New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-2-ThM

Boron-Containing Coatings II

Moderators: Dr. Marcus Hans, RWTH Aachen University, Germany, **Prof. Helmut Riedl**, TU Wien, Institute of Materials Science and Technology, Austria, **Prof. Johanna Rosén**, Linköping University, Sweden

8:40am **F4-2-ThM-3 Ternary Tungsten Boride Coatings with Improved Mechanical Properties Deposited by High-Power Pulsed Magnetron Sputtering from One Spark Plasma Sintered Target***, **Tomasz Mościcki**, R. Psiuk, J. Chrzanowska-Gizynska,* Institute of Fundamental Technological Research of Polish Academy of Science, Poland*; D. Garbiec,* Łukasiewicz Research Network – Poznań Institute of Technology, Poland **INVITED**

Today the deposition of protective coatings with magnetron sputtering is well known in scientific laboratories and in industry also. However, there is an increasing need to coat larger and heavier tools. Also, sometimes substrate materials shouldn't be deposited at temperature greater than 300˚C. This is a problem because some of novel materials like tungsten borides needs high substrate temperature (>400 ˚C) during deposition to obtain special mechanical properties. According to Thornton deposition model the deposition of films at lowered substrate temperature with exceptional mechanical properties (ZONE T) is possible by increasing of the energy of plasma. Such possibility gives a HIPIMS method. Additionally, this method allows to deposit defected by vacancies α-WB_2 structure which according to first-principles calculation possess exceptional mechanical properties.

In this presentation the influence of HIPIMS parameters like the pulse duration, frequency and power and also the bias voltage and substrate temperature on ternary tungsten borides films properties will be shown and discussed. The deposited at 350 ˚C coatings by High-Power Pulsed Magnetron Sputtering from one Spark Plasma Sintered W-Ti-B_{z-x} target are very hard (H>30 GPa) and possess high crack resistance. Additionally, they are thermally stable at temperature below 700 ˚C. The comparison between Titanium and Tantalum as a doping element will be presented also.

This work was financed by the National Centre for Research and Development (NCBR, Poland) under project no. TECHMATSTRATEGIII/0017/2019.

9:20am **F4-2-ThM-5 The Architectural Design of High-Temperature Protective Coatings: Improving the Oxidation Resistance of TMB_2 (TM = Hf, Ti, W) Thin Films***, **Sophie Richter**, T. Glechner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; B. Widrig, 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,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal (TM)-borides are well known for their high thermal stability, high melting points, and excellent mechanical properties such as high hardness and Young's modulus, making them suitable for a broad field of applications. However, TM-borides suffer from poor oxidation stability at high-temperature ranges. Therefore, improving the oxidation resistance is of great interest for coated high-performance components, where both – a combination of mechanical and oxidative resistance – are particularly desired.

Within this study an architectural approach to protect TMB_2 (TM = Hf, Ti, W) thin films from further oxidation is presented. For this purpose, different materials were investigated as protective layers on top of each boride system. The coatings have been deposited by PVD techniques. The phase formation, morphology, and mechanical properties (e.g., hardness and Young's modulus) of all as deposited thin films were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM), and nanoindentation. Thermogravimetric analyses up to 1400 °C in synthetic air was utilized to investigate the barrier function of these coatings with respect to the underlying TMB_2 against oxidation. Subsequently, the long-term oxidation behavior of the synthesized films in ambient air at 1200 °C for 30 h was examined. In particular, the HfB_2 and TiB_2 systems were characterized by their oxidation resistance. High-resolution characterization techniques (i.e. TEM, HR-TEM, EDX) confirmed the good adhesion between the barrier top layers, as well as the unaffected diboride coatings and the sapphire substrates, respectively.

Keywords: Protective coatings; Oxidation resistance; High temperature; PVD; Borides;

9:40am **F4-2-ThM-6 Stoichiometry, Structure, and Mechanical Properties of Superhard Zirconium Diboride Films Prepared by the High-Power Impulse Magnetron Sputtering***, **Viktor Šroba**, K. Viskupová, T. Roch, L. Satrapinskyy, M. Truchlý, T. Fiantok,* Comenius University, Bratislava, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics SAS, Slovakia*; B. Grančič, P. Kúš, M. Mikula,* Comenius University, Bratislava, Slovakia

Diborides of refractory transition-metals (TMB_2) especially from IVB (ZrB_2, TiB_2) are thanks to their excellent mechanical properties like high hardness or wear resistance and high thermal stability, given by high melting temperatures (above 3000 °C), promising ceramic materials for applications in extreme environments. Magnetron sputtering of TM diboride films from compound target is accompanied by the different angular distribution of sputtered boron and metal atoms which leads to the growth of overstoichiometric films $TMB_{2+\Delta}$ (B/TM > 2), The films have a nanocomposite structure consisting of stoichiometric crystalline TMB_2 nanofilaments surrounded by an amorphous boron tissue phase. The presence and volume fraction of the boron tissue phase relative to the crystalline phase significantly determines the mechanical properties and affects behavior of the films during high-temperature exposure in a real environment. The progressive technology of high-power impulse magnetron sputtering (HiPIMS) using pulsed plasma discharges leads to the efficient ionization of the target atoms, whose flux and kinetic energy can then be controlled by appropriate synchronization with the pulsed negative substrate bias. In this way, a better control of the composition (B/TM) of the diboride films can be ensured, which then leads to the formation or absence of the boron tissue phase.

Here in this work, HiPIMS (Hipster 6, Sweden) with synchronized substrate bias is used to prepare ZrB_x films where changes in deposition parameters (pulse width, frequency, phase shift) on stoichiometry, formation of nanostructure and mechanical properties are investigated using X-ray diffraction, scanning and transmission electron microscopic and nanoindentation techniques. All ZrB_x films exhibit understoichiometric composition ratio of B/Zr which vary from 1.5 to 1.9. The films have a crystalline character identified as hexagonal α-ZrB_2. A deeper insight into nanostructure shows changes in nanocomposite character of the films. Hardness of ZrB_x films is up to ~ 45 GPa and indentation Young's modulus of ~ 430 GPa.

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).

10:00am **F4-2-ThM-7 Exploring Phase Evolution and its Consequences on Mechanical Properties of a Novel HfB_2-AlB_2 Coating System***, **Samyukta Shrivastav**, D. Yun, K. Canova, J. Abelson, J. Krogstad,* University of Illinois at Urbana Champaign, USA

Thin films of ternary $Hf_xAl_{1-x}B_y$ were deposited using low temperature (200-300°C) chemical vapor deposition (CVD), using the precursors $Hf(BH_4)_4$ and AlH_3NMe_3.We hypothesized that the addition of Al would increase the oxidation resistance of HfB_y, which in the absence of Al oxidizes quickly at service temperatures of 700°C. One issue with aluminum alloying would be the formation of a soft phase that may deteriorate mechanical properties of the coating. Here, we report in detail on the phase and properties of $Hf_xAl_{1-x}B_y$ films. Due to the very low growth temperature, only ~ 0.09-0.1 on the homologous scale, it was not known whether the ternary films would be amorphous or crystalline, fully mixed or segregated, nonstoichiometric in B, or include elemental Al. We report that as-deposited $Hf_xAl_{1-x}B_y$ contains only metal diboride and that, remarkably, the films are nanocrystalline with grain sizes ~ 10 nm. This is in sharp contrast to as-deposited HfB_2, which is X-ray amorphous and has a metal sublattice density about half that of the crystalline phase. The concentration of aluminum is uniform throughout the coating thickness, indicating that the CVD reactions at the growth surface are kinetically in steady-state. We qualitatively evaluated the mechanical response using nanoindentation, to compare the effect of alloying on mechanical properties. AFM analysis of the indent on the as deposited $Hf_xAl_{1-x}B_y$ coatings shows elastic recovery, whereas HfB_2 exhibits considerable plastic response with outer pileup. These results show an improvement in mechanical response due to alloying, and negate the presence of a soft elemental Al phase.The improvement in mechanical properties could be due to the presence of an HfAlB ternary, which will be further explored using advanced chemical characterization techniques such as STEM-XEDS. We have also seen that the coatings form a uniform oxide at 700°C, and heat treatments do not seem to bring about any changes in microstructure and microscale phase segregations. We will also be showing our results for any nanoscale compositional fluctuations present due to heat treatments at 700°C, and the impact of such fluctuations and heat treatments on mechanical properties will also be demonstrated.

10:20am **F4-2-ThM-8 Challenges and Perspectives of Wear Resistant Boron-Containing Coatings***, **Jose L Endrino**,* Nano4energy SL, Spain*; J. Rao,* Cranfield University, UK*; T. Brzezinka,* Dell Technologies, UK*; A. Mendez, J. Santiago,* Nano4energy SL, Spain*; J. Molina,* Polythecnic University of Madrid, Spain **INVITED**

This invited talk will present two different cases studies related to the deposition of new generation of boron-containing coatings with highly ionized physical vapor deposition techniques such as filtered cathodic-arc evaporation and positive pulse high power impulse magnetron sputtering (HiPIMS). Although the deposition of boron-based compounds, brings in the prospect of hard coatings exhibiting very useful physical prospects, the brittle nature of borides, high melting points and characteristic compound formation introduces a unique set of challenges as well.

The first case study deals with the use of TiB2 for arc evaporation after first densifying its structure and adding non-metallic sinter additives such as C and TiSi2. Cylindrical cone-shaped cathode configuration is used and coating properties were compared to those obtained from monolithic TiB2 cathodes. Arc spots were found to stick at certain locations, leading to extensive local fracturing of the cathode. TiB2-C required the lowest current setting (40A) to trigger an arc and provided the best arc-spot stability and mobility. Carbon inclusions successfully prevented crack propagation, although they did not stop crack initiation, which resulted in high cathode flaking and poor target utilization. An appropriate distribution of magnetic fields from filtering and focusing coils was found to be essential for maintaining stable and mobile arc spots on TiB2-C and TiB2-TiSi2 cathodes.

The second case study deals with the optimization of nanostructured AlTiBN and AlCrBN coatings by tailoring metal ion fluxes and energies using HiPIMS with positive pulses. In this study, the formation of nanocrystalline grains embedded in an amorphous boron-rich phase provides enhanced toughness and wear resistance. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained using nanoscratch testing.

11:00am **F4-2-ThM-10 TiB_x Thin Film Synthesis from an Industrial-Sized DC Vacuum Arc Source***, **Igor Zhirkov**, A. Petruhins, A. Shamshirgar,* Materials Design, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden*; N. Hellgren,* Department of Computing, Mathematics, and Physics, Messiah University, USA*; S. Kolozsvári, P. Polcik,* PLANSEE Composite Materials GmbH, Germany*; J. Rosen,* Materials Design, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden

Titanium diboride exhibits outstanding properties promising for the next generation of hard and wear resistant coatings. However, for efficient physical vapor deposition (PVD) through DC vacuum arc, the field is comparatively unexplored due to challenges associated with the materials synthesis process. It is well known that arc deposition allows synthesis of coatings with a deposition rate unreachable for any other PVD technique. This, in turn, can make DC arc deposition a preferred method for sustainable materials engineering, reducing the carbon footprint of the thin film industry. This motivates development and investigation of arc processes for TiB_2 synthesis. Furthermore, previously reported attempts of TiB_2 arc depositions from a TiB_2 cathode mentions process instability, cracking of the cathode, and intensive generation of macroparticles, which in turn limits an evaluation of the process efficiency. In this work, we show consistent analysis of the cathode surface, the plasma composition, the film composition (from XPS) and (micro-)structure (from SEM, XRD), as well analysis of collected macroparticles. The study is done with an industrial scale arc plasma source, Hauzer CARC+, which utilizes plane cathodes of 100 mm in diameter. The cathode weight loss, the amount of the generated droplets and the deposition rate is also measured as a function of process parameters (arc current and pressure). Furthermore, we also investigate tuning of the process efficiency by modifying the cathode composition. Plasma analysis shows average ion energies consistent with the velocity rule, around 115 and 25 eV for Ti and B, respectively. The plasma ion composition shows approximately 40 % Ti and 60 % B, while the deposited films are understoichiometric in B. The film hardness is found to be above 30 GPa for all shown samples. The deposition rate is around 100 nm/min, while the cathode weight loss is around 0.3 gram/min. Altogether, the results show potential for the use of cathodic arc as an efficient and useful method for synthesis of metal borides.

11:20am **F4-2-ThM-11 Oxidation Behavior of Stochiometric $Ti_{0.35}Al_{0.65}B_2$ Coatings***, **Sebastian Lellig**,* Materials Chemistry, RWTH Aachen University, Germany, and Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; A. Navidi Kashani,* Materials Chemistry, RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, and Lawrence Berkeley Lab, USA*; M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

The oxidation resistance of stochiometric $Ti_{0.35}Al_{0.65}B_2$ coatings is investigated systematically in a TEM study at temperatures of 700 to 1000 °C and annealing times of 1, 4 and 8 h.
In the as deposited state, a native, amorphous aluminum oxide layer covers the surface as well as the grain boundaries of the lamellar structure. The oxidation behavior upon annealing is dominated by the formation of a partly amorphous and nanocrystalline aluminum oxide layer, whereby the crystallinity is increased with higher annealing temperatures. At higher temperatures, spinodal decomposition leads to the segregation of AlB_2 and TiB_2. Ti diffusion through AlB_2 regions is hindered due to the low solubility of Ti in AlB_2. Outdiffusion of Al from binary and ternary regions lead to a homogeneous concentration distribution over the whole film. Simultaneously, the diffusion of Al through the oxide layer is hindered by nanocrystalline and amorphous regions. At temperatures ≥ 920°C, it is evident that AlB_2 phase segregations decompose, whereby liquid Al is formed, leading to the disintegration of the film. It is reasonable to assume that the application temperature range of other AlB_2 segregation containing transition metal borides is restricted by the here identified decomposition process.

Author Index

Bold page numbers indicate presenter