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 Contents on the Microstructure, Mechanical Properties, and Corrosion Resistance of WTixB 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.

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