Topical Symposia
Room On Demand - Session TS2
New Horizons in Boron-Containing Coatings: Modeling, Synthesis and Applications

TS2-1 The Industrially Deposited W-B-C Coatings from Segmented Target*, Michael Kroker (kroker@physics.muni.cz)*, *P. Matej, P. Souček, L. Zábranský, V. Buršíková,* Masaryk University, Czechia*; V. Sochora, M. Jílek,* SHM, Czechia*; P. Vašina,* Masaryk University, Czechia

The coatings composed of transition metal (Me = Mo, W, Ta, Nb, …), boron, and carbon are promising candidates for next-generation hard protective coatings. The experimental studies are reporting a combination of high hardness and increased fracture resistance for Mo-B-C and W-B-C coatings, which are deposited using sputtering techniques at laboratory conditions. Such properties favor the use of Me-B-C coatings in the industry, where the demand for replacing the hard but brittle state-of-the-art ceramic coatings is significantly increasing.

For this study, the W-B-C coatings were sputter-deposited by non-reactive magnetron sputtering using an industrial system provided by the company SHM, Czech Republic. The system utilizes as a sputter source a cylindrical rotating segmented target composed of metal, boron carbide, and graphite segments. As an industrial standard, the planetary table capable of multi-axis rotation of substrates was used to simulate the batch coating of the tools. The depositions were carried out in both stationary regime and single-axis rotation regime to understand the differences between laboratory-like and industrial preparation of the coatings.

The properties of the W-B-C coatings were studied over a broad range of their chemical composition. Despite the coatings were mostly amorphous, they still exhibited high hardness (up to 30 GPa) and elastic modulus (up to 450 GPa). The coatings deposited in the rotation regime exhibited multilayered character due to different transport pathways of the light (B,C) and heavy (W) elements. Detailed analyses of their mechanical properties proved their superior fracture resistance compared to current ceramic based protective coatings. Low internal stress in the coatings together with good adhesion enabled to deposit sufficiently thick coatings on the test samples and tools used in forming applications. The application relevant testing was performed at the end-customers of SHM in the Czech Republic.

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TS2-2 Thermo-physical Properties of CVD Ti(B,N) Coatings*, Christina Kainz (christina.kainz@unileoben.ac.at)*, *N. Schalk, M. Tkadletz, C. Saringer,* Montanuniversität Leoben, Austria*; M. Winkler,* Fraunhofer Institute for Physical Measurement Techniques IPM, Germany*; A. Stark, N. Schell,* Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Germany*; J. Julin,* Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Germany*; C. Czettl,* Ceratizit Austria GmbH, Austria

Hard protective coatings are commonly subjected to temperatures up to 1000 °C, which has a significant influence on their thermo–physical properties and the associated performance in application. Within the present work, temperature dependent physical properties of chemical vapor deposited (CVD) coatings within the Ti(B,N) system were correlated with their chemical composition. High–energy X-ray diffraction experiments in inert atmosphere proved that CVD TiN, TiB_2 and ternary TiB_xN_y coatings with varying B contents are thermally stable up to 1000 °C. With increasing B content, the TiB_2 fraction in the coating increased gradually, whereas the grain size decreased. First order tensile strains of TiN and ternary TiB_xN_y coatings with different compositions decrease during heating. Contrary, TiB_2 exhibits compressive strain enhancement up to the deposition temperature, followed by strain relaxation thereafter up to 1000 °C. Nanocrystalline TiB_2 exhibits more pronounced grain growth during annealing compared to coarse grained columnar TiN. The mean thermal expansion coefficient decreases as the B content increases from $9.18\times10^{-6}\ K^{-1}$ in TiN to $7.95\times10^{-6}\ K^{-1}$ in TiB_2. The thermal conductivity decreases from 45 W/mK in TiN to 14 W/mK in TiB_2 and correlates with the grain size of the coatings. Annealing of TiB_2 resulted in an increment of the thermal conductivity (38 W/mK), which is ascribed to the less pronounced phonon scattering with increasing grain size and lower defect density. In summary, the present work provides a comprehensive overview of the thermo-physical properties of CVD coatings in the Ti(B,N) system filling a gap in the existing literature.

TS2-3 Chemical Shift in W-B-C Systems: Experiments and Modeling*, Jaroslav Ženíšek (jzenisek@mail.muni.cz)*, Masaryk University, Czechia*; P. Ondračka,* RWTH Aachen University, Germany*; P. Souček,* Masaryk University, Czechia*; D. Holec,* Montanuniversität Leoben, Austria*; M. Stupavská,* Masaryk University, Czechia*; J. Schneider,* RWTH Aachen, Germany*; P. Vašina,* Masaryk University, Czechia

This work discusses and reviews the generally accepted assumptions commonly used in the XPS bonding analysis of different materials. These are in the presented case applied to amorphous W-B-C materials with different compositions. We focus ourselves on the chemical shift of 4f electronic states of W atoms. In the W-B-C systems, the formation of binary W–B and W–C bonds leads to a shift in core-level to lower and higher binding energies, respectively, of W 4f core electrons due to the differences in the Pauling electronegativity of W, B and C. For the theoretical verification of this assumption we generated three amorphous W-B-C atomic models of different compositions (W:B:C ratios), calculated the W 4f core electron binding energies from *ab initio* methods and compared them with the measured XPS profiles of deposited W-B-C with the same W:B:C ratios. The atomic models reproduced the behaviour of the deposited systems in terms of XPS profiles. In the next step, we used the models to analyse the relationships between the W 4f electron binding energies and the local atomic environments of W atoms. It was found that the relative W 4f peak positions depend on the B/C ratio in the system, as was expected and as is commonly assumed in the bonding analysis. However, the relative amount of W and its density fluctuations in the volume of the unit cell on the other hand, which is usually omitted in the bonding analysis, also led to a chemical shift of the W 4f peak. Therefore, several series of amorphous W-B-C coating were deposited in a way to obtain amorphous coatings with compositions allowing to separate the effect of B/C ratio and the amount of W on the W 4f peak positions. The experimental positions of the W 4f peaks confirmed the theoretical predictions and have shown that general simplified assumptions based on electronegativity of elements need to be taken with care for precise chemical analysis of the bonding in W-B-C coatings.

TS2-4 Superior High-temperature Behavior of Amorphous Coatings from Quinary Hf-B-Si-C-N System*, Petr Zeman (zemanp@kfy.zcu.cz)*, *S. Zuzjakova, R. Cerstvy,* University of West Bohemia, Czech Republic*; E. Meletis,* University of Texas at Arlington, USA*; J. Vlcek,* University of West Bohemia, Czech Republic

Multielement ceramic coatings are appropriate candidates for high-temperature applications due to their excellent behavior at temperatures exceeding 1000°C. When the excellent oxidation resistance is combined with the thermal stability of a high optical transparency, they can be applied for high-temperature passive protection of optical and optoelectronical devices. On the other hand, a combination of the high oxidation resistance and the thermal stability of the electrical conductivity makes them suitable for capacitive pressure, vibration or tip clearance sensors in a severe oxidation environments.

The present work focuses on systematic investigation of high-temperature behavior of two amorphous Hf-B-Si-C-N coatings with different electrical and optical properties. The coatings were prepared by reactive pulsed dc magnetron co-sputtering of a B_4C-15%Hf-20%Si target in two Ar+N_2 mixtures (15% and 20% N_2 fractions). Particular attention is paid to thermogravimetric analysis and differential scanning calorimetry of the coatings in air and Ar, and to the evolution of the film structure, microstructure and elemental composition with increasing annealing temperature from 1100°C to 1700°C.

The coating prepared at the 15% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{22}C_6N_{40}$ and is electrically conductive, while the coating prepared at the 20% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{17}C_4N_{45}$ and is optically transparent. Both coatings are sufficiently hard (≈ 20 GPa) and exhibit a superior oxidation resistance up to 1600°C due to the formation of a nanocomposite diffusion barrier surface layer consisting of HfO_2 nanocrystallites surrounded by a borosilicate amorphous matrix. A small difference in the composition results, however, in a different thermal stability of the amorphous structure of the coatings above 1400°C. While the $Hf_7B_{23}Si_{17}C_4N_{45}$ coating underneath the oxide layer retains its amorphous structure, the $Hf_7B_{23}Si_{22}C_6N_{40}$ coating crystallizes into different phases (Si_3N_4, B(C)N, HfCN, HfB_2) with a unique self-organized structures [1,2].

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TS2-5 Application of the Heat Balance Integral Method to the Growth Kinetics of Nickel Boride Layers on Inconel 718 Superalloy

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The nickel-based superalloys are designed to meet industrial requirements to withstand higher temperatures during the long-term service. They have wide applications in the aerospace, marine, nuclear, and petrochemical industries due to their excellent oxidation and corrosion resistance. However, because their high nickel content, these alloys are susceptible to abrasive, erosive and adhesive wear damage. Boriding process is considered as an efficient method for improving the tribological properties of nickel-based superalloys. These superalloys were successfully borided by using different methods without impairing corrosion and oxidation resistance. Among the boriding processes, the powder-pack boriding is a highly effective and low-cost method to produce hard nickel borides with outstanding properties.

From a kinetic viewpoint, the growth kinetics modeling is very substantial to select the optimum values of boride layers' thicknesses matching the practical use of nickel-based superalloys in terms of wear conditions.

The Heat Balance Integral Method (HBIM) is an alternative to investigate the boriding growth kinetics of nickel-based superalloys. This approach, originally applied for analyzing thermal problems, is based on numerical resolution of a system formed by differential algebraic equations (DAE) under certain assumptions.

In the present work, new results about the growth kinetics of nickel boride layers on an Inconel 718 superalloy was estimated considering a diffusion model based on the HBIM. The boron diffusion coefficients in nickel boride layers were estimated in the temperature range of 1123 - 1223 K at different exposure times. In addition, the layers were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and Berkovich indentation techniques to determine the phases formed on the surface, the microstructure and the chemical composition across the depth of the layer-substrate, and the distribution of the hardness, respectively.

TS2-6 Influence of the Diffusion Annealing Process in the Corrosion Susceptibility of Cobalt Boride Layer Immersed in Hank's Solution

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The corrosion susceptibilities of the borided CoCrMo alloy exposed to the diffusion annealing process (condition I) and the borided CoCrMo alloy (condition II) immersed during 7 days in Hank's solution were evaluated. Firstly, the CoCrMo alloy was exposed to the powder-pack boriding process (PPBP) during 5 h at 1273 K, to obtain a biphasic layer (CoB-Co_2B) with a total thickness around 30 µm. Then, the diffusion annealing process (DAP) was performed in the borided CoCrMo alloy during 2h at 1273 K in an inert argon atmosphere to obtain a 30 µm of monophasic Co_2B layer. The potentiodynamic polarization technique was used to evaluate the corrosion resistance (R_p) using the linear polarization technique (LPR) and the corrosion current density (j_{corr}) from the Tafel extrapolation technique. In addition, the corrosion resistance estimated from conditions I and II were compared with the CoCrMo alloy (reference material). The results showed, in the 7th day of immersion in the Hank's solution, that the condition I (~357 kΩ cm^2) exhibited corrosion values ~24 times higher than those obtained by the condition II (~15 kΩ cm^2) reaching values close to the reference material (~385 kΩ cm^2). The corrosion behavior of the borided CoCrMo alloy exposed to the diffusion annealing process was attributed to: i) the presence of the monophasic Co_2B layer on the surface of the borided CoCrMo alloy, ii) the redistribution of Cr and Mo after the process, which increased the content of these elements at the surface of the borided alloy and iii) the inhibition of the B_2S_3 and $CrPO_4$ species, which has a detrimental effect on the corrosion behavior at the surface of borided CoCrMo alloy. Finally, the effect of the diffusion annealing process (condition I) reduced the corrosion susceptibility of the cobalt boride layer around 7% in comparison to the value of 96 % estimated for the borided CoCrMo alloy (condition II).

TS2-7 Pulsed-DC Powder-Pack Boriding: Growth Kinetics of Boride Layers on AISI 316 L Steel and Inconel 718 Alloy

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The conventional powder-pack boriding process (PPBP) is a surface hardening treatment, which results in the formation of boride layers to enhance the mechanical and chemical properties of the materials. Particularly, in the PPBP, the growth kinetics of the boride layers depends basically on the boriding temperature, the exposure time, and the content of the powder mixture (B_4C, SiC and KBF_4), using temperatures for the process in the range of 1123 to 1223 K with long exposure times (4 to 12 h).

Facing this problem, several studies have developed an alternative process to reduce exposure times in the formation of boride layers at the surface of various steels and alloys, using a direct current field in the powder-pack boriding process (PBDCF). During the process, the current flux between the electrodes follows the direction of the conventional current (from positive to negative), however, the migration of the boron atoms, on the surface exposed to the cathode, is opposite to the normal direction of diffusion, consequently, the growth of the boride layer is slower than that exposed to the anode.

Based on the aforementioned, this study develops a novel treatment called pulsed-DC powder-pack boriding (PDCPB). This treatment employs a DC power supply coupled to an electronic programable control device (EPCD) to generate timed cyclic polarity changes on the flux of ionized boron atoms. The effect of the pulsed DC current field provides a homogeneous boron diffusion during the PDCPB, which promotes the growth of similar boride layer thicknesses on both surfaces (anode and cathode) exposed to the direct current field. The PDCPB treatment was performed on the AISI 316 L steel and Inconel 718 alloy at temperatures of 1123 - 1223 K with different exposure times for each temperature. The powder mixture consisted of B_4C, SiC and KBF_4, supplying a current input of 5 A and polarity inversion cycles of 10 s.

Finally, the growth kinetics of the boride layers, in both materials, was established using a diffusion model that considers two mass balance equations at the growth interfaces, considering that the boride layers obey the parabolic growth law. The boron diffusion coefficients in the boride layers, were expressed as a function of the experimental temperatures using the Arrhenius relationship to estimate the boron activation energies. The results showed that the boron activation energies, estimated for the boride layers, decreased drastically (17% for the borided AISI 316 L steel and 31% for the borided Inconel 718 alloy) compared to those obtained for the conventional powder-pack boriding process.

TS2-8 Stoichiometry, Structure and Mechanical Properties of Co-Sputtered $Ti_{1-x}Ta_xB_{2\pm\Delta}$ Coatings

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Ternary transition metal diborides $M^1_{1-x}M^2_xB_2$ represent a promising class of materials for hard wear-resistant coatings [1]. By using co-deposition from two binary stoichiometric targets, it is possible to prepare a ternary system in a wide x range. However, the varying boron-to-metal ratio often embodies obstacles/difficulties in the evaluation of the effect of x on coating properties. The mechanisms that determine the resulting boron-to-metal ratio are dependent on the target material and may significantly alter the resulting coatings' properties [2].

We use magnetron co-sputtering from TiB_2 and TaB_2 stoichiometric targets to prepare AlB_2-prototype ternary $Ti_{1-x}Ta_xB_{2\pm\Delta}$ solid solution, with x in the range from 0 to 1. Using this technique, the boron-to-metal ratio (B/Me) varies with the actual Ti and Ta content. The boron-to–tantalum ratio can be increased by decreasing the TaB_2 target voltage, which has a considerable effect on the coating structure. Coatings with B/Me > 2 reveal highly textured nanocolumnar structure, while the coatings with B/Me < 2 tend to be nanocrystalline (without any preferred crystallite orientation) or amorphous. All the deposited coatings have a hardness higher than 32 GPa. The under-stoichiometric (B/Me < 2) coatings show material pile-up around the cube-corner indent edges, an indication for plastic flow and increased ductility.

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TS2-9 Effect of MB_2 (M = Zr, Ta, Nb, Hf, Ti, V, Cr) and W_2B_5 Target Composition on Plasma Properties and Thin-Film Stoichiometry During Magnetron Sputtering*, Igor Zhirkov (igor.zhirkov@liu.se),* Linköping University, Sweden*; F. Klimashin,* Linköping University, Sweden*; G. Greczynski,* Linköping University, Sweden*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan*; I. Petrov,* University of Illinois, USA, Linköping University, Sweden*; J. Rosen,* Linköping University, Sweden

DC magnetron sputtering (DCMS) is a widely used technique for the deposition of decorative, protective, and wear-resistive coatings. However, high power impulse magnetron sputtering (HiPIMS), due to the pulsed nature and higher peak current/power, is able to provide a much higher degree of sputtered atom ionization. This allows for a better control of the material flux, and a pathway for tuning of thin-film stoichiometry and microstructure. The physical vapor deposition synthesis of metal diborides (MB_2) is an expanding area of research and is primarily carried out by sputtering from a compound target. For both HiPIMS and DCMS, the material flux from the target goes through three primary stages – sputter ejection, plasma transport, and film deposition. The target composition is rarely preserved in the resulting film stoichiometry. In the present work, we have performed a systematic study of HiPIMS and DCMS plasmas generated from circular 5 cm diameter ZrB_2, TaB_2, NbB_2, HfB_2, TiB_2, VB_2, W_2B_5, and CrB_2 targets at Ar pressures of 3 and 20 mTorr. For all depositions, the average power is kept constant at 50 W, with HiPIMS being operated at a repetition rate of 100 Hz and a pulse length of 100 µs. Plasma characterization, including plasma chemistry and time- and charge-resolved ion energy distributions, is performed with a spectrometer-to-target distance of 15 cm. Corresponding films were deposited using the same geometry, for compositional characterization and a comparison to the plasma and target composition. The obtained results are discussed as a function of the material properties of the metal diboride targets, and in view of the differences in mass of the metal component. The study is aimed at developing an understanding of the synthesis of stoichiometric MB_2 using sputtering techniques.

TS2-10 Recent Process Development of Magnetron Sputtering Deposited Boron Carbide Thin Films for Neutron Detection at the European Spallation Source*, Chung-Chuan Lai (chung-chuan.lai@esss.se), C. Höglund, P. Svensson,* Detector Group, European Spallation Source ERIC, Sweden*; L. Robinson,* Detector Group, European Spallation Source ERIC,Sweden*; J. Birch, L. Hultman,* Thin Film Physics Division, IFM, Linköping University, Sweden*; R. Hall-Wilton,* Detector Group, European Spallation Source ERIC, Sweden

The construction of European Spallation Source (ESS) is aimed to build the brightest large neutron spallation source for research in material science. Since the decision made in 2009 to site ESS in Lund, Sweden, the staff in ESS has pushed forward the development in all fields to fulfill the goal of a world leading research facility. In line with increasing needs and costs for helium-3 (^3He), design and development of neutron detectors using boron-10 (^{10}B) gain practical value as a promising alternative for large area neutron detectors in ESS. Amorphous boron carbide (a-B_4C) is a common chemical form of choice for the detectors mainly due to its 80 at.% of B stoichiometry, chemical stability, and non-toxicity. In ESS Detector Group, a reliable and reproduceable direct-current magnetron sputtering deposition process for amorphous boron carbide (a-B_4C) coatings has been developed by ESS Detector Coatings Workshop in Linköping, Sweden, in collaboration with Linköping University. The process produces coatings with good adhesion to Al and Ti substrates, low H and O content, ~85 % mass density of bulk B_4C, and good radiation hardness. On top of this, the Coatings Workshop are continuously developing new processes of depositing a-B_4C coatings on a wider range of substrate materials or dimensions for the needs of various detector designs, e.g., PCB materials (G-10 and FR-4), other metals (Cu and Au), glass, Al foils with a thickness down to 18 mm, and removable substrates for stand-alone B_4C films. Characterization of the coatings helps to determine the influence of changing deposition parameters, such as substrate temperature, working pressure, and substrate materials, as well as a possible tradeoff of desired properties, such as low O content. We have also observed changes in the microstructure related to the difference in surface material and smoothness, which can further affect the physical properties or adhesion of the deposition films. Development of the coating processes has allowed the Coatings Workshop to be the go-to facility for institutes to search for a new generation of neutron detectors using $^{10}B_4C$ films, which is the core technology for more than half of the instruments in ESS.

TS2-11 Thermomechanical Properties and Oxidation Resistance of Ternary $W_{1-x}Ta_xB_{2-z}$ Coatings*, Christoph Fuger (christoph.fuger@tuwien.ac.at),* TU Wien, CDL-SEC, Austria*; V. Moraes,* Institute of Materials Science and Technology, TU Wien, Austria*; R. Hahn,* TU Wien, CDL-SEC, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Future tasks in many different fields of academia and industry are directed towards environmental sustainability, asking also for new advance in the field of protective coating materials. Especially, transition metal diboride based thin films exhibit a great potential to be applied in various applications because of their extreme refractory character as well as interesting electrical properties. Latest studies on various diborides emphasized their strong and weak points being on the one hand high hardness and phase stability in a wide range but on the other limited fracture and oxidation resistance. Alloying concepts involving transition metals (TM) such as W, Ta, or Zr forming ternary diborides ($TMI_{1-x}TMII_xB_{2-z}$) suggest to be a proper solution to overcome these restriction [1-3].

Therefore, within this study we provide a detailed insight on the thermomechanical properties and oxidation resistance of ternary $W_{1-x}Ta_xB_{2-z}$ thin films prepared by DC magnetron sputtering utilizing diboride based target materials. Based on theoretical investigations using density functional theory, we classified the two binary systems α-WB_{2-z} and α-TaB_{2-z} as highly ductile materials according to semi-empirical criteria e.g. Pettifor and Pugh. On behalf of structural investigations, we could confirm that single phased structured α-$W_{1-x}Ta_xB_{2-z}$ thin films are formed up to Ta contents of x=0.26. The addition of Ta also clearly enhances the phase stability in inert atmosphere shifting the decomposition of the metastable α- into the thermodynamically more stable ω-structure from 800 to 1400 °C for x=0.26. During oxidation treatments up to 800 °C the high Ta alloyed coatings outperform its counterparts, forming dense and stable oxide scale also after long exposure times (1000 min). In addition, these films were investigated by nanoindentation and in-situ micromechanical bending tests to evaluate the mechanical properties. The fracture toughness only slightly decreases with increasing Ta content from 3.7 to 3.0 $MPam^{1/2}$. In summary, the study highlights the potential of Ta alloyed WB_{2-z} coatings and confirms the strategy to form ternary or multinary diborides to expand the limitations in specific material properties.

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TS2-12 Fracture–Microstructure Relations of W-diboride Thin Films*, Rainer Hahn (rainer.hahn@tuwien.ac.at), C. Fuger,* TU Wien, CDL-SEC, Austria*; G. Habler,* University of Vienna, Austria*; H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Physical vapor deposited transition metal borides are an emerging class of materials. Their inherent promising properties range from ultra-low compressibility, highest thermal stability to chemical inertness, allowing an application as protective coating in quite harsh environments. Our recent ab initio calculations [1] suggest an attractive combination of high stiffness and appropriate high ductility for α-structured WB_{2-z} (space group 191, AlB_2-prototype, P6/mmm). This leads to an interesting combination of high hardness while maintaining a sufficient fracture toughness. The stabilization of the α-structure over the intrinsically favored ω-structure (space group 194, W_2B_5-prototype, $P6_3$/mmc) is based on omnipresent growth defects (e.g. various types of 0-dimensional vacancies) in the PVD process. However, next to the stabilized phases (hence prevalent bonding nature) also the morphology, especially column size and grain boundary interior, has a huge impact on the mechanical response.

Therefore, within this study we deposited various WB_{2-z} coatings using different deposition techniques as well as parameters to modify the crystallite size and grain boundary constitution but also predominating phases. Subsequently, the mechanical properties of these coatings in the as deposited and annealed state have been analyzed by means of nanoindentation, microcantilever bending tests, and micropillar compression testing. Depending on the coating morphology, which varies from nanocrystalline (amorphous) to crystalline fibrous grown structures, the hardness, indentation modulus, and fracture toughness obtains a strong variation. Hardness and indentation modulus can be varied between 31±2 to 42±2 GPa and 440±30 and 560±30 GPa, respectively. The most significant variation though was found in the fracture toughness of these coatings: We calculated values within the framework given by Matoy et al. [2] between 2.5 and 4.7 MPaVm. Furthermore, we critically evaluate the comparability of distinct micromechanical testing techniques assessing the fracture behavior also with respect to the residual stress state.

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TS2-13 Configurational and Vibrational Thermodynamics of Metastable Ternary $Ti_{1-x}Al_xB_2$ Alloys with Age-Hardening Potential, and their Constituent Binaries

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$Ti_{1-x}Al_xB_2$ metastable ceramic alloys were predicted in [1] to exhibit a tendency for isostructural decomposition despite the fact that binary TiB_2 and AlB_2 belong to the same hexagonal space group and have very similar lattice parameters. Due to the reported high hardness of TiB_2 and the prospect of age-hardening through isostructural clustering, these alloys could be good candidates for hard protective coatings on industrial cutting tools. In this work, we present theoretical predictions regarding phase stability and temperature dependence of structural parameters, based on first-principles density functional theory. The phase diagram for this ternary system is derived and shows an isostructural miscibility gap that closes only at temperatures beyond the melting temperatures of TiB_2 and AlB_2.

Out of the constituent binaries, TiB_2 is a well-studied line compound that has received more focus than AlB_2. In this work, initial phonon calculations of stoichiometric AlB_2 indicates that the thermal expansion trend does not follow experimental measurements as closely as TiB_2. Furthermore, it is known in the literature that there is an inherent metal deficiency present in AlB_2. Therefore, special attention is put on AlB_2 to further our fundamental understanding of the compound. We investigate configurational thermodynamics of metal vacancies, their origin in the electronic structure and their interplay with lattice vibrations. Through the use of cluster expansion, effective cluster interactions are obtained and used in Monte Carlo simulations in order to study vacancy order-disorder transition temperature and to derive a phase diagram. For a subset of vacancy structures, phonon vibrational contributions in the quasiharmonic approximation are calculated to obtain volume expansion for metal deficient AlB_2, and are compared with experimental measurements performed by our partners.

[1] B. Alling et al. "A theoretical investigation of mixing thermodynamics, age-hardening potential, and electronic structure of ternary $M^1_{1-x}M^2_xB_2$ alloys with AlB_2 type structure". Scientific Reports 5 2015, 09888.

TS2-14 Design of Under/Overstoichiometric Superhard $TaB_{2\pm x}$ Films

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Transition metal diborides (TMB_2) are very interesting due to their high temperature chemical stability and excellent mechanical properties. Growth of diboride films by physical vapor deposition (PVD) methods, such as magnetron sputtering from stoichiometric compounds, is accompanied by several interesting aspects. Different angular distribution of sputtered elements plays an important role leading to the formation of under/overstoichiometric nanocomposite films. The best-known superhard overstoichiometric TiB_{2+x} film consists of oriented α-TiB_2 hexagonal filaments embedded in the boron-rich tissue phase. In addition, thermodynamically non-equilibrium PVD processes lead in Nb-, Mo-, WB_2 to the synthesis of metastable structures by incorporating point defects such as vacancies. Understoichiometric $MoB_{1.6}$ and $NbB_{1.7}$ films form despite boron deficiency vacancy-containing α-nanofilaments surrounded by a boron matrix. In the case of slightly understoichiometric α-WB_{2-x} films, boron vacancies promote α-type of the structure exhibiting more ductile behavior in comparison with brittle character of stoichiometric ω-WB_2. Tantalum is probably the most interesting metal of the abovementioned transition metals of VB and VIB group due to its superior oxidation resistance and mechanical properties. Grančič et al. [1] sputtered TaB_{2-x} films from a stoichiometric compound. They drew attention to the significant impact of reflected Ar neutrals from heavy Ta atoms in the target toward the growing film. This led to a large re-sputtering of boron and formation of a significantly understoichiometric amorphous $TaB_{1.2}$ film. Only the maximum decrease in acceleration voltage reduced the energy of Ar neutrals resulting in the nanocrystalline $TaB_{1.7}$ film, but without the typical nanocolumnar character as in the other diborides. Here, we grow under/overstoichiometric $TaB_{2\pm x}$ films using High Target Utilisation Sputtering (HiTUS) technology where it is possible to independently change the kinetic energy of the argon particles accelerated towards the target (target voltage) while maintaining the same amount (target current). We used SRIM (Stopping and Range of Ions in Matter) simulation of sputtering processes and experiments supported by density functional theory (DFT) calculations to investigate the effect of reflected Ar neutrals on the chemical composition, structure and mechanical properties of tantalum diboride films.

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[1] B. Grančič, et al., Surface and Coatings Technology 367 (2019) 341–348.

TS2-15 Vacancies and Related Substoichiometry in Magnetron Sputtered Transition Metal Diboride Thin Films

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In the last couple of years, borides or diborides in particular, have drawn great attention in the development of protective coatings with exceptional properties. Their high melting points and excellent hardness are promising attributes to outperform nitride-based materials in various fields of applications.

Transition metal diborides tend to crystallize in two related but slightly different hexagonal structures. Whereas early TMB_2s have their stable configuration in the AlB_2-prototype (α-type, SG-191), late TMB_2s energetically prefer the W_2B_{5-x} prototype (ω-type, SG-194) showing a difference in the crystallographic ordering. Recent investigations on WB_2 have shown that in the case of thin films, the material crystallizes in the α-type, though its energetically preferred structure is the ω-type. Moreover, the thin films show a rather boron deficient chemical composition compared to measurements of bulk materials. On the contrary, HfB_2 clearly crystallizes in the α-type (bulk as well as thin films) with a tendency to an increased boron content.

In this study, we investigate the theoretical and experimental possible influences on stoichiometry, microstructure and the preferred structure type of various transition metal diborides. Therefore, we used Density Functional Theory calculations to study phase stabilities and the impact of point defects in combination with experimental variations on binary and ternary diboride systems such as HfB_2, CrB_2, $V(W)B_2$, or $W(Ta)B_2$.

TS2-16 INVITED TALK: Boron-containing Metallic-glass Coating: Unique Properties and Various Applications

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INVITED

A group of thin film metallic glasses have been reported to exhibit properties different from conventional crystalline metal films, though their bulk forms are already well-known for properties such as high strength because of their amorphous structure. Boron is one of the widely-used constituents for forming metallic glasses. Amorphous FeB-based alloys are excellent examples for this case, which have been developed for widely use as the energy efficient transformer core material. In this presentation, I will give a review of unique properties of this type of coating, followed by the first-ever metallic glass nanotube (MGNT) arrays on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter, with wall thicknesses of ~103 nm. Two examples are presented based on modifications of this scheme. First, the MGNT array is prepared on a heating device on Si wafers and, with an applied electric voltage to the heating device underneath, the array surface is functioned as biomimetic artificial suckers for thermally adhesion response in biological systems. Second, after modification of biotin, the MGNT array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin. The detection limit of the MGNT arrays for streptavidin is estimated to be 25 nM. Thus, the MGNT arrays may be used as a versatile platform for high-sensitive label-free optical biosensing.

TS2-18 XPS Analysis of TiB$_x$ Thin Films*, Niklas Hellgren* ***(nhellgren@messiah.edu)***, Messiah University, USA*; G. Greczynski,* Linköping University, Sweden*; M. Sortica,* Uppsala University, Sweden*; I. Petrov,* University of Illinois at Urbana Champaign, USA*; L. Hultman,* Linköping University, Sweden*; J. Rosen,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

We report on comprehensive analysis of TiB$_x$ thin films by x-ray photoelectron spectroscopy. Films were grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB$_2$ target in Ar discharge. By varyig the deposition parameters, the film composition could be tuned over the wide range $1.34 \leq B/Ti \leq 3.0$, as determined by elastic recoil detection analysis (ERDA) and Rutherford backscattering spectrometry (RBS). By comparing spectra over this wide range of compositions, we can draw new conclusions about how to interpret XPS spectra of TiB$_x$. By careful spectra deconvolution, the signals from Ti-Ti and B-B bonds can be resolved from those corresponding to stoichiometric TiB$_2$. The intensities of the off-stoichiometric signals can be directly related to the B/Ti ratio of the films. Furthermore, we demonstrate a way to obtain consistent and quantum-mechanical accurate peak deconvolution of the whole Ti 2p envelop, including plasmons, for both oxidized and sputter-cleaned samples. Due to preferential suttering of Ti over B, the film B/Ti ratio is best determined without sputter etching of the sample surface. This allows compositional determination, assuming extensive levels of oxygen has not penetrated below the sample surface. Fully dense films can be accurately quantified for at least a year after deposition, while under-dense samples do not give reliable data if the O/Ti ratio on the un-sputtered surface is ≥ 3.5. Titanium sub-oxides detected after sputter etching is also indicative of too much oxygen penetrating the sample, and quantification by XPS should not be trusted.

TS2-19 Mechanical Property Evaluation of VNbMoTaWCrB Refractory High-entropy Alloy Thin Films by Micropillar Compression and Nanoindentation*, Yen-Yu Chen* ***(cyy15@ulive.pccu.edu.tw)***, Chinese Culture University, Taiwan*; S. Chang,* National Tsing Hua University, Taiwan*; S. Hung, C. Wang,* National Taiwan University of Science and Technology, Taiwan*; J. Duh,* National Tsing Hua University, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan

Refractory high-entropy alloys (HEAs) show outstanding mechanical and thermal properties than traditional alloys. Recently, the application of HEA thin films as functional and protective coatings has been widely investigated. Following our previous studies on VNbMoTaW based refractory HEA thin films, the mechanical properties of the thin films were further investigated by micropillar compression and nanoindentation methods in this study. A series of VNbMoTaWCrB thin films were fabricated by a pulse direct current magnetron sputtering method. The hardness and elastic modulus of thin films were evaluated by nanoindentation. The yield strength of each HEA micropillar under uniaxial compression was analyzed. The elastic and plastic deformation behaviors and the fracture toughness of these HEA thin films were studied. The effect of Cr and B concentrations on the hardness, elastic modulus, and fracture toughness of VNbMoTaWCrB HEA thin films were also discussed in this work.

TS2-20 Effects of Stoichiometry and Individual Layer Thickness Ratio in the Quality of Epitaxial CrB$_x$/TiB$_y$ Superlattice Thin Films*, Samira Dorri* ***(samira.dorri@liu.se)***, N. Ghafoor, F. Eriksson, J. Palisaitis, B. Bakhit, L. Hultman, J. Birch,* Linköping University, IFM, Thin Film Physics Division, Sweden

Studies of single crystal artificial superlattices (SL) have been instrumental to understand hardening mechanisms at the nano-scale in transition metal (TM) nitride and carbide multilayers. The lack of such fundamental studies for TM diborides is the motivation for this study of CrB$_x$/TiB$_y$ (0001) SLs, grown epitaxially onto Al$_2$O$_3$ (0001) wafer substrates by direct current magnetron sputtering from compound diboride targets. Growth conditions for obtaining well-defined SLs with good interface quality are found at a sputter gas pressure of 4 mTorr Ar and a substrate temperature of 600 °C. 1-µm-thick SL films deposited with modulation periods Λ between 1 and 10 nm, and Λ = 6 nm SLs with TiB$_y$-to-Λ layer thickness ratios Γ ranging from 0.2-0.8 are characterized by means of HRTEM, STEM, EDX, EELS, XRD, ToF-ERDA, RBS, and XPS. It is found that SLs with Λ = 6 nm and Γ in the range of 0.3-0.4 exhibit the highest structural quality. The effects of Γ and the stoichiometries (B/TM ratio) of the CrB$_x$ and TiB$_y$ layers on the distribution of B in the SL structures are highlighted. We show that by increasing the relative thickness of TiB$_y$, the crystalline quality of SLs starts to deteriorate due to B segregation in over-stoichiometric TiB$_y$ layers, resulting in narrow epitaxial SL columnar growth with structurally-distorted boron-rich boundaries. An increase in relative thickness of under-stoichiometric CrB$_x$ on the other hand, enhances the SL quality and hinders formation of boron-rich boundaries. Detailed structural analyses, mechanical properties with hardness, and stress as well as possible solutions for further improved SL definition will be presented.

TS2-21 INVITED TALK: Boron-based Thin Film Materials for Future Neutron Technologies at the ESS*, Jens Birch* ***(jens.birch@liu.se)***, Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

The European Spallation Source (ESS), currently being built in Sweden, will be capable of delivering neutron beams more than an order of magnitude brighter than existing neutron sources, which will enable faster neutron scattering experiments on new materials using new techniques. For best utilization of the brightness, novel thin film based neutron-optical components, such as neutron mirrors and area detectors, are being developed. The Thin Film Physics division at Linköping University aims at developing novel thin film concepts enabling future neutron technologies.

Together with ESS, affordable ^{10}B -based thin film neutron converter coatings have been developed that allows for eliminating the present unsustainable use of the rare isotope ^{3}He in state-of-the-art neutron detectors. The primary material choice is magnetron sputter deposited B$_4$C, enriched in the neutron absorbing isotope ^{10}B. We have shown that ^{10}B$_4$C thin films can be grown by magnetron sputter deposition with properties that fulfill the requirements of mechanical and chemical stability as well as being radiation hard, while maintaining a high volume density of ^{10}B. For example1µm thick films with residual stress as low as 0.09 GPa can be grown by DC magnetron sputtering and by employing HiPIMS it is possible to lower the substrate temperature to ~100°C which is useful for sensitive substrates. This ^{10}B$_4$C thin film technology is proven superior to ^{3}He-based detectors and is chosen for most of the foreseen detectors for scattering, reflectometry, as well as time-of-flight inelastic spectroscopy at the ESS.

Novel solid-state neutron detector designs, requiring neutron converter filling of narrow high-aspect ratio wells and trenches in semiconductor surfaces, require conformal coverage CVD methods. We have recently shown that conformal coatings of BC$_x$ in wells with aspect ratios as high as 10 000:1 are possible using triethylborane, B(C$_2$H$_5$)$_3$ as precursor. This allows for future ^{10}B-based solid state neutron detectors with sensor pixels in the range of 10x10 µm^2 (rather than the present ~cm^2).

Nanometric metallic multilayers act as neutron mirrors and are key to guiding neutrons from source to experiment. By combining incorporation of ^{11}B in the multilayers with temporal ion-assistance modulation during sputter deposition, we obtain a significant reduction of interface width which, in turn, leads to significantly improved neutron reflectivities. For example in Ni/Ti:^{11}B multilayer mirrors reflectivity increased by 43% using this technique, implying up to 10x higher neutron flux throughput and significantly increased spectral range of future neutron guides.

TS2-23 Thermal and Mechanical Properties of (W,Zr)B$_{2-z}$ Coatings Deposited by RF Magnetron Sputtering Method*, Justyna Chrzanowska-Giżyńska* ***(jchrzan@ippt.pan.pl)***, R. Psiuk, P. Denis,* Polish Academy of Sciences, Poland*; Ł. Kurpaska,* National Centre for Nuclear Research, Poland*; T. Mościcki ,* Polish Academy of Sciences, Poland

W-Zr-B films with different stoichiometric ratio Zr/W were deposited by RF magnetron sputtering on silicon and tungsten carbide substrates. The coatings were deposited from plasma spark sintered targets using one-inch sputtering cathode. The impact of zirconium content on the film mechanical and thermal properties were investigated. Nano-indentation test was performed to analyze the hardness, Young modulus and subsequently flexibility of the films. It is shown that α-WB2 magnetron sputtered coatings alloyed with zirconium content 0 ⍰ 24 at% are superhard and in all investigated compositions possess similar hardness. In the same time Young modulus is decreasing about 10% what make deposited films more flexible. Obtained W-Zr-B films represent a new class of coatings which are simultaneously superhard H = 43±3 GPa, exhibit high values of the hardness and effective Young's modulus E* ratio H/E* >0.1, elastic recovery We > 60%. The results of thermal studies i.e. thermal shocking, annealing in vacuum and TGA show that deposited coatings are thermally stable at least to 800 °.

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