Topical Symposia

Room Pacific Salon 3 - Session TS4-1-MoM

Thin Film Materials for Flexible Electronics

Moderators: Oleksandr Glushko, Erich Schmid Institute of Materials Science, **Nicholas Glavin**, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

10:00am **TS4-1-MoM-1 2D Materials Based Epidermal and Implantable Conformable Bioelectronics***, **Nanshu Lu,*** University of Texas at Austin, USA **INVITED**

Bio-tissues are soft, curvilinear and dynamic whereas wafer-based electronics are hard, planar, and fragile. Such mismatch fundamentally impedes their integration with each other. As atomically thin, optically transparent, mechanically robust, and highly functional electronic materials, 2D materials are ideal for conformable bioelectronics. We have invented a cost- and time-effective “wet transfer, dry patterning” process for the freeform manufacture of graphene e-tattoos (GETs) [1-2]. Our GET has a total thickness of less than 500 nm, an optical transparency of ~85%, and a stretchability of more than 40%. Tensile fracture of PMMA-supported graphene has been experimentally investigated and different stages of fracture have been identified [3]. GET can be directly laminated on human skin exactly like a temporary transfer tattoo and can fully conform to the microscopic morphology of the skin surface via just van der Waals forces. Analytical models are developed to guide the GET design for full skin conformability even under skin deformation [4]. As a dry electrode, GET-skin interface impedance is found to be as low as medically used Ag/AgCl gel electrodes. GET has been successfully applied to measure electrocardiogram (ECG), electromyogram (EMG), electroencephalogram (EEG), skin temperature, and skin hydration. When applied around human eyes, imperceptible GET electrooculogram (EOG) sensors can capture eye movement with an angular resolution of 4 degrees, which can be used to wirelessly control a quadcopter in real-time [2]. In addition to noninvasive e-tattoos, we have engineered human eye-inspired soft implantable optoelectronic device using atomically thin MoS2-graphene heterostructure and strain-releasing, retina conformable designs [5]. The hemispherically curved image sensor array exhibits infrared blindness and successfully acquires pixelated optical signals. We propose the ultrathin hemispherically curved image sensor array as a promising imaging element in the soft retinal implant with minimum mechanical loading to the retina. Optical signals obtained by this curved image array can be converted to electrical stimulations applied to optic nerves to restore visualization.

[1] Ameri et al, Acs Nano 2017, 11 (8), 7634-7641.

[2] Ameri et al, npj 2D Materials and Applications 2018, in revision.

[3] Jang, et al. To be submitted 2017.

[4] Wang, et al. Journal of Applied Mechanics 2017, 84 (11), 111003.

[5] Choi, et al. Nat Commun 2017, 8, 1664.

10:40am **TS4-1-MoM-3 Performance Deterioration Characteristics of Silver-Nanoparticle-Printed Flexible Electric Wirings under Severe Bending Deformation***, **Shoji Kamiya**, H Izumi,* Nagoya Institute of Technology, Japan*; T Sekine,* Yamagata University, Japan*; Y Haga, H Sugiyama,* Nagoya Institute of Technology, Japan*; N Shishido,* Green Electronics Research Institute, Kitakyushu, Japan*; M Koganemaru,* Kagoshima University, Japan

One of the important issues in flexible electronic devices is certainly their mechanical robustness. For further development of devices and wider applications in markets, how to characterize performance deterioration behavior under large scale bending deformation and how such information should be shared among suppliers and users of devices must be established for the sake of quantitative risk management in the actual operation toward the society of so-called IoT or ubiquitous sensor networks.

Mechanical robustness of flexible devices is most commonly demonstrated by bending them to a certain curvature while they are working. However, such a demonstration is mere consolation because no one knows what happens with even a bit of severer curvature. Therefore, in order to appropriately understand their robustness, bending test must be once carried out to the end of possibility, i.e., to folding them in half, while their performance is being evaluated. This is indeed a similar concept to common strength tests of materials, where materials are loaded until breakage to know safety margins of operation conditions.

To examine such a concept on flexible devices, a new type of bending test method was proposed in this study. Silver nano-particle wirings printed on flexible films were selected for the actual experiment, since wirings are utilized as the component most commonly found in any kinds of flexible devices, and tested not only under monotonic but also repeated bending loadings. Depending on the levels of loading, their resistance increased not always gradually but occasionally also suddenly. Such sudden behavior could hardly be deduced with the data obtained under less severe loading conditions and in shorter time of testing.

On the basis of deterioration behavior of performance observed above as an example, a number of new possibilities will be discussed in the presentation to share knowledge for the evaluation of operation risks associated with flexible devices to be distributed as a new type of infrastructures in the next step of society.

11:00am **TS4-1-MoM-4 Characterizing the Mechanical Reliability of Flexible and Stretchable Conductive Inks on Polymeric Substrates***, **Gabriel Cahn,*** Georgia Institute of Technology, USA*; M Wolfe,* DuPont Photovoltaic and Advanced Materials, USA*; J Meth,* DuPont Electronics and Imaging, USA*; S Graham, O Pierron,* Georgia Institute of Technology, USA

Flexible hybrid electronic (FHE) devices are produced through precision printing of electrically conductive inks onto flexible substrates. A fundamental understanding of the inks’ conductivity evolution under mechanical strain is required to properly address mechanical reliability of these devices and develop better conductors for mechanically-demanding applications such as wearable devices. This work investigates the behavior of DuPont’s 5025 (“flexible”) and PE874 (“stretchable”) silver conductors under strain and on different polymer substrates (Kapton Polyimide (PI), Polyethylene Terephthalate (PET), and Thermoplastic Polyurethane (TPU)). Both inks are composite materials made of silver flakes embedded at high volume density within an insulating polymer matrix. While contacts between the flakes form electrically conductive pathways within the ink, their evolution under strain due to inhomogeneous deformation and local cracking, and the effect on conductivity has not been explored yet. This works specifically investigates this aspect using an *in situ* optical microscopy technique to measure the resistance evolution during monotonic, stress relaxation and creep loadings. As the applied strain is increased, the resistance of both inks increases as well, but at a much lower rate for PE874. Under stress relaxation, both inks see similar recovery in resistance, the amount of which is a function of the polymer substrate. The local deformation is investigated using digital image correlation to interpret these results and understand the role of polymer matrix and ink/substrate elastic modulus mismatch on ink conductivity.

11:20am **TS4-1-MoM-5 Printed Hybrid Materials for Flexible Electronic and Optoelectronic Devices***, E List-Kratochvil,* ***Felix Hermerschmidt,*** Humboldt-Universität zu Berlin, Germany **INVITED**

Beyond the use in home and office-based printers, inkjet printing (IJP) has become a popular structuring and selective deposition technique across many industrial sectors. More recently great interest also exists in new industrial areas like in the manufacturing of printed circuit boards (PCBs), solar cells, flexible organic electronic and medical products. In all these cases IJP allows for a flexible (digital), additive, selective and cost-efficient material deposition, which can be used in an in-line production process. Due to these advantages, there is the prospect that up to now used standard processes can be replaced through this low cost innovative material deposition technique. However, using IJP as a production process in manufacturing, beyond the use in research laboratories, still requires rigorous development of cost and performance optimised functional electronic inks and processes, in particular those allowing for the fabrication on low cost flexible substrates polyethylene terephthalate. By this means this important aspect also addresses the trend in industry for high-throughput, roll-to-roll device processing, where the use of common plastic substrates instead of glass poses problems concerning the thermal stability of the substrate and the mechanical stability of the deposited device layers, including the transparent conductive electrode (TCEs) against damages caused by substrate bending during the production and operation lifetime of the flexible devices. In this contribution we report on the design, realisation and characterization of novel low temperature processes for printed metals, active and passive IJP electronic devices on flexible low cost substrates. We will present examples of resistive memories, printed TCEs and related electrode structures for organic light emitting diodes and organic solar cells based on IJP. [1]

[1] F. Hermerschmidt, S. A. Choulis, E. J. W. List-Kratochvil, "Implementing Inkjet-Printed Transparent Conductive Electrodes in Solution-Processed Organic Electronics", Adv. Mater. Technol. (2019) 1800474.

Topical Symposia
Room Pacific Salon 3 - Session TS3+4-2-MoA

Surface Engineering for Lightweight Materials & Thin Film Materials for Flexible Electronics

Moderators: Klaus Böbel, Bosch GmbH, **Oleksandr Glushko**, Erich Schmid Institute of Materials Science, **Nicholas Glavin**, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

2:20pm **TS3+4-2-MoA-3 Electro-mechanical Reliability of Flexible Electronics: An Overview of Testing and Characterization Techniques***,* ***Oleksandr Glushko****, M Cordill,* Erich Schmid Institute of Materials Science, Austria

In this presentation an overview of three main mechanical test concepts will be given along with numerous examples of the reliability parameters which can be gained from these tests. Monotonic tensile test is a standardized technique which is used for characterization of general mechanical reliability parameters of a flexible system under tension. It will be shown how to describe general material behavior (from brittle to ductile), determine the crack onset strain or estimate the density and lengths of cracks with the help of tensile test combined with in-situ measurements of electrical resistance. Cyclic tensile (fatigue) testing is a well-established method to examine the stability of flexible components when small amounts of mechanical strain are repeatedly applied. Examples of different types of damage development with the cycle number will be given for materials with different microstructures. Finally, bending tests are required to prove the mechanical performance under conditions which closely simulate the real usage conditions of a flexible electronic device. Because there is no unified approach or standard for flexible electronics, different available bending test methods will be reviewed along with the typical cases of mechanical response. A special emphasize on the correlation between mechanical damage and the degradation of electrical conductivity will be made. It will be shown that, under given conditions, significant topological changes in metallization layers might occur without pronounced growth of measured electrical resistance.

2:40pm **TS3+4-2-MoA-4 Bending Fatigue of Al/Mo Bilayers on Polymer Substrates with Varied Al Layer Thickness***,* ***Patrice Kreiml****, M Rausch, V Terziyska,* Montanuniversität Leoben, Austria*; J Winkler,* Plansee SE, Austria*; C Mitterer,* Montanuniversität Leoben, Austria*; M Cordill,* Austrian Academy of Sciences, Austria

In traditional display technologies for rigid flat panel displays, magnetron sputter deposited Mo thin films, acting both as diffusion barrier and adhesion layer, are often used in combination with Al thin films, acting as charge carrying layer. With the increasing demand for flexible displays, for instance for the application in foldable smartphones, the mechanical limitations of these systems have to be systematically investigated and fully understood. *In situ* straining experiments, combining optical and electrical failure analyses, demonstrated the dominance of the brittle Mo layer on the bilayer fracture and increasing the Al-layer thickness has proofed to lighten its impact. Although general trends can be made visible from that approach, no quantified lifetime predictions under conditions close to reality can be drawn. Due to that a series of Al/Mo bilayers was magnetron sputter deposited on polymer substrates, keeping the thickness of the Mo layer at constant 30 nm and varying the thickness of the Al layer on top from 30 over 75 to 150 nm. These thin films were then tested on a custom-built bending device at different modi: (i) 20,000 cycles of compressive bending strains, (ii) 20,000 cycles of tensile bending strains and (iii) alternating 10 cycles compressive and 10 cycles tensile bending strains, leading to overall 20,000 cycles of mixed applied bending strains at strains of 0.5, 1.3 and 3.1 %. In combination with intermittent optical and resistance measurements, a quantification of the electro-mechanical behavior could be conducted. The data gained from these experiments reveal the physical limits of the Al/Mo system. It will be shown that an optimized thickness ratio, an adequate choice of bending load and bending strain lead to acceptable lifetimes for flexible back-plane electrodes.

3:00pm **TS3+4-2-MoA-5 Enabling High-Power Flexible Devices through Tailored Nanocomposite Interface Materials***,* ***Katherine Burzynski,*** University of Dayton, USA*; N Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA*; E Heller, M Snure, E Heckman,* Air Force Research Laboratory, Sensors Directorate, USA*; C Muratore,* University of Dayton, USA

Consumers and military personnel are demanding faster data speeds only available through fifth generation (5G) wireless communication technology. Furthermore, as wearable sensors and other devices become more ubiquitous, devices demonstrating enhanced flexibility and conformality are necessary. A fundamental challenge for flexible electronics is thermal management. Even on rigid substrates with significantly higher thermal conductivity than polymeric and other flexible substrates, the full potential of semiconducting materials is often thermally limited. The flexible gallium nitride (GaN) high electron mobility transistors (HEMTs) employed in this work are grown on a two-dimensional boron nitride (BN) release layer that allows the conventionally processed devices on sapphire wafers to be transferred using a polymeric stamp and placed onto a variety of rigid and flexible substrates. Characterization of the GaN device behavior on the as-grown sapphire wafers (prior to transfer) provide a baseline for evaluation of the thermal performance of engineered interfaces and substrates. With conventional substrates, device performance (specifically, the saturation current) is reduced when the device is transferred to polymeric substrates. The thermal dissipation is further restricted due to the addition of an adhesive layer to the substrate. Thermal imaging of devices in operation reveals that the current passing through an as-grown GaN transistor on a sapphire wafer reaches the target operating temperature at approximately five times the power of the same device transferred to a flexible substrate. Printable, thermally conductive nanocomposites integrating 1D, 2D, and 3D forms of carbon in a flexible polymer matrix, as well as metal nanoparticles, were developed to maximize heat transfer from GaN devices. The thermal conductivity of the candidate substrate materials was measured experimentally to have more than a 300 percent increase in thermal conductivity, and the performance of devices transferred to these novel flexible composite substrates was characterized. The measured thermal data was used in computational simulations to predict flexible substrate architectures effectively promoting point-to-volume heat transfer to further improve device performance. Additive manufacturing for engineered architectures of the flexible, thermally conductive substrate materials was demonstrated to substantially reduce the thermal limitation of high-power flexible electronics.

3:20pm **TS3+4-2-MoA-6 Plasma Polymers…A Family of Materials that is Full of Surprises***,* ***Rony Snyders,*** University of Mons, Belgium **INVITED**

Through the years, plasma polymerization has become a well-established technique for the synthesis of almost atomically flat functionalized organic thin films which are nowadays mostly used in the biomedical field. Nevertheless, in order to further extend the application fields of these materials (supports for nanoparticles, active surface for the detection of biomolecules…), a large surface area is often necessary. In this work, we develop plasma-polymer based platforms for the stabilization of gold nanoparticles that are active in the degradation of VOC molecules. In addition to the approach consisting to grow this material onto powders or paper substrates in order to increase the surface to volume ratio, we also develop strategies allowing for a structuration, at the micro/nano-scale, of these surafces. The present presentation will focus on this part of the work. It will be described how we have established a method that allow the self nano-structuration of plasma polymers coatings by adapting their mechanical properties. Specifically, it is demonstrated that a fine control of the latter by tuning of their crosslinking degree is a promising strategy to generated wrinkling phenomenon in these materials. In this context, our results unambiguously reveal the key role of the growth temperature on the mechanical properties of the deposited layer. Particularly, it has been reported that soft viscoelastic plasma polymer layer can be synthesized by depositing the coating at temperature below 273 K. Taking advantage of this discovery, it was possible to design nano/micro patterned surfaces by combining such a viscoelastic plasma polymer surfaces with a more elastic (plasma polymer) layer. The obtained patterns are generated by complex wrinkling and degassing mechanisms that will be discussed in the presentation.

4:00pm **TS3+4-2-MoA-8 Environmental Challenges of Thin Film Systems on Polymer Substrates for Space Applications***, Barbara Putz,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; G Milassin, C Semprimoschnig,* European Space Research and Technology Centre*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Multilayer thin film systems on flexible polymer substrates build up optical solar reflectors (OSR) for thermal insulation of satellites and spacecraft. During one year of operation a satellite in low earth orbit (LEO) typically encounters 6000 thermal cycles of +/ 100°C. Due to the different coefficients of thermal expansion between the individual layers and the substrate it is important to investigate the thermo-mechanical stability of the composites as a function of the cyclic heat load. Scanning electron microscopy and focused ion beam cross-sectioning revealed, that the Inconel-Ag-Teflon system, currently used as OSR material in orbit, forms through thickness cracks and cavities in the Ag layer during thermal cycling of +/- 150°C in a gaseous N_2 atmosphere. Crack and cavity formation start at very low cycle numbers, which is detrimental to the reflectivity (Ag) corrosion protection (Inconel) and considerably diminish the insulation capacity of the OSR. Combined in-situ surface imaging, film resistance (4 Point Probe setup) and film stress measurements (X-ray diffraction + $\sin^2\psi$) during straining revealed that also electro-mechanical properties of the bi-layer system are dramatically influenced, emphasizing the need to improve multilayer design and resistance of versatile metal-polymer compounds against thermal cycling. In this work, sputter deposited thin film metallic glasses (TFMG), combining metallic bonding and an amorphous microstructure, are introduced as novel coatings to overcome the problems of current multilayer OSR systems. Results indicate that this new and innovative type of thin films are ideal candidates to withstand the extreme thermal cycling as well as the harsh space environment.

4:20pm **TS3+4-2-MoA-9 Sputtered Thin Film Sensors for Self-sensing Composite Materials***, **Florian Cougnon**, A Lamberti, W Van Paepegem, D Depla,* Ghent University, Belgium

The wide-spread use of fibre-reinforced composite materials in big structures such as planes, windmills or pedestrian bridges, combined with the unacceptably high cost of material-failure, has vastly pushed the demand for structural health monitoring of composite materials. Structural health monitoring nowadays evolved from periodic quality inspections and surface-bounded sensing networks towards continuous monitoring of the entire in-service life time by sensing networks embedded in the material. In order not to degrade the structural integrity of the host material, the spatial dimensions of the embedded sensors should be as small as possible. Therefore we focus on the development of embedded thin film sensors – deposited by magnetron sputtering – such as thermocouples for measuring temperature and antennas for wireless measurements of strain and temperature through shift in resonance frequency. It is a challenging task to deposit well-performant thin film sensors onto temperature sensitive polymeric substrates. On the one hand, the electrical properties of the thin films mainly scale with the energy flux delivered towards the growing film. The temperature sensitivity of the substrate however demands tuning of the energy flux in order not to degrade the quality of the polymer. On the other hand, tuning the energy flux is often unambiguously correlated with an increased impurity flux towards the substrate. These impurities originate from residual gasses in the vacuum chamber and outgassing from the polymeric substrate and can have a large impact on the overall film properties as well. In this work, the link between energy flux, impurity flux and electrical properties of thin films grown by magnetron sputtering is unraveled from a fundamental point-of-view and exploited to fine-tune embedded thin film sensors towards applications for smart composite materials.

4:40pm **TS3+4-2-MoA-10 A New Method for Influencing Coating Properties on Polymer Substrates at Low Temperature: High Power Impulse Magnetron Sputtering (HIPIMS) with Positive Voltage Reversal***, **Ambiörn Wennberg**,* Nano4Energy SL, Spain*; M Simmons,* Intellivation, USA*; F Papa,* GP Plasma, Spain*; I Fernandez,* Nano4Energy SL, Spain

Current engineering and material advances are shifting manufacturing in many areas from solid bulk materials to flexible lightweight materials. Although these materials, such as polymers, are lightweight, flexible and tough, there are challenges to engineering coatings on such substrates as they insulating and not able to withstand high temperatures. This gives rise to the challenge of how to deposit high quality thin film coatings on such substrates. High Power Impulse Magnetron Sputtering (HIPIMS) has shown many advantages over conventional sputtering which is commonly used to deposit metals, metal nitrides and metal oxides on polymer web. With HIPIMS, a fraction of the target material will be ionized while the ion energy distribution function will shift to energies about 10 times greater than those for DC discharges. However, this increase in ionization and energy will give only modest changes on an unbiased substrate. With the addition of a positive voltage reversal pulse adjacent to the negative HIPIMS sputtering pulse, these ions can be accelerated towards the substrate providing energy for film nucleation and densification.

In this study, an industrial scale (330 mm wide web) web coater was used to deposit TiO2 and Cu coatings as well as other metal nitride and metal oxide coatings on PET at room temperature. Improvements in film density and grain size can be clearly seen compared to DC or pulsed DC sputtering. The effect on the index of refraction, extinction coefficient and barrier properties are also investigated.

5:00pm **TS3+4-2-MoA-11 Tribological Challenges and Surface Engineering Solutions for Extreme Environments and Lightweight Materials***, **Andras Korenyi-Both**,* Tribologix, Inc., USA **INVITED**

Moving mechanical assemblies that are used in extreme environments are often coupled with unique challenges for maintaining intended operational requirements. Conventional material selection becomes narrow and often native surfaces are not robust enough to handle extreme requirements. Surface modification techniques that are uniquely suited for special materials and their relevant operating environments must be carefully chosen from trusted knowledge bases or heritage based know-how. To further assure mission success modeling through simulation and specialized mechanical testing becomes critical. Surface analytical techniques, including in-situ data monitoring become an integral part of testing and simulation . To help offset the high costs often associated with placing moving mechanical assemblies in to extreme or high distance environments the choice of materials is further narrowed by intentional light-weighting for gains in economy. Lightweight material performance also needs to have careful attention placed on surface interactions and coating techniques to improve these surfaces are typically novel in nature. With a clear understanding of interacting surfaces, environmental factors, available options for treatments/coatings, risks associated with wear can usually be successfully mitigated. Several interesting and challenging extreme environment tribological cases are highlighted to provide further in-sight in to this area of science and engineering.

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™* 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 °C. 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.

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

This study is supported by the postdoctoral fellowship program to promote the academic career of women at TU Ilmenau for habilitation. The author, Anni Wang, would like to especially thank the financial add of internal research funding from TU Ilmenau for her traveling expanse to ICMCTF.

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.

Topical Symposia
Room Golden West - Session TS2-ThM

Icephobic Surface Engineering

Moderators: Alina Agüero Bruna, Instituto Nacional de Técnica Aeroespacial (INTA), **Jolanta-Ewa Klemberg-Sapieha**, École Polytechnique de Montréal, Canada

8:20am **TS2-ThM-2 Synthesis And Characterization Of Amphiphobic Hybrid Coatings For Industrial Applications***, **Giulio Boveri**, M Raimondo, F Veronesi,* Institute of Science and Technology for Ceramics, Italy

In the coming few years, the control of materials repellence against liquids is one of the biggest challenge to make innovation in many industrial fields. Gathering on the same material the ability of repelling liquids with physical properties (typically surface tension γ) in a wide range of values represents the topic of many scientific efforts. Materials wetting strictly depends on surface chemistry and reactivity and on structural features at nanoscale as well.

This work is based on the surface modification of aluminum substrates by deposition of thin layers of ceramic oxide nanoparticles, in particular Al_2O_3 and SiO_2 synthesized by sol-gel routes, in order to introduce nano features which, coupled with the organic modification of the surface chemistry, lead to an almost complete repellence against water (*superhydrophobicity*, contact angles approaching 180° and contact angle hysteresis <5°) and liquids with γ as low as 25 mN/m (*superhydrophobicity* plus *oleophobicity* = *amphiphobicity*). *Amphiphobic* materials are drawing much interest in different industrial sectors, such as naval, aerospace, energy and automotive, so that great efforts have been making to improve their durability and wearing resistance simulating their application in real environments.

Two different approaches were typically used to produce non-wetting surfaces: the so-called *Lotus Leaf* (*LF*) and the *Slippery Liquid Infused Porous Surfaces* (SLIPS) ones, both introducing textural and chemical modifications at surface level that, in turn, is working in a solid-liquid-air (LF) or liquid-liquid-air three phasic environment. Self-cleaning, anti-icing and anti-soiling behavior was assessed on these surfaces and the detected performances correlated to the nature of the coatings, other than to the physical state of the working interfaces.

Keywords: Amphiphobicity, hybrid coatings, ceramic nanoparticles, surface modifications.

8:40am **TS2-ThM-3 *In situ* Ice Growth Kinetics on Water-repellent Coatings in Atmospheric Icing Conditions***, **Jacques Lengaigne**, P Xing, É Bousser,* École Polytechnique de Montréal, Canada*; A Dolatabadi,* Concordia University, Canada*; L Martinu, J Klemberg-Sapieha,* École Polytechnique de Montréal, Canada

Ice accretion on the surface of airplanes during flight and in other similar situations presents significant safety concerns and economic loss. Icing occurs when micrometric Supercooled Water Droplets (SWD) impact at high speed and freeze on exposed components. Current de-icing systems (chemical agents, heaters or inflatable boots) are energy intensive and prone to failure. To address these shortcomings, research has focused on the development of so-called icephobic surfaces or coatings. These surfaces could provide an efficient passive protection: inhibiting ice nucleation, reducing ice growth or improving the efficiency of current de-icing technology. At the forefront of these new coatings, superhydrophobic surfaces, combining materials with low surface energy and high multiscale roughness, are regarded as one of the most promising avenues. In this work, we investigated the performance of water-repellent coatings against SWD ice accretion.

To replicate realistic SWD icing conditions, we used a small-scale icing wind-tunnel to generate microdroplets with diameters ranging from 10 to 90 µm, and an air speed of 10 m/s impinging at a temperature of -17 °C. The test section was equipped with a sample holder incorporating a thermoelectric module for heating/cooling the sample, a side camera to visually record the ice formation, and an *in situ* ice growth monitoring system. This latter module was developed to measure ice thickness during the testing cycle. It functions by following the displacement of a laser beam using a dedicated digital camera. Moreover, the laser spot spreading offers insights into the evolution of the roughness of the ice layer.

Three types of surfaces with different wettability and roughness R_q values were studied in this experiment: hydrophilic mirror-polished Ti-6Al-4V alloy (θ_c=74±1°, R_q= 51±4nm), hydrophobic spray coating (θ_c=107±1°, R_q= 0.35±0.04 µm) and superhydrophobic hierarchical spray coating (θ_c=173±3°, R_q= 12±2 µm).

The ice growth cycle follows a similar behavior on all samples: first the ice nucleation occurs followed by an incubation period before the continuous ice growth. Once the ice has formed a continuous layer, the growth rate is linear. It was found that the incubation period is longer when the surface is more hydrophobic. In fact, the superhydrophobic coating showed twice longer incubation time compared to the substrate. However, ice growth rate increased on the water-repellent coatings (up 34% faster on the superhydrophobic surface) compared to the pristine titanium alloy. Finally, de-icing of each sample showed that the conductive substrate is de-iced faster compared to both water-repellent coatings.

9:00am **TS2-ThM-4 Icephobic Elastomeric Surfaces?***, **Pablo Francisco Ibáñez**, F Montes Ruiz-Cabello, M Rodríguez Valverde, M Cabrerizo Vílchez,* Universidad de Granada, Spain

It is well-accepted that superhydrophobic surfaces may lead to interesting properties such as anti-fogging, self-cleaning, or anti-icing. However, some studies have reported that superhydrophobicity does not assure anti-icing/de-icing performance. Icephobic surfaces should hold three requirements: subcooled-water repellency, freezing delay and low ice-adhesion energy. Superhydrophobic surfaces are rough and ice adhesion is mostly increased by interlocking. Lubricant-Impregnated Surfaces (LIS) are also proposed to repel water. Moreover, there are evidences of that these surfaces also mitigate icing and reduce ice-adhesion. For this reason, we are investigating others approaches to prepare low ice-adhesion surfaces.

In this work, to absorb the surface shear stresses of freezing water, we focus on elastic hydrophobic surfaces such as fluorosilicones. We study the ice-adhesion strength on PDMS surfaces with different elastic modulus and thickness. Further, we study oil-infused elastomeric surfaces. Finally, we evaluate the durability of the prepared surfaces (wear, abrasion).

9:20am **TS2-ThM-5 Design and Fabrication of Superhydrophobic, Ice-phobic Coatings for High Voltage (HV) Power Lines Application***, **Mariarosa Raimondo**, G Boveri, F Veronesi,* ISTEC CNR - Institute of Science and Technology for Ceramics, Italy **INVITED**

The interaction between water under many different forms – dry or wet snow, ice, frost, rime or their combination – and materials is a complex matter to investigate, depending on many parameters, among which composition and surface texturing, outside temperature, wind velocity, etc. The deposition of water, ice, etc. on structural installations, facilities and infrastructures represents a huge problem in many cold regions. To overcome heavy risks on HV lines, such as the overloading and electricity blackout, new effective strategies - other than the mostly used based on the Joule effect, mechanical removal, electro-impulse methods and application of chemical de-icing fluids - need to be adopted.

New frontiers for superhydrophobic (SH) materials lie in their potential ability to hinder the interaction with water under many different forms so that they might be able to reduce snow, ice or even frost formation and accretion on structural installations, facilities and infrastructures under critical conditions (e.g. at temperatures below 0°C). Here, SH surfaces were obtained by deposition of hybrid nanostructured coatings on aluminum alloy cables commonly used for HV power lines. Two different design approaches to water repellence were pursued: the typical Lotus leaf (*LF*) and the one referring to Slippery Liquid-Infused Porous Surfaces (*SLIPS*), both obtained by the initial deposition of Al_2O_3 nanoparticles, followed by chemical hybridization with a fluoropolymer, plus additional infusion with an ultrasmooth, water-immiscible lubricant overlayer for *SLIPS*. Given the well-known role of surface texture on superhydrophobicity, sandblasted substrates with different roughness were used to assess its influence on the wetting-related performances. Indoor experimental test at lab scale revealed that superhydrophobicity involves the decreasing of shear stress on coated cables even if the ice adhesion strength varies in a more complex way depending on the surface roughness. Materials were also exposed outdoor at test facilities located in the west of Italian Alps, at an altitude of 959 m asl. At T of about -2°C under the conditions of dry snow with a low liquid water content (LWC) and spherical snowflakes morphology, *LF*-like designed sandblasted cables showed a significant delay (some hours) in snow deposition if compared to both the untreated and the *SLIPS* ones. This behavior stood out as the most relevant with respect to the other coated cables, whether smooth or sandblasted. However, under different conditions (-2°C < T < 0°C and wet snow with higher LWC), sandblasted *LF* materials seem to partially lose their ability of delaying show and ice accretion.

10:00am **TS2-ThM-7 Energy Saving Strategy for the Development of Icephobic Coating and Surface***, Y Zheng, J Wang, J Liu, K Choi, **Xianghui Hou,*** The University of Nottingham, UK

Aircrafts are frequently exposed to cold environments and ice accumulation on aircraft surface may lead to catastrophic failures. An appropriate solution of ice protection is a critical issue in the aerospace industry . In the R&D of icephobic coating, the current coating design target mainly aims on lowering the ice adhesion strength between the ice and the coating surface. However, as a passive ice protection approach, the use of icephobic coating is often combined with an active ice protection solution (e.g. electro-thermal heating and hot air bleeding), especially for the in-flight application where the reliability of ice protection must be ensured. Therefore, ice adhesion strength is no longer the sole criterion to evaluate the icephobic performance of a coating and a surface. It is a need to establish a better strategy for the design of icephobic coating and surface. In this work, an energy saving strategy has been proposed to assess the de-icing performance of the icephobic coating and surface when heating is involved. The energy consumed for the de-icing operation is used as the key criterion for the overall performance of icephobic coating and surface. Successful validation has been clearly obtained in the evaluation of the de-icing performance of selected coatings and surfaces, which demonstrates a new criterion on the R&D of icephobic coating and surface for ice protection.

10:20am **TS2-ThM-8 Anti-Icing Hard Steel Coating Modified With Polymer Particles***, P García, **Julio Mora,** A Agüero,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Icing is a severe problem, in particular on aircrafts, with important consequences in safety, energy consumption, ecologic impact, and economy. To fight it, ice protection systems have been developed and have evolved over the last decades, from the highly energy consumption active de-icing systems based on heating, and non-eco-friendly use of de-icing fluids on-ground, to the recent boom that have experimented the technology of passive, anti-icing materials, as well as alternative more efficient new active technologies.

Indeed, very attractive passive surface modification systems have been proposed, decreasing ice accretion and adhesion, but until now, these solutions are not durable and capable of withstanding the harsh conditions to which aircraft surfaces are exposed. A practical approximation would be the development of durable passive solutions that contribute to reduce the power required by the active deicing systems saving energy.

Durable anti-icing coatings with high thermal conductivity deposited over metallic aerodynamic surfaces have been developed and applied by HVOF (High velocity oxyfuel) thermal spray. Mixtures of powders of a high hardness steel and polymer particles were sprayed on stainless steel alloy 304L, and dense 50-100 microns coatings were obtained, with improved anti-icing properties in comparison with the untreated substrate. Extensive preliminary testing of the newly developed coatings has been carried out, including ice accretion in an icing wind tunnel (IWT), employing representative in-cloud icing conditions, allowing to obtain different types of ice: glaze, mixed-glaze, mixed-rime and rime ice. The developed systems showed a significant reduction in ice accretion in comparison with the untreated substrates, with some variations depending on the type of ice and the concentration of added polymer.

Moreover, the durability of the coatings was also examined by repeating icing cycles and by testing for sand and rain erosion resistance. The so tested samples maintained the hydrophobicity with a good water droplet mobility, and in general very promising results in terms of durability after repeated icing/deicing cycles in an IWT.

10:40am **TS2-ThM-9 Development of Superhydrophobic and Icephobic Coatings by Suspension Plasma Spraying***, **Ali Dolatabadi,** N Sharifi, R Attarzadeh, C Moreau, M Pugh,* Concordia University, Canada **INVITED**

Suspension plasma spraying (SPS) technique has been used to develop microtextured TiO_2coatings with a hierarchical surface roughness to develop superhydrophobic surfaces. Superhydrophobic coatings demonstrate extremely water repellent properties and can be potentially used for applications such as anti-icing, reduced drag and friction, self-cleaning and corrosion resistance purposes. The focus of this presentation is on engineering the hierarchical morphology or so-called “cauliflower” features using a parametric study approach to optimize the wetting properties of the coatings. It is demonstrated that by carefully designing and controlling the process parameters, rather fine and uniform dual-scale (hierarchical) surface textured coatings can be generated. Finally, icephobic performance of superhydrophobic surfaces are assessed both experimentally and also through a detailed numerical modeling of cloud-sized droplet impact and solidification.

11:20am **TS2-ThM-11 Minimum Required Thickness of a Hydrophobic Topcoat to withstand Cycling in an Icing Wind Tunnel***, **Stephen Brown,*** Ecole Polytechnique de Montreal, Canada*; J Lengaigne,* Polytechnique Montréal, Canada*; N Sharifi,* Concordia University, Canada*; L Martinu, J Klemberg-Sapieha,* Ecole Polytechnique de Montreal, Canada

Atmospheric icing occurs on aircraft when supercooled water droplets impact exposed surfaces, and quickly freeze in place. This leads to numerous issues such as increased fuel consumption, flight delays, and even crashes. Superhydrophobic surfaces have been shown to reduce icing by allowing droplets to bounce off the surface upon contact, as well as reducing ice adhesion compared to bare metals. A common technique for the creation of a superhydrophobic surface is to develop a surface with hierarchical roughness, and then to coat this surface with a hydrophobic material. If the hydrophobicity comes purely from the topcoat, however, then the durability of the entire system is limited to the durability of this topcoat.

In the present study, we explore the effect of topcoat thickness on sample durability, with the goal of defining a minimum required thickness to withstand repeated icing/deicing cycles. To achieve the desired hierarchical morphology, a ~100 µm TiO2 coating is first deposited on stainless steel by suspension-plasma-spray. Samples are then coated with a fluoropolymer by thermal evaporation, with thicknesses ranging from 7 to 75 nm. These surfaces show contact angles up to 164 ± 5 °, with hysteresis values as low as 5.8 ± 0.9 ° prior to cycling. The durability of the developed surfaces is tested by performing icing/deicing cycles in an icing wind tunnel, exposing the samples to supercooled microdroplets at a temperature of –10°C and a velocity of 43 m/s. Contact angle and contact angle hysteresis measurements are performed every 10 cycles. It is shown that samples with topcoats thinner than 20 nm completely lose their superhydrophobic properties after only 10 cycles, while samples with 75 nm topcoats retain at least some droplet mobility after as many as 100 cycles.

Topical Symposia
Room Grand Hall - Session TSP-ThP
Topical Symposia (TS) Poster Session

TSP-ThP-1 Surface Modification of Multiwalled Carbon Nanotubes for Electro-Thermal Heating in Ice Protection*, **Francesco Zangrossi**, F Xu, N Warrior, X Hou,* University of Nottingham, UK

Icing inevitably occurring on the surfaces of aircraft causes a serious concern of flight safety. Various de-icing strategies have been developed to overcome the icing problems on aircraft. Electro-thermal technique is categorized as heat generated by internal electrical component and transferred to the outer surface for ice protection. Given the increased use of composites on aircrafts structure, self-heating fibre reinforced polymer composite have been studied as de-icing system for the new generation aircraft. In the present work, electrical resistance of multi-walled carbon nanotubes (MWCNTs) was modified by two approaches: functionalisation by acid treatment and silver decoration techniques. The aim was to reduce the electrical resistance of the carbon nanotube networks. To evaluate the electrical resistance of carbon nanotubes, MWCNTs coated glass fibres samples prepared by filtration method. The results showed that MWCNTs treated by silver decoration via Tollen reaction had increased the electrical resistance. On contrast, the functionalisation by acid treatment of the carbon nanotubes reduced the resistance by approximate50%. Treated MWCNTs with improved electrical conductivity were used to produce multiwall carbon nanotube paper (MWCNP) and a composite structure with glass fibres and epoxy matrix. De-icing tests will be carried out to verify the electro-thermal performance in a climate chamber.

TSP-ThP-2 Nanostructured a-C:H:SiOx Coatings with Superhydrophobic Properties*, **Damian Batory**,* Lodz University of Technology, Poland*; J Lengaigne,* Ecole Polytechnique de Montreal, Canada*; A Jedrzejczak,* Lodz University of Technology, Poland*; S Brown, J Klemberg-Sapieha,* Ecole Polytechnique de Montreal, Canada

The main aim of the work was to obtain carbon and silicon based amorphous layers with different surface morphology allowing to obtain superhydrophobic properties. SiOx incorporated diamond-like carbon coatings with different thicknesses were synthesized onto reactive ion etched silicon wafers with previously deposited thin layer of gold. An island shape of the thin golden layer made it possible to obtain selectively etched pillar-like structure of silicon surface with morphology depending on the time of etching. A combination of different structures of the silicon substrates with three thicknesses of subsequently deposited a-C:H:SiOx layers enabled to obtain six sets of samples with respect to the thickness of the coatings and morphology of the substrate. The obtained coatings were characterized using scanning electron microscopy, Raman spectroscopy and atomic force microscopy. Finally the contact angle was measured using sessile drop technique. Additionally the contact angle hysteresis and roll-off angle were determined. As the result of the investigation it was noticed that the structure and morphology of the silicon substrates change with the time of etching. The deposition of a-C:H:SiOx coatings onto the reactive ion etched silicon substrates decreases the roughness parameters and surface area, which progress with increasing thickness. However, an optimal surface morphology correlated with a proper thickness of the coating resulted in contact angle exceeding 150 deg.

TSP-ThP-4 Structural Investigation of the Stability in Temperature of Some High Entropy Alloys*, **Monique Calvo-Dahlborg**,* University of Rouen Normandie-CNRS, France, Swansea University, UK*; U Dahlborg, J Cornide,* University of Rouen Normandie-CNRS, France*; S Mehraban,* College of Engineering, Swansea University, UK*; R Wunderlich,* University of Ulm, Germany*; N Lavery,* College of Engineering, Swansea University, UK*; S Brown,* Swansea University, UK

It has been shown in a previous study [1] that High Entropy Alloys (HEA) can be classified in three domains according to their e/a and r values, e/a being the number of itinerant valence electrons as calculated by Massalski [2] and r being the average radius for a 12 local neighborhood [3]. $CoCr_zFeNi$-XY (with X and Y = Al, Cu, Pd, Ru, Ti and z=0 or 1) HEAs from the three domains identified by e/a have been investigated in as cast conditions (T0), after 3 hours homogenization at 1100°C (T1) and after 3 hours annealing at 700°C (T3). The comparison is based mainly on diffraction and calorimetry results.

It is observed that for the alloys from domain I which contains fcc structures, the microstructure transforms from multi- to almost single-phase under homogenization. In Domain III which contains cubic (Bcc+B2) structures very small multi-structural changes are observed. The alloys in domain II have mixed structure which is changing under heat treatments. Morover, an additional heat treatment at T3 after homogenization leads in all domains to the appearance of other phases. All results are confirmed by the calorimetric results. The effect of heat treatments on hardness is discussed for some compositions.

[1] M. Calvo-Dahlborg, S.G.R. Brown. *J. Alloys and Compds* **724** (2017) 353-364. http://dx.doi.org/10.1016/j.jallcom.2017.07.074

[2] T.B. Massalski, *Materials Transactions* **51** (2010) 583-596. https://doi.org/10.2320/materia.49.192

[3] E.T. Teatum, K.A. Gschneidner Jr., J.T. Waber, 1968. Report LA-4003. UC-25. Metals, Ceramics and Materials. TID-4500, Los Alamos Scientific Laboratory.

TSP-ThP-6 Cu-nanoparticles /Polyfluoroacrylate Emulsion Nanocomposite Coating for Icephobic Applications*, T Barman, H Chen, J Liu, **Xianghui Hou**,* The University of Nottingham, UK

Atmospheric ice accumulation and adhesion on component surfaces often causes great concerns in various industries, especially for aerospace in which catastrophic accidents may occur under inflight or ground icing conditions. Applying icephobic coatings on the components surface has been considered as a promising solution for minimising the accumulation of ice and prompting the removal of the ice from the surface. In the present work, a nanocomposite coating has been developed by mixing Cu-nanoparticles with synthesized polyfluoroacrylate (PFA) emulsion and depositing the mixture on the substrates by spin coating method. Surface hydrophobicity of 140 ° was achieved on the surface of the nanocomposite coating, which has the average surface roughness (R_a) in the range of 0.2 to 0.3 µm. Ice adhesion of the coating was measured by centrifugal approach and it was found that the ice adhesion strength has been effectively reduced as compared to reference surface. De-icing performance of the coating was also evaluated using electro-thermal heating method and 35 % decrease in energy consumption was observed as compared to uncoated aluminium surface.

TSP-ThP-7 Surface Characteristics and Diffusion Phenomenon of $Ni_2FeCoCrAl_x$ Alloys Treated by Atmospheric Pressure Plasma*, **Chi-Ruei Huang**,* National United University, Taiwan*; J Duh,* National Tsing Hua University, Taiwan*; F Wu,* National United University, Taiwan

High entropy alloys, HEAs, recently attracted intense attention due to its outstanding performance in mechanical properties, thermal stability, sluggishness in diffusion, anti-sticking, corrosion resistance, etc… However the knowledge of the evolution of microstructure and surface characteristic of HEAs under treatments through atmospheric pressure plasma jet, APPJ, was limited. In present study, Al incorporated $Ni_2FeCoCr$ high entropy alloys were treated by APPJ to investigate the surface property evolution and diffusion characteristics on HEAs surface. The treatment parameters included gas source, input power, flow rate, and torch-surface distance, ranged from dry air to N_2, 850 to 1100 W, 35 to 50 sccm, and 15 to 50 mm, respectively. The slow and stable Ni showed limited diffusion and reaction even against highest power input under air. The surface microstructure and property evolution were attributed to the elemental redistribution of the active Al in the designed HEAs. The detailed concentration profiles, phase, and surface characteristics were analysed and discussed in consideration of concentration gradient, microstructure evolution, and chemical potential.

TSP-ThP-8 Development of Microwave Remote Plasma Source for New Surface Functionalization*, Y Isomura, Y Ikari, **Tadao Okimoto**, Y Tauchi, K Nishiyama,* Kobe Steel, Ltd., Japan*; H Toyoda, H Suzuki,* Nagoya University, Japan

We developed the so-called Twin-Roll Plasma Enhanced CVD (PECVD) integrated into an industrial roll to roll process for surface functionalization of a flexible substrate. In Twin-Roll PECVD process the winding rolls themselves function as the electrode for plasma discharge and hence provide a stable deposition process for a long time even for deposition of non-conductive films as compared to typical pulse PECVD process. In this technique, however, the direct plasma discharge occurs between the electrode winding rolls and hence the substrate material needs to be electrically non-conductive. The application of the direct plasma method to a conductive substrate is therefore practically limited.

We have been developing a microwave remote plasma source and its integration into roll to roll process as for demonstration of a new surface functionalization technique. In direct plasma discharge process such as in the case of Twin-Roll PECVD, for instance, ion bombardment/irradiation is expected during the film growth by application of a negative bias potential to the electrode. The ion bombardment effect is known to be quite effective for microstructural control of the growing film and hence the film properties. Application of bias voltage to the electrode is however not feasible when a conductive substrate is employed. In the remote plasma source developed, a positive bias potential is applied at a point of plasma source, and the plasma potential is increased with respect to a grounding substrate, accordingly. This source is a linear type exhibiting a possible plasma treatment on a large area with high uniformity. In this work we present the basic principle and function of this remote plasma source. We also demonstrate some applications thereof for film deposition, contributing towards a new technique for surface functionalization.

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