Topical Symposia
Room Royal Palm 4-6 - Session TS2
High Entropy and Other Multi-principal-element Materials

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

9:00am **TS2-4 Novel Properties and Nitriding Behavior of CoCrMnFeNi High-Entropy Alloy Prepared via Mechanical Alloying and Spark Plasma Sintering**, ***Akio Nishimoto***, *T Karimoto, C Nishi,* Kansai University, Japan

An equiatomic CoCrMnFeNi high-entropy alloy (HEA) exhibiting unique chemical and physical properties was synthesized via mechanical alloying (MA) and spark plasma sintering (SPS). The phase evolution, microstructure, mechanical properties, and nitriding behaviors of the HEA were investigated. The 30-h ball-milled alloy powder demonstrates excellent chemical homogeneity and a face-centered-cubic-structured solid-solution-refined morphology. The 30-h MA powder was subsequently consolidated via SPS at 700 °C–900 °C for 10 min. The sintered sample exhibits 93%–97% in relative density and 400–550 HV in Vickers hardness. The wear properties of the sintered sample improved compared with those of the casted sample. The effects of plasma nitriding at 500 °C–550 °C on microstructure and the mechanical performance of the HEA processed via MA-SPS were also investigated. The nitrided layer has a thickness of approximately 30 µm and a peak hardness level of 1300 HV near its surface. The nitrided sintered HEAs exhibit superior wear resistance compared to the casted HEA sample.

9:20am **TS2-5 Structural, Phase Stability, Thermodynamic and Elastic Properties of CoCrCuFeNi-(Nb_x, Al_x) High-entropy and Other Thin Films: Experimental and Ab Initio Investigations**, *C Li,* LSPM-CNRS, France*; B Braeckman, R Dedoncker,* Ghent University, Belgium*; Q Hu,* IMR-CAS, China*; L Belliard,* INSP-UPMC, France*; L Vitos,* KTH - Royal Institute of Technology, Sweden*; D Depla,* Ghent University, Belgium*;* ***Philippe Djemia,*** LSPM-CNRS, France

High entropy alloys are new class of multicomponent materials that renewed the metallurgy concepts by alloying several elements, at least five, with nearly equal concentrations. High mixing entropy can enable stabilization of one phase material by avoiding the formation of several intermetallic compounds. Among them, bulk CoCrCuFeNi solid solution with FCC structure has been among the first. Nevertheless, elaborating and characterizing their thin film counterparts is of newly increasing interest, providing different microstructures inherently due to a different process. Addition of a supplementary element can either increase the lattice distortion and/or favoured strong bonds formation with transition metals. These both effects on phase stability, structural and elastic properties are experimentally and theoretically studied with Nb and Al addition, respectively. Furthermore, as Nb is heavier than base elements, its addition also alters the growth conditions by the atomic peening effect. Fully dense films are then obtained with no modification of their mass density while mass density continuously decreased as a function of Al concentration.

Assessing the elastic properties of polycrystalline multicomponent alloys remains challenging as they relate on many attributes: the phase composition, texture, existence of lattice defects, impurities and porosities, grain size. Strategies should be employed to tackle this challenge by varying microstructure in a control manner and considering both single crystalline and polycrystalline materials.

This is the aim of the present work dedicated to polycrystalline cubic CoCrCuFeNi-(Alx, Nbx) films deposited by magnetron sputtering under Ar plasma discharges on a silicon substrate. In parallel, ab initio calculations were performed in the framework of the density functional theory using EMTO program providing theoretical data for the single crystal. Mass density r was determined by x-ray reflectivity measurements, while x-ray diffraction pole figure was employed to study texture effects and determine lattice parameters. Brillouin light scattering technique allows measuring sound velocity of surface acoustic waves (V_{SAW}) in thin films and thus estimating effective elastic constants (ρV^2). It can be conveniently combined with picosecond ultrasonics technique that measures the sound velocity of longitudinal waves (V_L) that are travelling forth and back within the film along the direction perpendicular to the film plane. We used this combination of techniques to measure the effective elastic constants C_{11}, C_{33}, C_{13} and C_{44} of our nanocrystalline and amorphous films.

9:40am **TS2-6 Carbon-containing High Entropy Alloys - A New Pathway to High-performance Materials?**, ***Stefan Fritze***, *P Malinovskis, L Riekehr, D Rehnlund, L Nyholm, E Lewin, U Jansson,* Uppsala University, Angstrom Laboratory, Sweden

High entropy alloys (HEAs) are a promising pathway to achieve new high-performance materials. While HEA thin films have been studied to some extent by experimental and computational materials science, there is only limited information available about the influence of carbon on HEA thin films, especially when prepared with physical vapor deposition techniques. In this study, we report on the influence of carbon on the structure and properties of three different HEA alloys in the CrNbTaTiW system, which are based on only strong carbide-forming transition metals. The metal composition of these alloys includes an approximately equimolar alloy, a Nb-rich alloy and finally a Ta/W-rich composition.

We have successfully deposited highly textured Cr-Nb-Ta-Ti-W-Cthin films by non-reactive unbalanced magnetron sputtering using one carbon and five metal targets. The films were characterized with SEM, XPS, XRD, TEM and nanoindentation. XRD analyses of these coatings show that all carbon-free Cr-Nb-Ta-Ti-W films crystallize in a simple bcc structure with a strong (110) orientation. The addition of 7 at.% carbon lead to an expansion of the unit cell, while retaining the bcc structure without formation of any additional carbide phases in the as-deposited state. As more carbon is added (40 at.%) a transition metal carbide (NaCl-type) structure is obtained.

The best mechanical properties were achieved for a Ta/W rich metal sublattice for all three carbon concentrations. An as-deposited $Cr_2Nb_8Ta_{44}Ti_2W_{44}$ films, exhibited a hardness of 14 Gpa. This is more than two times higher than expected from rule of mixture. The high hardness can be explained by a significant lattice strain due to large differences in atomic radii. Upon the addition of 7 at.% carbon the hardness increased by ~40 percent to 21 Gpa. The formation of a multicomponent carbide film at a carbon concentration of 40 at.% C, leads to a further hardness increase to 27 Gpa. Potential mechanisms for the formation of these extremely hard bcc alloys with carbon will be discussed. Finally, the effect of carbon addition on the corrosion properties was likewise investigated in 0.6 M NaCl environment. High pitting corrosion resistance was found for the $Cr_2Nb_9Ta_{40}Ti_2W_{40}C_7$ composition, with a corrosion potential of 0.23 V (vs. Ag/AgCl) and a transpassive region equal to hyper-duplex stainless steel (i.e. SAF3207HD).

10:00am **TS2-7 Radiation Hardness Of FeCrMnNi High-Entropy Thin Films**, ***Vladimir Vishnyakov***, *M Tunes, G Greaves, S Donnelly,* University of Huddersfield, UK

Thin films in the FeCrMnNi system were prepared by ion beam sputter deposition from elemental targets, which were deposited onto silicon, Zircaloy-4 and Ni superalloy (type 718) substrates at a temperature of approximately 350 K. Energy Dispersive X-Ray Spectroscopy and Transmission Electron Microscopy (TEM) were used to determine the elemental composition and the nanocrystalline structure respectively. In order to simulate neutron radiation damage the samples with closest to equimolar (±2 at%) composition were irradiated with 30 keV Xe^+ ions within a TEM at the MIAMI facility at the University of Huddersfield. The irradiation was performed at 573 K up to a fluence of approximately $1x10^{17}$ ions/cm², this corresponds to a damage level of 150 displacements per atom (dpa).

As the composition approaches the equimolar value, large grains were observed with sizes of hundreds of nanometres. The deviation from equimolar composition in the films only affected nanocrystallites size without traceable intermetallic presence.

During ion irradiation, the films have not shown any elemental segregation or dislocation loop formation. While the formation and growth of xenon bubbles was significantly suppressed. It is thus proposed that a fast defect recombination rate and slow defect diffusion in high-entropy alloys are responsible for the high radiation hardness of the high-entropy FeCrMnNi system.

10:20am **TS2-8 Reactive Sputtering of High Entropy Alloys with Nitrogen – Tuning the Unit Cell**, ***Robin Dedoncker***, *D Depla,* Ghent University, Belgium*; G Radnóczi,* Centre for Energy Research, Hungarian Academy of Sciences, Hungary

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. When deposited with magnetron sputtering, these alloys form solid solution thin films with a (111) out-of-plane fibre texture. In this present study, the effect on nitrogen addition on the growth of two different high entropy alloys, i.e. CoCrCuFeNi and CoCrFeMnNi is discussed. Thin layers were deposited from powder targets which were mounted on a two inch magnetron. Powder targets allow to design fast and in all desirable concentrations the high entropy alloy-thin films and derived compounds. The nitrogen uptake results in an enlargement of the unit cell. Gradually increasing the nitrogen/argon ratio produces a steady growth towards a stoichiometry nitride with the NaCl (B1)-structure. Other deposition parameters such as current discharge, target-substrate distance and pressure also have an influence on the arriving metal-to-nitrogen ratio and thus influence the size of the unit cell. The results can be summarized in a model for fine-tuning the unit cell of high entropy nitrides.

10:40am **TS2-9 Improved Resistance of Senary AlCrTaTiZrRu Under Bump Metallization to Interdiffusion and Reaction at Solder Joints***, **Wen-Yu Chen,*** National Tsing Hua University, Taiwan*; K Cheng,* National Chung Hsing University, Taiwan*; S Chang,* National Tsing Hua University, Taiwan

A thin layer of under bump metallization, e.g. Ni/Au, at solder joints is used to improve the wettability of molten solder to Cu pads but also to inhibit the rapid interdiffusion and over reaction between solder and the substrates. Under bump metallization needs to prevent solder joints from forming excessive brittle and detrimental intermetallic compounds, and plays an important role in the reliability of electronic devices. Multicomponent high-entropy alloys have been found to present excellent thermal stability and high diffusion resistance in recent years. Therefore in this study, an AlCrTaTiZrRu senary alloy was developed as under bump metallization to reduce the consumption rate and improve the lifetime of under bump metallization. Experimental results indicated that, after the reflow process of solder at 230-250°C, uneven intermetallic compounds obviously formed on a traditional Ni/Au substrate, and their thickness increased with reflow temperature. In comparison, only a thin interfacial reaction layer of only several tens of nanometers, rather than abundant intermetallic compounds, was observed between solder and the senary under bump metallization, revealing the high thermal stability of the AlCrTaTiZrRu high-entropy alloy. The wetting balance test suggested a good wettability of molten solder to the Ni/Au substrate, while the wetting of molten solder to the senary alloy was reduced. After dipping in molten solder at 250°C for one hour, a Cu substrate completely dissolved in the molten solder. However, the Cu substrate coated with the senary alloy layer remained, without an obvious loss, also suggesting the high thermal stability of the senary alloy.

Author Index

Bold page numbers indicate presenter