Protective and High-temperature Coatings
Room Town & Country C - Session MA5-2-ThA

Boron-containing Coatings II

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

1:20pm **MA5-2-ThA-1 Tuning Oxidation Resistance and Mechanical Properties of Diborides by Transition Metal Alloying Deposited by Combination of Magnetron Sputtering and Cathodic ARC Evaporation***, **Daniel Karpinski (d.karpinski@platit.com)**, P. Karvankova, C. Krieg,* PLATIT AG, Switzerland*; H. Joost, H. Frank,* Gesellschaft für Fertigungstechnik und Entwicklung Schmalkalden e.V., Germany*; A. Lümkemann,* PLATIT AG, Switzerland

Titanium diboride is currently the most widespread boride coating used in industry. Its most common application is machining non-ferrous metals, due to its outstanding properties such as high hardness 40–50 GPa, high elastic modulus ≥ 500 GPa, high chemical inertness, high melting point above 3000°C, and low propensity for sticking to soft metals. The main drawbacks of diborides are their generally low oxidation resistance (between 600-700°C for TiB_2) and brittleness. As productivity demands from customers rise, the cutting speed and feed rate of the tool increase as well, resulting in elevated temperatures at the contact point between the workpiece and the tool. Therefore, there is a strong incentive to increase the oxidation resistance and/or reduce the coefficient of friction of the coating. This study investigates the effect of alloying diboride materials with transition metals, altering the boron-to-metal coating stoichiometry (x = B/Me), mechanical properties, tribological properties, and oxidation resistance of the coating. A Platit Pi411 coating machine equipped with LACS® technology was used to synthesize the coatings. This technology enables magnetron sputtering to be performed from a central cylindrical cathode (SCiL®) while simultaneously running a cathodic arc evaporation process from cylindrical cathodes located in the chamber door (LARC®). For this study, the metal boride (MeB_x) coatings were deposited by concurrent magnetron sputtering of a MeB_2 target and cathodic arc evaporation of a Me target (Me = Ti, TiSi, Cr and Zr) to tune the coating stoichiometry and composition. Nanoindentation tests revealed that this alloying strategy can decrease the B-to-Me ratio from 2.0 to 1.5, resulting in a hardness drop from about 45 GPa to 35-40 GPa. Isothermal annealing tests conducted in air at 600°C for 1 hour showed that decreasing the B-to-Me ratio of the coating effectively doubles the oxidation resistance of the coating. In addition, it was found that the use of ternary boron alloys leads to an even more pronounced increase in oxidation resistance, up to threefold.

1:40pm **MA5-2-ThA-2 Coherent Coexistence of Crystalline Phases Enabled by Planar Defect Formation in Annealed $V_{1-x}W_xB_{2-\delta}$Films***, **Katarína Viskupová (katarina.viskupova@fmph.uniba.sk)**, B. Grančič,* Comenius University in Bratislava, Slovakia*; P. Švec Jr.,* Slovak Academy of Sciences, Slovakia*; T. Roch, M. Truchlý, V. Šroba, L. Satrapinskyy, M. Mikula, P. Kúš, T. Fiantok,* Comenius University in Bratislava, Slovakia

Transition metal diboride films are characterized by high mechanical hardness, wear resistance and chemical stability at elevated temperatures. Combination of these advanced properties makes them applicable as protective coatings for alloy-machining tools. Typical nanocomposite structure of these films, consisting of hexagonal P6/mmm columnar grains surrounded by boron tissue phase, leads to high hardness above 37 GPa [1]. However, formation of the boron tissue phase is not convenient in terms of brittle fracture and oxidation resistance, which are the main drawbacks of diboride films. Therefore, one of the ways to improve the properties is to reduce the boron to metal ratio and aim for understoichiometric films [2]. Here, it is important to understand, how the boron deficiency will be accommodated by the films' structure, because it can significantly affect the mechanical properties [3]. In this work, we study the effect of boron understoichiometry on structure in case of ternary $V_{1-x}W_xB_{2-\Delta}$ films prepared by magnetron sputtering and ex-situ annealed up to 1200°C. We present results of detailed structural analysis by high-resolution transition electron microscopy, which revealed interesting structural features, including several types of planar defects and coexistence of coherently linked orthorhombic and hexagonal phase accompanied by chemical decomposition.

[1] P.H. Mayrhofer, C. Mitterer, J.G. Wen, J.E. Greene, I. Petrov, Self-organized nanocolumnar structure in superhard TiB2 thin films, Appl. Phys. Lett. 86 (2005) 1–3, https://doi.org/10.1063/1.1887824.

[2] J. Thörnberg, B. Bakhit, J. Palisaitis, N. Hellgren, L. Hultman, G. Greczynski, P.O. Å. Persson, I. Petrov, J. Rosen, Improved oxidation properties from a reduced B content in sputter-deposited TiBx thin films, Surf. Coat. Technol. 420 (2021), https://doi.org/10.1016/j.surfcoat.2021.127353.

[3] K. Viskupová, B. Grančič, T. Roch, Š. Nagy, L. Satrapinskyy, V. Šroba, M. Truchlý, J. Šilha, P. Kúš, M. Mikula, Thermally induced planar defect formation in sputtered V1-xMoxB2-Δ films, Scripta Materialia, Volume 229, 2023, 115365, ISSN 1359-6462, https://doi.org/10.1016/j.scriptamat.2023.115365.

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).

2:00pm **MA5-2-ThA-3 Powder Synthesis and Application of Atmospheric Plasma Spraying Zirconium Diboride Coating***, **Ching Lee (tiger881217@gmail.com)**,* National Taipei University of Technology, Taiwan*; Y. Chen,* Researcher of National Chung-Shan Institute of Science & Technology, Taiwan*; Y. Chung,* Researcher of National Chung-Shan Institute of Science & Technology, Taoyuan city, Taiwan*; Y. Yang,* National Taipei University of Technology, Taiwan

Zirconium diboride has excellent properties such as high melting point, high thermal conductivity, high hardness, low theoretical density, good electrical conductivity, etc., making it suitable for the outer shell of supersonic spacecraft and missiles. As spacecraft or missiles will generate heat sources due to friction with the atmosphere at high altitudes, it is necessary to attach a layer of high-temperature refractory materials to prevent the heat generated externally from reaching the inside of the body. This experiment uses Atmospheric Plasma Spray (APS) to prepare self-synthesized zirconium diboride, and explores the coatings prepared under different spray conditions (current, surface speed, working distance). The coating was analyzed such as X-ray Diffraction, Scanning Electron Microscope, Crystallinity Analysis, Bond Strength Analysis, Micro Hardness Analysis, etc.

2:20pm **MA5-2-ThA-4 Annealing Twins in Sputtered Tantalum Boride Coatings***, **Branislav Grančič (branislav.grancic@fmph.uniba.sk)**, K. Viskupová, T. Fiantok,* Comenius University in Bratislava, Slovakia*; P. Švec Jr.,* Slovak Academy of Sciences, Slovakia*; V. Šroba, V. Izai, T. Roch, M. Truchlý, M. Mikula,* Comenius University in Bratislava, Slovakia

Magnetron sputtered transition metal diboride TMB_{2-x} coatings with significant substoichiometry are often amorphous in the as deposited state [1, 2]. Subsequent annealing at high temperatures can lead to formation of various crystalline phases [3]. In our work, we study the effect of annealing up to 1300°C on structure of substoichiometric $TaB_{1.2}$ films. Analysis by High Resolution Transmission Electron Microscopy revealed crystallization into orthorhombic Cmcm structure with high density of annealing twin lamellae. Using ab-initio calculations we show that the formation of stacking faults on {110} planes are energetically favorable and accumulation of such defects can lead to formation of orthorhombic Pnma phase with similar formation energy as Cmcm phase. Moreover, the thermally induced structural changes were accompanied by coatings' hardness increase from 27 to 34 GPa.

[1] B. Grančič, M. Pleva, M. Mikula, M. Čaplovičová,L. Satrapinskyy, T. Roch, M. Truchlý, M. Sahul, M. Gregor, P. Švec,M. Zahoran, P. Kúš, Stoichiometry, structure and mechanical properties of co-sputtered $Ti_{1-x}Ta_xB_{2\pm\Delta}$ coatings, Surf. Coat. Technol. 367 (2019) 341–348, https://doi.org/10.1016/j.surfcoat.2019.04.017.

[2] K. Viskupová, B. Grančič, T. Roch, L. Satrapinskyy, M. Truchlý, M. Mikula,V. Šroba, P. Ďurina, P. Kúš, Effect of reflected Ar neutrals on tantalum diboride coatings prepared by direct current magnetron sputtering, Surf. Coat. Technol. 421 (2021), https://doi.org/10.1016/j.surfcoat.2021.127463.

[3] K. Viskupová, B. Grančič, T. Roch, Š. Nagy, L. Satrapinskyy, V. Šroba, M. Truchlý, J. Šilha, P. Kúš, M. Mikula, Thermally induced planar defect formation in sputtered $V_{1-x}Mo_xB_{2-\Delta}$ films, Scripta Materialia, Volume 229, 2023, 115365, ISSN 1359-6462, https://doi.org/10.1016/j.scriptamat.2023.115365.

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).

2:40pm **MA5-2-ThA-5 Constitution, Microstructure and Properties of Magnetron Sputtered CrB_2-TiB_2 and CrB_2-ZrB_2 Thin Films***, V. Ott,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; H. Riedl, T. Wojcik,* Vienna University of Technology, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; P. Mayrhofer,* Vienna University of Technology, Austria*; **Michael Stueber (michael.stueber@kit.edu)**,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal diboride thin film materials can provide interesting property profiles related to wear, oxidation and corrosion resistance, preferably at higher temperature and thermomechanical loads. To achieve such properties, intense efforts have recently been undertaken with regard to the microstructural design of diborides. These include for example different alloying strategies, incorporation of Si, formation of core-shell structures, defect engineering and advanced hybrid PVD processes for sophisticated thin film growth. However, the database on phase formation, microstructure and properties for PVD thin films in some material systems of interest is still surprisingly limited in comparison to transition metal nitrides and carbides. This study aims to contribute such information on DC magnetron sputtered thin films in the binary systems CrB_2-TiB_2 and CrB_2-ZrB_2. For both systems, a combinatorial approach for thin film deposition was followed, using segmented ceramic targets. The composition, phase and microstructure formation, characterized by EPMA, XRD and TEM methods, are systematically described for a broad compositional window in both systems. Selected mechanical properties, such as indentation hardness and modulus, as well as elastic and plastic deformation energies in micro indentation, are discussed versus the thin films' constitution and microstructure. Special focus is laid on the potential formation and impact of solid solution structured diboride thin films in the two quasi-binary systems that exhibit significantly different phase diagrams in thermodynamic equilibrium.

3:00pm **MA5-2-ThA-6 Fracture Characteristics of Si Containing Ternary and Quaternary Transition Metal Diborides***, **Anna Hirle (anna.hirle@tuwien.ac.at)**, A. Bahr, O. Beck, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria

Alloying with silicon or Si-based phases is an efficient approach to improve the oxidation resistance of transition metal diborides (TMBs). It is well established for bulk ceramics [1,2] but was also recently verified for thin film TMBs such as CrB_2, HfB_2, or TiB_2 [3,4]. Adding these strong oxide formers to diborides results in highly dense and protective SiO_2-based scales, whereas the amount of Si required differs between ternaries (pure Si addition) and quaternaries (alloying via disilicides), respectively. In more detail, alloying of $TaSi_2$ and $MoSi_2$ into TiB_2 thin films not only reduces the amount of Si needed to provide excellent oxidation resistance but also minorly influences the mechanical properties. For quaternary TiB_2 based coatings, hardness values of 36 GPa ($TaSi_2$) and 27 GPa ($MoSi_2$) compared to around 38 GPa of the binary system have been achieved. Interestingly, for ternary Ti-Si-$B_{2\pm z}$ films the mechanical properties vary in a wide range ceasing 20 GPa while exhibiting similar oxidation stabilities. All these coatings crystalized in the α-AlB_2 structure type with a preferred 0001 orientation being decisive for highest hardness.

Meanwhile the oxidation behavior and mechanical properties have been thoroughly described for ternary and quaternary TMBs so far [3,4] the fracture characteristics of these coating materials are rather unexplored. Based on a recent study [4] the fracture toughness (K_{IC}) of binary $TiB_{2\pm z}$ is known to be highly dependent on the amount of tissue phase present at the grain boundaries.

Therefore, this study aims to unravel the fracture resistance of Si containing ternary and quaternary TMBs, focusing on alloying routes with disilicides. A set of different coating compositions has been deposited by non-reactively DC magnetron sputtering using a broad set of composite targets TiB_2, TiB_2/$TiSi_2$ (90/10 & 80/20 mol%), TiB_2/$TaSi_2$ (90/10 & 80/20 mol%) and TiB_2/$MoSi_2$ (85/15 & 80/20 mol%). The elastoplastic behaviour involving also fracture characteristics such as K_{IC} are evaluated by micro-mechanical testing methods, such as cantilever bending or pillar compression testing, as well as nanoindentation. For an in-depth understanding, these results are correlated with detailed structure-morphological investigations using XRD, SEM, TEM, or ERDA/RBS.

[1] GB. Raju, et al,. J Am Ceram Soc. 2008;91(10):3320–3327.

[2] GB. Raju, et al., Scr Mater. 2009;61(1):104–107.

[3] T. Glechner, et al., Surf. Coat. Technol. 434 (2022) 128178.

[4] A. Bahr, et al.,Materials Research Letters. 11 (2023) 733–741.

3:20pm **MA5-2-ThA-7 Yttrium Tetraboride Thin Films – Thermal Evolution of the Nanostructure and Mechanical Properties***, **Marek Vidiš (marek.vidis@fmph.uniba.sk)**, M. Truchlý, V. Izai, T. Fiantok, T. Roch, L. Satrapinskyy,* Comenius University Bratislava, Slovakia*; Š. Nagy,* Slovak Academy of Sciences, Slovakia*; M. Mikula,* Comenius University Bratislava, Slovakia

Ultra-high temperature ceramics based on transition-metal diborides (TMB_2) attract attention due to their excellent chemical and mechanical properties. However, their practical application is limited by their inherent brittleness. The Y-B system offers a number of stoichiometric phases with a wide range of mechanical properties. The YB_2 has the lowest Young's modulus among the TMB_2, while the YB_6 is predicted to be a ductile ceramic. On the other hand, the YB_4 has the highest hardness among the Y-B phases, a melting temperature of 2800 °C, and a high flexural strength of 317 MPa. However, only a limited amount of knowledge is available about its properties in the form of a thin film. In this work, we focus on YB_4 thin film prepared by High Target Utilization Sputtering (HiTUS) technology using a stoichiometric YB_4 target. We report the evolution of the chemical composition, nanostructure, and mechanical properties after vacuum annealing up to 1300 °C. The EDS/WDS analyses show a slight over-stoichiometry of the sputtered film with a B/Y ratio of 4.7, a low oxygen content below 2 at.%, and a stable chemical composition with no boron loss. The as-deposited film is X-ray amorphous with a hardness of 23.4 GPa and a low Young's modulus of 281 GPa. After annealing at 800 °C, a partial crystallization occurs, and small regions with the tetragonal YB_4 phase in the amorphous matrix can be recognized. Further annealing leads to the grain coarsening of the YB_4 phase and formation of smaller grains of the cubic YB_6 phase. According to the XRD and HR-STEM, the coherence domain size increases from 26 nm to 44 nm for the YB_4 phase and from 7 to 53 nm for the YB_6 phase. The changes in the nanostructure are reflected in the mechanical properties of the film. The hardness increases to 26.4 GPa at 1000 °C, while a relatively low Young's modulus of 322 GPa is maintained. The ductile/brittle response to the mechanical loading is examined by cube-corner indentation. In the case of as-deposited film, a material pile-up at the edges with no crack formation is observed, indicating a ductile behavior of the X-ray amorphous film. After annealing, a crack formation is observed at the corners of the indents, which is a sign of a more brittle response. To conclude, the exceptional properties of YB_4 ceramic are confirmed in the form of thin sputtered films and are maintained even after high temperature loading. Therefore, the YB_4 thin film is a suitable candidate for example in superlattice architecture, where it would play the role of a medium-hard but less brittle layer in order to improve the overall toughness and thermal shock resistance of the coating.

Author Index

Bold page numbers indicate presenter