New Horizons in Coatings and Thin Films
Room Town & Country C - Session F2-2-TuA

High Entropy and Other Multi-principal-element Materials II

Moderator: Erik Lewin, Uppsala University, Sweden

2:00pm **F2-2-TuA-2 Structure and Properties of Refractory MoNbTaW+X (X = Ti,V,Cr,Mn,Hf) High Entropy Alloy Thin Films Deposited by HiPIMS**, *G. Gruber,* Montanuniversität Leoben, Austria*; A. Lassnig, S. Zak, C. Gammer, M. Cordill,* Austrian Academy of Sciences, Austria*; **Robert Franz (robert.franz@unileoben.ac.at)**,* Montanuniversität Leoben, Austria

Refractory high entropy alloys (HEAs) represent a new class of materials that show promising properties, such as high hardness, good thermal stability and sluggish diffusion, which makes them suitable for various potential applications. Within this study a series of refractory HEAs was deposited using high power impulse magnetron sputtering keeping the base alloy MoNbTaW constant and adding a fifth element: Ti, V, Cr, Mn or Hf. The targets used for the synthesis of each alloy contained all five elements in an equimolar concentration. As analysed by X-ray diffraction and transmission electron microscopy, all films showed a bcc solid solution phase structure in as-deposited state. Further, the thermal stability of the films was analysed by annealing in vacuum up to 1200 °C revealing that the bcc phase is stable to a temperature of at least 1000 °C. Changes in the residual stress state and mechanical properties due to annealing were studied by the wafer

curvature method and nanoindentation, respectively. The performed work is intended to contribute to a comprehensive understanding about phase and thermal stability of refractory HEA thin films.

2:20pm **F2-2-TuA-3 Effect of Rare-earth yttrium Addition on Microstructure and Thermal Stability of Refractory TiTaZrHfW High Entropy Film**, ***Mohamed EL GARAH (mohamed.el_garah@utt.fr)**,* University of Technology of Troyes , France*; L. PATOUT, A. CHARAI,* Aix Marseille University , France*; F. SANCHETTE,* University of Technology of Troyes , France

High entropy alloys (HEAs) are of considerable interest due to their superior properties. Since 2004, they are defined as quasi- or equimolar alloys and they consist, at least, of five elementary elements with an atomic percentage ranging from 5 to 35 at.% [1-3]. High Entropy Films (HEFs) have been also reported to have excellent properties such as good wear [4] and corrosion resistance [5] and excellent thermal stability [6]. Rare earths have excellent physical and chemical properties. They play an interesting role to improve the performance of the coatings. The effect of the addition of yttrium Y as a rare earth element, on the microstructure, the mechanical properties and on the thermal stability of TiTaZrHfW refractory film is studied. A series of $(TiTaZrHfW)_{100-x}Y_x$ films were synthesized using magnetron sputtering technique. Y content is varied by changing the discharge current applied to Y target. No change of the films microstructure is observed when Y is added with small amount, however with high Y content new phases are formed. The phase evolution is evaluated by calculating the thermodynamic criteria ΔHmix, ΔSmix, Ω and δ and the result are compared to the experimental analysis. Nanoindentation measurements indicate a degrading of mechanical properties when the film is doped with Y element. The highest values of hardness and Young's modulus are obtained for TiTaZrHfW film at 9.69 GPa and 111.63 GPa respectively. Moreover, thermally stability of TiTaZrHfW film without and with Y element is investigated.

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[2] Cantor, I. Chang, P. Knight, A. Vincent, Microstructural development in equiatomic multicomponent alloys, *Mater. Sci. Eng. A*, **375**, 213-218 (2004)

[3] W. Zhang, P.K. Liaw, Y. Zhang, Science and technology in high-entropy alloys, *Sci. China Mater.*, **61**(1), 2-22 (2018)

[4] Cheng, J. B.; Liang, X. B.; Xu, B. S., Effect of Nb addition on the structure and mechanical behaviors of CoCrCuFeNi high-entropy alloy coatings. Surf. Coat. Tech. 2014, 240, 184-190

[5] Hsueh, H.-T.; Shen, W.-J.; Tsai, M.-H.; Yeh, J.-W., Effect of nitrogen content and substrate bias on mechanical and corrosion properties of high-entropy films $(AlCrSiTiZr)_{100-x}N_x$. Surf. Coat. Tech. 2012, 206 (19-20), 4106-4112

[6] Sheng, W.; Yang, X.; Wang, C.; Zhang, Y., Nano-crystallization of high-entropy amorphous $NbTiAlSiW_xN_y$ films prepared by magnetron sputtering. Entropy 2016, 18 (6), 226

2:40pm **F2-2-TuA-4 Investigation of Strain Stabilization in Aluminum-Based High Entropy Sublattice Nitride Films**, ***Balint Hajas (balint.hajas@tuwien.ac.at)**, A. Kretschmer, A. Kirnbauer, P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien University, Vienna, Austria

Hard protective coatings allow for increased lifespan of machining tools and more versatile fields of application. Less than two decades ago the world of material science was introduced to the so called "high entropy alloys" (HEAs), a field that has since seen enormous growth in popularity. Applying the concept of metallic HEAs, which typically consist of a solid solution of at least five primary elements in near equiatomic composition, we developed various nitride and oxy-nitride coatings, where at least five different metals (in near equiatomic composition) share the same metal-sublattice. Hence, essentially their metal-sublattice is high entropic, however, for simplicity these will be named high entropy nitrides respectively oxynitrides.

Based on Density Functional Theory calculations, several Al-based single-phase high entropy nitride systems were selected for further experimental investigations. The selection criterion was basically their ability to delay the wurtzite AlN phase formation (essentially through strain stabilization) upon exposure to elevated temperatures. In addition to these high entropy nitrides, also their oxynitrides and Si-alloyed nitrides were developed, all of which by reactive magnetron sputtering.

The primary investigation focused on how the mechanical properties such as hardness and fracture toughness of the nitride coatings changed due to vacuum annealing up to 50 hours, and how the oxynitrides related to those results, and whether the formation of the wurtzite phase could be detected. The secondary investigation was aimed towards the oxidation resistance of the coatings, and if the additional silicon could delay the oxidation process. Their characterization includes X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, nanoindentation and cube-corner indentation.

4:00pm **F2-2-TuA-8 Magnetron Sputtering of Hard and Strong Multicomponent (HfNbTiVZr)C Thin Films**, ***Barbara Osinger (barbara.osinger@kemi.uu.se)**, S. Fritze, L. Riekehr, E. Lewin, U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden

Thin films of the high entropy alloy HfNbTiVZr have shown promising mechanical properties and interesting charge transfer effects, reducing atomic size mismatch and in turn the lattice distortion δ. Being able to tune the electronic structure is especially interesting for the design of multicomponent carbides, as their desirable properties are a result of their bond character. This, along with general properties of group 4-6 carbides, like ceramic hardness, high wear resistance and ultra-high temperature strength, motivates the investigation of the (HfNbTiVZr)C system.

This study focused primarily on multicomponent carbide (HfNbTiVZr)C thin films with varying carbon concentrations (0–44 at.%), synthesised by non-reactive DC magnetron sputtering. All carbide films exhibit a single solid solution phase with NaCl-type structure and a lattice parameter of approximately 4.53 Å. The hardness increases to 34 GPa compared to 10 GPa for the metallic films. Additionally, phase stability based on films deposited at elevated temperatures (300-700°C), compared with predictions made by CALPHAD methods, will be discussed.

4:20pm **F2-2-TuA-9 Comparative Study of Reactively and Non-Reactively Sputtered High-Entropy Metal-Sublattice Carbides**, ***Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at)**, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Within this work, we report on the phase formation and thermal stability of high entropy metal-sublattice carbides to provide a further insight to a more extensive understanding of the high-entropy effect, according to which, based on the Gibbs-free energy, such materials should be stabilised in the high-temperature regime. Therefore, (Hf,Ta,Ti,V,Zr)C coatings were reactively and non-reactively sputtered from a single powder-metallurgically produced composite target (either metallic or consisting of the respective binary carbides). Reactively sputtered coatings were synthesised using an C_2H_2 – Ar mixture with different $C_2H_2/(C_2H_2+Ar)$ ratios (f_{C2H2}). After deposition, the coatings were investigated in as-deposited state and after vacuum annealing between 800 and 1200°C. The structure and morphology, the chemical composition, the mechanical properties, and the thermal stability of the coatings were investigated by scanning electron microscopy, X-ray diffraction, and nanoindentation.

The non-reactively sputtered as well as reactively sputtered coatings with f_{C2H2}= 20 % show a single-phased face-centred cubic (fcc) structure. The hardness for the non-reactively sputtered HESCs is with ~41 GPa higher than that of the reactively sputtered one which exhibits a hardness of 35 GPa. This indicates that due to the use of C_2H_2 also regions of amorphous carbon form, which slightly weaken the coating already in the as-deposited state. After vacuum annealing up to 1200 °C the non-reactively sputtered coatings maintain a hardness of ~40 GPa indicating retarded softening mechanisms due to sluggish diffusion. Additionally, powdered free-standing coating material was investigated by XRD in as deposited state and after vacuum annealing up to 1300 °C. The results of these investigations show, independent of the synthesis route, no phase transformation within the investigated temperature range. This behaviour was also observed in previous studies on different material classes such as nitrides, borides, and oxides indicating a stabilisation due to the high-entropy metal sublattice.

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