Topical Symposia
Room Pacific Salon 3 - Session TS1-1-WeM
High Entropy and Other Multi-principal-element Materials I

Moderators: Diederik Depla, Ghent University, **Ulf Jansson**, Uppsala University, Angstrom Laboratory

8:00am **TS1-1-WeM-1 Effect of Nitrogen Content on the Microstructure and Mechanical and Tribological Properties of Magnetron Sputtered FeMnNiCoCr Nitride Coatings**, ***Chuhan Sha***, *P Munroe,* University of New South Wales, Australia*; Z Zhou,* City University of Hong Kong, Hong Kong*; Z Xie,* University of Adelaide, Australia

Extensive research has been carried out on high entropy alloys (HEAs) in bulk form. These alloys exhibit many attractive physical and mechanical properties, and more recently are being investigated in the form of thin film coatings. In pursuit of improved mechanical performance of HEA coatings, nitrides based on these compositions have been investigated in this study. We have examined a series of FeMnNiCoCr nitride coatings deposited onto M2 steels using a DC closed field unbalanced magnetron sputtering system. The target was composed of a FeMnNiCoCr alloy in equal atomic ratio. The nitrogen content in the nitride coatings was controlled by nitrogen gas flow rate. The phase compositions, microstructure, mechanical, and tribological properties of the as-prepared coatings were examined by XRD, TEM/EDS, nanoindentation, scratch and wear tests. A phase transformation from FCC to BCC, with higher nitrogen contents was observed in these coatings. A relatively high hardness value of ~17 GPa was measured in the coating with the highest nitrogen content. A reduction in the adhesion strength with increasing nitrogen content was also found by the scratch test. In contrast, an improved wear resistance was achieved at higher nitrogen concentrations. It is believed the evolution of mechanical and tribological properties is related with the compositional changes and phase transformations as a function of gas flow rate. That is, the low-nitrogen content coatings exhibit FCC structures with higher ductility and toughness, whilst the high-nitrogen content coatings exhibit BCC structures but greater brittleness.

8:20am **TS1-1-WeM-2 Reactive Sputtering of High Entropy Alloys with Nitrogen – The Effect of Enthalpy and Entropy**, ***Robin Dedoncker***, *D Depla,* Ghent University, Belgium

High entropy alloys are a new class of materials with at least 5 different metals in near-equimolar concentrations with promising properties such as a high degree of corrosion resistance and mechanical strength. Despite the multi-elemental composition, these alloys can form simple solid solutions when they are deposited by magnetron sputtering. The formation of a solid solution was initially believed to origin from the large contribution of the entropy of mixing, but this has recently become subject of discussion. Upon sputtering in a mixed argon/nitrogen atmosphere, a nitride is formed. This nitride shows a rock salt (B1) structure, with the metals in solid solution on the cation sites. Studies on different alloys where the incorporation of nitrogen was investigated, reveal a Langmuir adsorption mechanism. The latter could be quantified with the calculation of the sticking coefficient of nitrogen on each alloy. This made it possible to examine the influence of enthalpy and entropy, and to reveal what the role of both thermodynamic quantities are in the phase formation of these alloys.

8:40am **TS1-1-WeM-3 Compositional Variations and Resulting Structure-property Correlations in Multicomponent Al-Cr-Nb-Y-Zr-N Thin Films**, *K Johansson, A Srinath,* Uppsala University, Sweden*; L Nyholm,* Uppsala University, Angstrom Laboratory, Sweden*;* ***Erik Lewin,*** Uppsala University, Sweden

Initial studies on multicomponent Al-Cr-Nb-Y-Zr-based nitride coatings exhibited a single NaCl-type (B1) solid solution phase, and promising corrosion performance in electrochemical testing.[1] Further studies have now been conducted. Samples have once more been synthesised using reactive magnetron deposition from elemental and segmented targets. Coating composition has been varied, both with regards to nitrogen (from pure alloy to nitride) and metals (several different multicomponent compositions, as well as ternary references). Samples have been analysed using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electron microscopy (SEM and TEM). The present results are combined with the previously attained results where coating have been deposited under different process conditions,[1] to attain an overview of structure and properties of multicomponent coating materials within the Al-Cr-Nb-Zr-Y-N system. Pure alloy samples, as well as samples with lower amounts of nitrogen show both diffuse scattering connected with amorphous alloys, as well as broad diffraction peaks pointing to the presence of a nanocrystalline alloy phase. Thus low nitrogen content coatings are nanocomposites with nanocrystallites in a metallic amorphous matrix. For nitrogen contents above about 37 at.% (corresponding to a N_2/Ar ratio of 1), only a single NaCl-type crystalline phase is observed, without any indications of secondary phases. Coating performance has been evaluated using polarisation tests, as well as more in-depth electrochemical testing. The formed passive layer has been investigated with hard X-ray photoelectron spectroscopy (HAXPES) for non-destructive depth profiling. Also mechanical testing, using nanoindentation, has been performed.

[1] K. Johansson et al. *Multicomponent Al-Cr-Nb-Y-Zr-N Thin Films*, poster presentation (TSP-6) at 45th**ICMCTF**, San Diego 2018.

9:00am **TS1-1-WeM-4 Exploring High Entropy Alloy Core Effects in Multi-principal Transition Metal-Al-Si-N, and Multi-principal Boride PVD Thin Films**, ***Kumar Yalamanchili***, *F Doris, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Switzerland

Several metallic high entropy alloys (HEA), also known as multi-principal element alloys were reported with fascinating structural and functional properties. These properties are mainly attributed to (1) unpredicted favourable cocktail mixture of alloying elements, (2) a severe distortion of their lattice, (3) sluggish diffusion kinetics, and most importantly (4) formation of entropy stabilized solid solutions enabled by a high configurational entropy (S_{config} > 1.61 *R)*, where *R is* the gas constant.

Recent studies also indicate that HEA core effects are operative in ceramic alloys. It was experimentally shown that the entropy predominates the thermodynamic landscape, resulting in a reversible entropy stabilized solid solution in an equimolar mixture of MgO, CoO, NiO, CuO and ZnO [1]. In contrast, entropy stabilization could not be achieved in (AlTiVNbCr)N alloy [2]. This leads to a question of what should be the pre-qualifying criterion to form entropy stabilization in ceramic alloys.

In this contribution, we have explored the above mentioned HEA core effects in two different alloy system with an estimated S_{config} 1.4 R in their cation sub-lattice, (a) multi-principal transition metal (Ti,Nb,V,Cr,W)-Al-Si-N, and (b) multi-principal (Ti-Zr-Ta-Hf-Cr) B_2 alloys. Nitride alloys are synthesized in a reactive arc and boride alloys are synthesized in *S3p^{TM}* process in thin film form.

As deposited nitride alloys crystallized in a metastable *cubic* B1 (*NaCl*) and boride alloys crystallized in hexagonal AlB_2 structure, with a hardness of 40 GPa. Subsequently, these films are subjected to post vacuum annealing up to a temp of 1100 ^oC. Key properties like structural and hardness evolution as a function of annealing temperature, indentation-induced fracture resistance, and high temp. Oxidation resistance of the multi-principal high entropy alloys are measured and compared with their selective low entropy binary and ternary alloys. These observations are cross-compared with above mentioned HEA core effects.

Ref:

[1] C.M. Rost, et al., Nat. Commun. 6 (2015) 8485

[2] K.Yalamanchili et al., Thin Solid Films, Vol.636, 346-352, 2017

9:20am **TS1-1-WeM-5 Mechanical Properties and Corrosion Resistance of Magnetron Sputtered Co-Cr-Fe-Mn-Ni-C Thin Films**, ***León Zendejas Medina***, *P Berastegui,* Uppsala University, Sweden*; L Nyholm, U Jansson,* Uppsala University, Angstrom Laboratory, Sweden

In this project we aim to deposit thin films which combine high hardness and wear resistance with a high ductility and oxidation resistance. This combination of properties is uncommon as there is often a trade-off between hardness and ductility. Multicomponent or high entropy alloys (HEAs) are a new generation of materials, which is corrosion resistant and has characteristically high strength compared to traditional alloys. There are many HEAs with promising qualities, but the correlation between the mechanical properties and corrosion behavior is less well studied.

The HEA CoCrFeMnNi system with small amounts of C was chosen as a starting point. Carbon is known to increase the corrosion resistance and strength of metal films [1]. However, in the CrCoFeNi system, the ductility starts decreasing above 4 at-% C due to carbide formation [2]. By using magnetron sputtering, which can form metastable phases, the formation of carbides can be suppressed, and the amount of carbon increased beyond the maximum equilibrium solubility. In this project we have used combinatorial sputtering to study the influence of C on the two alloy systems CrFeNi and CrCoFeMnNi.

In the first system, targets of Fe, Cr, Ni and graphite were used to deposit compositional gradient films with up to 10 at-% C at 300 °C. The structure was a mixture of fcc, bcc and σ-phases. All films were highly ductile, and the addition of carbon gave an increase in both hardness and ductility. Films as hard as 11 GPa were obtained for near-equimolar metal contents and 10 at% C. No indication of carbide formation was observed, suggesting that the carbon was dissolved on interstitial sites in the structure. The corrosion of the films was investigated with impedance and potentiodynamic polarization measurements in 0.6 M NaCl. The carbon containing films exhibited higher pitting corrosion resistance than a 316L steel reference.

In a second set of experiments, a compound CoCrFeMnNi HEA and a graphite target were used to deposit gradients with up to 20 at-% C. The structure was a mixture of fcc and bcc, and the crystallinity decreased with increasing carbon content. The hardness at 10 at-% C was 15 GPa, an increase compared to the carbon free films at 7 GPa. The corrosion behavior of the films, and the influence of carbon, have been studied and will be described in more detail.

[1] Fritze, S. et al. Hard and crack resistant carbon supersaturated refractory multicomponent nanostructured coatings. *Sci. Rep.*, 8:14508, 2018.

[2] Huang, T. D. et al. Effect of carbon addition on the microstructure and mechanical properties of CoCrFeNi high entropy alloy. *Sci China Tech Sci*, 61(1):117-123, 2018.

9:40am **TS1-1-WeM-6 Thermal Property Evaluation of V-Nb-Mo-Ta-W and V-Nb-Mo-Ta-W-Cr-B High-entropy Alloy Thin Films***, **Sheng-Bo Hung**, C Wang,* National Taiwan University of Science and Technology, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

Refractory high entropy alloys (HEAs) have drawn lots of attentions from researchers and industries because of their outstanding properties, such as high hardness, good wear resistance, and good corrosion resistance and stable thermal properties. In this work, the V-Nb-Mo-Ta-W and carbon contained V-Nb-Mo-Ta-W-B-C refractory HEA thin films were fabricated by a sputtering system on the Al_2O_3, AISI304 stainless steel, AISI420 stainless steel and P-type (100) Si wafers substrates. The structures of thin films were determined by an X-ray diffractometer. The cross-sectional morphologies of thin films were examined by a field emission scanning electron microscopy (FE-SEM). A nanoindenter and scratch test were used to evaluate the hardness and adhesion properties of thin films, respectively. The thermal properties of the V-Nb-Mo-Ta-W and V-Nb-Mo-Ta-W-B-C coatings were evaluated at the temperature ranging from 500 to 1000 ^{o}C. The influence of carbon contents on the thermal stability of the V-Nb-Mo-Ta-W and V-Nb-Mo-Ta-W-B-C coatings were discussed in this study.

11:00am **TS1-1-WeM-10 Structure, Mechanical Properties and Thermal Stability of Magnetron Sputtered HfTaVWZr High-entropy Boride Coatings***, **Alexander Kirnbauer**, C Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; P Polcik,* Plansee Composite Materials GmbH, Germany*; P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

In the field of materials research, a novel alloying concept of so-called high-entropy alloys (HEAs), has gained particular attention within the last decade. These alloys contain 5 or more elements in equiatomic or near-equiatomic composition. Properties, like hardness, strength, and toughness can be attributed to the specific elemental distribution and are often superior to those of conventional alloys. In parallel to HEAs also high-entropy ceramics (HECs) moved into in the focus of research. These consist of a solid solution of 5 or more binary borides, carbides, nitrides, or oxides. Within this work, we investigate the structure and mechanical properties of thin films based on the high-entropy materials concept with emphasis on their behaviour at elevated temperatures, as their structural integrity should be improved with increasing temperature according to the Gibbs free energy.

Therefore, HfTaVWZr boride coatings were synthesised in a lab-scale sputter deposition facility using a single powder-metallurgically produced composite target (nominal target composition 20 mole % of HfB_2, TaB_2, VB_2, W_2B_5, and ZrB_2, respectively). The coatings crystallise in a single-phased hexagonal α-structure (AlB_2 prototype) with a fine columnar morphology. The hardness in as-deposited state is 45.6 ± 1.5 GPa and these films can thus be considered super hard. The structural evolution of free-standing powdered coating material upon annealing was investigated by DSC and X-ray diffraction, showing only marginal structural changes between 900 and 1200 °C, which can be interpreted by a stabilisation due to the high-entropy effect. Upon annealing up to 1400 °C slight indication for the initiation of decomposition processes is given by emergence of low intensity XRD peaks. Yet, the hardness after annealing at 1400 °C remains at least ~42 GPa.

Compared to their binary boride constituents a significant structural stability and mechanical enhancement at elevated temperatures could be achieved by applying the high-entropy concept to HfTaVWZr boride thin films.

Author Index

Bold page numbers indicate presenter