New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-3-ThM

New Horizons in Boron-Containing Coatings III

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Helmut Riedl**, TU Wien, Austria, **Johanna Rosén**, Linköping University, Sweden

8:40am **F4-3-ThM-3 Synthesis of MoAlB Thin Films ContainingMoB MBene Regions***, R. Sahu,* Max-Planck-Institut für Eisenforschung GmbH, RWTH Aachen University, Germany*; D. Bogdanovski, S. Evertz, P. Pöllmann, D. Holzapfel, E. Mayer, J. Achenbach,* RWTH Aachen University, Germany*; S. Zhang,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; C. Scheu,* Max-Planck-Institut für Eisenforschung GmbH, RWTH Aachen University, Germany***; Jochen M. Schneider (schneider@mch.rwth-aachen.de)***,* Materials Chemistry, RWTH Aachen University, Germany

Two-dimensional (2D) inorganic transition metal boride nanosheets are emerging as promising post-graphene materials in energy research due to their unique properties. State-of-the-art processing strategies are based on chemical etching of bulk material synthesized *via* solid-state reaction at temperatures above 1000 °C. Here, we report the direct formation of MoB MBene domains in an MoAlB thin film by Al deintercalation from MoAlB in the vicinity of AlO_x regions. Hence, based on these results a straightforward processing pathway for the direct formation of MoB MBene-AlO_x-heterostructures without employing chemical etching is proposed here.

Furthermore, the nanolaminated ternary boride MoAlB exhibits a promising high-temperature oxidation resistance due to the formation of a dense alumina scale. While bulk synthesis of MoAlB requires temperatures larger than 1000 °C with up to 40% of excess Al in the feedstock, here we report the temperature range for the formation of single phase, orthorhombic MoAlB synthesized by magnetron sputtering from a stoichiometric target is 450 – 650 °C. Lower synthesis temperatures yield the formation of amorphous films, while at 700 °C, impurity phases form in addition to orthorhombic MoAlB. Amorphous MoAlB films were observed by in-situ X-ray diffraction to crystallize between 545 and 575 °C. Hence, we infer that the formation of orthorhombic MoAlB thin films issurface diffusion mediated below 545 °C. As bulk diffusion is activated between 545 and 575 °C the synthesis of fully dense MoAlB films with a maximum hardness of 15 ± 2 GPa and a Young's modulus of 379 ± 30 GPa at 600 °C is surface and bulk diffusion mediated.

9:00am **F4-3-ThM-4 On the Surpassing Fracture Toughness of TiB_2±z Thin Films***,* ***Christoph Fuger (christoph.fuger@tuwien.ac.at)****, A. Hirle, R. Hahn, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG , Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Their unique material characteristics make transition metal diboride-based thin films to perfect candidates for replacing state of the art protective and functional coatings. Not only machining tools but also high-precision components (e.g. turbine blades) within aircrafts and turbines used for energy production demand for surface improving materials. Mechanical properties like hardness, Young's modulus and fracture toughness of the thin films are essential to protect the components from impacting mechanical stresses, especially against sudden impacts at high stress levels. Well-known for their superior hardness, various TMB_2 exhibit enhanced resistance against fracture exceeding K_{IC} values of well-established nitride-based coating materials (e.g. TiN or $Ti_{1-x}Al_xN$) and are therefore perfect aspirants for various industrial applications.

Here, we focus on magnetron sputtered non-stoichiometric $TiB_{2\pm z}$ exhibiting outstanding mechanical properties. Beside super hardness of 45.90 ± 1.20 GPa and Young's modulus of 524.27 ± 14.10 GPa the coatings exhibit a fracture toughness of K_{IC} = 4.79 ± 0.57 MPa√m – tested via different micro-mechanical testing procedures. Detailed TEM and TEM-EELS investigations elucidate, that the distinct excess of boron predominates the constitution of the precipitating tissue phases around the columnar growth morphology. Due to covalently bonded boron-boron bonds the cohesive grain boundary strength is enhanced, impeding severe intercolumnar crack growth. The study highlights the great potential of $TiB_{2\pm z}$ for new applications in the field of high-performance components and reveal the importance of a detailed understanding of the grain boundary strength for fracture tough thin films.

Keywords: Fracture Toughness; Transition Metal Diborides; TiB_2; Tissue Phase; Micro-mechanical Testing;

9:20am **F4-3-ThM-5 Revealing the Beauty of Imperfection in Novel Diboride Coatings by Transmission Electron Microscopy***,* ***Justinas Palisaitis (justinas.palisaitis@liu.se)****,* Linköping Univ., IFM, Thin Film Physics Div., Sweden **INVITED**

Transition metal diborides (TMB_2) are considered as an extremely hard ceramics owning to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes TMB_2 coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1,2].Currently, magnetron sputtering is the primary technique for obtaining TMB_2 coatings. Typically obtained TMB_2 coatings are overstoichiometric in boron (B/TM>2) [3]. Recent addition of novel understoichometic variants of TMB_2 coatings (B/TM<2) have greatly widened their compositional range [3-8]. As the field of non-stoichiometric TMB_2 coatings is starting to open, this work offers the first systematic investigation into the different types of extended planar defects presented in the TMB_2 coatings throughout the wide compositional and elemental range. Atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects. Distinct types of planar defects residing on the {1-100} planes have been identified that are accompanied with or without local compositional changes. The characteristic atomic structures and factors leading to the formation of these planar defects in TMB_2 coatings will be presented.

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10:00am **F4-3-ThM-7 Thermally Induced Structure Evolution and Improved Oxidation Behavior of Ternary $Ta_{1-x}Al_xB_{2+\Delta}$ Hard Thin Films***,* ***Viktor Šroba (viktor.sroba@fmph.uniba.sk)****,* Comenius University, Bratislava, Slovakia*; T. Fiantok,* Comenius University in Bratislava, Slovakia*; M. Truchlý, T. Roch, B. Grančič,* Comenius University, Bratislava, Slovakia*; P. Švec,Jr.,* Institute of Physics, Slovak Academy of Sciences, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics SAS, Slovakia*; V. Izai,* Comenius University, Bratislava, Slovakia*; T. Glechner,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, Austria*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria*; P. Kúš, M. Mikula,* Comenius University, Bratislava, Slovakia

Diborides of transition metals (TMB_2) from IIIB to VIB group are due to their excellent mechanical properties and thermal stability promising materials for hard thin films used in extreme environments. Notable example being overstoichiometric $TiB_{2+\Delta}$ with value of hardness up to 60 GPa. However, formation of volatile boric acid (H_3BO_3) at elevated temperatures in air (450 °C for $TiB_{2+\Delta}$) and low fracture toughness expressed by high values of elastic modulus (500-600 GPa for $TiB_{2+\Delta}$) significantly reduce application potential of binary diboride coatings [1]. Alloying with aluminum to form ternary systems is well-proven method leading to improved oxidation resistance and higher hardness due to age hardening as a result of spinodal decomposition. This effect was theoretically predicted in $TiAlB_2$ by Alling et al. [2] and experimentally confirmed by Mockute et al. [3] in which decomposition of $TiAlB_{2+\Delta}$ films during annealing at 1000 °C led to increase in hardness from 32 to 37 GPa.

Here, we present structural evolution and oxidation behavior of ternary $Ta_{1-x}Al_xB_{2\pm\Delta}$ films. Experimental results obtained on magnetron co-sputtered $Ta_{1-x}Al_xB_{2\pm\Delta}$- films were supported by density functional theory (DFT) calculations on $TaAlB_2$ system. Addition of aluminum resulted in decrease of hardness from ~34 GPa for amorphous $TaB_{1.21}$ films to ~29 GPa for $Ta_{0.75}Al_{0.25}B_{2.14}$ films with typical 0001 texture of hexagonal α-AlB_2 type structure. Positive effect of aluminum alloying in improvement of oxidation behavior was observed during thermogravimetric analysis (TGA) with onset oxidation temperature of approx. 700 °C for $Ta_{0.75}Al_{0.25}B_{2.14}$ films compared to 600 °C for $TaB_{1.21}$ films.

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10:20am **F4-3-ThM-8 Mapping the X-B-C Systems: Search for the Elusive X_2BC Phase***, **Pavel Soucek (soucek@physics.muni.cz)**, S. Debnarova, M. Alishahi, S. Mirzaei, M. Kroker, L. Zabransky, V. Bursikova,* Masaryk University, Czechia*; Z. Czigany, K. Balazsi,* Centre for Energy Research, Hungary*; M. Hans, D. Holzapfel, S. Mraz, J. Schneider,* RWTH Aachen, Germany*; P. Vasina,* Masaryk University, Czechia **INVITED**

Binary borides and binary carbides have been known for many decades. Their outstanding mechanical, electrical and thermal properties made them indispensable in the industry, either in bulk or as thin films. The idea of combining these systems into a ternary X-B-C system naturally evolved. Such systems in the form of bulk have been investigated since the 1950s. The X has been from all of the s, p d and f blocks of the periodic table of the elements. Different structures were found. The orthorhombic Mo_2BC phase, being the first with the X_2BC stoichiometry, was described by Jeitschko in 1963 [1]. This structure attracted interest for its superconducting properties. Sixty years later, this is still the only synthesised X_2BC phase.

An interest in the X-B-C thin films can be traced to the mid-1980s, with experimental work accelerating in the 1990s. The focus was on the Ti-B-C system in the form of multilayers or in the form of a crystalline-crystalline nanocomposite. Superior mechanical properties of this system were described. A renaissance of the X_2BC phases, this time in the form of the thin films, has begun in 2009 when the Mo_2BC phase was prepared by direct current magnetron sputtering [2]. This phase was no longer studied for its superconducting properties, in which other materials superseded it, but for its highly unusual combination of high hardness and moderate ductility. Theoretical studies describing other crystalline ternary X_2BC phases predicting the thermodynamic possibility of their preparation together with even better mechanical properties followed [3]. Since then, several different systems from these predictions have been studied, including W-B-C, Nb-B-C and Ta-B-C. No definitive proof of the existence of any X_2BC phase apart from the original Mo_2BC phase was found. This contribution will cruise through the ups and downs of this research in the last decade. It will be shown that thin films from these systems can have interesting mechanical and thermal properties even without the formation of the desired and elusive X_2BC phase. It will be discussed why these phases won't form even under energetically very harsh conditions such as HiPIMS. We will also sketch the possibilities for the future directions of the studies of the X_2BCs.

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11:00am **F4-3-ThM-10 Industrial Deposition of W-B-C Coatings: Properties and Process Modelling***, **Michael Kroker (kroker@physics.muni.cz)**, P. Souček, L. Zábranský, V. Buršíková,* Masaryk University, Czechia*; V. Sochora, M. Jílek,* SHM s.r.o., Czechia*; P. Vašina,* Masaryk University, Czechia

W-B-C coatings have the potential to replace current state-of-the-art hard protective coatings in the industry owing to their unprecedented combination of high hardness and increased fracture resistance, as the brittle fracture is the most limiting shortcoming of the traditional hard protective coatings based on ceramics such as TiN, CrN, AlN, and their combinations. So far, only a few studies have dealt with industrial deposition of the W-B-C coatings.

This study shows the properties of W-B-C coatings industrially deposited by non-reactive magnetron sputtering using a system provided by SHM, Czech Republic. The system utilizes a single cylindrical sputter source fitted with a segmented target composed of tungsten, boron carbide, and graphite segments. The segmented target provides for the adaptation of the coatings' chemical composition by rearranging the position of individual segments. As an industrial standard, the planetary table capable of multi-axis rotation of substrates was used to simulate batch coating of the tools. The depositions were carried out in both stationary and single-axis rotation regimes to understand the differences between laboratory-like and industrial preparation of the coatings.

W-B-C coatings were studied over a broad range of chemical compositions. Although the coatings were mostly amorphous, they still exhibited high hardness (up to 29 GPa) and elastic modulus (up to 440 GPa). Detailed analyses of their mechanical properties proved their superior fracture resistance compared to current ceramic-based protective coatings. The comparison of the fracture resistance was possible using the instrumental indentation technique and indentation tip with a very small curvature radius (cube-corner diamond tip) and very thick coatings. This method induced cracking in the coating without the significant influence of the substrate.

To further ease the industrial utilization of these coatings, a simple yet powerful model was developed to predict the influence of the target setup and the influence of movement and placement of the substrates in the chamber. The modelling procedure was based on freeware SDTrimSP for the sputtering processes and SiMTra for the particle transport. The results showed very good agreement in terms of chemical composition as well as the relative thickness of the coatings. They were able to identify the crucial difference between the laboratory-like and industrial preparation of the W-B-C coatings.

11:20am **F4-3-ThM-11 Magnetron Sputter Deposition of Boron Carbide Films on Tilted Substrates***, **Swanee Shin (shin5@llnl.gov)**, L. Bayu Aji,* Lawrence Livermore National Laboratory, USA*; J. Bae,* General Atomics, USA*; A. Engwall, M. Nielsen, J. Hammons,* Lawrence Livermore National Laboratory, USA*; X. Zuo, B. Lee,* Argonne National Laboratory, USA*; X. Lepro Chavez, P. Mirkarimi, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Many applications of boron carbide films call for deposition onto non-planar substrates in the regime when the substrate normal is tilted away from the main deposition flux direction. Properties of boron carbide films deposited on such tilted substrates have not been previously studied, and the underlying physics of boron carbide film growth in the oblique angle deposition regime remains poorly understood. Here, we present results of our systematic study of the effect of substrate tilt on properties of boron carbide films deposited by direct current magnetron sputtering. The influence of the working gas (Ar vs Ne) on the deposition rate and film properties will also be discussed.

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