J. Houska, S. Haviar, R. Cerstvy, Petr Zeman (zemanp@kfy.zcu.cz),* University of West Bohemia, Czechia

Transition metal nitride and boride coatings with high hardness and wear resistance prepared by magnetron sputter deposition have become popular materials for many engineering applications. Since these coatings are ceramic materials, they deform predominantly elastically before catastrophic failure. One way to improve their toughness is combining them with a non-ceramic phase in a heterogenous nanocomposite structure that allows them to absorb strain energy to a certain level through plastic deformation. As a result, nanocomposite coatings with balanced mechanical properties, in addition to other functional properties, can be developed.

Recently, we have demonstrated that dual-phase nanocomposite Zr-Cu-N coatings can be prepared by the one-step process of reactive magnetron sputter deposition. The nanocomposite structure of these coatings is based on a hard nitride phase represented by ZrN and a soft phase, which can be prepared either as metallic ductile Cu or as amorphous ZrCu alloy with metallic glass behavior, depending on the deposition conditions. In the present work, we follow up on this research and investigate the possibility of preparing dual-phase nanocomposite coatings also within the ternary Zr-Cu-B system by non-reactive magnetron sputter deposition, focusing on the compositions corresponding to the stoichiometric ZrB_2 and ZrCu phases.

The Zr-Cu-B coatings were deposited in argon using four unbalanced magnetrons equipped with two ZrB_2 targets, one Zr target, and one Cu target. The magnetrons with the ZrB_2 and Zr targets were operated in dc regimes, while that with the Cu target in a high-power impulse regime. All coatings were deposited onto rotating substrates with rf biasing at different substrate temperatures. The elemental composition of the coatings was variedso that the stoichiometry of both potential phases remained the same, but only the volume fraction was changed.

The obtained results show that the structure of Zr-Cu-B coatings deposited without external heating is amorphous for all compositions investigated. Increasing the substrate temperature promotes the crystallization of the coatings, leading to the formation of a dual-phase nanocomposite structure based on a nanocrystalline ZrB_2 phase and an amorphous ZrCu phase. This effect becomes more pronounced as the volume fraction of the ZrCu phase decreases. Mechanical properties such as hardness and stress are affected by the volume fractions of both phases and exhibit a dependence on the substrate temperature. The structural investigations are complemented by ab-initio simulations, which show very good agreement with experimental results.

10:40am **MA5-1-ThM-9 High-Rate Deposition of Ultrathick Boron Carbide Coatings for Inertial Confinement Fusion***, **J. B. Merlo (merlo3@llnl.gov)**, K. Kawasaki, J. Forien, S. Gonzalez, G. Taylor, S. Shin, L. Bayu Aji, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Boron carbide has attractive properties for several applications, including fuel capsules for inertial confinement fusion (ICF). For ICF applications, boron carbide needs to be in the form of a hollow spherical shell, about 2 mm in diameter, with a wall thickness of about 100 microns. Sputter deposition of such non-planar ultrathick coatings with submicron density uniformity has many challenges. Remaining challenges include relatively low deposition rates, delamination and fracture due to residual stress, and the growth of nodular defects. Here, we systematically study effects of the deposition rate and substrate tilt on properties of amorphous boron carbide films deposited by planar magnetron sputtering on stationary substrates. Our focus is on optimizing the deposition rate and minimizing residual stress and the density of nodular defects. As a result of this systematic study, we demonstrate low-stress, ultrathick boron carbide films fabricated by magnetron sputtering with deposition rates approaching 10 microns per hour.

11:00am **MA5-1-ThM-10 Taking Advantage of Unique Lattice Sites – How to Find New Boron-Based Materials Through Large-Scale Stability Predictions***, **Martin Dahlqvist (martin.dahlqvist@liu.se)**, A. Carlsson, J. Rosen,* Linköping University, IFM, Materials Design, Sweden

Boron-based materials are highly desirable for their promising mechanical properties, rendering them ideal for various industrial applications. Previous experimental work has demonstrated that mixing two metals at a given ratio can result in preferential occupation of different lattice sites, leading to chemically ordered phases, e.g., W_2CrB_2 and W_4CrB_3. However, to experimentally identify new materials with improved properties, being simultaneously composed of abundant elements, is a challenging task. A useful tool for such mission is phase stability calculations which have proven to be useful for identifying stable and synthesizable candidates. In this work, we have searched for known binary metal borides which have two unique metal sites in their respective prototype structures, that may have potential for forming chemical order when mixing two metals, M' an M''. The metal sites in these prototypes were then pair-wise decorated by combing 44 different elements resulting in over 20 000 ternary compounds. The thermodynamic phase stability of these compounds was assessed by evaluating the formation enthalpy with respect to competing phases. Almost 200 compounds were identified as stable, and for selected systems mechanical and elastic properties were calculated.

Functional Thin Films and Surfaces
Room Palm 1-2 - Session MB3-1-ThM

Nanomaterial-based Thin Films and Structures I

Moderators: Ondrej Kylian, Charles University, Prague, Czechia, **Jörg Patscheider**, Evatec AG, Switzerland

8:00am **MB3-1-ThM-1 Dual Scale Structures Based on Nanocolumns and Nanoparticles***, **Lidia Martinez (lidia.martinez@icmm.csic.es)**,* ICMM-CSIC, Spain*; J. García-Martín,* IMN-CSIC, Spain*; Y. Huttel,* ICMM-CSIC, Spain **INVITED**

Like the formation of alloys that combines the properties of different elements resulting in novel materials, the combination of different shapes and dimensions also leads to materials having novel properties, especially at the nanoscale. We will first briefly present the ultra-high vacuum physical methods used to grow the Nanocolumns (NCs) by Glancing Angle Deposition (GLAD) [1-2] and Nanoparticles (NPs) fabricated by means of a Multiple Ion Cluster Source (MICS) [3-4], highlighting the control over chemical composition, shape and dimensions of the fabricated nanostructures.Later, we will present some examples where the combination of NCs and NPs leads to synergic effects using materials like gold, silver, titania or iron oxide. In particular, we will present some examples of application as antibacterial coatings [5], photo-induced self-cleaning surfaces [6], SERS substrates [7], controlled wettability or catalysis among others.

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4. D. Llamosa et al., "The ultimate step towards a tailored engineering of core@shell and core@shell@shell nanoparticles", Nanoscale 6, 13483 (2014).

5. D. Medina-Cruz et al., "Synergic antibacterial coatings combining titanium nanocolumns and tellurium nanorods", Nanomedicine: Nanotechnology, Biology, and Medicine 17, 36–46 (2019).

6. F. Fresno et al., "Photo-Induced Self-Cleaning and Wettability in TiO2 Nanocolumn Arrays Obtained by Glancing-Angle Deposition with Sputtering", Adv. Sustainable Syst., 2100071 (2021).

7. G. Barbillon et al., in preparation.

8:40am **MB3-1-ThM-3 MGA Nanoparticle Thin Films for Enhanced Hydrogen Gas Sensing: Synthesis, Modeling, and Characterization***, **Stanislav Haviar (haviar@kfy.zcu.cz)**, T. Kozák, K. Shaji,* University of West Bohemia, Czechia*; T. Košutová,* Charles University, Czechia*; B. Prifling, V. Schmidt,* Ulm University, Germany*; J. Čapek,* University of West Bohemia, Czechia

Thin films formed by nanoparticles from various metal oxides (WO_x, CuO_x, PdO_x) were synthesized using a magnetron-based aggregation cluster source (MGA). The mixing ratios of the oxide particles were adjusted to achieve the best conductometric sensorial response toward hydrogen gas.

(i) Single-material films were investigated utilizing electron microscopy, energy dispersive and photoemission spectroscopies and small-angle x-ray scattering (SEM, TEM, EDS, XPS, SAXS).

(ii) Results of these analyses were used as an input for hard-sphere packing algorithm simulations generating models of synthesized mixed-materials films.

(iii) Optimized finite element modeling was used to calculate the conductivity of modeled films. Various material parameters were adjusted to receive a quality estimation of mixed-materials behavior.

(iv) Output of the simulation was used as a lead for synthesizing films with optimum ratios of materials to generate nanoheterojunction-rich materials.

(v) Promising candidates were assembled as conductometric gas sensors and tested towards hydrogen gas.

In the talk, the details of MGA system orchestration will be discussed. Special attention will also be paid to the simulation strategy and the process of simulation results verification.

See illustrative figures in the Supplemented file.

[1] Batková; Kozák, T.; Haviar, S.; et al. *Surf. Coatings Technol.* 2021, **417**

[2] Haviar, S.; Čapek, J.; Batková, Š.; et al. *Int. J. Hydrogen Energy* 2018, **43**

[3] Shaji, K., Haviar, S., Zeman P et al. *Surf. Coatings Technol.*Controlled sputter deposition of oxide nanoparticles-based composite thin films, *submitted*

9:00am **MB3-1-ThM-4 Enhanced Dimer Sputtering and Production of Nanoparticles by Pulsed Magnetron Discharge**, *P. Čurda,* University of South Bohemia, Czechia*; R. Hippler,* University of Greifswald, Germany*; M. Cada,* Institute of Physics, Czech Academy of Sciences, Czechia*; **Ondřej Kylián (ondrej.kylian@gmail.com)**,* Charles University, Czechia*; Z. Hubicka,* Institute of Physics, Czech Academy of Sciences, Czechia*; V. Stranak,* University of South Bohemia, Czechia

This study investigates the initial stage of nanoparticle formation in physical vapor deposition processes, emphasizing the role of atomic dimers as cluster nuclei. The process of metal nanoparticle formation and growth by gas aggregation starts with the release of free metal atoms and nuclei through magnetron sputtering followed by thermalizing collisions and by atom attachment and coagulation. By employment of energy-resolved mass spectrometry and scanning electron microscopy imaging, dimers originating in the discharge gas phase ($ArCu^+$, Ar_2^+) and dimers sputtered directly from the target (Cu_2^+) were examined. Our findings reveal that sputtered Cu_2^+ dimers which carry the high-energy tail of the Thompson distribution play a crucial role as nanoparticle nuclei. Haberland's concept aggregation source confirmed that the population of Cu_2^+ dimers is directly proportional to the mass transported by nanoparticles. The gas aggregation process can be optimized for enhanced nanoparticle production by the employment of a pulsed discharge, which leads to increased energies of impinging Ar ions and enhanced sputtering of metal dimers. There exist optimal conditions, where the dimer production is increased, but the plasma is not too hot for the nuclei and nanoparticles to decay. Under such conditions, the production rate can be increased by a factor of 10. This enhancement in nanoparticle yield is achieved with the same invested power as for the DC sputtering. Furthermore, the proposed mechanism and the role of dimers may be material-independent, as qualitative agreement was also observed for Ag nanoparticles. This research contributes to a deeper understanding of the fundamental mechanisms governing the early stages of nanoparticle synthesis through physical vapor deposition.

Acknowledgment

The research was financially supported by the Czech Science Foundation through the project GACR 21-05030K and by the Ministry of Education, Youth and Sports of the Czech Republic through the project "Solid state physics for the 21st century" CZ.02.1.01/0.0/0.0/16_019/0000760.

9:20am **MB3-1-ThM-5 Plasma Polymer - Ag Nanocomposites: Is the Gas Aggregation Source of Nanoparticles an Appropriate Technique for Their Synthesis?**, ***Zdenek Krtous (krtousz@gmail.com)**, T. Kosutova, P. Pleskunov,* Charles University, Prague, Czech Republic*; B. Baloukas, L. Martinu,* Polytechnique Montréal, Canada

Metamaterials or metasurfaces represent the emerging field of nanotechnologies focusing on pushing the limits of the standard optical coatings. One of the most promising types of metamaterials are plasmonic nanocomposites based on metallic nanoparticles. The usefulness of such materials was demonstrated for absorbers, plasmonic coloration, transparent electrodes and optical filtering. In this project, we investigate a classical type of plasmonic metamaterials – silver nanoparticles embedded in a plasma polymer matrix, prepared by simultaneous co-deposition of both organic and metallic components. The organic matrix is prepared by the recently developed Plasma Assisted Vapour Thermal Deposition (PAVTD). The PAVTD allows one to control the chemical composition and, as a result, the optical and mechanical properties of the matrix within a wide range. We investigate two different cases of synthesis of metallic nanoparticles. In the first case, which could be considered a more classical approach, the nanoparticles are formed by co-deposition of silver atoms by magnetron sputtering. The silver atoms form nanoparticles inside the polymeric matrix. The growth rate of the matrix limits the size of the growing inclusions. In the second case, the Gas Aggregation Source (GAS) was used to fabricate nanoparticles in the gas phase. Subsequently, pre-fabricated nanoparticles are landing on and being embedded into the growing matrix. Due to the different nanoparticle growth mechanisms, the optical properties of such nanocomposites are not equivalent even at similar filling factors. Finally, the applicability of the PAVTD – GAS films is demonstrated by the fabrication of a nanocomposite-based Bragg´s reflector.

9:40am **MB3-1-ThM-6 Fabrication of Ag-modified $BaTiO_3$ Nanorod Arrays and their Properties of Piezo-Photoelectric Catalysis**, ***Yu-Han Hsu (emilyanna5428@gmail.com)**, K. Chang, Y. Chiu,* National Cheng Kung University (NCKU), Taiwan

α-Fe_2O_3 is an attractive n-type semiconducting material in the visible-light photocatalytic application because of its characteristic of narrow energy band gap characteristics for absorbing the visible light. The optical property can be tailored through morphology control, elemental doping, or compositing with other materials. However, studies on the α-Fe_2O_3 nanorod arrays with the metalic nanoparticles directly through hydrothermal processes for the fabrication still lacking. In this study, well-aligned α-Fe_2O_3 nanorod arrays/Au nanoparticles were synthesized through a facile hydrothermal reaction and solution-based method. To optimize the morphology of Fe_2O_3 nanorod arrays for compositing with Au, hydrothermal parameters, including concentrations and types of precursor solutions, reaction time, and temperatures, were manipulated. And then, it composited with different amounts and sizes of Au nanoparticles, finding an optimized condition for the visible-light photocatalytic application with the LSPR effect from nanogold. X-ray diffraction and scanning electron microscopy were employed to determine the phase and morphology of the resultant composite samples. In addition, the interfaces between the materials were observed from the transmission electron microscopy. Uv-vis spectroscopy was utilized to measure the absorption and the energy band gaps of the materials, which were significant for building the energy band diagram of the system. The composites were further used in the visible-light photocatalytic application.

Keywords: α-Fe_2O_3 nanorod arrays, Au nanoparticles, hydrothermal reaction, LSPR, visible-light photocatalysis

10:20am **MB3-1-ThM-8 Combinatorial Approach of Zr-Ti-Al Thin Films: Understanding Glass-Forming Behavior, Morphological Changes, and Thermal Stability**, ***Zil Fernández-Gutiérrez (zil.fernandez-gutierrez@univ-lorraine.fr)**, D. Pilloud, S. Bruyère, S. Hupont, J. Pierson,* Institut Jean Lamour - Université de Lorraine, France

The advancement of nanotechnology relies significantly on developing thin film metallic glasses (TFMGs), given their distinct attributes such as high strength and corrosion resistance at the atomic level. The exploration of new TFMG systems holds the potential to revolutionize technology, enhancing performance and durability across applications in electronics, coatings, and medical devices. In this study, we employed a combinatorial approach to investigate the glass-forming ability of Zr-Ti-Al thin films synthesized through magnetron co-sputtering. Our findings demonstrate that controlled variations in chemical composition influence the amorphous or crystalline state of the layers, with an observed reduction in grain size with increasing the Al content. The SEM images illustrate notable modifications in surface and cross-sectional morphology. However, despite the glassy form, electrical property determinations reveal that TFMGs maintain consistent electrical characteristics with their ternary crystalline counterparts of Zr-Ti-Al films. Values ranging between approx. 100 and 200 µΩ·cm have been measured for either crystalline or amorphous films. Lastly, the thermal stability of Zr-Ti-Al TFMGs was assessed through TEM and Raman analyses following annealing processes. The crystallization starts at temperatures higher than 300 °C. Since the annealing has been performed in air, the formation of oxides (ZrO_2 and TiO_2) has been evidenced by Raman.

10:40am **MB3-1-ThM-9 The Impact of Laser Annealing on Electrical Resistivity and Mechanical Properties in Highly(111)-Oriented Nanotwinned Ag Thin Films**, ***Tsai-Shaun Kuo (shirlley.kuo2000@gmail.com)**, C. Yang, F. Ouyang,* National Tsing Hua University, Taiwan

Recently, with the trend of miniaturization in microelectronic devices, resistivity plays a crucial role in the performance of electronic devices. Isothermal furnace annealing is usually conducted to enable grain growth to possess lower resistivity on interconnects; however, furnace annealing is usually time-consuming. By approach of locally abnormal grain growth, the electrical resistivity could be much more improved and still remains good mechanical properties.

In this study, we proposed using laser annealing to facilitate the grain growth on the highly (111)-oriented nano-twinned Ag thin film. The laser pulse frequency was fixed at 100 Hz, the pulse width was fixed to 1 ms and the laser is incident from the side of the silicon substrate to heat the film in purpose to avoid high reflectivity of the silver thin film surface. The laser annealing experiments were conducted with low laser annealing power (8.54, 16.44, 19.08, 24.35 W) in long annealing time (3 and 5 minutes) or high laser annealing power (50, 60 W) win short annealing time (4-10 seconds). For temperature controlment, the thermal couple was used to measure the temperature in the central of substrate during the laser annealing process. Dual-beam focused-ion beam system (FIB) was used to observed the cross-sectional microstructure images of as-deposited and laser annealed silver films. And the surface orientation was analysed by electron backscatter diffraction (EBSD). X-ray Diffractometer (XRD) was introduced in detecting the preferred orientation. The surface microstructure was investigated by Scanning electron microscope (SEM). Finally, four-point probe was used to detect the resistivity and Nanoindenter (NIP) was used to study the hardness.

Exceptional abnormal grain growth of Ag films can be achieved at 210 ℃ in 3 min, being much faster and lower temperature than furnace annealing. The microstructural and property evolution during laser annealing and the corresponding mechanism were discussed in detail below.

11:00am **MB3-1-ThM-10 Stainless-steel Nano-Pyramid Structure Coating to Enhance Oil/Water Separation***, **Helmi Son Haji (d11104807@mail.ntust.edu.tw)**, J. P. Chu,* National Taiwan University of Science and Technology, Taiwan

The process of separating oil and water is crucial for modern human life. Oil waste can affect living environments and impact human health. Various industries require breakthroughs in this field, including the food, petrochemical, oil mining and semiconductor industries. The urgent need for oil waste treatment causes a growing focus on the research of oil effluent. An oil-water separation process's scalability, efficacy and efficiency are crucial factors in the successful purification of oily wastes. Therefore, this research proposed a highly scalable, low-cost production method for fabricating membranes with outstanding selectivity and permeability. The proposed membrane comprises mixed cellulose ester (MCE) with stainless steel (SS) nano-pyramidal structure coating on its surface. The unique morphological characteristics of nano-pyramidal stainless-steel coating exhibit superhydrophilic properties and superoleophobic underwater, which prevent oil adhesion and enable exceptional oil separation performance, achieving an impressive efficiency of up to 99% in the process of filtering oil with various solutions, reaching high recyclability up to 99% in four cycles, also have good stability performance at low until high temperature (60℃), and compatible with diverse environmental conditions from acidic (pH 1) to alkaline (pH 14) [1].

Keywords: Stainless-steel, Coating, MCE.

11:20am **MB3-1-ThM-11 Study of Interfacial Reactions in Artificially Nanolayered Mg-Mo-N Thin Films***, B. Julien, **Andriy Zakutayev (andriy.zakutayev@nrel.gov)**,* National Renewable Energy Laboratory, USA

Ternary nitrides are an exciting class of materials for various applications such as hard coatings, LEDs, magnets, superconductors, or topological materials. Many of the most interesting nitride phases are predicted to be metastable. In bulk synthesis, reactions necessary occur at the interfaces, and so solid-state diffusion is required to drive complete nucleation. This leads to condition of high temperature and long-time reactions, which can bypass metastable phases.

Thin-film synthesis of ternary nitrides often leads to cation-disordered structure yet predicted unstable by thermodynamics calculation. Post-deposition thermal annealing can sometimes overcome energetic barriers and lead to nucleation of the layered targeted phase. However, the kinetic window is often narrow and requires high temperatures to trigger atomic diffusion. Therefore, nanolayered thin-film structures with designed diffusion lengths and interface densities offer an opportunity to overcome this situation.

To investigate the interfacial nucleation, we propose to reduce the atomic diffusion length (typically ~1um in bulk synthesis) by fabricating multilayer nanolaminate structures of the binary precursors, as a model system. Post-deposition annealing, interlayer thickness, and the multilayer period modulation are studied as a mean to control the structural properties of the nitride thin films.

In this study, we focus on the Mg-Mo-N system, in which $MgMoN_2$ phase is predicted to be thermodynamically stable and exhibits a natural layered structure built up by alternating layers of edge-sharing MgN_6 octahedra and MoN_6 trigonal prisms. This makes it a good candidate for this work as in a thermodynamics point of view, the structure tends to naturally form a layered structure and should be more favorable to nucleate from a layered precursor.

The nanolayered films are fabricated by RF co-sputtering, using a computer-controlled sputtering chamber featuring programmable shutters in front of each sputter cathode, allowing us to control the modulation sequence during the deposition. One major challenge here is to minimize the interfacial roughness during the deposition, limiting the intermixing at the interfaces. Once co-calibration of deposition rate and composition is established for both binary phases, a set of multilayer films with different modulation period and composition are characterized by X-ray reflectivity and diffraction. The morphology and the composition of the interfaces are further characterized by electron microscopy.

Tribology and Mechanics of Coatings and Surfaces
Room Town & Country B - Session MC3-2-ThM

Tribology of Coatings and Surfaces for Industrial Applications II

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Rainer Cremer**, KCS Europe GmbH, Germany, **Stephan Tremmel**, University of Bayreuth, Germany

8:00am **MC3-2-ThM-1 Interactions between Coatings/Surfaces and Lubricants: How to Manage the Tribochemical Wear in ZDDP-lubricated DLC Coatings?***, **Maria Isabel De Barros (maria-isabel.de-barros@ec-lyon.fr)**,* Laboratory of Tribology and System Dynamics Ecole Centrale de Lyon, France **INVITED**

Solid and liquid lubrication play a key role in reducing energy consumption and wear behaviour of mechanical parts. Regarding the high importance of Diamond-Like-Carbon (DLC) coatings in the transportation and wind energy sectors, it is necessary to investigate their friction and wear mechanism in lubricated conditions. For these DLC films, mainly carbon and hydrogen are known to have a high chemical inertia under static conditions towards their environment. But in a lubricated sliding contact, a kind of complex "chemical reactor" is operating under severe dynamic conditions. The reason based on mainly the possibility of breaking of C-H and C-C bonds under the effect of shear, which leads to the emergence of C° free radicals or "dangling bonds" on the rubbed surface of thecoatings. A wide variety of tribochemical reactions with the lubricant molecules follow at the contact asperities, areas subjected to high pressure.

It was recently showed that very hard sp3-hybridized hydrogen-free amorphous carbon (ta-C) lubricated in the presence of the ZDDP (zinc-dialkyldithiophosphate) additive shows significant wear, associated with the absence of phosphate- type tribofilm formation. The wear is related to a preferential reactivity between the sulphur atoms released by the ZDDP and the reactive carbon atoms formed on the ta-C surface. In contrast, the softer DLCs, hydrogenated DLC and non-tetrahedral a-C, show much lower wear rates and the formation of ZDDP-derived tribofilms with higher coefficients of friction. Thus, the decomposition of ZDDP appears to be governed primarily by contact pressure at the bearing asperity scale, but the surface and subsurface sulphur transport that leads to tribofilm formation or significant wear and, results in a change in material properties at the nanoscale, depends on both stiffness and surface chemistry. In this context, the understanding of the reactivity of different DLC coatings representative of the variety of DLC found on the market and industrial applicationsin terms of H content and mechanical properties, and the interplay of mechanical and chemical contributions is of primary importance. Ultimately, itis targeting to optimize "multi-functional DLC surfaces", combining mechanical properties and surface chemistry, to better control their friction and wear performances in application.

8:40am **MC3-2-ThM-3 Coating of Plastic Parts with Tetrahedral Amorphous Carbon for Wear Protection Using Laser-Arc Technology***, B. Gebhardt, M. Holzherr, M. Kopte, H. Pröhl, R. Seifert, **Marc Tobias Wenzel (Wenzel.MarcTobias@vonardenne.com)**,* VON ARDENNE, Germany*; F. Kaulfuß, F. Härtwig,* Fraunhofer IWS, Germany

Laser-arc technology is a well-established method to produce hydrogen free ta-C coatings. Such coatings are known to provide outstanding wear properties and reduced friction for a variety of applications like piston rings, tappets, motorcycle chains or cutting tools.

Plastic components are ubiquitous in industry and everyday life. The use of plastic parts instead of metal components enables savings in cost, weight, and energy. Yet, coating of plastics with ta-C poses challenges due to the low hardness and limited temperature resistance of the substrates.

Injection molded plastics are shown to be suitable for ta-C coating on industrial scale using laser-arc. Reinforced and non-reinforced parts of PA12 and PEEK have been coated and investigated. The promising coating variants were transferred to a gear system. In dry operation the ta-C coating increased the lifetime by a factor of five.

In addition, we will present an up-scaled laser-arc module allowing increase of productivity and reduction of coating cost.

9:00am **MC3-2-ThM-4 Investigation of the Mechanical and Tribological Properties of TiBCN Thin Films***, **Cennet Yıldırım (cennetyildrm@gmail.com)**,* Turkish Energy, Nuclear and Mineral Research Agency – Boron Research Institute / Istanbul Technical University, Türkiye, Turkey*; Ö. Kısacık, H. Doyuran, C. Eseroğlu,* Turkish Energy, Nuclear and Mineral Research Agency – Boron Research Institute, Türkiye, Turkey*; E. Kaçar,* Hakkari University, Türkiye, Turkey

Recently, coatings with a nanocomposite structure have become increasingly significant compared to monolithic coatings, owing to their advantageous properties such as high hardness and wear resistance. Particularly, the impact of boron and carbon on coating hardness has led to a growing application of boronrich and carbide-rich nanocomposite coatings. In the scope of this study, nanocomposite films with a TiBCN structure were produced on M2 HSS using titanium and B_4C magnetron targets. To enhance adhesion on steel surfaces, Cr-CrN bond layers were deposited using the cathodic arc physical vapor deposition (CaPVD) technique, and films with different compositions were subsequently produced by varying the power of titanium and B_4C targets. Cross-sections of the produced films were examined using electron microscopy, and surface morphologies, as well as film thicknesses, were determined. Phases formed were analyzed by XRD, Raman, and FTIR, and changes in bond structures and depth profiles were identified using XPS. The hardness of the produced films was measured using the nanoindentation method, and adhesion was examined through scratch tests. Wear behaviors against alumina balls were investigated at different temperatures ranging from room temperature to 600 °C. Wear volumes were determined using optical profilometry, and wear rates and friction coefficients were calculated. The formed tribo-films were characterized using XPS analysis. It was observed that the amount of boron and carbon incorporated into the films had an influence on hardness and wear behaviors.

9:20am **MC3-2-ThM-5 Investigating the Influence of B, C, and N on the Tribo-mechanical Properties of the Chemically Complex TiSiBCN Thin Film using Design of Experiments***, W. Tillmann, **Julia Urbanczyk (julia.urbanczyk@tu-dortmund.de)**, A. Ebady,* Institute of Materials Engineering, TU Dortmund University, Germany*; A. Thewes, G. Bräuer,* Institute for Surface Technology, TU Braunschweig, Germany*; N. Lopes Dias,* Institute of Materials Engineering, TU Dortmund University, Germany

TiSiBCN thin films show promising properties like high hardness and improved tribological behavior. Adjusting the chemical composition can tailor the properties of these thin films. To investigate this influence, usually one element is varied. However, the interplay and influence of especially the light elements B, C and N on the tribo-mechanical properties of chemical complex TiSiBCN thin films remain unclear. Therefore, a Design of Experiment using a Central Composite Design (CCD) was employed to investigate the influences of these light elements on the tribo-mechanical properties of TiSiBCN thin films. TiSiBCN with varying chemical compositions were grown in a magnetron sputtering process by adjusting the cathode power of TiB_2/$TiSi_2$ composite targets and the gas flow rates of C_2H_2 and N_2.

X-ray diffraction (XRD) analysis revealed crystalline phases based on Ti, TiN, TiC, and TiB_2, with varying degrees of crystallinity dependent on the chemical composition. Depending on the chemical composition, the TiSiBCN thin films demonstrate a broad spectrum of mechanical properties, with hardness and elastic modulus ranging from 20.2 to 39.7 GPa and from 222.3 to 405.0 GPa, respectively. Notably, the B content significantly affects the mechanical properties, with the highest hardness and elastic modulus observed at 46.0 at.–% B. In tribometer tests against Al_2O_3 under dry friction at room temperature, the TiSiBCN thin films also exhibit a broad spectrum of tribological properties, with the coefficients of friction (CoF) between 0.62 and 0.89 and wear rates between 6.4×10^{-5} and 12.2×10^{-5} mm^3/Nm. The lowest CoF of 0.62 with a wear rate of 7.7×10^{-5} mm^3/Nm is obtained for TiSiBCN with high amounts of 31.1 at.-% C and 33.5 at.–% N, while high 31.7 at.–% C and low 11.2 at.–% N contents favor the lowest wear rate of 6.4×10^{-5} mm^3/Nm with a CoF of 0.74. The tribological results reveal the significant influence of C and N on friction and wear, with TiSiBCN displaying reduced friction and wear tending to have lower hardness. Consequently, TiSiBCN thin films with either high hardness or enhanced friction and wear performance are attainable by adjusting the chemical composition.

Depending on the application requirements, the content of the light elements is decisive for the properties of TiSiCN thin films. The CCD provides insights into the intricate interplay between the chemical composition and tribo-mechanical performance of TiSiBCN. Adjusting the concentrations of B, C, and N within TiSiBCN is crucial for tailoring the tribo-mechanical behavior to meet the specific requirements of applications.

9:40am **MC3-2-ThM-6 Effect of Alloy Modification on the Wear Protection Coatings Made of Ni- and Co-Based Materials and Surface Machinability via Ultrasonic Milling Process***, **Maraike Gräbner (maraike.graebner@tu-clausthal.de)**,* Clausthal University of Technology, Institute of Welding and Machining, Germany*; M. Giese,* Federal Institute for Materials Research and Testing, Germany*; K. Treutler,* Clausthal University of Technology, Intitute of Welding and Machining, Germany*; S. Lorenz, V. Wesling,* Clausthal University of Technology, Institute of Welding and Machining, Germany*; D. Schröpfer, T. Kannengießer,* Federal Institute for Materials Research and Testing, Germany

The development of technologies for climate-neutral energy generation is an important contribution to the reduction of greenhouse gases, whereby the efficient use of material systems is a key factor. Wear-resistant coatings are required for highly efficient and economical steel components in plant, process and power plant engineering to withstand the high corrosive, tribological, thermal and mechanical stresses. Co alloys are utilized as wear protection coatings for steel components that are customized to the specific application. The research area of interest is the substitutability of Co alloys with Ni-based wear protection systems. This research endeavour considers the price and supply uncertainties as well as the escalating demands on corrosive load-bearing capacity at elevated temperatures.

The wear-resistant alloys NiMoCrSi (Colmonoy C56) and CoMnCrSi (Tribaloy T400) have been modified through various alloying additions and subsequently applied to a carbon-manganese steel S355 using the Plasma Arc Transferred Arc (PTA) welding process. The influence of the alloying additions on the microstructure as well as on the formation of the hard phases of the build-up welds is compared. The inclusion of the alloying element Nb, for instance, results in the formation of a more refined hard phase and reduces the machining force required for the C56 and T400. The incorporation of Al results in an enhancement of the cutting forces for the C56, as the hard phases exhibit more needle-like structures. Al reduces the cutting forces of the T400. The wear potential of the modified build-up welds of the C56 and T400 is also being examined In the industrial sector, there is a growing demand for functional surfaces of superior quality. Therefore, it is imperative to ensure the machinability of the wear protection layers to achieve clearly defined contours. The machinability of the build-up welds is investigated using ultrasonic milling. The optimization of the demanding machining conditions through alloy modifications of the Co- and Ni-based alloys without impairing the wear protection potential and using the ultrasonic-assisted milling process is a joint project of BAM and ISAF at Clausthal University of Technology (Fosta P1550/IGF 21959 N).

10:20am **MC3-2-ThM-8 An Alternative Thermal Route to Improve an Aluminum Alloy Mechanical and Tribological Properties through Deposition of NiP Coating***, R. Davies,* Pontificia Universidade Católica do Parana, Brazil*; M. Soares,* Universidade Tecnologica Federal do Parana, Brazil*; F. Amorim, P. Soares, C. Neitzke, **Ricardo Torres (ricardo.torres@pucpr.br)**,* Pontificia Universidade Católica do Parana, Brazil

This research aims to improve the main limitations of aluminum alloys: mechanical and wear resistance through the deposition of the nickel-phosphorus (NiP) coating. Due to the natural formation of a dense oxide layer on the aluminum surface, the NiP deposition process often becomes more costly. Furthermore, it is common for NiP coatings to undergo a post-heat treatment to increase hardness due to crystallization and Ni3P precipitation and further increase adhesion through the interdiffusion layer with the substrate. Finding an adequate interdiffusion temperature is challenging, as aluminum significantly decreases its mechanical properties. It would probably soften or even melt if subjected to an interdiffusion temperature of around 400 ºC. This work aimed to find a suitable process for depositing an autocatalytic nickel-phosphorus coating on AlCu4Ti aluminum alloy in an alternative thermal route using the aluminum typical aging temperature and time treatment to create an interdiffusion layer between NiP and aluminum substrate in a single step. The typical aging temperature of the alloy was investigated, i.e., 200 ºC, as well as the minimum temperature for the beginning of Ni3P precipitation, i.e., 250 ºC.

The SEM and EDS analyses showed a NiP layer of about 40 µm, well adhered, homogeneous, without substrate exposure, and a high phosphorus content (≈ 10%) formed in the aluminum alloy surface. The interdiffusion and aging treatment condition at 250ºC/16h resulted in the highest hardness of both aluminum and NiP coating.

10:40am **MC3-2-ThM-9 High-Temperature Tribology of Cathodic Arc Deposited Altin Protective Coating***, Aljaž Drnovšek (aljaz.drnovsek@ijs.si), P. Šumandl,* Jožef Stefan Institute, Slovenia*; Ž. Gostenčnik,* jožef Stefan Institute, Slovenia*; J. Kovač, M. Čekada,* Jožef Stefan Institute, Slovenia

The AlTiN coating is a popular hard coating for high-temperature applications. However, the most commonly used method for depositing this coating on cutting tools, cathodic arc evaporation, can result in a relatively rough surface due to micro-droplet emission. This roughness and embedded droplets in the coating matrix can significantly affect the coating's wear and friction properties.

Our objective was to assess the wear and friction properties of the AlTilN coating during both the running-in and steady-state periods under varying temperature conditions. To evaluate the performance of the AlTiN hard coating, we conducted tribological tests using a high-temperature ball-on-disc tribometer. The tests were conducted using an Al_2O_3 ball as a counter body at different temperatures. We varied the test duration at specific temperatures, ranging from 50 up to 140,000 cycles, to examine the effect of test length on the coating's wear and friction properties.

The results indicated that the coating experienced the highest wear during the room temperature test. Conversely, the wear during the running-in phase and steady-state friction were the lowest at 250ºC. As the temperature increased, the wear rate rose, which we attributed to increased tribo-oxidation and fatigue caused by the high test lengths. Ultimately, the coating delaminated from the WC-Co substrate at the highest temperature. The asperities on the coating surface due to micro-droplets played a significant role in friction and wear behaviour, as they were a primary source of wear particles and the first spots of oxidation on the coating. We show that the running-in phase depends mainly on the surface condition (asperities density) at room temperature tests. In contrast, at high temperatures, the formation of a stable tribo-oxide layer in the wear track elongates this period.

We conducted detailed 3D profilometry, SEM and FIB analyses on numerous samples to determine the wear mechanisms at different stages of high-temperature wear. In addition, we conducted secondary-ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy studies to evaluate the extent of oxidation and identify different species present in the oxide layer.

The combination of these analyses allowed us to gain a comprehensive understanding of the wear mechanisms and behaviour of the AlTiN coating at high temperatures. We could identify the dominant wear mechanisms and how they evolved over test length by analysing the samples at different wear stages.

11:00am **MC3-2-ThM-10 Nanomechanical and Tribological Properties of Conversion Coatings for Railway Rolling Bearing Applications***, Esteban Broitman (esteban.daniel.broitman@skf.com), A. Ruellan,* SKF - Research and Technology Development, Netherlands*; R. Meeuwenoord,* SKF Research and Technology Development, Netherlands*; D. Nijboer, V. Brizmer,* SKF - Research and Technology Development, Netherlands

In this study, different conversion coatings have been compared in terms of friction performance based on a single-contact oil-lubricated tribometer and on a grease-lubricated double row bearing friction test rig ran under relevant operating conditions for a railway application. Conversion layers like zinc-calcium-phosphate, manganese-phosphate and tribological black-oxide deposited onto AISI 52100 bearing steel have been compared to uncoated steel in terms of nanomechanical and tribological properties.

Our results demonstrate that the optimum tribological black-oxide conversion layer can reduce friction by more than 25% on rolling/sliding raceway contacts (ball-on-disk) and up to 80% on the sliding flange contacts (roller-on-disk), which share a significant portion of power losses in roller bearing units. Results at the bearing level demonstrate that the same optimum conversion layer can reduce the running torque by approximately 30% compared to the current products both at low and intermediate speeds relevant to intercity trains.

Reference

Broitman, E.; Ruellan, A.; Meeuwenoord, R.; Nijboer, D.; Brizmer, V. *Comparison of Various Conversion Layers for Improved Friction Performance of Railway Wheel-End Bearings*. Coatings **13** (2023) 1980.

11:20am **MC3-2-ThM-11 Impact of Fiber Orientation and Oxidation on Wear Performance of Carbon-Carbon Composites***, Hamid Mohseni (Hamid.Mohseni@prattwhitney.com), X. Fang, L. Dawag, C. Winder,* Pratt & Whitney, USA

Carbonaceous matrix reinforced with continuous or discontinuous carbon-based fibers comprises the building block of carbon-carbon (C/C) composites, one of the prominent and versatile aerospace materials. The range of constituents in C/C composites, such as carbonaceous matrix, oxidation resistant impregnation, fiber types, size, volume, orientation, weaving pattern, lay-ups, and densification method, potentially allows to achieve a unique combination of properties. This design flexibility presents numerous opportunities to achieve application-specific and novel wear resistant composites. In this investigation, two class of C/C composites each with three different fiber orientations in non-oxidized and pre-oxidized (to 5 and 10 % weight loss) condition were subjected to a reciprocating sliding wear test against Inconel 718 plates at 375°C. Whereas the average wear depth was in the 10^{-2} mm range for all the samples regardless of non-oxidized or oxidized conditions, the samples with fiber orientation perpendicular to the reciprocal sliding exhibited almost 75% higher wear. Microstructural investigation of worn and unworn samples using SEM/EDS revealed severe cracking at the interface of fibers and carbonaceous matrix that resulted in fiber pull-out and evolution of wear debris. Raman spectroscopy revealed higher D/G band intensity for the worn area that indicated higher concentration of defects induced by reciprocating sliding at the interface of perpendicular fibers and carbonaceous matrix. Presence of pre-existing porosities was found to be the precursor for wear-induced cracking and formation of wear debris. Furthermore, carbonaceous solid-lubricant transfer film was discovered on the Inconel 718 plate that justified the significantly lower average wear depth (10^{-3} - 10^{-4} mm) compared to the corresponding C/C composite samples.

11:40am **MC3-2-ThM-12 Tribological Insights of Nickel – and Cobalt – Based Alloys in Extreme Conditions***, Pantcho Stoyanov (pantcho.stoyanov@concordia.ca),* Concordia University, Canada

Nickel- and cobalt – based alloys are widely used as structural components in demanding environments due to their excellent stability (i.e., resistance to mechanical and chemical degradation) at elevated temperatures. These superalloys were primarily developed to meet the demand of jet engine and industrial gas turbine engine blades operating at extreme temperature ranges. Unfortunately, while intensive alloy and process development activities for these high-temperature alloys have been performed over the last few decades, their tribological behavior (i.e., friction and wear) has received little attention. With the increasing demand in temperature and spread of application of these alloys to other static and dynamic components in the engine, there is a clear need for a better understanding of their tribological behavior.

The main purpose of this study was to critically investigate the friction and wear behavior of Co- and Ni- based materials under low and high temperature environmental conditions. The ultimate goal was to identify the underlying interfacial processes leading to the observed tribological behavior. Thus, a series of studies on the friction and wear behavior of Ni-based and Co-based superalloys was conducted using a custom build high temperature fretting wear apparatus.In addition, ex situ analysis was performed on the worn surfaces using XPS, AFM, and cross-sectional SEM imaging of the near-surface region. The results showed a clear correlation between the third body formation process (e.g. oxide layer formation, transferfilms) and the tribological behavior of the superalloys as a function of temperature. The low friction and wear of these material systems at elevated temperatures is attributed to the formation of a lubricious 'glaze layer'. Depending on the contact conditions, stable lubricous oxides will form above a critical temperature and provide sufficient wear resistance as long as the system continuously operates at these temperatures.

12:00pm **MC3-2-ThM-13 Cr Doping Modification for Tribological Behavior of Cr/a-C Multilayer Coatings Against PEEK Under Diverse Operational Conditions***, Xiaohui Zhou (zhouxiaohui@nimte.ac.cn),* Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Considering the increasing demands for wear-resistant materials used for various frictions with dynamic sealing parts, we employed hybrid magnetron sputtering technology to fabricate Cr/a-C multilayered coatings with and without Cr-doping modification for comparison. The tribological behaviors of coatings when paired with Polyether ether ketone (PEEK) balls was focused under different friction environments evolving atmosphere, NaCl solution, olyalphaolefin (PAO) oil, and water-in-oil (W/O). The results demonstrated that the tribological properties of all friction pairs was strongly influenced by the surrounding environment. In the atmosphere and NaCl solution, the addition of Cr promoted the formation of a-C transfer film, thereby yielding the stable and low friction characteristics. However, the dominant factor contributing to the tribological performance shifted from the coatings themselves to the PAO oil film with PAO medium. In the case of W/O solution, both the facile reactivity of Cr and the intrinsic instability of W/O mixture accelerated the existence of Cr_2O_3, which caused the more severe wear. The current observations not only identified the tribological failure mechanism of Cr/GLC coatings with and without Cr doping modifications in conjunction with PEEK counterparts, but also addressed the importance of designing and fabrication of adaptive lubricant coatings for harsh multi-environment applications.

Coatings for Biomedical and Healthcare Applications
Room Palm 3-4 - Session MD1-2-ThM

Surface Coatings and Surface Modifications in Biological Environments II

Moderator: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

8:40am **MD1-2-ThM-3 The Biocompatibility of Thermal Sprayed Bioactive Glass Hydroxyapatite Composited Coatings***, **Pin-Jie Chen (mtou335@gmail.com)**, C. Wu, R. Chung, Y. Yang,* National Taipei University of Technology, Taiwan

In recent years, with the trend of demographic changes and aging, the demand for medical care has continued to rise, and the demand for orthopedic medical devices has increased day by day. In order to maximize the benefits of biomedical composite materials. This experiment uses flame spraying (FS) to coat the surface of Ti-6Al-4V to study the effects of modified hydroxyapatite composite coatings prepared with different proportions of bioactive glass powder on bone healing in rats. help. The experiment will be divided into two parts for discussion. The first part is the microstructure observation, phase composition analysis, mechanical properties and bonding strength test of the modified hydroxyapatite composite coating. The acetylene flow rate will be 1.60 Nm3/hr, the spray gun speed is 250 mm/s, the spraying distance is 125 mm, and the number of flame spray (FS) sprays is 2 times for animal experiments; the second part is the observation of the bone healing situation of the modified hydroxyapatite composite coating, The coated round rods were implanted into the femurs of 6-week-old SD rats for 2 weeks and 4 weeks. Finally, microstructure and through-compression tests were conducted to test the implant bonding strength.

9:00am **MD1-2-ThM-4 Mineralization Ability and Inflammatory Reaction of HFOB 1.19 and THP-1 Cells on the Surface of the Borided AISI 316 L Steel***, **Erick Japhet Hernandez-Ramirez (japhet_hdez@hotmail.com)**, R. Perez Pasten Borja, Y. Marquez-Flores, N. Hernandez-Delgado,* Instituto Politecnico Nacional, Mexico*; I. Mejia-Caballero,* Universidad Autonoma Metropolitana, Mexico*; I. Campos-Silva,* Instituto Politecnico Nacional, Mexico

Metal-based implants, including stainless steel, titanium-based alloys, and cobalt-based alloys, are the most commonly used materials in orthopaedic implants. They are favored for their cost-effectiveness, exceptional durability, and advantageous mechanical properties. Stainless steel, in particular, offers an economical alternative that can help reduce costs in public health services. However, its wear and corrosion behavior in body fluid environments can lead to various corrosion-related failures, exacerbated by the release of metal ions, such as chromium and nickel, or fretting debris from the steel.

To enhance the performance of stainless steel, a FeB-Fe_2B layer developed through the boriding process has been applied to 316 L stainless steel. This boride layer generally improves wear and tribocorrosion resistance on the stainless surface. In addition, cytotoxicity results indicate satisfactory properties with regard to the effects on the survival and proliferative activity of human fibroblasts, osteoblasts, and macrophage cells on the surface of the borided AISI 316 L steel.

The hFOB 1.19 (osteoblast cells) mineralization and the evaluation of nitric oxide formation in THP-1 (macrophage cells) on the surface of borided AISI 316 L steel were obtained in this study. The FeB-Fe_2B layer on the stainless steel was developed using a novel method called the pulsed-DC powder pack boriding process at 900ºC for 3600 s, with a 5 A current intensity and cyclic polarity changes of 10 s, resulting in a total boride layer thickness of 20 µm. The mineralization ability of hFOB 1.19 adhered to the borided surface during 1 – 28 days of exposure was analyzed with the alizarin red S assay, while the inflammatory reaction of THP-1 cells to borided AISI 316 L steel was estimated by the Griess reaction after 10 days of exposure. Both assays were also replicated in non-borided AISI 316 L steel.

Notably, for mineralization, the Gompertz and Michaelis-Menten models were used to describe the evolution of the calcium compounds and alkaline phosphatase over the borided and non-borided surfaces.

Based on the mineralization results, it was evident that the FeB-Fe_2B layer promoted osteoconductive and osteoinductive properties, rendering it a promising bioactive layer. Consequently, the THP-1 cells in contact with the borided surface exhibited a controlled inflammatory reaction, with $NaNO_2$ values measuring below 3µM.

9:20am **MD1-2-ThM-5 Tribological Composite Coatings Prepared by Cold Spray***, **Sima Alidokht (saalidokht@mun.ca)**,* Department of Mechanical and Mechatronics Engineering, Memorial University of Newfoundland, Canada **INVITED**

The cold spray process stands out as a cutting-edge coating technology within the thermal spray family. Its versatility spans from component repair to additive manufacturing. Initially, cold spray research predominantly focused on metallic materials within the first decade since its inception. Cold spray suitability is confined to materials exhibiting ductility at high strain rates. While metals remain primary in cold spray, recent research explores developing metal matrix composites, particularly for tribological purposes. This presentation touches upon a number of tribology fundamentals and principles underpinning the deposition of metal matrix composites via cold spray. It provides an overview of advancements in fabricating tribological coatings through this method. Strategies involving powder characteristics and process parameters optimization to enhance coating quality and retain ceramic or solid lubricant will be covered. Despite successful measures in controlling the retention, these changes might unintentionally impact the coatings' tribological properties. The focus will be on the tribology aspects of composite coatings manufactured through cold spray. The presentation also covers structural, chemical, and mechanical changes in third bodies during sliding, offering insights into wear processes influencing cold-sprayed composite coating's wear resistance and friction characteristics. Lastly, we will discuss potential future trajectories for metal matrix composites produced via cold spray and their suitability for tribological applications.

10:20am **MD1-2-ThM-8 Bio-Tribocorrosion Performance of AISI 316 L Steel Enhanced by Pulsed-DC Powder-Pack Boriding***, **Alan Daniel Contla-Pacheco (aldani.90@hotmail.com)**,* TecNM/Tecnologico de Estudios Superiores de Jocotitlan, Mexico*; I. Mejia-Caballero,* Universidad Autonoma Metropolitana-Azcapotzalco, Mexico*; A. Delgado-Brito, V. Castrejon-Sanchez,* TecNM/Tecnologico de Estudios Superiores de Jocotitlan, Mexico*; R. Perez Pasten-Borja, I. Campos-Silva,* Instituto Politecnico Nacional, Mexico

Stainless steel, titanium and CoCrMo alloys are commonly employed in the fabrication of biomedical implants, particularly for artificial replacements like hip and knee joints, owing to their mechanical strength and corrosion resistance. Among these materials, AISI 316 L steel stands out for its corrosion resistance, biocompatibility, affordability, and nonmagnetic properties, making it a frequently utilized biomaterial. However, low hardness and poor tribological properties are the important disadvantages of AISI 316 L steel. In this sense, boriding process is known to increase the surface properties of AISI 316 L steel; the resulting boride layer has excellent wear resistance due to its high hardness, thermal and chemical stability, and adhesion to the substrate material.

This study presents novel insights into the bio-tribocorrosion resistance of borided AISI 316 L steel when immersed in calf serum. Initially, the boride layer (FeB-Fe_2B) on the steel surface was formed through pulsed-DC powder pack boriding at 950 ºC for 0.5 h, using a 10 A of current intensity, and inverse polarity cycle changes every 10 s. Subsequently, a diffusion annealing process, at 1000ºC during 3 h in an inert atmosphere, was conducted on the borided AISI 316 L steel to induce a microstructural change in the layer, resulting in the development of a monophasic Fe_2B layer. In both experimental conditions, the bio-tribocorrosion experiments were performed following the procedure disclosed in the ASTM G119-09 standard; a ball-on-flat tribometer connected with a three-electrode-chemical cell was used for this purpose. The experiments were also replicated in the AISI 316 L steel (reference material).

The results indicated a wear-corrosion regime for both borided AISI 316 L (FeB-Fe_2B) steel and borided steel exposed to diffusion annealing (Fe_2B), characterized by a material loss ratio of corrosion to wear (C/W) approximately 0.2. The regime was significantly influenced by the boride layer, enhancing the bio-tribocorrosion resistance on the material surface by approximately 2 times compared to the reference material. In contrast, the reference material exhibited a wear-dominated regime (C/W= 0.095) attributed to passive film removal and high contact pressure in the tribopair, resulting in an increased total material loss rate due to wear.

10:40am **MD1-2-ThM-9 SERS Substrates Based on Self-Organized Dimple Nanostructures on Polyethylene Naphthalate Films Produced via Oxygen Ion Beam Sputtering**, *S. Lee,* KIMS, Republic of Korea*; **Jun-Yeong Yang (yjy8184@kims.re.kr)**,* Korea institute of materials science, Republic of Korea

Surface-enhanced Raman spectroscopy (SERS) utilizes metal nanostructures to enhance the intensity of Raman signals. Although many methods have been developed for fabricating SERS nanostructures, most involve multiple steps. Herein, we employed oxygen ion beam sputtering (IBS), a one-step technique suitable for processing flexible substrates in roll-to-roll processes for mass production, Specifically, one-step oxygen IBS was used to fabricate self-organized dimple nanostructures, whose area and roughness could be controlled using the ion irradiation [https://www.sciencedirect.com/topics/physics-and-astronomy/ion-irradiation] energy density, on the surfaces of polyethylene naphthalate films. Gold nano-tips for SERS were subsequently obtained by evaporating gold onto the dimple nanostructures. Finite-difference time-domain (FDTD) simulations revealed that nano-tip structures with spacings of less than 10 nm increased the localized E-field enhancement, which improved the SERS signal. Fabrication at a low energy density (5.8 J/cm^2) produced more nano-tips with spacings of less than 10 nm, corresponding to a density of 61.4 nano-tips/μm2. SERS analysis conducted with methylene blue at 638 nm and 785 nm demonstrated that the Raman signal intensity was stronger for SERS substrates fabricated with low energy density (5.8 J/cm^2) than for substrates fabricated with high energy density (17.3 J/cm2), because of the high density of nano-tips on the former substrate.

11:00am **MD1-2-ThM-10 Design and Fabrication of a Hybrid IrOx/Polydopamine Thin Film via a Co-Electrodeposition Process as a Bendable Bio-Interface Microelectrode Array**, ***Hung-Yu Chen (bryan950396@gmail.com)**, M. Tsou,* National Taipei University of Technology, Taiwan*; K. Tso, K. Sasagwa, J. Ohta,* Nara Institute of Science and Technology, Japan*; P. CHEN,* National Taipei University of Technology, Taiwan

Iridium oxide (IrOx) is a promising electrode material for implantable neural therapeutic devices owing to its remarkable performance on bio-interfaces. We demonstrate a unique chemical formula to co-electrodeposit hybrid iridium oxide thin film with polydopamine (PDA) on a flexible Parylene C substrate. In a mild alkaline solution, electrochemical deposition facilitated the formation of inorganic/organic nanoparticle (NP) corona structures. The NP-corona with an order atomic structure enabled enhanced electrochemical stability and bioactivity. The incorporated PDA contributed to nanorough surface structures that led to higher current storage capacity (CSC) and lower impedance than that of pristine IrOx. The IrOx/PDA microelectrode array also demonstrates an excellent sensitivity to dopamine which is an important neurotransmitter related to brain diseases. In addition, the hybrid IrOx/PDA thin film reveals an impressive mechanical property. In a bending test of 15,000 cycles, the hybrid IrOx/PDA thin film retains 90% of its initial CSC without any physical crack or delamination. Our results provide solid evidence of fabricating a robust flexible electrode for neural interfaces for potential use in implantable electronic devices.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP2-1-ThM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

Moderators: Martin Rudolph, Leibniz Inst. of Surface Eng. (IOM), Germany, **Tetsuhide Shimizu**, Tokyo Metropolitan University, Japan

9:00am **PP2-1-ThM-4 Metal-Ion Synchronized HiPIMS of AlN and AlScN for Piezoelectric Applications**, *J. Patidar,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; S. Bette,* aixACCT systems GmbH, Aachen, Germany*; O. Pshyk,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R. Kessels,* aixACCT Systems GmbH, Aachen, Germany*; **Sebastian Siol (sebastian.siol@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Ionized physical vapor deposition (PVD) techniques, such as High Power Impulse Magnetron Sputtering (HiPIMS), offer unique opportunities to control the microstructure of thin film materials by accelerating ions onto the growing film using substrate-bias potentials. At moderate acceleration potentials, the increase in ad-atom mobility often leads to improved crystalline quality and texture. This, in turn, enables the deposition of high-quality thin films at low deposition temperatures. However, gas-ion incorporation can limit the feasibility of such synthesis approaches for defect-sensitive materials. In recent years, HiPIMS processes with a synchronized pulsed substrate bias have been developed with the goal to selectively manipulate the kinetic energy and momentum transfer of the film-forming species, particularly the metal ions. These processes hold remarkable potential to significantly reduce the defect concentration and stress in HiPIMS-deposited films, potentially unlocking a host of new applications for the technique.

In this presentation, I will showcase our latest work on the development of reactive metal-ion synchronized HiPIMS processes for the growth of piezoelectric AlN and AlScN thin films. It will be shown how highly textured, c-axis oriented AlN and AlScN films can be grown using reactive metal-ion synchronized HiPIMS. Here, even unconventionally moderate substrate bias potentials of up to only -30 V already lead to significant improvements in the films' properties. Most strikingly, the application of a substrate bias facilitates the deposition at oblique deposition angles and on structured substrates, while also significantly reducing the fraction of undesirable misoriented grains. A detailed characterization of the piezoelectric coefficients of the materials show values comparable to the current state-of-the-art. In addition, for AlScN in particular, the phase formation and stress state can be tailored by applying different biasing schemes and combinations of different sputter modes (i.e., HiPIMS or DCMS, or hybrid). Importantly, it will be shown that the applicability of these types of processes can be significantly extended, even on insulating substrate materials.

The goal of this presentation is to demonstrate the tremendous potential of synchronized HiPIMS processes for the deposition of defect-sensitive materials, especially in applications where tailoring microstructure and texture of the thin film materials is important.

9:40am **PP2-1-ThM-6 Optimization of Deposition Parameters of Titanium Oxide Films by Taguchi Method**, ***Shih-Yang Hsu (pupuyang0120@gmail.com)**,* Department of Materials and Mineral Resources Engineering, Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei, Taiwan*; B. Lou,* Chemistry Division, Center for General Education, Chang Gung University, Taoyuan, Taiwan*; J. Lee,* Department of Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan*; Y. Yang,* Department of Materials and Mineral Resources Engineering, Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei, Taiwan

Titanium dioxide thin film exhibits excellent photocatalyst effect, antibacterial ability, and optical performance, which makes it widely studied and applied in related applications. Due to its antibacterial and transparent performance, the TiO_2 film can be deposited on touch screens and touch panels to prevent the infection of microorganisms. This work used a superimposed high power impulse magnetron sputtering and mid-frequency (HiPIMS-MF) sputtering system to deposit TiO_2 films on 304 and 420 stainless steel, silicon wafers, and glass slide substrates. Through the Taguchi method, nine batches of TiO_2 thin films were grown under different deposition processing parameters, including the HiPIMS frequency, HiPIMS duty cycle, working pressure, and substrate bias. The cross-sectional morphology of the film was observed with a field emission scanning electron microscope. the phase structure of the film was analyzed with an

X-ray diffraction analyzer, and the hardness and adhesion of thin films were measured with a nanoindentation instrument and a scratch tester. The antibacterial and transmittance properties of TiO_2 thin films were examined. The Taguchi method was employed to investigate the optimal deposition conditions using signal-to-noise ratio and analysis of variance (ANOVA), discussing and optimizing the impact of process parameters on the antibacterial and transmittance properties of TiO_2 thin films.

10:20am **PP2-1-ThM-8 Phase Transformation of Boron Carbon Nitride Coatings Deposited by High-Power Impulse Magnetron Sputtering**, *H. Nagakura, H. Komiya,* Tokyo Metropolitan University, Japan; *Y. Touta,* Tokyo Metropolitan Industrial Technology Research Institute, Japan; *I. Fernandez,* Nano4Energy, Spain; *R. Boyd, U. Helmersson, D. Lundin,* Linköping University, Sweden; ***Tetsuhide Shimizu (simizu-tetuhide@tmu.ac.jp)***, Tokyo Metropolitan University, Japan

To realize the growth of cubic boron nitride (c-BN) towards a full-scale industrial application of this coating materials, this work has been aimed to understand the discharge physics and growth kinetics in reactive high-power impulse magnetron sputtering (HiPIMS) of B_4C target in Ar/N_2 gas mixtures. One of the most significant challenges to industrialize the c-BN coating is the significant degradation of film adhesion due to the high residual stresses during the cubic phase formation. While the key to nucleate c-BN phase is a formation of "nano-arches" by ion bombardment on turbostratic BN phase (t-BN), the bombardment by the gas ions, such as Ar^+ ions, leads the entrapment of the gas atoms into the crystal lattice, causing the increase in residual stress. On the other hand, time-transient discharge of HiPIMS makes the time separation of ion arrivals to the substrate and it enables the tuning of incident ions and the independent control of its kinetic energy by the use of synchronized pulsed substrate biasing technology. This would realize the selective ion bombardment of film forming species, expecting to result in efficient momentum transfer without introducing film stresses through the rare gas incorporation. In addition, this great feature of HiPIMS discharge allows us to systematically isolate the influencing factors and will dramatically advance the understanding of nucleation physics of c-BN. In this study, the impact of ion acceleration schemes, including DC bias, synchronized pulsed bias and bipolar pulse configurations and its process parameters, such as the pulse duration, delay time and the substrate bias potential are thoroughly investigated, based on the mass-spectroscopy study of reactive HiPIMS discharge of B_4C target in Ar/N_2 gas mixture. In addition to the great importance of bias potential, the obtained results clearly show the effect of the synchronized pulse duration and the time delay on the chemical bonding states of B-C-N films and its mechanical properties, owing to the time domain of accelerated ions during film growth. By focusing on the average momentum transfer per deposited atoms at each biasing conditions, role of mass and flux of incident ions on the formation of c-BN bonding state are discussed.

10:40am **PP2-1-ThM-9 Thick and Smooth Nanostructured Cr Coatings with Enhanced HiPIMS Ionization**, ***Ricardo Serra (ricardo.serra@dem.uc.pt)***, University of Coimbra, Portugal; *S. Adebayo,* University of Coimbra, Nigeria; *J. Oliveira,* university of coimbra, Portugal

In sputtering deposition processes the atomic shadowing effect, originated from the preferential deposition of obliquely incident atoms on higher surface points of any substrate, drives the formation of open columnar anisotropic microstructures, with columns interspersed with voids or underdense regions. The effect increases the surface roughness as the film thickness increases and undermine their performance, also limiting the maximum achievable thickness of films. Energetic ion bombardment during film growth counteracts the atomic shadowing effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and triggering re-deposition processes. However, film surface bombardment with highly energetic particles forms higher density of defects, disrupting the crystalline structure of the films and adding compressive internal stress.

In a previous work was shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment.

Thick chromium films were prepared by DOMS, with different levels of ionization to test and study the influence on the film growth conditions and respective coating properties, like structure and surface morphology. An electrostatic flat probe mounted at the substrate location was used to characterize the saturated current density of positive charges bombarding the substrate during film growth, evaluating the flux of positive ions bombarding the growing film. Film hardness decreases with increase of thickness, however, Young's Modulus values remain close to Cr bulk value. The films have [110] preferential orientation depending on the bombarding conditions.

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11:00am **PP2-1-ThM-10 Implementation of HiPIMS Technology in Different Industrial Sectors**, ***IVAN FERNANDEZ (IVAN.FERNANDEZ@NANO4ENERGY.EU)***, NANO4ENERGY SL, Spain

After 20 years of continuous development by several research groups and companies it is now clear that real industrial breakthroughs for the high-power impulse magnetron sputtering (HiPIMS) technology are happening. HiPIMS is a state-of-the-art tool for applying high demanding metal and ceramic coatings with superior properties for applications such as: metal fabrication process (machining, stamping, molding or other tools), functional decorative, trench filling in semiconductor industry, or tribological (H-free DLC coatings with reduced friction, high hardness and enhanced thermal stability). Despite the great perspective and the positive forecasts for HiPIMS-technology since its' discovery in 1999, it has taken more than 15 years for the real industrial breakthrough to start. For example, the deposition rate of HiPIMS is still considered to be rather low compared with conventional magnetron sputtering and even more so when compared to cathodic arc-deposition. Another issue is the complexity of use due to the large number of adjustable process parameters. It is not only the HiPIMS power supply, which itself has more controllable parameters than any traditional power supply, what contributes to this great deposition technology. It is also the process regulation (monitoring), the magnetron system (magnetic configurations), the gas flow, the pumping speed, etc.

Apart from the traditional use of HiPIMS which is being currently implemented by the industry, it has been recently demonstrated that the application of a positive voltage reversal pulse adjacent to the negative sputtering pulse (Bipolar HiPIMS) gives rise to the generation of high fluxes of energetic ions. This solution allows unprecedented benefits for the coating industry, such as the energetic deposition onto insulating or grounded substrates, improved coverage on 3D parts or components, or even substrate etching. Also, Dual Magnetron HiPIMS operation is implemented more often in combination with multiple magnetron sources for the large production of high-end decorative coatings. A few examples of implementation of HiPIMS technology in industrial systems as well as the experimental results obtained in different configurations will be presented in this talk.

11:20am **PP2-1-ThM-11 Impact of Energetic Film-Forming Particles in Ion Beam Sputter Deposition of Epitaxial Ga_2O_3 Thin Films**, ***Dmitry Kalanov (dmitry.kalanov@iom-leipzig.de)***, *Y. Unutulmazsoy, J. Gerlach, A. Lotnyk, J. Bauer, A. Anders, C. Bundesmann,* Leibniz Institute of Surface Engineering (IOM), Germany

Ion beam sputter deposition (IBSD) is an energetic deposition technique, which provides intrinsic heating and kinetic assistance to the growing film by energetic particles arriving at the substrate surface, which affect various thin film properties such as density, microstructure, and forming phase. In IBSD, the kinetic energy distributions of film-forming particles can be controlled by changing process parameters, including the sputtering geometry, the flux, and the energy of primary ions. This is especially important for the growth of epitaxial thin films since it is necessary to find the optimal energetic assistance while minimizing the damage to the crystal lattice.

In this study, reactive IBSD is used for deposition of epitaxial Ga_2O_3 thin films on $Al_2O_3(0001)$ substrates.The influence of process parameters such as substrate temperature, kinetic ion energy, ion beam current, sputtering geometry, oxygen pressure, and deposition time on the properties of the epitaxial films is investigated. The kinetic energy distributions of ions in the film-forming flux are measured by using a combined mass and energy analyzer and the resulting films are characterized regarding growth rate, roughness, crystalline structure, and microstructure. The impact of energetic bombardment by film-forming particles on the thin film structure is analyzed, and a significant change in crystalline quality is observed above the threshold in the average energy of film-forming particles (around 40 eV for the sputtered Ga^+ ions).

11:40am **PP2-1-ThM-12 Quantification of the Negative Oxygen Ion Yield*, Diederik Depla (diederik.depla@ugent.be),*** Ghent University, Belgium

Many thin film applications are based on oxides. The optimization of the oxide properties is an on-going process and requires a deep understanding of the deposition process. A typical feature of reactive (magnetron) sputter deposition is the presence of negative oxygen ions. The presence of negative ions in gas discharges was already postulated in the very first paper on sputtering by Grove.

In a magnetron oxygen containing discharge, two groups of ions can be identified based on their energy. Low energy ions are generated in the bulk of the discharge. The high energy ions are emitted from the oxide or oxidized target surface. As these ions are generated at the cathode, they are accelerated by the electrical field towards the growing film. Depending on the discharge voltage and the powering method, their energy is typically several tenths to hundreds electron volt. As such the ions can have a strong impact on the film properties. Nevertheless, despite the many illustrative studies on the impact of negative oxygen ions, quantification is often lacking as the negative ion yield is only known for a few oxides. A compilation of several literature sources permits not only the prediction of the negative ion yield, but also a comparison amongst different oxides.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country D - Session TS4-1-ThM

Coatings and Surfaces for Thermoelectrical Energy Conversion and (Photo)electrocatalysis I

Moderators: Clio Azina, RWTH Aachen University, Germany, **Carlos Tavares**, University of Minho, Portugal

8:00am **TS4-1-ThM-1 Inorganic Thermoelectric Films for Harvesting Waste Heat Near Room Temperature: Opportunities and Challenges*, Rui Shu (rui.shu@liu.se),*** Linkoping University, Sweden, USA **INVITED**

The abundance of untapped low-grade heat presents a significant opportunity for sustainable energy solutions. However, current recovery technologies often fall short due to their lack of cost-effectiveness. Effectively harnessing this waste heat holds the promise of fostering a more sustainable society. Notably, inorganic thermoelectric bulk materials have shown promise in capturing waste heat near room temperature, offering potential applications in energy harvesting and thermal cooling.

However, challenges persist, including limited thermoelectric performance when transitioning to thin films and hindered large-scale implementation due to the scarcity and costliness of elemental Te. Adapting high-performance inorganic bulk thermoelectric materials into consistent thin films remains a significant obstacle.

This presentation explores the opportunities and challenges associated with using inorganic thermoelectric films for waste heat recovery at room temperature. Recent research advancements focusing on materials like Mg_3Bi_2 and transition-metal-nitride-based thin films are highlighted. Notably, these materials circumvent the use of scarce and brittle tellurium, with Mg_3Bi_2-based substitutes showing promise as alternatives to commercially used Bi_2Te_3. Our study aims to pave the way for the practical utilization of highly efficient inorganic thermoelectric films in energy harvesting applications.

8:40am **TS4-1-ThM-3 Retaining Crystallinity of as-deposited Thermoelectric Fe_2VAl-based Thin Films Grown from DCMS and HiPIMS*, Ludwig Enzlberger (ludwig.enzlberger@tuwien.ac.at),*** TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvari,* Plansee SE, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Thermoelectric materials have gained much attention in recent years due to their ability to directly interconvert electrical and thermal energy via the Seebeck/Peltier effect. This can be used to convert waste heat back into usable electrical energy, making thermoelectrics very interesting materials in a world with increasing demand for renewable and efficient utilisation of energy. The efficiency of this process is generally dependent on three parameters - the thermopower *S*, the electrical conductivity *σ* and the thermal conductivity *λ* - which are represented together in the dimensionless Figure of Merit *ZT*.

Among thermoelectrics, Heusler and half-Heusler materials have shown to be promising candidates, due to their high Seebeck coefficients at room temperature and their high electrical conductivity, while generally higher thermal conductivity is often a drawback in thermoelectric performance.

In 2019, Hinterleitner *et al.* managed to produce magnetron sputtered thin films of bcc-$Fe_2V_{0.8}W_{0.2}$Al with an exceptionally high Seebeck coefficient, Power Factor and Figure of Merit, but the samples needed to be heat-treated for one week to crystallize from their initially amorphous state.

In this work, we present Fe_2VAl-based full-Heusler thin films retaining their crystallinity during sputter deposition. By tuning deposition temperature, bias potential and pulse on-time we managed to fabricate films of $Fe_2V_{0.8}W_{0.2}$Al in a W-type bcc-structure on silicon and austenite substrates. These films were analysed using XRD, EDX, electron microscopy and by measurement of transport data (resistivity, Seebeck coefficient). Thermal conductivity of the films was derived from measurements of thermoreflectance and specific heat capacity.

9:00am **TS4-1-ThM-4 Thermoelectrical Investigations of TaC-Based Superlattice Protective Coatings*, Barbara Schmid (barbara.schmid@tuwien.ac.at),*** *S. Lin, T. Schöngruber, N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Bühler-Paschen,* TU Wien, Austria*; L. Mitterhuber,* Materials Center Leoben, Austria*; D. Ingerle,* TU Wien, Austria*; S. Kolozsvari,* Plansee SE, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides (TMC) and nitrides (TMN) feature high melting points up to 4000 °C and superior thermal stability and are therefore regarded as ultra high temperature ceramics (UHTC). Those materials are well-established in the realm of protective coatings. Superlattice architecture can impact a plethora of different material characteristics such as mechanical, chemical and electric properties. Inspired by preliminary DFT high-throughput screenings, we developed TiC/TaC and TiN/TaC superlattice coatings exhibiting bilayer periods between 2 and 50 nm via non-reactive DC magnetron sputtering. Those materials exhibit high hardness and fracture toughness and are therefore immaculate choices as protective coatings. These superlattice materials also exhibit decent thermal stability and electrical conductivity, which motivated us to calculate their thermoelectrical properties via DFT using BoltzTraP and VASP. The experimentally determined Seebeck coefficients exhibit a significant bilayer-period-dependence. By conducting Time Domain Thermoreflectance investigations, we also derived their figure of merit (ZT) values.

9:20am **TS4-1-ThM-5 Exploring the Potential and Challenges of Solution-Processed Inorganic Thermoelectric Materials***, M. Ibáñez,* Institute of Science and Technology Austria (ISTA), Austria*; **Tobias Kleinhanns (Tobias.Kleinhanns@ist.ac.at),*** Institute of Science and Technology, Austria **INVITED**

Over the past few years, there has been a significant surge in interest surrounding solution-based techniques due to their cost-effectiveness and scalability in the production of high-performance thermoelectric materials. This approach involves the synthesis of particles in a solution, followed by their purification and thermal processing to yield the desired dense polycrystalline material. In contrast to traditional methods, solution-based syntheses offer the ability to manipulate particle characteristics, including size, shape, crystal structure, composition, and surface chemistry, to an unprecedented degree. This fine-tuned control over powder properties opens up distinct opportunities for crafting thermoelectric materials with meticulously controlled microstructural attributes.

In this presentation, our primary focus will be on Ag2Se, an important thermoelectric material for harnessing thermoelectricity at or near room temperature, an area where the selection of high-performing materials is currently limited. While Ag2Se shows great promise, the main problems are the large discrepancy in the reported thermoelectric properties and difficulties in replicating its exceptional performance. These discrepancies often stem from the intricate control of defects within the material, such as vacancies, interstitial atoms, dislocations, grain boundaries, and precipitates.

We will show that our solution-based synthesis method enables precise defect control, especially avoiding fluctuations in stoichiometry. Additionally, we will illustrate how we can fine-tune microstructural defects, including strain, dislocations, and grain boundary density, leveraging the characteristic phase transition of Ag2Se during the sintering process. Our results will highlight that besides stoichiometry, the microstructure is crucial for tuning Ag2Se transport properties and how this control can be provided by our novel synthetic route. Furthermore, we will highlight the sustainability and scalability of our approach, where solvents can be recycled and energy consumption minimized, contributing to a more environmentally friendly production process.

10:20am **TS4-1-ThM-8 3D Nanoscale Spatial Imaging of Doped ZnO and TiO_2 Transparent Thermoelectric Thin Films**,
J. Ribeiro, F. Correia, H. Faria, University of Minho, Portugal*; A. Welle, T. Boll,* Karlsruhe Institute of Technology (KIT), Germany*; **Carlos Jose Tavares (ctavares@fisica.uminho.pt)**,* University of Minho, Portugal

Transparent thermoelectric materials are a promising technology for touchscreen displays and solar cell applications, rendering a sustainable powering of the device. In order to enhance the thermoelectric performance, the material must have a high Seebeck coefficient and high electrical but low thermal conductivity. This work focuses on the effect of doping on ZnO and TiO_2-based thin films deposited by DC magnetron sputtering. The properties of the films depend strongly on the dopant type and concentration. On the one hand, it has been documented that Al and Ga doping can improve the electrical properties in ZnO, as can Nb doping in TiO_2. On the other hand, introducing heavier elements (such as Bi, Sb or Nb) into the metal-oxide matrix hinders phonon-mediated heat conduction, and consequently reduces the thermal conductivity, which is a promising approach. Atom Probe Tomography and Time-of-Flight Secondary Ion Mass Spectrometry are powerful tools to determine the composition and inherent homogeneity within the thin films, as well as to investigate the cation and anion segregations to interfaces and grain boundaries. For the ZnO-based films, Al and Ga dopants are homogeneously distributed within the crystals, with the exception of Bi, which is not incorporated in the ZnO wurtzite cell and segregates at the grain boundaries and at the triple junctions. Thus, Bi contributes to grain boundary scattering of phonons and contributes less to the reduction of the thermal conductivity, in comparison to Ga-, Al-, and Sb-doping in ZnO. For the Sb-doped ZnO thin films, a larger Zn content was registered at the triple junctions of the grain boundary. As for the Nb-doped TiO_2 thin films, Nb is homogeneously distributed into the TiO_2 matrix and no grain boundaries are visible. However, the composition varies depending on the deposition conditions, where the Nb content inside the film changes depending on the oxygen content controlled through the reactive O_2 flow during the sputtering depositions.

10:40am **TS4-1-ThM-9 Ni-B-based Polyalloy Electrocatalyst Coatings Deposited by MSPVD for Efficient Oxygen Evolution Reaction**,
***Kubilay Sahin (ahink@uni.coventry.ac.uk)**,* Institute for Clean Growth and Future Mobility, Coventry University, Department of Metallurgy, University of Mons (UMONS), UK*; V. Vitry,* Department of Metallurgy, University of Mons (UMONS), 23 Place du Parc, B-7000 Mons, Belgium., Belgium*; A. Cobley,* Institute for Clean Growth and Future Mobility, Coventry University, Priory St, Coventry, CV1 5FB, UK.*; J. Graves, G. Pourian Azar,* Institute for Clean Growth and Future Mobility, Coventry University, UK

Molecular hydrogen has been considered as one of the best green energy sources due to its high energy density [1]. Water splitting is a highly promising approach to generate molecular hydrogen without any damage to environmental health. However, electrocatalyst materials, which are generally expensive noble elements, are required to complete the reactions efficiently and sustainably. Due to their excellent features such as low cost, high abundance, high corrosion resistance and durability, catalytic activity, and good synergistic effect with other elements, Nickel-based electrocatalysts have been reported as one of the most valuable alternatives to expensive noble metals [2]. Electrodeposition, electroless plating, hydrothermal deposition, and physical vapour deposition are some of the used techniques to synthesize Nickel-based electrocatalysts. Electroless nickel-boron plating is a remarkably beneficial technique to produce Ni-B coatings with outstanding features such as hardness, wear resistance, and corrosion resistance. In recent studies, Ni-B coatings have also demonstrated encouraging catalytic activity with remarkable stability [3]. While Ni-B coatings have been extensively studied for various applications, there is not enough research on their catalytic applications.Furthermore, there is no existing literature regarding the deposition of Ni-B coatings utilising a technique other than electrodeposition or electroless plating. However, the Magnetron Sputtering Physical Vapour Deposition (MSPVD) technique has the capability of producing Ni-B coatings with porous and tunable structures together with easy alloyability to further improve the electrochemical performance.

The current study is designed to investigate the electrocatalytic performance of Ni-B-based polyalloy coatings produced by MSPVD. Polyalloy coatings were co-deposited using a Ni-B and transition metal targets such as Fe, Co, and Mo. The coatings were deposited at different deposition parameters such as chamber pressure, substrate type and different chemical compositions. The electrocatalytic performance of the coatings was compared to see the effect of boron, alloying elements, morphology and crystal structure for the Oxygen Evolution Reaction. Superior features like low overpotentials, high stabilities, and high surface areas were obtained after the electrochemical analyses such as Linear sweep voltammetry, cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy under alkaline conditions. The results showed promising efficiencies and stabilities for highly tunable, cost-effective Ni-B-based electrocatalyst coatings.

11:00am **TS4-1-ThM-10 Role of Grain Boundaries in the Stress Corrosion Cracking of Nanoporous Gold Thin Films**,
***Aparna Saksena (a.saksena@mpie.de)**,* Max-Planck Institut für Eisenforschung GmbH, Germany*; A. El-Zoka,* Imperial College London, UK*; A. Saxena, E. Hatipoglu,* Max-Planck Institut für Eisenforschung GmbH, Germany*; J. Schneider,* RWTH Aachen University, Germany*; B. Gault,* Max-Planck Institut für Eisenforschung GmbH, Germany

For its potential as catalyst, nanoporous gold (NPG) prepared through dealloying of bulk alloys has been extensively investigated. NPG thin films can offer ease of handling and better tunability of the chemistry and microstructure of the nanoporous structure. They are however prone to intergranular cracking during dealloying, limiting their stability and potential applications. Here, we systematically investigate the grain boundaries in Au28Ag72 (± 2 at.%) thin films. We observe that a sample synthesized at 400 °C is 2.5 times less prone to cracking than one synthesized at RT. This correlates with a higher density of coincident site lattice (CSL) grain boundaries, especially coherent Σ3, increased, which appear resistant to cracking. Nanoscale compositional analysis of random high-angle grain boundaries reveals prominent Ag enrichment up to 77 at.%, whereas Σ3 coherent twin boundaries show a Au enrichment of up to 30 at.%. The misorientation and the chemistry of grain boundaries have a crucial role in their dealloying behavior, which controls the cracking. Our results provide a target for optimizing the longevity application of NPG thin films for possible applications.

11:20am **TS4-1-ThM-11 Metal/Oxide Heterostructure as Hydrogen Evolution Reaction Electrocatalyst**,
***Thi Y Phung Nguyen (phungnguyen0398@gmail.com)**,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; J. Ting,* National Cheng Kung University (NCKU), Taiwan

In response to the growing demand for sustainable energy sources, there has been a concerted effort to develop efficient electrocatalysts for the hydrogen evolution reaction (HER). Previous researches indicate the need to improve consistent efficiency and stability at high current densities (⩾ 500 mA/cm2) over 100 hours. In this study, we have investigated metal/oxide heterostructure HER electrocatalysts. The heterostructure is noble-metal free and synthesized using a hydrothermal method followed by thermal reduction for controlling the alloy/oxide ratio. Various characterization techniques, including scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and in-situ Raman spectroscopy are used to examine the obtained heterostructures. Furthermore, the electrochemical performance is evaluated using linear sweep voltammetry, electrochemical impedance spectroscopy, cyclic voltammetry, and electrochemical specific surface area analyses. We demonstrate highly efficient and stable heterostructure HER electrocatalyst. This work contributes to cost-effective and sustainable hydrogen production, with significant implications for renewable energy integration.

11:40am **TS4-1-ThM-12 Copper-Based Porous Surfaces for Electrocatalytic CO_2 Reduction**,
***Maria José Lima (mjlima@fisica.uminho.pt)**, S. Viana,* University of Minho, Portugal*; J. Castro, S. Carvalho,* University of Coimbra, Portugal

The United Nations (UN) has identified carbon dioxide (CO_2) as a greenhouse gas (GHG) that is present in the atmosphere as an environmental issue in Goal 13 for climate action.

Decreased CO_2 emissions and participation in a circular economy are crucial to achieving these goals. To include CO_2 in a circular economy, capture and electroreduction of CO_2 into long-chain hydrocarbons or alcohols (C2+) can be the solution. From a material perspective, copper-based catalysts are active and selective cathodes capable of producing hydrocarbons, increasing the Faradaic efficiency of the CO_2RR to C2+ molecules.

Enhancing electrochemical active sites can be an additional strategy to improve CO_2RR. Different strategies can produce porous electrodes, thus increasing the electrochemical active surface area (ESCA) and the CO_2-catalyst interaction. One technique that produces porous materials is the anodization process, an electrochemical process capable of producing a thin oxide layer at the metallic surface.

In this work, we systematically optimized the anodization parameters of metallic copper (Cu) to develop Cu_xO_y porous electrodes. Different anodization parameters were studied, such as voltage, time, electrolyte concentration, and distance between the anode and the cathode.

Materials characterization was made by SEM, EDS, and XRD, where it was possible to observe a higher porosity and Cu_2O crystalline phase obtained using 0.1 M of K_2CO_3 and applying 25 V for 15 min. In fact, lower applied potentials show a compact surface with cracks. Increasing the potential to 25 V favors the formation of hollow tubes, whereas a further increase to 50 V results in structure compaction.

Electrochemical analyses, such as linear sweep voltammetry and cyclic voltammetry, will be shown to discuss the involved redox reactions of organic and inorganic species. The ESCA calculation of each electrode material will permit an understanding of how it correlates with morphology.

Focused Topic Session
Room Town & Country C - Session FTS-ThL

Focused Topic Session

12:20pm **FTS-ThL-1 The World of Scientific Publishing: A Publisher's Perspective**, ***Biswanath Dutta (b.dutta@elsevier.com)***, Elsevier, Netherlands

Publishing research articles is of pivotal importance in the scientific career of a researcher. A scientist without publishing his or her scientific results in a reputable (electronic) journal will not receive the necessary recognition or scientific respect. It is often a major challenge for early career researchers with little or no experience of writing research articles to present their research outcome in a structured fashion. In this presentation, I will discuss different areas of scientific publishing such as (i) how to write a research article and (2) how to publish a research article. I will introduce the publication workflow and explain the different stages involved in the workflow. For the choice of journal, I will explain different models of scientific publishing, including subscription and open access models. The knowledge of best practices in scientific publishing will help early-career researchers of having their manuscripts accepted in state-of-the-art scientific journals. Finally, I will also touch upon subjects such as publishing ethics as well as the usage of Artificial Intelligence in publishing.

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM3-1-ThA

Accelerated Thin Film Development: High-throughput Synthesis, Automated Characterization, and Data Analysis I

Moderators: Davi Marcelo Febba, NREL, USA, **Sebastian Siol**, Empa, Switzerland, **Andriy Zakutayev**, NREL, USA

1:40pm **CM3-1-ThA-2 Collaborative Intelligence in Thin Film Research for Clean Energy Technologies**, ***Shijing Sun (shijing@uw.edu)***, University of Washington, USA **INVITED**

Addressing global environmental challenges, particularly in the realm of energy storage and conversion, necessitates innovative approaches. In this context, artificial intelligence (AI) has emerged as a transformative tool, catalyzing the discovery of new materials. However, the practical application of computational models in laboratory settings presents distinct challenges. This talk will explore the evolving role of AI in scientific research, focusing on its capacity to enhance rather than replace human expertise. This synergy paves the way for advanced collaborative efforts in the development and analysis of thin films.

Drawing from my experience as both an experimentalist and a materials data scientist in academic and industrial settings, I will showcase data-driven approaches that accelerate the formulation of precursors for solution-processed thin films. Additionally, I will delve into how AI-assisted image characterisation can effectively detect imperfections and establish crucial structure-property correlations. These advancements are particularly significant in the pursuit of clean energy solutions, demonstrating the integral role of AI in accelerating scientific innovation in thin film technology.

2:20pm **CM3-1-ThA-4 Discovery and Design of a New Functional Amorphous Nitride: Y-W-N**, ***Oleksandr Pshyk (oleksandr.pshyk@empa.ch)**, S. Zhuk, J. Patidar, A. Wieczorek,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Sharma, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; C. Cancellieri,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; V. Stevanovic,* Colorado School of Mines, USA*; S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Amorphous thin films are employed in many applications and offer unique characteristics, which are not observed in their crystalline counterparts.

We present the discovery and design of amorphous Y-W-N ceramic thin films. We performed an exploratory synthesis and high-throughput characterization of $Y_{1-x}W_xN$ thin films. The compositions are performed using combinatorial, reactive radio-frequency magnetron co-sputtering of Y and W targets in Ar/N_2 atmosphere, resulting in materials libraries with orthogonal composition and deposition temperature gradients. This allows for a rapid screening of the synthesis phase space. A composition window within $0.1 \le x \le 0.85$ is covered, whereas the substrate temperature (T_s) is varied from 80 ℃ up to 600 ℃. High-throughput screening of the composition and structure of the libraries by means of XRF and XRD reveals a wide composition range of $0.2 \le x \le 0.6$ where thin films grow with an amorphous structure without precipitation. Moreover, the amorphous structure shows remarkable temperature stability of up to 600 ℃. Optical properties mapping using an automated high-throughput UV−vis photo-spectroscopy system suggests a band gap of >2.5 eV and confirms the phase purity showing only negligible sub band gap absorption. The band gap can be tuned by varying the cation composition, whereas the highest absorption onset for $Y_{1-x}W_xN$ thin films is found for Y-rich samples with x=0.3 implying an optical band gap of ~3.3 eV. Mechanical properties mapping using an automated nano-indentation system shows that the hardness of $Y_{1-x}W_xN$ thin films with $0.3 \le x \le 0.5$ doesn't change significantly as a function of T_s and the highest hardness of 9.45±0.05 GPa is found for samples with x=0.5 while the increase of Y concentration deteriorates hardness down to 8.45±0.06 GPa for films with x=0.3. A representative pair of amorphous $Y_{1-x}W_xN$ thin films with x=0.3 and 0.5 are selected for a detailed study. A thorough structural and compositional analysis of the latter films by means of high-resolution TEM reveals a homogeneous amorphous structure of the films with no signs of elemental segregations or crystallization. To comprehend the application potential of these materials, a comprehensive study of a wide range of functional and physical properties is performed including a set of optical and dielectric constants, diffusion barrier performance, oxidation resistance, and thermal stability. Experimental findings are corroborated by theoretical calculations for a better understanding of a complex relationship between the elemental composition of amorphous $Y_{1-x}W_xN$ thin films and their physical and functional properties.

2:40pm **CM3-1-ThA-5 Deposition of Highly Crystalline AlScN Films Using Synchronized HiPIMS – From Combinatorial Screening to Piezoelectric Devices**, ***Jyotish Patidar (jyotish.patidar@empa.ch)***, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; S. Bette,* aixACCT Systems GmbH, Germany*; O. Pshyk, K. Thorwarth,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R. Kessels,* aixACCT Systems GmbH, Germany*; S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Piezoelectric thin films are crucial for many technologies, in particular for RF components for telecommunication. Wurtzite Aluminum Nitride (w-AlN) is one of the most widely used material for these types of applications. Recently, Aluminium Scandium Nitride (AlScN), is becoming more popular due to its increased piezoelectric coefficient. Highly crystalline and textured thin films are essential for high-performing piezoelectric devices. In our prior work, we demonstrated that metal-ion synchronized HiPIMS (MIS-HiPIMS) with moderate substrate bias potentials can offer key advantages in the deposition of these materials.[1] Here we explore how these concepts can be applied to AlScN films.

In AlScN films, high Sc concentrations enhance the piezoelectric response by softening of the phonon modes. However, high Sc content can also lead to structural frustration and precipitation of cubic ScN (c-ScN). Investigating the Sc non-equilibrium solubility and structural evolution upon scandium alloying is experimentally involved and thus rarely discussed. In our work, we employ a combinatorial approach for an accelerated estimation of the solubility limits and optimization of film's properties, for varying synthesis environments. We investigate different synthesis routes by hybrid co-sputtering of Al/Sc in a reactive environment through a combination of direct current magnetron sputtering (DCMS) and HiPIMS processes, along with different biasing strategies.

The combinatorial screening reveals a striking correlation between the ion kinetic energy and non-equilibrium Sc solubility. In addition, certain deposition modes prove to be more resilient against structural frustration than others. Particularly, a reduction of misaligned grains is observed with the application of a negative substrate bias potential. Based on the results from the screening, uniform $Al_{0.8}Sc_{0.2}N$ thin films were deposited on Ti/Pt contacts, for each synthesis strategy. Detailed characterization of these films show that based on the chosen synthesis modes, the stress state can be tailored from -1.5 to 1.5 GPa. On the other hand, measurements of the piezoelectric coefficient $d_{33,f}$ show a performance comparable to the current state-of-the-art.

The results of this study showcase how high-throughput experiments can facilitate the development of complex sputter processes but also highlight the potential of synchronized HiPIMS processes for the deposition of piezoelectric thin films and other defect-sensitive materials.

[1] Patidar, Jyotish, et al., Surface and Coatings Technology (2023), 129719.

3:00pm **CM3-1-ThA-6 Advancing Metallic Glasses for Biomedical Applications: A Comprehensive Study on CuAgZr Alloys Using Combinatorial Synthesis, High-Throughput Characterization, and Machine Learning**, ***Krzysztof Wieczerzak (krzysztof.wieczerzak@gmail.com)***, Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory of Mechanics of Materials and Nanostructures, Switzerland

This work presents a study on CuAgZr metallic glasses (MGs), highlighting their potential in biomedical applications due to their exceptional strength, corrosion resistance, and antibacterial properties. Our research employs a novel approach combining combinatorial synthesis, high-throughput characterization, and machine learning to explore the mechanical properties of these alloys. We introduce the material library of CuAgZr alloys produced using direct current magnetron sputtering (DCMS) and employ advanced characterization methods to assess their composition, structure, and mechanical properties. A key finding of our study is the significant influence of high oxygen content in Cu-rich regions, a result of post-deposition oxidation, on the mechanical behavior of these alloys. This insight is pivotal in understanding the role of oxygen in synthesized alloys and its correlation with the growth mechanism and chemical composition. The introduction of the "Scanning Indenter" device in our study marks a significant technological advancement, enabling the automatic mapping of full wafers and integration of various characterization techniques like X-ray fluorescence (XRF) X-ray diffraction (XRD), and nanoindentation. This facilitates a multimodal dataset creation, enhancing our understanding of material properties. Our findings also reveal the critical impact of nanoscale structural features on plastic yielding and flow in these alloys, with a notable correlation between atomic size mismatch, oxygen content, and hardness. Furthermore, we demonstrate the efficacy of machine learning, particularly the multi-layer perceptron (MLP) algorithm, in predicting the hardness of untested alloys, offering valuable insights for future research. This study not only sheds light on the mechanical properties of CuAgZr MGs but also underscores the potential of integrating combinatorial synthesis, high-throughput characterization, and machine learning for the development of new metallic glasses with enhanced strength and economic feasibility.

4:00pm **CM3-1-ThA-9 Accelerating Materials Discovery by Combining Combinatorial Synthesis of Thin-Film Libraries, High-Throughput Characterization and Data Science***, Alfred Ludwig (alfred.ludwig@rub.de),* Ruhr University Bochum, Germany **INVITED**

Discovery of new materials is a key challenge in materials science: e.g., new materials for sustainable production/storage/conversion of energy carriers are necessary to improve existing and to enable future energy systems. Efficient methods for discovery and optimization of new materials are necessary: Thin-film combinatorial materials science (1) is presented as an effective means to produce large datasets on new materials. This approach is useful for validation of theoretical predictions (e.g., from high-throughput computations), and production of large, consistent and complete experimental datasets which can be used for materials informatics. The approach comprises fabrication and processing of thin-film materials libraries by combinatorial sputter deposition processes and optional post-deposition treatments, followed by the high-throughput characterization of the different thin-film samples contained in these libraries, and finally the organization of the acquired multi-dimensional data in adequate databases as well their effective computational analysis and visualization. The importance of defining adequate screening parameters and according designs of materials libraries is addressed. High-throughput material characterization methods are automated, fast, and mostly non-destructive: examples are EDX, XPS and RBS for composition, XRD for crystal structure, high-throughput test stands for temperature-dependent resistance (phase transformation), magnetic, optical and mechanical properties as well as scanning droplet cells for (photo)electrochemical properties screening. Results for up to quinary systems are visualized in the form of composition-processing-structure-function diagrams, interlinking compositional data with structural and functional properties. The talk will cover and discuss examples of combinatorial discoveries and development of new materials in different materials classes and forms (films, nanoparticles) with a focus on compositionally complex materials. Furthermore, a new approach to accelerate atomic-scale measurements for complex alloys is presented as well as applications of materials informatics to accelerate and improve the materials discovery process.

4:40pm **CM3-1-ThA-11 Autonomous Sputter Synthesis and Data Management for Nitride Thin Films***, Davi Febba* ***(davimarcelo.febba@nrel.gov)****, K. Talley, K. Johnson, S. Schaefer, S. Bauers, J. Mangum, R. Smaha, A. Zakutayev,* National Renewable Energy Laboratory, USA

Autonomous experimentation has emerged as an efficient approach to accelerate the pace of materials discovery. Although instruments for autonomous synthesis have become popular in molecule and polymer science, solution processing of hybrid materials, and nanoparticles, examples of autonomous tools for physical vapor deposition are scarce yet important for the semiconductor industry.

Moreover, sputtering reactors usually available in the market can be challenging to incorporate into an autonomous workflow, mainly due to the lack of comprehensive programming support. This makes it difficult to interface the instruments with optimization and active learning routines, common to an autonomous setup. To overcome these limitations, we recently designed and built a highly automated co-sputtering reactor featuring extensive programming capabilities and support for server-client interactions with other programming languages [1].

Furthermore, this high vacuum instrument is equipped with four cathodes, each with a dedicated channel for plasma monitoring via optical emission spectroscopy. It allows the exploration of a wide substrate temperature range, from cryogenic temperatures up to 1000 °C, in addition to RF and DC substrate biasing. Additional capabilities include real-time deposition data logging of sputtering parameters (such as power, voltage, pressure, gas flow), control of gas distribution to individual targets, time-sequenced shutters, and turbo gate position. All of these enable the user to execute complex programmable synthesis recipes.

In this presentation, we will discuss the details of this unique sputtering instrument and its integration with Python routines, resulting in an autonomous workflow for the synthesis of nitride thin films with controlled composition [1]. Moreover, we will also outline the integration of the time-series data automatically generated by this sputtering instrument with the research data infrastructure (RDI) [2]. NREL's RDI catalogs experimental data from inorganic thin films experiments at NREL and enables the High-Throughput Experimental Materials Database (HTEM-DB) (https://htem.nrel.gov/) [3], which stores information about synthesis conditions, chemical composition, crystal structure, and optoelectronic properties of materials.

[1] APL Mater 11, 071119, 2023

[2] Patterns, 2, 100373, 2021

[3] Scientific Data 5, 180053, 2018

Protective and High-temperature Coatings
Room Town & Country C - Session MA5-2-ThA
Boron-containing Coatings II

Moderators: Martin Dahlqvist, Linköping University, Sweden, **Anna Hirle**, TU Wien, Austria

1:20pm **MA5-2-ThA-1 Tuning Oxidation Resistance and Mechanical Properties of Diborides by Transition Metal Alloying Deposited by Combination of Magnetron Sputtering and Cathodic ARC Evaporation***,* ***Daniel Karpinski (d.karpinski@platit.com)****, P. Karvankova, C. Krieg,* PLATIT AG, Switzerland*; H. Joost, H. Frank,* Gesellschaft für Fertigungstechnik und Entwicklung Schmalkalden e.V., Germany*; A. Lümkemann,* PLATIT AG, Switzerland

Titanium diboride is currently the most widespread boride coating used in industry. Its most common application is machining non-ferrous metals, due to its outstanding properties such as high hardness 40–50 GPa, high elastic modulus ≥ 500 GPa, high chemical inertness, high melting point above 3000°C, and low propensity for sticking to soft metals. The main drawbacks of diborides are their generally low oxidation resistance (between 600-700°C for TiB_2) and brittleness. As productivity demands from customers rise, the cutting speed and feed rate of the tool increase as well, resulting in elevated temperatures at the contact point between the workpiece and the tool. Therefore, there is a strong incentive to increase the oxidation resistance and/or reduce the coefficient of friction of the coating. This study investigates the effect of alloying diboride materials with transition metals, altering the boron-to-metal coating stoichiometry (x = B/Me), mechanical properties, tribological properties, and oxidation resistance of the coating. A Platit Pi411 coating machine equipped with LACS® technology was used to synthesize the coatings. This technology enables magnetron sputtering to be performed from a central cylindrical cathode (SCiL®) while simultaneously running a cathodic arc evaporation process from cylindrical cathodes located in the chamber door (LARC®). For this study, the metal boride (MeB_x) coatings were deposited by concurrent magnetron sputtering of a MeB_2 target and cathodic arc evaporation of a Me target (Me = Ti, TiSi, Cr and Zr) to tune the coating stoichiometry and composition. Nanoindentation tests revealed that this alloying strategy can decrease the B-to-Me ratio from 2.0 to 1.5, resulting in a hardness drop from about 45 GPa to 35-40 GPa. Isothermal annealing tests conducted in air at 600°C for 1 hour showed that decreasing the B-to-Me ratio of the coating effectively doubles the oxidation resistance of the coating. In addition, it was found that the use of ternary boron alloys leads to an even more pronounced increase in oxidation resistance, up to threefold.

1:40pm **MA5-2-ThA-2 Coherent Coexistence of Crystalline Phases Enabled by Planar Defect Formation in Annealed $V_{1-x}W_xB_{2-\delta}$Films***, Katarína Viskupová (katarina.viskupova@fmph.uniba.sk), B. Grančič,* Comenius University in Bratislava, Slovakia*; P. Švec Jr.,* Slovak Academy of Sciences, Slovakia*; T. Roch, M. Truchlý, V. Šroba, L. Satrapinskyy, M. Mikula, P. Kúš, T. Fiantok,* Comenius University in Bratislava, Slovakia

Transition metal diboride films are characterized by high mechanical hardness, wear resistance and chemical stability at elevated temperatures. Combination of these advanced properties makes them applicable as protective coatings for alloy-machining tools. Typical nanocomposite structure of these films, consisting of hexagonal P6/mmm columnar grains surrounded by boron tissue phase, leads to high hardness above 37 GPa [1]. However, formation of the boron tissue phase is not convenient in terms of brittle fracture and oxidation resistance, which are the main drawbacks of diboride films. Therefore, one of the ways to improve the properties is to reduce the boron to metal ratio and aim for understoichiometric films [2]. Here, it is important to understand, how the boron deficiency will be accommodated by the films' structure, because it can significantly affect the mechanical properties [3]. In this work, we study the effect of boron understoichiometry on structure in case of ternary $V_{1-x}W_xB_{2-\Delta}$ films prepared by magnetron sputtering and ex-situ annealed up to 1200°C. We present results of detailed structural analysis by high-resolution transition electron microscopy, which revealed interesting structural features, including several types of planar defects and coexistence of coherently linked orthorhombic and hexagonal phase accompanied by chemical decomposition.

[1] P.H. Mayrhofer, C. Mitterer, J.G. Wen, J.E. Greene, I. Petrov, Self-organized nanocolumnar structure in superhard TiB2 thin films, Appl. Phys. Lett. 86 (2005) 1–3, https://doi.org/10.1063/1.1887824.

[2] J. Thörnberg, B. Bakhit, J. Palisaitis, N. Hellgren, L. Hultman, G. Greczynski, P.O. Å. Persson, I. Petrov, J. Rosen, Improved oxidation properties from a reduced B content in sputter-deposited TiBx thin films, Surf. Coat. Technol. 420 (2021), https://doi.org/10.1016/j.surfcoat.2021.127353.

[3] K. Viskupová, B. Grančič, T. Roch, Š. Nagy, L. Satrapinskyy, V. Šroba, M. Truchlý, J. Šilha, P. Kúš, M. Mikula, Thermally induced planar defect formation in sputtered V1-xMoxB2-Δ films, Scripta Materialia, Volume 229, 2023, 115365, ISSN 1359-6462, https://doi.org/10.1016/j.scriptamat.2023.115365.

This work was supported by the Slovak Research and Development Agency (Grant No. APVV-21-0042), Scientific Grant Agency (Grant No. VEGA 1/0296/22), European Space Agency (ESA Contract No. ESA AO/ 1-10586/21/NL/SC), and Operational Program Integrated Infrastructure (Project No. ITMS 313011AUH4).

2:00pm **MA5-2-ThA-3 Powder Synthesis and Application of Atmospheric Plasma Spraying Zirconium Diboride Coating***, **Ching Lee (tiger881217@gmail.com)**,* National Taipei University of Technology, Taiwan*; Y. Chen,* Researcher of National Chung-Shan Institute of Science & Technology, Taiwan*; Y. Chung,* Researcher of National Chung-Shan Institute of Science & Technology, Taoyuan city, Taiwan*; Y. Yang,* National Taipei University of Technology, Taiwan

Zirconium diboride has excellent properties such as high melting point, high thermal conductivity, high hardness, low theoretical density, good electrical conductivity, etc., making it suitable for the outer shell of supersonic spacecraft and missiles. As spacecraft or missiles will generate heat sources due to friction with the atmosphere at high altitudes, it is necessary to attach a layer of high-temperature refractory materials to prevent the heat generated externally from reaching the inside of the body. This experiment uses Atmospheric Plasma Spray (APS) to prepare self-synthesized zirconium diboride, and explores the coatings prepared under different spray conditions (current, surface speed, working distance). The coating was analyzed such as X-ray Diffraction, Scanning Electron Microscope, Crystallinity Analysis, Bond Strength Analysis, Micro Hardness Analysis, etc.

2:20pm **MA5-2-ThA-4 Annealing Twins in Sputtered Tantalum Boride Coatings***, **Branislav Grančič (branislav.grancic@fmph.uniba.sk)**,* *K. Viskupová, T. Fiantok,* Comenius University in Bratislava, Slovakia*; P. Švec Jr.,* Slovak Academy of Sciences, Slovakia*; V. Šroba, V. Izai, T. Roch, M. Truchlý, M. Mikula,* Comenius University in Bratislava, Slovakia

Magnetron sputtered transition metal diboride TMB_{2-x} coatings with significant substoichiometry are often amorphous in the as deposited state [1, 2]. Subsequent annealing at high temperatures can lead to formation of various crystalline phases [3]. In our work, we study the effect of annealing up to 1300°C on structure of substoichiometric $TaB_{1.2}$ films. Analysis by High Resolution Transmission Electron Microscopy revealed crystallization into orthorhombic Cmcm structure with high density of annealing twin lamellae. Using ab-initio calculations we show that the formation of stacking faults on {110} planes are energetically favorable and accumulation of such defects can lead to formation of orthorhombic Pnma phase with similar formation energy as Cmcm phase. Moreover, the thermally induced structural changes were accompanied by coatings' hardness increase from 27 to 34 GPa.

[1] B. Grančič, M. Pleva, M. Mikula, M. Čaplovičová,L. Satrapinskyy, T. Roch, M. Truchlý, M. Sahul, M. Gregor, P. Švec,M. Zahoran, P. Kúš, Stoichiometry, structure and mechanical properties of co-sputtered $Ti_{1-x}Ta_xB_{2\pm\Delta}$ coatings, Surf. Coat. Technol. 367 (2019) 341–348, https://doi.org/10.1016/j.surfcoat.2019.04.017.

[2] K. Viskupová, B. Grančič, T. Roch, L. Satrapinskyy, M. Truchlý, M. Mikula,V. Šroba, P. Ďurina, P. Kúš, Effect of reflected Ar neutrals on tantalum diboride coatings prepared by direct current magnetron sputtering, Surf. Coat. Technol. 421 (2021), https://doi.org/10.1016/j.surfcoat.2021.127463.

[3] K. Viskupová, B. Grančič, T. Roch, Š. Nagy, L. Satrapinskyy, V. Šroba, M. Truchlý, J. Šilha, P. Kúš, M. Mikula, Thermally induced planar defect formation in sputtered $V_{1-x}Mo_xB_{2-\Delta}$ films, Scripta Materialia, Volume 229, 2023, 115365, ISSN 1359-6462, https://doi.org/10.1016/j.scriptamat.2023.115365.

This work was supported by the Slovak Research and Development Agency (Grant No. APVV-21-0042), Scientific Grant Agency (Grant No. VEGA 1/0296/22), European Space Agency (ESA Contract No. ESA AO/ 1-10586/21/NL/SC), and Operational Program Integrated Infrastructure (Project No. ITMS 313011AUH4).

2:40pm **MA5-2-ThA-5 Constitution, Microstructure and Properties of Magnetron Sputtered CrB_2-TiB_2 and CrB_2-ZrB_2 Thin Films***, V. Ott,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; H. Riedl, T. Wojcik,* Vienna University of Technology, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; P. Mayrhofer,* Vienna University of Technology, Austria*; **Michael Stueber (michael.stueber@kit.edu)**,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal diboride thin film materials can provide interesting property profiles related to wear, oxidation and corrosion resistance, preferably at higher temperature and thermomechanical loads. To achieve such properties, intense efforts have recently been undertaken with regard to the microstructural design of diborides. These include for example different alloying strategies, incorporation of Si, formation of core-shell structures, defect engineering and advanced hybrid PVD processes for sophisticated thin film growth. However, the database on phase formation, microstructure and properties for PVD thin films in some material systems of interest is still surprisingly limited in comparison to transition metal nitrides and carbides. This study aims to contribute such information on DC magnetron sputtered thin films in the binary systems CrB_2-TiB_2 and CrB_2-ZrB_2. For both systems, a combinatorial approach for thin film deposition was followed, using segmented ceramic targets. The composition, phase and microstructure formation, characterized by EPMA, XRD and TEM methods, are systematically described for a broad compositional window in both systems. Selected mechanical properties, such as indentation hardness and modulus, as well as elastic and plastic deformation energies in micro indentation, are discussed versus the thin films' constitution and microstructure. Special focus is laid on the potential formation and impact of solid solution structured diboride thin films in the two quasi-binary systems that exhibit significantly different phase diagrams in thermodynamic equilibrium.

3:00pm **MA5-2-ThA-6 Fracture Characteristics of Si Containing Ternary and Quaternary Transition Metal Diborides***, **Anna Hirle (anna.hirle@tuwien.ac.at)**, A. Bahr, O. Beck, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria

Alloying with silicon or Si-based phases is an efficient approach to improve the oxidation resistance of transition metal diborides (TMBs). It is well established for bulk ceramics [1,2] but was also recently verified for thin film TMBs such as CrB_2, HfB_2, or TiB_2 [3,4]. Adding these strong oxide formers to diborides results in highly dense and protective SiO_2-based scales, whereas the amount of Si required differs between ternaries (pure Si addition) and quaternaries (alloying via disilicides), respectively. In more detail, alloying of $TaSi_2$ and $MoSi_2$ into TiB_2 thin films not only reduces the amount of Si needed to provide excellent oxidation resistance but also minorly influences the mechanical properties. For quaternary TiB_2 based coatings, hardness values of 36 GPa ($TaSi_2$) and 27 GPa ($MoSi_2$) compared to around 38 GPa of the binary system have been achieved. Interestingly, for ternary Ti-Si-$B_{2\pm z}$ films the mechanical properties vary in a wide range ceasing 20 GPa while exhibiting similar oxidation stabilities. All these coatings crystalized in the α-AlB_2 structure type with a preferred 0001 orientation being decisive for highest hardness.

Meanwhile the oxidation behavior and mechanical properties have been thoroughly described for ternary and quaternary TMBs so far [3,4] the fracture characteristics of these coating materials are rather unexplored. Based on a recent study [4] the fracture toughness (K_{IC}) of binary $TiB_{2\pm z}$ is known to be highly dependent on the amount of tissue phase present at the grain boundaries.

Therefore, this study aims to unravel the fracture resistance of Si containing ternary and quaternary TMBs, focusing on alloying routes with disilicides. A set of different coating compositions has been deposited by non-reactively DC magnetron sputtering using a broad set of composite targets TiB_2, $TiB_2/TiSi_2$ (90/10 & 80/20 mol%), $TiB_2/TaSi_2$ (90/10 & 80/20 mol%) and $TiB_2/MoSi_2$ (85/15 & 80/20 mol%). The elastoplastic behaviour involving also fracture characteristics such as K_{IC} are evaluated by micro-mechanical testing methods, such as cantilever bending or pillar compression testing, as well as nanoindentation. For an in-depth understanding, these results are correlated with detailed structure-morphological investigations using XRD, SEM, TEM, or ERDA/RBS.

[1] GB. Raju, et al,. J Am Ceram Soc. 2008;91(10):3320–3327.

[2] GB. Raju, et al., Scr Mater. 2009;61(1):104–107.

[3] T. Glechner, et al., Surf. Coat. Technol. 434 (2022) 128178.

[4] A. Bahr, et al.,Materials Research Letters. 11 (2023) 733–741.

3:20pm **MA5-2-ThA-7 Yttrium Tetraboride Thin Films – Thermal Evolution of the Nanostructure and Mechanical Properties**, ***Marek Vidiš (marek.vidis@fmph.uniba.sk)***, *M. Truchlý, V. Izai, T. Fiantok, T. Roch, L. Satrapinskyy,* Comenius University Bratislava, Slovakia*; Š. Nagy,* Slovak Academy of Sciences, Slovakia*; M. Mikula,* Comenius University Bratislava, Slovakia

Ultra-high temperature ceramics based on transition-metal diborides (TMB_2) attract attention due to their excellent chemical and mechanical properties. However, their practical application is limited by their inherent brittleness. The Y-B system offers a number of stoichiometric phases with a wide range of mechanical properties. The YB_2 has the lowest Young's modulus among the TMB_2, while the YB_6 is predicted to be a ductile ceramic. On the other hand, the YB_4 has the highest hardness among the Y-B phases, a melting temperature of 2800 °C, and a high flexural strength of 317 MPa. However, only a limited amount of knowledge is available about its properties in the form of a thin film. In this work, we focus on YB_4 thin film prepared by High Target Utilization Sputtering (HiTUS) technology using a stoichiometric YB_4 target. We report the evolution of the chemical composition, nanostructure, and mechanical properties after vacuum annealing up to 1300 °C. The EDS/WDS analyses show a slight over-stoichiometry of the sputtered film with a B/Y ratio of 4.7, a low oxygen content below 2 at.%, and a stable chemical composition with no boron loss. The as-deposited film is X-ray amorphous with a hardness of 23.4 GPa and a low Young's modulus of 281 GPa. After annealing at 800 °C, a partial crystallization occurs, and small regions with the tetragonal YB_4 phase in the amorphous matrix can be recognized. Further annealing leads to the grain coarsening of the YB_4 phase and formation of smaller grains of the cubic YB_6 phase. According to the XRD and HR-STEM, the coherence domain size increases from 26 nm to 44 nm for the YB_4 phase and from 7 to 53 nm for the YB_6 phase. The changes in the nanostructure are reflected in the mechanical properties of the film. The hardness increases to 26.4 GPa at 1000 °C, while a relatively low Young's modulus of 322 GPa is maintained. The ductile/brittle response to the mechanical loading is examined by cube-corner indentation. In the case of as-deposited film, a material pile-up at the edges with no crack formation is observed, indicating a ductile behavior of the X-ray amorphous film. After annealing, a crack formation is observed at the corners of the indents, which is a sign of a more brittle response. To conclude, the exceptional properties of YB_4 ceramic are confirmed in the form of thin sputtered films and are maintained even after high temperature loading. Therefore, the YB_4 thin film is a suitable candidate for example in superlattice architecture, where it would play the role of a medium-hard but less brittle layer in order to improve the overall toughness and thermal shock resistance of the coating.

Functional Thin Films and Surfaces
Room Town & Country B - Session MB3-2-ThA

Nanomaterial-based Thin Films and Structures II

Moderators: **Ondrej Kylian**, Charles University, Prague, Czechia, **Vladimir Popok**, Aalborg University, Denmark

2:20pm **MB3-2-ThA-4 Polymer-Supported Hydrophobic Functional Surfaces: A Smart SERS-Active Substrate**, ***Mohmmad Kamal Hossain (kamalhossain@kfupm.edu.sa)***, *A. Matin, A. Ulhamid,* King Fahd University of Petroleum and Minerals, Saudi Arabia

Smart and active surfaces of metal, particularly noble metal nanostructures, have been long desired due to their capabilities to show multifunctional properties. However, the development of such platforms remained challenging. In this work, a simple and two-step process was demonstrated to develop polymer-supported multifunctional surfaces. Commercially available polycarbonate (PC) was treated to turn the active surface hydrophobic with an average wetting contact angle (WCA) as high as 110.5°. The formation of nano-flowers with a coverage density of $9.29\times10^6/cm^2$ on the top of fine base nanostructures was confirmed by a high-resolution field emission scanning electron microscope (FESEM). Further decoration of such a hydrophobic surface with metal facilitated the achievement of a hydrophobic metal nanostructured surface. In this context, the petals of nano-flowers and fine base nanostructures were well decorated with functional metals such as silver (Ag) and thus the active surface remained hydrophobic with an average WCA as high as 106.6°. Abundant sharp spikes on the top of narrow hills and dips, as revealed in the high-resolution FESEM investigation, were speculated to be the reason behind this hydrophobic characteristic. High-resolution FESEM revealed broadened hills and dips that support the Cassie-Baxter model to demonstrate the scenario. Sessile drop tests were carried out to record average WCA and to understand the wetting characteristics of pristine PC, treated PC and Ag-decorated pristine and treated PC. A plausible mechanism for such hydrophobic characteristics as well as the transition from a hydrophobic state to a hydrophilic state has been elucidated. To demonstrate the surface-enhanced Raman scattering (SERS) activity, the specimen was incubated with the Raman active dye, Rhodamine 6G. Strong enhancement in SERS activity was recorded and the plausible reason behind such enhancement was elucidated. Such a straight forward and hand-on strategy in devising SERS-active substrates not only shows the cost-effective process, but also paves the way for a generic route to designing polymer-templated electronics.

2:40pm **MB3-2-ThA-5 AFM-SEM Imaging for TEM Grid Mounted Nanomaterials**, ***Kerim Arat (kerim.arat@qdusa.com)***, *S. Spagna,* Quantum Design Inc., USA

Microscopists employing Transmission Electron Microscopy (TEM) alongside TEM-based Energy Electron Loss Spectroscopy (EELS) to study the properties of nano-materials often need to assess physical parameters like heights and cross-sectional shapes of the samples under examination. Due to the typical sub-five nanometer thickness of membranes in TEM grids, conducting Atomic Force Microscopy (AFM) measurements on grid-mounted samples is currently arduous and time-intensive. This paper introduces a fully integrated AFM and Scanning Electron Microscope (SEM) correlative workstation, facilitating direct sample imaging on a TEM grid using both techniques. This seamlessly integrated and user-friendly AFM-SEM microscopy workstation unlocks unparalleled measurement capabilities at the nanoscale, particularly for complex geometries. The AFM-SEM imaging of TEM grid-mounted samples streamlines measurement workflows, leading to enhanced data output rates. Additionally, the platform supports easy expansion of functionalities, such as elemental analysis through Energy Dispersive X-ray Spectroscopy (EDS). The diverse array of AFM modes available (including Contact, Tapping, Off-resonance, Conductive, Magnetic, and Electrostatic) enables the extraction of various physical properties from the sample.

3:00pm **MB3-2-ThA-6 Sputtering onto Liquids: Towards the Synthesis of Ultra-Fine Nanoparticles**, *H. Lasfargues, L. Freymann, S. Shankar, M. Momma, T. Schneider,* ***Clio Azina (azina@mch.rwth-aachen.de)***, RWTH Aachen University, Germany

Physical vapour deposition approaches are highly versatile techniques which allow the deposition of a variety of material systems typically under thin film form. While thin films are the most common outcome of vapour-based deposition methods, nano-objects, such as nanoparticles, can also be produced by switching conventional solid substrates with liquid ones. Herein, the concept of sputtering onto liquids will be introduced. SoL is a technique which allows the synthesis of ultra-fine (<10 nm) nanoparticles in a vacuum-compatible liquid. While this approach has existed for more than 50 years, the mechanisms of nanoparticle formation are still not fully described. In fact, the effect of the plasma on the synthesis and stability of the suspensions is rarely discussed in the literature. Herein, we will attempt to identify the effects of the sputtered atoms kinetic energy and flux on the size of Ag nanoparticles sputtered onto polyethylene glycol and castor oil. From the systematic study it is shown that the flux and kinetic energy of the sputtered atoms have a combined effect on the nanoparticle size distribution. In addition, the functional groups of the liquids also impact the growth by stabilizing the incoming species despite their potentially elevated kinetic energies.

3:20pm **MB3-2-ThA-7 Superhard Hexagonal Tib$_2$/Hf Single Crystal Superlattices for Toughness Enhancement***, Naureen Ghafoor* ***(naureen.ghafoor@liu.se),*** Linköping University, Sweden*; N. Koutná, S. Lin,* TU Wien, Austria*; F. Angáy, M. Lorentzon, F. Eriksson, L. Hultman, J. Birch,* Linköping University, Sweden

We present combined experimental and theoretical investigations on iso-structural TiB_2/Hf superlattices, demonstrating the impact of individual layer thicknesses on the hardness and toughness.*Ab initio* calculations suggest that hexagonal alpha-structured TiB_2 and hexagonal close-packed Hf exhibit a basal-plane lattice and shear modulus mismatch of 0.16 Å (5.4%) and 200 GPa, respectively, hence providing a basis for hindering dislocation glide across interfaces. Superlattices are deposited using ion-assisted magnetron sputter deposition, designed with a modulation period of 5 nm (to allow for theoretical modeling of the structure), where the individual layer thicknesses range from 1 to 4 nm, as analyzed by XTEM, XRD, ERDA, and XPS. Superhard single crystal TiB_2/HfB_2 diboride superlattices with 40 GPa nanoindentation hardness form at lower Hf thicknesses and at high growth temperatures. Furthermore, structural characterization reveals boron diffusion from overstoichiometric TiB_2 into Hf layers, resulting in single crystal TiB2 and understoichiometric HfB_2, in response to the high negative enthalpy of Hf-B. Thanks to self-diffusion, no strain build-up and epitaxial breakdown of superlattice layers are observed in films with period numbers as high as 375. We show that for achieving TiB_2/Hf superlattice, it is critical to reduce boron diffusion by controlling the TiB_2 stoichiometry. Consequently, nanoindentation combined with microcantilever bending testing will be presented in relation to structural and mechanical predictions by *ab initio* calculations as well as machine-learning-potential molecular dynamics, where the latter uses a moment-tensor-type potential developed and carefully validated for the purpose of this study.

4:00pm **MB3-2-ThA-9 Study on Improving the Performance of Zinc Oxide Piezoelectric Pressure Sensor by Doping Vanadium***, Heng-Chi Chu* ***(juliachu2000@gmail.com),*** *S. Brahma, J. Huang,* National Cheng Kung University (NCKU), Taiwan

Piezoelectric effect is a phenomenon in which positive and negative ions are displaced generating electric polarization with the application of stress on the materials having non-centrosymmetric crystal structure. Zinc oxide possesses both piezoelectric and semiconductor properties. The applied pressure generates piezo-potential thereby creating a Schottky barrier at the interface of the semiconductor and the metal electrode that can be modulated by the variation of the strain. This characteristic can be applied to fabricate the piezoelectric pressure sensors devices based on ZnO/doped ZnO and investigate the stress sensitivity. However, the low piezoelectric coefficient (12.4 pC/N) of ZnO restricts further development zinc oxide based piezoelectric devices. Consequently, we doped zinc oxide with vanadium and doping of smaller ionic radius vanadium at the zinc sites enhanced electric polarization and improved the piezoelectric coefficient. Furthermore, vanadium doping induced changes in the grain size and energy band structure and influenced the performance of the piezotronic effect. We employed radio frequency magnetron co-sputtering to deposit V doped ZnO thin films by using zinc oxide and vanadium pentoxide as targets and V doping concentration was controlled by the variation of the working power of vanadium pentoxide target. Subsequently, we fabricated a pressure sensor by depositing gold electrodes to create a Schottky barrier and investigated the piezoelectric stress sensitivity. SEM results revealed that vanadium doping led to the grain size reduction. XPS analysis of the oxygen spectrum indicated that doping led to surface adsorbates and an increase in intrinsic defects. The XPS spectra of vanadium showed the presence of both V^{5+} (V^{3+}) ions at low (high) V doping concentrations. As the doping concentration increased, the proportion of V^{5+} decreased due to the redox effects, shifting to V^{3+} with a larger radius. This trend aligns with the piezoelectric coefficient. UV-vis and UPS analyses provided insights into the energy band structure. Vanadium doping shifted the Fermi level towards the conduction band, resulting in a smaller work function and band gap compared to undoped zinc oxide. This induced a more stable Schottky barrier and improved carrier transport mechanism. In the piezoelectric stress sensitivity test, vanadium doping effectively enhanced current and stress sensitivity. However, higher doping concentration decreased the sensitivity due to the lower piezoelectric coefficient. In summary, our research aims to combine the above analyses to identify optimal sputtering parameters, thereby enhancing the performance of piezoelectric pressure sensors.

4:20pm **MB3-2-ThA-10 Glancing Deposited Wide Band Gap Zirconia Nanohelical Metamaterial Platforms:Unveiling Broad-Band UV-Active Chirality***, Ufuk Kilic* ***(ufukkilic@unl.edu),*** University of Nebraska - Lincoln, USA*; M. Hilfiker,* Onto Innovation Inc., USA*; S. Wimer,* University of Nebraska - Lincoln, USA*; C. Argyropoulos,* Pennsylvania State University, USA*; E. Schubert, M. Schubert,* University of Nebraska - Lincoln, USA

Chirality is a property of asymmetry in molecules or objects that cannot be superimposed onto their mirror images. This symmetry breaking phenomenon is fundamental to various fields such as chemistry, biology, physics, and materials science. Optical manifestation of chirality known as circular dichroism is the differential absorption response of the object to the incoming left- and right- handed circularly polarized light. However, chirality found in nature is very weak, almost impossible to spectrally control, and mostly emerges in the vacuum ultraviolet (VUV) part of the spectrum [1]. Utilizing metamaterial platforms to boost chirality and to detect these chiral molecules presents challenges, as many are designed for the operation in the infrared (IR) to the visible spectral range [1,2]. The utilization of ultra-wide band gap metal oxides in nanostructure fabrication has received limited attention in the literature, particularly concerning their chiral properties [2]. In this study, we explored the fabrication of zirconia (ZrO_2) thin films using electron beam evaporated glancing angle deposition (GLAD) technique. This recently emerging bottom-up fabrication technique is known for its capacity to produce various 3D nano-morphologies over wafer-scale area.

Leveraging the substrate manipulation arm, the normal incidence of the particle flux onto the surface leads to the fabrication of flat, uniform, thin films of ZrO_2. Through generalized spectroscopic ellipsometry (GSE) technique, we extracted the frequency dependent complex dielectric function and performed critical point model dielectric function analysis to identify the band-to-band transitions within near-IR to VUV spectral range. On the other hand, impinging the particle flux on the sample substrate at extremely oblique angle (85.5^o) together with continuous rotation of sample (24 sec/rev) permits the fabrication spatially coherent, well-oriented nano-helices. Hence, we experimentally detected VUV-active strong circular dichroism responses from ZrO_2 nano-helical metamaterials using the Mueller matrix GSE technique. Furthermore, we employed finite element modeling (FEM) to theoretically verify these responses and observed that the chiral response can be tailored in terms of magnitude and spectral position using structural parameters of nano-helices. Furthermore, we envision a potential use of these chiral metamaterials in areas which include high power required chiroptic photonic/electric circuit designs, UV active topological insulators, chiral sensor technologies.

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Coatings for Biomedical and Healthcare Applications
Room Palm 3-4 - Session MD2-ThA

Medical Devices: Bio-Tribo-Corrosion, Diagnostics, 3D Printing

Moderators: Steve Bull, Newcastle University, UK, **Hamdy Ibrahim**, University of Tennessee at Chattanooga, USA

2:00pm **MD2-ThA-3 Corrosion Risk Analysis of CoCrMo alloy as a Function of Microstructure: Biomedical Applications***, **Maansi Thapa (mthapa3@uic.edu)**,* University of Illinois at Chicago, USA*; Y. Sun, B. Keaty, M. Mathew, C. Takoudis, M. Daly, D. Ozevin,* University of Illinois - Chicago, USA

CoCrMo alloys are widely used in orthopedic implants and various biomedical applications, exhibit excellent corrosion resistance and mechanical properties. However, it has raised concerns about inferior corrosion behavior and subsequent side effects due to metal ion release. While the electrochemical nature of this alloy is well studied, the microstructure's effect needs further research. The objective of this study is to evaluate corrosion behavior of CoCrMo alloys in two microstructures: unbanded (transverse) and banded (longitudinal).

Six CoCrMo disks (11x7mm) were prepared and polished following metallographical protocol for a surface finish of <50 nm. The unbanded CoCrMo rod was cut perpendicular to the axis, while the banded CoCrMo rod was cut parallel to the axis. The electrolyte used was bovine calf serum (30 g/L proteins) with a pH of 7.6 to simulate the joint environment. The electrochemical test followed ASTM G61 standard using a three-electrode system: the sample as the working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a graphite rod as the counter electrode. The typical protocol involved: open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and cyclic polarization curve. Using Tafel's estimation, the corrosion potential (E_{Corr}) and corrosion current (I_{Corr}) were determined. EIS data was utilized to generate Bode and Nyquist plots and construct an equivalent electric circuit to determine polarization resistance (R_p) and double layer capacitance (C_{dl}). The corroded surfaces were characterized by white light microscopy, SEM, and EBSD.

Our study showed that the CoCrMo specimens with unbanded microstructures exhibited increased corrosion resistance (E_{corr}: -0.678 V vs SCE, I_{corr}: 1.85E-06 A/cm^2) compared to banded microstructures (E_{corr}: -0.736 V vs SCE, I_{corr}: 5.05E-06 A/cm^2). The EIS data supported this observation, revealing higher R_p and lower capacitance. SEM observations revealed larger pitting in the banded microstructure compared to unbanded. Previously, Jacob et al.[1] reported superior fretting-corrosion behavior of unbanded microstructures and potential risk of banded microstructures under an infected environment.

The banded microstructure, with increased grain boundary exposure, heightens the risk of intergranular and galvanic corrosion. Further exploration is needed to understand microstructural mechanisms and develop strategies to inhibit increased corrosion risk. Our investigation emphasizes the vital role of material composition and configuration in microstructural and corrosion behavior.

(1)Manthe, J *Mech. Behavior of Biomed Materials*. **2022**.

2:20pm **MD2-ThA-4 Comparative Study of Composite Coatings on Magnesium for Biomedical Devices***, V. Patil,* University of Tennessee at Chattanooga, USA*; B. Williams,* University of Arkansas, USA*; J. Rich,* University of Tennessee at Chattanooga, USA*; M. Elsaadany,* University of Arkansas, USA*; **Hamdy Ibrahim (hamdy-ibrahim@utc.edu)**,* University of Tennessee at Chattanooga, USA

Magnesium (Mg) and its alloys exhibit a biodegradable nature in aqueous environments, rendering them appealing for diverse biomedical applications where permanent existence in the body is not advisable. However, the utilization of Mg for bone fracture repair faces notable challenges, primarily stemming from its constrained mechanical strength and rapid corrosion rates. To address these issues, extensive research has been directed towards the development of biocompatible coatings that can offer Mg the necessary protection in vivo. In this study, we have formulated various composite coatings and conducted a comprehensive assessment of their properties, including corrosion rates, biocompatibility, adhesion strength, and surface morphology. The evaluated composite coatings were derived from three distinct processes: Plasma Electrolyte Oxidation (PEO), sol-gel coating, and polymer dip coating. Results indicated a substantial enhancement in corrosion resistance within the sol-gel coated composite group. Moreover, the polymer-coated groups demonstrated superior osseointegration and biocompatibility. This investigation underscores the feasibility of producing biocompatible magnesium-based implants with enhanced strength and controlled corrosion properties through the application of diverse composite coatings.

2:40pm **MD2-ThA-5 Laser-Induced Graphene Coatings on Polymers for Biomedical Devices***, **Mostafa Bedewy (mbedewy@pitt.edu)**,* University of Pittsburgh, USA **INVITED**

Nanocarbons like graphene and related materials are promising for various biomedical applications; however, major manufacturing challenges still hinder our ability to scalably produce graphene with tailored morphology and surface chemistry, especially on flexible and polymeric substrates. While chemical vapor deposition (CVD) processes enable the synthesis of high-quality graphene, the typically high temperatures in such reactors limit the choice of substrates to silicon, quartz, metals or other temperature-resistant materials. On the other hand, emerging flexible devices, such as implantable surgical meshes and biosensors require the fabrication of such nanocarbon coatings and electrodes directly on polymers. Unlike different transfer techniques of CVD-grown nanocarbons, or printing methods from inks, this talk will focus on a bottom-up approach for directly growing different types of graphenic nanocarbons on aromatic polymers by laser irradiation.The speaker will present an approach that leverages this direct-write process, often referred to as laser-induced graphene (LIG), for creating spatially-varying morphologies and chemical compositions of LIG electrodes, by leveraging gradients of laser fluence. Three distinct morphologies are identified, and process control map is generated for maximizing the electrical conductivity of these porous graphene for biomedical devices. Moreover, this talk will introduce a method for controlling heteroatom doping of LIG based on controlling the molecular structure of the polymer being lased, i.e. by introducing sulfur- and fluorine- containing backbones.We demonstrate superhydrophobic and parahydrophobic surface properties for the fluorine-doped LIG patterns. We also show antibacterial properties of LIG coated surgical devices. Finally, a demonstration of these functional doped LIG electrodes as electrochemical biosensors will be presented for the detection of the neurotransmitter dopamine with nanomolar sensitivity.

3:20pm **MD2-ThA-7 Microfluidic Device for the Isolation, Detection, and Purification of Exosomes Based on Metallic Nanostructure Arrays***, **Alfreda Krisna Altama (alfredakrisna@gmail.com)**, Y. Hsiao, C. Chen,* National Taiwan University of Science and Technology, Taiwan*; R. Haliq,* National Taiwan University of Science and Technology, Indonesia*; P. Yiu,* Ming Chi University of Technology, Taiwan*; P. Wu, J. Chu,* National Taiwan University of Science and Technology, Taiwan

Due to their low cost, rapid processing, and ability to analyze even minuscule samples, microfluidic devices are widely used in disease detection and specimen separation. In this study, metallic nanostructure arrays (MeNTAs) with tube-like features are embedded into microfluidic devices for immunoaffinity-based detection and efficient exosome isolation. MeNTA candidates were evaluated based on their ability to withstand mechanical stress during microfluidic operations, X-ray diffraction, zeta potential, and electrostatic interactions. The $Zr_{60}Cu_{25}Al_{10}Ni_5$ thin film metallic glass (Zr-TFMG) exhibited superior mechanical properties and a negative zeta potential compared to other materials. (e.g., Cu, Bronze, Ag, 7075Al, Ti64, 718Ni, SS316, Cu-TFMG, W-TFMG, and Al-TFMG). The resultant microfluidic device featured Zr-based MeNTAs with an interdigital electrode in a microchannel. In testing with derived exosomes (liquid biopsy of 500 µL), the device achieved a 95.3% exosome recovery rate within 1 hour while resisting nonspecific binding to HeLa-derived exosomes (recovery rate < 0.1%). The device facilitated the isolation of 1 x 10^8 exosome particles per mL for electrochemical impedance spectroscopy detection and allowed efficient release of captured exosomes via cyclic voltammetry operations. The proposed Zr-MeNTA microfluidic device holds significant potential for the isolation, detection, and purification of exosomes in liquid biopsy samples for cancer diagnosis, as mentioned by Hsiao et al. (2023).

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP2-2-ThA
HiPIMS, Pulsed Plasmas and Energetic Deposition II

Moderators: Simizu Tetuhide, Tokyo Metropolitan University, Japan, **Martin Rudolph**, Leibniz Inst. of Surface Eng. (IOM), Germany

2:00pm **PP2-2-ThA-3 Strategies for Low Temperature Reactive Deposition of Crystalline TiO_2 Thin Films**, ***Tomas Kubart (tomas.kubart@angstrom.uu.se)***, Uppsala University, Department of Electrical Engineering, Sweden **INVITED**

Titanium dioxide thin films have a multitude of different applications. While the amorphous TiO_2 has excellent optical properties and very good conductivity, the presence of defects leads to an increased recombination. For this reason, crystalline thin films of TiO_2 are desirable for photocatalysis as exemplified by plasmonic photoconversion devices for production of chemical molecules or oleophobic surface treatment by photofixation of SO_2 on anatase surfaces. In general, there is a great interest in deposition techniques that enable phase control of oxide thin films with TiO_2 being the prominent example.

This contribution deals with reactive HiPIMS deposition of TiO_2 thin films. First, experiments with a relatively long target-to-substrate distance are presented. It is shown that in the absence of substrate heating, all deposited films are X-Ray amorphous. Despite that, films prepared by an optimized HiPIMS process exhibit up to 3 times higher photocatalytic activity evaluated by photodegradation of stearic acid, as compared to reference pulsed DC films prepared using the same setup. High oxygen partial pressure is required to achieve the enhanced photocatalytic performance. Increased ion energy, however, has a detrimental effect on the photoactivity. The deposition conditions have also pronounced impact on the crystallization kinetics of the thin films as illustrated by in-situ GIWAXS studies.

When the target-to-substrate distance is reduced, the crystallinity of the as-deposited films is greatly improved. Growth of anatase as well as rutile can be achieved by changing the total deposition pressure. Even here, the HiPIMS process facilitates crystallization of the films as compared to pulsed DC. The deposition, however, results in a pronounced unintentional heating of the substrate. The heat input to the substrate is characterized and results from alternative experiments are presented.

In summary, the HiPIMS deposited films clearly outperforms the ones prepared by pulsed DC. Although the exact growth conditions are dependent on the deposition geometry and specifics of the deposition setup, some general trends can support the process development.

2:40pm **PP2-2-ThA-5 Plasma Dynamics of Individual HiPIMS Pulses Investigated by High-Frame-Rate Camera**, ***Matjaz Panjan (matjaz.panjan@ijs.si)***, Jozef Stefan Institute, Slovenia

Plasma of high-power impulse magnetron sputtering (HiPIMS) discharges is not azimuthally homogenous instead it is concentrated in dense angular regions called spokes [1]. These regions are organized in periodic or quasi-periodic patterns, typically have triangular shape and rotate with velocities of several km/s. Spokes are also present in other types of magnetron discharges. They have been observed in DC magnetron sputtering [2] and RF magnetron sputtering discharges [3].

In this work, we studied the dynamics of HiPIMS plasma with microsecond time resolution using a high-frame-rate camera. The individual pulses were investigated for different Ar pressures (0.25-2 Pa) and peak currents (10-400 A). The experiments show three distinct stages in the plasma dynamics and self-organization with increasing discharge current. From the pulse onset and up to currents of 25-50 A the dynamics is similar to one observed in DCMS discharges. Spokes rotate in the -**E×B** direction with velocities from 4 km/s to 15 km/s and exhibit elongated triangular shape. The growth rate in discharge current strongly influences the spoke velocity – spokes rotate faster for higher growth rates. This DCMS-like stage is followed by a chaotic plasma reorganization with the formation of irregular patterns and complex spoke propagation. As current increases above approximately 50 A, plasma starts to form regular patterns with triangular spoke shape. During this stage, spokes rotate in the **E×B** direction with velocities from 6 km/s to 9 km/s. The spoke velocity depends on the pressure but is practically independent of the discharge current. Spokes rotate faster at lower pressures than at higher pressures. Remarkably similar plasma evolution is observed for pulses with comparable discharge current waveforms.

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3:00pm **PP2-2-ThA-6 PowerFlex 500CG: A New HiPIMS Machine for Microtools Coating**, ***Tommaso Ceccatelli Martellini (tommaso.ceccatellimartellini@protectim.com),*** Protec Surface Technologies, USA; *G. Coletta,* Protec Surface Technologies, Italy

A new PVD platform for the deposition of ultra-smooth hard coatings on microtools is introduced: the PowerFlex 500CG. This PVD machine is based on HiPIMS technology and allows the reliable deposition of multiple industrial coatings (TiSiN-based, AlCrN-based or sputter taC) for demanding applications such as high precision machining of hardened steel (HRC60), TiAlV or Al-alloys. The current cutting applications require coatings with extremely high smoothness, durability, and thermal resistance as well as tailored stress and toughness. The performance of the PowerFlex 500CG machine will be described in this paper, including its new etching protocol allowing in-situ microtool edge preparation or a stable reactive sputtering process to improve deposition rate. Finally, a comparison with the industrial benchmark coatings for high precision machining is presented.

3:20pm **PP2-2-ThA-7 Toward Decoupling the Effects of Kinetic and Potential Ion Energies: Ion Flux Dependent Structural Properties of Thin (V,Al)N Films Deposited by Pulsed Filtered Cathodic Arc**, ***Yeliz Unutulmazsoy (yeliz.unutulmazsoy@iom-leipzig.de)***, *D. Kalanov, K. Oh,* Leibniz Institute of Surface Engineering (IOM), Germany; *S. Karimi Aghda,* RWTH Aachen University, Germany; *J. Gerlach, N. Braun,* Leibniz Institute of Surface Engineering (IOM), Germany; *F. Munnik,* Helmholtz-Zentrum Dresden - Rossendorf, Germany; *A. Lotnyk,* Leibniz Institute of Surface Engineering (IOM), Germany; *J. Schneider,* RWTH Aachen University, Germany; *A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany

Multiply charged ions formed in pulsed filtered cathodic arc process carry significant kinetic and potential energy which contributes to the formation of dense, adherent and macroparticle-free thin films. While the impact of kinetic ion energy on thin film formation during energetic processes such as cathodic arc deposition is well explored, the effects of ion potential energy are less known. We aimed to decouple the contribution of ion kinetic and potential energy regarding the structural effects on the forming thin films. To reach that goal, different arc source configurations are utilized in the filtered cathodic arc experiment including biasing the plasma in relation to the grounded substrate and applying an external magnetic field at the source. Charge-state-resolved energy distribution functions of ions measured at the substrate positions revealed the differences in plasma properties between the arc source configurations, and applying external magnetic field is found to be the primary tool to increase the ratio of multiply charged ions. Thin films of metastable cubic (V,Al)N films are deposited using different electrical configurations and characterized in detail. The resulting thin films demonstrate the possibility to deposit crystalline films without substrate heating due to “atomic scale heating” stemming from the high flux of multiply charged ions, namely the ions carrying significant kinetic and potential energy, in the case of an external magnetic field. However, additional complexity added by the high flux needs further research to distinguish the sole effects of ion flux and ion potential energy on the structure of a forming thin film.

4:00pm **PP2-2-ThA-9 On Working Gas Rarefaction in High Power Impulse Magnetron Sputtering**, ***Kateryna Barynova (barynova.k.a@gmail.com)***, University of Iceland; *M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany; *S. Suresh Babu,* University of Iceland; *J. Fischer,* Linkoping University, Sweden; *N. Brenning, M. Raadu,* KTH Royal Institute of Technology, Sweden; *D. Lundin,* Linkoping University, Sweden; *J. Gudmundsson,* University of Iceland

The ionization region model (IRM) is applied to explore working gas rarefaction in high power impulse magnetron sputtering discharges operated with graphite, aluminum, copper, titanium, zirconium, and tungsten targets. The various contributions to working gas rarefaction including electron impact ionization, kick-out by the sputtered species, and diffusion, are evaluated and compared for the different target materials, and over a range of discharge current densities. For all cases the working gas rarefaction is found to be significant, and to be caused by several processes. Their relative importance varies between different target materials. In the case of a graphite target, electron impact ionization (by both primary and secondary electrons) is the dominating contributor to the working gas rarefaction, with 65 – 69% contribution, while the sputter wind kick-out, has almost negligible influence. In the case of a copper and tungsten targets, the kick-out dominates. The main factor determining the relative contribution of the kick-out by the sputtered species to working gas rarefaction appears to be a multiplication of the mass of the target atom, the cohesive energy, which determines the most probable velocity with which the sputtered particles leave the target, and the self-sputter yield.

4:20pm **PP2-2-ThA-10 Tough Plasmonic Titanium Nitride Films Deposited by High Power Impulse Magnetron Sputtering***, E. Muir,* Sheffield Hallam University, UK*; R. Bower, P. Petrov,* Imperial College of Science, Technology and Medicine, UK*; **Arutiun P. Ehiasarian (A.Ehiasarian@shu.ac.uk),*** Sheffield Hallam University, UK

TiN is one of the most plasmonically active and environmentally robust materials with photocatalytic function. However thin films suffer from high optical losses due to a high uptake of C and O impurities at grain boundaries. Densification of the microstructure through High Power Impulse Magnetron Sputtering (HIPIMS) deposition improves the optical properties, however the influence of plasma chemistry is not known. This study utilises constant-current HIPIMS as a technology to achieve high pulse-to-pulse reproducibility and overall operational stability in the discharge in a wide operating window. Time-resolved optical emission spectroscopy reveals a gas-rich ignition phase with duration of 30 µs which develops into a metal-rich phase where the metal component is continuously pumped over 70 µs while the plasma density remains constant. A steady metal-dominated state is reached for pulse durations above 100 µs. Films deposited during the ignition stage were markedly different than those deposited when the discharge develops into the "pumping" and "steady state" regimes, for a constant peak and average power. Differences are observed in the crystallographic texture shifting from a strong (111) to a stronger (200) component confirmed by XRD pole figures, and H_{IT}^3/E_{IT}^2 ratio (toughness) increasing dramatically from 0.2 to 0.3 GPa for a nano-hardness increase from H_{IT} = 33 to 34 GPa. The changes are correlated with the grain morphology observed by AFM. All films were deposited without heating or substrate bias and exhibited excellent plasmonic properties with a single wavelength of electric permittivity near zero and low optical losses represented by the imaginary component of the electric permittivity as determined from modelling of ellipsometry data. The antimicrobial properties of the films will be discussed.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country D - Session TS4-2-ThA

Coatings and Surfaces for Thermoelectrical Energy Conversion and (Photo)electrocatalysis II

Moderators: Clio Azina, RWTH Aachen University, Germany, **Carlos Tavares**, University of Minho, Portugal

1:40pm **TS4-2-ThA-2 Multifunctional Materials for Emerging Technologies***, **Federico Rosei (federico.rosei@units.it),*** University of Trieste, Italy **INVITED**

This presentation focuses on structure property/relationships in advanced materials, emphasizing multifunctional systems that exhibit multiple functionalities. Such systems are then used as building blocks for the fabrication of various emerging technologies. In particular, nanostructured materials synthesized via the bottom–up approach present an opportunity for future generation low cost manufacturing of devices [1]. We focus in particular on recent developments in solar technologies that aim to address the energy challenge, including third generation photovoltaics, solar hydrogen production, luminescent solar concentrators and other optoelectronic devices. [2-40].

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2:20pm **TS4-2-ThA-4 Enhanced Photoelectrochemical Water Splitting on $ZnCo_2O_4$ Electrodes in Chloroplasts Driven by Spin Injection***, **Chien-Yu Lin (n56111453@gs.ncku.edu.tw),** Y. Su,* National Cheng Kung University (NCKU), Taiwan

This work demonstrated the photoelectrochemical water splitting efficiency of spinel-structured $ZnCo_2O_4$ on carbon paper substrate as photoelectrode and also coating on chloroplasts. $ZnCo_2O_4$ is p-type transition metal oxide semiconductor and could be synthesized by hydrothermal method and different annealing temperature, showing nanoparticles in morphology. Furthermore, we extracted the chloroplasts from chlorella to make it coat on $ZnCo_2O_4$ electrodes as protection layer, which also could be boosting the photosynthesis reaction when the water splitting process goes on. We observed the applied bias photon-to-current efficiency (ABPE) by changing spin quantum states, and the chloroplasts photoelectrochemical water splitting cell shows a splendid efficiency of hydrogen production. Accordingly, the device can be successfully applied on energy storage and conversion, suggesting the great potential of the applications in electronic, catalysis, and solar applications.

2:40pm **TS4-2-ThA-5 Piezoelectricity-Assisted Photocatalyst of BiOBr-Based Composites on a Flexible Substrate***, **Thi Nghi Nhan Nguyen (nghinhan2410@gmail.com)**, K. Chang,* National Cheng Kung University (NCKU), Taiwan

A novel 3D network of BiOBr flakes was grown on carbon fiber (CF) substrates through a straightforward chemical deposition process. The BiOBr-based composites served as catalysts for photodegradation and as photoelectrodes for photoelectrochemical cells. The p-n junction formation was determined by Mott–Schottky measurements which was also confirmed through high-resolution transmission electron microscopy and X–ray photoelectron spectroscopy. The piezoelectric properties of BiOBr were verified using piezoresponse force microscopy. The photoelectrochemical performance of samples was assessed through various techniques, including linear sweep voltammetry, chronoamperometry [https://www.sciencedirect.com/topics/chemistry/chronoamperometry], amperometry andcyclic voltammetry. Under simultaneous illumination and mechanical pressure, the Ag_2O/BiOBr composite demonstrated a photocurrent of approximately 20.0 mA cm^{-2} at 1.23V, showcasing a remarkable enhancement over 4 and 20 times compared to individual BiOBr and Ag_2O, respectively. The maximum applied bias photon to current efficiency values of Ag_2O/BiOBr composite with external stress was approximately 2.7 % at 0.9V. Additionally, a glucose sensor based on Ag_2O/BiOBr composite exhibited a high sensitivity of 400 µA cm^{-2} mM^{-1}, within a detection glucose range of 0.1–12 mM. The Ag_2O/BiOBr-based photolectrodes showed excellent stability and repeatability in glucose detection. Furthermore, the CuS/BiOBr composite displayed outstanding performance in TC degradation. The effectiveness of the BiOBr composites was attributed to the p-n junction formation, piezoelectric potentials, substantial active surface area and advantageous band positions.

3:00pm **TS4-2-ThA-6 Hydrothermal Synthesis of (Ba,Sr)TiO_3/AgBr Films and Their Application for the Visible-light Piezo-photocatalysis***, **Yen-Lun Chiu (0953065268v@gmail.com)**, K. Chang, S. Han,* National Cheng Kung University (NCKU), Taiwan

Perovskite-nanostructured films are attractive because of their excellent characteristics. Different kinds of properties can be obtained, e.g., dielectric properties, piezoelectricity, and thermoelectricity, from different materials. With the hydrothermal fabrication, the perovskite materials can be synthesized in a facile way with lower power consumption. However, studies on this topic directly through hydrothermal processes for the fabrication of perovskite-nanostructured films are still lacking. In this study, well-aligned (Ba,Sr)TiO_3 nanorod arrays composited with p-AgBr were synthesized through the hydrothermal reaction for visible-light piezo-photocatalytic application. The hydrothermal parameters, including concentrations of precursor solutions, reaction time, temperatures, different types of ion species, and the surfactants used for the reaction, were manipulated. X-ray diffraction and transmission electron microscopy were employed to determine the phase and microstructure of the resultant samples. The amplitude of the piezoresponse (d_{33}) was measured through a piezoresponse force microscope for the materials. The photoelectrochemical activity of the samples were also studied for related applications. An energy band diagram was constructed to elucidate a potential mechanism for the remarkable activity.

Keywords: perovskite-nanostructured films, hydrothermal, $(Ba,Sr)TiO_3$ nanorod arrays, p-AgBr, piezo-photocatalysis

3:20pm **TS4-2-ThA-7 Advances in Piezo-Photothermal Effect Enhanced Photocatalytic Activities of Heterostructure Composites***, **Van Ty Tran (tranvanty108@gmail.com)**, D. Chen,* National Cheng Kung University (NCKU), Taiwan

This study focusses on developing heterostructure composites to enhance the efficiency of piezoelectric and photothermal-assisted photocatalytic processes for pollutant degradation and photoelectrochemical water splitting. The $Ag_2O/BiFeO_3$ and CuS/MoS_2 composites were fabricated through a hydrothermal method. The morphologies and microstructures of the samples are analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy. The composites exhibit a low band gap, indicating their capacity to absorb light in the Vis-NIR range. The conductive type of the samples and p-n junction formation is determined through Mott Schottky (M-S) measurements. The formation of a p-n junction facilitates the separation of electron-hole pairs, thereby improving the efficiency of the photocatalyst. Additionally, the induced piezoelectric potential in the piezoelectric material promotes photocatalytic activity by reducing the recombination of photogenerated charges. Under irradiation, the generated heat further supplies kinetic energy to photogenerated carriers, enhancing reaction rates in photocatalytic processes. The piezoelectric composite demonstrates the ability to produce $\bullet O^{2-}$, $\bullet OH$, and h^+ through photocatalysis, effectively degrading pollutants like tetracycline (TC) and Rhodamine B (Rh B) through oxidation. The degradation efficiency of the TC solution was further increased to 95% for CuS/MoS_2 composite in 30 min, which was higher than that of individual components. Moreover, The $Ag_2O/BiFeO_3$ heterostructure exhibited excellent photocatalytic degradation of Rhodamine B and TC, and photoelectrochemical water splitting activity.

4:00pm **TS4-2-ThA-9 Photoelectrochemical Properties of Chlorophyll Coating on Cu_2O Photocatalyst by Mediating Charge Transfer Characteristic***, **Yu-Teng Wu (wuyuteng22@gmail.com)**, Y. Su,* National Cheng Kung University (NCKU), Taiwan

Metal oxide semiconductors have impressive applications in the field of photo electrochemistry. This study utilizes electrochemical deposition to generate nano-thin films of cuprous oxide, applying them in green energy sources. During the photoelectrochemical (PEC) process, cuprous oxide faces issues of instability and insufficient durability due to photo-induced corrosion in aqueous solutions. To address this, the natural photosensitizing material chlorophyll is adhered to enhance charge transfer efficiency and provide a better surface electric field distribution. Additionally, the chlorophyll layer effectively isolates the aqueous solution from direct contact with cuprous oxide, enhancing sample stability. Detailed research results, including atomic force microscopy (AFM) and electrostatic force microscopy (EFM) surface electric field analyses, along with electrochemical methods, confirm that Chlorophyll/Cu2O exhibits superior stability and durability, enhancing the overall value of this PEC cell.

4:20pm **TS4-2-ThA-10 Ligand Modified Bimetallic Metal-Organic Frameworks Electrocatalysts for Urea Oxidation Reaction***, **Hui Chuan Chen (jace52112@gmail.com)**,* National Cheng Kung University (NCKU), Taiwan*; T. Nguyen,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; J. Ting,* National Cheng Kung University (NCKU), Taiwan

In the quest for energy efficiency, electrocatalytic urea oxidation reaction (UOR) is a promising alternative to oxygen evolution reaction (OER) due to the favorable thermodynamics, meanwhile, it is also an environmentally friendly strategy.

In this regard, metal-organic framework (MOF) materials have the advantages of high specific surface area, high porosity, structural adjustability, etc., providing abundant metal active sites to achieve high efficiency electrocatalytic performance. However, due to the poor conductivity of MOF, the charge transfer ability is limited. In order to improve the shortcoming, ligand having redox activity is introduced. This ligand can not only adjust the synergistic effect of metal clusters and organic ligands to increase the charge transfer ability, but also can be an additional adsorption sites to promote the adsorption/desorption ability of intermediates. In this study, we report ligand modified bimetallic MOF synthesized via a low temperature hydrothermal method, this optimized bimetallic MOFs exhibits an outstanding UOR performance with high catalytic activity, low resistance and excellent electrochemical stability.

Keywords: MOFs, urea oxidation reaction (UOR), electrocatalyst

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Golden State Ballroom - Session CM-ThP

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films (Symposium CM) Poster Session

CM-ThP-1 Localized Surface Plasmon Resonance of Silver Nanoparticle Thin Films on Moissanite: Simulation, Fabrication, and Characterization*, **Tsung-Jen Wu (d09224004@ntu.edu.tw)**, S. Song, W. Chen,* National Taiwan University, Taiwan*; W. Lin,* National Taiwan University of Science and Technology, Taiwan*; M. Phan,* National Taiwan University, Taiwan*; S. Tseng,* National Synchrotron Radiation Research Center, Taiwan

The fabrication and characterization of silver nanoparticle (Ag NPs) thin films on a moissanite (silicon carbide) substrate and their inherent localized surface plasmon resonance (LSPR) properties were investigated in this study. The preliminary phase of this investigation employed Finite-Difference Time-Domain (FDTD) simulations to anticipate the LSPR effects and the resultant hue of the films. The size of the silver nanoparticles was maintained within a range of 10-25 nm, producing a greenish yellow hue attributed to the LSPR effect.

Two methods were harnessed to produce these size-specific Ag NP films. The first approach involved a dual-target co-sputtering technique utilizing silver and silicon dioxide. It prompted the spontaneous formation of Ag NPs, leading to a visible coloration due to the LSPR effect. The other method involved a single-target sputtering of silver, followed by an annealing process to foster the emergence of Ag NPs, yielding a characteristic color induced by the LSPR effect.

CM-ThP-2 Greybox-Models to Describe the Wear Behavior of Coated Cutting Tools*, K. Bobzin, C. Kalscheuer,* ***Nina Stachowski (stachowski@iot.rwth-aachen.de)**,* Surface Engineering Institute (IOT) - RWTH Aachen University, Germany

The real application behavior of coated carbide tools can neither be satisfactorily measured, nor described within existing models with the current state of research. The wear development, beginning tool failure as well as the remaining tool life cannot be accurately identified or predicted. This inhibits the knowledge-based qualification of coated tools for more efficient cutting processes. In the current state of research, the tribological system of machining must be evaluated and repeatedly analyzed for every small change in the cutting condition. This is despite the fact that both involved disciplines of production and material engineering have already detailed whitebox models. However, not all available data from both disciplines can be integrated into these models.The main objective is therefore to combine the existing whitebox models with new data driven blackbox models in greybox models. These new greybox models are used to determine the temporal changes of the tools in use, which cannot be described in purely deterministic terms, right up to the end of their service life. Further developments in machining, material and coating technology enable the evolution of new methods for analyzing and simulating the wear behavior of coated cutting tools. This includes the investigation of time- and temperature-dependent coating properties such as indentation modulus, indentation hardness, thermal diffusivity and surface roughness with increasing cutting time. Such changes have not been considered in simulation models up to now. However, by taking such data into account, the description of the wear behavior can be probably significantly more accurate. Another key factor within the SPP 2402 is the data storage as well as the comparison of measurement methods. This enables a better estimation of quality within all participating consocial projects. The final greybox models allow the description of the time-dependent changes in the material properties and the stress collective during machining.

CM-ThP-3 Flow Curve Determination of TiAlSiN Coatings Using Nanoindentation and Iterative FEM Simulations*, K. Bobzin,* ***Christian Kalscheuer (kalscheuer@iot.rwth-aachen.de)**, X. Liu,* Surface Engineering Institute - RWTH Aachen University, Germany

Physical vapor deposition (PVD) coatings are extensively employed to improve the service life of tools under high thermomechanical load in forming processes. The wear resistance of coatings is highly related to their mechanical properties, especially elastic and plastic properties that can be delineated by the flow curve. Consequently, the accurate determination of the flow curve holds paramount significance in the coating development process. While the elastic modulus can be easily measured using nanoindentation, other flow curve parameters are difficult to determine. The current analytical Juliano approach for determining the yield stress lacks precision and becomes challenging to use when the Juliano signal is not obvious, particularly evident in the investigated TiAlSiN coatings that exhibit minimal plastic behavior. Therefore, an easier and more precise flow curve determination method is required. In this study, flow curves of TiAlSiN coatings are determined combining nanoindentation and iterative finite element simulations (FEM). Initially, nanoindentation using a spherical indenter is performed accompanied by the measurement of time-load and time-displacement curves. Then the nanoindentation is simulated time-dissolved using FEM based on the load at each time step directly derived from the time-load curve. The flow curve parameters in FEM including the Young's Modulus E, yield stress Y, strain hardening coefficient B and strain hardening exponent n are iteratively adjusted by comparing the experimental and simulated time-displacement curves until a good match between two curves. Consequently, the flow curve can be obtained from the FEM model with the best match. The simulated time-displacement curves with physically reasonable flow curve parameters have a good agreement to the experimental time-displacement curves of various TiAlSiN coatings. The method uses FEM simulations to determine all flow curve parameters without measuring the Young's Modulus using nanoindentation and determining the yield stress using the Juliano approach.

CM-ThP-4 Material Property Distributions of Sputter-Deposited Thin Films on a Two-Dimensional Diagram with Incident Particle Energy and Substrate Temperature*, **Ichiro Ikeda (ichiro-ikeda@osakavacuum.co.jp)**, K. Kuroshima,* Osaka Vacuum, Ltd., Japan*; Y. Gotoh,* Department of Electronic Science and Engineering, Kyoto University, Japan*; M. Iguchi, S. Sugimoto,* Osaka Vacuum, Ltd., Japan

Recently, we have confirmed that Anders' structure zone model (SZD)[1] is applicable to the case of conventional magnetron sputtering[2-3]. TheSZD shows the difference of the film structure on a two dimensional diagram with the normalized incident particle energy and normalized substrate temperature. Based on the fact that the properties of the films depend upon the film structure, we assumed that the distribution of mechanical or electrical property is also well expressed on this two-dimensional diagram. We named the diagram the material property diagram (MPD)[4].

In this study,we attempted to make MPDs ofelectrical conductivity and optical reflectancedistribution of Ti films. Titanium thin films were deposited under various deposition conditions. The deposition conditions were translated to the particle energy incident on a film surface using the computer simulation[2-3] to identify the deposition condition on MPD. From the accumulated data, we drew contour lines for each film property. As a result, it was confirmed that contour lines for electrical conductivity were arranged in parallel to ZONE border on SZD. The electrical conductivity is well explained by the SZD, reflecting the fact that film structure. On the other hand, the contour lines for the optical reflectance were not arranged in parallel to the ZONE border of the SZD. The optical reflectance has relationship different from the film structure. The film property will be well expressed on the MPD, and the diagram differs depending on the material and property itself. About the film property distribution, we confirmed little difference between equipments.

We made the simulation program calculating the sputtering condition from the requested film property value (ex. the conductivity) using the MPD on the assumption that the MPD does not depend on the sputtering condition and the equipment. We may be able toleave out the experience, the intuition or the test sputtering by the use of this program.

References

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Nagoya, October 31-November 2, 2023.

[2] K. Kuroshima et al., International Conference on Metallurgical Coatings & Thin Films 2024,

San Diego, May 19-24, 2024 (to be presented).

[3] A. Anders, Thin Solid Films, **518**, 4087 (2010).

[4] I. Ikeda et al., Annual Meeting of the Japan Society of Vacuum and Surface Science 2023,

Nagoya, October 31-November 2, 2023.

CM-ThP-5 AI-Enabled Construction and Prediction of Atomic Models for Thin-Film Heterostructures via Materials Genome Approach*, Po-Liang Liu (pliu@dragon.nchu.edu.tw), J. Dai,* National Chung Hsing University, Taiwan

Successful heteroepitaxial film growth enables the integration of heterogeneous films despite lattice mismatches. Exceptional heteroepitaxial films alleviate lattice mismatch stress and diminish material defect density, resulting in smoother surfaces and reduced deposition time for subsequent thin-film epitaxial growth. This study introduces a materials genome approach to predict heterostructures. Employing this novel method, we explore new thin-film heterostructures on flexible muscovite mica substrates. As flexible electronic devices rapidly advance, traditional epitaxial substrates are being supplanted by flexible alternatives, yielding substantial economic benefits. While polymers are commonly used for such devices, they suffer from poor thermal stability, low solvent resistance, and a low thermal expansion coefficient. Layered muscovite mica materials have emerged as a promising solution. Muscovite mica, with its two-dimensional layered structure, can be easily divided into flakes, offering mechanical flexibility, optical transparency, and high thermal stability. We have successfully developed a novel artificial intelligence-generated heterostructure for studying the GaN(001)/Muscovite(001) heterostructure. Our findings reveal that the GaN thin film, characterized by the gene T1, epitaxially grows on muscovite substrate models characterized by gene arrangements S1 and S3. The heterojunction demonstrates the potential to form 12 Ga-O bonds, with a calculated lowest interface energy of −1.21 eV/Å^2.

CM-ThP-8 In-Situ Characterization of the Crystallization Kinetics of Sputtered TiO_2 Thin Films*, Daniel Félix Fernandes (daniel.f.fernandes@angstrom.uu.se),* Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden*; J. Hérnandez,* Madrid Institute for Advanced Studies in Nanoscience (IMDEA Nanoscience), Ciudad Universitaria de Cantoblanco, C/ Faraday 9, 28049 Madrid, Spain*; J. Martínez,* ALBA Synchrotron, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallés, Barcelona, Spain*; T. Kubart,* Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden, Spain

Crystalline TiO_2 thin films are attractive owing to their photocatalytic, electronic, and optical properties.Anatase is the lower-temperature metastable phase of this material system and is the desired phase in many applications.While the phase formation can be controlled by both the deposition and post-depositionannealing temperatures, it is often desireable to reduce the overall thermal budget. Forthe large majority of cases, the employed temperaturesfor the crystallization of suchfilms areconsiderablyhigh, making it incompatiblewith heat-sensitive substrates.

In this study, the crystallization kinetics of TiO_2thin films during post-deposition annealing is investigated.These were grown by reactive magnetron sputtering at different temperatures and the kinetics assessedby in-situ Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS), with synchrotron radiation. The films were heated for 2 hours and, using an adapted Avrami model for phase change kinetics, the crystallization times were compared for three annealing temperatures: 225, 250 and 300°C. The growth conditions achieved in pulsed-DC (pdcMS) and High Power Impulse Magnetron Sputtering (HiPIMS) were investigated. For both techniques, the influence of the mode of reactive operation, the ionization of the sputtered flux and the deposition temperatures were studied.

All studied films were X-ray amorphous in their as-deposited state. However, the depositionconditions have a significant impact on the transformation kinetics. The results show that the deposition temperature is the single most influential parameter. While the reactive mode of operation also affected the transformation dynamics, HiPIMS was found to facilitate sthe crystallization compared to pdcMS films, and generally promoteda faster formation of the anatase phase. Additionally, from the GIWAXS experiments, a set of optimal growth conditions are identified for ex-situpost-deposition annealing. The optimized conditions were investigated for a 2 hour periodat 250°C. In all cases, anatase was achieved. Depending on the growth conditions, specific anatase planes were favored, as seen in GIXRD measurements.

CM-ThP-9 On the Utility of SiMTra Analysis for Forecasting Atomistics of Confocal Deposition of Bimetal Alloys*, Kyle Dorman (krdorma@sandia.gov), R. Kothari, N. Bianco, M. Kalaswad, C. Sobzcak, R. Dingreville, D. Adams,* Sandia National Laboratories, USA

Nanocrystalline thin films feature the potential for enhanced or altered material properties compared to their bulk single crystal counterparts. Assessing thermally stable binary metal systems that feature solute enrichment of grain boundaries (J.R. Trelewicz et al., PRB, 2009) for specific material properties, it is a complex task to survey the full compositional range. High-throughput methods of combinatorial sputtering (McGinn, ACS Comb. Sci., 2019) and complementary high-throughput automated data collection systems potentially permit swift accumulation of a large quantity of data on a broad selection of alloy compositions, if provided.

In this poster, we describe the application of the binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films, 2012) to the challenge of efficient guidance of depositions to access a large range of compositions in a minimal set of depositions. A series of compositionally varied Cu-Ag and Ni-Pt bimetal alloy thin films were prepared by pulsed DC magnetron sputter deposition with varied sputter power and gun-tilt angle. SiMTra simulations provided estimates of film composition for the employed sputter chamber geometry and parameters involved with the simultaneous confocal sputter deposition of each pair of elements. The result is demonstrated with the near-full range of composition achieved, in only three depositions for Cu-Ag, onto 112 samples of 1 cm2 per 150 mm-diameter silicon wafer. The simulation results are presented in comparison to verifying Wavelength Dispersive Spectroscopy (WDS), to demonstrate the degree of accuracy with which SiMTra can specify the binary composition. Successful modeling of film compositions relied on the use of accurate global angular distributions of each elemental target which accounts for target erosion geometry, redeposition, material specific ejecta distributions, and sputter yield amplification with incidence angle following the method of Boydens et al. (Thin Solid Films, 2013). Additionally, we investigate the potential role of off-normal- vs. normal-oriented local ejecta distributions on final film composition by varying these orientations within separate simulations for comparison with WDS. Finally, we present other SiMTra outputs including the energy and incidence angle distributions of species arriving at the film growth surface, which are being used to optimize key film properties such as film hardness and resistivity.

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CM-ThP-10 Investigation of Battery Electrode as a Function of Process Variables*, Tatyana Kravchuk (tkravchu@ford.com), S. Peczonczyk, T. Misovski, M. Trought, B. Emley, A. Straccia,* Ford Motor Company, USA

Studying the elemental distribution and morphology in Li-ion battery electrodes prepared under various drying conditions is crucial for comprehending the connection between processing conditions and battery performance. Efficiency in time, cost, and energy usage are common goals in large-scale battery manufacturing, and a deeper understanding of these connections can aid in the development of precise drying protocols for ensuring consistent and high-performance Li-ion batteries at a large scale.

This study describes an analysis performed using Time-of-Flight Secondary Ion Mass Spectroscopy on electrode coatings prepared under various drying conditions, including different temperatures of system components and airflow. The significance of sample preparation is underscored, with a discussion of various methods such as ion milling and microtoming. Subsequently, differences in element distribution and surface morphology between electrodes processed under different conditions are investigated. Experimental findings obtained via TOF-SIMS are compared to those obtained through other surface-sensitive techniques and to those predicted by computational simulation methods. Lastly, the implications of the results for manufacturing are deliberated.

CM-ThP-11 Actually Measuring Thin Film Elastic Constants by Combined X-ray Microdiffraction and Micromechanical Testing, ***Rebecca Janknecht (rebecca.janknecht@tuwien.ac.at)***, Institute of Materials Science and Technology, TU Wien, Austria; *R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria; *J. Todt, M. Meindlhumer,* Department Materials Science, Montanuniversität Leoben, Austria; *A. Davydok,* Helmholtz-Zentrum Hereon, Institut für Werkstoffphysik, Germany; *P. Polcike, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J. Keckes,* Department Materials Science, Montanuniversität Leoben, Austria; *H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Direction-dependent X-ray Elastic Constants (XECs) measurements are far from routine and pose significant technical challenges. While nanoindentation offers insights into reduced Young's modulus, accessing direction-dependent XECs necessitates innovative methodologies due to inherent challenges compared to bulk materials (e.g., tensile testing). Although ab initio Density Functional Theory (DFT) calculations offer theoretical input, discrepancies persist between model systems and real-world properties, primarily due to a lack of available experimental data for newly emerging—and often chemically and structurally complex—material systems.

Our study addresses this gap by proposing a novel experimental approach to measure XECs, combining synchrotron microdiffraction and micropillar compression testing to investigate the in-situ stress-strain relation within TiN-based physical vapor deposited (PVD) thin films. Our investigation focuses on two individual ceramic TiBN coatings with boron contents up to 10 at.%, where linear elastic failure prevails. By employing in-situ uniaxial testing at P03 beamline of PETRA III synchrotron at DESY in Hamburg, Germany, we create a controlled environment for the determination of the stress in loading direction and strain in three directions to calculate orientation-dependent Poisson's ratios and Young's modulo, facilitating the calculation of XECs for crystal orientations 111, 200, and 220. By correlating our experimental results with ab initio calculations, our study provides a robust and new method for validating theoretical predictions and advancing thin film material testing and design.

CM-ThP-12 The Influence of Cantilever Geometry on the Measured Fracture Toughness of Hard Coatings, ***Rainer Hahn (rainer.hahn@tuwien.ac.at)***, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *S. Kolozsvari, P. Polcik,* Plansee Composite Materials GmbH, Germany; *C. Jerg,* Oerlikon Surface Solution AG, Liechtenstein; *H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Fracture toughness, K_{IC}, is an essential material property representing the resistance to crack propagation in the most prevalent opening mode. The fracture toughness should be correspondingly high to prevent premature failure of a material or a thin film with subsequent environmental exposure of the substrate. As a result, toughness is an important safety factor when designing protective coating materials exposed to mechanical loads. The fracture toughness of coatings is typically determined using micromechanical methods due to the small dimensions. The microcantilever bending test should be particularly mentioned here, as it determines the intrinsic K_{IC} without possible substrate influences.

This study investigated the influence of the cantilever geometry, particularly the distance between the point of force application and the position of the predefined crack. For this purpose, cathodic arc evaporated TiN was selected as a reference material, and a series of cantilevers were fabricated via focused ion beam (FIB) milling, and subsequently tested with an in-situ indentation stage within the SEM. The calculated fracture toughness was found to be dependent on the distance: as the distance increased, the values decrease to a subsequently constant K_{IC}. In summary, this study discusses failure sources for any over- and under-estimations due to geometrical aspects and provides guidelines for properly conducting and interpreting microcantilever bending tests estimating K_{IC}.

CM-ThP-13 e-Poster Presentation: Finite-Temperature Shear Deformation and Phase Transformations of Transition Metal Diborides MB_2 (M=Ti, Ta, W, Re) via Machine-Learning-Potential Molecular Dynamics, ***Shuyao Lin (shuyao.lin@tuwien.ac.at)***, TU Wien, Institute of Materials Science and Technology, Austria; *D. Holec,* Montanuniversität Leoben, Austria; *D. Sangiovanni, L. Hultman,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *P. Mayrhofer, N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal diborides (MB_2s) adopt three types of layered hexagonal structures (α, γ, ω) which are different stackings of the metallic sublattice, thus, may be inter-changeable by a displacive transformation. To test this hypothesis, we develop machine learning interatomic potentials (MLIPs) targeted to molecular dynamics simulations of finite-temperature tensile and shear deformation. The chosen material systems, MB_2, M=(Ti, Ta, W, Re), exemplify different energetic preference for the α, γ, ω phase polymorphs. Following the MLIP fitting procedure, a detail validation for atomic-to-nanoscale simulations is presented using a relevant ab initio dataset (including snapshots of ab initio molecular dynamics simulations on shear-induced phase transformation) as well as through the concept of the extrapolation grade. Consequently, the here-developed MLIPs are employed for room-temperature simulations of {0001}[$\overline{1}2\overline{1}$0] and {0001}[10$\overline{1}0$] shear deformation with nanoscale-sized supercells. Our results reveal a significant impact of the phase prototypes on the shear strength, which is the highest for the energetically most favourable stackings. Shear-induced phase transformations are predicted for TiB_2 and TaB_2. The transformations can be aided by applying additional tensile or compressive strain along the hexagonal [0001] axis. For WB_2 and ReB_2, a nucleations of other defects (e.g. local amorphization or lattice rotation) is typically favoured over changes in the stacking sequence. Our comprehensive study provides insights into the phase-dependent mechanical properties of MB_2 and underscores the strength of machine-learning-potential molecular dynamics for understanding mechanical response of ceramic materials under application-relevant conditions.

CM-ThP-14 Angle-Resolved XPS Characterisation of Thin Films Using Hard X-Rays, ***Tom Swift (tswift@kratos.com)***, *J. Counsell,* Kratos Analytical Limited, UK; *C. Tupei, Y. Li,* Nanyang Technological University, Singapore

High-energy X-ray photoelectron spectroscopy (XPS) was employed to analyze the structure and chemical composition of HfOx thin films deposited on Alumina substrates. The ongoing trend of shrinking device dimensions has led to an increased use of atomic layer deposition (ALD) to enhance uniformity and control of layer thickness. ALD's capability to deposit high dielectric constant (high-k) films has facilitated its widespread application in optical, optoelectronic, and electronic devices.

Using standard Al Kα excited XPS enabled the determination of film thicknesses up to 7nm. However, accurate quantification of the Si 2p peak from the substrate became challenging beyond this thickness. Employing Ag Lα excitation resulted in electrons with higher kinetic energy for the same photoemission peak, effectively increasing the overlayer's attenuation length. In practical terms, this led to a roughly twofold increase in the sampling depth.

In this study, high-energy Ag XPS (Ag Lα radiation - 2984eV) was utilized in a conventional angle-resolved XPS (ARXPS) experiment. The ARXPS data was analyzed using algorithms connected with physical data parameters based on thermodynamic models, maximizing entropy to achieve the best-fit solution [1]. This process generated a reconstructed depth profile over a greater sampling depth provided by the higher energy excitation source. This approach allowed the non-destructive elucidation of the structure of ALD thin films of hafnia, alumina, and a combination of the two. Importantly, the use of the higher photon energy excitation source eliminated the need for destructive depth profiling using Ar-ion beams, reducing the risk of ion beam-induced chemical changes.

The focus of this investigation encompassed film thickness, chemistry at the interfaces, and the efficacy of Ag Lα-excited XPS for such applications.

[1] K. Macak, SIA 43(13) 2011

Surface Engineering - Applied Research and Industrial Applications
Room Golden State Ballroom - Session IA-ThP

Surface Engineering - Applied Research and Industrial Applications (Symposium IA) Poster Session

IA-ThP-1 Application and Practice of Surface Aluminization Treatment in Zinc Pot Equipment of Hot Dip Galvanizing Production Line, ***Lu Wang (4986208@qq.com)***, BAOSTEEL, China

hot dip galvanizing is a process of coating the surface of a steel strip with a zinc layer to prevent corrosion. This process is widely used in industries such as automobiles, home appliances, and construction. During the hot dip galvanizing process, various components on the galvanizing line are immersed in the high-temperature molten zinc liquid in the zinc pot, which has a certain degree of corrosiveness and can cause corrosion to components such as sink rolls, stabilizing rolls, zinc pumps, and snout. In the continuous hot dip galvanizing process of strip steel, due to the corrosiveness of the high-temperature molten zinc liquid in the zinc pot, the service life of some components in the galvanizing equipment is concise, with an average service life of only 12-15 days. This seriously restricts the production efficiency of continuous hot dip galvanizing, increases economic costs, and also affects product quality. Parts in direct contact with high-temperature molten zinc on the galvanizing line are required to resist zinc corrosion and thermal shock.

The use of thermal spraying technology for surface coating treatment of components in zinc pots can have a certain anti-corrosion effect, but it cannot be widely used due to its high cost. This article introduces an aluminizing technology that involves placing components in a molten aluminum pot for hot dip aluminum pot, and then diffusing at a temperature of 800-950 ℃ to transform all the aluminum plating layers on the hot-dip aluminum surface into aluminum iron compound layers, forming a diffusion type aluminizing layer. This thin film can effectively prevent the corrosion of zinc solution on components and also inhibit the formation of zinc dross on the surface of components.

Through experiments, we found that after muffle furnace annealing, a uniform and dense Al2O3 film is formed on the surface of aluminized stainless steel. Aluminum oxide has unique properties that metal and organic polymer materials do not have. Aluminum oxide films have excellent wear resistance, corrosion resistance, heat resistance, high-temperature oxidation resistance, insulation, and other properties. The Al2O3 film isolates the steel substrate from the zinc liquid, preventing mutual diffusion and reaction between Fe and Zn atoms. The Al2O3 film serves as an isolation layer, which can prevent corrosion of the steel substrate by zinc liquid. The cost of this surface aluminizing treatment is much lower than that of thermal spraying, which not only prolongs the service life of the components but also significantly reduces maintenance costs.

IA-ThP-3 The Behavior of Surface-Activated Fine Particles with Variation of Acoustic Field, ***Hyo-Soo Lee (todd3367@kitech.re.kr)***, Gaetbeol-ro 156, Republic of Korea; *K. Kim, T. Choi,* Sejong University, Republic of Korea; *J. Lee,* Kongju National University, Republic of Korea

In recent times, the presence of nano-particles in media such as air and water has become a major concern due to environmental pollution.

Traditional methods like physical filtering or electromagnetic charging have not been sufficient to solve this problem. To address this issue, a new technology has been investigated which involves the use of acoustic fields to move, collide, and agglomerate the nanoparticles present in the media.

The acoustic fields were created using frequencies ranging from 20Hz to 20kHz and sound pressures ranging from 0 to 100dB. The density of the media was varied with specific acoustic fields, and the agglomeration of nanoparticles was observed. This new approach has shown promise in reducing the levels of nanoparticles in polluted media.

It is worth noting that the technology's effectiveness in agglomerating nanoparticles depends on various factors such as the size and shape of the particles, the density of the media, and the specific acoustic fields used. Therefore, further research is needed to determine the optimal conditions for different types of nanoparticles.

IA-ThP-5 e-Poster Presentation: Bismuth Thin Film Electrodes, *B. Frontana-Uribe, V. Ugalde-Saldivar, A. Hernandez-Gordillo, A. Vazquez,* Universidad Nacional Autónoma de Mexico; ***Sandra E. Rodil (srodil@unam.mx)***, Universidad Nacional Autonoma de Mexico

Bismuth film electrodes (BiFE) for trace metal detection using electroanalytical techniques have been researched since 2000, after the demonstration that the BiFE could substitute mercury drop or mercury film electrodes, leading to a safer and eco-friendly solution. However, after more than 20 years of research, the BiFEs are not yet available for commercial use. In this work, bismuth-based thin films produced by magnetron sputtering have been tested for detecting trace metals and organic molecules of interest. Moreover, the stability of the Bismuth-based electrodes in different non-aqueous solutions has been studied, aiming to use the electrodes for the electrosynthesis of organic molecules.

Pure bismuth, bismuth-tin, and bismuth-indium films were deposited on both smooth and rough glass substrates. These were used as the working electrodes in a three-electrode electrochemical cell, where different electroanalytical techniques were used to detect metal ions or organic molecules of interest, such as acetaldehyde. The same electrodes were also tested for the electrosynthesis of organic molecules, which constitutes a sustainable method to produce high-value chemicals without using catalysts.

The results are summarized to present the potential use of bismuth-based electrodes produced by a physical vapor deposition technique for detecting cadmium, zinc, acetaldehyde, and insulin. The Bi-In electrode was tested to drive the cathodic reduction of benzophenone using Cyrene™/EtOH (1 : 1) as a green solvent mixture. Interestingly, the Bi–In electrode yielded a 56% of the pinacolic compound. Such reaction can be used to prepare alcohols and diols from the electrochemical reduction of carbonyl compounds, such as aldehydes and ketones.

IA-ThP-6 Fabrication of TiO_2 Nanotube/SiNW Arrays Structure at Different Synthesis Parameters for Solar Cell Application, ***Ai-Huei Chiou (ahchiou@gs.nfu.edu.tw)***, *Z. Lin,* National Formosa University, Taiwan

Titanium dioxide is renowned for its non-toxicity, high chemical stability, and excellent photocatalytic activity, making it widely applicable in areas such as photocatalysis, photodegradation, and solar energy-related applications. Various methods, including hydrothermal synthesis, sol-gel techniques, and anodization, can be employed to obtain titanium dioxide nanostructures. Among these methods, anodization is favored by many researchers for its simplicity, cost-effectiveness, and ease of observation.

This study utilizes the anodization method to prepare a novel hybrid silicon nanowire array structure and explores its feasibility for application in solar cells. The research primarily focuses on the preparation of titanium dioxide nanotube structures, comparing the results of nanoscale structures with non-nanoscale structures in solar energy measurements.

Currently, most anodization methods used for preparing titanium dioxide nanotubes utilize platinum metal as the cathode, despite its better stability, it is expensive. The anode is typically made of pure titanium foil or sheet. In this study, a novel structure is proposed, involving the deposition of a seed layer on the anode silicon nanowire array, and using a pure titanium plate as the cathode for anodization. The study investigates structural changes under different experimental parameters.

The research employs a trial-and-error approach to sequentially adjust parameters such as electrolyte water content, current, voltage, and film thickness to confirm the conditions for subsequent anodization. A magnetron sputtering machine is used to deposit titanium on the silicon nanowire array, and finally, anodization is employed to prepare a divergent structure of titanium dioxide nanotubes.

SEM observations indicate that with appropriate water content, current, voltage, and film thickness, a complete pore morphology can be obtained. Raman analysis reveals TiO2 lattice peaks under different growth times, confirming the prepared TiO2 has a rutile structure. Additionally, UV-Vis analysis shows that when the substrate is non-nanoscale, the reflectance is approximately 80%, but when the substrate is a silicon nanowire, the reflectance decreases with increasing TiO2 thickness. In terms of electrical properties and solar energy analysis, the TiO2 nanotube/Si structure demonstrates a conductivity of 8.856×10^{-7} S/cm and a photovoltaic conversion efficiency of 2.31×10^{-3}, while the TiO_2 nanotube/SiNW Arrays Structure exhibits a similar conductivity of 8.856×1010^{-7} S/cm and a higher photovoltaic conversion efficiency of 5.46×10^{-3}.

IA-ThP-7 Process-Awared Compact Modeling to Obtain Consistent Performance for Various Gate-All-Around Structures Due to Vertical Oxidation and Etching Process of 3D Charge Trapping Flash Memory*, Sunghwan Cho (joboss9999@gmail.com),* Samsung Electronics Co., Republic of Korea

To address the scaling limitations of conventional planar flash memory, gate-all-around (GAA) charge trapping flash (CTF) memory has emerged as the most promising alternative, offering significantly larger storage capacity and reduced disturbance. However, as more layers are stacked vertically and feature sizes are decreased, it becomes increasingly challenging to manage vertical processes like etching or oxidation, leading to variations in geometry such as hole radius or tunneling oxide thickness, respectively. Furthermore, unexpected process variations along the word lines (WLs) pose challenges for circuit designers in optimizing conditions for consistent performance, primarily due to the absence of a framework based on circuit simulation. Therefore, in this study, we introduce a compact modeling approach aimed at delivering optimized solutions for achieving uniform performance after program and erase operations along the WLs, thereby reducing the effects of process variations inherent in vertical GAA structures within 3D CTF memory devices such as hole etching and vertical oxidation. The program and erase performance exhibit unexpected differences due to variations in the etching process and vertical oxidation within gate-all-around structures, resulting in variations in hole radius and tunneling oxide thickness along the WLs, as shown in Fig. 1 and 2. We presented diverse variations in hole radius and tunneling oxide thickness across three representative GAA structures (trapezoid, entasis and iterated trapezoid in Fig. 1). Then, utilizing the proposed workflow outlined in this paper, we extracted optimized WL gate biases to ensure a uniform electric field along the WLs, as shown in Fig. 3. Finally, we presented the variation in program speed across different locations within a string and demonstrated consequent uniform performance using SPICE simulation, as shown in Fig. 4. As a valuable framework, the proposed compact modeling enables circuit designers to optimize design schemes for consistent behavior in 3D CTF memory devices.

IA-ThP-8 Disruption of Cell Wall Using Non-Thermal Plasma for Recovery of Intracellular Lipid to Be Used as Bio Lubricant*, JOSÉ GERALDO PRADELLA (jpradella51@gmail.com),* Universidade do Vale do Paraiba, Brazil

Rhodosporidium toruloides stands out as a highly promising oleaginous yeast, renowned for its capacity to amass substantial quantities of intracellular neutral lipids. These lipid reservoirs hold significant commercial value across diverse industries such as biofuels, food production, chemicals, pharmaceuticals, and bio lubricants. Leveraging non-thermal plasma for yeast cell wall disruption presents a distinct advantage in preserving the integrity of these sought-after intracellular components. The cultivation process of this oleaginous yeast involves two distinct stages, each utilizing specific culture media. The inoculum phase employs Saboraud medium, while the production phase utilizes a defined medium with a C/N optimized ratio. Following the fermentation stage, the harvested material undergoes centrifugation, with the discarded supernatant paving the way for subsequent non-thermal plasma treatment. This plasma process, executed in triplicate with five samples, incorporates variations in exposure time—ranging from 5 to 30 minutes—while keeping other parameters constant. Characterization of the samples, both before and after plasma treatment, involves comprehensive analysis using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and tribometer assessments. Notably, tribometer evaluations employ the treated samples as a biolubricant interface between a 316L plaque and sphere. The results display a progressive disruption of the yeast cell wall upon exposure to non-thermal plasma, with noticeable effects emerging as early as 5 minutes and culminating in complete destruction within the 30-minute timeframe. The FTIR was used to analyses the bio lubricant structure before and after friction tests. This study underscores the immense potential of non-thermal plasma as a groundbreaking technique for efficiently extracting lipids through cell wall disruption, thereby contributing to the advancement of sustainable bioprocessing and bio lubricant production.

Protective and High-temperature Coatings
Room Golden State Ballroom - Session MA-ThP

Protective and High-temperature Coatings (Symposium MA) Poster Session

MA-ThP-1 Predictive Modeling and Experimental Validation of Phase Formation in High-Entropy Alloys Thin Films*, Salah-eddine Benrazzouq (salah-eddine.benrazzouq@univ-lorraine.fr), J. Ghanbaja, S. Migot, J. Pierson, V. Milichko,* Institut Jean Lamour - Université de Lorraine, France

High-entropy alloys (HEAs) introduce a new class of materials that challenge existing theories on phase stability due to their complex, multi-element composition. Initially theorized to gain stability from the significant entropy associated with mixing five or more elements, these alloys have garnered interest for their potential applications. However, the scientific community has yet to develop a robust model that can predict with certainty which element mixtures will form a single-phase alloy. In this investigation, we try some predictive model grounded in thermodynamics to forecast the phase behavior of high-entropy alloys (HEAs). By computationally analyzing the enthalpies of binary compounds, the model identifies combinations of elements likely to form single-phase alloys. This method has successfully pinpointed all previously known single-phase HEAs and excluded compositions that result in multiple phases. Moreover, we have experimentally validated numerous new single-phase alloy compositions proposed by our model.

Subsequently, this work employed X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) to characterize the structural and microstructural properties of the films, specifically the Cantor alloy (CrMnFeCoNi) with additional elements like Pt, Cu, Ti, Zr, Al, and Ag. We found that the CrMnFeCoNi base alloy, along with its Pt and Cu variants, retained a homogeneous FCC crystalline structure. In contrast, the Al-modified films underwent a phase transformation from FCC to a mixed FCC+BCC structure and eventually to a singular BCC phase. The Ti and Zr variants exhibited amorphous structures at certain concentrations, whereas the Ag-doped films presented a multiphase structure with silver precipitates embedded in the Cantor alloy matrix.

Our findings show that some alloys consistent alignment between the predicted phases using thermodynamic criteria and the actual observed phases, even when the synthesis conditions are far from equilibrium. This consistency suggests a significant role of underlying thermodynamic factors in determining the phase stability of HEAs thin films.

MA-ThP-3 Optimizing Temperature Stability in Non-Reactively Sputtered (Hf,Ta,Ti,V,Zr)B-C-N Coatings by Design of the Non-Metal Sublattice*, A. Kretschmer, **Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at)**,* TU Wien, Institute of Materials Science and Technology, Austria*; R. Frost, D. Primetzhofer,* Uppsala University, Sweden*; H. Rojacz, E. Badisch,* AC2T Research GmbH, Austria*; M. Hans, J. Schneider,* RWTH Aachen, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

In the past, we have studied the system (Hf,Ta,Ti,V,Zr)B-N with exceptional hardness and thermal stability, but the coatings contained a significant amount of C impurities, which may have influenced the properties [1]. To investigate the impact of C in this system, we have deposited new coatings with a TiN target, on which we placed diboride and/or carbide pieces of the metals Hf, Ta, V, and Zr. We have varied the composition by using either only diborides, only carbides, or different mixtures of the two material types to make 5 coatings containing either N and B, N and C, or all three. The B concentration varies between 42 and 0 at%, the C content between 25 and 0 at%, and the N content is stable at around 30 at% in all coatings. The Ti makes up roughly 20 at%, while the other metals are in the range between 2 and 5 at%. X-ray diffraction (XRD) shows a weakly textured single-phase fcc solid solution in all coatings. The FWHM of the 200 reflex ranges from 2 ° in the C-free coating down to 0.5 ° in the B-free coating, indicating different grain sizes. This is confirmed by transmission electron microscopy, revealing fine columnar growth in the 2.3 to 3.2 µm thick coatings, with especially fine grains in the B-richer coatings. Electron diffraction confirms that no secondary phases are present. We annealed the coatings in a vacuum furnace at 1000, 1200, and 1400 °C for 10 min, followed by XRD and nanoindentation. The coatings stay stable up to 1200 °C and start decomposing at 1400 °C. The as-deposited hardness of all coatings lies between 36 and 38 GPa, and is maintained after annealing at 1000 °C. After annealing at 1200 °C, the coatings containing only C or only B both soften to ~34 GPa, while the coatings with both C and B do not lose any hardness at this temperature. Only after annealing at 1400 °C does the hardness of all coatings drop below 30 GPa. The exceptional thermal stability of the solid solution was confirmed by atom probe tomography, which shows no onset of decomposition despite the high B content even after annealing at 1200 °C. Only after the 1400 °C annealing, a TiB_2 phase is formed.

[1] Kretschmer, A., Kirnbauer, A., Pitthan, E., Primetzhofer, D., Yalamanchili, K., Rudigier, H., & Mayrhofer, P. H. (2022). High-entropy alloy inspired development of compositionally complex superhard (Hf,Ta,Ti,V,Zr)-B-N coatings. *Materials & Design*, *218*, 110695. https://doi.org/10.1016/j.matdes.2022.110695

MA-ThP-4 Unravelling Diffusion Processes and Morphology Changes of Ternary and Quaternary Diborides During High-Temperature Oxidation*,* ***Sophie Richter (sophie.richter@tuwien.ac.at),*** *A. Bahr, T. Glechner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; O. Hunold, J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; P. Felfer,* Department of Materials Science and Engineering, FAU Erlangen, Germany*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria

Transition metal diborides (TMBs) are currently in the focus of diverse academic and industrial research studies, as they obtain a unique mix of properties. Here, especially their mechanical strength, chemical inertness, but also electrical conductivity is in focus [1]. However, the oxidation resistance is a weak point in binary TMBs and strongly limits a broad application. Therefore, to improve the oxidation resistance of transition metal diborides (TMB_2) at high temperatures (T > 1000 °C), alloying approaches using silicon (Si) as a strong oxide-forming element have been successfully established [2,3]. However, both ternary (TM-Si-B) and quaternary (e.g., TM-Mo-Si-B by alloying TMB_2 with $MoSi_2$) diborides have shown pore formation due to phase transitions and diffusion processes during oxidation above 1100 °C. Over extended periods of time (t > 1000 h), these pores significantly weaken the protective function of these coatings and depict a major challenge. In this study, physical vapor deposited ternary and quaternary transition metal diborides are investigated to study the influence of different alloying elements on the pore formation. In more detail, the influence of additional elements such as Mo or Ta based on disilicide alloying to TMBs is in focus. High-resolution techniques such as transmission electron microscopy (TEM), elastic recoil detection analysis (ERDA), Rutherford backscattering spectrometry (RBS), and atom probe tomography (APT) are used to gain insights on the prevailing phase transformations, diffusion processes and hence pore formation. These results are correlated with mechanical analysis to assess the tolerance with respect to porosity.

[1] M. Magnuson et al., Review of transition-metal diboride thin films, Vacuum. 196 (2022) 110567.

[2] T. Glechner et al., Influence of Si on the oxidation behavior of TM-Si-B2±z coatings (TM = Ti, Cr, Hf, Ta, W), Surf. Coat. Technol. 434 (2022) 128178.

[3] A. Bahr et al., High-temperature oxidation resistance of ternary and quaternary Cr-(Mo)-Si-B2-z coatings — Influence of Mo addition, Surf. Coat. Technol. 468 (2023) 129733.

MA-ThP-5 Influence of Mo on DCMS and HiPIMS Deposited TiB_{2+z} Thin Films*,* ***Anna Hirle (anna.hirle@tuwien.ac.at),*** *P. Dörflinger, R. Hahn, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria

Titanium diboridethin films deposited by physical vapor deposition are typically attributed to inherent brittleness. Theoretical predictions by DFT assessing the elastic constants revealed that the formation of ternary Ti-Mo-$B_{2\pm z}$ might be a suitable approach to gain a less brittle character.

In the present study, the accompanying experiments to the theoretical investigations have been conducted. Three different target compositions were used for the non-reactive growth of ternary $Ti_{1-x}Mo_xB_{2\pm z}$ thin films: TiB_2/MoB 95/5 mol%, TiB_2/MoB 90/10 mol%, and TiB_2/MoB 80/20 mol%. The binary TiB_{2+z} system was deposited with a TiB_2/C 99/1 wt.% target. In addition, direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HiPIMS), were employed in order to investigate the influence of different deposition techniques – hence ionization degrees.

The structural and mechanical properties of the coatings were characterized by a broad variety of methods, such as scanning electron microscopy, X-ray diffraction analysis, and nanoindentation. The chemical composition was determined by inductively coupled plasma optical emission spectrometry and elastic recoil detection analysis. To verify the suggested enhancement on the brittle behavior of $Ti_{1-x}Mo_xB_{2\pm z}$ fracture characteristics such K_C or K_{IC}have been determined by cube corner indentation and in-situ micro-mechanical bending tests, respectively. Alloying of Mo leads to an increase in Ti content and a decrease in B content for both DCMS and HiPIMS deposited coatings. In contrast, the Mo content is significantly lowered while using HiPIMS. All coatings exhibit α-structured (SG191) $Ti_{1-x}Mo_xB_{2\pm z}$ solid solutions. An increased hardness for both binary and ternary thin films, with a maximum value of 45 ± 1 GPa (TiB_{2+z}) and a minimum 28 ± 0.8 GPa (~ 6 at.% Mo) can be obtained by using HiPIMS. Overall, this study highlights the influence of Mo additions on the structure-mechanical properties of $TiB_{2\pm z}$ using different growth techniques.

MA-ThP-7 Impact of the B/Ti-ratio on Microstructure, Mechanical Properties, and Thermal Stability of DCMS and HiPIMS TiB_2 Thin Films*,* ***Ludwig Enzlberger (ludwig.enzlberger@tuwien.ac.at),*** TU Wien, Institute of Materials Science and Technology, Austria*; M. Podsednik,* TU Wien, Austria*; S. Kolozsvari,* Plansee SE, Germany*; A. Limbeck,* TU Wien, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Titanium diboride is widely known as a superhard material achieving an indentation hardness of 40 GPa and beyond. Coatings of TiB_2 produced by DC magnetron sputtering (DCMS) are typically in the superstoichiometric regime regarding the B/Ti-ratio in a range of $TiB_{2.4}$ to $TiB_{3.5}$. This surplus in Boron is attributed to a different radial distribution of Boron and Titanium during the deposition process and forms a tissue phase which is highly relevant for the material's mechanical properties.

A reduction of Boron content in the coating would thus mean a reduction of tissue phase formed and consequently a clear change in e.g., hardness or fracture toughness. Earlier works have already shown an increase in fracture toughness (measured by microcantilever bending) of DC-sputtered TiB_2 when reducing the B/Ti-ratio from 4.4 to 2.1. There have also been reports of even higher fracture toughness in understoichiometric $TiB_{1.43}$ produced through high power impulse magnetron sputtering (HiPIMS) and measured by cube corner indentation, while films grown by DCMS showed a decrease in K_C with decreasing B-content.

Here we address this discrepancy, via detailed studies of DCMS as well as HiPIMS developed $TiB_{2\pm z}$ thin films with B/Ti-ratios varying between 1.5 and 3.2. The stoichiometry of DCMS-grown films is adjusted by placing Ti-pieces at the target race track, while that of HiPIMS-grown films is adjusted by varying the pulse on-time. The B/Ti-ratios are measured by ICP-OES and the mechanical properties are characterized by nanoindentation (Hardness, Young's Modulus) as well as cube corner indentation for K_{IC}. Vacuum annealing treatments with subsequent detailed transmission electron microscopy studies as well as nanoindentation experiments clarify the impact of the B/Ti ration on these important characteristics.

MA-ThP-8 Synthesis and Characterization of $AlMgB_{14}$ Thin Films*,* ***Erwin Peck (erwin.peck@tuwien.ac.at),*** *A. Kirnbauer,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

When it comes to the protection of tools and the increase of their lifetime, protective coatings with high hardness, good wear resistance, and low coefficients of friction are commonly used. Typically, nitrides, carbides, and borides –specifically metal-diborides such as TiB_2, ZrB_2, and TaB_2 – are selected as protective coating materials.

Here, we concentrate on more complex borides, $AlMgB_{14}$, and study their microstructure, mechanical properties, thermal stability, and wear resistance.

$AlMgB_{14}$ is a very promising material with reported high hardness (even superhardness, > 40 GPa), high thermal stability, and very low coefficients of friction. We developed $AlMgB_{14}$ coatings by magnetron sputtering, using a single composite $AlMgB_{14}$ target, and varying the substrate temperatures between 300 and 600 °C. All of these coatings were amorphous in their as-deposited state with hardness increasing from 29.3±1.6 GPa to 42.1±1.5 GPa upon increasing the substrate temperature from 300 to 600 °C. Simultaneously, their indentation moduli only increase from 373±17 to 497±14 GPa and their residual compressive stresses vary between -2 and -3 GPa. Their fracture toughness values – derived from cube corner indentation experiments – increase from 3.72±0.46 to 5.15±0.22 MPa√m with increasing substrate temperature. To gain information about the thermal stability of the coatings, they were vacuum annealed up to 1050 °C and subsequently investigated by TEM, XRD and nanoindentation.

MA-ThP-9 Non-Reactive Magnetron Sputtering of Al-N Coatings, ***Balint Hajas (balint.hajas@tuwien.ac.at)**, A. Foki, T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S. Kolozsvari,* Plansee SE, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Hard protective coatings allow for increased lifetime of machining tools and more versatile applications. Although AlN-based coatings have a rich history in material science with various improvements for their production, little is known about non-reactive deposition using ceramic AlN compound targets. Aluminium nitride in its hexagonal close packed (hcp) wurtzite-type structure has the highest thermal conductivity among ceramic materials, a large electromechanical coupling factor and temperature stability, as well as a high acoustic velocity.

Reactive deposition of such AlN coatings is studied in-depth, showing that especially for sputtering the resulting microstructure and consequently properties (next to deposition rate) hugely depend on the N2-partial pressure used. Alternatively, such nitrides can also be prepared non-reactively using nitride compound targets. Here, we use powder metallurgically prepared AlN compound targets to prepare coatings with pulsed DC magnetron sputtering with a 3” target and a 6” target.

The primary investigations focused on how the mechanical properties such as hardness and indentation modulus depend on various deposition conditions, such as sputtering power density, pulse frequency, substrate temperature, substrate-to-target distance and plasma condition. Additionally, several experiments were conducted by adding H_2 to Ar to study the effect of a reducing agent during the ion-etching of the substrate as well as during the deposition of the AlN film. To counteract understoichiometry, we added sometimes N_2 as well.

Detailed investigations by X-ray diffraction reveal that all coatings were single-phase hcp-structured, with various amounts of an amorphous phase and/or a metallic Al, depending on the deposition conditions. The highest hardness obtained for such films is 26.9 GPa. With the addition of H2 to the working gas Ar, the discharge became more stable even for high power densities, allowing for a deposition rate of up to 1 µm/h.

MA-ThP-10 Effects of the Modulation Period and Ratio on Mechanical Properties and Oxidation Resistance of WB_2/AlB_2 Superlattices, ***Chun Hu (chun.hu@tuwien.ac.at),*** Institute of Materials Science and Technology, TU Wien, Austria*; R. Hahn,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; T. Wojcik, R. Janknecht, N. Koutná, P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Superlattice structures offer a unique playground for simultaneous hardness and fracture toughness enhancements by tuning the layer thicknesses and volume ratio of the layer constituting materials. The superlattice effect has been widely studied within the cubic transition metal nitrides but nearly unexplored for hexagonal transition metal diborides (TMB). Here we focus on the nanolayered WB_2/AlB_2 system, where already one of the chosen materials, AlB_2, is nearly unreported despite its great potential for increasing the typically low oxidation resistance of TMB. Aiming to combine exceptional mechanical properties and oxidation resistance, we develop WB_2/AlB_2 superlattice thin films with different modulation periods (λ, 3-50 nm) and thickness ratios (η, WB_2/AlB_2=1, 2, 3). All superlattices reveal single-phase AlB_2-type structure. With the template effect of the WB_2 layers, the AlB_2 layers are supported for their crystallization as single phase AlB_2-type layers, even for deposition parameters which would otherwise result in a dual phase constitution of Al and AlB_{12}. TEM investigations of selected samples reveal clearly coherent interfaces between WB_2 and AlB_2 layers. Nanoindentation studies show that these WB_2/AlB_2 superlattice films facilitate the superlattice effect for hardness, which we rationalize with the shear modulus mismatch and modulation period. Among the WB_2/AlB_2 superlattices studied here, the one with λ of 3 nm and η of 2 shows the highest hardness (33.1 GPa), compared to the 26.6 GPa calculated from rule of mixing. Isothermal oxidation experiments demonstrate significantly improved oxidation resistance of WB_2/AlB_2 superlattices compared with WB_2 monolithic thin film.

MA-ThP-11 Effect of Preplaced Graphene and Graphite Films on Stellite 6 Metallurgical Coatings*, J. Sippel,* PG-MEC/ Universidade Federal do Paraná, Brazil*; W. de Oliveira,* Universidade Estadual de Ponta Grossa, Brazil*; J. Ribeiro da Cruz Alves,* Instituto Senai de Inovação - Sistema de manufatura e Processamento a laser, Brazil*;* ***Ana Sofia C. M. d'Oliveira (sofmat@ufpr.br)***, Universidade Federal do Paraná, Brazil

Protective coatings are a key player on a sustainable development of equipment with a longer and better service life**.** This goal motivates the search for better coatings offering the opportunity to put together new materials and efficient processing techniques. Carbon-based compounds are materials widely studied for their unique properties which are distinct from others engineering materials due to a variety of atomic arrangement. These materials exhibit excellent mechanical, thermal and tribological properties. An approach to use these materials is tailoring a metal matrix composite focusing on improved performance through the he distribution of carbon compounds in the matrix. This study is part of an ongoing project on the development of carbon-base compounds metallic matrix hardfacing coatings by Plasma Transferred Arc (PTA). PTA process is a hardfacing process that uses feedstock in the powder form that melts in a plasma arc column allowing for the customization of coatings. Although literature reports coatings reinforced with carbon compounds materials were produced by powder metallurgy before deposition by PTA. This work assesses the impact of pre-deposited layers of graphene and graphite on Co based (Stellite 6) coatings processed by PTA, particularly at the interface with the substrate. Deposition was carried out on AISI 304L stainless steel, with and without predeposited films of graphite and graphene, with a surface Sq roughness of 1.4 µm for better anchoring of the preplaced micro/nanoparticles of graphite and graphene, respectively. The geometry at the cross section of single beads showed the dilution of coatings with modifying particles being higher than pure that of Stellite 6 coating. EDS analysis showed an increased presence of iron in the coating, explained by increased dilution. EBSD characterization revealed a larger heat affected zone in the substrate of graphene-modified coating, exhibiting smaller grains due to recrystallization, comparing with others processed coatings, suggesting that this material increases thermal transfer from the plasma arc to the substrate. The Vickers microhardness shows graphite improves hardness and graphene reduces it. Nanoscratch testing on the coatings near the fusion line revealed lower wear rate in the graphene-modified coating when compared to the Co-based coatings with and without graphite. The contributions of this research include: (1) advances on identifying viable techniques for processing graphite and graphene enriched coatings, (2) understanding the influence of graphene and graphite in Stellite 6 hardfacing coatings.

MA-ThP-12 Modified High Hardness Steel Coating for Biomass Combustion Boilers, ***Alina Agüero Bruna (agueroba@inta.es)***, Ctra. Ajalvir km 4, Spain*; M. Gutierrez, S. Rodríguez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Biomass is a renewable, CO_2 neutral source of energy. However, the efficiency of biomass combustion plants is not as high as that currently obtained with fossil fuels. Biomass plants currently operate at a maximum temperature of 550º C in order to reduce corrosion caused by the very aggressive species present in biomass combustion. In the European project BELENUS, new materials and coatings are being evaluated, aiming to increase the operating temperature to 600 ºC and consequently the plant efficiency. Among the different coatings that are being studied, a high hardness steel modified with Al, applied by HVOF thermal spray has shown a very promising performance in the laboratory when exposed to a model biomass environment including KCl deposits, for 8000 h. Moreover, the coating has also been tested in pilot plants burning eucalyptus and wheat straw at 600º C for 2000 h and the results indicate high resistance to corrosion. Microstructure analysis of the tested samples by SEM, EDS and XRD, was performed in order to study the coating evolution in these environments as well as the protection and degradation mechanisms.

MA-ThP-13 Effect of Austenite Stability on Pack Aluminizing of Stainless Steels, ***Bryant Hernandez (bdh@cpp.edu)**, C. Sullivan, L. Rodriguez, V. Ravi,* California State Polytechnic University, Pomona, USA

Austenitic stainless steels are extensively used in a range of engineering applications. When high temperatures are involved, oxidation is an issue that may affect service life. In certain use conditions, phenomena such as molten salt attack may also be relevant. Under these adverse operating conditions, it would be advisable to modify the surface of stainless steel components for ensuring reliability and additional life. In this study, the surfaces of stainless steels were aluminized using the halide-activated pack cementation process. The particular focus of this study was to investigate the relationship between the stability of austenitic stainless steels and aluminide coating characteristics, e.g., thickness and morphology. Aluminizing of SS 304 and SS 330 resulted in mass gains per unit area. An inverse relationship between the austenite stability of these stainless steels and the respective aluminide coating thicknesses was obtained. Other stainless steels being studied include SS304L, SS301, and SS302B. It is notable that these alloys have lower austenite stabilities than SS 304 and SS 330. The results of these studies will be discussed and placed in context with respect to previous studies from this group and others. The results of these studies will provide valuable insights for industrial applications where the surfaces of austenitic stainless steels need to be protected against high temperature degradation.

MA-ThP-14 Co-Deposition of Chromium and Silicon on Nickel, and Iron-Based Alloys*, Catherine Sullivan (cdsullivan@cpp.edu), B. Hernandez, L. Rodriguez, A. Coronado, V. Ravi,* California State Polytechnic University, Pomona, USA

Halide activated pack cementation is a surface modification process in which, typically, a single element is deposited onto the surface of an alloy and subsequently incorporated into the substrate through diffusion. For some applications, it would be desirable to co-deposit more than one element simultaneously onto the substrate surface. During service life, this co-deposited surface would offer improved resistance to degradation in high temperature environments. The current study focuses on chromium-silicon codeposition process studies via halide activated pack cementation. Coatings containing chromium are expected to improve the corrosion resistance of the alloy, while the presence of silicon should improve the erosion resistance, thereby providing a dual benefit when co-deposited. The results of the co-deposition process for pure nickel and selected ferrous alloys will be presented and discussed. The discussion will incorporate coating characterization including phase analysis using x-ray diffraction, microstructural characterization using optical and scanning electron microscopy, and elemental analysis using energy dispersive spectrometry.

MA-ThP-15 Corrosion Behavior of Galvanized Coils in Coastal Warehouse Environment*, **Baiyou Fang (Fangby88@163.com)**,* Baosteel-NSC Automotive steel Sheets Co., Ltd, China

To investigate the corrosion failure of packed galvanized coils in a coastal warehouse, a scanning electron microscope with energy disperse spectroscopy and a Raman spectrometer were employed to observe corrosion morphologies of rusty surfaces and detect their chemical compositions. In general, two types of rusts were distinguished, the white grey and the red brown, in which the white corrosion product was a mixture of ZnO, $Zn(OH)_2$, $Zn_4SO_4(OH)_6$ and $Zn_5(CO_3)_2(OH)_6$, and the brown one was mainly composed of γ-FeOOH. In light of these, the corrosion mechanism was determined for the galvanized sheets. Due to the day-and-night temperature difference and high humidity, condensation took place readily, providing electrolyte for corrosion process. Further the zinc coatings react with O_2, H_2O, CO_2 and SO_2 depositing on the surface of galvanized sheet during the initial stage of corrosion, resulting in the white corrosion product. After the exhausting of galvanizing effect in the local area, the steel substrate started to corrode, and thus the red brown product formed.

MA-ThP-16 Development of Zr-Ta Anticorrosion Coatings for Nuclear Applications Using PVD HiPIMS Technology*, **Cécile Marsal (cecile.marsal@cea.fr)**,* Commissariat à l'Énergie Atomique et aux énergies alternatives Centre de Saclay, France

Reprocessing of spent fuel is essential to establish a sustained nuclear cycle, as it enables reusable materials to be recycled and waste to be limited. This retreatment requires the use of nitric acid, which is particularly corrosive for the materials making up the equipment used for fuel reprocessing. However, most of the materials that efficiently passivates in the reprocessing media are expensive, which hinders their direct use. Alternatively, they can be used as coating, the protective performance on which may be further enhanced by mixing two or more complementary elements.

In this study, the corrosion resistance in a nitric acid environment of zirconium-tantalum and zirconium-chromium coatings of distinct compositions on 304L stainless steel was scrutinized. Coatings were elaborated by High-Power Impulse Magnetron Sputtering (HiPIMS), using a tandem target setup allowing for combinatory synthesis of high quality adherent coatings made of Cr-Zr or Ta-Zr solid solutions. The adherence, composition and microstructure of coatings were then characterized by SEM and XRD. Immersion tests in nitric acid demonstrated the appreciable gain in substrate protection with respect to the aggressive environment used for fuel reprocessing.

Authors: Cécile MARSAL[1], Amélie FRISON[1], Beatriz PUGA[2], Michel L. SCHLEGEL[1]

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MA-ThP-17 Study on Physical Phenomena During Precise Cutting with Novel WCCo/cBN Composite Cutting Tools Equipped with Various Anti-Wear Coatings*, **Szymon Wojciechowski (szymon.wojciechowski@put.poznan.pl)**, R. Talar, P. Zawadzki,* Poznan University of Technology, Poland

Recent research on the development of modern tool materials with improved cutting-performance focuses on the production of hybrid materials combining the advantages of carbides and superhard materials (cBN and PCD). Examples of such materials are novel WCCo/cBN composites obtained by pulse-plasma sintering (PPS). However, the preliminary studies reveal that during cutting of hard-to-cut materials with these novel WCCo/cBN cutting tools an intense built-up-edge (BUE) formation, together with adhesion wear can appear. Thus, in order to improve the cutting ability of WCCo/cBN materials, the anti-wear coatings can be applied. This work is focused on the analysis of physical phenomena and tool wear during turning of spheroidal cast iron with coated (with TiN and TiAlN coatings) and uncoated WCCo/cBN tools. The conducted studies involved the evaluation of a fundamental cutting process physical indicators, as cutting forces and vibrations. Moreover, an updated Merchant cutting model was applied for a determination of the average coefficient of friction on the rake face. The proposed approach considered both the shearing forces related to the chip formation mechanisms, as well as the edge forces related directly to rubbing phenomena occurring between the flank face of a tool and workpiece. Ultimately, the tool wear mechanisms and tool life of the uncoated and coated WCCo/cBN inserts were identified and compared with ones obtained during cutting with a coated and uncoated cemented carbide tools. The obtained results showed the presence of a built-up-edge (BUE) on the flank face of the uncoated WCCo/cBN tool throughout the entire range of cutting speed. In the case of WCCo/cBN inserts with TiN and TiAlN coatings, a BUE was also observed, however, its intensity was significantly lower comparing to that obtained during cutting with the uncoated BNDCC tool. The highest tool life was obtained during grooving with the WCCo/cBN inserts with TiAlN coatings and then with WCCo/cBN inserts equipped with TiN coatings. The tool life obtained for a cemented carbide inserts with TiAlN coating was significantly lower than that for a WCCo/cBN TiAlN insert.

MA-ThP-18 Fabrication and Characterization of Titanium-doped Indium Tin Oxide Thin Film*, **Mohammad Kamal Hossain (kamalhossain@kfupm.edu.sa)**, A. Ulhamid,* King Fahd University of Petroleum and Minerals, Saudi Arabia

Metal-doped indium tin oxide (M-ITO), particularly Gd, In and Al-doped ITO has emerged as an efficient transparent conducting oxide (TCO) to facilitate high mobility and transparency as needed for photo-active devices such as solar cell and a light-emitting diode. However, most of these metals are scarce, and such M-ITO thin film requires special care to fabricate and achieve the best optoelectronic properties suitable for solar cell applications. In this work, we have fabricated tin (Ti)-doped ultrathin ITO film (called hereafter ITO:Ti) through a co-sputtering technique with and without nitrogen (N_2). A detailed and systematic study has been carried out by changing the doping percentage and treating it at different annealing temperatures. Ti doping within ITO thin films was controlled by changing the deposition power provided to the DC gun. Field emission electron scanning microscope (FESEM), SEM-aided energy dispersion spectroscopy (EDS), UV-absorption and transmission, X-ray diffraction (XRD), Hall effect, and ellipsometry were used to perform topographical, optical, and electrical characterizations. The samples were annealed for 2 hours at 200, 400, and 600 ^{o}C before being investigated. The impact of Ti doping inside ITO with and without N_2 has been elaborated. Preliminary visual inspection confirmed that the degree of Ti doping altered transparency and shifted the specimen toward opaqueness. The same samples, however, were more transparent after being annealed at higher temperatures. In the instance of N_2 environment, Ti doping was shown to have less of an effect on lowering transparency. UV-Vis measurements revealed that the transparency decreased with increasing Ti doping. The band gap and Urbach energy were estimated for samples containing and not containing N_2. SEM and SEM-aided EDS were used to explore detailed topography and elemental confirmation, respectively. A solar simulator was used to assess the performance of a conventional solar cell with and without the presence of the aforementioned thin films. Due to space limitations, more information is not included in this article. Experimental details and further elaboration of the results will be presented at the event and in the conference proceedings.

Functional Thin Films and Surfaces
Room Golden State Ballroom - Session MB-ThP

Functional Thin Films and Surfaces (Symposium MB) Poster Session

MB-ThP-1 Effective Ways to Enhance the Performance of n-MoS_2/p-CuO Heterojunction Based Self-Powered Photodetectors, ***Davinder Kaur (davinder.kaur@ph.iitr.ac.in)***, Indian Institute of Technology Roorkee, India

The present study investigated two effective routes to improve the response time and the detection range for the n-MoS_2/p-CuO heterostructure (a conventional p-n heterojunction). In the first rectification, an insulating aluminium nitride (AlN) layer was inserted in between the molybdenum disulfide (MoS_2)and cupric Oxide (CuO) layer, which eventually converted the conventional p-n heterojunction to Semiconductor-Insulator-Semiconductor (SIS) with a superior carrier tunneling mechanism. Interestingly, the fabricated heterostructure exhibits self-powered and broad-range photoresponse. The response time (rise time and fall time) of the fabricated n-MoS_2/p-CuO heterojunction decreases from 93.35 ms and 102.68 ms to 11.31 ms and 12.73 ms with the insertion of ultrathin insulating AlN Layer. The higher responsivity and ultrafast photoresponse in n-MoS_2/AlN/p-CuO (SIS) heterojunction can be ascribed to the carrier tunneling mechanism through the ultrathin-insulating AlN layer. Moreover, the detection range can be enhanced up to the UV region by adding a layer of MoS_2 quantum dots (QDs) on the surface of the MoS_2 layer in the fabricated heterostructure. The fabricated n-MoS_2 QDs/n-MoS_2-/AlN/p-CuO heterostructure shows photoresponse in a broad range from UV to NIR radiations. The obtained results demonstrate the n-MoS_2-/AlN/p-CuO (SIS) heterostructure with the addition of MoS_2 QDs shows excellent potential for next-generation ultrafast optoelectronics applications.

KEYWORDS: MoS_2, CuO, Quantum Dots, Photodetectors, Heterojunction, broad-range, and ultrafast.

MB-ThP-2 Porous Metal/Metal-Oxide Nanostructured Coatings Produced Using Gas Aggregation Sources of Nanoparticles as Recyclable SERS-Active Platforms, *A. Hanková, D. Novák, N. Khomiakova, E. Kočišová, M. Procházka,* ***Ondřej Kylián (ondrej.kylian@matfyz.cuni.cz)***, Charles University, Prague, Czech Republic

Due to their low cost, chemical and thermal stability, and unique electronic, optical or bioresponsive properties, metal-oxides (MeO) have become almost irreplaceable materials in an impressive range of modern technologies, such as (photo)catalysis, sensing, detection, or energy harvesting. In many cases, the functional properties of MeO may be enhanced by their nanostructuring that increases the specific surface and facilitates physicochemical phenomena like adsorption and diffusion of chemical species. One possibility of producing these materials relies on the deposition of highly porous transition metal (e.g. Ti, V, Nb, W) nanoparticle films by magnetron-based gas aggregation sources followed by the subsequent annealing of such formed nanoparticle films that assures their controllable oxidation and crystallization. The aim of this study is to demonstrate that further improvement of the functional properties of MeO nanoparticle-based films may be achieved if they are decorated with sputter-deposited noble metal nanostructures. In this way, different functionalities intrinsic to metal-oxide and metal components may be successfully combined or enhanced. As shown in this study, such metal/MeO nanomaterials are highly interesting as novel platforms for surface-enhanced Raman spectroscopy (SERS), in which the noble metals act as highly SERS-active component, while the transition MeO due to its photocatalytic characteristics provides the possibility of highly effective re-cycling of the platforms after cleaning them with UV light irradiation.

This work was supported by the grant GAČR 21-05030K from the Grant Agency of the Czech Republic.

MB-ThP-3 Exploring the Magnetoelectric Functionality in PMN-PT/FSMA Multiferroic Heterostructure for Flexible MEMS Applications, ***Diksha Arora (diksha@ph.iitr.ac.in)***, *D. Kaur,* Indian Institute of Technology Roorkee, India

Flexible microelectromechanical systems (MEMS) are poised to scaffold technological innovations in the domains of wearable sensors, implantable health monitoring systems and touchless human-machine interactivity. In this study, a cost-effective and flexible magnetoelectric heterostructure comprising thin films of $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$(PMN-PT) and ferromagnetic shape memory alloy (Ni-Mn-In, FSMA) over flexible stainless steel and Ni substrates has been reported. The growth of the tetragonal structured pure perovskite phase of PMN-PT thin film without any pyrochlore impurity is confirmed by the dominant (002) orientation in the XRD pattern. The magnetoelectric coupling characteristics of the flexible PMN-PT/FSMA multiferroic heterostructure have been explored for magnetic sensor and nonvolatile memory applications. The influence of phase fraction, anisotropy and poling on magnetoelectric coefficients has been thoroughly studied to obtain the optimum magnetoelectric coupling. A notable magnetoelectric coupling coefficient of ~4.1 $Vcm^{-1}Oe^{-1}$ at 250 Oe of H_{DC} has been obtained, making it promising for room-temperature magnetic field sensors. These results have been explained by an analytical model based on strain-mediated magnetoelectric coupling between interfacially coupled PMN-PT and FSMA layers of the multiferroic heterostructure. The electric field-controlled switching of magnetoelectric coefficient observed in PMN-PT/FSMA heterostructure is beneficial for high-density nonvolatile memory devices. The flexible ME heterostructure displays excellent mechanical endurance up to 2000 bending cycles. The remarkable response of such flexible magnetoelectric heterostructures at room temperature makes them promising for flexible magnetic field sensors, nonvolatile memory, spintronics and multifunctional device applications.

MB-ThP-4 A Carbon Nanotubes-Based Microwave Resonator for Ammonia Gas Sensing, ***Hsuan-Ling Kao (snoopy@mail.cgu.edu.tw)***, *Y. Tsai,* Chang Gung University, Taiwan

Carbon nanotubes (CNTs) have been used as gas-sensing material owing to their high specific surface areas and structural porosities that enable rapid responses and high sensitivity at room temperature. Fully inkjet printing technology promotes the green process using by digital controlled pattern in required location to offer fast, material saving, low cost, high substrate selectivity, and low annealing temperature. In this work, Inkjet-printed CNT films can be conferred with the appropriate resistance for embedding into transmission-type resonators for gas sensing by controlling droplet spacing (DS) and layer number. CNTs films as sensing layers and silver films as conductive layers to realize gas sensors using fully inkjet printing technology. Gas sensors, including resistive and microwave resonator sensors, were inkjet-printed on CLTE-MW to measure their response in the presence of ammonia. Gas responses of CNT films with regular electrode and interdigital electrode patterns were compared by resistive-type gas sensors. CNTs with the IDE pattern can provide large contact areas between the silver film and CNTs for the provision of more effective conductive paths, this resulting in stable sheet resistance and high response. The resistance of the sensing films embedded into the transmission-type microwave resonators should be as low as possible to avoid affecting loss. A microwave resonator consisting of two open-loop ring resonators coupled to each other by an interdigital structure was proposed as a microwave gas sensor. CNT films with the IDE pattern were embedded at the edge of the interdigital structure. The repeatability of the resonator under exposure to 700 ppm NH_3 for 20 cycles was examined. The exposure time to NH_3 gas at each step was 60 s and then, pure N_2 was injected into test chamber for 90 s at the recovery step. The average sensitivities of insertion loss and resonant frequency were 9.5 mdB and 353 kHz for 20 cycles, respectively. The results demonstrated that the CNT films with IDE pattern embedded in transmission-type microwave resonator provided two-dimensional response values in NH_3 sensing through electromagnetic transduction, thereby providing wireless sensor applications.

MB-ThP-5 Investigating 2D-Materials Using Correlative Spectroscopy & Microscopy, *T. Nunney,* Thermo Fisher Scientific, UK; ***James Lallo (james.lallo@thermofisher.com)***, Thermo Fisher Scientific, USA; *P. Mack, R. Simpson, H. Tseng,* Thermo Fisher Scientific, UK

Across a wide range of application areas, understanding the chemistry and structure of surfaces and interfaces is crucial. In the last fifty years, X-ray photoelectron spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry, and advances in instrumentation have enabled it to keep pace with the requirements for both academia and industry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry, but the limit on spatial resolution for XPS can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using just XPS.

Other experimental techniques which are unable to match the surface selectivity of XPS are able to provide complementary information to extend the data from XPS. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This can be a perfect complement to XPS analysis, so long as the same points of interest can be identified. Molecular spectroscopy, such as FTIR or Raman, can also provide complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures using the wide range of spectral libraries available for those techniques.

In this poster, we will describe how a correlative approach using both surface analysis instrumentation and scanning electron microscopy can be used to characterize 2D nanomaterials. Samples of MoS_2 grown on Si substrates have been investigated using XPS, Raman and SEM to determine their composition and structure. To facilitate co-alignment of the analysis positions when moving between the instruments, special sample carriers and software alignment routines have been developed.

MB-ThP-6 $CsPbI_3$-Based Perovskite Thin Film Using All Vacuum Deposition Process, ***HYO SIK CHANG (hschang@cnu.ac.kr)**, M. Jeong, j. Park,* Chungnam National University, Republic of Korea

We deposited $CsPbI_3$ films using a co-evaporation method, and optimized the film thickness and heat treatment. UV-vis and PL analysis confirmed the presence of a peak at 710nm wavelength, indicating the absorption and emission properties of the a-phase $CsPbI_3$ perovskite film. The use of vacuum co-deposition for $CsPbI_3$ deposition allows for excellent uniformity and thickness control, leading to optimized film thickness. To make inorganic $CsPbI_3$ perovskite solar cell, the phase change temperature must be lowered and a low phase change temperature of less than 200 °C is required. We have developed low phase change temperature $CsPbI_3$ with additive deposition. In this study, we manufactured a perovskite solar cell by combining the co-deposited $CsPbI_3$ perovskite with an inorganic charge transport layer using atomic layer deposition (ALD). ALD NiOx and SnO_2 films used as a hole transport layer and electron transport layer (ETL). Efforts are underway to apply vacuum co-deposition of $FAPbI_3$ and $CsPbI_3$ perovskite to tandem perovskite-Si solar cell applications.

MB-ThP-7 Synthesis and Characterization of AlCrTiZrSiW High Entropy Alloy Coating by High-Power Impulse Magnetron Sputtering, *C. Chang,* Ming Chi University of Technology, Taiwan*; J. Tang,* Lunghwa University of Science and Technology, Taiwan*; **Bo-Ruei Lu (M11188027@mail2.mcut.edu.tw)**, J. Tsao, M. Lin,* Ming Chi University of Technology, Taiwan*; F. Yang,* National Taiwan University of Science and Technology, Taiwan

High-entropy alloy coating feature high hardness, excellent thermal stability, and corrosion resistance. They have been considered as promising candidates for next-generation surface coating material because of their advantageous properties.In recent years, the popular high power impulse magnetron sputtering (HIPIMS) surface technology has attracted considerable attention due to the ability to produce coatings with excellent properties. It is preferable to replace high entropy alloy target with a co-sputtering method involving the use of more targets(single element metal target) simultaneously, which can greatly reduce the process cost.

In this study, AlCrTiZrSiW high-entropy alloy coating deposited on the various substrates (SKH-9 high-speed steel, SUS304 stainless steel, Si wafer) by HIPIMS technology.To obtain the Non- equimolar high-entropy alloy coatings was adjusted by varying the output power of Al and CrSi target (Zr 、TiSi、W target power was fixed). Detailed investigation was performed on the microstructure, mechanical properties and corrosion resistance of the resulting coatings. XRD and nanoindenter measurement results indicated that the coating exhibited an amorphous structure with a hardness value between 9.0 to 10.8 GPa. In addition, the coating with hydrophobic and corrosion resistance was verified via contact angle and electrochemical potentiostat test.The corrosion resistance of the AlCrTiZrSiW high-entropy alloy coating (Rp=28.3 $\Omega cm^2 \times 10^5$) is ~27 times that of the SUS304 stainless steel.

MB-ThP-8 Increasing the Sensitivity of ZnO Piezoelectric Pressure Sensor by Vanadium Doping, ***Heng-Chi Chu (juliachu2000@gmail.com)**, S. Brahma, J. Huang,* National Cheng Kung University (NCKU), Taiwan

ZnO is a common semiconductor material recently, due to its piezoelectric property, it can be used to fabricate the piezoelectric devicessuch as pressure sensor for monitoring the human health. Beside, doping vanadium(V) into ZnO can boost up the device performance because of increasing the piezoelectric coefficientandthe p-type carrier concentration. In our research, we will prepare the thin film V doped ZnO piezoelectric pressure sensor by RF magnetron sputtering system with different working power. After deposition, we will annealing the sample at Ar atmosphere. XRD,SEM&EDS were observed the structure, surface morphology and doping concentration. XPS results show the V^{5+} amount will reduce with higher doping concentration, and these trends were similar with the piezoelectric coefficient. The optical measurement will analysis by UV-vis, UPS, PL&RAMAN, these suggest the defect properties and energy level. When we enhance the doping concentration, the intrinsic defect will decrease, however, the lattice arrangement becomes disorder because the zinc sites were replaced by the vanadium. Finally, the sensor current sensitivity will discus by the I-V curve. when the V concentration is about 0.24 at%, piezoelectric coefficient and carrier concentration can reach the balance, promoting the device’s sensitivity significantly.

MB-ThP-9 Location-Dependent Super-amphiphobic Nano-Structured Films Deposited by Tubular Microwave Plasma, ***Ta-Chin Wei (tcwei@cycu.edu.tw)**, Y. Shen,* Chung Yuan Christian University, Taiwan

Super-hydrophobic and oleophobic surfaces have attracted much interest for both fundamental research and practical applications. In this study, Teflon-like fluorocarbon films with different nano-structures were deposited on various substrates by microwave-generated C2H2F4/CF4 plasma. The reactor was a tubular quartz tube with diameter of 5 cm and length of 80 cm. The substrates were placed in 20 different locations along the gas flow direction in upstream region, discharge region, and afterglow region. It was found that the surface morphology of the deposited film was very location dependent. The fluorocarbon films deposited in upstream and afterglow region consisted of nano-particulate structure with F/C atomic ratio of about 2.0, namely the Teflon-like structure. However, the fluorocarbon film was rough and thick with a low F/C atomic ratio when substrate was located in the discharge region. Interestingly, Teflon-like fluorocarbon films with vertical nano-wall structure could be deposited only on substrates located in the end of upstream region and in the beginning of the afterglow region. It was also found that water contact angle on the Teflon-like nanowall or nano-particulated film was above 160° and the CH2I2 contact angle was above 140°. Moreover, by using the same operating parameters, we successfully deposited transparent super-amphiphobic fluorocarbon nanowall film onto various substrates such as glass, copper, polycarbonate, and etc. Moreover, we found that Teflon-like films with nano-wall structure could also be deposited onto various porous substrates. Finally, from the time evolution of the deposited film, the growth mechanism of nano-wall structure film was realized.

MB-ThP-10 Enhancing Oxygen Evolution Reaction Performance with Sputter-Deposited High Entropy Alloy Thin Film Electrocatalysts, ***Siang-Yun Li (m98l0217@gmail.com)**, T. Nguyen, Y. Su, Y. Shen, C. Liu, J. Ruan, K. Chang, J. Ting,* National Cheng Kung University, Taiwan

Thin film catalyst, giving a different morphology, provides a significant advantage over catalyst particles for gas evolution reaction.Taking the advantages of sputter deposition, we hereby report high entropy alloy (HEA) thin film electrocatalyst for oxygen evolution reaction (OER).We investigate the catalyst characteristics not only in its as-deposited state but also during and after the OER.For comparison, unary, binary, ternary, and quaternary thin film catalysts were prepared and characterized.The surface electronic structure modification due the addition of a metal is studied experimentally and theoretically using density function theory calculation.We demonstrate that sputtered FeNiMoCrAl HEA thin film exhibits OER performance superior to all the reported HEA catalysts with robust electrocatalytic activity having a low overpotential of 220 mV at 10 mA cm^{-2}, and excellent electrochemical stability at different constant current densities of 10 and 100 mA cm^{-2} for 50 h.Furthermore, we have investigated the microstructure transformation during the OER, which is important for the understanding of the OER mechanism provided by HEA electrocatalyst.Such finding would contribute to future catalyst design.

MB-ThP-11 Transition Metal Nitride Anti-Reflective Coatings*, Barbara Schmid (barbara.schmid@tuwien.ac.at), B. Hajas, N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria*; J. Blaschke,* TU Wien, Austria*; P. Polcik,* Plansee SE, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Anti-reflective (AR) coatings are of high importance for our everyday lives in the field of optics, for example in visual aids and photography equipment. Lesser known, those coatings are also essential in the realm of photovoltaics like solar cells, because they are able to reduce the reflectivity of the material surface. There is a plethora of different design approaches to this topic. Within our work, we want to change the optical properties of hard TiC/TaC superlattice protective coatings without sacrificing superior mechanical properties. Using DC magnetron sputtering, we create nano-scale transition metal nitride-based (AlN and ZrN) thin films exhibiting different material characteristics. We investigate the influence of deposition parameters and film thickness on the optical properties of our materials system. Apart from structural and morphological investigations and the determination and comparison of mechanical properties of our material systems, we conduct optical investigations using differential reflectance spectroscopy (DRS).

MB-ThP-12 Enabling Robust Chemical State Analysis of Sn-Based Perovskites *via* Auger Parameter Analysis in XPS*, A. Wieczorek, Sebastian Siol (Sebastian.Siol@empa.ch),* Empa – Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Sn-based perovskites exhibit compelling properties such as reduced toxicity and lowered band gaps over those purely based on Pb. As a result, they are of increasing interest for photovoltaic applications in single-junction and all-perovskite tandem applications.[1]

For high performances, control of the oxidation state and interfacial chemistry is paramount, which can be determined using X-Ray photoelectron spectroscopy (XPS). However, the minor chemistry related shifts of the Sn core level emission complicate the analysis, especially for semiconducting materials. Here, surface band-bending as well as differences in the work function can be particularly pronounced.

In this presentation, we demonstrate that studies based on the modified Auger parameter α' provide a robust method to resolve different chemical states in Sn-based perovskites. Using a set of reference samples, we identified a high sensitivity to the halide, resulting in a shift of up to $\Delta\alpha' = 2$ eV between $ASnI_3$ and $ASnBr_3$-type polycrystalline perovskite thin-films.[2] Observed dependencies of α' on the Sn oxidation state and local chemistry provide a framework that enables reliable tracking of degradation as well as X-site composition for Sn-based perovskites and related compounds. Recently, we successfully applied this framework on Sn-based perovskite nanocrystals to ensure the absence of Sn(IV) impurities upon optimized synthesis procedures.[3]

The higher robustness and sensitivity of such studies not only enables more in-depth surface analysis of Sn-based perovskites than previously performed, but also increases reproducibility across laboratories. Due to the facile data analysis, this method is ideal for high-throughput studies that are increasingly being adopted in the development of new semiconducting materials.[4]

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MB-ThP-13 Pvd Deposition of Tin Based Antimultipacting Thin Films for Applications in Particle Accelerators*, Yanis Pisi (yanis.pisi@grenoble-inp.fr),* CNRS, Université Paris-Sud, France

The multipactor phenomenon is a critical issue that can occur in particle accelerators. To improve the performance of components used in particle accelerators, we have chosen to develop a materials approach with innovative coatings.

The SEY is the ratio of the number of secondary electrons to the number of incident electrons (primary electrons). To avoid the multipactor effect, the ratio must be less than 1. Currently, most materials have an SEY greater than 1 [1].The investigated coatings based on nitride or carbide titanium because the SEY ratio is intrinsically low [2,3]. My work consists to elaborate based TiN (TiO_xN_y, TiN, TiN_xC_y) thin films and study their properties. Another approach concerns the investigation of thin layers consisting of alternating layers of NbN and TiN. The preferred deposition method is PVD (Physical Vapor Deposition) by cathodic pulverisation. We will present the results obtained as a function of coating nature: (i) firstly, the physical properties (such as electrical properties by 4-point measurements) and chemical characterisations (such as the layer composition determined by XPS analysis); (ii) the values of secondary electron emission yields at the fully conditioned state (see Table, the surface was conditioned by electron bombardment). In this work, we study the SEY without the effects of roughness, which is known to significantly influence the SEY.

Reference	Layer	Substrat	Roughness (nm)	SEY
This work	TiNC	Si	0,5	1,01
This work	Multilayer NbN/TiN	Si	1	0,99
[1]	TiNC	Si	High	0,97
[2]	TiZrVC	Si	High	0,93

Table: SEY values of different thin films obtained PVD

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MB-ThP-14 Influence of Oxygen Partial Pressure and Temperature on the Optical and Electrical Properties of NiO_x Thin Films obtained by r.f. Sputtering*, E. Osorio-Urquizo, Francisco David Mateos-Anzaldo (dmateos@uabc.edu.mx), M. Curiel-Alvarez, R. Nedev, O. Pérez-Landeros, B. Valdez-Salas, N. Nedev,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico

Nickel oxide (NiO_x) thin films were deposited by r.f. magnetron sputtering on n-type silicon and corning glass substrates. The deposition conditions were 60 W of power during 6 minutes, a pressure of 5 mTorr and different substrate temperatures in the range of 25-200 °C. The partial pressure between O/Ar was varied between 0 and 4 %. Prior to deposition, the substrates were cleaned in an ultrasonic bath with acetone, isopropyl alcohol and deionized water for 5 min each and dried with high-purity nitrogen after each step. Besides, the target was pre-sputtered for 15 min. MOS capacitors were fabricated by deposition of gold and aluminum as top and back contacts using thermal evaporation.The thickness and optical constants of the films were obtained by spectroscopic ellipsometry. Measurements of current-voltage (I-V) and capacitance-voltage (C-V) dependences were carried out to study the effect of temperature and oxygen partial pressure on the electrical properties of the NiO_x thin films. The obtained results indicate that it is possible to obtained high quality films at low r.f. power that are viable for applications in electronic devices.

MB-ThP-15 Characterization of Tin Oxide deposited by ALD for EUV Photoresist Applications*, Sangwoo Lee (runlej@sju.ac.kr), T. Choi,* Sejong University, Republic of Korea*; I. Choi, J. Park, J. Yang,* TES Co., Ltd, Republic of Korea

At present, metal oxide photoresists are being explored as alternatives to chemically amplified resists. The metal oxide film may take the form of a photosensitive metalorganic oxide film, such as an organotin oxide. The deposition process may involve the reaction of an organotin oxide with carbon dioxide. Notably, organotin compounds exhibit high sensitivity to extreme ultraviolet (EUV), facilitating the attainment of high-resolution patterning. The strength and dissociation mechanism of carbon bonds are factors that can be associated with EUV photosensitivity in dry photoresist. SnO_x photoresists are introduced as materials for EUV resist with high absorptivity and excellent etch resistance. A comparative analysis was conducted on SnO_x thin films deposited via TALD and PEALD at various deposition temperatures and reactant ratios. We focus on the optical, chemical, and electrical properties of the SnO_x thin films under various deposition conditions, with a specific emphasis on the influence of the carbon ratio. Additionally, we will evaluate and discuss their etch properties.

MB-ThP-17 Effect of the R.F. Power and Thermal Annealing on the Properties of NiO_X Thin Films*, Roumen Nedev (roumen.nedev@uabc.edu.mx), F. Mateos-Anzaldo, M. Curiel-Alvarez, O. Pérez-Landeros, E. Osorio-Urquizo, B. Valdez-Salas, N. Nedev,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico

NiO_x thin films were deposited by RF sputtering in Ar atmosphere on n-Si and glass substrates. During the deposition the RF power was varied between 5 W and 60 W, while the deposition time was fixed at 9 min. Three deposition temperature of 25 °C, 50 °C and 100 °C were used. The samples deposited on Si were separated in three groups. The first group was furnace annealed at 450 °C in N_2 atmosphere for 1 h. The second one was treated by Rapid Thermal Annealing (6 min, 550 °C), while the third group was kept as control. Metal/NiO_x/n–Si heterostructures were prepared by deposition of Au electrodes through a mask.

The thicknesses and optical constants of the layers were determined by spectroscopic ellipsometry. XRD measurements were used to determine the effect of deposition temperature and thermal annealing on the crystallinity of the films. The Au/NiO_x/c-Si structures were electrically characterized by current-voltage (I-V) and capacitance-voltage (C-V) measurements. The I-V dependences showed formation of p-n heterojunction diodes with properties, which depend on the r.f. power, deposition temperature and annealing.

MB-ThP-20 Nano Indentation Pop-in Response on Basal Plane of 4H Hexagonal SiC Surface*, Jacob C. Huang (jacobc@faculty.nsysu.edu.tw),* National Sun Yat-sen University, Taiwan

The nano-scaled mechanics for the hexagonal 4H SiC single-crystal surface (with a bandgap of 3.26 eV) is examined by using nanoindentation testing on the {0001} basal plane. The 4H SiC material was prepared by Prof. M. C. Chou's lab via the Czochralski process. The as-grown crystal surface has been examined carefully by X-Ray diffraction (XRD) to confirm the 4H hexagonal structure, with the basal plane lying on the horizon plane and the c-axis parallel to the growth direction. The (0004) peak at 2q=35.5° is the only peak appeared, ensuring the well-grown surface orientation with minimum defects. The lattice parameters, a and c, are determined to be 0.3073 and 0.1006 nm, respectively. Through the analysis of XRD rocking curves, it is confirmed that there should be minimum defects inside the as-grown SiC surface.

Nanoindentation tests were performed using the continuous stiffness method (CSM), up to a maximum depth of ~950 nm on the (0001) basal plane surface. The average elastic modulus and hardness calculated from depth ranging from 300~800 nm over nine indents were ~500 GPa and ~42.5 GPa, respectively. In addition, the first few pop-in loads and displacements are captured from the deviations from a perfect Hertizian contact curve fitted to the load-displacement curve. By using rough estimation for the yield stress from hardenss by a factor about 2.5 (Tabor's assumption), we estimate the yield stress to be about 42.5/2.5 ~ 17.0 GPa. The first pop-in loads, pop-in hardness, and pop-in stresses can all be measured. The first pop-in stress is usually termed as the incipient stress, associated with the first initiation of the activation of dislocations (nucleation or gliding of diloscations). The average incipient stress for the first dislocation activity is about 16.1 GPa, slightly below the overall yield stress. From the first pop-in displacement, about 10 nm, it is likely to be a result of the micropipe threading screw dislocations (with a Burger's vector of c-axis, namely, ~1 nm). This suggests that the first pop-in could be caused by these screw dislocations gliding for 10 Burger's vectors. The understanding of dislocation incipient pop-in as a function of applied load would give the insight for subsequent influence for various functional properties of 4H SiC.

MB-ThP-21 2D Chemical Mapping of Nanoscale Functional Material using Soft X-ray STXM*, Namdong Kim (east@postech.ac.kr),* Pohang Accelerator Laboratory, Republic of Korea

Soft x-ray nanoscopy employing the scanning transmission x-ray microscope (STXM), which can provide chemical structural information of materials at tens of nanometer scale, has become a powerful study in analytical microscopic research. The nanoscopy beamline in the Pohang Light Source is operating currently at the optimum condition in its focused beam size ~30 nm and photon energy resolution < 0.1 eV in the soft x-ray energy range (200-1650 eV).

Basically, based on different x-ray absorption contrast depending on chemical states, we have studied structural and electronic properties of nanoscale defects or domains formed on various two-dimensional (2D) materials including graphene, hBN, MoS_2, WSe_2, and topological insulators such as Bi_2Se_3 thin film as well as energy materials. We will here introduce briefly the 2D nanoscale chemical mapping of such functional materials.

Moreover, as for Li-ion batteries, we investigated in-situ annealing effect on Ni-rich NCM cathode materials from RT to high temperature by measuring Ni, Co, Mn L_3-, and O K-edge absorption spectra. In-situ thermal degradation is induced by annealing. And oxygen reduction is preferentially observed on the edges of smaller particles at 400 °C.

KEYWORDS: 2D chemical mapping, soft x-ray nanoscopy, STXM, 2D materials, energy materials

MB-ThP-23 Exploring HiPIMS-Deposited TixN and TixAlyN Films for Oxygen Evolution Reaction (OER) Catalysis*, Wan-Yu Wu (wywu@nuu.edu.tw),* National United University, Taiwan*; J. Ting,* National Cheng Kung University (NCKU), Taiwan*; Y. Tsai,* National United University, Taiwan*; S. Li,* National Cheng Kung University (NCKU), Taiwan*; Y. Lin,* National Chung Hsing University, Taiwan

Sustainable energy technologies are fundamentally linked to electrochemical reactions, notably the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which are critical in electrolysis cells. OER, characterized by its sluggish kinetics, is a bottleneck in the efficiency of molecular oxygen generation, highlighting the necessity for advanced catalyst development. While precious metals like Ir, Ru, and their oxides (IrO2, RuO2) are prevalent in current research, their scarcity, cost, and low durability limit practical applications, urging the discovery of viable alternatives. This study explores metal nitrides, specifically TixN and TixAlyN films deposited on nickel foam using High Power Impulse Magnetron Sputtering (HiPIMS), as potential OER catalysts. Despite traditionally higher OER overpotentials, these heterostructured metal nitrides demonstrate promising activity and remarkable long-term stability, even in strong alkaline electrolytes. The capability of producing these films with precise crystalline structure and stoichiometry via scalable magnetron sputtering positions them as compelling substitutes to conventional precious metal catalysts, showing lower overpotentials compared to commercial RuO2 and paving the way for their application in large-scale clean energy solutions.

MB-ThP-24 Characterization of Protective AlCrON Thin Films for Application on Sensor Thin Films in Fused Layer Modeling Processes*, W. Tillmann, Julia Urbanczyk (julia.urbanczyk@tu-dortmund.de), M. Mainz, P. Bengfort, N. Lopes Dias,* TU Dortmund University, Germany

In plastic processing, the use of sensor thin films is gaining interest for inline measurement to ensure stable process control. However, due to the corrosive and abrasive characteristics of molten plastics, the application of an appropriate protective coating becomes imperative to ensure the functionality of the sensor films. AlCrON thin films demonstrate favorable protective attributes for this purpose. The tribo-mechanical and electrical properties are inherently influenced by the oxygen content. Therefore, a systematic variation of O_2 gas flow rates (10 to 30 sccm in steps of five) during the mid-frequency magnetron sputtering process was employed resulting in the O contents rise from 12.2 at.-% for 10 mln O_2 to 57.6 at.–% for 30 mln O_2. Simultaneously, a change of a polycrystalline structure containing CrN, Cr_2N, and hexagonal AlN to an amorphous structure with increasing O content for AlCrON is observed. This affects the tribo-mechanical properties. The highest polycrystallinity was reached at 25.2 at.–% O resulting in a H/E maximum, with a maximum in hardness of (37.6 ± 2.8) GPa and an elastic modulus of (361.2 ± 20.7) GPa. Here, also the lowest coefficient of friction (CoF) at elevated temperatures was reached with 0.43 against polypropylene (PP) and 0.23 against polyamide (PA). The low CoF correlates with a lower wetting ability of the AlCrON thin film. Regarding the electrical properties AlCrON thin films show insulating characteristics dependent on the O content. The electrical resistance increases with higher O content while the dielectric stregth tends to increase with higher crystallinity.

A first attempt to apply a functional copper layer within an Al_2O_3 and AlCrON system was successful, showing promise for enhanced functionality. However, further investigation is needed to fully understand its potential and optimize its performance.

The results show that AlCrON thin films offer promising protective qualities for sensor applications in plastic processing. By adjusting the oxygen content, their tribo-mechanical properties can be optimized for reduced friction and enhanced durability, while their insulating properties are promising for maintaining the functionality of the sensors.

MB-ThP-25 Synthesis of Highly-Textured Wurtzite AlN Thin Films on Nitrogen-Terminated Metal Surfaces*, **Oleksandr Pshyk (oleksandr.pshyk@empa.ch)**, J. Patidar, S. Zhuk, S. Siol,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

AlN thin films in wurtzite structure are used in a broad range of piezoelectric applications such as microelectromechanical systems (MEMS) due to their high acoustic velocity, chemical resistance, thermal stability and linear piezoelectric response. Especially, for piezoelectric applications AlN thin films have to demonstrate a high crystalline quality and exhibit a pronounced out-of-plane c-axis orientation.

Typically, this necessitates the growth at elevated temperatures. It has been demonstrated that deposition on certain metallic substrates can improve the crystallinity and texture of sputter-deposited AlN [1]. However, despite the widespread application of metallic templates for the deposition of AlN, only few systematic studies of the stabilization mechanisms are reported.

In this work, we present a systematic study of AlN thin film growth on chemically and structurally different metallic seed layers. The deposition sequence used in these experiments is pre-sputter metal targets in Ar (1)/ RF magnetron sputter deposition of a metal layer (2)/ pre-sputter Al-target in Ar (3)/ pre-sputter Al target in Ar+N_2 (4)/ AlN deposition by reactive DCMS (5). All steps are performed at room temperature to eliminate the effects of temperature while (4) ensures metal layer exposure to N_2 for 1 min.

We demonstrate that AlN films grown on different low-work function metals show markedly improved texture and crystallinity compared to films grown on glass. To differentiate between either a chemical or a structural templating effect we vary the metal-layer thickness from 115 nm down to less than 1 nm and to tune their crystallinity and their substrate coverage. The AlN grain size strongly correlates with the glass substrate coverage by the metal layers. However, it appears much less important if the metal templates are crystalline or amorphous. It is therefore likely that the stabilization mechanism is chemical in nature.

UHV-transfer XPS studies on freshly sputtered metal layers demonstrate the formation of a thin layer of metal nitride on the surface of W and Al thin films upon short-term exposure to the N2-containing process gas, even at room temperature. The conditions were chosen equivalent to the environment in the sputter chamber leading up to the AlN deposition. We therefore assign the promotion of AlN nucleation and growth on low-work function metal substrates to the chemical effect set by a complete N2 substrate surface termination and the associated preferential c-axis polarization. The revealed mechanism extends the fundamental understanding of the AlN growth process on different metallic substrates beyond strain-driven mechanism or AlN/metal interface symmetry considerations.

MB-ThP-26 Synthesis of Epitaxial a-Ga_2O_3 Thin Films on Sapphires by Pulsed Laser Deposition*, **Heungsoo Kim (heungsoo.kim.civ@us.navy.mil)**, M. Mastro, A. Piqué,* Naval Research Laboratory, USA

Gallium oxide (Ga_2O_3) is an emerging ultrawide-bandgap semiconductor for high power electronics and ultraviolet photonics. Among various Ga_2O_3 crystal structures, a α-Ga_2O_3 has gained a great interest because its bandgap (>5.3 eV) is far wider than that of common β-Ga_2O_3 (4.5 – 5.3eV). Thermodynamically stable β-Ga_2O_3 thin films have been successfully synthesized by various deposition techniques. However, the growth of metastable α-Ga_2O_3 thin films is more challenging process because the formation of α-Ga_2O_3 is only stable for the first few monolayers and easily converted from α-Ga_2O_3 to β-Ga_2O_3 during high temperature post growth treatment. In this work, we have explored an effective route for growing relatively thick epitaxial α-Ga_2O_3 films on *m*-plane and *a*-plane sapphire substrates by pulsed laser deposition (PLD). First, we have grown Ga_2O_3 films at various substrate temperatures (560 – 720 °C) while the background pressure was kept at 3 mTorr of oxygen. Second, the effect of oxygen background pressure was investigated in an oxygen pressure range between 1 and 50 mTorr while the substrate temperature was fixed at 720 °C. The crystal structure and film quality of all Ga_2O_3 thin films were then investigated by high-resolution X-ray diffraction (XRD). For films grown on *a*-plane sapphires, pure α-Ga_2O_3 films can be obtained at only high growth temperatures (> 720°C) while the β-Ga_2O_3peaks are appeared as the growth temperature is lowered below 720 °C. For films grown on *m*-plane sapphires, pure α-Ga_2O_3 film can be obtained at all temperature ranges (560 – 720 °C) while the film crystallinity improved as the growth temperature increases. We will present details of optimization processes to grow pure α-Ga_2O_3 films along with structural and optical properties of Ga_2O_3 films.

This work was supported by the Office of Naval Research (ONR) through the Naval Research Laboratory basic research program.

MB-ThP-27 High Responsivity GaS Nanobelt Metal-Semiconductor-Metal Photodetector with Ni Contact*, **Chun-Yi Lin (gary12305112@gmail.com)**, C. Wang,* National Taiwan University of Science and Technology, Taiwan

Two-dimensional GaS is an important member of group III_A–VI_A semiconductors possessing exceptional optoelectronic properties. In this work, 2D GaS nanobelts (NBs) were successfully synthesized via the vaper-liquid-solid (VLS) method and the structure, morphology, and chemical composition of the as-prepared nanobelts are extensively investigated. Furthermore, GaS nanobelts are fabricated into photodetector with Ni contacts through electron beam lithography (EBL), electron beam evaporation and lift-off processes. The photodetector determines the photodetectors exhibited a dark current smaller than 500 fA while demonstrating remarkably high responsivity, external quantum efficiency (EQE) and detectivity is tens mAW^{-1}, ~10^4 % and ~10^{13} Jones, respectively. Moreover, they displayed repeatable ON−OFF switching behavior, which with a fast response time is ~60 ms under the 405 nm excitation. Given the very low dark current, the GaS nanobelts were characterized as p-type semiconductors via MOSFET measurements under 405 nm excitation, with a measured mobility of ~10^{-3} cm^2 V^{-1} s^{-1}.

To further enhance the performance of the devices,GaS/Ni heterostructure devices were formed through rapid thermal annealing (RTA). Post-annealing,the devices exhibited metallic behavior with a conductivity of ~10^3 $\Omega^{-1}cm^{-1}$ with high annealing temperature. On the other hand, low-temperature annealing resulted in the formation of Ni_xGaS/GaS heterostructures. These findings present a novel approach to enhancing the responsivity of GaS photodetectors with Ni contacts, offering promise for future high-performance optoelectronic systems.

MB-ThP-29 The Effect of the Precursors and Chemical Vapor Deposition Process on the Synthesis of Two-Dimensional Molybdenum Nitride Nanomaterials*, C. Peng, B. Lin, H. Chen, L. Chen, **Sheng-Kuei Chiu (skuechiu@o365.fcu.edu.tw)**,* Feng Chia University, Taiwan

Transition metal nitrides (TMNs) are crucial in influencing a wide range of physical and chemical characteristics due to their layered structure. They find applications in energy storage, sensors, electronics, spintronics, and catalysis. TMNs have a 2D structure that contains several active sites on the surface or edge, which contribute to their exceptional catalytic activity. Ongoing research is increasingly focused on developing methods to synthesize 2D TMNs. There are several defects in the structure of 2D TMN created using solution-based chemical synthesis, such as the hydrothermal technique. When fluorine, hydroxyl, or other oxygen-containing groups are on the surface of 2D TMNs, they become less reactive than they were before. Obtaining the desired effect from the use of TMNs synthesized by the hydrothermal process is challenging. The chemical vapor deposition (CVD) method has recently been approved as a way to make high-quality 2D transition metal nitrides (TMNs) that do not have any functional groups on the surface. We present a novel technique for producing an extremely thin, two-dimensional molybdenum nitride nanomaterial via chemical vapor deposition. Molybdenum nitride can be synthesized on a SiO2/Si wafer by the CVD process. It undergoes an ammoniation reaction with the transition metal disulfide (MoS2) and substitutes it with the transition metal nitride (MoN). By using a range of material testing devices, the precise composition and structure of the material are verified. This verification process aims to synthesize exceptionally reactive TMNs by carefully manipulating experimental conditions. The ultimate goal is to further the use of 2D TMNs in nanoelectronic components in the future.

MB-ThP-30 Optical Properties of Nanoscale Multi-Layered Ti/taC Thin Films*, K. Oh, **JiWon Park (pjw000605@naver.com)**,* Korea Aerospace University, Republic of Korea*; J. Kim,* KIMS, Republic of Korea*; Y. Kim,* Yonsei University, Republic of Korea*; S. Lee,* Korea Aerospace University, Republic of Korea

For the decade, it has been shown that diamond-like carbon (DLC) coatings are very promising anti-reflection (AR) and protective coatings for solar cell.However, tetrahedral amorphous carbon (ta-C) coatings with extremely high hardness, smooth surface, excellent wear resistance, and better thermal stability than DLC have been paid much attention to an alternative protective coating materials. Additionally, optical properties of the taC coating could be improved by various metals doping. In this study, various contents of Si were doped in the taC coating to improve the mechanical and optical properties of tacC coatings. A filtered cathodic vacuum arc (FCVA) and magnetron sputter hybrid system was used to synthesize the metal doped taC coating. As the Ti concentration increased, the mechanical properties of the coatings decreased. The hardness and elastic modulus of the taC coating (50 and 435 GPa)decrease down to 14 and ~223 GPa. Xray photoelectron spectroscopy (XPS) C 1 s spectra showed that both the Ti atomic percent and TiC bond percent increased with sputtering power. In addition, Tidoped taCcoatings showed an improved transmittance in all wavelength ranges when the sputtering powers were relatively low, comparing with undoped taC coating. Tribological behaviors of the Tidoped taC coatings were ubvestigagted and the results showed that with increasing sliding distance, the CoF and the wear rate increased regadless of the Ti and Ti-C contendt in the Ti-doped taC coatings. Experimental details and further results will be presented.

MB-ThP-31 Vernier Ellipsometry Sensing with Ultralow Limit-of-Detection and Large Dynamic Range by Tuning of Zero-Reflection Points*, Y. Zhang, M. Thawda Phoo, F. Yishu, X. Li, Y. Lam,* ***Juan Antonio Zapien (apjazs@cityu.edu.hk)****,* City University of Hong Kong

Optical sensors using zero-reflection points (ZRPs) enable excellent sensitivity due to accompanying phase singularities and the steepest slope of the reflectivity curve. Reflection zeros have been demonstrated at different spectral regions under very specific conditions in the angle of incidence (AoI) and polarization state. However, manipulation of the darkness points for multiple spectral positions and polarizations has not been achieved yet. Here, we report the collaborative and synergic operation of three ZRPs in a simple platform formed by a lithography-free, three-layer, metal-dielectric-metal structure where careful design and efficient manipulation of these ZRPs results in an optical sensor with unsurpassed, experimentally demonstrated, limit of detection ~2x10^{-8} RIU. The synergic operation of the proposed sensor relies on: i) strong coupling between *p*-pol surface plasmon polariton and *p*-pol photonic waveguide modes with experimentally demonstrated reflection suppression, Rabi splitting and phase singularities; ii) simultaneous implementation of two orthogonally polarized ZRPs and wavelength-interrogation mode of operation leads to spectral overlap of *s*-pol photonic modes with the coupled, *p*-pol resonances; and iii) ellipsometry-based sensing where the relatively insensitive *s*-pol ZRPs provide internal references to boost the sensor performance in terms of the amplitude ratio (ψ) and phase difference (Δ) of the *s*- and *p*-polarized reflectance thereby naturally forming a refinement measuring scale akin to a Vernier scale. Remarkably, the precise manipulation of the double dark points via the AoI control enables a second metric that yields ultrahigh sensitivity and can be reset to the original spot over a large dynamic range, thereby avoiding the trade-off between sensitivity and dynamic range. This occurs because the AoI acts an additional degree of freedom to tune and reset the sensor to its original ZRPs while keeping track of the total accumulated change. The strength of these capabilities has been demonstrated for a biosensor of SARS-CoV-2 spike (S2) protein that can track the full functionalization process of the chip surface and then reset to its best sensing conditions to perform real-time dose-dependent detection of the S2 spike protein. Our work provides a new and powerful strategy for the development of optical sensors, perfect light absorbers, pyroelectric detectors, and phase modulators.

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MB-ThP-32 Optical and Protective Coatings Synthesized by Magnetron Sputtering*, E. Aubry,* FEMTO-ST (UMR CNRS6174)/UTBM, France*;* ***Pascal Briois (pascal.briois@utbm.fr)****,* FEMTO-ST (UMR CNRS 6174)/UTBM, France

The consortium of Opti-Reve project is composed by Surcotec and He-arc for the Swiss part and Gaggionne and UTBM for the French part. This project aims to develop a new technological solution (optical and protective coatings) in order to improve the quality of optical polymer components thanks to new functionalities brought to the surface by PVD technology, notably the corrosion resistance and the wear, as well as the brightness.

As part of this study, we first theoretically defined the material presenting the best reflection for the application but also its thickness. Based on the theoretical results, an adequate protective coating is determined. From the experimental point of view, the films were sputtered by magnetron sputtering from metallic targets in a neutral argon atmosphere for the reflective layer, then in a reactive atmosphere for the protective layer. The thin films were characterized by SEM, XRD for the morphological and structural parameters, the optical properties were determined by spectrophotometry. The first results obtained will be presented as well as future work.

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Tribology and Mechanics of Coatings and Surfaces
Room Golden State Ballroom - Session MC-ThP

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces (Symposium MC) Poster Session

MC-ThP-1 Influence of Cobalt Content on the Adhesion of TiAlN and AlTiN/TiSiN Coatings on WC-Co Substrates*,* ***Bruna Michelle de Freitas (bruna.michelledefreitas@gmail.com)****, R. Diego Torres, D. Stolle da Luz Weiss, P. Cesar Soares Junior, C. Augusto Henning Laurindo,* Pontificia Universidade Católica do Paraná, Brazil*; F. Lacerda Amorim,* Pontificia Universidade Catolica do Paraná, Brazil

Coatings based on Ti-Al-N-Si, deposited by the physical vapor deposition (PVD) process, aim to increase the working life of machining tools. In this way, the mechanical properties of the substrate interfere with the adhesion of these coatings, reflecting on their performance. Cemented carbide, one of the most used materials for cutting tool manufacturing, is a composite consisting of tungsten carbide (WC) plus a binder phase. The binder content, typically cobalt (Co), defines its main characteristics: hardness, elastic modulus and determining its application [1]. However, the effect of cobalt composition in the cemented carbide substrate and how its variation affects the mechanical properties and adhesion of PVD coatings is not extensively investigated [2]. Therefore, the objective of this study is to evaluate the adhesion and mechanical properties (hardness (H), elastic modulus (E), and the H/E ratio) of Ti-Al-N-Si-based coatings (TiAlN and AlTiN/TiSiN) deposited by the PVD process on cemented carbide substrates with different Co concentrations (6, 8, and 10%). The surface properties of the substrates and coatings were assessed using scanning electron microscopy (SEM) with an attached energy-dispersive X-ray spectroscopy (EDS) system, X-ray diffraction (XRD), and roughness measurements. For the evaluation of mechanical properties, nanoindentation tests were performed, and adhesion was evaluated through indentation testing and scratch testing. The results show that the hardness and elastic modulus of the substrates are affected by the Co content, and the AlTiN/TiSiN coating has the highest hardness due to the presence of Si in its composition, along with higher roughness from the deposition process. In general, higher Co content in the substrate negatively affects adhesion. Through the scratch test, it was observed that the TiAlN coating has better adhesion to the substrate. Additionally, for a higher H/E ratio, there is greater adhesion for both coatings (TiAlN and AlTiN/TiSiN), and this adhesion is higher in cemented carbide substrates with low Co content.

[1] CHEN C. et al., Additive manufacturing of WC-Co cemented carbides: process, microstructure, and mechanical properties, **Additive Manufacturing**, **2**023.

[2] CHEN Y. et al., Cohesive failure and film adhesion of PVD coating: Cemented carbide substrate phase effect and its micro-mechanism, **International Journal of Refractory Metals and Hard Materials**, 2023.

MC-ThP-2 The Multi-Component Alloy Powder Manufacturing and Coating on Router Cutters for Carbon Fiber Composite Materials*,* ***Sung-Mao Chiu (smchiu@mail.mirdc.org.tw)****, H. Hsueh,* Metal Industries R&D Centre, Taiwan

This research focuses on the manufacturing of the key component of high-end cutting manufacturing in aerospace, the milling tools for cutting carbon fiber composite materials. By integrating the multi-component alloy $Al_xCr_yNbSiTi_z$ coatings, including alloy composition design, simulation, powder manufacturing and sputtering target block manufacturing to establish the customized long-life and high value performance special coating technology of cutting tools. Multi-component alloy nitride coating by PVD sputtering process shows high hardness ≧30GPa, water droplet contact angle: ≧ 90°, high temperature resistance ≧1000℃, coating adhesion: ≧ 60N. After field verification of composite cutting tools show increasing the tool life by more than 30% compared with the current tool life used by the industry.

The developed technology will fill the gap in coating technology in domestic cutting tool manufacturing industry, and finally integrate with the verification of cutting performance in the laboratory and field test, to achieve the goal of significant improving cutting performance in cutting aircraft parts made by carbon fiber composite materials.

MC-ThP-3 Application of *In Situ* Hydrogen Charging During Micromechanical Testing of Thin Films*, **Szilvia Kalacska (szilvia.kalacska@cnrs.fr)**,* CNRS LGF, Mines St. Etienne, France

Understanding mechanisms of deformation in thin films at the sub-micron scale is the key for designing new compositions for industrial applications. It requires the determination of strains/stresses [1], dislocation distribution [2] and the overall microstructure evolution, which is often extremely challenging. Microstructural processes during external mechanical loading are hard to observe due to the complex multiscale nature of the phenomenon. If hydrogen is present in the solid, it can cause embrittlement or enhanced cracking, when the material is subjected to stress. This would eventually lead to the reduced lifetime or critical failure of the component. Although it is known for a long time that hydrogen causes degradation of mechanical performance in metals, the microscale mechanisms remain a subject of debate. Direct H-detection within the lattice is an extremely challenging task, (continuous diffusion and outgassing issues). Microstructure observations are still mostly performed post mortem on bulk samples.

In situ H-charging is therefore essential for thin film experiments. Samples can be loaded electrochemically through the back surface [3], using a cell compatible with high-vacuum (HV) scanning electron microscopes (SEM). This way, H diffuses into the lattice from the back, avoiding contamination to the surface of interest. The developed system will be presented, focusing on the coupling of the cell with the nanodeformation stage by performing nanoindentation experiments on H-charged thin films.

References:

[1] S. Wang, S. Kalácska, X. Maeder, J. Michler, F. Giuliani, T. B. Britton, The effect of δ-hydride on the micromechanical deformation of a Zr alloy studied by in situ high angular resolution electron backscatter diffraction, *Scripta Materialia* 173 (2019) 101-105. doi: 10.1016/j.scriptamat.2019.08.006

[2] S. Kalácska, *et al.*, Investigation of geometrically necessary dislocation structures in compressed Cu micropillars by 3-dimensional HR-EBSD, *Materials Science and Engineering A* 770 (2020) 138499. doi: 10.1016/j.msea.2019.138499

[3] J. Kim, C. C. Tasan, Microstructural and micro-mechanical characterization during hydrogen charging: An in situ scanning electron microscopy study*, International Journal of Hydrogen Energy* 44 (12) (2019) 6333-6343. doi: 10.1016/j.ijhydene.2018.10.128

MC-ThP-4 Shrouding Gas Plasma Deposition Technique for Generating Wear Resistant ZnO/WS_2 Composite Films on PEEK*, **Dietmar Kopp (dietmar.kopp@joanneum.at)**,* Leobner Straße 94a, Austria

In this study, zinc oxide/tungsten disulfide (ZnO/WS_2) composite films were generated by an atmospheric pressure plasma jet (APPJ) equipped with a shrouding gas attachment on polyether ether ketone (PEEK) discs. The friction and wear properties of the ZnO/WS_2 composites sliding against 100Cr6 counterpart balls were intensively investigated by using a rotational ball-on-disk setup under dry sliding conditions at ambient room conditions. The deposited and worn coating areas were observed with a scanning electron microscope (SEM). The results indicated that low friction ZnO/WS_2 composite films have the potential to protect PEEK against mechanical motion. However, the tribological performance of the coatings are strongly dependent on the plasma-process settings (i.e. plasma current, dwell time of the powder particles in the plasma jet). In fact, there is a significant tribological improvement of the composite films in contrast to the uncoated PEEK by a factor of three.

MC-ThP-5 Wear and Corrosion Characterization and Parametric Optimization of Nb-doped Hydrogenated Diamond-like Carbon (a-C:H) Coatings*, **Ihsan Efeoglu (iefeoglu@atauni.edu.tr)**, Y. Totik, G. Gulten, B. Yaylali, M. Yesilyurt,* Atatürk University, Turkey*; R. Gunay, G. Kara, B. Altintas,* TUSAS ENGINE INDUSTRIES (TEI), Turkey

This study focuses on enhancing the wear and corrosion resistance of AISI 4130, a chromium-molybdenum alloy steel, through the application of a functional coating. Targeting various industrial uses, notably in the aerospace and automotive industries, the research aims to improve the durability and performance of AISI 4130. As the functional coating, niobium-doped hydrogenated diamond-like carbon (a-C:H:Nb) coatings were deposited using a closed-field unbalanced magnetron sputtering technique under various parameters, which were systematically optimized following the Taguchi L_9 orthogonal array method. The microstructural properties of the coatings were analyzed using a scanning electron microscope, and their crystallographic characteristics were determined using X-ray diffraction, providing a comprehensive understanding of the coating structure. To evaluate the mechanical properties, nanoindentation tests were employed, offering precise measurements of hardness and elasticity. The tribological characteristics of the DLC films were assessed using a pin-on-disc tribometer, examining their wear resistance and frictional behavior under ambient air. These comprehensive analyses reveal the a-C:H:Nb coating potential for applications requiring enhanced surface properties, combining enhanced superior tribological and corrosion performance.

MC-ThP-6 Improving Tribological Properties of Al 7075 Alloy by Two-Step Soft Plasma Electrolytic Oxidation*, **Thiago de Lima Gontarski (thiago.gontarski@pucpr.edu.br)**, G. Caetano, J. dos Santos Junior, B. Leandro Pereira, R. Diego Torres, P. Soares,* Pontifical Catholic University of Paraná, Brazil

The trend of using aluminum (Al) alloys in various industrial sectors, including naval, automotive, and aerospace, can be attributed mainly to their high specific strength. However, their relatively lower resistance to wear and corrosion could limit their applications. To address this, Plasma Electrolytic Oxidation (PEO) has emerged as an effective method to enhance the mechanical, chemical, and thermal properties of Al alloys. Hence, this study aims to evaluate the impact of sample exposure time during the PEO process on the tribological properties of the Al7075. Specimens of Al7075 were abraded with silicon carbide sandpapers of #220 grit. Subsequently, all samples were cleansed with acetone and air-dried at ambient temperature. The PEO procedure was carried out in two stages. It employed a unipolar power source, a stainless steel counter electrode, and a silicate-based electrolyte. The first stage of PEO was the same for all samples, and it involved applying a voltage of 300V and a current of 0.5 A for one minute. The second stage was carried out with a voltage of 350V, and a current of 0.3 A, with varied exposure durations for each sample: 3, 5, 10, and 20 min. The morphology, chemical composition, and crystalline phases were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-ray Diffraction. The friction and wear properties of the samples were determined by dry linear reciprocating sliding tests in a ball-on-plate setup, using an Anton-Paar universal tribometer. An applied load of 5 N and a sliding speed of 2.5 cm/s were maintained, with a reciprocating stroke of 6 mm. The test distance was set at 40 m at 25°C and a relative humidity of 50%. SEM analyses post-PEO process revealed that surface layers of the Al substrate were characterized by numerous pores and a flattened topography. The smoothest and thickest layer was achieved with the 20-minute PEO treatment. EDS results indicated that Al and O elements were predominantly present in all coatings after various exposure times. The coefficients of friction recorded were 0.557 for the substrate, and 0.501, 0.540, 0.442, and 0.427 for the PEO treatments of 3, 5, 10, and 20 min, respectively. Concurrently, wear rates were measured at 2.84, 1.79, 2.06, 1.97, and $1.34x10^{-3}mm^3/Nm$ for the same conditions. The oxide layer with the most advantageous tribological performance was that which formed over 20 min; it withstood rupture for in excess of 1600 cycles, compared to the other layers, which failed between 700 to 800 cycles. In conclusion, the longest exposure time during the mild PEO treatment correlated with the most favorable tribological properties.

MC-ThP-8 Mechanical and Tribological Behavior of Nanolayered Sputtering MoN/MoWN Coatings*, W. Hsu, **Fan-Bean Wu (fbwu@nuu.edu.tw)**,* Department of Materials Science and Engineering, National United University, Taiwan

This research investigated the microstructure, mechanical and tribological behavior of the molybdenum nitride, MoN, molybdenum tungsten nitride, MoWN, single layers and the nanolayered MoN/MoWN, films through reactive radio frequency magnetron sputtering, RFMS, technique. The nanolayered MoN/MoWN was prepared with fixed 50 nm MoWN building layers and MoN building layers with a thickness of 25 to 50 nm. These layers were alternately stacked to form a multilayer film with a total thickness of approximately 1 µm. The MoN single building layers presented a nanocrystalline structure while well crystalline feature was found for the MoWN layers. Through microstructure analysis, the nanolayered MoN/MoWN with a building bilayer of 25/50 nm/nm possessed continuous growth of MoWN columnar crystals along B1-MoN(111). On the contrary, the through-layer columnar grain was suppressed by the 50/50 nm/nm MoN/MoWN stacking. For mechanical and tribological behavior,the wear track of the M-50/50 multilayer film was shallower and narrower as compared to those of the 25/50 MoN/MoWN multilayer film. The superior wear resistance was attributable to the effective inhibition of continuous growth of columnar crystals by a thicker MoN building layer. Additionally, the 50/50 multilayer MoN/MoWN film exhibited larger compressive residual stress which was beneficial for hardness and tribological characteristics.

MC-ThP-10 Influence of Carbon and Boron Additions on the Wear Resistance of Fe_3Al Based Laser Claddings*, H. Rojacz, K. Pichelbauer, M. Varga,* AC2T Research GmbH, Austria*; **Paul Heinz Mayrhofer (paul.mayrhofer@tuwien.ac.at)**,* TU Wien, Institute of Materials Science and Technology, Austria

Strengthened iron aluminides exhibit excellent mechanical properties up to 600°C, and are promising candidates to replace Co-, Cr- and Ni- rich coatings for high temperature wear protection. To improve their hardness, different strengthening mechanisms can be chosen accordingly. For this study, precipitation hardening with carbon and/or boron was used to strengthen Fe_3Al-based iron aluminides. Carbon and boron were alloyed in the range from 0-20 at.% as well as combined up to 10 at.% each to precipitate carbides, borides and carboborides to show the influence on microstructural evolution, hardness as well as wear resistance. A thorough material analysis of the developed laser claddings materials and the present phases was conducted using scanning electron microscopy, electron backscatter diffraction, hot hardness testing, nanoindentation as well as high temperature abrasion testing. Results show that the hardness can be significantly increased from ~260 HV10 (claddings without any strengthening of the Fe_3Al phase) to ~850 HV10 with boride precipitations (20 at.% B). Strengthening with carbon and boron leads to a hardness of ~670 HV10 due to the formation of carboborides as well as graphite islands (10 at.% B and 10at.% C). Alloying with carbon causes the formation of graphite lamellae as well as perovskite-type carbides $Fe_3AlC_{0.6}$ and lower hardness of a max. of ~350 HV10 at 20 at.% C. Wear results indicate a strong dependence on the present phases, whereas a significant reduction of the wear rates can be pointed out when strengthened; comparable to classical FeCrC-based hardfacings, but with the advantage of a significantly reduced ecological impact.

MC-ThP-11 Understanding Stress in Sputter-Deposited Ti-Zr-N Alloy Films*, E. Chason, **Tong Su (tong_su@brown.edu)**, Z. Rao,* School of Engineering, Brown University, USA

Understanding and controlling residual stress in sputtered metal-nitride films is important because of the impact it can have on their properties.Numerous studies have quantified the stress for different systems and processing conditions and modeling has attempted to explain the stress in terms of the underlying kinetic processes.Although ternary nitride alloys are used in many applications, there is much less understanding of stress in these systems relative to the binary alloys.In this work, we present results of stress in TiZrN, TiN and ZrN at different growth rates and pressures.Comparison of the ternary alloy with the two constituent binary alloys sheds light on how the addition of a second metal element modifies the stress. The results are interpreted in terms of mechanisms that have been proposed for explaining the stress generation in sputter-deposited films. These include tensile stress due to island coalescence and compressive stress due to insertion of excess atoms into the grain boundary and the effect of energetic particle bombardment.

MC-ThP-12 Cyclic Laser Thermal Shock Resistance and Mechanical Properties of AlCrSiN/AlTiSiN Multilayer Hard Coatings*, **Ming-Xun Yang (u6au6vmp711@gmail.com)**,* National Formosa University, Taiwan*; C. Chang, B. Chang, Y. Chang,* National Formosa University, Taiwan

In recent years, the quaternary coatings such as AlCrSiN and AlTiSiN were excellent potential candidates for wear resistance applications due to excellent thermally stability and oxidation resistance. However, for demanding operations such as the interrupted cutting and piercing, a typical failure mechanism of these tools is cyclic thermal fatigue. Such hard coatings may suffer cracking and spalling due to the high temperature cycling impact. A hard coating with multilayer architectures possesses excellent thermal stability and oxidation resistance which is attributed to the multielement composition and multilayer structure. In this study, the cyclic thermal fatigue shock test was developed to investigate the thermal fatigue failure mechanisms of the AlCrSiN and AlTiSiN monolayered coatings and multilayered AlCrSiN/AlTiSiN coatings. The failure mechanisms of the prepared coatings under the constant and cyclic thermal shocks were compared and analyzed. Several instruments were used to analyze the characteristics of the coatings. Emission electron probe microanalyzer (EPMA) was employed for elemental composition analyses, and grazing incidence X-ray diffraction (GIXRD) was utilized to analyze the crystal structure and phases of the coatings. Field emission scanning electron microscopy (FESEM) and field emission transmission electron microscopy (FETEM) were used to observe the cross-sectional microstructures. The coatings were also subjected to scratch tests to determine the adhesion strength of the deposited coatings. A nanoindentation tester was used to measure the hardness and elastic modulus. Ball-on-disk tests were used for the tribological analyses. In this case, ball-on-disk tests were used to evaluate the wear and abrasion resistance of the coatings. The results showed that the AlTiSiN/AlCrSiN multilayer coating exhibited improved mechanical properties and wear resistance due to the multilayer structure. SEM observations of the surface morphology of the thin films after single and 100 cycles of laser irradiation revealed that the AlTiSiN/AlCrSiN coatings showed less laser-induced thermal cracks, indicating excellent thermal fatigue performance of the multilayer coatings compared to respective monolayer coatings.

MC-ThP-13 Fracture Toughness of Borided AISI 1045 Steel with a Diffusion Annealing Process*, A. MENESES AMADOR,* Instituto Politécnico Nacional, Mexico*; A. OCAMPO RAMIREZ,* Universidad Veracruzana, Mexico*; A. Ballesteros-Arguello, J. Ceron Guerrero, **FELIPE NAVA LEANA (felnaval@gmail.com)**,* Instituto Politécnico Nacional, Mexico

A numerical-experimental study of the fracture toughness of iron borides obtained by cross-sectional scratch test was carried out. The iron borides were formed on an AISI 1045 steel. The powder-pack boriding process was developed at 1000 °C and 4 h of exposure time. The diffusion annealing process was performed on the borided steel at a temperature of 1000 °C with 4.5 h of exposure using SiC powder.The scratch tests were carried out on the cross-sections of borided material using a CSM Revetest-Xpress commercial equipment with a Vickers indenter. The scratch distance was of 1.2 mm with a load range from 5, 10 and 15 N. The applied loads and damage observed at the samples surface (with half cone geometry) were used to estimate the fracture toughness of the system. The numerical model based on the finite element method of the cross-sectional scratch test was developed considering the same test conditions. The numerical results were used to establish parameters employed in the methodology of fracture toughness by cross-sectional scratch testing.

MC-ThP-14 Influence of Cu Addition on Microstructure, Mechanical and Tribological Properties of Fe/NbC Coatings Produced on Tool Steel Using Laser Surface Alloying*, **Dariusz Bartkowski (dariusz.bartkowski@put.poznan.pl)**,* Poznan University of Technology, Poland*; P. JURČI,* Slovak University of Technology in Bratislava, Slovakia*; A. BARTKOWSKA,* Poznan University of Technology, Poland*; P. GOGOLA,* Slovak University of Technology in Bratislava, Slovakia*; D. PRZESTACKI, A. PATALAS, M. ROGALEWICZ, P. POPIELARSKI, P. SIWAK,* Poznan University of Technology, Poland

The work presents the influence of manufacturing parameters on properties of Fe/NbC composite coatings metallurgically bonded with tool steel substrate during the laser surface alloying. The Fe/NbC coatings were produced in two stages. In the first stage, an pre-coat in the form of paste was applied on substrate. In the second stage, pre-coat was remelted using a 3 kW diode laser beam. Three laser beam powers: 350 W, 500 W and 650 W were used. Various variants of powder mixture to produce pre-coats were applied: 100% NbC, NbC/4%Cu, NbC/8%Cu and NbC/12%Cu. The amounts of individual components were determined by weight. The main goal of the research was to check the possibility of producing composite coatings reinforced with NbC particles. The influence of copper addition on the properties of these coatings was investigated. Microstructure, microhardness, chemical composition tests using energy-dispersive X-ray spectroscopy and phase composition tests using the X-ray diffraction method were carried out. For tribological tests the Ball-on-Flat sliding wear method was used. The Fe/NbC coatings were analyzed both for adhesion using bronze balls and for abrasion using two types of balls - steel and tungsten carbide. The pressure forces of individual balls were selected in such a way that the average contact stresses in accordance with Hertz's theory were 1 GPa. Basic mechanical properties were determined using the nanoindentation method. It was found that it is possible to produce composite coatings metallurgically bonded to steel substrate, in which the reinforcing phase is NbC, and the role of the matrix is played by iron taken from the substrate or a mixture of iron and copper introduced with the pre-coat. It was found that some of the NbC particles were melted completely and released in situ in the matrix. However, some of these particles remain in the primary form. It was found that increasing the copper content in pre-coat leads to decrease in the microhardness of the coating matrix. In the case of coatings without copper, the hardness of 800 HV was achieved, and in the case of the addition of 12% Cu, the maximum hardness was 600 HV. However, this was the hardness of matrix without taking into account the reinforcing particles in the form of primary NbC carbides. Similar relationships occurred in the case of wear resistance. In this study design of experiment methods, which made it possible to determine the significance of the impact of researched input variables of the manufacturing process on the properties of obtained coatings were used.

MC-ThP-15 Microstructure, Mechanical and Tribological Behavior of Fe/Mo2c Coatings Produced by Laser Surface Alloying on Tool Steel, *D. BARTKOWSKI, A. BARTKOWSKA,* Poznan University of Technology, Poland*; P. JURČI, M. KUSY,* Slovak University of Technology in Bratislava, Slovakia*; D. PRZESTACKI, **Michał ROGALEWICZ (michal.rogalewicz@put.poznan.pl)**, P. SIWAK, P. POPIELARSKI,* Poznan University of Technology, Poland

The work presents the influence of manufacturing parameters on the microstructure and properties of metallurgical Fe/Mo_2C composite coatings produced in the laser surface alloying process. Tool steel was used as the substrate. The coatings were produced in two stages. In the first stage, pre-coats based on Mo_2C powder were produced. Thicknesses of these pre-coats were 150 µm, 250 µm and 350 µm. In the second stage, pre-coats were remelted with steel substrate using a 3 kW diode laser beam. A constant laser beam scanning speed of 3 m/min and three laser beam powers: 500 W, 700 W and 900 Wwere used. The aim of the studies was to determine the possibility of producing coatings with a composite microstructure, where the matrix will consist of iron from the substrate and Mo_2C particles will be the reinforcing phase. Microstructure tests using a scanning electron microscope, microhardness tests, chemical composition tests using the energy-dispersive X-ray spectroscopy method and phase composition tests using the X-ray diffraction method were carried out. Basic mechanical properties were checked using nanoindentation. Wear resistance tests were also carried out. To determine friction properties Amsler type method was used. Hardened steel was used as a counter specimen. It was found that it is possible to produce composite coatings metallurgically bonded to the substrate, in which the reinforcing phase is Mo_2C and the role of the matrix is played by iron from the steel substrate. This work presents the model for producing this type of coatings. It was found that the laser beam power and the thickness of pre-coats have influence on obtained Fe/Mo_2C coatings properties. Thanks to the use of design of experiments methods, the significance of the influence of the tested production parameters on the properties of the obtained coatings was determined. It was found that increasing the laser beam power leads to a decrease in the hardness of Fe/ Mo_2C coatings. The most favorable hardness and wear resistance are obtained for coatings produced using pre-coat thickness of 150 µm and 250 µm. Further increasing the thickness of the pre-coat results in deterioration of mechanical and operational properties. This is related to the reduced amount of matrix material in the coating and thus the lack of a matrix binding the Mo_2C particles.

MC-ThP-16 Mechanical Properties, Microstructure and Tribological Behavior of TaC Coatings Produced Using Laser Surface Alloying on Monel®400 Alloy, *A. BARTKOWSKA, D. BARTKOWSKI,* Poznan University of Technology, Poland*; P. JURČI,* Slovak University of Technology in Bratislava, Slovakia*; D. PRZESTACKI, **Paweł POPIELARSKI (pawel.popielarski@put.poznan.pl)**, P. SIWAK, A. MIKLASZEWSKI, M. ROGALEWICZ,* Poznan University of Technology, Poland

The work presents the characteristics of metallurgical TaC coatings produced on the single-phase Monel®400 alloy using the laser surface alloying method. The coatings were produced in two stages. In the first stage, pre-coats based on TaC powder were produced. They had a thickness of 260 µm +/- 10 µm. In the second stage, pre-coats were remelted with a Monel®400 alloy substrate using a 3 kW diode laser beam. A constant scanning speed of laser beam: 3 m/min and three laser beam powers: 350 W, 450 W and 550 W were used. Microstructure tests using a scanning electron microscope and microhardness tests were carried out. Additionally chemical composition tests using the Energy-dispersive X-ray spectroscopy method and phase composition study X-ray diffraction were investigated. The basic mechanical properties of the produced coatings were determined using nanoindentation. Tribological tests were also carried out. Test method for linearly reciprocating Ball-on-Flat sliding wear was used. The produced coatings had a composite microstructure with a clearly separated TaC reinforcing phase from the nickel-copper based alloy matrix. It was found that it is possible to create composite coatings on the Monel®400 alloy while simultaneously implementing this alloy from the substrate to the coating as a matrix. Based on the conducted studies, it was found that the increase in the laser beam power has influence on decrease of content of the reinforcing phase. The microstructure influences both microhardness results and wear resistance. In the matrix area microhardness ranging from 400 HV to 700 HV were obtained, but much higher values (even over 1600 HV) were observed in the areas significantly changed by the melted TaC carbide. The significance of influence of laser beam power on individual mechanical properties was determined. It was taken into account that increasing the power of the laser beam contributed to a change in the microstructure, including the complete melting of some primary TaC particles and their separation as secondary carbides.

MC-ThP-17 Influence of Differently Manufactured TiAl Targets on the Structural and Tribo-Mechanical Properties of Arc-Evaporated TiAlN Thin Films, ***Finn Ontrup (finn.ontrup@tu-dortmund.de)**, N. Lopes Dias,* TU Dortmund University, Germany*; D. Stangier,* Oerlikon Balzers Coating Germany GmbH, Germany*; N. Denkmann, A. Meijer, S. Jaquet, J. Debus, D. Biermann, W. Tillmann,* TU Dortmund University, Germany

The cutting performance and service life of WC-Co milling tools can be improved through the application of TiAlN thin films. Among the different Physical Vapor Deposition (PVD) methods, arc evaporation is widely employed to coat cutting tools due to its high deposition rate and excellent adhesion of the thin films. The TiAl targets are typically produced either by smelting or powder metallurgical methods, depending on the Al/Ti ratio. Smelting is commonly employed for Al/Ti ratios up to 1, while powder metallurgy becomes necessary for Al/Ti ratios exceeding 1. The impact of different deposition parameters on the arc evaporation process is well studied, while little is known about the influence of the target manufacturing route on the resulting tribo-mechanical properties. Differences in the manufacturing route manifest themselves in the microstructure of the targets, which in turn results in different arc conditions at the target surface during deposition and may also cause a droplet formation. Therefore, TiAlN thin films are deposited by advanced plasma assisted (APA) arc sources, using smelting and powder metallurgical TiAl targets at three distinct working pressures (8500, 5000 and 3000 mPa).

The correlation between the target and the deposition conditions is analyzed with respect to quantity and type of droplets within the thin film. These measurements are supplemented by 3D optical roughness measurements of the thin film surface. Scanning electron microscopy SEM is used to analyze the morphology and topology, while the chemical composition is determined by microprobe analysis as well as tip-enhanced Raman scattering. Additionally, the influence of the different target types on their phase composition is evaluated employing X-ray diffraction. The hardness and the coefficient of friction are determined to examine the tribo-mechanical behavior of the thin films on cemented carbide substrates. These comprehensive analyses provide insights into the relationship between the target manufacturing route and the resulting structural, physico-chemical and tribo-mechanical properties of TiAlN thin films. The results will enhance the fundamental understanding of the interaction between target type and thin film properties of arc-evaporated TiAlN.

MC-ThP-18 Formation of TiB_2/TiB Layers on Ti_6Al_4V Alloy: Adhesion and Wear Resistance, *J. Escobar-Hernández, G. Rodríguez-Castro, J. López-Rodríguez, A. Meneses-Amador, A. Cruz-Ramírez, **T. N. Cabrera-Yacuta (tcabreray1800@alumno.ipn.mx)**,* Instituto Politécnico Nacional, Mexico

Adhesion and wear of Titanium borides (TiB_2 and TiB) formed on Ti_6Al_4V alloy wereevaluated by scratch tests. The powder-pack boriding at 1100 °C during 10, 15 and 20 h under inert argon atmosphere was applied to Ti6Al4V alloy. TiB2 and TiB phases were identified on the surface of Ti alloy with maximum thicknesses of 9.3 and 8.6 µm, respectively. By instrumented indentation, hardnesses were determined around 42 GPa for TiB2 and 24 GPa for TiB. The Rockwell C tests classify the adhesion of the systems as acceptable (HF3 type), regardless of the layer thicknesses. While in the scratch tests, the behavior of the coefficient of friction increased from 0.2 to 0.6 as the indenter penetrates and the damage mechanisms identified were hertzian cracks, chipping, and spallation. After, the multi-pass scratch test was employed to evaluate wear behavior at subcritical loads (40 and 50% of chipping critical load) applying 100 cycles. According to the results, the friction coefficient was not affected by the titanium boride thicknesses, but the wear rate reached its maximum reduction at 20 h of boriding with 3,7 x$10^{-3}$$mm^3$/N*m.

MC-ThP-19 Effect of MoS_2 Additive on Corrosion and Tribocorrosion Property of Plasma Electrolytic Oxidation Coating on Titanium*, N. Zheng,*

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Plasma electrolytic oxidation (PEO) technology as a novel and attractive surface engineering process has been widely used for preparation of functional oxide coatings on light alloys such as aluminum, magnesium, zirconium, and titanium. In this study, we fabricated the MoS_2 decorated composite oxide layers on pure titanium by using PEO treatment under pulsed DC power with unipolar mode in alkaline phosphate- and aluminate-based solutions with 0~3 g/L MoS_2 nanoparticle additions. The influence of MoS_2 nanoparticle addition on the microstructure, mechanical property, corrosion resistance and tribocorrosion behavior of PEO composite coating on pure titanium was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), field-emission electron probe microanalysis (FE-EPMA), surface profilometry (α-step), scratch adhesion testing, pin-on-disc wear testing and potentiodynamic polarization measurement in 3.5 wt% NaCl solution. The experimental results obtained from scratch adhesion testing and potentiodynamic polarization measurements show that PEO composite coating with 2.5 g/L MoS_2 nanoparticlesaddition exhibits optimal adhesion strength and corrosion resistance. Furthermore, the results of XRD and SEM-EDS indicate that regardless of the presence or absence of MoS_2 nanoparticle additives, the PEO composite coatings on pure titanium are primarily composed of aluminum titanate (Al_2TiO_5) and rutile-phase titanium dioxide (TiO_2). The FE-EPMA data reveal that MoS_2 particles are mainly well distributed at the interface between the PEO coating and pure titanium substrate.The tribocorrosion behavior of MoS_2 nanoparticle decorated PEO composite coatings was carried out by potentiodynamic polarization measurement in 3.5 wt% NaCl solution under wear mode. As similar to static potentiodynamic polarization measurement, the PEO composite coating with 2.5 g/L MoS_2 nanoparticles addition also displays optimal tribocorrosion resistance in this study. In summary, the adhesion strength, wear resistance and corrosion/tribocorrosion resistance of Al_2TiO_5–rutile TiO_2 composite coating on pure titanium can be improved by increasing MoS_2 nanoparticles addition. The optimal concentration of MoS_2 additive is 2.5 g/L.

MC-ThP-20 An Improved Statistical Nanoindentation Methodology*,*

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The principle of statistical nanoindentation proposed ca. 2006 is based on performing a relatively large number (many hundreds/few thousands) of single indentation tests in a grid and analyzing the indentation elastic modulus and hardness with statistical methods. Many authors have claimed that this method can be used to study composite materials, showing that mechanical properties, number, and volume of the different composite phases could eventually be deduced and predicted by only using the nanoindentation technique.

In this presentation, we first review the previous work done in statistical nanoindentation by different researchers, highlighting the main problems that have been encountered and possible proposed solutions. In the second part, we study and report the statistical nanoindentation of three composite model samples, in the form of a soft Al2124 matrix embedded with hard SiC particles. We propose a novel heuristic wavelet technique to filter the measurement noise from the raw nanoindentation data as an attempt to obtain a more robust statistical nanoindentation methodology. Furthermore, a Finite Elements modeling will be used to analyze the response of the nanoindenter regarding the position of the hard particles. Our modeling will show many mistakes made by authors in previous publications. Finally, we will introduce results on bearing steels. Hardness histograms generated by Statistical Nanoindentation will demonstrate unique characteristics (fingerprints) for the different analyzed steels.

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MC-ThP-21 Adhesive Strength and Diffusion Model for Borided Ti6Al4V Alloy*, A. MENESES AMADOR, G. RODRIGUEZ CASTRO,*

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In this work, the Ti6Al4V alloy was hardened by powder-pack boriding process at temperatures from 1000 to 1100 °C for 10, 15 and 20 h. The boride layers formed on the Ti6Al4V alloy were examined by scanning electron microscopy and X-ray diffraction, while their mechanical behavior was evaluated by Berkovich nanoindentation and Hertzian contact. The growth kinetics of the boride layer formed on Ti6AL4V alloy was investigated based on the boron activation energy. The boride layer consisted of an outer TiB_2 layer and a TiB whiskers sub-layer. A diffusion model was proposed to estimate the boron activation energies in the TiB_2 and TiB layers, where values of 91.2 and 146.5 kJ mol^{-1} were obtained considering the experimental data of the thicknesses of the boride layers. Young's modulus and hardness were at the range of 350-400 GPa and 20-25 GPa for TiB and TiB_2 phases, respectively. The sample with the thinnest layer thickness showed the highest adhesive strength under Hertzian contact. Finally, finite element method was used to obtain the stress field in the layer-substrate system caused by the contact loads.

MC-ThP-22 Influence of Ti Content on the Tribological Behavior of Ti:MoS_2 Coatings Under Reciprocating Electrified Contact Conditions*,*

***N.K. Fukumasu (newton.fukumasu@usp.br)**, M. Danelon, A. Tschiptschin, I. Machado, R. Souza,* University of São Paulo, Brazil

The possibility of improving the durability and efficiency of heavy-loaded mechanical transmission systems by controlling external parameters is paramount in next-generation automotive powertrain and energy generation systems. Using electric current to control surface chemistry during the relative motion between two surfaces could allow electrified contacts to present reduced friction and wear, reducing energy consumption and enhancing overall system performance. The use of coatings with advanced 2D materials, such as molybdenum disulfide, may promote excellent solid lubrication under high contact stresses and pure sliding conditions. In this work, MoS_2coatings were deposited using pulsed D.C. magnetron sputtering technique with MoS_2 (purity of 99.99%) and Ti (purity of 99.9%) targets, in which changes in the power applied to the Ti target allowed the variation of the final Ti doping concentration at Ti:MoS_2 composite coatings. Reciprocating electrified tribological tests were carried out with the ball-on-plane configuration. Three electrified conditions (non-electrified, ball as cathode and ball as anode) and five Ti doping concentrations were tested. In all cases, uncoated AISI 52100 balls were pressed with a 10 N normal load against Ti:MoS_2 coated glass substrates. Tangential ball velocity was set at 3 mm/s with 4 mm stroke movement distance. Results indicated that electrification of the contact induced lower COF than the non-electrified conditions, for coatings with lower Ti concentration. Raman Spectroscopy of inner regions of the wear tracks indicated the presence of crystalline MoS_2 compared to as-deposited coatings. Coherence correlation interferometry analyses of wear tracks indicated wider tracks for the cases in which the ball was set as the cathode of the system. Also, under this condition, optical and scanning electron microscopy results showed high coating damage for all tested Ti concentrations. Results suggest that electrical potential polarity may promote selective desorption of coating ions that change surface chemistry, influencing the formation and composition of tribofilms that develop during the sliding motion and the friction and wear behavior of the tribosystem.

Coatings for Biomedical and Healthcare Applications
Room Golden State Ballroom - Session MD-ThP

Coatings for Biomedical and Healthcare Applications (Symposium MD) Poster Session

MD-ThP-1 Investigation of Silver/Copper Diffusions in the Matrix of Amorphous Carbon Thin Films Produced by Magnetron Sputtering, ***Hailin Sun (hailin.sun@teercoatings.co.uk)**,* Teer Coatings Ltd, UK

The environment inside a spacecraft is ideal not only for the members of the crew onboard, but also for bacteria and fungi to grow. The proliferation of harmful microorganisms can become a hazard for the human crew as well as for the safe running of equipment. In our previous work, we used magnetron sputtering to develop amorphous carbon coatings doped with silver and copper for antimicrobial application in space stations, and the benefits of the bactericidal properties added by silver- and copper-doping were shown under both terrestrial gravity and micro-gravity conditions [1]. In addition, these thin films are scratch-resistant and wear-resistant with high hardness, providing a long lifetime which is critical for the applications in a space station.

The prepared Ag- and Cu-doped amorphous carbon coatings showed a slow diffusion of Ag from the carbon matrix to the surface, eventually replenishing the Ag at the surface lost due to daily wear and tear. Such diffusion process is a key factor in the coating performance: if too fast, the antimicrobial lifetime of the coating would be shorter, if too slow the bactericidal efficiency of the coating would be affected. Therefore, it becomes apparent and critical to identify the key factors that influence the Ag diffusion rate in a carbon matrix, and also to understand how they influence it.

In this work we report the latest study on Ag and Cu diffusion in Ag- and Ag/Cu-doped amorphous carbon coatings. Samples with the same concentration of Ag and different concentrations of Cu have been prepared and annealed in oven at 100 ^{0}C, 150 ^{0}C and 200 ^{0}C to speed up the diffusion process of the metals. With the combination of RBS (Rutherford Backscattering Spectrometry) and ToF-ERD (time of flight elastic recoil detection) the elemental depth profile is accurately measured, which is supported by XPS data to investigate the chemical state of the species at the surface. Preliminary results have shown that higher temperature causes a higher diffusion rate, and the addition of copper has slowed down the diffusion rate of silver, which is confirmed also by cross-section SEM images. Interestingly, XPS data show how Ag retains always its metal state and does not oxidize, while Cu bonds with carbon, oxygen and hydrogen to form more complex molecules such as Cu(II) carbonate dihydroxide.

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MD-ThP-2 Enhanced Biomedical Implant Surfaces: Stainless Steel Modification Through Hipims-Coated Titanium and Peo Treatment, ***Bruno Pereira (brnlp7@gmail.com)**,* Pontifícia Universidade Católica do Paraná, Luxembourg*; L. Fontana,* Universidade do Estado de Santa Catarina, Brazil*; C. Lepienski,* Universidade Federal do Paraná, Brazil*; P. Soares,* Pontifícia Universidade Católica do Paraná, Brazil

The main causes of failures in implantable devices are often attributed to bone reabsorption, due to a mismatch in elastic modulus at the implant-bone interface, as well as and bacterial infections. Plasma electrolytic oxidation (PEO) is a versatile surface modification technique for metals, such as Titanium (Ti), and is capable of producing coatings that exhibit a reduced elastic modulus. Moreover, this method can incorporate bactericidal elements, such as Copper (Cu), achieving a durable antibacterial effect. However, PEO is not directly applicable to stainless steel, which is frequently employed as biomaterial. In this study, austenitic stainless steel was coated with titanium using High Power Impulse Magnetron Sputtering (HiPIMS). The Ti-coated steel (SS-Ti) was subsequently subjected to the PEO process to improve the surface properties essential for implantable devices. The PEO process involved an electrolyte mixture of calcium acetate, calcium glycerophosphate, and copper sulphate. Post-PEO surfaces were examined by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Crystalline structures were characterized using X-ray diffraction (XRD), while the thickness of the layers was measured through cross-sectional analysis. Nanoindentation tests were employed to measure the hardness (H) and elastic modulus (E) of the layer, while nano-scratch tests were performed to evaluate the layer adhesion. The resulting coating presented a homogeneous, porous oxide structure containing calcium (Ca), phosphorus (P), sulphur (S), copper (Cu), and crystalline anatase (TiO2). The modified oxide layer was approximately 4 µm thick. Nanoindentation tests indicated a considerable reduction in the elastic modulus (~50%) compared to SS, while the scratch tests showed strong adhesion of the Ti+oxide layer to the SS substrate, with no exposure of the SS substrate in the scratched regions. The resulting coating, due its properties, displayed potential for use in biomedical applications.

MD-ThP-3 Nanospectroscopy and Nanochemical Imaging Using Photothermal AFM-IR on Biomolecular Sensors and Hydrated Self-Assembled-Monolayers, ***Nafiseh Samiseresht (nasajobjo@gmail.com)**,* MPI für Eisenforschung GMBH, Germany*; G. Figueroa-Miranda, D. Mayer,* Forschungszentrum Juelich GmbH, Germany*; M. Rabe,* MPI für Eisenforschung GMBH, Germany

Nanostructured self-assembled-monolayers (SAMs) on solids are common platforms for functionalizing and controlling chemical and physical properties of surfaces with applications in diverse fields such as corrosion, catalysis and bio-sensors. Here Resonance enhanced AFM-IR is used to obtain nanoscale topographic information and spectroscopic, i.e. chemical information on such systems [1], in order to better understand the interplay between nanostructure and function. A tunable pulsed quantum cascade including four chips and a fast optical parametric lasers provides the IR source in the ranges of 910-1900 cm^{-1} and 2700-3900 cm^{-1}. Using a gold coated silicon cantilever on gold substrate provided high sensitivity to detect monolayer and single molecule.

First, results on aptamer SAMs on gold used as SARS-CoV-2 biosensors will be presented. Tapping mode AFM-IR was employed to characterize the surface after each fabrication step and after analyte binding to the receptor layer to provide insight to molecular conformational and structural variation as well as chemical composition of this system. Binding of single molecule proteins was detected.

Second, biomolecule-repellent oligoethylene glycol (OEG)-based SAMs on gold were studied. In such systems the molecular conformation of OEG and the structure of interfacial water are thought to strongly influence the repellent character [3]. Tapping mode AFM-IR investigation of water films adsorbed on nano-domains of OEG SAMs were performed under elevated relative humidity and provided structural details of the OEG moieties and adsorbed H_2O.

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MD-ThP-4 Development of Hierarchical Surfaces Coated with Zinc Nanoparticle-Doped Polycaprolactone on 316LVM Stainless Steel Substrate for Biomedical Applications, ***Tarciana Dieb Toscano (tarcianadieb@gmail.com)**,* Pontifícia Universidade Católica do Paraná (PUCPR), Brazil*; A. Bhattacharjee,* Colorado State University, USA*; K. C. Popat,* George Mason University, USA*; P. Soares,* Pontifícia Universidade Católica do Paraná (PUCPR), Brazil

The use of 316LVM stainless steel in medical implants, while advantageous due to its mechanical strength and biocompatibility, poses a significant challenge in the form of bacterial infections. These infections occur when bacteria adhere to the implant surface, forming biofilms that are resistant to antibiotics and immune responses. This can lead to persistent infections, causing complications such as implant failure, the need for surgical revision, and prolonged patient suffering. It is known that nanostructured and biomimetically textured surfaces have demonstrated superiority over smooth surfaces in bacterial inactivation and reduction of bacterial adhesion. Bacterial inactivation through surface morphology can occur through a physical-mechanical mechanism. By integrating bactericidal elements into these nanostructured surfaces, it is possible to create a route for physical-mechanical and chemical inactivation. Thus, the surface of 316LVM steel was modified using the cathodic plasma electrolytic oxidation process, followed by acid etching to promote surface nanostructuring. This nanostructured surface was subsequently coated with polycaprolactone doped with zinc oxide nanoparticles (nP-ZnO/PCL). The objective of this study is to evaluate the morphological, topographical, and chemical properties, along with the wettability and electrochemical response of the textured surfaces. Additionally, the effect of surface texturing on the adhesion of the nP-ZnO/PCL coating was investigated. The bactericidal effect of the nanotextured and nP-ZnO/PCL-coated surfaces was also assessed using Staphylococcus aureus bacteria. For this purpose, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), contact angle measurements using a sessile drop goniometer, and evaluation of the electrochemical response through potentiodynamic polarization tests were employed. Coating adhesion to the substrate was assessed through scratch tests. The bactericidal effect was evaluated using colorimetric assays and live/dead bacterial quantification. The results showed that the application of cathodic plasma electrolytic processes in conjunction with acid treatment successfully induced surface nanostructuring. There was an improvement in corrosion resistance properties and an increase in surface contact angle for the textured and coated samples, along with a significant reduction in bacterial adhesion. It was also observed that the zinc oxide-doped polymeric coating exhibited better adhesion on textured surfaces compared to polished material.

MD-ThP-5 Catastrophic Corrosion in Metal Guitar Strings with or Without DLC Films Using Artificial Sweat*, C. Andrés Velásquez Andrade,* Universidade do Vale do Paraiba, Brazil*; N. Pereira Alves Granado,* IGTPAN, Brazil*; **Lucia Vieira (lvs.lucia@gmail.com)**,* Universidade do Vale do Paraíba - Univap, Brazil

Diamond-like carbon (DLC) film was deposited on electric guitar strings to evaluate corrosion under the impact of artificial sweat at a constant temperature of 37 degrees Celsius. The objective was to assess the effect of corrosion on the change in string mass over time and the string tonality variation. The process involves the application of a DLC by plasma-enhanced chemical vapor deposition (PECVD), recognized for its corrosion-resistant film. The strings' mass changes due to exposure to artificial sweat were measured over 240 hours, focusing on mass variation to obtain information on the strings' durability and corrosion resistance. The results show that all strings suffered corrosion, and the tonality (frequency variation of the notes) varied due to the film of the strings. The results can help design electric guitar strings with better tonal qualities and corrosion resistance. Understanding how external elements such as sweat affect the integrity of the DLC film contributes to the sound quality and longevity of the strings.

Keywords: (mass variation; Corrosion; artificial sweat; nickel plated steel; Raman; guitar strings; DLC; PECVD)

Plasma and Vapor Deposition Processes
Room Golden State Ballroom - Session PP-ThP
Plasma and Vapor Deposition Processes (Symposium PP) Poster Session

PP-ThP-2 Modeling and Synthesis of Long Scale Coherence Time Vacancy Defects in Silicon Carbide via Pulsed Uv Laser and Photonic Curing for Industrial Scale Qubit Manufacturing*, N. Khatoon, S. Khalili, **Douglas Chrisey (douglasbchrisey@gmail.com)**,* Tulane University, USA

Qubits have unique capability to exhibit superposition and entanglement which makes them stand out to exist in multiples states simultaneously with ability to perform parallel computations. Serving as a fundamental building block of Quantum computers (QC) which leverages the superposition and entanglement of Qubits to perform quantum parallel operations at exponential speed. The applications of QC include cryptography, solving optimization problems, materials science, drug discovery and materials science. IBM Quantum System One is the first QC powered by 127-Qubits reported by RPI of Troy, NY. The unmatching wonders of Qubits comes with certain challenges to make and build QC such as their susceptibility to environmental noise and decohering, and difficulty in their fabrication and scalability. In this work we utilized pulsed UV laser and a broad spectrum (220-1500 nm) intense and short (0.03–100 ms) pulsed light (called photonic curing) to create and anneal the vacancy defects in silicon carbide (SiC) respectively. The study of vacancy formation will help to explore the mechanism of defect formation after laser irradiation as well as the mechanism of the subsequent photonic annealing of residual damage. The combination of these processes will give us an extensive combinatorial library of data to be used to train a deep learning neural network algorithm to predict the best possible Qubit defect architectures, processing conditions, and their expected performance. Excimer lasers like ArF (10 nsec, 193 nm) are efficient in creating color centers with 6.42 eV photons and can even etch SiC at a high enough laser fluence, < 2 J/cm^2. We propose to use an ArF excimer laser or a quintupled YAG (266 nm) and to optimize the conditions for different defect constructs and test their efficacy as defect-based Qubits.The as created defects will then be selectively annealed using photonic curing, which initiates rapid transformations, and reactions due to non-equilibrium processes. The acquired dataset will serve as the foundation for crafting a machine learning algorithm. This algorithm will be trained using innovative open-ended material selections to ensure statistically reliable predictions for future Qubit outcomes, with accuracy that can be empirically verified. Combination of Pulsed UV laser and photonic curing offers an instantaneous and roll-to-roll compatible approach for large-scale synthesis of Qubits.

PP-ThP-4 Recirculating Atmospheric Inductively Coupled Plasma (Icp) Beam Systems for Conversion of Si Sawdust in Si Nanoanode*, **Michael ryaboy (miryboy@gmail.com)**,* UC Berkeley, USA

Policies encouraging the reuse of waste products are becoming increasingly popular so as to avoid the negative impact on the environment and human health. Nowadays, silicon ingots are into strips a few hundreds of microns thick (wafers) that are the base of solar cells. Inefficiently, ca. 45–55% of such costly Si is lost simply as sawdust in the cutting process. Doping by the boron and phosphorus of Si wafers inevitably makes waste very toxic. The amount of waste produced by industry is increasing all the time, while the Earth's capacity to decompose these residues is declining. Idea to convert this waste into the cheap raw material for another fossil-less source of energy like Li-ion battery, especially their important electrode like Si anodes looks very attractive as the WIN-WIN solution both for environmental and clean energy.
The conventional thermal recycling process that involves the one-passed high-temperature treatment requests a lot of energy. Therefore, our method of recirculation through the multi-pass penetration of the high-temperature area of the swirling plasma stream for incremental downsizing is more rational.

The first objective of this proposal is to develop a method of recycling of Si waste in the high-temperature in the plasma loop using the multi-step plasma-thermal plasma recirculation process. Such recycling involves three stages. The first stage consists of in the conversion of the Si sawdust into the Si melted droplets in thermal plasma flowing in a non-oxidant environment; the second stage consisted in the superficial incremental vaporization of the shells of the melted droplets; the third stage consisted in collecting the downsized Si nanoparticles on the current collector to manufacture the Si anode, simultaneously preventing its oxidizing during the whole process operation.

PP-ThP-5 Recyclable Thin Coatings Deposited by Means of Plasma-Assisted Techniques on Polymer Foils for Food Packaging Applications*, **Francisco A. Delfin (Francisco.Delfin@fh-wels.at)**, C. Forsich, M. Schachinger, S. Augl,* University of Applied Sciences Upper Austria*; S. Brühl,* National University of Technology, Regional Faculty of Concepción del Uruguay (UTN – FRCU), Argentina*; C. Burgstaller, D. Heim,* University of Applied Sciences Upper Austria

The prevalent pollutant in our lands and oceans today is plastic litter. Emphasizing waste recycling is crucial to counter this environmentally harmful issue. Nonetheless, the recycling process faces challenges when items such as food packaging consist of multiple layers of diverse polymers co-extruded together to ensure adequate barrier properties. A solution to this problem lies in applying thin coatings using plasma-assisted techniques on single-layer polymer foils, which can provide similar resistance to water and oxygen permeation. Considering the nanometric thickness of these coatings, it is feasible to recycle them without significant problems.

In this study, thin coatings deposited on polymer foils using two plasma-assisted techniques are compared: Plasma-Assisted Chemical Vapor Deposition (PA-CVD), employing a bipolar DC pulsed discharge, and Magnetron Sputtering Physical Vapor Deposition (MS-PVD). Carbon and silicon-based coatings were obtained with PA-CVD using acetylene C_2H_2 and hexamethyldisiloxane (HMDSO) as precursors, respectively. MS-PVD was used to deposit carbon, silicon, and aluminium coatings. Polypropylene (PP), Low Density Polyethylene (LDPE) and Polyethylene Terephthalate (PET) with a thickness of approximately 20 µm were used as substrate. The effect of coating thickness (directly correlated to deposition time) and chemical composition on the barrier properties was examined. Characterization included Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Surface Free Energy (SFE), Water Vapor Transmission Rate (WVTR) and Oxygen Transmission Rate (OTR).

The FTIR spectra of the Si-coated films exhibited a characteristic band at around 1075 cm^{-1}, corresponding to the asymmetric stretching vibrations of Si–O–Si. Carbon based coatings displayed a broad band at around 1600 cm^{-1} related to C=C bonding vibrations. Raman spectra of carbon coatings showed the typical D and G bands which are characteristic of amorphous carbon. SFE was about 45 mN/m for carbon- and about 20 mN/m for silicon-based coatings, while that of the untreated polymers is in average 30 mN/m. SEM cross-sections allowed for an estimation of coating thickness between 50 and 150 nm, which is considered to be neglected in conventional recycling processes. Depending on thickness and chemical composition, barrier properties improved by 20 to 50%, with Al-PVD coating showing the best performance with an improvement of up to 10 times.

PP-ThP-6 Design and Manufacturing of Low-Cost Atomic Layer Deposition System to obtain Semiconductor and Dielectric Thin Films*, J. Navarro-Rodríguez, F. Mateos-Anzaldo,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico*; **Jesús Román Martínez-Castelo (jesus.roman.martinez.castelo@uabc.edu.mx)**,* Facultad de Ingeniería, Mexicali-Universidad Autónoma de Baja California, Mexico*; A. Pérez-Sánchez, J. Ruiz-Ochoa,* Facultad de Ciencias de la Ingeniería y Tecnología, Valle de las Palmas-Universidad Autónoma de Baja California, Mexico*; A. Gaytán-Pérez,* Facultad de Ciencias de la Ingeniería y Tecnología-Valle de las Palmas-Universidad Autónoma de Baja California, Mexico*; H. Tiznado-Vázquez,* Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México*; N. Nedev,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico

This work describes the design and manufacturing of a lab-made ALD system. In the system, the chamber reactor was designed using SolidWorks software and machined with a lathe. The chamber is of aluminum and has an internal diameter of 3.5 inches, with two entries for precursors with a diameter of 1/64 inch, and one exit with a diameter of 1/2 inch. To dose the precursor and the oxidant, two 3-way diaphragm valves were used. This type of valves allow a continuous flow of nitrogen as carrier gas and permit formation of high- and low-pressure zones, which allow a high-speed deposit. To heat the system, a flat circular resistance controlled by a PID was used. The control of all the system is carried out using a graphical interface of LabView.

PP-ThP-7 Neon Addition to the Plasma for Enhanced Ionization in the Deposition of Cr films by HiPIMS-DOMS*, **João Carlos Oliveira (joao.oliveira@dem.uc.pt)**,* University of Coimbra, Portugal*; S. Adebayo,* University of Coimbra, Nigeria*; R. Serra,* University of Coimbra, Portugal

In magnetron sputtering-based deposition processes, particles that arrive at oblique angles relative to the growing film's surface promote the atomic shadowing effect which, ultimately, results in porous and underdense columnar microstructures. Energetic particles bombardment helps to prevent this effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and/or triggering re-deposition processes. However, bombarding the film's surface with highly energetic particles comes with a heavy cost: the formation of a high density of defects, which disrupts the crystalline structure of the films, and the creation of compressive stresses.

In a previous work, the authors have shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material[1]. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment. The most straightforward route to achieve high ionization of the sputtered species in HiPIMS is to increase the peak power. However, this also increases the average energy of the sputtered species and brings about energetic bombardment. Partially replacing Ar by Ne in the process gas promotes an increased mean electron energy which increases plasma ionization, as the ionization energy of Ne (21.56 Ne) is significantly higher than that of Ar (15.75 eV). In this work, partial substitution of Ar by Ne in the DOMS process gas was investigated as a mean to increase the ionization degree of the sputtered species without increasing their average energy.

In this work, Cr thin films were deposited by DOMS in pure Ar and mixed Ar + Ne plasmas up to 60 % Ne. Adding Ne to the plasma resulted in 25 % increase in the ions saturation current density (ISCD) as measured by an electrostatic flat probe placed at the substrate location. All the deposited films have a dense and compact columnar microstructure with an almost complete [110] out of the plane preferential orientation. The lattice parameter of the Cr films increased with increasing Ne content in the plasma while their surface roughness decreased from 6 to 3 nm. The hardness and young's modulus of the Cr films were evaluated by nanoindentation.

PP-ThP-8 Study of Transitional Element Dopants on CeO_2 Thin Films for Resistance Random Access Memory Application*, A. Sun,* Department of Chemical Engineering and Materials Science, Yuan Ze University, Taiwan*; **Sea-Fue Wang (sfwang@mail.ntut.edu.tw)**,* Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei 106, Taiwan

In this study, an RF magnetron sputtering method was employed to fabricate a 60 nm CeO_2 film as the insulating layer for Resistive Random-Access Memory (RRAM). Platinum (Pt) layers, each 100 nm thick, were utilized as the upper and lower electrodes. To investigate the impact of doping elements on device characteristics, elements such as La, Nd, Sm, Gd, and Y were introduced into the insulating layer. The findings revealed that La doping resulted in the most stable operation with the lowest operating voltage. The device exhibited excellent non-volatile properties, achieving over 2000 switching cycles, and maintained data storage for more than 10^4 seconds.

X-ray Photoelectron Spectroscopy (XPS) analysis indicated that the metal elements in the doped film were bound with oxygen rather than existing in a pure metal state. Based on these results, it is hypothesized that the conductive path in the film is composed of oxygen vacancies. The controlled formation and breakage of conductive filaments by the input voltage allow the device to undergo high and low resistance state changes, showcasing its potential application in resistive memory technologies.

Furthermore, XPS analysis of bond energies suggested that doping weakened the interaction between Ce and O, making it easier for oxygen ions to migrate. This effect contributes to a reduction in the working voltage of the device.

PP-ThP-9 Mechanical Properties Thermal Stabilities of Multilayered AlCrBN/AlTiSiN Hard Coatings*, **Chung-En Chang (abcd0214milk@gmail.com)**, T. Tsai, H. Feng, M. Yang, Y. Chang,* National Formosa University, Taiwan

AlCrN and AlTiN coatings have been applied widely in cutting tools and mold dies because of good mechanical properties, tribological properties and oxidation resistance as resulting from the incorporation of Al into CrN and TiN. The AlCrN coating possesses good oxidation resistance even at 1000 °C while the AlTiN has high hardness at high temperature. To make further improvement of these two coatings, multilayer coatings with alternate AlTiN and AlCrN layers have been designed. In addition, it is known that adding Si and B to coatings can effectively enhance their mechanical properties. Through combining the characteristics of Si and B, multicomponent and multilayer AlCrBN/AlTiSiN coatings were prepared using an electro-magnetic controlled cathodic arc ion plating method, and their thermal stabilities at high temperature up to 900 °C and 1000 °C were studied to align with the requirements of high-temperature applications. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM) equipped with energy-dispersive X-ray spectroscopy (EDS). In this study, multilayered AlCrBN/AlTiSiN coatings were deposited using cathodic arc evaporation with periodic layering structures. Nanoindentation measurements and SEM/TEM observations revealed that when the samples were subjected to vacuum annealing at 900 ºC, the addition of Si and B not only suppressed the unfavorable formation of h-Cr_2N and w-AlN phases that would deteriorated mechanical properties, but also resulted in the phenomenon of increased coating hardness due to the formation of nanometer-sized c-TiN and c-AlN after the phase decomposition of the coating. In comparison, the hardness of AlCrN coatings decreased continuously with increasing temperature due to the absence of inhibiting h-Cr_2N formation. And, strengthening mechanisms from the phase decomposition was not observed in this AlCrN at high temperature. The AlCrBN/AlTiSiN coatings exhibited the capability to maintain or even enhance their mechanical properties at high temperature. In addition to the improved oxidation resistance, secondary hardening mechanism at high temperature could contribute to the successful application of such coatings in high-temperature environments.

PP-ThP-10 CVD Equipment: Yesterday, Today and Tomorrow, ***Anne Zhang* *(anne.zhang@ihi-bernex.com)***, *H. Strakov,* IHI Bernex AG, Switzerland

Bernex coating systems are used worldwide to produce coatings on metal / ceramic compounds for the purpose of reducing wear and/or friction, providing corrosion and oxidation protection,or obtainingother specific surface characteristics. The CVD coating processes are based on chemical reactions on hot surfaces between reactant gases, which directly yield the solid coating material. One of the advantages of CVD resides in the ability to coat a wide range of materials with complex shapes, even porous and hollow ones, and is also suitable for coating internal surfaces. Applications include industrial components, aerospace, cutting inserts, forming/molding/extrusion tools, etc.

Bernex coating systems cover various CVD technologies, including Chemical vapor aluminizing (CVA), Chemical vapor infiltration (CVI) and CVD with solid metalorganic precursors (MOCVD). These systems are highly modular and provide significant process flexibility. Based on customer requirements, the systems can be pre-configured upon purchase, or extended at any time. This not only includes hardware and software components, but also comprises external units and accessories.

Coatings developed by Bernex will be presented, along with new process modules and general improvements on hardware and software modules. An insight of future developmentswill also be provided.

PP-ThP-11 Target Erosion Simulation in Full 3D for Optimization of Target Utilization in Magnetron Sputtering, ***Kryštof Mrózek* *(mrozek@plasmasolve.com)***, *P. Zikán, A. Obrusník,* PlasmaSolve s.r.o., Czechia

Target utilization – fraction of target material sputtered over its lifetime - is one of the important factors in total cost of magnetron sputtering processes. One approach to increasing target utilization is movement of target surface, relative to magnetic field – for example rotation of cylindrical target. However, this approach is not always possible (e.g., for planar targets), or cost-efficient as it adds complexity and moving parts to the cathode design.

Another way of optimizing the target utilization is through the magnetic field. Electrons are trapped by the magnetic field, move above target, and ionize the gas. Created ions then impact the target surface and sputter its material. By changing the shape of the magnetic field, it might be possible to extend the ionization region, thus increasing the area of target impacted by ions (therefore eroded). However, it is very difficult, time-consuming, and expensive to do this optimization experimentally. Each magnetic field configuration has to be tested on separate cathode, the cathode has to be eroded for a long time in order for erosion grove to be visible, only several cathodes can be tested at a time (4-8, depending on the coater), and large part of the target material is wasted.

Reliable target erosion model solves all of the aforementioned issues. Presented model, developed by PlasmaSolve within the OPTIMISM project, predicts the shape of racetrack and profile of an erosion grove based on full 3D geometry of a cathode (cylindrical, planar), pressure, power level, and, most importantly, shape and strength of an arbitrary external magnetic field. The model is based on an iterative Monte Carlo algorithm. The computation takes from a few hours (for ca 50 cm cathodes) to about a day (for 4 m glass coater cathodes). Thanks to this, the model can serve as a fast prototyping tool for target erosion optimization studies in real geometries.

This contribution will present a brief overview of the model and its results for different cathode geometries, metallic and poisoned state of the target and different topologies of the magnetic field, with focus on the effect of the magnetic field on racetrack shape and target utilization.

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PP-ThP-12 Synthesis and Characterization TiAlZrTaNbN Coatings Obtained by High-power Impulse Magnetron Sputtering, *I. Gonzalez Avila, J. Gónzalez Lozano, O. Piamba Tulcan,* ***Jhon Jairo Olaya Florez* *(jjolaya@unal.edu.co)***, Departamento de Ingeniería Mecánica y Mecatrónica, Universidad Nacional de Colombia

TiAlZrTaNbN coatings were obtained by High-Power Impulse Magnetron Sputtering and deposited on superalloys and Ti alloy substrates. The effect of working pressure and bias voltage on hardness, corrosion and wear resistance was investigated and correlated with the microstructure of the samples. The microstructure, morphology and chemical composition of the coatings were analyzed by X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy. The sample porosity and corrosion resistance were studied by electrochemical methods. The mechanical properties were evaluated by means of nanoindentation, and the tribological properties was studied with pin-on-disk technique. The pulse power and current peak have been affected by working pressure which modified significantly the films properties. The relationship between growth conditions, microstructure, wear and corrosion resistance is presented and discussed in this work. Finally, the effect of substrate-coating system and the deposition parameters are highlighted in order to further enhance HiPIMS coatings properties.

PP-ThP-13 Residual Stress Analysis in 30 µm thick High-Speed PVD Coatings, *K. Bobzin,* surface Engineering Institute - RWTH Aachen University, Germany*; C. Kalscheuer,* ***Max Philip Moebius* *(moebius@iot.rwth-aachen.de)***, *P. Hassanzadegan Aghdam,* Surface Engineering Institute - RWTH Aachen University, Germany

Several studies focus on the impact of residual stress in coatings, predominantly synthesized by conventional physical vapor deposition (PVD) techniques like Arc PVD and Magnetron Sputtering (MS). High-Speed PVD (HS-PVD) is a PVD variant based on hollow cathode gas flow sputtering. It enables the deposition of thick PVD coatings s >20 µm in contrast to Arc or MS-PVD, where coating thickness is limited due to compressive residual stress. Therefore, the effect of the residual stress on coating and compound properties of several HS-PVD coatings was analyzed for the first time in this study.

The aim is to evaluate the influence of diverse substrate materials, different coating systems, and process parameters on the residual stress state in HS-PVD coatings. Herein different coatings systems like AlCrN and AlCrO, were deposited at different process parameters such as reactive gas flow, deposition time, and bias voltage. The residual stress of oxide coatings with s ≈ 30 µm, deposited on WC-CO and steel X40CrMoV5-1, was analyzed using X-ray diffraction (XRD) and the $\sin^2\psi$ method. For the nitride coatings, in addition to the XRD method, the residual stresses were measured by the focused ion beam-digital image correlation (FIB-DIC) ring-core method to investigate different measuring methods.

With increasing coating thickness, a reduced compressive residual stress is determined by both analysis methods. AlCrN and AlCrO coating systems show higher adhesion strength with increasing thickness. Moreover, AlCrO coatings deposited on WC–Co indicate higher residual stresses than coatings deposited on steel substrate.

Using HS-PVD, the deposition of thicker coatings with simultaneously higher adhesion strength is possible, which is typically a limitation of Arc and MS-PVD. Additionally, lower residual compressive stresses are unexpectedly observed at higher coating thickness. This indicates an outstanding research demand to investigate, how an increased coating thickness in HS-PVD leads to reduced residual stresses.

PP-ThP-14 Corrosion and Tribocorrosion Behavior of DlC/CNx/CrC/Cr Multilayers Deposited by Hipims in Synthetic Seawater, ***Martin Flores* *(martin.fmartinez@academicos.udg.mx)***, *L. Flores, L. López,* Universidad de Guadalajara, Mexico*; A. González,* Unversidad Autónoma de Tamaulipas, Mexico

Diamond-like carbon (DLC), CNx and CrC coatings have a wide range of potential applications to reduce the sliding friction and improve wear and corrosion resistance of bearings and other components. AISI 4317 steel is used in bearings of crane grabs for the transport of minerals with sulfur and fluor content in port facilities. These steels suffer from tribocorrosion and corrosion promoted by chloride ions at the port and the ions from the minerals. The multilayers were deposited by High Power Impulse Magnetron Sputtering (HIPIMS). The ion etching using Ar ions cleans the substrate and the metal ion etching (Ar^+ and Cr^+) promotes a good adhesion of the film. In this work the metal ion etching was performed with a delay in the synchronized polarization pulse of the substrate with respect to the applied to the Cr target, the ion energy distribution function was studied for each plasma used to deposit the multilayers. This work reports the results of the potentiodynamic polarizations to evaluate the corrosion and the measurements of open circuit potential during the tribocorrosión tests. Synthetic seawater was used as electrolyte. The structure of Cr and CrC layers was studied by XRD. Raman spectroscopy was used to study the sp2 and sp3 bonds of DLC and CNx. The results show an improvement in the corrosion and tribocorrosion resistance of the samples coated with the multilayer.

PP-ThP-15 Stable Hybrid HiPIMS/RF Sputtering Process on a Single Magnetron for arc-free Deposition of Compact Oxide Films, *A. Fromm,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; **Caroline Adam (c.adam@physik.uni-kiel.de)**,* Fraunhofer Institute for Mechanics of Materials IWM, MELEC GmbH, Kiel University, Germany*; F. Meyer,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; G. Mark, J. Löffler,* MELEC GmbH, Germany*; M. Thomas, M. Wirth, F. Burmeister,* Fraunhofer Institute for Mechanics of Materials IWM, Germany

Thin, insulating coatings are required for electronics, sensors and medical technology. Most of them are deposited by reactive magnetron sputtering and involve an RF or MF excitation of the plasma (radio/mid frequency). However, this often results in sub-stoichiometric layers with process-induced, but undesired residual porosity. With HiPIMS (high power impulse magnetron sputtering), significant advantages over conventional sputtering processes can be achieved, such as the production of coatings with high adhesion and almost bulk density. However, the deposition rates are lower when compared to an RF or MF process with the same average power. In addition, process stabilization is not trivial due to high peak currents and short pulse durations. Instabilities are induced by arcing between insulating areas on the target, leading to droplet formation, which significantly reduces the achievable film quality [2]. To overcome these difficulties, we have for the first time investigated the combination of an RF and HiPIMS excitation in a single magnetron.

Therefore, a HiPIMS generator from Melec company was combined with a RF-Generator and connected to a single magnetron. To avoid back reflections, a special RF-Filter was used.Al_2O_3 layers were deposited in a hybrid RF/HiPIMS process using a metallic Al target and O_2 as reactive gas, with variations in power and pulse parameters.

A stable reactive hybrid RF/HiPIMS process on a single magnetron, with higher process stability when compared to a simple HiPIMS process, has been demonstrated for the deposition of Al_2O_3 layers. The number of arcing events could be significantly reduced. A higher deposition rate with higher nano hardness of the deposited coatings could be achieved [5].

A proof of principle for a combination of RF and HiPIMS excitation in one source has been established and opens up a new route for the arc-free deposition of Al_2O_3 and other oxidic layers. Further investigations will include the influence and optimization of pulse parameters as well as the relationship of average HiPIMS and RF power. For a pulsed superposition of RF and HiPIMS, further developments of ultrafast impedance matching techniques are also necessary.

[1] Surf Coat Tech 122.2-3 (1999), p. 290–293.

[2] Surf Coat Tech 257 (2014), p. 308–325

[3] Surf Coat Tech 250 (2014), p. 32–36.

[4] J of Vac Sc & Tech A 30.6 (2012), p. 061504.

[5] C. Adam "Untersuchungen zur plasmagestützten Abscheidung von Al2O3-Schichten im reaktiven hybriden MF/HF-HiPIMS-Sputterprozess", Thesis Freiburg 2023.

Topical Symposium on Sustainable Surface Engineering
Room Golden State Ballroom - Session TS1-ThP

Coatings for Batteries and Hydrogen Applications - TS1 Poster Session

TS1-ThP-1 Formulating Advanced Materials for Energy Storage using Composite Solid- State Electrolyte Incorporating Al-Doped LLZO (Al-LLZO) in NCM811 for Solid State Lithium- Metal Batteries, *C. Yang,* Ming Chi University of Technology, Taiwan*; **Adere Tarekegne Habte (aderetarekegn@gmail.com)**,* Ming Chi University of Technology, Ethiopia

The development of advanced materials for energy storage devices has been of utmost importance for the transition towards clean and renewable sources of energy. In this context, solid-state lithium metal batteries have shown promising features such as high energy density, good ionic conductivity, and safer performance than conventional batteries. The primary aim of this research work is to develop a free-standing composite solid-state electrolyte (CSE) that incorporates Al-doped Lithium Lanthanum Zirconium Oxide (LLZO) into NCM811 for solid-state lithium-metal batteries followed by solution casting method. The researcher used various characterization techniques such as XRD, FT-IR, EIS, and SEM to analyze the structural and morphological properties as well as the impedance of the solid-state composite electrolyte. This material gives 4.9 x 10^{-4} Scm^{-1}ionic conductivity at room temperature. The NCM811/CSEs/Li exhibited after 100 cycles a specific capacity of 125.35 mAhg-1 and^{-1}and a capacity retention of 99.08 % at ambient temperature and with the rate of0.2C.

TS1-ThP-2 Corrosion Stability and Electrical Conductivity of PVD Coated Electrolyzer Bipolar Plates, ***Martin Welters (welters@kcs-europe.com)**,* KCS Europe GmbH, Germany*; N. Kruppe,* Schaeffler Technologies AG & Co. KG, Germany*; R. Cremer,* KCS Europe GmbH, Germany*; M. Öte, N. Bagcivan,* Schaeffler Technologies AG & Co. KG, Germany

Bipolar plates (BPP) are one of the essential components of electrolyzer stacks for the generation of pure hydrogen by water electrolysis. In order to replace conventional and expensive titanium based BPP, stainless steel becomes more and more important against the background of increasing production volume due to cost and functional reasons. On the other hand, some requirements exist, which limit the use of stainless steel BPP in electrolyzers. Firstly, due to harsh corrosive conditions, the application of the stainless steel BPP requires the protection against corrosion. Secondly, the electrical conductivity of BPP must remain constantly low over the entire service life.

As part of the H2Giga StacIE joint project, KCS Europe developed titanium-based PVD protection layers for stainless steel BPP in order to fulfill the demanding requirements of water electrolysis. In addition to the functional suitability of the coatings, the economic viability and suitability for large-scale production was kept in mind. Therefore, the coatings were deposited by means of a tailored inline coating system, applying PVD technology. The coating system enables an easy scale up to larger production quantities in future. Measurement of Interfacial Contact Resistance at 10 bar and Linear Sweep Voltammetrie of the coatings revealed promising results regarding corrosion stability and electrical conductivity prior and after electrochemical cell tests on laboratory scale adapting electrolyzer cell conditions.

TS1-ThP-3 PVD Core-Shell-Catalysts for Water Electrolysis, ***Jan-Ole Achenbach (achenbach@kcs-europe.com)**,* KCS Europe GmbH, Germany*; M. Berger,* Institute of Technical and Macromolecular Chemistry, Germany*; M. Pilaski,* The Hydrogen and Fuel Cell Center - ZBT, Germany*; R. Cremer,* KCS Europe GmbH, Germany

The expected increasing demand of hydrogen in the upcoming years requires adequate electrolysis capacities in order to be able to serve the market. One technology for mass production of hydrogen is the alkaline polymer membrane water electrolysis (AEM-WE). Heart of AEM-WE are the catalysts, which enable the decomposition of water at low energy input. Therefore, the availability of sufficient and suitable catalysts is a limiting factor for high H_2 production volumes.

Within the research project H2Giga AlFaKat, KCS Europe follows up the approach of replacing the usual expensive catalysts containing precious metals by cheaper core-shell particles. Therefore, particles of a suitable low-cost material are activated by the deposition of a more expensive catalyst material by means of physical vapor deposition (PVD). For the realization, a coating demonstrator was developed and validated in the project. Thereby, the basic suitability, the efficiency and useability for mass production of the concept as well as the coating growth, homogeneity and properties were investigated. Analyses of the core-shell-particles showed a homogeneous coating of the core particles after processing by PVD coating demonstrator. Further investigations regarding catalytic activity revealed high activity of new PVD catalyst. In this context, a comparison confirmed similar activity of PVD core-shell-catalyst and pure catalyst. Thereby, only the top layer of the core-shell-catalyst is active, meaning the same performance at significantly less material input. The results prove, that a reduction of catalyst material by Core-Shell-concept is possible.

TS1-ThP-4 Production of Cost-Effective Precious Metal Free Bipolar Plates for Future High Demand, ***Sijia Yang (yang@kcs-europe.de)**,* KCS Europe GmbH, Germany*; J. Kapp, V. Lukassek,* The hydrogen and fuel cell center ZBT GmbH, Germany*; R. Cremer,* KCS Europe GmbH, Germany

Objective of the R&D project "BipolarPilot" was the economic mass production of bipolar plates, which form the heart of fuel cells and represent around 30% of the total system costs. Together with its research partner The hydrogen and fuel cell center ZBT GmbH, KCS Europe has both developed appropriate PVD coatings as well as an inline PVD pilot coating system in order to enable mass production of cheap and corrosion stable stainless steel Bipolar plates.

While batch coaters are coating units with only one cycle-time limiting coating chamber, inline systems are coating units that enable a continuous processing and coating with short cycle times. Thus, the pilot coating unit has been designed with a future high demand for bipolar plates in mind.

KCS Europe's coatings for bipolar plates have been tested based on DoE specifications. The deposited coatings were investigated in detail by ZBT. Both, the electrical properties and the corrosion behavior under application conditions were investigated. KCS Europe's coatings for bipolar plates are homogenous precious metal free coatings. Investigations at ZBT proved, that the coatings beat the various limitations given by the DOE (Department of Energy) of the United States to meet the stack conditions. The contact resistance of all investigated coatings was determined below 0.6 mΩcm^2 and thus well below the DOE limit of 10 mΩcm^2. Moreover, the corrosion current identified by polarization test of all coatings meet the target values for bipolar plates defined by the DOE (lower than 1 µA/cm^2).

TS1-ThP-5 Hydrogen Diffusion in Protective Coating Materials*, P. Rückeshäuser, A. Bahr, W. Zhao, R. Hahn, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; T. Stelzig, F. Rovere,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; **Helmut Riedl (helmut.riedl@tuwien.ac.at)**,* Institute of Materials Science and Technology, TU Wien, Austria

Introducing hydrogen-based energy production, storage, and conversion technologies implies materials withstanding hydrogen's specific, reactive behavior. Durability-related issues such as hydrogen embrittlement in structural components or corrosion-induced phenomena in fuel cell or electrolyzer technologies are of significant interest in transitioning to green and sustainable energy supplies. In more detail, the stimulated interaction of hydrogen with the topmost micrometers and the microstructural features of materials will play a predominant role. Therefore, using physical vapor deposited (PVD) coating materials to protect and functionalize material surfaces will be critical in diverse future applications.

Degradation mechanisms related to hydrogen occur at multiple length scales, involving different strategies for exposure or treatments. These strategies are typically divided into the two hydrogen-related material research worlds: (i) electrochemical degradation setups and (ii) and non-electrochemical treatments as a collective term for pressure/gas-related setups. Nevertheless, the broad field of hydrogen-related applications is increasingly merging. Consequently, the different degradation strategies primarily focus on electrochemical test setups as they are highly versatile.

Therefore, in this study, the interaction of hydrogen with well-known protective coating materials such as TiN, CrN, ZrN, or TiAlN and AlCrN is described by an electrochemical Devanathan-Stachurski permeation setup. Different sets of these ceramic coating materials have been deposited on ferritic steel sheets through sputter and arc-evaporation technologies with varying deposition parameters. Subsequently, the coatings have been electrochemically loaded, and parameters such as diffusion coefficients, permeability, or permeation reduction factors are estimated. These results are correlated with the coatings' microstructural appearance before and after hydrogen testing using a set of diverse high-resolution techniques such as SEM, TEM, XRD, and micro-mechanical testing methods.

Keywords: Protective coatings; Hydrogen; Electrochemical testing; PVD; Nitrides;

Topical Symposium on Sustainable Surface Engineering
Room Golden State Ballroom - Session TS3-ThP
Solar Thermal Conversion - TS3 Poster Session

TS3-ThP-1 Tailoring the Structural, Optical and Electrical Properties in Perovskite Nickelates Through the Tilt Control of $Nd_{1-x}Sm_XNiO_3$ Thin Films*, **Zil Fernández-Gutiérrez (zil.fernandez-gutierrez@univ-lorraine.fr)**, T. Easwarakhanthan, S. Bruyère, D. Pilloud, S. Barrat, F. Capon,* Institut Jean Lamour - Université de Lorraine, France

Rare-earth nickelates ($RNiO_3$) are functional oxides with a vast landscape of properties, with the metal-insulator transition (MIT) being the most attractive one. This latter can be modified by varying the *rare-earth* atomic composition ($R'_{1-x}R_xNiO_3$) and the consequent tilt of the crystalline structure. However, obtaining solid solutions of this perovskite family is even more complex due to the specific composition control and the bottleneck that has been their synthesis over the years. Even so, this work aims to customize the thermochromic behavior of the layers to enhance infrared thermal regulation in solar collectors between 60 and 80 °C. Therefore, $Nd_{1-x}Sm_xNiO_3$ thin films were synthesized using reactive magnetron sputtering and air-annealing. Comprehensive XRD and TEM analysis confirms the efficient synthesis of various crystallized nickelates within the $SmNiO_3$ to $NdNiO_3$ range. This methodology facilitates the tunability of MIT temperatures between -80 and 120 °C as Sm atoms progressively replace Nd atoms. Optical performance, assessed through FTIR spectroscopy, aligns with literature-reported MIT temperatures. Additionally, a detailed examination of the structural, electrical, and electronic properties of the $Nd_{0.2}Sm_{0.8}NiO_3$ combination is presented. Lastly, ellipsometry measurements reveal a metal-like to dielectric-like phase change in the imaginary part of the dielectric function with photon energy, while the real part indicates oxidation in the upper film volume. These findings advance the understanding of $Nd_{1-x}Sm_xNiO_3$ nickelate thin films and their potential applications in thermochromic devices for solar energy utilization.

TS3-ThP-2 Trigeneration Plants Based on Solar Selective Surfaces of Carbon*, **Jose L. Endrino Armenteros (jlendrino@uloyola.es)**, E. Valbuena Niño,* Universidad Loyola Andalucia, Spain*; F. Montero-Chacón,* Universidad Loyola Andalucía, Spain*; A. Sandoval, M. Zurita,* Universidad Loyola Andalucia, Spain

The SSC material is one of the major components in solar-driven trigeneration technologies. The optical properties determine the efficiency of the energy conversion from the concentrated sun irradiation. Solar receivers are usually maintained under vacuum as to limit convective thermal losses, the absorber coating is typically designed to operate without oxidative atmosphere. The development of a solar receiver, able to operate under air, is a challenge to reduce some of the costs. It is also a way to lower the complexity of existing linear CSP technologies. Although standard solar troughs receivers operate inside an annulus with a pressure of less than 10-4 mbar, the proposed trigeneration technology will require the SSC material to operate in an oxidizing (ambient air) atmosphere and avoid critical troubleshoots due to accidental glass breakage and an unexpected vacuum loss.

Solar absorber layers based on nanocomposite materials (a-C:MeC) are here proposed. These nanocomposites are suitable candidates for medium-temperature solar absorber applications. Pure a-C thin films in combination with group 4, 5, and 6 transition metals form a number of exceptionally stable interstitial carbides. These carbides are characterized by high melting points, high thermal and electrical conductivity, and high reflectivity in the entire UV-Vis-IR spectral range. The presence of these carbides stabilizes the nanocomposite microstructure at this range of temperatures. Different microstructures and morphologies nanocomposite layers are here explored in combination with the Infrared (IR) layer made of titanium nitride (TiN) and a defect free alumina antireflective (AR) layer.

In addition, a simulation platform which we can run several scenarios that include, but are not limited to, hospitals, supermarkets, schools, residences, etc. will provide information on the trigeneration plant (i.e., heating, cooling, and electricity loads) for given scenarios using carbon-based coating materials.

Topical Symposium on Sustainable Surface Engineering
Room Golden State Ballroom - Session TS4-ThP
Coatings and Surfaces for Thermoelectrical Energy Conversion and (Photo)electrocatalysis - TS4 Poster Session

TS4-ThP-1 Dopant-defect Engineering in SnS_2 Thin Films for Improved Gas-phase Photocatalytic CO_2 Reduction*, **Tadios Tesfaye Mamo (tadios.tesfaye@aau.edu.et)**,* Department of Chemistry, National Taiwan University, Taiwan*; M. Qorbani,* Center for Condensed Matter Sciences, National Taiwan University, Taiwan*; A. Hailemariam,* Department of Applied Chemistry, National Yang-Ming Chiao Tung University, Taiwan*; A. Sabbah,* Center for Condensed Matter Sciences, National Taiwan University, Taiwan*; S. Kholimatussadiah,* Department of Physics, National Taiwan University, Taiwan*; C. Huang,* Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan*; L. Chen,* Center for Condensed Matter Sciences, National Taiwan University, Taiwan*; K. Chen,* Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan

To address the issue of CO_2 amount increment in the Earth's atmosphere, various semiconductor photocatalysts have been employed to convert CO_2 into valuable products. Designing an efficient photocatalyst that can activate the CO_2 molecule with the least amount of activation energy is one of the challenging problem. In this regard, we report a combined experimental and computational analysis on a thin film of SnS_2 doped with phosphorous ions at various ion doses. Thermal evaporation followed by sulfurization and ion implantation processes were used to prepare the regulated amount of phosphorous ion-implanted 20-nm SnS_2 thick thin films. Our findings reveal that phosphorous doping synergistically enhances light harvesting by lowering the band gap and energetically stable CO_2 binding sites with the lowest activation energy. The optimized P-SnS_2 photocatalyst has a three times higher CO_2 conversion rate than the pristine one, with a high selectivity of about 92% towards CH_4 formation. Because Phosporous play a vital role in the activation of CO_2 by serving as an active site and due to its low electronegativity, it increases the charge density of the Sn atom adjacent to it. Also, P-doping affects the charge density of the neighboring S atom by serving as a bridge to improve the charge distribution between Sn and S. This degree of electron density alteration would facilitate the electron transfer in the photocatalytic reaction.NAP- In-situ XPS and XAS results with formation energy, Bader charge, and Gibbs free energy calculations are used to carefully assess the overall impact of phosphorus in the SnS_2 sample. DFT calculations accord well with the experimental findings and help us to know the reaction pathway. We anticipate that our result will motivate additional ion implantation research to modify the material's active site for CO_2 reduction and examine its CO_2 conversion capability and related optical and charge transfer behavior.

TS4-ThP-2 e-Poster Presentation: Copper-Based Coatings on Polylactic Acid for Electrocatalytic CO_2 Reduction*, M. Lima,* University of Minho, Portugal*; J. Castro,* ***Sandra Carvalho (sandra.carvalho@dem.uc.pt)****,* University of Coimbra, Portugal

The climate crisis caused by global warming is recognized by the United Nations (UN) as a trigger for catastrophic effects such as weather extremes and natural disasters. Carbon dioxide (CO_2) emissions constitute about three-quarters of the total greenhouse gases (GHG) released and have gathered global attention due to their significant contribution to global warming.

Developing new catalytic processes can accelerate the transition to a more sustainable Earth. Electrocatalytic methods are the most promising of all the catalytic processes because they are energy efficient, selective, easy to control, and flexible. They are also known as the most viable solution for the CO_2 reduction reaction (CO_2RR).

Metallic copper has notable electrical conductivity, making it suitable for many electrode-based applications. Additionally, copper-based materials were reported to be active and selective electrocatalysts capable of producing hydrocarbons from the CO_2RR. However, the updated version of the Element Scarcity—EuChemS Periodic Table by the European Chemical Society brings attention to the limited abundance of copper. Ensuring a sustained supply of this element is a significant challenge. Utilizing thin film coatings to produce electrodes is a potentially practical approach to mitigating element shortages. Furthermore, Cu-based electrodes using a polymeric skeleton can provide several benefits concerning cost, material accessibility, and weight.

This work used polylactic acid (PLA) as the substrate for Cu-based electrodes. PLA is widely used in additive manufacturing, a low-cost technique that enables the fabrication of 3D-structured electrodes. Magnetron sputtering (PVD technique) was applied to develop copper metallic surfaces on PLA. Different coatings with Cu/CuO_x/Cu layers were produced. Anodization was a secondary technique applied to enhance the electrochemical active surface area. The CuO_x in the middle of the coating might act as a barrier material to stop the oxidation reaction during the anodization process while maintaining film adhesion. The chemical and morphological characterization of the resulting films will be discussed, as well as the electrochemical properties for CO_2RR applications.

TS4-ThP-3 Two-Dimensional Ruddlesden–Popper Phase of B-site substituted $Ca_{n-1}Mn_{n-3}Nb3O_{3n+12-}$ (n=4,5,6) Perovskite Nanosheets Integration with Chlorella vulgaris for Electrochemical Water Splitting*,* ***Yao-Yuan Chang (m56111135@gs.ncku.edu.tw)****, C. Chang, Y. Su,* National Cheng Kung University (NCKU), Taiwan

Two-dimensional (2D) perovskite nanosheets have emerged as potential candidates for hydrogen production and spintronic devices due to their large surface area, special optical, electric, magnetic, and structural properties. In this study, we synthesized 2D Ruddlesden–Popper (RP) phase perovskite nanosheets $Ca_{n-1}Mn_{n-3}Nb_3O_{3n+1}^-$ (n=4,5,6) to tune their physicochemical properties and catalytic performances via soft chemistry process. In this configuration, manganese (Mn) partially substitutes niobium (Nb) at the B-site within the niobate perovskite lattice structure exhibited positive influences in water splitting applications.The combination of CMNO nanosheets with Chlorella on the photoelectrode surface has demonstrated improved photoelectrochemical performance, especially for CMNO (n=6) nanosheet.This research contributes to the future outlook for sustainable energy solutions by unique properties of 2D perovskite oxide nanomaterials in conjunction with bio-inspired components.

Keywords: two-dimensional, Ruddlesden–Popper phase perovskites, Chlorella vulgaris, water splitting,magnetic

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM3-2-FrM

Accelerated Thin Film Development: High-throughput Synthesis, Automated Characterization, and Data Analysis II

Moderators: Davi Marcelo Febba, NREL, USA, **Sebastian Siol**, Empa, Switzerland, **Shijing Sun**, University of Washington, USA

8:20am **CM3-2-FrM-2 Combinatorial Synthesis and High-Throughput Characterization of Cu-Ag and Ni-Pt Thin Films Fabricated by Confocal Magnetron Sputter Deposition**, ***Kyle Dorman (krdorma@sandia.gov)***, *R. Kothari, N. Bianco, M. Kalaswad, C. Sobzcak, S. Desai, J. Custer, S. Addamane, M. Jain, F. DelRio, B. Boyce, R. Dingreville, D. Adams,* Sandia National Laboratories, USA

Nanocrystalline thin films feature the potential for enhanced or altered material properties compared to their bulk single crystal counterparts. While such possibilities are frequently limited by a lack of thermal stability, nanocrystalline thin films comprised of binary metal alloys such as $Pt_{0.9}Au_{0.1}$ have demonstrated greater resistance to annealing (P. Lu et al., Materialia, 2019) which is consistent with predicted thermodynamic preferences for a minority solute element to enrich and stabilize grain boundaries (J.R. Trelewicz et al., PRB, 2009). Recent studies on Pt-Au binary thin films have emphasized the role of grain boundary character in this solute stabilization (C. M. Barr et al., Nanoscale, 2021), and means of high-throughput combinatorial synthesis (McGinn, ACS Comb. Sci., 2019) have been developed to complement automated characterization and simulation capacity. To further develop understanding of the properties and synthesis of similar nanocrystalline binary metal systems, the suite of tools developed for Pt-Au analysis is now turned towards Cu-Ag and Ni-Pt combinations in search of optimized material properties and greater comprehension of nanocrystalline systems. Our study utilized simultaneous confocal sputter deposition of each pair of elements, with pulsed DC magnetron methods directing single element sources with a variety of approaches. The result, with the substrate fixed rather than rotated and the employment of photolithography, is a varied atomic composition across 112 samples on a single 150 mm diameter wafer. A series of such depositions, varying the gun-tilt angle and power at each cathode, allows swift examination of nearly the full range of alloy compositions. Wavelength Dispersive Spectroscopy, Atomic Force Microscopy, X-ray Diffraction, X-ray Reflectivity, sheet resistance, optical profilometry and nanoindentation were employed for high-throughput and fast-paced analysis. The binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films, 2012) assisted with the deposition design to minimize the necessary quantity of sample batches, and enabled analysis of the energetic and compositional properties of the wafer at deposition with respect to the resultant hardness, modulus, film density, crystal texture, resistivity, and chemical stability for the case of tarnishing Cu-Ag combinations. The resulting correlations are examined with a goal of optimization of nanocrystalline material properties and identifying the corresponding fabrication conditions.

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8:40am **CM3-2-FrM-3 Combinatorial Screening of Al-Si-N-O Protective Coatings with Tunable Refractive Index**, ***Stefanie Frick (stefanie.frick@empa.ch)***, *A. Wieczorek, K. Thorwarth, O. Pshyk, J. Patidar, S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Rising requirements of next-generation technologies lead to an increasing demand for multifunctional thin-film coatings. In order to accelerate the co-optimization of the functional properties of these coatings, combinatorial materials synthesis in combination with high-throughput automated characterization and data analysis is instrumental. The quaternary material system Al-Si-N-O is a promising candidate for protective optical coatings due to the hardness of its nanocomposite phase at low Si contents [1] and the tunability of the refractive index via the variation of the oxygen content [2]. In this work, thin film combinatorial libraries were deposited via reactive Hybrid Al-HiPIMS/Si-DCMS covering a significant fraction of the quarternary phase space by applying orthogonal anion- and cation gradients. Different approaches to obtain intentional oxygen gradients in combinatorial libraries, including varying localization of gas inlets as well as target configurations, will be addressed and the respective advantages and drawbacks will be discussed. Cation spreads mainly between 5 and 35 cation % Si were investigated as well as various oxygen contents depending on the respective anion gradient approach. Subsequently, the libraries were comprehensively characterized via automated mapping procedures with XPS, XRD, nanoindentation and UV-Vis spectroscopy. The latter allowed for automated refractive index determination employing the envelop method for transmission spectra according to Swanepoel [3]. The analysis of the data sets reveals the achievement of an indentation hardness of 20-24 GPa over a range of 10-35 cation % of Si corresponding to a refractive index of 2.03-2.05 in a pure nitride library. In addition, it is shown that the refractive index can be reduced down to 1.57-1.71 for a nearly pure oxide library and higher silicon contents (15-57 cation % Si) at the expense of hardness values of 7-9 GPa. The comprehensive combinatorial data sets allow for deeper insights in the composition-structure-property relationship in this complex material compared to experiments based on serial experimentation. Finally, the influence of the application of an RF bias at the insulating substrates, for an acceleration of the incident ions, on the film properties will be elaborated.

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9:00am **CM3-2-FrM-4 From Automated to Autonomous Thin Film Deposition Experiments**, ***Andriy Zakutayev (andriy.zakutayev@nrel.gov)***, NREL, USA **INVITED**

In this presentation, I will discuss recent progress towards demonstration of autonomous thin film deposition experiments in a highly automated combinatorial co-sputtering instrument at NREL. The autonomous operation will be demonstrated on the example of thin film reactively sputtered ternary nitride materials used for energy and electronic applications. A conceptual extension to other materials classes (e.g. oxides) ans other deposition methods (e.g. molecular beam epitaxy) will be discussed. A relation of autonomous deposition instruments to autonomous electrical characterization instruments, data processing pipelines, and high throughput computational reference data will be discussed.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country D - Session IA2-3-FrM

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications III

Moderator: Ta-Chin Wei, Yuan Christian University, Taiwan

8:00am **IA2-3-FrM-1 Study of Piezo-photocatalytic Performance of p-CoS-n-$NaNbO_3$ Junction Composite**, ***Man-Yu Hsiao (n56121288@gs.ncku.edu.tw)***, *T. Nguyen, K. Chang,* National Cheng Kung University (NCKU), Taiwan

Piezoelectric materials have been applied to the application of photocatalysis, photoelectrochemical cells, and pressure sensors. Furthermore, their heterojunction composites can enhance the photocarrier separation through a built-in electric field, and induced piezoelectric potentials can also minimize photocarrier recombination, improving photocatalytic efficiencies. In this talk, detailed studies on piezoelectric $NaNbO_3$, CoS-$NaNbO_3$ composites, and their associated piezo-related applications will be discussed. Various morphologies of $NaNbO_3$ were tuned via facile hydrothermal methods by the adjustments of heating times and temperatures, solution concentrations, and precursor types (Fig. 1-3, Supplement). Crystal phases of the samples were determined using XRD. Morphology and microstructures of $NaNbO_3$ and their composites were examined by SEM and TEM. Optical properties of the samples were investigated using UV–Vis spectroscopy. The sample's conductivity types were determined through Mott-Schottky measurement. Piezoelectric properties were directly measured via piezoresponse force microscopy (PFM). Furthermore, piezo-photocatalytic applications of $NaNbO_3$ and CoS-$NaNbO_3$composites were also explored, and the performance was elucidated using a constructed energy band diagram. Our results reveal that the photocatalytic effectiveness of the CoS-$NaNbO_3$ composite is attributable to the robust formation of p–n junctions, piezoelectric potentials, substantial amounts of active surface areas, and band positions.

8:20am **IA2-3-FrM-2 Enhanced Metal Surface Finishing with EPPo: Innovative Strategies for Ti 6Al-4V Alloys***, **Nicolas Laugel (nicolas.laugel@manchester.ac.uk)**, A. Matthews, A. Yerokhin,* The University of Manchester, UK

Electrolytic plasma polishing (EPPo) emerges as a promising technique for the precision removal and refinement of metals' surface layers. Its applications are experiencing growing interest, particularly in improving the finishing of lightweight alloys produced through additive manufacturing (AM). While the AM of metals holds immense potential to revolutionize global production, it faces a persistent challenge of achieving satisfactory final surface quality. To tackle this challenge, effective post-treatment methods are crucial, and EPPo emerges as an ideal solution.

The EPPo process involves placing the workpiece as the anode in an electrolytic cell and applying DC voltages in the hundreds of volts. The resultant energy release at the interface induces various physical and chemical reactions, ultimately influencing the processes governing the working surface's dissolution and allowing more precise control. EPPo employs electrolyte compositions that are safer for the workplace and the environment compared to traditional electropolishing methods, albeit with a slower material removal rate. Nevertheless, it preserves the advantages of contactless and geometry-independent polishing, aligning ideally with the advantages of additive manufacturing.

EPPo holds particular significance in its application on titanium and its alloys, a class of materials highly valued across various industries for their exceptional strength-to-weight ratio, corrosion resistance, and biocompatibility. They also present a valuable testing ground for EPPo due to their challenging electrodissolution characteristics, particularly the interference caused by the formation of insoluble oxides that create passivation layers, hindering the EPPo process itself in a positive feedback loop. This investigation specifically focuses on the impact of electrolyte on the surfaces generated through the EPPo of Ti 6Al4V alloy.

As EPPo has been transitioning from laboratory to industrial scales in recent years, electrolyte replacement has emerged as a significant and unexpected obstacle to cost-effective implementation. Notably, considerable downtime arises with the associated waste management tasks and inertia in temperature change of larger volumes. This study explores novel, environmentally friendly, non-aqueous electrolytes with deep eutectic solvents and their unique advantages in the application of EPPo to valve metals such as titanium and aluminium. Furthermore, it examines the ageing process in conventional fluoride-based aqueous electrolytes, providing insights from both chemical and surface science perspectives, along with proposed mitigations.

8:40am **IA2-3-FrM-3 Optimization of Plasma Electrolytic Polishing for 304 Stainless Steel Using Taguchi Method***, **Chun-Wei Chang (yiwenz988@gmail.com)**, N. Zheng, C. Tseng,* Ming Chi University of Technology, Taiwan, Republic of China

Plasma electrolytic polishing (PEP) is an advanced and efficient surface treatment technique widely employed across various industries. These particles induce chemical reactions on the material surface, thereby achieving fine polishing and enhancement of surface properties. In this study, we focused on utilizing a low concentration of ammonium sulfate ($(NH_4)_2SO_4$) aqueous solution to perform plasma electrolytic polishing on 304 stainless steel surfaces. The Taguchi experimental method was employed to assess the effects of different PEP parameters such as process time, voltage, electrolyte concentration, and temperature on the surface roughness,wettability and corrosion resistance of the PEP-treated stainless steels. Optical microscopy (OM) and scanning electron microscopy (SEM) were utilized to capture the changes in surface defects on 304 stainless steels after PEP processes, while a white light interferometer was used to evaluate surface roughness and flatness. Water contact angle measurements were conducted to assess the hydrophilicity/hydrophobicity of the PEP-treated 304 stainless steels. Additionally, the corrosion resistance properties were evaluated by using potentiodynamic polarization curve measurements in 3.5 wt% NaCl solutions. The experimental results performed by Taguchi analysis reveal that the electrolyte concentration is the most significant parameter affecting the effectiveness of plasma electrolytic polishing for 304 stainless steels, and followed by process time, voltage, and temperature. The OM and SEM images indicate that the removal of surface defects is increasing by increasing the process time, maximum voltage, and electrolyte concentration. The experimental data measured by the white light interferometer reveal that the lowest surface roughness of 0.061 μm and optimal surface flatness are achieved at PEP parameters of 6 minutes, 320 volts, and 5 wt% ammonium sulfate concentration. However, the wettability of PEP-treated 304 stainless steels obtained by water contact angle measurements indicates that an enhancement in hydrophobicity for PEP-treated surfaces, with the contact angle increasing from 73.8° before PEP to a maximum of 96.6° after PEP in 5 wt% ammonium sulfate solution. Furthermore, the pitting resistance for PEP-treated 304 stainless steels evaluated by potentiodynamic polarization curves measured in 3.5 wt% NaCl solution demonstrates that the highest pitting nucleation potential (E_{np}) and the largest passive region, indicating superior corrosion resistance properties, achieve on PEP-treated surface after PEP in 5 wt% ammonium sulfate solution.

9:00am **IA2-3-FrM-4 Structure Design and Degradation Mechanism of Amorphous Carbon Coatings on Metallic Bipolar Plates***, **Hao Li (lh@nimte.ac.cn)**, P. Guo, A. Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Proton exchange membrane fuel cell (PEMFC) is important on the development of hydrogen energy and fuel cell technology. However, in the acidic working environment of the PEMFC, the metallic bipolar plates (BPs), as a core component in PEMFC, will face to the problems of dissolution and corrosion, which directly determines the output power and service life of the PEMFC. Therefore, improving the conductivity and corrosion resistance of the metallic BPs is one of the key technologies that need to be tackled in the PEMFC field, affecting the competitiveness of the hydrogen energy and fuel cell industry.

The amorphous carbon (a-C) coating can endow metallic BPs with excellent corrosion resistance and conductivity. Besides, the scale cost advantage of a-C coating is significant. It can be prepared by physical vapor deposition technology, and has great application potential in metallic BPs of PEMFC. However, the preparation of a-C coating with excellent performance and the realization of stable low interface contact resistance (ICR) are still great challenges in this field. In addition, the degradation mechanism of a-C/metallic BPs after long-term operation is not clear, which seriously limits the development of corrosion-resistant and conductive a-C materials and technologies.

In view of the above problems, this paper fabricated a series of a-C coatings for the surface modification of metallic BPs under PEMFC conditions, and explored the relationship between the microstructure and bonding composition of coatings and corrosion resistance and conductivity, revealed the failure mechanism of the coatings modified metallic BPs, prepared a-C coating with high conductivity and corrosion resistance, and put forward a new idea of interface optimization of the coating modified metallic BPs.

9:20am **IA2-3-FrM-5 Automated Laser Cleaning/Ablation as a Novel Tool in Aerospace Manufacturing***, **Dmitri Novikov (dnovikov@ipgphotonics.com)**,* IPG Photonics, USA

This presentation will explore the progress in laser technology that has made them the tool of choice for mass manufacturing, with a focus on laser cleaning/ablation. Laser technology has revolutionized the way we manufacture, maintain, repair, and overhaul aerospace components. Thorough cleaning is a critical step in these processes, whether before coating, surface polishing or roughening, or any joining operations like welding or brazing. Currently, three main technologies are used for coating stripping and surface preparation for coating: abrasive grit blasting, abrasive water jetting, and chemical cleaning/stripping. However, these technologies negatively impact the environment and health and are slow and expensive. This presentation aims to introduce a laser cleaning solution that can replace these legacy technologies. Although laser cleaning/ablation is known in the industry, its use is limited due to the limited access to correct laser sources and concerns of part damage by laser heat. The presentation will showcase successful laser cleaning applications for different cleaning/ablation tasks, resulting in improved productivity, repeatability, direct cost savings, and part performance improvements in quality. Laser technology has proven to be a game-changer in the manufacturing industry.

Coatings for Biomedical and Healthcare Applications
Room Palm 3-4 - Session MD3-FrM

Bioactive Surfaces

Moderators: Valentim A.R. Barão, University of Campinas (UNICAMP), Brazil, **Sandra E. Rodil**, Universidad Nacional Autónoma de México

8:20am **MD3-FrM-2 Electrochemical Aspects of Interaction between Surface Engineered Metal Implants and Biological Environment***, **Aleksey Yerokhin (Aleksey.Yerokhin@manchester.ac.uk)**,* University of Manchester, UK **INVITED**

Interfacial redox reactions involving charge transfer between metallic biomaterials and biological environment are of particular interest for development of new generation of biomedical implant devices. Controlling reaction kinetics can help achieving the targeted biological functionality such as osteogenic and biocidal activity, or drug-release ability of surface engineered smart and multifunctional implants; this is also important when minimising corrosion rates to enhance long-term performance of permanent metal implants or controlling degradation behaviour of bioabsorbable implants. Extensive exploratory research at the interface of biomedical and materials engineering often takes advantage of lab-scale electrochemical methods for express assessment of relevant implant properties. However interpreting results of the tests that were originally designed to evaluate aqueous corrosion of metals in engineering applications and are now being adopted to study more complex interactions between implants and biological environment is not straight forward. This talk will revisit electrochemical fundamentals of most common corrosion tests based on potentiodynamic polarisation and frequency response analysis, with a focus on implications for the assessment of implant material degradation in vitro and relevance of obtained characteristics to the implant performance in vivo. Discussions will be provided into effects that composition of simulated biological media, implant surface state and test conditions may have on basic kinetic parameters of anodic and cathodic processes, including exchange current densities, Tafel slopes and limiting current densities, and how these are reflected in polarisation curves. Attention will further be drawn to the multistage nature of the interfacial charge transfer process and correct evaluation of contribution from different stages to the overall corrosion kinetics that inform the strategies for environmental degradation control of biomedical implant materials.

9:00am **MD3-FrM-4 New Approach for Controlling Peri-Implant Infections Integrates Multifunctional Photocatalytic Coating and Photodynamic Therapy – an in Vitro and in Vivo Study***, **Valentim A. R. Barão (vbarao@unicamp.br)**, B. Nagay, R. Costa, C. Dini, A. Santos,* University of Campinas (UNICAMP), Brazil*; L. Cintra,* Sao Paulo State University (UNESP), Brazil*; N. da Cruz, L. Faverani,* São Paulo State University (UNESP), Brazil*; J. van den Beucken,* Radboudumc, Netherlands

Although peri-implant infections reduce the longevity of dental implants, there is still no gold-standard therapeutic strategy. Therefore, here we developed a visible light-responsive multifunctional bismuth (Bi)-TiO_2 coating on titanium (Ti) surface to optimize the properties of dental implants and enhance antimicrobial photodynamic therapy (aPDT)-mediated microbial reduction. Bi-TiO_2 experimental coating was synthesized via plasma electrolytic oxidation (PEO). TiO_2 and polished Ti were controls. Topographic, physicochemical, tribological, structural and photocatalytic properties were analyzed. In vitro microbiological assays were performed under different light times (0, 1 and 5 min). In vitro cytocompatibility was evaluated in mesenchymal cells and gingival fibroblasts. The antimicrobial activity and inflammatory response were investigated in vivo (in a subcutaneous tissue of rats). PEO created rough, superhydrophilic and crystalline surfaces, with higher hardness values and tribological performance compared to Ti control ($p<0.05$). Bi-TiO_2 was not cytotoxic and enhanced the microbial reduction mediated by aPTD ($p<0.05$) by presenting photocatalytic activity under visible light. The combination of Bi-TiO_2 and aPDTreduced microbial viability and modulated the inflammatory response in vivo ($p<0.05$). The Bi-TiO_2 coating is a promising strategy for rehabilitation with dental implants as it presents optimized surface properties and enhances microbial reduction and inflammatory modulation mediated by aPDT.

Note: This study was supported by the Sao Paulo Research Foundation (FAPESP, Brazil) (grant numbers: 2019/17238-6 and 2022/16267-5).

Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP5-FrM

Plasma Surface Interactions and Diagnostics

Moderator: Arutiun P. Ehiasarian, Sheffield Hallam University, UK

8:00am **PP5-FrM-1 The Role of Plasma in Plasma Enhanced Atomic Layer Deposition***, **Scott Walton (scott.walton@nrl.navy.mil)**, D. Boris, M. Johnson, V. Wheeler,* US Naval Research Laboratory, USA*; M. Sales, P. Litwin,* NRC, USA*; J. Woodward,* US Naval Research Laboratory, USA*; S. Rosenberg,* Lockheed Martin Space Advanced Technology Center, USA*; J. Hite, D. Pennachio, M. Mastro,* US Naval Research Laboratory, USA **INVITED**

Plasma-enhanced atomic layer deposition (PE-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce amorphous, crystalline, and epitaxial films of varying types and characteristics. The plasma-based advantages come at the cost of a complex array of process variables that can drastically impact the growth modes and resulting film properties. Accordingly, understanding the process-structure-property relationship is both critical and challenging. We approach this problem by combining plasma diagnostics and material characterization techniques. Plasma diagnostics are used to inform the choice of process conditions for PE-ALD systems including VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the plasma used in commercial and research PE-ALD tools. In particular, we assess the spatial variation of plasma parameters, flux and energy of ions reaching the substrate surface, and the relative fractions of atomic and molecular species generated in the plasma under a variety of operating powers, gas pressures, and gas input flow fractions typically used to grow nitride, oxide, and fluoride films. Changes in plasma parameters are then linked with changes in growth modes and film properties using both ex situ and in situ characterization techniques. Select example systems including AlF_3, InN, TiO_2 and Ga_2O_3, will be discussed. This work supported by the Naval Research Laboratory base program.

8:40am **PP5-FrM-3 Navigating the Complexity of Microwave Plasma-Assisted ALD During AlN and TiN Fabrication***, **Caroline Hain (caroline.hain@empa.ch)**, K. Maćkosz,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Guerra,* Swiss Cluster AG, Switzerland*; T. Nelis,* BFH, Bern University of Applied Sciences, Switzerland*; J. Michler, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Plasma-based atomic layer deposition (ALD) techniques are becoming increasingly relevant, offering extended control over process parameters such as temperature range, precursor/co-reactant chemistries and surface reactions. This freedom allows for a wider choice of substrates and thin film materials, as well as the ability to precisely tailor material properties critical to specific applications. Nevertheless, the complexity introduced by plasma necessitates a more detailed understanding of the deposition environment. This study aims to characterise *in situ* the surface reactions occurring during electron cyclotron resonance (ECR) microwave plasma-assisted ALD and their influence on the deposited films, in this case using the examples of aluminium nitride (AlN) and titanium nitride (TiN). Trimethylaluminium (TMA) and tetrakis(dimethylamido)titanium (TDMATi) were used as precursors for AlN and TiN, respectively, with plasma-activated nitrogen serving as co-reactant. Two types of time-of-flight mass spectrometers (ToFMS) were used to identify neutral and ionic species produced during the sequential ALD cycles. Optical emission spectroscopy (OES) was utilized to identify the nitrogen species produced during the nitrogen plasma step, while Langmuir probe measurements determined the plasma spatial potential, density, and electron temperature as a function of microwave power and distance from the source. Finally, the chemical composition, thickness, density, and structure, as well as surface uniformity of deposited AlN and TiN thin films were investigated via a combination of scanning and transmission electron microscopy (SEM/TEM), X-ray reflectometry (XRR) and ellipsometry. This work offers insights on the complexity of plasma-assisted ALD processes and paves the way for informed optimisation and application-based customisation of deposited thin films.

9:00am **PP5-FrM-4 Advanced Ion Energy Measurement Tools to Understand the Effect of Ion Energy on Film Properties***, Thomas Gilmore (thomas.gilmore@Impedans.com),* Impedans, Ireland

In any plasma assisted deposition process, ion surface interactions can influence the film properties significantly. Ion energies determine if deposition, sputtering or implantation occurs, while ion flux determines the rate of this processing. The ion/neutral ratio impacts the thin film properties. Measuring these values for various chamber conditions can not only aid in process development, but also facilitate process transfer, as these ion parameters are the direct process drivers.

We, at Impedans Ltd, offer solutions to the requirements of ion energy and flux measurements. Our collection of sensors includes the Semion, Quantum and Vertex RFEAs for wafer level measurements. In this talk we will demonstrate the role of energetic ions in plasmas and how they affect the properties of materials etched or deposited in plasma processing. We will show how to use measured ion flux, ion energies and ion-neutral fractions to optimize industrial plasma-assisted processes. The *Semion RFEA* measures the ion energies hitting a surface, the ion flux, negative ions, and bias voltage at any position inside a plasma chamber using an array of integrated sensors [1-3] over a region of 300 mm large size wafer with down to 44 ns time resolution. On the other hand, the *Quantum system* is an energy resolving gridded quartz crystal microbalance (QCM), used to measure the ion-neutral fraction hitting a surface inside a plasma reactor. This instrument also measures the etching/deposition rate, ion energy, ion flux and bias voltage [4, 5]. The Vertex RFEA design has a variable aspect ratio (AR), controlled using a potential difference between its grids. A variable AR controls the ion angular spread passing through the sensor for detection. The Vertex product produces a plot of ion energy distribution versus AR [6].

We will highlight the successful measurements done by our RFEA product range in selected applications (like pulsed source and /or bias, tailored waveform biasing, etc) enabling better control of film properties of different materials and various plasma chemistries.

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9:20am **PP5-FrM-5 Plasma Polymerization Processes***, Dirk Hegemann (dirk.hegemann@empa.ch),* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Plasma polymer films are deposited via reactive intermediate species as formed in a low temperature plasma. Over the last decades, the understanding of the mechanisms behind plasma polymerization processes has steadily been improved, which will be discussed. Basically, the highly non-equilibrium conditions provide an average energy per molecule in the plasma, known as specific energy input (SEI), yielding plasma chemical reactions by inelastic collisions (excitation, dissociation, and ionization). Due to the related energy distribution, the probability for the activation mechanism to produce film-forming species can be described by a simple Arrhenius-like equation, where temperature is replaced by SEI. The potential of this approach to optimize plasma polymerization processes for surface functionalization is demonstrated on the basis of siloxanes, hydrocarbons, and further gaseous mixtures.

Hexamethyldisiloxane (HMDSO) has been well studied in the past revealing insights into the plasma chemical reaction pathway, which can thus be used as a model monomer following Arrhenius-like behaviour. Nano-scaled controlled film deposition is obtained considering the flux of film-forming radicals, etchants, and energetic species. Thus, dense to porous, hydrophilic to hydrophobic films can be generated. Such films are investigated for the chemical modification of catalytic substrates, as durable barrier layers and bioactive surfaces.

Furthermore hydrocarbon molecules are mixed with reactive gases such as CO_2 or NH_3 to investigate the penetration of radicals into complex 3D structures, which is studied using cavity techniques. Various applications in technical and biomedical fields will be presented.

Finally, an outlook is given about the applicability of the presented approach for plasma gas conversion based on comparable plasma chemical processes.

Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP7-FrM

Modeling and Data-Driven Methods for Process Design, Analysis and Control

Moderator: Petr Zikán, PlasmaSolve s.r.o., Czechia

10:20am **PP7-FrM-8 Insights on Plasma Processing from Multi-Scale Physical and Data-Driven Modeling***, L. Vialetto,* Stanford University, USA*; T. Gergs,* Kiel University, Germany*; I. Chaerony Siffa,* Leibniz Institute for Plasma Science and Technology (INP), Germany*; C. Stüwe,* Kiel University, Germany*; T. Mussenbrock,* Ruhr University Bochum, Germany*; M. Becker,* Leibniz Institute for Plasma Science and Technology (INP), Germany*; **Jan Trieschmann (jt@tf.uni-kiel.de)**,* Kiel University, Germany **INVITED**

The theoretical description of plasma processing provides a formidable task that has been addressed by analytical modeling and numerical simulation for decades. Although the continuous increase in compute power has enabled simulation studies of the gas discharge physics in great detail, many open questions remain. This is reasoned by the extremely complex dynamics of multi-component plasmas facing solid surfaces, involving a large number of processes in the plasma and in the solid, as well as their plasma-surface interaction. The time and length scales of these physico-chemical processes span many orders of magnitude. Well separated scales often allow for the description of a given phenomenon on its respective scales, paired with a hierarchical coupling. This coupling is often rather static and realized via oversimplifying assumptions (e.g., tabulated coefficients), and may be biased-by-experience. Advantage can be taken from more unbiased data-driven approaches, which are derived from high fidelity data obtained from physical models at the lower scales. Moreover, the description of certain physical mechanisms may be substituted by data-driven sub-models (e.g., electric field calculation or transport parameters from a kinetic description). Correspondingly, a hierarchy of physical and data-driven models may be derived, linking global process quantities (e.g., pressure, voltage, current) to microscopic process quantities (e.g., thin film composition, electrical properties).

This approach is exemplified by the investigation of a low-pressure partially-magnetized capacitively coupled radio frequency discharge for the sputter deposition of silicon oxide thin films. The model is implemented in the OpenFOAM framework, extended by a Particle In Cell/Monte Carlo Collisions (PIC/MCC) implementation and coupled to a system of fluid equations for the neutral background. The surface evolution is described by a system of rate equations, which takes into account physical sputtering, chemisorption, physisorption, and surface diffusion of adatoms. The dynamics of physical sputtering are included using an artificial neural network model trained on surface kinetics data with varying stoichiometry from Monte Carlo simulations. It is argued that the versatility of the implementation also allows to use this model in a broader range of applications, such as plasma etching.

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11:00am **PP7-FrM-10 Utilizing Digital Twin Technology for Automated Coating Recipe Development***, **Petr Zikan (zikan@plasmasolve.com)**, A. Obrusnik,* PlasmaSolve s.r.o., Czechia

Recent developments in the field of coating technology have seen a rise in the adoption of process modeling and digital twin tools. The primary motivation for this shift is the extended duration and unpredictability of process transfers and scaling in coating applications. Moreover, these technologies are now beginning to contribute to energy reduction in coating processes.

In our previous work, we introduced a Digital Twin model for coaters, integrated into the MatSight framework by PlasmaSolve. This model demonstrated high accuracy in predicting the composition and key performance characteristics (such as hardness and residual stress) of coatings, utilizing a dataset of only eight characterized samples for training. This achievement was made possible by a hybrid process model that merges simulations of physical processes and chemistry with machine learning techniques. By incorporating knowledge of the coater's physical limitations, the model significantly reduced the need for extensive training experiments.

This contribution advances our research by tackling an inverse problem: using the Digital Twin model to create a coating recipe based on defined material specifications. These specifications include the number of layers, the thickness and composition of each layer, and the target hardness/residual stress for the complete stack. The model generates a recipe file compatible with coater operations, allowing for immediate implementation and validation of model predictions.

Furthermore, we illustrate how the Digital Twin model can be seamlessly integrated with other PVD simulation tools, offering a comprehensive view of the coating process. A case in point is the integration with the MatSight Coating Uniformity App, which enhances understanding of the coating's thickness distribution and the variations in ion bombardment and composition across a 3D object.

11:20am **PP7-FrM-11 Open-Source Plasma Modelling for Thin-Film Technologies with the Simulation Tool PICLas**, ***Paul Nizenkov (nizenkov@boltzplatz.eu)****, A. Mirza, S. Copplestone, J. Beyer,* boltzplatz - numerical plasma dynamics GmbH, Germany

Simulating technical plasmas or highly rarefied gases in vacuum chambers presents a significant challenge due to the complexity of processes such as electron kinetics and strong non-equilibrium effects. To address these challenges, gas kinetic approaches are often employed. These approaches describe the medium not as a continuum, but as a stream of particles, including atoms, ions, and electrons.

This talk introduces PICLas, an open-source simulation tool originally developed for the simulation of space systems such as atmospheric re-entry & electric propulsion and now applied in various technical fields for simulating plasma processes. PICLas is based on gas kinetic approaches, utilizing particle methods like Particle in Cell (PIC) and Direct Simulation Monte Carlo (DSMC). A distinctive feature of PICLas is its modular structure, which allows the software to be used either as a pure DSMC or pure PIC solver. Combining these methods opens up exciting possibilities, such as simulating collisional plasmas.

The development of an intelligent graphical user interface aims to make this complex modeling more accessible to technical developers. This interface leverages modern web-based technologies and other open-source projects for cost-effective development. The talk will demonstrate how these technologies, combined with PICLas, can streamline the pre-processing, simulation setup, and post-processing in numerical simulation projects. Furthermore, the talk shall present different application examples, where the code has been tested and validated for thin-film technologies.

Topical Symposium on Sustainable Surface Engineering
Room Town & Country C - Session TS3-FrM

Solar Thermal Conversion

Moderators: Telmo Echániz, University of the Basque Country, Spain, **Marcus Hans**, RWTH Aachen University, Germany

8:00am **TS3-FrM-1 Application of Surface Engineering Solutions in Concentrating Solar Power Key Components**, ***Ramón Escobar-Galindo (rescobar1@us.es)****,* University of Seville, Spain*; J. Sanchez-Lopez, T. Rojas,* CSIC-University Sevilla, Spain*; H. Barshilia,* CSIR-National Aerospace Laboratories, India*; M. Krause,* Helmholtz Zentrum Dresden-Rossendorf, Germany **INVITED**

Thermal conversion of solar energy into electricity is one of the most efficient methods of harvesting renewable energy. In this regard, the development of new materials is crucial to improve the performance of concentrating solar power (CSP) plants. The future developments of thermosolar plants demand, among others, (1) mirrors with higher reflectivity, better protection, and lower costs, (2) absorber receiver components operating at higher temperatures, with wavelength selective capabilities, or (3) more stable materials under corrosive environments (i.e. molten salts) (see Figure 1). In this presentation, a review of surface engineering concepts (i.e. tailoring of multilayer materials, control of the interface design) applied to thermosolar energy will be discussed. Examples from our own research on the design, characterization, and thermal testing of ultra-reflective dielectric multilayer mirrors[1] and solar selective coatings (SSCs) for high-temperature applications[2,3,4] will be presented. In the former, we have demonstrated the design, using a genetic algorithm, and manufacture, using Physical Vapour Deposition (PVD) techniques, of metal-dielectric multilayered solar mirrors that can outperform silver reflectors commonly employed in thermosolar and photovoltaic systems. In the latter, the thermal stability of SSCs based on metal oxynitrides prepared by PVD was studied after high-temperature annealing of the samples performed in air (*ex-situ*) and in vacuum (*in-situ*).

(1) A. Jiménez-Solano et al. *Aperiodic Metal-Dielectric Multilayers as Highly Efficient Sunlight Reflectors*. **Advanced Optical Materials** 5,9 (2017) 1600833

(2) T.C, Rojas Ruiz et al. *High-temperature solar-selective coatings based on Cr(Al)N. Part 2: Design, spectral properties and thermal stability of multilayer stacks***. Solar Energy Materials & Solar Cells. 218** (2020) 110812

(3) R. Escobar-Galindo et al. *Solar selective coatings and materials for high-temperature solar thermal applications*, **Chapter 13 in "Sustainable Material Solutions for Solar Energy Technologies",** Elsevier, 2021

(4) K. Niranjan et al. *WAlSiN-based solar-selective coating stability-study under heating and cooling cycles in vacuum up to 800 °C using in situ Rutherford backscattering spectrometry and spectroscopic ellipsometry*. **Solar Energy Materials & Solar Cells**. 255 (2023) 112305

8:40am **TS3-FrM-3 Development and Thermal Characterization of High-Temperature Coating Materials for Solar Thermal Energy Conversion***,* ***Renkun Chen (rkchen@ucsd.edu)****,* University of California, San Diego, USA **INVITED**

Coating is fundamentally important and ubiquitous for solar thermal energy conversion. From low temperature solar water heaters to intermediate parabolic trough solar collectors to high temperature solar towers, solar absorbing coatings play an important role. In this presentation, I will introduce our work over the past few years. Specifically, we have developed coatings based on high-temperature stable spinel oxide nanoparticles with ultra-high solar absorptance. The spinel oxide nanoparticles are synthesized with a scalable hydrothermal process. In the first application, the particles are mixed with silica resin to form a slurry for coating. The slurries can be spray coated onto substrates with a scalable process followed by standard curing and sintering processes. The coating on steel and Inconel substrates shows high solar absorptance (with solar to thermal conversion efficiency over 90% for 1000-sun at 800 oC absorber temperature). The coatings also exhibit superior thermal stability after long thermal isothermal ageing tests at 800 oC and thermal cycling tests from room temperature to 800 oC. This scalable coating process can be applied to cylindrical solar collector tubes with liquid heat transfer fluid (e.g., molten salts) in solar towers. In the second application, the black spinel nanoparticles are coated onto particulate heat transfer media (HTM) based on sand or ceramic particles of a few hundred microns in diameter. The black coating can greatly enhance the solar absorptance of sand HTM, and can also lead to stable solar absorptance of Carbo ceramic particles. We also developed high-entropy version of black nanoparticles which show remarkable stability against grain growth and can be used to coat thermochemically active particles to simultaneously increase the solar absorptance and suppress particle sintering, which is important to sustain high reaction kinetics of the thermochemical materials.

9:20am **TS3-FrM-5 Smart Coatings for Concentrated Solar Thermal: from Optical Design and Plasma Synthesis to Performance and Durability Assessment***,* ***Audrey Soum-Glaude (Audrey.Soum-Glaude@promes.cnrs.fr)****, A. Diop,* PROMES-CNRS, France*; A. Mahammou, D. Ngoue,* PROMES-CNRS, Perpignan University, France*; A. Grosjean,* EPF Montpellier, France*; B. Plujat, S. Quoizola,* PROMES-CNRS, Perpignan University, France*; A. Bousquet, E. Tomasella,* University Clermont Auvergne, France*; L. Thomas,* PROMES-CNRS, Perpignan University, France **INVITED**

Half of our energy consumption is heat for industrial processes and buildings. Contrary to solar PV and wind where electricity is directly produced, in solar thermal technologies, solar radiation is harvested by a solar receiver and converted into heat. In concentrated solar thermal (CST) technologies, solar radiation is concentrated by mirrors on the receiver to increase temperature. The generated heat can be stored more efficiently and at lower cost than electricity, providing great dispatchability and mitigating the intermittency of the solar resource. Solar thermal is thus a major solution for sustainable energy production, complementary to PV and other renewables. Additionally, the hybridization of PV and CST solar technologies can take advantage of the low cost of PV electrical production and the thermal storage of CST to produce both electricity and heat on demand.

To increase solar-to-heat conversion efficiency, the metallic surface of CST receivers can be covered with Solar Selective Absorber Coatings (SSACs) with high absorptance (i.e., low spectral reflectance) in the solar range, and low thermal emittance (i.e., high spectral reflectance) in the infrared range to limit radiative thermal losses. These coatings must also be resistant to high temperatures in air and high thermomechanical stresses, particularly for CST where they are exposed to harsh working conditions for long durations.

Similarly, for PV/CST hybridization, compact systems where PV cells are installed on solar concentrators to produce electricity, and CST thermal absorbers placed at their focus to produce heat, require spectrally selective mirror coatings. The latter must transmit part of the solar radiation to the underlying PV cells (typically from 400 to 1100 nm) and reflect the rest towards the CST thermal solar receiver.

In both types of surfaces, such spectrally selective behavior is obtained by combining advanced optical design and optimization of the coatings with their experimental synthesis, microstructural and thermo-optical characterization, and aging studies including aging under representative solar irradiation. In this paper, this complete development strategy will be illustrated with two examples of coating developments carried out at PROMES-CNRS laboratory: $[W/SiCH]_n$ and $W/WSiCH/TaO_xN_y$ multilayer stacks for CST high temperature SSACs and $[SiO_2/TiO_2]_n$ for selective “PV mirrors” for PV/CST hybridization, deposited by PVD and PECVD techniques.

10:20am **TS3-FrM-8 Controlling Infrared Emissivity of Thermochromic VO_2 Films via V_2N Precursor Thickness for Enhanced Solar Thermal Regulation***,* *A. Garcia-Wong, D. Pilloud, S. Bruyère, S. Migot, S. Hupont, F. Capon,* ***Jean-François Pierson (jean-francois.pierson@univ-lorraine.fr)****,* Institut Jean Lamour - Université de Lorraine, France

The control of infrared (IR) radiation is crucial for applications related to solar radiation. Thanks to the IR properties modification during its metal-insulator transition, monoclinic vanadium dioxide (m-VO_2) is an excellent material for solar thermal regulation device development. Yet, these applications are linked to substrate IR properties on which the VO_2 is deposited.

In this study, we propose a novel method for tuning the sign of the VO_2 IR-emissivity without changing the substrate. Thermochromic VO_2 films have been synthesized by air oxidation of reactively sputtered V_2N films deposited on silicon substrates. As-deposited vanadium nitride films have been oxidized in air at 550 °C. The structure of the VO_2 films has been characterized using X-ray diffraction and Raman spectrometry. Transmission electronic microscopy combined with electron energy loss spectroscopy (EELS) bring relevant information to describe the oxidation mechanism of V_2N. At the interface between the remaining V_2N film and the formed VO_2 one, a thin layer of VN of 20 nm thick has been evidenced. At this oxidation temperature, the annealing duration to obtain efficient thermochromic VO_2 films is fixed to 3 minutes. The initial precursor (V_2N) thickness is the key parameter for tuning the IR properties. V_2N films with low thickness allow the formation of thermochromic VO_2 films with negative emissivity switch (approx. -0.2) while thick V_2N films allow positive emissivity switch (approx. 0.2). Our findings introduce a different strategy for IR emissivity control on thermochromic devices.

10:40am **TS3-FrM-9 Emissivity and Reflectivity Measurements of Coatings for Solar Applications***,* ***Telmo Echaniz (telmo.echaniz@ehu.eus)****, I. Gonzalez de Arrieta, M. Sainz-Menchon, J. Gabirondo-Lopez, G. Lopez,* University of the Basque Country, Spain

Widespread adoption of concentrated solar power relies on lowering its operational costs, which requires efficient absorbing materials capable of withstanding high temperatures. This motivates the development of coating materials based on oxides. Unfortunately, these materials do not always feature appropriate optical properties, which means that strategies to increase their solar absorptances must be carried out. This work reports on the optical characterization of high-absorbing coatings. For that, directional spectral infrared emissivity measurements up to 600 ºC, integrating sphere and bidirectional reflectance measurements in the UV-Vis-NIR range at room temperature have been performed. Spectral directional emissivity measurements were performed in the HAIRL emissometer using using a DTLaGS detector between 1.43 and 25 µm and the sample was placed between 10 and 80º every 10º for each directional measurement [1]. This emissometer is equipped with a Bruker Vertex 80v FTIR spectrometer that possesses an IR integrating sphere. Once the spectra were obtained, the emissivities were integrated along the electromagnetic spectrum and the solid angle to obtain total hemispherical emissivity values. Bidirectional reflectance measurements were performed between 350 and 2500 nm in a Cary UMA device. They were measured in both s and p polarizations, from which the unpolarized reflectance function was reconstructed. Measurements in the off-specular directions were also measured to complement these data and allow estimation of the total reflectance, weighted by the solar spectrum. Both the infrared emissivity and the BRDF measurements allowed obtaining the conversion efficiency.

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