Wednesday Afternoon, May 22, 2019

Topical Symposia
Room Pacific Salon 3 - Session TS1-2-WeA
High Entropy and Other Multi-principal-element Materials II

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

2:00pm **TS1-2-WeA-1 Structure and Mechanical Properties of Refractory Type High-entropy Alloy Thin Films Deposited by Vacuum-arc***, **Martin Kuczyk**, U Nimsch, O Zimmer, J Kaspar, F Kaulfuss, A Leson, M Zimmermann, C Leyens,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany

High-entropy alloys (HEA), comprised of five or more principal elements in near equimolar ratios, have attained increasing attention, since they have demonstrated many exciting properties such as high hardness and wear resistance, high strength at elevated temperatures and high thermal stability or a desirable balance of structural and functional properties. Hence, it is supposed that coatings from HEAs will also exhibit such promising properties.

In the current work a series of refractory type HEA metal and nitride thin films were synthesized by means of vacuum-arc deposition technique. For this pre-alloyed targets of TiVNbZrMo, TiVNbZrHf and TiNbZrHfTa were vaporized in argon and nitrogen atmosphere. The film microstructure was analyzed applying high resolution electron microscopy (SEM and TEM) as well as X-ray diffraction. Moreover nanoindentation was used to determine the hardness and elastic modulus of the different coatings.

The results of the structural analysis reveal, that all metallic coatings exhibit a single phase bcc and all nitride layers a single phase fcc structure with more or less strong columnar grain growth. The hardness of the metallic HEA coatings is typically about 10 GPa, whereas the hardness of the nitride coatings is above 25 Gpa, clearly depending on the chosen material system.

Due to their high hardness the obtained multi-element nitride coatings are regarded as promising candidates for cutting tool application. It is furthermore concluded, that further improvement of mechanical properties of the metallic and nitride HEA coatings should be feasible by additionally applying a nanostructured design.

2:20pm **TS1-2-WeA-2 Templated Stacking of Organic/Inorganic Semiconductors Crystals Upon Coalescence, Assembly and Split Behaviors of High-entropy Ferroelectric Lamellar Crystals***, **Jr-Jeng Ruan**, C Pan, J Ting, K Chang, Y Su,* National Cheng Kung University, Taiwan

The cocrystallization of multiple principle elements with near-equimolar ratio has been widely pursued as an approach to create high-entropy alloys, which likely involves plentiful spatial distribution patterns of constituent elements within crystal lattices and therefore fruitful physical properties. In the field of organic materials, the cocrystallization of two disparate organic compounds is also feasible, but, nevertheless is rarely found. Upon the random incorporation of trifluoroethylene (TrFE) and vinylidene fluoride (VDF) motif within random copolymer poly(vinylidene fluoride trifluoroethylene) (PVDF-TrFE), possible routes of cocrystallization of VDF and TrFE motifs are studied, and several ferroelectric crystalline phases were found able to grow concurrently. For the development of each crystalline form, there is an appropriate composition range of TrFE motif, instead of a specific composition. Above the Curie temperature, all the crystals transform into the high-temperature phase, and unique secondary crystallization behaviours are involved, which initiates lamellar coalescence and assembly. As a result, previous crystals lattices composed of various compositions and helical conformers are integrated together into one crystals, rendering the high-temperature lattice packing as a kind of high-entropy crystalline form.

For the transportation of charge carrier within organic/inorganic semiconducting thin films, continuous pathways are realized to critically rely on stacking and growth pattern of semiconductive crystals. Hence, based on initiated coalescence and assembly behavior of crystalline lamellar of PVDF-TrFE, adjustable stacking pattern of PVDF-TrFE lamellar crystals upon the mixing with poly(methyl methacrylate) (PMMA) have been further studied and adopted as the guiding template for the crystallization of organic/inorganic semiconductors. With the presence of regular stacking arrays of ferroelectric PVDF-TrFE lamellar crystals, oriented crystals growth of convention organic semiconductor like 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) and fullerene derivative of [6,6]-phenyl C61 butyric acid methyl ester (PCBM) has been identified. In addition, oriented crystallization of 2D lead-free perovskite $(PEA)_2SnI_4$ crystals were explored in this research as well, which is classified as a kind of 2D materials and less subject to environmental moisture. Based on unveiled guiding effects of stacking arrays of PVDF-TrFE lamellar crystals, the physics and also possible routes to harvest the merits of coexistent constituent phases have been acknowledged.

2:40pm **TS1-2-WeA-3 Angular-dependent Deposition of High Entropy Alloy Thin Films by DCMS, HiPIMS and Cathodic Arc***, **Ao Xia**,* Montanuniversität Leoben, Austria*; A Togni,* University of Modena and Reggio Emilia, Italy*; S Hirn,* Montanuniversität Leoben, Austria*; L Lusvarghib,* University of Modena and Reggio Emilia, Italy*; R Franz,* Montanuniversität Leoben, Austria

In recent years, high entropy alloys (HEAs) have emerged as a new class of materials. These typically metallic alloys consist of 5 to 13 metallic elements in an approximately equimolar ratio. Studies conducted on HEA bulk materials revealed promising combinations of properties, such as high strength, corrosion resistance, high wear resistance, high hardness and sluggish diffusion. While research on bulk HEAs has seen quite a boost over the past years, HEAs as thin films are still a relatively unexplored area.

The current work examines the influence of different physical vapor deposition methods on structure, chemical composition and properties of HEA thin films at different deposition angles. MoNbTaVW and AlCuCrTaTi HEA thin films were deposited by cathodic arc deposition (CAD), direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HIPIMS). The HEA thin films were deposited on Si substrates which were positioned at angles from 0° up to 90° in steps of 15° with respect to the cathode surface normal. The achieved coating thickness varied from 0.3 to 3.2 µm depending on deposition technique and angle. According to scanning electron microscopy and X-ray diffraction, the HEA thin films revealed a smooth surface with columnar growth characteristics and a bcc crystal structure regardless of the deposition method. The chemical composition of the coatings was analyzed by energy dispersive X-ray spectroscopy which revealed, e.g., that W and Ta, the heaviest elements in the composition, are the most abundant elements at a deposition angle of 0° in the MoNbTaVW films deposited by CAD. However, their atomic percentage decreases with increasing deposition angle and at 90° the HEA thin films were enriched in V, the lightest element. Finally, mechanical properties of the synthesized HEA thin films were determined by nanoindentation to compare the impact of the deposition technique on the hardness and elastic modulus of the synthesized HEA films.

3:00pm **TS1-2-WeA-4 Combustion Synthesis of High Entropy Alloys Thin Films: AlCrFeNi, AlCrCuFeNi, and AlCoCrFeNi***, **Anni Wang**, M Hopfeld, T Kups, D Flock, H Romanus, L Kellmann, H Rupapara, P Schaaf,* Technische Universität Ilmenau, Germany

This study presents combustion synthesized High Entropy Alloy (HEA) thin films through physical vapor deposition (PVD). By that, metallic multilayer coatings were produced with different multilayer scales in a total thickness of around 900 m. AlCrFeNi, AlCrCuFeNi, and AlCrCoFeNi were selected due to their large negative enthalpy of formation and superior physical and chemical properties. Several stacking sequences of CrNi, AlFe, CoFe, Cu were deposited onto an as-prepared Ni-Al reactive layer on a Cu substrate; afterward, the coatings were removed from the Cu substrate to form a free-standing HEA thin film. Two fabrication methods were conducted in comparison: combustion synthesis via spark ignition and thermal treatment via rapid thermal annealing. The propagation velocity and temperature during combustion synthesis were monitored by using a high-speed camera and a pyrometer. The reaction products were then analyzed b y means of a scanning electron microscope (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) to identify the phase transformation and stability related to the layer stacking as well as annealing temperature. The compositional profile and uniformity were measured via EDX analysis with SEM, and Auger electron spectroscopy. A spark voltage of 12 V for stacking layers of 30 nm was shown to be sufficient despite the unstable and partial reaction. In the reacted region, grain sizes of 200 to 300 nm were observed from TEM images. In contrary to the annealed samples with random texture, the combustion synthesized ones showed highly textured HEA thin films as seen from XRD patterns. In this research, a new synthesize path for developing HEA thin films is first introduced, and the attempt to optimize a stable reaction through individual metal layers and thickness is demonstrated.

Acknowledgment

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3:20pm **TS1-2-WeA-5 Nanostructured Highly Concentrated Solid Solution Alloy Coatings on a Zirconium Based Alloy**, *M Tunes, S Donnelly,* Institute for Materials Science, University of Huddersfield, UK*; P Edmondson,* Oak Ridge National Laboratory, USA*; **Vladimir Vishnyakov,*** University of Huddersfield, UK

Highly Concentrated Alloys (HCAs) are a class of multicomponent alloys formed with two or more elements in close to equiatomic composition. The materials are lately also known as High Entropy Alloys (HEA). The alloys have enhanced phase stability in extreme environments. Aiming at to establish a protective coating on Zr-based alloys (or Zircaloys), equiatomic and non-equiatomic thin films from the FeCrMnNi system were deposited on both Si and Zircaloy-4 substrates at room temperature by ion sputtering. The microstructural features of the films has been performed by means of Transmission Electron Microscopy (TEM). The non-equiatomic thin film exhibited polycrystalline structure with nanometre-sized grains while in the equiatomic thin film, grains are bigger with sizes around of 100-200 nm. Planar defects, surface roughening and Ar bubbles were also observed in the microstructure of the films. Current theories of concentrated solid solution alloys and crystal nucleation have been applied to reflect on the results. Metallic alloys are well suited to form protective coatings on Zircaloys for the future Accident Tolerant Fuel (ATF) reactor assemblies.The experimental results obtained demonstrate the possibility of depositing highly concentrated solid solution alloy thin films as protective coatings for future ATF systems using Zircaloys as the nuclear-fuel cladding material at low homologous temperature. A study on their radiation resistance conducted using *in situ* TEM heavy ion irradiation will also be presented.

3:40pm **TS1-2-WeA-6 High Temperature Electrical Conductivity and Oxidation Resistance of V-Nb-Mo-Ta-W High Entropy Alloy Thin Films***,* ***Yen-Yu Chen,*** Ming Chi University of Technology, Taiwan*; S Hung, C Wang, W Wei,* National Taiwan University of Science and Technology, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

Multi-principal element alloys, such as high entropy alloys (HEA), show outstanding thermodynamic, mechanical or thermal properties as compared with pure metals or binary alloys. Among several kinds of HEAs, the refractory element containing HEAs exhibit relatively high thermal stability and better mechanical properties at elevated temperature. In this study, the V-Nb-Mo-Ta-W high entropy alloy thin films with and without nitrogen doping were deposited on the substrate of AISI 316 stainless steel by a magnetron sputtering process. The oxidation resistance and electric conductivities of HEA thin films at elevated temperatures were evaluated for high temperature application. Crystal phases, chemical compositions, microstructures and mechanical property of these thin films were characterized by the x-ray diffraction, energy dispersive spectra, scanning and transmission electron microscopes, and nanoindenter, respectively. The electrical conductivity of V-Nb-Mo-Ta-W thin films are around 10^7 S-cm^{-1}. The electrical conductivities of V-Nb-Mo-Ta-W and V-Nb-Mo-Ta-W-N thin films gradually decreased when the oxidation temperature increased. The decreasing tendency of electrical conductivity is due to the surface oxidation of thin films and formation of amorphous phase. The influence of nitrogen content, microstructure and phase evolution on the oxidation resistance and electrical conductivity of thin films under high temperature conditions will be discussed in this work.

4:00pm **TS1-2-WeA-7 Micro-mechanics of High Entropy Alloys: Size Effects and Rate Sensitivity***,* *Y Xiao, R Spolenak, **Jeffrey M. Wheeler,*** ETH Zürich, Switzerland **INVITED**

High-entropy alloys (HEAs) are comprised of four or more major alloying elements, where the individual elements typically exhibit concentrations between 5 and 35 at%. These alloys demonstrate exceptional properties (e.g. high strength, high toughness, good corrosion performance, et cetera) and represent a fascinating new field of metallurgy and materials science. Over the last few years, great advances have been made to understand the mechanical behavior of these alloys in the micron and submicron regimes. However, a systematic, experimental investigation of the influence of increasing the number of major components on the fundamental plasticity mechanisms is still missing. In this study, the deformation behavior of the medium-entropy alloy CrCoNi and high-entropy alloy FeCrCoNi is compared with more traditional unary and binary alloys (pure Ni and NiCo) by using *in situ* strain rate jump micropillar compression. This allows us to simultaneously determine both size effects and rate effects, which give a fingerprint of the fundamental plasticity behaviour, from a single sample set. From these results, we discuss the relationship between solid solution strengthening mechanisms and the number of major alloying elements and how this quantitatively relates to the observed deformation mechanisms.

4:40pm **TS1-2-WeA-9 Is the Entropy of High Entropy Ceramics High?***,* ***Jochen Michael Schneider,*** *S Evertz, D Neuß, M Steinhoff, D Holzapfel,* RWTH Aachen University, Germany*; S Koloszvári,* Plansee Composite Materials GmbH, Germany*; P Polcik,* PLANSEE Composite Materials GmbH, Germany*; H Rueß,* RWTH Aachen University, Germany

Several reports have extended the high entropy alloy notion to ceramics and ultrahigh temperature ceramics. Here the configurational entropy of several so called ceramic high entropy alloys is estimated. Furthermore, (TiCrMoW)N, (TiVNbTa)N, (VNbTaCrMoW)N and (TiVZrNbHfTa)N thin films were grown and their thermal stability was evaluated. Based on the obtained thermal stability data of compounds with similar configurational entropy the conceptual significance of the high entropy ceramics notion is critically appraised.

5:00pm **TS1-2-WeA-10 Next Generation Entropy Stabilized Material***,* ***Jyh-Ming Ting,*** *J Ting, K Chang, Y Su,* National Cheng Kung University, Taiwan

High entropy alloy (HEA) has been one of the most focused materials in the last decade and continues to be one that is still drawing a tremendous amount of attentions from academia and industry. While the research and development of HEA is being conducted world-wide, recent attention has also been paid to high entropy oxides (HEOs) and nitrides (HENs). Limited studies have shown the synthesis of various HEOs that exhibits unique structures and improved, unexpected properties. The studies in HEOs and HENs are still in its infant stage such that unlimited explorations are there. Also, in these studies, the vast majority of the materials are made in bulk, including powders. As a result, we have recently launched a study to investigated HEOs and HENs thin films as well as powders. Combinatorial deposition techniques are applied to make the films and non-conventional, facile methods are used to made the powders. The resulting materials, including a number of new HEOs, are subjected to microstructural analysis and a number of different physical/chemical characterizations. In particular, the thin film samples are investigated with tools that are capable of mapping the characteristics of the entire films. The materials are also examined for use in energy generation/storage and photocatalysis.

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