Protective and High-temperature Coatings
Room Palm 3-4 - Session MA3-2-TuA

Hard and Nanostructured Coatings II

Moderators: 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-TuA-1 Designing Nanocrystalline Alloys and Compounds: Unraveling Compositional and Microstructural Pathways to Exceptional Properties***, **Rostislav Daniel [rostislav.daniel@unileoben.ac.at]**, Michal Zitek, Tobias Ziegelwanger,* Montanuniversität Leoben, Austria*; Ranming Niu,* The University of Sydney, Australia*; Edoardo Rossi, Marco Sebastiani,* Università degli studi Roma Tre, Italy*; Petr Zeman, Stanislav Haviar,* University of West Bohemia, NTIS, Czechia*; Jozef Keckes,* Montanuniversität Leoben, Austria **INVITED**

This talk presents advanced methods in combinatorial synthesis and microstructural design to achieve extraordinary properties in multielement alloys and layered coatings. Using the CrCuTiW alloy system as a primary example, we demonstrate how large compositional variations and the limited miscibility between elements lead to diverse self-assembled multicomponent phases,combining solid solutions, nanocomposites, and metallic glasses. These structures exhibit unexpected combinations of hardness and elastic modulus, demonstrating the potential for unique property tailoring.

In a second example, a cross-sectional combinatorial synthesis of nanostructured CrMnFeCoNi alloy is employed to address the thermal stability of this metastable alloy. This approach enables an in-depth analysis of segregation kinetics in the primary phase at moderate temperatures (50-450°C) resulting in the formation of a variety of coexisting phases that enhance alloy strength while maintaining ductility and fracture toughness. This approach demonstrates its capability to provide insights into the thermal behavior of complex, metastable microstructures and allows for controlled property enhancement.

Additionally, the talk emphasizes a bio-inspired approach to compositional and microstructural design withina layered Zr-Cu-N system, where antibacterial properties are combined with enhanced fracture toughness and stress resistance. These multifunctional coatings represent a new class of sustainable materials, suitable for both hard and smart coating applications.

Our methodology integrates advanced multi-technique characterization tools, including 2D (XRD, EDX) and 3D (nano-XRD, nanoindentation) mapping capabilities, combined with transmission electron microscopy and atom probe tomography. These techniques facilitate a rapid assessment of processing-structure-property relationships in these novel nanostructured alloys, bridging the gap between theoretical predictions and practical applications. Together, these methodologies provide a pathway to the design of next-generation multifunctional layered architectures,tailored down to the nanoscale, to enable exceptional mechanical and functional properties and robust thermal stability.

2:20pm **MA3-2-TuA-3 Evolution of the Pulsed-DC Powder-Pack Boriding Process: Exploring Low-Temperature Boride Layer Formation***, **J.L. Rosales-Lopez [jrosalesl1401@alumno.ipn.mx]**[1], M. Olivares-Luna, L.E. Castillo-Vela, I.E. Campos-Silva,* Instituto Politécnico Nacional, Mexico

This study rigorously investigates the transformative potential of the Pulsed-DC Powder-Pack Boriding (PDCPB) process to catalyze boride layer formation on AISI H13 steel at remarkably reduced temperatures (600°C, 650°C, and 700°C) under substantial current densities ($\sim$952mA·cm^{-2}) and significantly minimized exposure times of 1800s, 2700s, and 3600s. Enabled by the implementation of a custom high-capacity power supply, this innovation generates the essential electric field to support boriding at unprecedented low temperatures. Traditionally, achieving similar results in AISI H13 required treatments at temperatures exceeding 900°C with exposure times of at least 14400s, underscoring the extraordinary advancement represented by this approach.

Through meticulous microstructural and physicochemical analyses using SEM–EDS and XRD, the study reveals substantial findings: at a mere 600°C, PDCPB successfully produced dense, biphasic FeB+Fe_2B layers with thicknesses ranging from ~8μm to ~17μm, uniformly distributed across the sample surfaces. Remarkably, and contrary to established reports on borided AISI H13, the substrate retained its α-phase microstructure without transformation to the α'-phase, and the interface between the boride layer and substrate remained free of any diffusion zone. This breakthrough not only introduces significant commercial scalability for low-temperature boriding but also opens possibilities for further innovations, potentially achieving effective boriding near the 530°C threshold. The insights presented mark a seminal advancement in boriding technology, with vast implications for industrial applications and the future of materials engineering.

2:40pm **MA3-2-TuA-4 Three-Fold Superstructured HfN/HfAlN Multilayers***, **Marcus Lorentzon [marcus.lorentzon@liu.se]**[2],* Linköping University, IFM, Thin Film Physics Division, Sweden*; Rainer Hahn,* TU Wien, Institute of Materials Science and Technology, Austria*; Lars Hultman, Justinas Palisaitis,* Linköping University, IFM, Thin Film Physics Division, Sweden*; Johanna Rosen,* Linköping University, IFM, Materials Design Division, Sweden*; Grzegorz Greczynski, Jens Birch, Naureen Ghafoor,* Linköping University, IFM, Thin Film Physics Division, Sweden

Brittleness and poor fracture toughness are limiting factors for the application of hard protective coatings. To resolve these issues, we explore multilayer superlattice (SL) coating designs based on $HfN_{1.33}$ and $Hf_{0.76}Al_{0.24}N_{1.15}$. We achieve high-quality single-crystal films and superlattices with superior mechanical characteristics by epitaxial growth on MgO(001) substrates using ion-assisted reactive magnetron sputtering at high temperatures.

The structure and properties of monolithic single-crystal $HfN_{1.33}$ and $Hf_{0.76}Al_{0.24}N_{1.15}$ are studied to evaluate the SL-coating performance. Overstoichiometric HfN_y exhibits metal-like ductility in micropillar compression tests, with easy dislocation nucleation and movement along multiple {111}<110> slip systems, which results in significant strain hardening and a doubled ultimate strength at 17% strain, compared to the yield point at 2%. The improved ductility is attributed to point defects—vacancies and nitrogen interstitials—forming a checkerboard superstructure of hyper-overstoichiometric and near-pristine domains. In contrast, HfAlN shows improved hardness and yield strength in pillar compression, however, it fails by strain-burst with fractures on the {110}<110> slip system. These properties stem from strain fields, pinning dislocations, which develop between coherent Hf- and Al-rich nanodomains, formed by surface-initiated spinodal decomposition. In addition, the domains similarly self-organize into a checkerboard superstructure.

Thus, by combining overstoichiometric $HfN_{1.33}$ and $Hf_{0.76}Al_{0.24}N_{1.15}$ in SLdesigns with equal layer thicknesses but varying bilayer period of 20 nm, 10 nm, and 6 nm, fascinating three-fold superstructured SLs are created by checkerboard superstructuring in 1) the HfN layers and 2) the HfAlN layers, as well as 3) the multilayer structure itself. While the interfaces provide dislocation pinning to maintain an equally high hardness as $Hf_{0.76}Al_{0.24}N_{1.15}$, about 20% higher than $HfN_{1.33}$, other multilayer effects and inherent ductility of $HfN_{1.33}$ enhance the toughness through coherency strains, crack-tip blunting or deflection. The SLs are analyzed using X-ray diffraction, reciprocal space maps, high-resolution z-contrast scanning transmission electron microscopy, selected area electron diffraction, nanoindentation, and micropillar compression tests. Post-mortem imaging of the pillars reveals the underlying plastic deformation mechanisms. Superlattice effects enhance mechanical performance, combining properties of both materials for coatings with high hardness and improved toughness, ideal for advanced protective applications.

3:00pm **MA3-2-TuA-5 Effects of Different Interlayer Layers on Residual Stress Relief in γ-MoN/Ti and γ-MoN/Mo Thin Films***, **Ding-Hsuan Yang [dave35116@gmail.com]**, Jia-Hong Huang,* National Tsing Hua University, Taiwan

Transition metal nitrides have been widely used due to their outstanding properties such as wear resistance, high corrosion resistance and excellent mechanical properties. γ-Mo_2N coating is becoming more popular in terms of high temperature tribological properties, which results from the formation of Magnéli oxide phase. However, residual stress from the deposition of the hard coatings is a common issue that may decrease the adhesion strength and fracture toughness. Adding a metal interlayer is a convenient method to relief the residual stress of hard coatings. The purpose of this research was to compare the behavior of stress relief by using different metal interlayers, Ti and Mo. In this study, the Ti and Mo

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[1] **Graduate Student Award Finalist**

[2] **Graduate Student Award Finalist**

interlayers were deposited by DC-unbalanced magnetron sputtering, while the γ-Mo$_2$N coatings with Ti and Mo interlayer were deposited using high pulsed power magnetron sputtering on Si (100) substrates. The γ-Mo$_2$N layer thickness was maintained at 1000 nm with three different interlayer thicknesses controlled at 50, 100, and 150 nm. The overall residual stress of the bilayer coatings was determined by the laser curvature method (σ_{LCM}), while individual layer stress was evaluated by the average X-ray strain method (σ_{AXS}). Contrary to our expectations, the results show that σ_{LCM} values are consistently higher than σ_{AXS}, suggesting that the Ti and Mo interlayer cannot effectively relieve stress through plastic deformation. The Ti interlayer may be partly converted to TiN due to the reaction of N_2 gas or N_2^+ ions with the pre-deposited Ti, and consequently the interlayer cannot be plastic deformed to relieve stress. In contrast, due to the high elastic constant of Mo, the compressive residual stresses in the Mo interlayer is higher than that in γ-Mo$_2$N coating, where the stress is higher than the yield strength of Mo metal, indicating that Mo interlayer cannot serve as a buffer layer to relieve residual stress of γ-Mo$_2$N coatings.

4:00pm **MA3-2-TuA-8 Highly Stacked Ge0.8Si0.2 Nanosheets Fabricated by Wet Etching of MBE-Grown Superlattice Films***, Zefu Zhao, Dun-Bao Ruan,* FZU-Jinjiang Joint Institute of Microelectronics, College of Physics and Information Engineering, School of Advanced Manufacturing, Fuzhou University, China*; Kai-Jhih Gan,* FZU-Jinjiang Joint Institute of Microelectronics, College of Physics and Information Engineering, School of Advanced Manufacturing, Fuzhou University,, China*; **Qian Cheng Yang [455783022@qq.com]**,* FZU-Jinjiang Joint Institute of Microelectronics, College of Physics and Information Engineering, School of Advanced Manufacturing, Fuzhou University, China*; Kuei-Shu Chang-Liao,* Department of Engineering and System Science, National Tsing Hua University, Taiwan*; Jie-yin Zhang,* SongShan Lake Materials Laboratory, Center for Semiconductor Heterogeneous Materials and Devices, Dongguan 523830, China*; Shenglin Pan,* FZU-Jinjiang Joint Institute of Microelectronics, College of Physics and Information Engineering, School of Advanced Manufacturing, Fuzhou University, China

This work demonstrates a novel wet etching approach to fabricating a 3-stacked Ge0.8Si0.2 nanosheet structure, which holds significant promise for advancing next-generation transistor technologies. As the semiconductor industry approaches the 2 nm node, transistors with nanosheet architectures are emerging as strong contenders to replace FinFETs due to their superior electrostatic control over short channels, enabling enhanced performance and power efficiency. In this study, high-quality and atomically flat superlattice Ge0.8Si0.2 layers were epitaxially grown using molecular beam epitaxy (MBE), providing an ideal platform for nanosheet fabrication. The key innovation lies in the utilization of HNO_3-based wet etching, which exploits the high selectivity of Ge over Ge0.8Si0.2 to achieve precise and uniform etching, resulting in three stacked Ge0.8Si0.2 nanosheets with exceptional channel uniformity. To mitigate lattice mismatch and confine misfit dislocations, an undoped Ge buffer layer was grown on a Si wafer, serving as a critical intermediate layer. Reciprocal space mapping (RSM) analysis confirms the successful realization of a fully relaxed Ge buffer layer and strained Ge0.8Si0.2 nanosheets, highlighting the structural integrity and strain engineering of the fabricated stack. This work not only provides a scalable and cost-effective method for nanosheet fabrication but also paves the way for the integration of GeSi-based nanosheet transistors in future sub-2 nm technology nodes, offering a pathway to further miniaturization and performance enhancement in semiconductor devices.

4:20pm **MA3-2-TuA-9 A T*EM* and Nanoindentation Study of the Correlation between Composition, Structure and Mechanical Properties of the AlCu Thin Film System***, **Dániel Olasz [olasz@student.elte.hu]**, Quang Chinh Nguyen,* Eötvös Loránd University, Hungary*; Noémi Szász, György Sáfrán,* HUN-REN Centre for Energy Research, Hungary

AlCu alloys in their bulk form are of great importance of the industry, including construction and aerospace and also their study has been instrumental in understanding the precipitation hardening effect in alloys. However, they are less frequently studied in their thin film form, with existing research mainly focusing on low alloying concentration cases. The aim of the present research is to investigate over the whole compositional range the correlation between composition, structure and mechanical properties in the AlCu thin film system.

By applying the micro-combinatorial approach, 15 discrete $Al_{1-x}Cu_x$ ($0 \le x \le 1$) films having a thickness of 1.7 um and different compositions were deposited on a single Si substrate through DC magnetron sputtering of Al and Cu in a single vacuum run. Nanoindentation measurements have demonstrated that even for pure Al and Cu, the layers exhibit significant strength in comparison to their bulk counterparts. The hardness increases substantially with increasing alloying concentration, reaching a maximum of about 16 GPa in the vicinity of ~50 at% Cu composition. For these layers, which display the highest strength, the loading stage of the indentation curves exhibits a step-like behavior, indicative of non-continuous deformation. Furthermore, the indentation experiments on the layer system provide an excellent opportunity to gain a deeper understanding of the indentation size effect (ISE), as the hardness of the layers at low alloying concentrations is independent of the applied maximum indentation force, whereas a clear sensitivity to ISE can be observed for layers containing 40-70 at% Cu. A comprehensive TEM study over the whole Al-Cu composition range using cross-sectional FIB TEM lamellae revealed microstructural features such as grain size, crystal structure, presence of non-equilibrium phases and layer growth mechanisms. This, together with the nanoindentation results, led to an understanding of the deformation mechanisms at work during indentation and hence to an explanation of the surprising mechanical properties of thin AlCu layers.

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