Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-3-TuM

PVD Coatings and Technologies III

Moderators: Frank Kaulfuss, Fraunhofer Institute for Material and Beam Technology (IWS), **Jyh-Ming Ting**, National Cheng Kung University, **Qi Yang**, National Research Council of Canada

8:00am **B1-3-TuM-1 PVD-AlTiN with High Al Content – How to Overcome the "Magic" 67%-Limit**, ***Fred Fietzke****, T Modes, O Zywitzki,* Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP, Germany

Since first investigations in the 1980's, TiAlN has become the most widespread coating material for wear protection in cutting applications. For the use at high temperatures, its corrosion resistance can be further improved by increasing the aluminum content in the cubic rock salt (Ti,Al)N phase. However, the solubility of Al in this phase is limited, and above a certain threshold AlN with hexagonal wurtzite structure is formed in addition. This leads to a sharp drop of hardness and a general deterioration of wear resistance.

Whereas the application of CVD techniques allows the deposition of single phase cubic $Al_xTi_{1-x}N$ layers with x > 0.8, the accepted state of the art for PVD is a maximum x-value of 0.67.

To find out how the effective maximum-x-value depends on the deposition conditions, a co-sputtering approach was used and compositionally graded layers with increasing Al content in growth direction were deposited. By FE-SEM investigation of cross sections in crystal orientation contrast it could be shown that the microstructure is changed at a certain depth, from large columnar crystallites with lateral dimensions of about 60 nm to a nanocrystalline structure with globulitic crystallites in the range of 10 nm.

XRD measurements showed that the initially deposited columnar structure is single-phase cubic, whereas the nanocrystalline layer arising on top is hexagonal with wurtzite structure. Hardness measurements by nanoindentation gave results up to 40 GPa for the lower and around 20 GPa for the upper layer. The depth profiles of chemical composition were determined by GD-OES. The results show that the layers are stoichiometric and exhibit aluminum gradients of different slope.

The location of the phase change from cubic to hexagonal could be affected by deposition conditions like pressure, temperature, and bias voltage. By optimization of the process parameters, it was possible to shift the phase transformation from x-values of 0.67 to 0.75.

8:20am **B1-3-TuM-2 PVD Methods and Coatings for Protection of Aero Engine Components**, ***Uwe Schulz****, R Naraparaju, R Braun, N Laska,* German Aerospace Center (DLR), Germany **INVITED**

Advanced aero engines aim at reduced specific fuel consumption and increased thrust-to-weight ratio. This ultimately calls for materials with increased high temperature capability and lightweight components that are pushed to its limits. Usage of coatings offers the potential to prolong lifetime, to increase operating temperatures, and to protect turbine components. Several PVD coating techniques that are used to protect turbine parts will be presented.

Thermal barrier coatings (TBCs) are applied to increase lifetime and efficiency of turbine blades and vanes in aero-engines and land-based gas turbines by reducing the average metal temperature and mitigating the detrimental effects of hot spots. The presentation highlights the interplay between processing, microstructure, and lifetime of the coatings that are produced by electron beam-physical vapor deposition (EB-PVD. Those coatings possess a superior strain and thermo-shock tolerance due to their columnar microstructure. The influence of substrate material, bond coat composition, and top coat composition is discussed. New topcoat chemistries have been developed that offer low thermal conductivity, improved sinter resistance, higher phase stability, and especially enhanced resistance against degradation by volcanic ash and calcium-magnesium alumino-silicate (CMAS) deposits that are ingested in aero-engines during the flight. The presentation provides results on several new TBCs, especially their behavior under the influence of deposits and under thermo-cyclic loading.

Gamma-TiAl based alloys are attractive light-weight materials for high temperature applications in automotive and aero engines. However, their oxidation resistance is poor at temperatures above 800°C. To improve the oxidation behavior of TiAl components, the use of protective coatings is a suitable method. Furthermore, the application of TBCs on TiAl would allow a further increase in operating temperature of internally cooled components. In the presentation several alumina forming coatings such as PtAl, Ti-Al-Cr based coatings and TBCs of yttria partially stabilized zirconia (YSZ) are discussed. They were deposited on gamma-TiAl alloys using magnetron sputtering and electron-beam physical vapour deposition, respectively. The oxidation behavior of the protective layers and the lifetime of the TBC systems are presented in the temperature range between 900 and 1000°C performing thermal cyclic tests.

PVD methods are also capable to protect CFRPs against erosion which is another damaging effect in aero-engines. Here multilayers of metallic and hard coatings are favored to effectively protect the underlying material.

9:00am **B1-3-TuM-4 High-temperature Nanoindentation and Microcantilever Deflection Tests of CrAlN and CrAlSiN Hard Coatings**, ***Aljaž Drnovšek***, Montanuniversität Leoben, Austria*; H Vo,* University of California Berkeley, USA*; A Xia, M Rebelo de Figueiredo,* Montanuniversität Leoben, Austria*; S Koloszvári,* Plansee Composite Materials GmbH, Germany*; S Vachhani,* Bruker Nano Surfaces, Germany*; P Hosemann,* University of Californa at Berkeley, USA*; R Franz,* Montanuniversität Leoben, Austria

Mechanical properties of protective coatings are commonly determined by nanoindentation methods. The development of nanoindentation in recent years led to new ex-situ and in-situ systems that are capable of measuring mechanical properties such as hardness, elastic modulus and fracture toughness at high temperatures (HT). For hard protective coatings it is of paramount value to gain knowledge of their mechanical properties close to the real operation temperature.

In the current work, we tested two magnetron sputter deposited coatings that are widely used in industrial cutting applications, namely CrAlN and CrAlSiN. Although the coatings consist of similar elements, the addition of Si interrupts the columnar growth of CrAlN coatings resulting in a nanocomposite composed of CrAl(Si)N grains surrounded by an amorphous SiN_x grain boundary phase. We measured their HT hardness and elastic modulus up to 700°C in steps of 100°C. The hardness value reduced from 30 GPa and 36 GPa for CrAlN and CrAlSiN, respectively, by approximately 2 GPa per temperature step. In contrast to a gradual decrease of hardness over the whole temperature range for CrAlN, the hardness of CrAlSiN revealed only minor changes at temperatures exceeding 500 °C. The HT fracture toughness was measured by microcantilever deflection using in-situ nanoindentation. These measurements were conducted in a similar way as the hardness measurements, up to 700°C in 100°C steps. We found that the trend is similar to the HT hardness results with CrAlSiN exhibiting a slightly better performance.

This data set is intended to serve as a first step towards a more comprehensive understanding of the HT mechanical properties of hard coatings which is vital for their further development and improvement for use in HT applications.

9:20am **B1-3-TuM-5 On Crystallization and Oxidation Behavior of $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ Thin-film Metallic Glasses Compared to a Crystalline $Zr_{54}Cu_{46}$ Thin-film Alloy**, ***Michaela Kotrlová****, M Zítek, P Zeman,* University of West Bohemia, Czech Republic

Zr- and Cu-based metallic glasses are one of the most studied systems because of their high crystallization temperature and a wide supercooled liquid region. Their unique properties make them attractive for miscellaneous applications. An important prerequisite to use them in industry is their ability to resist an oxidizing environment at elevated temperatures.

Therefore, this work is focused on the investigation of the crystallization and oxidation behavior of $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ thin-film metallic glasses and on the comparison of their oxidation behavior with that of a crystalline $Zr_{54}Cu_{46}$ thin-film alloy. The amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ thin-film metallic glasses were prepared by non-reactive magnetron co-sputtering of Zr, Hf and Cu in pure argon. The magnetrons with the Zr and Hf targets were operated in dc regimes while the magnetron with the Cu target in high-power impulse regime. Several as-deposited $Zr_{54}Cu_{46}$ films were post-annealed in high vacuum to create a crystalline thin-film alloy of the identical composition. The non-isothermal crystallization behavior of the amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ films and the effect of a substitution of Hf for Zr on the crystallization process were studied by differential scanning calorimetry. The oxidation behavior of the amorphous and crystalline $Zr_{54}Cu_{46}$, and amorphous $Zr_{27}Hf_{27}Cu_{46}$ films was investigated by thermogravimetric analysis.

The results showed that the $Zr_{54}Cu_{46}$ film crystallized at a lower temperature (≈ 422°C) and in two successive steps in contrast to the $Zr_{27}Hf_{27}Cu_{46}$ film (≈ 477°C). The activation energy of the $Zr_{27}Hf_{27}Cu_{46}$ film was higher for all conversion fractions, which indicates that the substitution of Hf for Zr enhanced the thermal stability of the glassy state. Dynamical thermogravimetric curves revealed that the onset of the oxidation of the amorphous $Zr_{54}Cu_{46}$ film (≈ 475°C) was shifted by about 120°C to a higher temperature than for the crystalline $Zr_{54}Cu_{46}$ film. Moreover, the substitution of Hf for Zr shifted the onset of the oxidation to an even higher temperature (≈ 550°C). As for oxidation kinetics, all isothermal thermogravimetric curves in the temperature range from 400 to 575°C obeyed the parabolic law. The activation energy of the oxidation process was 112, 143 and 208 kJ/mol for the crystalline $Zr_{54}Cu_{46}$ film, and the amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ films, respectively. The highest activation energy for the $Zr_{27}Hf_{27}Cu_{46}$ film indicates that the most protective oxide layer was formed on the surface of this film.

9:40am **B1-3-TuM-6 On the Origin of Multilayered Structure of W-B-C Coating Prepared by Non-Reactive Magnetron Sputtering from a Single Segmented Target***, **Michael Kroker**, P Soucek, M Fekete, L Zabransky, V Bursikova,* Masaryk University, Brno, Czech Republic*; P Zikan, A Obrusnik,* Plasma Solve, Brno, Czech Republic*; Z Czigany, K Balazsi,* Hungarian Academy of Sciences, Hungary*; P Vasina,* Masaryk University, Brno, Czech Republic

Machining tools are routinely coated with thin films to enhance their performance and durability. Nowadays used hard protective coatings exhibit high hardness and high stiffness; however, these positive features are often accompanied by negative brittle deformation behaviour, which facilitates formation and spreading of cracks. This leads to a premature degradation of the coated tool. A solution would be to prepare coatings simultaneously exhibiting high hardness together with enhanced ductility. Recently, there has been an increased interest in crystalline metal-boron-carbon based coatings [1] with X2BC stoichiometry which is inherently nanolaminated within the unit cell. According to the ab-initio models [1], these materials should exhibit an unusual combination of high stiffness and moderate ductility. A systematic theoretical study revealed that the nanolaminates with X = W should exhibit the best mechanical properties [1] making them the best candidates for experimental synthesis. Thus W-B-C coatings were sputter deposited in non-reactive atmosphere onto substrates performing a planetary motion around a central rotating cylindrical target composed from boron-carbide, tungsten and graphite segments in an industrial scaled deposition system of company SHM, Sumperk, Czech Republic. The coatings were deposited at the temperature of 450 °C and bias of -100 V by direct current magnetron sputtering. The SEM and TEM cross-section view revealed the presence of multilayered structure. The pattern of the multilayered structure was dependent on the type of planetary rotation around the central target. According to EDX and GDOES, the multilayered structure consisted of tungsten-rich layers alternating with boron- and carbon-rich layers. The whole structure consisted of thin layers with the thickness not exceeding 15 nm. The number of the multilayers was correlated with the number of the revolutions the sample performed during the deposition process. The multilayered structure was attributed to different transport pathways of heavy (W) and light (C and B) atoms sputtered from the target and scattered by working gas. 3D DSMC model was developed to explain the transport of sputtered atoms. The model is using the experiment geometry and initial velocities of sputtered particles calculated by TRIM. Results obtained with this model are in good agreement with experiment.

[1]H. Bolvardi, J. Emmerlich, M. to Baben, J, von Appen, R. Dronskowski, J.M. Schneider, Systematic study on the electronic structure and mechanical properties of X BC (X = Mo, Ti, V, Zr, Nb, Hf, Ta and W), J. Phys.-Condens. Mat. 25 (2013) 045501.

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