Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-4

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

1:50pm **B1-4-2 Combinatorial Exploration of the High Entropy Alloy System Fe-Mn-Ni-Co-Cr**, ***Alexander Kauffmann,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany*; M Stüber, H Leiste, S Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; S Schlabach, D Szabó,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK)*; B Gorr,* University of Siegen, Germany*; H Chen,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany*; H Seifert,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; M Heilmaier,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany

The concept of high entropy alloys (HEA) differs from conventional alloy design strategies by increasing the number of base elements as well as their concentrations. Rather than being composed of a single principal element and minor additions for obtaining desired microstructures and materials properties, HEAs are chemically complex composed of multiple principal elements in almost equiatomic ratios. Here, the basic intention is to maximize the configurational part of entropy and stabilizing disordered, single-phase materials with simple crystal structures. Nevertheless, configurational entropy is not the sole decisive factor for the thermodynamic stability of particular phases. Accordingly, efficient theoretical as well as experimental methods have to be conducted in order to screen the vicinity of the center of five or more component systems.

The FeMnNiCoCr HEA crystallizes face-centered cubic and is one of the few examples of HEAs which can be tailored by means of classical metallurgical processes. Thus, FeMnNiCoCr has attracted most interest by the scientific community among the class of HEAs so far. Its outstanding mechanical properties are resulting from a complex interplay of the impact of lattice distortion and an interplay of deformation twinning and dislocation slip. In order to experimentally separate fundamental parameters like stacking fault energy which are strongly depending of Fe, Mn and Ni content and lattice distortion which are influenced by Cr and Mn content, deviations from the almost equimolar composition are necessary.

For exploring the phase field of the solid solution within the Fe-Mn-Ni-Co-Cr system, we use a combinatorial thin film method in the present contribution. The films are prepared by magnetron sputtering from a Fe-Mn-Ni-Co-Cr multi-element target with circular sectors onto Si substrates. The compositions of the prepared films with a thickness of about 5 µm were obtained by EDX. In the as-deposited state, the disordered solid solution is found in the near equimolar region of the films. The lattice parameter of bulk material obtained from conventional metallurgy could be verified. The microstructure of the obtained thin film in the center of the quinary system is examined by using TEM (FIB lift out) and 3D-APT. In addition, the results on the center of the phase diagram are complemented by analyses towards the binary border systems which are in our case Mn-Fe, Fe-Co, Co-Ni, Ni-Cr as well as Cr-Mn. Here, disordered solid solutions with fcc, bcc, hcp and alpha-Mn structure type crystal structure were found. The appearance of all phases is discussed based on CALPHAD calculations.

2:10pm **B1-4-3 The Effect of Mo-Cu Cathode Composition on Thin Film Synthesis and DC Vacuum Arc Characteristics**, ***Igor Zhirkov,*** Linköping University, IFM, Sweden*; P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Rosen,* Linköping University, IFM, Sweden

Mo-Cu alloys demonstrate high electrical and thermal conductivity, low coefficient of thermal expansion, and good high-temperature performance. The material properties are dependent on how well Mo and Cu can be mixed. Classical methods such as powder metallurgy and/or infiltration are limited due to the Mo/Cu grain size. An alternative synthesis method is vacuum arc, which allows generation of metallic flux even from refractory materials, and which also provide an increased Mo-Cu intermixing. In this work, we have studied the influence of $Mo_{1-x}Cu_x$ cathode composition (x = 0, 0.05, 0.1, 0.15, 0.3, 0.63, 0.95, 1 (wt%)) on plasma generation and materials synthesis in a DC vacuum arc discharge. It is found that the stability of the arc process is strongly correlated to the cathode composition. Highest stability, together with the lowest cathode potential (~ 19 V), is detected for the $Mo_{0.37}Cu_{0.63}$ (wt%) cathode, while the $Mo_{0.95}Cu_{0.05}$ (wt%) cathode shows the most unstable arc process with the highest cathode potential (~ 28 V). Moreover, plasma properties such as total intensity of ion flux, ion kinetic energy and ion charge state are all found to be strongly dependent on the relative Mo/Cu ratio. The intensity of macroparticle generation as well as the size of the droplets also correlate with the relative fraction of Cu within the cathode. However, there is an inverse correlation between the visually observed intensity of the macroparticle flux and the number of droplets on the resulting films. In particular, for the cathodes with low Cu content, there is an increased abundance of visually observed macroparticles while the films are (close to) free of droplets. The thickness and elemental composition of the deposited films also demonstrate a dependence on the elemental composition of the cathode. The obtained results are discussed in the light of a very limited solubility between Mo and Cu, surface and material properties of new and used Mo-Cu cathodes, and features resulting from high temperatures of the cathode surface during the arc process.

2:30pm **B1-4-4 Towards High-Rate Magnetron Sputter Deposition: Influence of Discharge Power on Deposition Process and Coating Properties**, ***Christian Saringer,*** *R Franz,* Montanuniversität Leoben, Austria*; K Zorn,* MIBA High Tech Coatings, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Magnetron sputtering offers the possibility of depositing a vast variety of functional coatings and is nowadays widely established in research and industry. Its main advantage is the great versatility, which is owing to the possibility of freely adjusting the conditions during film growth, like the degree of thermalization, the substrate temperature and the ion bombardment. Thus, the mechanical, optical and structural properties of the coatings can be tailored on laboratory and industrial scale. However, the applicability is often limited due to the large amount of energy that is inherently dissipated into heat, resulting in a low deposition rate. Therefore, the increase of deposition rate is of great interest in order to improve productivity and cost-efficiency. Raising the overall power introduced to the process can be perceived as an approach for elevating the deposition rate which is, however, also affecting the properties of the resulting coatings. Within this work, we therefore studied the influence of the target power on the sputter deposition process and resulting coating properties during reactive and non-reactive sputtering. Chromium, titanium, TiN, TiO_2 and carbon coatings were deposited at different average power densities of up to 34 W/cm² in DC and pulsed DC mode. The coatings were examined by X-ray diffraction, scanning electron microscopy and nanoindentation experiments, which revealed that their mechanical and structural properties are significantly affected by the power density. It was also found that by controlling the discharge power it is possible to effectively influence the transition between metallic and poisoned mode during the reactive sputtering of titanium in N_2 as well as O_2 containing atmospheres. Additionally, conducted plasma investigations employing Langmuir probe analysis and optical emission spectroscopy revealed further details about the relations between discharge and coating properties contributing to establish a comprehensive understanding of high-rate magnetron sputter deposition.

2:50pm **B1-4-5 High Temperature Solid PVD Lubricants Based on Vanadium**, ***Vjaceslav Sochora,*** *M Jilek, Jr., O Zindulka,* SHM, s.r.o., Czech Republic

The increase of the production in the industry demands higher cutting speeds of the tools. A higher speed means higher forces which increase the working temperature and decrease the tool life. One of the solutions is to use PVD coatings with a very good thermal stability or we can use a film with a low friction coefficient in high temperatures. In our work, we focus on the high temperature lubricant PVD coatings based on vanadium that are very promising for cutting and forming applications.

The studied systems were CrVN, VAlN, AlCrVN and VAlSiN prepared by the low voltage arc. The disadvantage of these systems is a narrow functional temperature interval that determines the specific application for the film.

We investigated the dependence of the hardness on the amount of vanadium in the film and then annealed the deposited coatings in the air at the temperatures of 500 – 700 °C and researched the change in hardness and oxidation rate. We also examined the structure by using SEM.

In the next step, we used face-turning test to simulate the real conditions to assess the friction properties of the coatings. The parameters of the cutting tests were set to achieve the thermal load from 550 °C to 700 °C.

The presence of vanadium in the system has a significant influence on the friction and enables to optimize the process application like hobbing or aluminum die casting.

3:10pm **B1-4-6 Grain Size-Dependent Metastable Phase Formation*, Marcus Hans,*** *D Music,* RWTH Aachen University, Germany*; D Kurapov, J Ramm, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Switzerland, Liechtenstein*; J Schneider,* RWTH Aachen University, Germany

Physical vapor deposited (PVD) TiAlN is the benchmark hard coating system utilized in metal cutting and forming applications today. However, phase formation prediction efforts by density functional theory (DFT) calculations for TiAlN are often inconsistent with experimental data. It is well known that the phase stability is affected by chemical composition, temperature as well as pressure. Recently, the impact of point defects on the phase stability [1] and the consequences of processing conditions in an industrial deposition system for the phase stability [2] were evaluated.

Here we consider for the first time the impact of grain size on the stability of metastable TiAlN coatings by relating calculated surface and volume energy contributions to the total energy. Typical grain sizes determined for PVD TiAlN are < 50 nm and, hence, these coatings contain domains with large surface-to-volume ratios. Our starting hypothesis is that the energetic "penalty" associated with the formation of these grain surfaces (= interfaces) will affect the experimentally determined stability. Therefore, we investigated the grain size-dependent phase stability of cubic and wurtzite $Ti_{1-x}Al_xN$ theoretically by considering a surface energy term in addition to the volume energy term. With this approach critical grain sizes for metastable phase formation are identified as a function of the Al concentration x.

$Ti_{1-x}Al_xN$ coatings were synthesized combinatorially by cathodic arc deposition and the here proposed, grain size dependent phase stability calculation is found to be consistent with experimental phase formation data. The results provide evidence that the extent of phase stability regions of TiAlN critically depends on the grain size. While these thoughts have been overlooked in the past we will demonstrate that the grain size-dependent phase formation is equally relevant for other material systems with large surface-to-volume ratios.

References:

[1] M. Hans, M. to Baben, D. Music, J. Ebenhöch, D. Primetzhofer, D. Kurapov, M. Arndt, H. Rudigier, J. M. Schneider, *Effect of oxygen incorporation on the structure and elasticity of Ti-Al-O-N coatings, synthesized by cathodic arc and high power pulsed magnetron sputtering*, J. Appl. Phys. 116 (2014) p. 093515.

[2] M. Hans, M. to Baben, Y.-T. Chen, K. G. Pradeep, D. M. Holzapfel, D. Primetzhofer, D. Kurapov, J. Ramm, M. Arndt, H. Rudigier, J. M. Schneider, *Substrate rotation-induced chemical modulation in Ti-Al-O-N coatings synthesized by cathodic arc in an industrial deposition plant*, Surf. Coat. Technol. 305 (2016) 249-253.

3:30pm **B1-4-7 Nanoengineering Periodically Structured SiCu Thin Film Anodes for Rechargeable LIBs*, Billur Deniz Polat Karahan,*** *B Bilici,* Istanbul Technical University, Turkey*; O Eryilmaz,* Argonne National Laboratory, USA*; K Amine,* Argonne National Laboratory, USA, United States of America*; O Keles,* Istanbul Technical University, Turkey

In the quest for a radically better lithium-ion battery, a promising direction is suggested so-called “silicon (Si) composite” anodes, in which the negative electrode contains a higher proportion of Si with another material. In the current technology, while the Si composite electrodes have the potential to have far higher energy density, long cycle life and high reversibility are still not satisfactorily provided due to intrinsic properties of Si such as low electrical conductivity and high volumetric changes upon cycling.

Therefore, in this work, to create electron conduction pathway in the electrode and to increase the ductility of the film 10%at. Cu atoms are co-deposited with Si. Then to induce homogeneously distributed interspaces in the electrode structured composite thin film has been engineered by glancing angle electron beam deposition (GLAD) method. This process enables to deposit coatings of any materials without a need of binders or any conductive additives. Plus, various structures from nanocolumns to helices might be deposited by optimizing the evaporation rate of source materials, the incident angle and the azimuthal rotation rate of the substrate.

An innovative approach involving adaptation of ion assistance to GLAD has been also proposed in this study. The well adherent composite nanostructures are expected to provide large reaction area with Li, facile stress relaxation (to prevent electrode pulverization or delamination), effective electrical contacts with the substrate and short Li diffusion distances.

To evaluate the electrochemical performances of the structured composite films, two samples have been deposited on Cu collector with different evaporation rates: quartz crystal microbalances of Cu and Si show 0.4-4 Å/s and 0.9-10 Å/s for Samples 1 and 2, respectively. The morphological analyses show that depending on the evaporation rates of sources the structure of the film changes which affects their performances in cycling.

3:50pm **B1-4-8 Thin Film Metallic Glass: Novel Coating Providing High Toughness and Low Friction*, Chia-Chi Yu,*** *J Chu,* National Taiwan University of Science and Technology, Taiwan*; Y Shen,* University of New Mexico, USA

The amorphous nature of thin film metallic glasses (TFMGs) provides outstanding mechanical properties, including high strength, large elastic limits, and excellent corrosion and wear resistance. The grain boundary-free structure of TFMGs produces an exceptionally smooth surface and low surface free energy, resulting in high hydrophobicity and a low coefficient of friction.

In this study, magnetron sputtering was used in the deposition of Zr-based TFMG coatings with the aim of enhancing the bending and fatigue properties of bulk metallic glasses (BMGs). A TFMG coating was shown to increase the plastic strain of BMG by 9.2%, without sacrificing its extraordinary strength. This was also shown to increase the fatigue endurance-limit of BMG by ~33%, from 300 MPa for bare BMG to 400 MPa for TFMG-coated BMG. The results of transmission electron microscopy and nanoindentation testing revealed that TFMGs are able to withstand enormous shear strain without fracturing. Used as a coating on syringe needles, the low coefficient of friction of TFMG (∼0.05) reduced the insertion forces by ∼66% and retraction forces by ∼72%, when tested on polyurethane rubber blocks.

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