Protective and High-temperature Coatings
Room Palm 5-6 - Session MA5-2-ThM

Boron-containing Coatings II

Moderators: Anna Hirle, TU Wien, Austria, **Martin Dahlqvist**, Linköping University, Sweden

8:40am **MA5-2-ThM-3 Influence of Boriding Treatment on the Tribological Performance of Tool Teel Repaired by Wire and Arc Additive Manufacturing**, ***Cesar Resendiz [resendiz.cesar@tec.mx]***, Tecnologico de Monterrey, Mexico

Interest in reconditioning metallic components has grown as a means to reduce industrial waste. Electric arc-based repair methods, including additive manufacturing techniques like Wire and Arc Additive Manufacturing (WAAM), impact microstructure and mechanical properties due to high heat input. Moreover, data on the reliability of components repaired through these methods under demanding tribological conditions remain limited. This study presents a tribological characterization of borided WAAM-repaired tool steel. To simulate tool damage, a groove measuring 6.35 mm in width and 3 mm in depth was created in AISI D2 steel samples using a spherical milling cutter. Material deposition was then manually performed by a certified technician using Gas Tungsten Arc Welding (GTAW) with ER308L wire, chosen for its availability and cost-effectiveness. Samples were subjected to three different conditioning treatments: (a) quenching and tempering followed by welding restoration (QTR treatment), (b) welding restoration followed by quenching and tempering (RQT treatment), and (c) welding restoration followed by boriding treatment (RB treatment). The physico-chemical characteristics of all samples were analyzed through optical microscopy and Raman spectroscopy. Mechanical surface properties were evaluated using instrumented indentation tests, while the adhesion of the boride coating on BT samples was assessed with VDI testing. Wear resistance and coefficient of friction (CoF) in both repaired and unrepaired regions of all sample types were measured using a micro-abrasion machine rig equipped with a load sensor. Wear scars were analyzed through scanning electron microscopy to identify dominant wear mechanisms. The results revealed that wear resistance in the repaired regions of QTR and RQT samples was significantly lower than that in their corresponding unrepaired regions. However, RB-treated samples exhibited consistent mechanical properties and tribological behavior, with improved wear resistance in both the repaired and unrepaired regions compared to QTR and RQT samples.

9:00am **MA5-2-ThM-4 Micromechanical Properties of $Ti_{1-X}Mo_XB_{2\pm z}$ Coatings Deposited by DCMS and HiPIMS**, ***Anna Hirle [anna.hirle@tuwien.ac.at]***, Christian Doppler Laboratory for Surface Engineering of High-performance Components,TU Wien, Austria*; Philipp Dörflinger, Rainer Hahn,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; Christian Gutschka, Tomasz Wojcik,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien,, Austria*; Maximilian Podsednik,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; Szilard Kolozsvári, Peter Polcik,* Plansee Composite Materials GmbH, Germany*; Carmen Jerg,* Oerlikon Surface Solutions AG, Liechtenstein*; Helmut Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, Austria

A promising strategy for enhancing the limited fracture characteristics of sputtered transition metal diboride (TMB_2) thin films, including hardness and fracture toughness, is the formation of ternary diborides. Theoretical predictions based on density functional theory (DFT) indicate that Mo alloying in TiB_{2+z} may prove beneficial in reducing the inherent brittleness of such diboride coatings. The present study aims to provide experimental investigations of ternary $Ti_{1-x}Mo_xB_{2\pm z}$ coatings prepared by direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HiPIMS) to validate the predictions and to investigate the influence of different deposition techniques.

A series of coatings was deposited using target compositions of TiB_2/C 99/1 wt. %, TiB_2/MoB 95/5 mol %, and TiB_2/MoB 90/10 mol %, resulting in coating compositions ranging from 0 at. % Mo to 4.7 at. % Mo. A variety of analytical techniques, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction analysis (XRD), were employed to characterize the microstructural properties. The chemical composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). To investigate the micromechanical properties of the ternary $Ti_{1-x}Mo_xB_{2\pm z}$ coatings, including hardness, fracture toughness, and fracture strength, nanoindentation, in-situ cantilever bending tests, and micropillar compression tests were employed.

The present study demonstrates that HiPIMS processes result in a considerable enhancement of hardness, fracture toughness, and fracture strength compared to DCMS. Specifically, the hardness of the HiPIMS coatings was enhanced from 38.8 ± 1.7 GPa to 43.7 ± 1.2 GPa, while the fracture toughness increased by 0.4 MPa√m and the $R_{p0.2}$ value rose by approximately 2 GPa. In comparison, the DCMS coatings exhibited a consistent decline in mechanical properties with increasing Mo content. Our findings highlight the significance of the energetics of growth conditions for novel ternary diboride systems.

9:20am **MA5-2-ThM-5 Tuning Properties of Diborides by Transition Metal Alloying Deposited by Combination of Magnetron Sputtering and Cathodic ARC Evaporation**, *Daniel Karpinski, **Keith Thomas [k.thomas@platit.com]**, Pavla Karvankova,* PLATIT AG, Switzerland*; Hannes Joost, Heiko Frank,* GFE-Schmalkalden e.V., Germany*; Pavel Soucek, Petr Vasina,* Institute of Physics and Plasma Technology, Masaryk University, Czechia*; Fedor Klimashin, Johann Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; Jan Kluson,* PLATIT a.s., Czechia*; Christian Krieg, Andreas Lümkemann, Hamid Bolvardi,* PLATIT AG, Switzerland

Titanium diboride is currently themost widespreadmetal boride (MeB_x) coating used in industry due to itsoutstanding properties such as high hardness >40 GPa, high melting point >3000 °C, and low propensity for sticking to soft metals.The main drawbacks of diborides are their generally low oxidation resistance (<800°C for TiB_2) and brittleness. This study investigates the effect of alloying MeB_xwithtransition metalson the structure, mechanical and tribological properties, and oxidation resistance of the coating. The coating deposition was performed in a Platit Pi411 machinewith LACS® technology which includes simultaneous magnetron sputtering from a central cylindrical cathode (SCiL®) and a cathodic arc evaporation from cylindrical cathode located in the chamber door (LARC®). Here, the MeB_x target was sputtered, and cathodic arc evaporation of Ti or Cr target was used for alloying thecoating. XRD, HRTEM structure study, nanoindentation and isothermal annealing in air at Ta=600–900°C revealed that by alloying of MeB_xwe can form the nanolaminate microstructure, tune the hardness and modulus, and enhance oxidation resistance of the coating, respectively.

10:20am **MA5-2-ThM-8 Effect of Duty Cycle on the Microstructure and Mechanical Properties of Titanium Diboride Thin Films Deposited by High-Power Pulsed Magnetron Sputtering**, *Jian-Fu Tang,* National Kaohsiung University of Science and Technology, Taiwan Jian-Fu Tang, Taiwan*; **Min-Yi Lin [M12188007@o365.mcut.edu.tw]**,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan, ROC*; Fu-Sen Yang,* Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taiwan, ROC*; Chi-Lung Chang,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan, ROC

With the rapid advancement of modern technology, the growing development of 5G and artificial intelligence (AI) has led to a substantial increase in demand for printed circuit boards (PCB). Enhancing the performance of cutting tools used in PCB drilling has become essential to meet supply and application needs, especially in the application of non-ferrous metal materials. Surface treatments aimed at improving tool wear resistance, high-temperature durability, anti-adhesion properties, hardness, and overall lifespan are common strategies in the industry. Titanium diboride (TiB_2) and titanium diboride-based nitride films, known for their high hardness, excellent wear resistance, high-temperature stability, and thermal conductivity, are ideal coating materials for cutting tools.

This study used high-power impulse magnetron sputtering (HiPIMS) to investigate the microstructure and mechanical properties of TiB_2 films deposited under various duty cycles. Five samples were prepared under identical target power output (3.5 kW) and frequency (200 Hz), using different duty cycle settings: 3%, 5%, 10%, 25%, and DC.The analysis results indicate that the peak power density increases with the duty cycle decrease. Energy dispersive spectroscopy (EDS) analysis also confirmed that the film composition was consistent with the alloy target proportions. Nanoindenter analysis shows that as the duty cycle decreases, the hardness increases significantly, from 28.3GPa to 43.2GPa, and the residual stress increases, from -0.21GPa to -6.18 GPa. This can be attributed to the higher peak power density effect. In addition, all samples showed good adhesion (HF1~HF2), excellent wear resistance (< 8.4×10^{-7} $mm^3N^{-1}m^{-1}$), and lower friction coefficient (0.39 to 0.55), indicating that TiB_2 films have potential in PCB drilling application.

Keywords: TiB_2, duty cycle, high power impulse magnetron sputtering, hardness, residual stress

10:40am **MA5-2-ThM-9 TiB_2/Hf Superlattices: Exploring Mechanical Strength, Fracture Toughness, and Stress-Strain Behavior***, **Naureen Ghafoor [naureen.ghafoor@liu.se]**, Firat Angay, Marcus Lorentzon,* Linköping University, IFM, Sweden*; Rainer Hahn,* TU Wien, Austria, Sweden*; Michael Meindlhumer,* University of Leoben, Austria*; Lars Hultman, Jens Birch,* Linköping University, IFM, Sweden

We present experimental investigations on iso-structural TiB_2/Hf superlattices, exploring the impact of layer thickness on hardness, toughness, and fracture resistance. Ab initio calculations, which guided material selection, reveal a basal-plane lattice and shear modulus mismatch of 0.16 Å (5.4%) and 200 GPa between TiB_2 and Hf, hindering dislocation glide at interfaces. Superlattices were deposited with periods ranging from 2 to 10 nm and were characterized by XTEM, XRD, and ERDA for structural and compositional details. High hardness (40 GPa) and structural integrity were achieved at lower Hf thicknesses and higher growth temperatures, with boron diffusion from TiB_2 into Hf forming single-crystal TiB_2 and understoichiometric HfB_2. No strain buildup or epitaxial breakdown was observed in films with up to 375 periods, attributed to self-diffusion. Pillar compression tests were performed to measure stress-strain curves and determine fracture values of the superlattices. A strong correlation between the metallic Hf layer and ceramic TiB_2 was observed, with fracture stress varying across samples—some exhibited values up to 22 GPa, while others showed localized plasticity. Fracture stress showed minimal dependence on the superlattice period, suggesting that morphology did not significantly influence mechanical behavior, as all coatings exhibited similar column diameters. Plasticity was attributed to localized slip, which was visible in SEM and analyzed in TEM. Boron and oxygen diffusion in Hf layers impedes flow, increasing strength but reducing elongation, consistent with the Hall-Petch effect. The high strength of Hf restricts dislocation motion, particularly in thin superlattices, while TiB_2's single-crystal structure eliminates easy fracture paths, enhancing toughness. Assuming similar trends to nitrides, TiB_2/Hf superlattices are expected to exhibit significantly higher fracture stresses. Based on the Young's moduli of TiB_2 (~400 GPa) and Hf (~80 GPa), a maximum outer fiber strain of 4% in bending would result in ~16 GPa in TiB_2 and ~3.2 GPa in Hf. The Hall-Petch effect further strengthens the material, with flow stress estimates between 4.7-6.7 GPa in tension, while bending primarily affects the outer layers. The difference in Young's moduli between TiB_2 and Hf contributes to high fracture toughness, highlighting TiB_2/Hf superlattices as promising materials for applications requiring high hardness, toughness, and fracture resistance.

11:00am **MA5-2-ThM-10 Production of Thin Films of Cubic Boron Nitride with Almost No Residual Stresses by Pulsed Laser Deposition and Laser Stress Relaxation***, **Falko Jahn [jahn@hs-mittweida.de]**,* Mittweida University of Applied Sciences, Germany*; Thomas Lampke,* University of Technology Chemnitz, Germany*; Steffen Weissmantel,* Mittweida University of Applied Sciences, Germany

For decades boron nitride has been researched as a coating material due to its outstanding mechanical, thermal and chemical properties. Especially the cubic phase (c-BN) as second hardest material known so far with high thermal and chemical resistance has driven the desire to make this material usable for industrial applications. Pulsed Laser Deposition has been one of the few deposition techniques with deposition rates of several tens nm per minute, high enough for industrial needs [1]. However, like other deposition techniques, PLD produced c-BN-coatings show very high compressive intrinsic stresses which limits the film thickness to a few hundred nm.

We present a method to produce thin films of cubic boron nitride which contain almost no residual stresses. These thin films were deposited using Ion Beam Assisted Pulsed Laser Deposition as sublayers of 100 nm film thickness on silicon substrates. Applying a modified laser stress relaxation technique [2], we were able to reduce the intrinsic compressive stresses in these sublayers from 10 GPa to less than 1 GPa.

Alternating deposition and stress relaxation of such sublayers successively enables film thicknesses relevant for industrial applications, such as wear resistant coatings. One possibility is to stack relaxed pure phase c-BN-sublayers in order to obtain applicable cubic boron nitride coatings. Another possibility is the combination of c-BN-sublayers with hard h-BN-sublayers to form multilayer system with increased mechanical properties. These h-BN-sublayers produced by PLD show indentation hardnesses in the range of 15 – 25 GPa, which allows the whole multilayer system to be superhard with indentation hardness above 40 GPa.

[1] S. Weissmantel, G. Reisse, Pulsed laser deposition of cubic boron nitride films at high growth rates, Diamond and Related Materials 10 (2001) 1973–1982. https://doi.org/10.1016/S0925-9635(01)00386-7.

[2] S. Weissmantel, G. Reisse, D. Rost, Preparation of superhard amorphous carbon films with low internal stress, Surface and Coatings Technology 188-189 (2004) 268–273. https://doi.org/10.1016/j.surfcoat.2004.08.070.

11:20am **MA5-2-ThM-11 Influence of Deposition Parameters on the Microstructure, Mechanical and Anti-Corrosion Characteristics of (Hfvtizrw)B2 High Entropy Alloy Boride Thin Films***, **Jun-Xing Wang [wangxing1470@gmail.com]**,* Ming Chi University of Technology, Taiwan*; Bih-Show Lou,* Chang Gung University, Taoyuan, Taiwan*; Riedl-Tragenreif Helmut,* Technische Universität Wien, Austria*; Jyh-Wei Lee,* Ming Chi University of Technology, Taiwan

In recent years, the exceptional mechanical and physical properties of highentropy alloy (HEA) boride thin films have garnered significant attention, sparking interest among the global industrial community, academia, and researchers. This study selected $(HfVTiZrW)B_2$ HEA boride as the target material to sputter $(HfVTiZrW)B_2$ HEA boride films under different substrate temperatures by high power impulse magnetron sputtering.

The results indicated that as the deposition temperature increases from 200°C to 500°C, the HEA boride films consistently exhibited a hexagonal close-packed (HCP) structure. Composition analysis and bonding energy assessments revealed that all films were metallic diborides.The highest hardness of 38.0 GPa was obtained for the film deposited at 500°C. The wear coefficient of friction was from 0.33 to 0.57. An excellent wear rate of 2.98×10^{-6} mm/N·m was achieved.

Observations from high-resolution transmission electron microscopy revealed that the grain size of the films increased from 11.39 ± 0.84 nm to 27.25 ± 3.59nm as deposition temperature increased from 200 to 500°C. The corrosion resistance of the HEA boride films in the 0.5 M H_2SO_4 aqueous solution was 38.89 times greater than that of 304 stainless steel. Furthermore, good oxidation resistance of HEA films in dry air atmospherebelow 600°C was observed. In summary, this study demonstratedthe $(HfVTiZrW)B_2$ HEA boride films exhibitedpromising applications as protective coatings for cutting tools and forming dies.

11:40am **MA5-2-ThM-12 Comparative Analysis of Oxidation Behavior and Mechanical Properties of $Hf_{0.24}Al_{0.06}B_{0.70}$ vs. $Hf_{0.35}B_{0.65}$ Thin Films***, **Eva B. Mayer [mayer@mch.rwth-aachen.de]**, Janani D. Ramesh,* RWTH Aachen University, Germany*; Zsolt Czigány,* Centre for Energy Research, Hungary*; Marcus Hans,* RWTH Aachen University, Germany*; Daniel Primetzhofer,* Uppsala University, Sweden*; Lukas Löfler, Jochen M. Schneider,* RWTH Aachen University, Germany

To improve the oxidation behavior of HfB_2 films for applications at high temperatures the addition of Al is a promising approach, however, at the expense of the mechanical properties, as the addition of 20 at.% Al causes a reduction in E-modulus by ~27 %. Therefore, the oxidation behavior and mechanical properties of magnetron sputtered $Hf_{0.35}B_{0.65}$ and$Hf_{0.24}Al_{0.06}B_{0.70}$ thin films are compared. ERDA, XRD and STEM data are employed to identify changes in composition, phase and oxide thickness, respectively, before and after isothermal oxidation in ambient air at 700°C for 1, 4 and 8 h each.

The addition of 6 at % of Al leads to the formation of an amorphous passivating oxide scale, exhibiting only 9.7 % of the scale thickness obtained on $Hf_{0.35}B_{0.65}$ after 8 h of oxidation. Nanoindentation measurements indicate that, the hardness and elastic modulus of $Hf_{0.24}Al_{0.06}B_{0.70}$ (35.6 ± 1.5 GPa and 501.4 ± 13.4 GPa) do not significantly differ from $Hf_{0.35}B_{0.65}$ (34.8 ± 1.0 GPa and 494.4 ± 13.8 GPa).

Hence, the incorporation of 6 at. % Al into HfB_2 improves the oxidation behavior by an order of magnitude, while the reduction in stiffness remains within the error range of the measurement.

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