New Horizons in Coatings and Thin Films
Room Pacific E - Session F2-ThA

High Entropy and Other Multi-principal-element Materials

Moderators: Dr. Erik Lewin, Uppsala University, Sweden, **Prof. Dr. Jean-François Pierson**, IJL - Université de Lorraine, France

1:20pm **F2-ThA-1 Data Driven Methods Enable Rational Design of High Entropy Materials for Hydrogen Storage***, **Matthew Witman**, V. Stavila, M. Allendorf,* Sandia National Laboratories, USA **INVITED**

Data-driven modeling in recent years has ushered in a new paradigm for rapid discovery of useful materials across a plethora of domains in the physical and materials sciences. These methods become particularly invaluable when investigating applications of high-entropy materials, where the combinatorial growth of explorable chemical space makes brute-force experimentation or first-principles simulation intractable. To assess the primary figure(s) of merit for 10,000s of possible materials for a given application and down-select only top candidates for more rigorous examination, accurate and efficient machine learning and data-driven techniques are required. This talk will survey a variety of data-driven (high entropy) hydride discovery exemplars representing efforts between Sandia and a large international collaboration group. These range from traditional machine learning approaches for direct hydride thermodynamic property prediction to modern graph neural networks, trained as DFT surrogate models, that feed sampling-intensive first principles simulations. These modeling strategies can rapidly screen hydride thermodynamic properties and therefore experimentally target new materials or rationally tune existing ones for various hydrogen storage or compression use cases. Coupled with additional simple objectives (i.e., raw material costs), multi-dimensional Pareto optimal materials can therefore be identified, targeted, and synthesized.

2:00pm **F2-ThA-3 Effect of Mo Content on the Corrosion and Tribocorrosion Behavior of $(CoCrFeNi)_{100-x}Mo_x$ HEA Thin Films Deposited by HiPIMS***, **Alessandro Togni**, R. Tinazzi,* Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Italy*; S. Deambrosis, E. Miorin, F. Montagner, C. Mortalò, V. Zin,* Institute of Condensed Matter Chemistry and Technologies for Energy, National Research Council, Italy*; G. Bolelli, L. Lusvarghi,* Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Italy

Based on a multi-principal-element-design concept, high-entropy alloys (HEAs) feature enhanced mechanical strength, excellent thermal stability, and superior wear and corrosion resistance, making them promising candidates for applications in harsh environments. Moreover, the microstructure and properties of HEAs can be fine-tuned by changing their composition or by alloying them with additional elements, boosting their application potential even further. Therefore, HEA-based protective films with suitably designed compositions could improve the wear and corrosion resistance of low-cost substrate materials under various service conditions. In this work, $(CoCrFeNi)_{100-x}Mo_x$ HEA thin films were deposited on Si and AISI 304 stainless steel substrates by high-power impulse magnetron sputtering (HiPIMS) using pure Mo and equiatomic CoCrFeNi targets. The effect of Mo content on the microstructure, mechanical properties, and corrosion and tribocorrosion behavior of the films was investigated by adjusting the Mo target-to-substrate distance. Higher amounts of Mo favored the formation of a dense microstructure, resulting in higher hardness values. The potentiodynamic polarization curves revealed that the corrosion resistance of the films in 3.5 wt.% NaCl solution is not significantly affected by Mo concentration. Differences were found, however, in terms of tribocorrosion behavior. With increasing Mo content up to 12 at.%, the wear rate of the films gradually decreased. Above this value, further Mo addition resulted in increased material loss. The obtained results aim to contribute to a comprehensive understanding of the corrosion and tribocorrosion behavior of HEA thin films in artificial seawater to broaden their application in marine engineering.

2:20pm **F2-ThA-4 Corrosion Behavior of Sputter-Deposited CoCrNiFeAl High Entropy Alloy***, A. Korra,* University of Tennessee at Chattanooga, USA*; H. Raji,* Florida Institute of Technology, USA*; **Hamdy Ibrahim**,* University of Tennessee at Chattanooga, USA*; S. Saedi,* Florida Institute of Technology, USA

Multicomponent or High-entropy alloys (HEA) are the new generation of alloys with exceptional properties such as high strength and hardness, excellent thermal stability at high temperatures, and remarkably good fatigue. Recently HEA thin films have attracted significant attention due to their superior corrosion resistance and emerged as potential candidates to meet demanding requirements for selected extreme applications, particularly in the nuclear, turbine, and aerospace industries. Prominent advantages of HEAs are primarily derived from their ability to stabilize as a single-phase crystalline structure when specific alloy design criteria are met. HEA thin films have been fabricated using a wide range of technologies including laser cladding, arc cladding, electrodeposition [https://www.sciencedirect.com/topics/materials-science/electrodeposition], and spraying. However, magnetron sputtering is one of the most desirable fabrication methods due to lower growth temperatures, precise control, good film-forming ability, high efficiency, and good film adhesion. In this work, CoCrNiFeAl (at.%) was deposited by Radio Frequency (RF) magnetron sputtering to evaluate its corrosion behavior. While homogenization is a common post-processing treatment in metallurgy, the process for HEA can be entirely different from regular alloys due to the slow/sluggish diffusion and phase transformation rate in HEAs. To understand the effects of homogenization on the sputter target deposited HEAs, heat treatments in the range of 800-1100 °C were performed and the microstructure, phase stability, hardness, and corrosion behavior were investigated. While the results obtained from both Calphad modeling and experiments showed that homogenization is a strong mechanism for improving the corrosion resistance in HEA composition, it was also concluded that hominization temperature can play an important role in the formation of phases that can significantly deteriorate the corrosion resistance. The conclusion was drawn from the fact that lower homogenization temperatures led to the formation of an undesirable sigma phase in the microstructure that was decomposed to a secondary BCC single phase in the alloys treated at higher temperature ranges.

2:40pm **F2-ThA-5 Mechanical Properties of Low Density Ternary Titanium-rich Medium-entropy Alloy with Heterogeneous Structure***, **Che-Wei Chang**,* Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Taiwan*; P. Chen, S. Jang,* Institute of Material Science and Engineering, National Central University, Taiwan*; C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Taiwan

At present, global warming is becoming more and more serious. We plan to reduce the weight of the material to reduce energy loss during transportation. Therefore, we expect the medium entropy alloy to have good mechanical properties, and it can also have low density characteristics, so we choose alloys to carry out. In follow-up studies, the mechanical properties of alloys have always been an important issue for researchers. It is well known that the strength and ductility of alloys compete with each other. It has been pointed out that the heterostructure allows alloys to exhibit good strength and ductility simultaneously. Therefore, we attach our alloys to rolling and annealing and expect to obtain a heterostructure. X-ray diffractometer (XRD) and electron backscatter diffractometer (EBSD) was used to observe the changes in crystal structure and microstructure of the alloy under different annealing time. Finally, we perform tensile tests to obtain the mechanical properties of the alloys and compare the microstructural evolution between them.

3:00pm **F2-ThA-6 Charge Transfer Effects in Multicomponent Materials – Shown by Ab-Initio Calculations and X-Ray Photoelectron Spectroscopy XPS***, **Barbara Osinger**,* Uppsala University, Angstrom Laboratory, Sweden*; L. Casillas-Trujillo,* Linköping University, Sweden*; R. Lindblad,* Uppsala University, Angstrom Laboratory, Sweden*; B. Alling,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden*; I. Abrikosov,* Linköping University, Sweden*; E. Lewin,* Uppsala University, Angstrom Laboratory, Sweden

Multicomponent materials have opened a vast landscape for complex compositions and interesting properties. They exhibit complex bonding, due to their diverse chemical environment, as a result of the extensive alloying, typically involving 5 or more elements. Ab-initio calculations, using density functional theory (DFT) and X-ray photoelectron spectroscopy (XPS), were used to investigate the electronic structure of multicomponent thin films based on the HfNbTiVZr system. The charge transfer was evaluated theoretically using relaxed, non-relaxed, as well as elemental reference structures using a fixed sphere size model to quantify the charge transfer. High-resolution XPS spectra were obtained from HfNbTiVZr and (HfNbTiVZr)C magnetron sputtered thin films.

The HfNbTiVZr alloy shows core level binding energy shifts and peak broadening, compared with metal references, which are in good agreement with shifts calculated from DFT simulations, where charge

transfer between the metal atoms is observed. The charge transfer follows the general electronegativity trend, and results in a reduced atomic size mismatch and lattice distortion δ, compared with estimates based on tabulated atomic radii. Similarly, the (HfNbTiVZr)C carbide films exhibit core level binding energy shifts and broadening effects, as a result of their complex chemical environment.

This study demonstrates the importance of chemical bonding and environment when discussing multicomponent materials. Moving beyond the concept of an ideal solid solution and considering the bonding in more detail opens up a deeper understanding and the possibility of tuning the electronic structure. This would be especially interesting for the design of multicomponent materials, as many desirable properties are a result of their bond character.

3:20pm **F2-ThA-7 Toughness Estimation of High Entropy Nitride Coatings by Tensile Testing**, ***Martin Kuczyk***, *T. Krülle,* Technische Universität Dresden, Germany*; M. Zawischa, M. Leonhardt, O. Zimmer, J. Kaspar,* Fraunhofer IWS, Germany*; C. Leyens, M. Zimmermann,* Technische Universität Dresden, Germany

High Entropy Nitrides (HEN) are an interesting material system intended for sophisticated wear and high-temperature applications. Being closely linked to the group of so-called high entropy alloys, which were discovered independently by Cantor and Yeh in the early 2000s [1,2], they consist of five or more nitride-forming constituents in a near equimolar ratio as well as 50 at% nitrogen forming single-phased fcc microstructures. Multiple works have shown that through the use of HEN superior hardness close to or in some cases well into the superhard range (H > 40 GPa) can be achieved while also maintaining high thermal stability [3,4].

For the possible use as protective tool coatings, not only hardness and thermal stability are important factors but also toughness. A method that might be suitable for high throughput screening of coating toughness is tensile testing of coated substrates. The description of critical strains at which first cracks in the coating appear as well as the development of the crack density with increasing applied strain can be used to reasonably estimate coating toughness values.

In this work, three HEN coatings are compared to (AlTi)N via tensile testing. The three coatings are (AlCrTaTiZr)N, (AlCrNbSiTIV)N and (HfNbTaTiVZr)N and were chosen based on previous works of the author [4]. The applicability of that method for the screening of coating toughness is discussed by comparing the results with other more established methods for the estimation of fracture toughness such as micro-beam bending.

It could be shown that tensile testing is a feasible method for high throughput screening of coating toughness.

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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. Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes. Adv. Eng. Mater. 2004, 6, 299–303, doi:10.1002/adem.200300567.

3. Li, W.; Liu, P.; Liaw, P.K. Microstructures and properties of high-entropy alloy films and coatings: A review. Materials Research Letters 2018, 6, 199–229, doi:10.1080/21663831.2018.1434248.

4. Kuczyk, M.; Krülle, T.; Zawischa, M.; Kaspar, J.; Zimmer, O.; Leonhardt, M.; Leyens, C.; Zimmermann, M. Microstructure and mechanical properties of high entropy alloy nitride coatings deposited via direct current cathodic vacuum arc deposition. Surface and Coatings Technology 2022, 448, 128916, doi:10.1016/j.surfcoat.2022.128916.

3:40pm **F2-ThA-8 Synthesis and Characterisation of (Gd,Hf,Sc,Ti,Zr)-Oxide Coatings**, ***Alexander Kirnbauer***, *E. Peck, M. Derflinger,* 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

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. Especially oxides are of great interest as they can serve as oxidation protection coatings at high temperatures. A very common oxidation-protection coating is α-Al_2O_3, usually synthesised by chemical vapour deposition as very high temperatures are required to form the stable α form. Another interesting oxide for use at high temperatures is HfO_2 as it exhibits the highest melting point within the group of oxides besides Thorium oxide. As HfO_2 crystallises, similar to ZrO_2, in three different crystal structures, the desired cubic high-temperature modification is hard to stabilise. Within this work we report on the phase formation and mechanical properties of (Gd,Hf,Sc,Ti,Zr) oxide coatings. High-entropy metal sublattice oxides were synthesised using reactive magnetron sputtering utilising a single equiatomic target consisting of Gd, Hf, Sc, Ti, and Zr. For synthesis of oxide coatings different $O_2/(Ar+O_2)$ flow ratios were used to investigate the influence of reactive gas flow on the structure and mechanical properties. X-ray diffraction analysis show that the coatings crystallise in a single-phase fcc structure. Nanoindentation measurements revealed hardness values of ~20 GPa and an indentation modulus of ~ 250 GPa. Furthermore, transmission electron microscopy investigations were done to get more detailed information about the growth morphology and crystal structure of the oxide coatings. To investigate the structural stability at elevated temperatures, vacuum annealing treatments and subsequent XRD and nanoindentation measurements were done.

4:00pm **F2-ThA-9 Functional Materials for Energy Applications**, ***Susan Sinnott***, Pennsylvania State University, USA **INVITED**

The development of new functional materials for use as battery electrodes, for catalysis, and for electronic devices is an ongoing area of research. Structure-property relationships are determined using a combination of experimental characterization and high-fidelity computational methods. Here, first-principles density functional theory (DFT) calculations are used to investigate functional two-dimensional inorganic materials and high-entropy oxides (HEOs). Two-dimensional materials have properties that strongly depend on composition, defects, and surface structure. This presentation will focus on two-dimensional metal dichalcogenides and metal dichalcogenide/metal carbide heterostructures that have unique properties related to electron confinement within these layered materials. The computational predictions are compared to experimental data to advance design of two-dimensional materials for electronic devices. Similarly, the controlled synthesis of functional HEOs are being investigated, including J14 [(Mg, Co, Cu, Ni, Zn)0.2O] and F1 [Ce, La, Pr, Sm, Y)0.2O2-δ] where δ indicates oxygen vacancies. In this case, DFT calculations are being employed to help explain recent findings of structural dependencies on growth conditions for J14 and to reveal structure-transport composition trends in F1, a leading high-ion conductor. The synergies between experimental synthesis, characterization, and modeling is a focus of the presentation.

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