New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-1-WeA

Boron-Containing Coatings I

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

2:00pm **F4-1-WeA-1 Improving the Oxidation Resistance of TiB_2 Coatings by TM-silicide Alloying (TM = Ti, Ta, Mo)**, ***Ahmed Bahr*[1]**, *O. Beck, T. Glechner, A. Grimmer, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; E. Ntemou, D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

TiB_2 is considered a promising candidate among the family of transition metal diborides (TMB_2) to be applied in several high-performance applications under extreme conditions. In particular, the unique strength of TiB_2 is based on its high melting temperature (~3225 °C), high thermal shock resistance, and chemical inertness. However, the wide applicability of TiB_2 as a protective coating is still limited due to its poor high-temperature oxidation resistance by forming volatile, non-protective Ti- and B-based oxide scales. Si-alloying of TMB_2 provides a successful route to enhance the high-temperature oxidation resistance up to 1200 °C [1, 2]. Yet, the high Si content usually leads to the deterioration of the mechanical properties of these films [3].

Here, we investigated new alloying routes for sputtered TiB_2 coatings based on $TMSi_2$ secondary phases (TM = Ti, Ta, Mo) for achieving the challenging compromise between good mechanical properties and high oxidation resistance. We employed DC magnetron sputtering technique to synthesize TiB_2 alloyed coatings with different $TMSi_2$ phases from compound targets. The alloyed coatings were characterized in terms of chemical composition, phase constitution, and mechanical properties using high-resolution characterization techniques.Moreover, the oxidation kinetics within the alloyed Ti-(TM)-Si-B were studied at different temperature regimes up to 1400 °C, accompanied with detailed morphological characterization of oxide scales formed.

Keywords: Diborides; TiB_2; PVD; Protective Coatings; Oxidation; Mechanical Properties;

[1] T. Glechner, H.G. Oemer, T. Wojcik, M. Weiss, A. Limbeck, J. Ramm, P. Polcik, H. Riedl,Influence of Si on the oxidation behavior of TM-Si-B2±z coatings (TM = Ti, Cr, Hf, Ta, W), Surf. Coat. Technol., (2022) 128178.

[2] T. Glechner, A. Bahr, R. Hahn, T. Wojcik, M. Heller, A. Kirnbauer, J. Ramm, S. Kolozsvari, P. Felfer, H. Riedl,High temperature oxidation resistance of physical vapor deposited Hf-Si-B2±z thin films, Corrosion Science, 205 (2022) 110413.

[3] B. Grančič, M. Mikula, T. Roch, P. Zeman, L. Satrapinskyy, M. Gregor, T. Plecenik, E. Dobročka, Z. Hájovská, M. Mičušík, A. Šatka, M. Zahoran, A. Plecenik, P. Kúš,Effect of Si addition on mechanical properties and high temperature oxidation resistance of Ti–B–Si hard coatings, Surface and Coatings Technology, 240 (2014) 48-54.

2:20pm **F4-1-WeA-2 Quaternary CrTaBN: Experimental and Theoretical Insights Into a Novel Coating Material with Promising Mechanical Properties and Exceptional Thermal Stability**, ***Christina Kainz,*** Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; L. Patterer, D. Bogdanovski,* Materials Chemistry, RWTH Aachen University, Germany*; H. Krüger,* Institute of Mineralogy and Petrography, University of Innsbruck, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; I. Letofsky-Papst,* Institute for Electron Microscopy and Nanoanalysis and Center for Electron Microscopy, Austria*; M. Pohler, C. Czettl,* Ceratizit Austria GmbH, Austria*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany*; C. Mitterer,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Austria **INVITED**

Owing to their combination of excellent thermal stability, outstanding oxidation resistance and beneficial mechanical properties, ternary CrTaN coatings have recently received increasing interest for use in demanding applications. Although the addition of B to ternary transition metal nitride coatings is an effective strategy to improve their mechanical properties and thermal stability, studies on quaternary CrTaBN coatings are not available in literature. The present work provides a comprehensive overview on the microstructure, phase composition and thermal stability of $Cr_{0.69}Ta_{0.20}B_{0.11}N$ coatings grown by cathodic arc evaporation. Lab–scale X–ray diffraction yielded only the fcc-$Cr_xTa_{1-x}N$ solid solution being present as crystalline phase of the coating. X–ray photoelectron spectroscopy, however, confirmed the presence of B–N bonds. A combination of atom probe tomography and transmission electron microscopy showed that B forms nanoscale segregations, which seem to be preferably located at the grain boundaries. The thermal stability of CrTaBN was investigated by complementary application of X-ray photoelectron spectroscopy, atom probe tomography and *in–situ* high–temperature synchrotron X-ray diffraction. Annealing the coating at 1000 °C provokes no change in the crystalline phase composition, but induces a reduction of the B content and the formation of B–metal bonds. These findings on phase composition and thermal stability of the coating were furthermore compared to density functional theory calculations. Finally, *in-situ* high–temperature synchrotron X-ray diffraction and nanoindentation confirmed that CrTaBN allows for an exceptional oxidation resistance up to 1100 °C with simultaneous high hardness (32±2 GPa). The thorough investigation of phase composition and microstructure of CrTaBN at ambient and elevated temperatures provides the basis for a fundamental understanding of this novel coating system.

3:00pm **F4-1-WeA-4 Transition Metal Diboride Superlattices: Combination of *Ab Initio* and Experimental Approach for Investigation of Ceramic Thin Films with Improved Ductility and Fracture Toughness**, ***Tomáš Fiantok,*** Comenius University, Slovakia*; N. Koutná,* Linköping University, IFM, Sweden*; V. Šroba,* Comenius University, Slovakia*; M. Meindlhumer,* Austrian Academy of Sciences, Austria*; T. Roch, M. Truchlý, M. Vidiš, L. Satrapinskyy, M. Gocník,* Comenius University, Slovakia*; D. G. Sangiovanni,* Linköping University, IFM, Sweden*; M. Mikula,* Comenius University, Slovakia

Demanding high temperature mechanical applications create an opportunity to exploit the potential of transition metal diboride based thin films (TMB_2, TM = Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, Ta, W) due to their very high hardness and temperature stability. However, the industrial use of these materials is limited by their brittle behavior under high-temperature mechanical loads which results in the initiation and propagation of cracks leading to permanent failure.

One of the approaches to suppress the inherent brittleness of TM diboride films is the concept of superlattices (SL) – i.e., formation of alternating chemically and/or structurally modulated nanolayers. Such SL structures ensure efficient dissipation of accumulated energy in the vicinity of an already formed crack due to its deflection, blunting and stopping at the interface between the flexible and stiff layers.

In our work, using density functional theory (DFT) calculations, we predict the structural stability and theoretical ductility of 184 TMB_2 SL systems, where we search for suitable candidates exhibiting improved fracture toughness.

In the next step, we experimentally focus on the magnetron co-sputtered TiB_2 – TaB_2 films with different bi-layer period where we performed micromechanical bending tests on the film cantilevers which confirmed the

[1] **Graduate Student Award Finalist**

positive superlattice effect on improving the fracture resistance. In addition, for a more detailed explanation of the obtained results, the films are investigated using X-ray diffraction, and transmission electron microscopy. Mechanical properties (hardness and indentation modulus) are measured by nanoindentation techniques.

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).

The calculations were carried out using the resources by the Swedish National Infrastructure for Computing (SNIC)—partially funded by the Swedish Research Council through Grant Agreement (VR-2015-04630)—on the Clusters located at the National Supercomputer Centre (NSC) in Linköping"

3:20pm **F4-1-WeA-5 Tissue Phase Affected Fracture Toughness of Nano-Columnar TiB_{2+z} Thin Films***, **Anna Hirle**, C. Fuger, R. Hahn, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; M. Weiss,* Institute of Chemical Technologies and Analytics, TU Wien, A-1060 Vienna, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria

Despite being intensively investigated and already established in industry as protective coatings for aluminium machining [1] or diffusion barriers [2], Titanium-Diboride (TiB_2) is still not fully understood. In particular, for the fracture behaviour and the corresponding material characteristic (intrinsic fracture toughness, K_{IC}) the literature presents only little descriptions. So far it is known that the mechanical properties (H and E) of TiB_2 are highly dependent on the crystal orientation [3] and the amount of tissue phase present [4], which in turn can be influenced by the choice of coating parameters. To figure out, if this also affects the fracture behaviour, we synthesized a broad stoichiometric variation from $TiB_{2.07}$ up to $TiB_{4.42}$ by DC magnetron sputtering and thoroughly determined their structural, morphological and mechanical properties. By using micro-mechanical test set-ups (in-situ microcantilever bending tests) the intrinsic fracture toughness was investigated in relation to the chemical and hence morphological variation. In addition, information about the stress states within the thin films were obtained by nanobeam (synchrotron) experiments. The presence of a B-rich tissue phase was confirmed by HR-TEM analysis, showing that the grain size is decreasing with increasing B content, which is accompanied by an increase in tissue phase fraction. The dominance of the tissue phase is progressing with increasing B, also forcing smaller column sizes (from ~10 to < 5 nm) [5]. A change in Boron content from $TiB_{2.22}$ to $TiB_{4.42}$ leads to a decrease in fracture toughness from 3.55 ± 0.16 MPa√m to 2.51 ± 0.14 MPa√m of these superhard films. In summary, this study underlines the influence of stoichiometry and the potential of tissue phase engineering on the mechanical properties of TiB_{2+z} based thin films.

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[5] C. Fuger et al., Revisiting the origins of super-hardness in TiB2+z thin films – Impact of growth conditions and anisotropy, Surf. Coat. Technol. (2022) 128806.

3:40pm **F4-1-WeA-6 Characterization of Ti-Al-La-B-N Hard Coating and Cutting Tool Application***, **Shin Takayama**, T. Ishigaki, M. Takahashi,* Mitsubishi Materials Corporation, Japan **INVITED**

Current machining applications require new developments in the field of hard coatings to achieve excellent precision and effective processes. TiAlN thin films are well established due to their good thermo-mechanical properties. Recently, we reported TiAlLaBN films by sputtering. In the report the addition of La into the TiAlN lattice was shown to increase film hardness and H/E which correlates with film toughness. The microstructure of the film composes fine grain crystals with a size of 5 nm. However, the relationship between the microstructure of the TiAlLaBN film and its mechanical properties is still unclear. It is necessary to understand the relationship to maximize the cutting performance. The microstructure of the film can be varied by changing the deposition rate. Increasing the deposition rate may change the crystal grain size, leading to coarse grain microstructure. In this study, we investigate the changes in microstructure and mechanical properties by changing the deposition rate in order to improve the cutting performance.

Two different deposition approaches of sputtering and CAE (Cathodic Arc Evaporation) were used for changing the deposition rate. Ti-Al alloy added with 2 mol% LaB_6 was used as metal target. So as to prepare the metal target including unstable La, it was stabilized by combining with boron to form the LaB_6 compound. The deposition rate in CAE was 144 nm/min which was faster than in sputtering, 104nm/min. From the cross-sectional SEM observation and TEM images, the TiAlLaBN film of 144 nm/min was found to be a fine columnar structure with a width of 10 nm and length of 30 nm. The film hardness H and H/E of the fine-grained TiAlLaBN were H=40.1 GPa and H/E=0.095, then those of columnar structure were H=35.3 GPa and H/E=0.096, where E is elastic modulus. Both increased compared to H=31.3 GPa and H/E=0.065 for conventional TiAlN by CAE. The hardness of the TiAlLaBN film with fine-grained structure was found to be larger than that of columnar structure, while film toughness H/E was almost the same regardless of their different structures.

Milling cutting performance of TiAlLaBN with columnar structure was evaluated on ductile cast iron that was widely used for automobile parts. The TiAlLaBN with columnar structure showed 1.25 times better performance than TiAlN by CAE. The observation of the cutting edges indicated that TiAlLaBN with columnar structure reduces crack damage on the rake face by 20%. This is because the addition of La improves the film toughness and oxidation resistance. TiAlLaBN coatings deposited by stabilization with boron is expected to be an important material for future cutting.

4:20pm **F4-1-WeA-8 Mechanical Properties and Thermal Stability of ZrBSiTaN Films***, **Kuo-Hong Yeh**,* National Taiwan Ocean University, Taiwan*; L. Chang,* Ming Chi University of Technology, Taiwan*; Y. Chen,* National Taiwan Ocean University, Taiwan

ZrBSiTaN films were fabricated on silicon and AISI 420 stainless steel substrates through direct current magnetron co-sputtering. ZrB_2, Ta, and Si targets were used. The power applied on the Si target and the nitrogen flow ratio of the reactive gas were the variables in the sputtering processes. The effects of Si and N contents on the mechanical properties and thermal stability of ZrBSiTaN films were investigated. The results indicated that all the as-deposited ZrBSiTaN films formed amorphous structures. The supplement of reactive gas with a nitrogen flow ratio of 0.4 resulted in that the ZrBSiTaN films exhibited a high N content of 60 at.%. The increase of Si content from 0 to 42 at.% in ZrBSiTa films decreased the hardness and Young's modulus values from 19.1 to 14.3 GPa and 264 to 242 GPa, respectively, whereas the increase of Si content from 0 to 21 at.% in ZrBSiTaN films increased the hardness and Young's modulus values from 11.5 to 14.0 GPa and 207 to 218 GPa, respectively. The amorphous BN and SiN_x phases played the vital role in the variations of structural and mechanical properties of ZrBSiTaN films. The thermal stability test was conducted at 800 °C for 10 min within purged Ar gas in a rapid thermal annealing furnace. The ZrBSiTa films oxidized with the residual oxygen in the vacuumed furnace, which was accompanied with the formation of ZrO_2, Ta_2O_5, and $TaSi_2$ phases, whereas the ZrBSiTaN films maintained amorphous structures. Further exploration on the oxidation behavior of ZrBSiTaN films will be studied.

4:40pm **F4-1-WeA-9 Formation of Orthorhombic MAB Phase $Mo_{1-x}Cr_xAlB$ Solid Solution Thin Films***, **Peter J. Poellmann**, D. Bogdanovski, S. Lellig, M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; D. Holzapfel, P. Zoell, S. Karimi Aghda,* Materials Chemistry, RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

$Mo_{1-x}Cr_xAlB$ thin films were deposited by combinatorial magnetron sputtering at temperatures between 450 °C and 700 °C. Subsequent analysis by XRD, EDX, ERDA, and TEM revealed the compositional phase formation range to be between $0.38 \le x \le 0.76$ for orthorhombic MAB phase $Mo_{1-x}Cr_xAlB$, consistent with previous ab initio predictions, and can hence be rationalized by composition-induced changes in chemical bonding. For samples with lower x, the formation of Cr_2AlB_2, Cr_3AlB_4, and Cr_4AlB_6 side phases has been observed, again in accordance with theoretical and experimental literature data.

5:00pm **F4-1-WeA-10 Application of AlTiBN Coating for Cutting Tools for Exotic Materials Machining***, **Yuta Suzuki**, H. Kanaoka,* Sumitomo Electric Hardmetal Corporation, Japan

In recent years, the machining of difficult-to-cut materials, such as heat-resistant alloy and titanium alloy, has been increasing for aircraft, energy and medical markets. When cutting exotic alloys, the workpiece material is likely to adhere onto the cutting edge of a tool, resulting in a sudden fracture of the cutting edge of the tool. The tool life is significantly shorter than that of tools for cutting general steel. This study was intended to investigate the mechanical property and cutting performance of AlTiBN coating in order to solve the serious problems. AlTiBN coating was deposited on cemented carbide by arc ion plating method using nitrogen as reaction gas and Al-Ti-B alloys with B contents of 0, 2, 5 and 10 at. % were used as target materials. The mechanical properties of the coatings were measured by nano-indenter and the microstructure was evaluated by X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The cutting performance was evaluated by milling test of Ni-based heat-resistant alloy, and then tool life and damage to the coating at the early stage of machining were evaluated.In conventional PVD coatings for cutting tools, Cr and Si has often been added to AlTiN in order to increase hardness and heat resistance, achieving high wear resistance. However, these methods increase hardness as well as Young’s modulus, which reduces toughness of coating. In heat-resistant alloy and Titanium alloy milling, coatings with a high Young’s modulus tends to develop internal cracks, leading to early destruction of the coatings. In this research, we developed an innovative coating with high hardness and low Young's modulus for difficult-to-cut materials milling. Optimizing B content of AlTiBN coating, we realized low Young's modulus of 504 GPa while maintaining high hardness of 38 GPa. This is probably because the pure AlTiN changed to a mixed crystal structure of cubic and hexagonal by the addition of B. When the cutting performance of this AlTiBN coating was evaluated in milling for Ni based super alloy, material equivalent to Inconel 718, it was found that internal cracks were suppressed at the initial stage of processing. As a result, cemented carbide tool with the AlTiBN coating achieved approximately 1.6 times longer tool life than that with B-free AlTiN coating. As described above, the AlTiBN film with high hardness and low Young's modulus has not only excellent wear resistance but also excellent toughness, so it is expected to contribute to the improvement of productivity in aircraft, energy and medical markets.

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