New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-2-WeA

New Horizons in Boron-Containing Coatings II

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

2:00pm **F4-2-WeA-1 Understanding and Optimizing the Properties of Superhard Metal Borides**, ***Sarah Tolbert (tolbert@chem.ucla.edu)***, University of California, Los Angeles, USA **INVITED**

In this talk, we will examine a family of super-hard materials based on late transition metal borides.These materials are exciting because, unlike diamond, they can be synthesized at atmospheric pressure.The materials were initially constructed using three very simple design rules:1) use late transition metals to create high electron density so that the materials are incompressible; 2) add boron to build strong covalent bond to prevent slip and generate hard materials; 3) use solid-solution effects to further tune materials properties.While these ideas is incredibly simple, they have also proven to be very effective.In this talk, we will thus use a combination of materials synthesis, indentation measurements, and high-pressure diffraction to gain an understanding of how the hardness in this family of materials can be tuned based on chemical composition and bonding motifs.We will specifically take advantage of non-hydrostatic high pressure X-ray diffraction methods to directly probe both elastic lattice deformations and the onset of plastic deformation in a wide range of materials in a lattice specific manner.To gain a global understanding of the family of materials we will move from metal (M) rich MB phases, to more conventional MB_2 and MB_4 type materials, and finally to very high boron content MB_{12} type materials.In all cases, the goal will be to correlate structure and bonding with hardness.Finally, we will end with some new studies on nanoscale versions of these materials, where nanoscale architecture is combined with bonding constraints to further improve hardness.

2:40pm **F4-2-WeA-3 Si alloyed Transition Metal Diborides - A Novel Class of Oxidation Resistant Coating Materials**, *T. Glechner, L. Zauner, R. Hahn, A. Bahr, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; **Helmut Riedl (helmut.riedl@tuwien.ac.at)***, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Surface protection of highly stressed components used in aviation or energy production is of great interest, especially to extend the operation ranges in oxidative high-temperature environments. Here, transition metal (TM) ceramics are a suitable class to resist such conditions. However, studies on a drastic improvement of the oxidation resistance of TM-diborides based coatings are relatively rare, as up to now many studies focus on the synthesis and mechanical properties of such films.

Therefore, within this study we suggest the combination of TM-boride based coating materials – as a high temperature stable ceramic – with the excellent oxide former Si, resulting in coatings with outstanding oxidation resistance, tested up to 1500 °C. Various TM-Si-$B_{2\pm z}$ (TM=Ti, Cr, Hf, Ta, W) films have been sputter deposited and subsequently oxidized in a DTA/TG setup to study their oxidation kinetics. Above certain Si contents, Ti-Si-$B_{2\pm z}$, Cr-Si-$B_{2\pm z}$, and Hf-Si-$B_{2\pm z}$ coatings exhibit strongly retarded oxidation kinetics obtaining k_p values below 10^{-11} $kg^2m^{-4}s^{-1}$ at 1100 °C. Long term oxidation tests at 1200 °C (up to 60 h in ambient air on hard substrates) confirmed the superior protective capability of these coatings, with i.e. $Hf_{0.20}Si_{0.23}B_{0.57}$ possessing an oxide scale thickness of only 1.5 µm after 60 h. Along with a broad set of high-resolution characterization techniques (i.e. HR-TEM, APT) the study introduces this new class of hard coatings for oxidation protection at ultra-high temperatures.

Keywords: Oxidation Resistance; Transition Metal Ceramics; Thin Films; Borides; UHTC;

3:00pm **F4-2-WeA-4 High-Power Impulse Magnetron Sputter Deposition of TiB_x Thin Films: Effect of Pulse Length and Peak Current**, ***Niklas Hellgren (nhellgren@messiah.edu)***, Messiah University, USA*; I. Zhirkov,* Linköping University, IFM, Thin Film Physics Division, Sweden*; M. Sortica,* Uppsala University, Sweden*; A. Petruhins, G. Greczynski,* Linköping University, IFM, Thin Film Physics Division, Sweden*; I. Petrov,* University of Illinois at Urbana-Champaign, USA*; L. Hultman, J. Rosen,* Linköping University, IFM, Thin Film Physics Division, Sweden

We report on titanium boride, TiB_x, thin films grown by high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target. Commonly HiPIMS studies are conducted in constant power mode, so when the pulse length in changed, so is the peak current and/or frequency. Here we independently vary pulse length (t_{on} = 50 – 200 µs) and peak current density (J_{peak} = 0.5 – 2 A/cm^2), while keeping the pulse frequency constant at f = 100 Hz. Thus, the total power vary depending on deposition condition. All other parameters were kept constant; substrate-target distance d = 6.5 cm, Ar pressure p_{Ar} = 10 mTorr, substrate temperature T_s = 500 °C, and substrate bias V_s = - 60 V.

The resulting films are all under-stoichiometric with B/Ti ranging from 1.3 to 1.9, as determined by ToF-ERDA and RBS. For any given t_{on}, the B/Ti ratio increases monotonically as J_{peak} increase from 0.5 to 2 A/cm^2. The trend is more complex as a function of t_{on}; in most cases, the highest B/Ti is observed for t_{on} = 100 µs, and decreases for both higher and lower t_{on}. The exception is for J_{peak} = 2 A/cm^2, where B/Ti increased slightly when increasing t_{on}.

The trends are discussed in terms of variations in both the total atom deposition flux, as determined from ERDA and RBS, and B^+, Ti^+ and Ar^+ ion flux measured by time- and energy-integrated mass spectrometry. Especially the Ti and Ti^+ fluxes saturate for the highest values of t_{on} and J_{peak}, which explains the highest film B/Ti ratios. This is also accompanied by a transition from strongly 001-textured films to predominantly 101-texture.

3:20pm **F4-2-WeA-5 Effect of Ar Particles on the Growth and Mechanical Properties of ZrB_{2+x} Films**, ***Tomas Fiantok (tomas.fiantok@fmph.uniba.sk)***, *T. Roch,* Comenius University, Bratislava, Slovakia*; P. Svec,* Academy of Science, Bratislava, Slovakia*; M. Truchly, V. Sroba, M. Mikula,* Comenius University, Bratislava, Slovakia

Highly demanding aerospace applications create an opportunity to exploit the promising potential of transition metal diboride based thin films (TMB_2, where TM = Ti, Zr, Nb, Ta, Mo, W) due to their high hardness and wear resistance. But their real use is still limited by brittle character and low oxidation resistance at elevated temperatures. TMB_2 films are most often prepared by physical vapor deposition (PVD) methods such as magnetron sputtering from stoichiometric compound targets in an inert argon atmosphere. The deposition processes are accompanied by (i) different angular distribution of sputtered boron, and metals, respectively, leading to the growth of overstoichiometric TMB_{2+x} films; (ii) the energy of reflected Ar neutrals causing resputtering and lead to grow a substoichiometric vacancy-containing TMB_{2-x} films. Here, we would like to demonstrate the effect of Ar particles on the structure, mechanical properties, and oxidation resistance of ZrB_{2+x} films. The films were deposited by high target utilization sputtering (HiTUS) technology where it is possible to independently change the kinetic energy of the argon ions accelerated toward the target (steering of target voltage) while maintaining the same amount (constant target current). Therefore, we have grown nanocrystalline ZrB_{2+x} films over a wide concentration range (x ~ 0.02 ÷ 2.1) with hardness values in range of 45.5GPa ± 1.2 GPa ÷ 8.3 GPa ± 0.3GPa. The films have a brittle character, expressed by Young's moduli, with the highest value of 480.9 GPa ± 8.8 GPa for $ZrB_{2.11}$. X-ray diffraction analysis confirmed the presence of hexagonal ZrB_2 phase with different preferred orientations depending on stoichiometry of the films. The highest oxidation resistance exhibited $ZrB_{2.27}$ films with onset temperature of ~ 750°C. Due to better understanding of the obtained results a deeper insight into nanostructure via transmission electron microscopy was performed. Mechanical behavior of ZrB_{2+x} was explained by density functional theory calculations.

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3:40pm **F4-2-WeA-6 Accurate Composition Depth Profiling of Light Elements in Thin Films Using Ion Beams - What Can Be Achieved?***, Daniel Primetzhofer (daniel.primetzhofer@physics.uu.se),* Uppsala University, Sweden **INVITED**

For compound materials, subtle differences in stoichiometry often significantly alter the material properties of interest. This fact becomes particular important for compound systems for which a wide range of different compositions is accessible during synthesis as exemplified by transition metal carbides and borides. However, while accurate data on the composition on such compound samples containing light chemical species is thus of critical relevance, only very few methods can accurately provide the information requested. Ion beam-based analysis offers a unique toolbox to access the sample chemistry of such systems by a number of different non-destructive composition depth profiling techniques.

In this contribution we will illustrate the potential of ion beam analytical techniques in the characterization of light species ranging from hydrogen to oxygen while simultaneously providing reliable concentration depth profiles of the heavier constituents. Particular emphasis will be given to boron containing systems of different nature, i.e. thin films as well as multilayered or ion-implanted systems. At first, the underlying principles of ion-beam based analysis will be reviewed, illustrating the general characteristics and advantages of the methodology. These include amongst others minimum sample-preparation, non-destructive analysis, as well as typically fast measurements and analysis.

Subsequently, we will present a number of different ion-beam based methods by showcasing how they can answer specific scientific questions ranging from lattice location of hydrogen interstitials in energy storage materials to accurate measurements of the stoichiometry of borides as used for hard coatings. The methods presented will include tools capable of high-resolution depth profiling of specific isotopes as in nuclear resonance analysis or elastic backscattering spectrometry as well as methods providing composition depth profiles of the whole sample inventory on nanometer depth scales as enabled by Time-of-Flight Elastic Recoil Detection Analysis. We will discuss the achievable accuracy as well as limitations of the techniques also in comparison to other analytical approaches. Finally, we will also discuss, how a combination of methods can be employed to further increase the accuracy of analysis.

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