New Horizons in Coatings and Thin Films
Room On Demand - Session F2

High Entropy and Other Multi-principal-element Materials

F2-1 Combinatorial Design of High Entropy Alloys: A Rational Approach in Thin Film*, Elise Garel (elise.garel@grenoble-inp.fr),* *H. Van Landeghem, R. Boichot,* SIMAP, Grenoble-INP, CNRS, France

High entropy alloys (HEAs) have been studied since 2004 for their exceptional mechanical properties. While conventional alloys are composed of one or two main elements plus addition elements, HEAs are designed with five or more principal elements. The development strategy of these alloys usually focuses on the interior region of the composition space. Among them, refractory high entropy alloys (RHEAs) are studied as an alternative to nickel superalloys that could, for instance, be used in aerospace or for energy production.

Improving the properties of a RHEA by the usual method of trial-and-error requires synthesizing and characterizing many different bulk alloys to cover the entire composition space. For five elements, exploring a 5 to 35% molar fraction range, with a variation of 0.1%, would represent 2.43×10^{12} possible samples to make. Thus, using this historical approach, with such a space to explore, new interesting alloys (probably not optimized) would be discovered essentially by applying a rule of thumb.

This study aims at developing a method to systematically explore an entire n-elements composition space with the minimum number of experiments, focusing on the particular quinary alloy Zr-Ti-Nb-Mo-Cr. Linear gradients of composition are synthesized by depositing thin films through a modified confocal Magnetron Sputtering deposition technique, choosing each set of targets so that these gradients pass by at least three points of an augmented centroid mixture design, to guarantee a uniform screening.

In a n-elements space, it has been demonstrated that there are $(3^n-2^{n+1}+1)/2$ possible gradients, that pass several times by each point of the mixture design. For five elements, there are 90 potential samples to deposit. It is then possible, depending on the preference of the experimenter – such as exploring preferentially the centre or the borders of the composition space - to choose a certain number of gradients among all the possibilities. In the case of a five elements RHEA, about 20 samples (meaning 20 experiments) are enough to screen the entire composition space.

All of these deposited alloys are to be characterized (composition, micro-hardness and phases) to build a database that links composition, structure and properties. A Machine Learning approach is tested to evaluate whether or not it is possible to build a reliable predictive model that would allow to define the RHEA compositions that optimize the alloy properties.

Ultimately, samples of optimized compositions would be cast in ingots in order to confirm on bulk samples the properties discovered with the thin film approach.

F2-2 Systematic Investigation of the Impact of Pure Metal Addition on AlCuMgZn Multi Principal Element Alloys*, Johannes Kirschner (johannes.kirschner@tuwien.ac.at),* *R. Gaschl,* Vienna University of Technology, Austria*; J. Bernardi,* USTEM, Vienna Technical University, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria*; C. Simson,* LKR Leichtmetallkompetenzzentrum Ranshofen, Austria

The design and synthesis of new materials and alloys is a crucial element in various technical areas, from the design of more energy-efficient mobility solutions to the construction of mechanically more robust alloys. Multi-Principal Element Alloys (MPEAs) show great potential as previous studies have shown that certain quaternary and quinary alloys containing approximately equal amounts of their constituents were superior to conventional alloys. The prediction of compatible elements and their optimal composition, especially in the area of light metals, represents a major challenge in this field and up to date, there is a lack of reliable models and concepts.

Multi-component layers (thickness of 10 µm) were co-deposited by magnetron sputtering and thereafter thermally treated to reveal the complex correlation between chemical composition, crystallography, mechanical properties and morphology. Quaternary systems including the elements Al, Mg, Zn and Cu were chosen to prepare samples in different compositions on a single substrate. Special emphasis was given to the increase of the relative Cu content with approximately the same ratios of the other alloying materials. Scanning electron microscopy in combination with energy dispersive X-ray spectroscopy and X-ray diffraction showed that the addition and increase of Cu have immense effects on the crystallographic phase formation. A wide concentration range in the Cu rich regime was observed (Cu content > 65 at%), in which a single phase system was formed. This range is characterized by significant indentation hardness variations and changes in microstructure. The obtained results were compared with the effects of the quantitative variation of the other constituents to evaluate the impact of different metals and metal classes (alkaline earth metals, transition metals, post-transition metals) on the system properties. Furthermore, the effects of the addition of a 5th element on the structure and crystallography of the alloy were investigated. These results establish a better understanding of the correlation between different metals in a complex system and expand the concept of high entropy alloys to the class of light metals to develop low density alloys. They should also provide valuable information for alloy synthesis using traditional methods such as melt synthesis.

Acknowledgements

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F2-3 Improving Phase Stability, Hardness and Oxidation Resistance of Reactive Magnetron Sputtered ($Al_vCr_wNb_xTa_yTi_z$)N Thin Films by Si-alloying*, Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at),* Institute of Materials Science and Technology, TU Wien, Austria*; K. Yalamanchili,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Rudigier,* OC Oerlikon Management AG, Switzerland, Liechtenstein*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloyed nitrides are promising materials for hard coatings. One major drawback is a lack of oxidation resistance in most coatings, which limits high-temperature applications in ambient conditions. In this work we report a method to increase the oxidation resistance while also improving thermal stability of the alloy, and higher resistance to the hardness drop induced by elevated temperature annealing.

($Al_vCr_wNb_xTa_yTi_z$)N coatings were formed in a cubic (c) solid solution in thin film form by reactive magnetron sputtering in N_2-atmosphere using a powder metallurgically prepared metal target (Plansee) with nominal composition of 20 at% of each element. Si was alloyed by placing different numbers of pieces (about 2x2x0.4 mm^3 each) of Si on the cathode racetrack during deposition. The hardness and indentation modulus of the as-deposited samples were 32.6 ± 2.0 GPa and 462 ± 23 GPa without Si, and 35.4 ± 1.1 GPa and 328 ± 14 GPa with Si, respectively. X-Ray Diffraction (XRD) measurements of the samples after vacuum annealing to temperatures up to 1200 °C revealed that Si delays the decomposition from 1000 °C to 1200 °C. After vacuum annealing to 1100 °C we measured a hardness of 30.3 ± 2.5 GPa and 38.1 ± 1.3 GPa as well as an indentation modulus of 445 ± 25 GPa and 430 ± 11 GPa for the samples without and with Si, respectively.

We gauged the oxidation resistance of the coatings by placing the samples in a furnace in ambient air at 850 °C for 0.5, 1, 5, 10, 30 and 100 h. After these durations we extracted the samples from the hot zone and analysed them with XRD and Energy-Dispersive-X-Ray-Analysis. With increasing Si-content the oxidation resistance improved significantly.

Based on our results we can conclude that this type of high entropy nitride coatings, especially when alloyed with Si, provides excellent thermomechanical properties as well as oxidation resistance.

F2-4 Carbon Containing Multicomponent Alloys with High Hardness, Ductility and Corrosion Resistance*, León Zendejas Medina (leon.zendejas.medina@kemi.uu.se),* Uppsala University, Sverige*; G. Lindwall,* KTH - Royal Institute of Technology, Sweden*; E. Pascalidou,* Uppsala University, Sweden*; L. Riekehr,* Uppsala University, Angstrom Laboratory, Sweden*; M. Tavares da Costa,* Uppsala University, Sweden*; S. Fritze,* Uppsala University, Angstrom Laboratory, Sweden*; K. Gamstedt,* Uppsala University, Sweden*; L. Nyholm, U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden

The development of fuel cells is a field in need of new multifunctional materials for corrosive environments. The cell components need to withstand the high potentials and low pH in the cell while simultaneously meeting many additional material requirements. In this study, we focus on finding coatings for corrosion protection of bipolar plates in PEM fuel cells. The high demands on the corrosion resistance must be combined with high mechanical stability and formability, to allow for roll-to-roll deposition followed by stamping to a customized pattern of flow channels. The

coatings must, therefore, meet high demands on three points: corrosion resistance, hardness, and ductility.

To achieve this, we have explored carbon addition to multicomponent films deposited by magnetron sputtering. Adding carbon is a known way to overcome the hardness-ductility trade-off [1] and improve the corrosion resistance of thin films, as long as the formation of crystalline carbides is avoided. The Cantor alloy, CrMnFeCoNi, was chosen as a starting point due to the high concentration of weak carbide forming elements. The alloy composition, combined with the high quenching rate during sputter deposition, improves the chances of carbide suppression.

The selection of new compositions was first explored by thermodynamic calculations using CALPHAD. The films were characterized using a range of techniques, from XRD, SEM, EDS, TEM, XPS to HAXPES and XAS at a synchrotron. Electrochemical measurements and mass spectrometry were used to understand the corrosion mechanisms. Nanoindentation was used to obtain mechanical parameters, while fragmentation tests on polyimide substrates were performed to investigate the crack resistance [2].

The addition of carbon to the alloy resulted in the amorphization of the material, starting from 6 at-% C, with no evidence of free carbon or a segregated carbide phase. The change in structure was accompanied by an increase in both hardness and crack resistance, and the addition of carbon greatly improved the corrosion resistance. In the second part of the study, Mo and W were added to the alloy as a way to increase the corrosion resistance further. The effects on structure and material properties will be presented in more detail.

References:

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2. Tavares da Costa, M. V., et al. Surf. Coatings Technol. 370, 374–383 (2019).

F2-5 Structural and Mechanical Properties of AlTiTaZr(-N) Medium Entropy Films (MEF) Obtained by DC Magnetron Sputtering in Dynamic Mode*, **Mohamed El Garah (mohamed.el_garah@utt.fr)**, S. Achache,* LASMIS, CNRS- Université Technologique de Troyes, France*; A. Michau, F. Schuster,* CEA, Université Paris-Saclay, France*; F. Sanchette,* LASMIS, CNRS-Université Technologique de Troyes, France

Since their introduction by Yeh and Cantor[1, 2], High Entropy Alloys (HEAs) reveal attractive physical and chemical properties. Similar to that, High Entropy Films (HEFs) have been also reported to possess excellent mechanical and physical properties such as good wear[3] and corrosion resistance[4] as well as an excellent thermal stability.[5] They open up new promising possibilities to various functional material applications; especially they can be used as protective coatings to deal with extreme environments.

New AlTiTaZr medium entropy films (MEFs) are elaborated by using direct current magnetron sputtering of four pure metallic targets. The films are deposited in various argon-nitrogen gas mixtures on glass, silicon and sapphire positioned in the center and in the target's axis of a rotating substrates holder. Crystallographic structure evolution, as a function of the nitrogen content, is predicted by calculating the phase selection criteria. The theoretical predicted structures are consistent with X-ray diffraction analysis results. Without nitrogen, the films are amorphous, and by increasing the N_2 content in the gas mixture, they are single phased faces centered cubic (FCC). A {200} preferential growth of AlTiTaZr(-N) films is favored in the targets axis position with increased nitrogen flow rate, whereas those in the center position of substrates holder grow preferentially with {111} planes parallel to the substrates surface.

Hardness and Young's modulus are improved with increasing of the nitrogen flow. The highest values were obtained for those in the targets axis position and reach 24.64 GPa and 148.4 GPa for the hardness and the Young's modulus, respectively. These films were annealed at 600 °C and 900 °C in vacuum and their thermal stability is discussed.

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(2) Yeh, J.-W.; Chen, S.-K.; Lin, S.-J.; Gan, J.-Y.; Chin, T.-S.; Shun, T.-T.; Tsau, C.-H.; Chang, S.-Y. , , 299.

(3) Cheng, J. B.; Liang, X. B.; Xu, B. S.*Coat. Tech.***2014**, *240*, 184.

(4) Hsueh, H.-T.; Shen, W.-J.; Tsai, M.-H.; Yeh, J.-W. , , 4106.

(5) Sheng, W.; Yang, X.; Wang, C.; Zhang, Y. , , 226.

F2-6 Mechanical Properties of Multilayered NbMoTaW Alloy Films with Cyclic Gradient Concentration*, Y. Chen, **Chun-Yen Chen (lover0614revol@gmail.com)**,* National Taiwan Ocean University, Taiwan

Conventional High-entropy alloy films have been fabricated through sputtering using a target of multi-principal-element materials with equal proportions in chemical compositions. In this study, NbMoTaW alloy films were prepared using a four-gun cosputtering apparatus with four pure-element targets. Moreover, the rotation speeds of the substrate holder were controlled at 1–30 rpm, which resulted in that the films exhibited a multilayer structure stacked with cyclic gradient concentration. The uniformity of the multilayered alloy films was improved with increasing the substrate holder rotation speed. The mechanical properties and crystalline phases of the NbMoTaW alloy films were investigated. The results indicated that the NbMoTaW alloy films prepared with a substrate holder rotation speed of 30 rpm exhibited a single body centered cubic(bcc) phase, a hardness of 12.9 GPa, and a Young's modulus of 287 GPa. The phase evolved into a combination of plural bcc phases as the substrate holder rotation speed was decreased to 1–10 rpm. All the NbMoTaW alloy films exhibited a Young's modulus level of 282–289 GPa. The NbMoTaW alloy films prepared at 10 rpm exhibited a high hardness of 14.1 GPa.

F2-7 Unveiling Microplasticity Mechanisms in Metallic Glasses with the Help of Polymer-supported Thin Films*, **Oleksandr Glushko (oleksandr.glushko@unileoben.ac.at)**,* Montanuniversität Leoben, Leoben, Austria*; C. Mitterer, J. Eckert,* Montanuniversität Leoben, Austria

The main, if not only, mechanism of plastic deformation in metallic glasses is *shear banding* – formation of strongly localized bands with high shear displacement within them. Despite at least a decade of intense research, shear bands are still not fully understood. This unfortunate situation can be explained by the fact that shear banding is a very fast kinetic process which can hardly be temporally resolved in an in-situ experiment. Additionally, the high amount of elastic energy which is released upon shear band propagation leads to catastrophic fracture of free-standing tensile samples through propagation of a single shear band across the whole specimen. Here, we use polymer-supported thin film metallic glasses (TFMGs) to capture the dynamics of shear bands under tensile loading.

By means of in-situ resistance measurements, in-situ optical microscopy as well as quasi-in-situ SEM and FIB characterization, different stages of evolution of shear bands and cracks with increasing strain are detected and described. Two distinct types of shear bands appear in polymer-supported $Pd_{80}Si_{20}$ and $Au_{60}Ag_{20}Si_{20}$ (deposited by co-sputtering) TFMGs with increasing strain: (i) the "out-of-plane" shear bands (the direction of shear is not in the film plane) which are formed at about 2% strain and develop quickly into through-thickness cracks and (ii) in-plane shear bands (the direction of shear is within the film plane) which appear after crack density saturation (at about 10% strain) and do not lead to crack formation. If the film thickness is reduced below 15 nm, the formation of shear bands is suppressed and the film can deform up to strains of about 6% elasto-plastically (i.e. without cracking) showing formation of homogeneously distributed short nanocracks at higher strains [1]. It is demonstrated, that with increasing applied strain, new in-plane shear bands can easily intersect the existing ones, whereupon the intersected shear bands become inactive and cannot carry further plastic deformation. This mechanism can lead to effective strain hardening of metallic glasses. Not intersected shear bands are shown to be softer than the non-deformed matrix and the deformation is localized there if the sample is unloaded and re-loaded.

Presented results demonstrate that formation of shear bands of specific type in thin film metallic glasses under tensile loading does not always lead to film failure. The "only" problem is to learn how to promote formation of favorable shear bands and suppress formation of unfavorable shear bands.

[1]O. Glushko, *et al.* Exceptional fracture resistance of ultrathin metallic glass films due to an intrinsic size effect. *Sci Rep***9,** 8281 (2019)

F2-8 Phase Formation and Structural Properties of AlSiTaTiZr Multicomponent Thin Film Alloys*, **Felipe Cemin (lipecemin@gmail.com)**, M. Jimenez,* UNICAMP, Brazil*; L. Leidens,* Universidade de Caxias do Sul, Brazil*; R. Merlo,* UNICAMP, Brazil*; C. Figueroa,* Universidade de Caxias do Sul, Brazil*; F. Alvarez,* UNICAMP, Brazil

The increasing demand for advanced materials combining unique and unusual properties has encouraged the study of new multicomponent alloys. High entropy alloys (HEA) were originally designed as simple solid-solution structures composed of at least five principal elements (3d transition metals) in near-equiatomic composition, yielding exceptional mechanical properties. In recent years, the field has grown to include

refractory and noble metals as well as low-density elements. Moreover, these alloys now include intermetallic phases, ceramic compounds, thin films, architected microlattices, *etc*. When considering HEA thin layers composed by functional elements such as Ti, W, and Zr, the as-deposited product is often amorphous (or nanocrystalline), due to the relatively large atomic size difference (resulting in sluggish diffusion) and 'rapid quenching' effect in sputtering deposition, prompting glassy metal formation.

In the pursuit of understanding these new materials in the non-bulk, thin film form, we have investigated key parameters leading to film crystallization and phase formation in an AlSiTaTiZr multicomponent system, due to its potential application in the field of high-temperature, oxidation-resistant coating materials. Therefore, metallic films were grown by radio-frequency magnetron sputtering at different deposition conditions with the goal to tune adatom diffusivity, grain nucleation, and ultimately the microstructure and properties of the films. Although the deposition method is essentially controlled by kinetic factors, thermodynamic calculations can help to predict possible phase formation. Therefore, thermodynamic simulations using the CALPHAD method were employed in post-annealed samples. The chemical composition of the films was controlled by proper designing of a sectioned, circular target containing slices ("pizza shaped target") of different elements. This approach differs from most of strategies using powder targets or co-deposition methods (multiple metal targets). The chemical bonds were analyzed by XPS revealing the presence of silicides and aluminades of the transition metals in both amorphous and crystalline metallic samples. Moreover, a microstructural characterization was performed using XRD and AFM. Post-thermal annealing prompts the metallic glass structure into a complex crystalline structure of several coexistent compounds, expected by thermodynamic calculations. Special focus is given to the entropy and enthalpy role on the phase formation and stability.

F2-9 XPS Core-Level Shifts, Local Lattice Distortions and Charge Transfer in HfNbTiVZr Refractory High Entropy Alloy*, **Luis Casillas-Trujillo (luis.casillas.trujillo@liu.se)***, Linköping University, IFM, Sweden*; B. Osinger, R. Lindblad, D. Karlsson, S. Fritze, K. von Fieandt,* Uppsala University, Angstrom Laboratory, Sweden*; B. Alling,* Linköping University, IFM, Sweden*; U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden*; I. Abrikosov,* Linköping University, IFM, Sweden*; E. Lewin,* Uppsala University, Angstrom Laboratory, Sweden

Ab-initio simulations of HfNbTiVZr high-entropy alloy using density functional theory (DFT) have been combined with experimental studies of the thin film material using X-ray photoelectron spectroscopy (XPS) to investigate lattice distortions, charge transfer and XPS core level shifts in the alloy. The lattice distortions obtained from the DFT simulations show that the size mismatch among the constituent elements is reduced in the alloy, causing a considerable reduction of the assumed lattice distortion effect commonly estimated with metallic radii. We show that this size reduction is due to the charge redistribution caused by the different local chemical environments, which was evaluated using a fixed sphere model that compared the relaxed, non-relaxed, and elemental reference structures. Finally, the theoretical core level shifts (CLS) values calculated from the DFT-simulated high entropy alloy show good agreement with the experimentally observed core level binding energy shifts, as well as peak broadening due to a range of chemical surroundings obtained by XPS measurements of a thin film deposited by sputter deposition.

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