Topical Symposia
Room Sunrise - Session TS4
Materials Modeling and Simulation

Moderators: Thomas Mussenbrock, BTU Cottbus, David Holec, Montanuniversität Leoben, Austria

1:30pm **TS4-1 From the Atomic Interaction to Thermodynamic and Mechanical Properties of Materials***, **Ralf Drautz**,* Ruhr-Universität Bochum, Germany **INVITED**

Density functional theory (DFT) provides a solid basis for the simulation of materials properties. In some cases the computational expense of DFT makes the sampling of thermodynamic observables or the calculation of dynamic variables difficult. We coarse grain the interatomic interaction from DFT at two levels of approximation to allow for faster and larger simulations. First, a tight-binding model is derived from a second-order expansion of DFT in a minimal basis. The parameters in the tight-binding model are obtained directly from minimal basis DFT calculations. In a second step the tight-binding model is approximated locally and analytically, resulting in the analytic Bond-Order Potentials (BOPs). Because of the derivation of BOPs from DFT, the contributions of magnetism and charge transfer to bond formation are directly taken into account. The BOPs are orders of magnitude faster than DFT and allow for the direct sampling of thermodynamic observables.

I will discuss the application of the BOPs to simulating finite temperature magnetism in iron, in particular the ferromagnetic to paramagnetic phase transformation and the alpha-gamma transition and the prediction of some mechanical properties. I will further discuss atomic simulations for phase stability, nucleation and solid-solid transformations with relevance to high-temperature materials.

2:10pm **TS4-3 Molecular Dynamics Study of Titanium Oxynitride Surface Properties***, **Tobias Gergs**, J Trieschmann,* Ruhr University Bochum, Germany*; T Mussenbrock,* BTU Cottbus, Germany

Mechanical properties of metal oxynitride hard coatings depend on the preceding film growth through fundamental surface processes and thermodynamic driving forces. While the latter aspects were recently studied for titanium nitrides, the influence of substitutional oxygen requires further investigation. The absence of theoretical approaches reported in the literature is mainly due to unavailable purely classical potentials to describe titanium oxynitrides. A second reason might be computational limitations of ab-initio methods. So far solely the bulk properties have been addressed by means of density functional theory in the literature. Initially in this work, on the basis of these referenced calculations [1], the recently published COMB3 (3rd generation charge optimized many body) semi-classical potential for heterogeneous titania/titanium nitride systems is characterized and validated. Subsequently, the validated potential is utilized to systematically investigate the inherent thermodynamic driving forces for varying nitrogen/oxygen compositions at the surface. For this study, independent atom configurations are generated with a modified version of the combinatorial SOD (site-occupancy disorder) code, taking into account the broken symmetries of the (001), (110) and (111) surfaces. The resulting slabs are relaxed and characterized with the molecular dynamics code LAMMPS (large-scale atomic/molecular massively parallel simulator). With the validation of the semi-classical potential for titanium oxynitride and a discussion of the influence of a substitutional oxygen contribution, a first step towards the modeling of the corresponding film growth is presented.

[1] J. Graciani, S. Hamad, and J. F. Sanz, Phys. Rev. B **80**, 184112 (2009).

Financial support provided by the German Research Foundation (DFG) in the frame of the collaborative research centre SFB-TR 87 is gratefully acknowledged.

2:30pm **TS4-4 Distribution of O Atoms on Partially Oxidized Metal Surfaces According to Ab-initio Calculations, and the Consequences for Sputtering of Individual Metal Oxides***, **Jiri Houska**, T Kozak,* University of West Bohemia, Czech Republic

We investigate the oxidation of a wide range of metal surfaces by density functional theory. The metals of interest will include those studied in Ref. 1 (Al, Ag, Cu, Ti, Zr, Hf) as well as those studied more recently. We go through a wide range (235 per metal) distributions of O atoms on a partially oxidized metal surface. First, we focus on the qualitative information whether the preferred distribution of O atoms is heterogeneous (stoichiometric oxide + metal) or homogeneous (substoichiometric oxide). We find that the former is energetically preferred e.g. for Al, while the latter is energetically preferred e.g. for Ti, Zr and Hf. Second, we correlate these qualitative results with the known formation enthalpies of oxides of various compositions. Third, we provide the quantitative values of adsorption energies corresponding to the energetically preferred O atom distribution for various partial coverages of various metals by O. We find that the absolute values of the adsorption energies increase with the surface oxygen coverage e.g. for Al, and decrease e.g. for Ti, Zr and Hf. Fourth, we demonstrate one use of these results by presenting Monte Carlo simulations of sputtering. Fifth, we utilize the theoretical results in order to explain the experimental results, such as the time dependence of the magnetron voltage during sputter cleaning of oxidized metal targets (monotonous e.g. for Al but non-monotonous e.g. for Ti).

2:50pm **TS4-5 First-principles Study of Adsorption and Diffusion of Oxygen on the Surface of TiN, ZrN, HfN and the Effect of Al on Oxidation Resistance of TiN Coatings***, **Fangyu Guo**,* Central South University, China

Using first-principles calculations based on the density functional theory, we systematically study the adsorption and diffusion behaviors of single oxygen (O) atom on the (001) surface of nitride coating s of TiN, ZrN and HfN. When adsorbing at the top(N) site, the adsorption energy of TiN is much lower than the value of ZrN and HfN. The O atom is more likely to stabilize adsorbed on the ZrN and HfN surfaces. The diffusion behavior of O atom is investigated through determining the minimum energy pathways (MEP) and diffusion barrier on the (001) surface of these metal nitrides. O atom tends to diffuse on the (001) surface from one top(N) site to neighboring top(N) sites via the hollow site for all the three nitrides. It is also found that diffusion of O atom on the (001) surface of TiN is easier than that of ZrN and HfN. On the three nitrides surface, the adsorption of O on the TiN(001) surface is most unstable. This is a good explanation for a experimental phenomenon that the oxide thickness of TiN is smaller than that of ZrN under the same oxidation conditions.

In order to further increase oxidation resistance of TiN coating, the third elements are added to the TiN coating. TiAlN is widely used as protective coating for cutting and forming tools due to the high hardness combined with good oxidation and wear resistance. We used the special quasirandom structure (SQS) approach to represent the random Nacl structure TiAlN systems and address the effect of Al on the oxidation resistance of TiN by means of *ab initio* molecular dynamics simulations. The forming process of oxides of TiAlN coatings was investigated at 1123k and 773k.

3:10pm **TS4-6 Metastable Phase Formation of Pt-X (X= Ir, Au) Thin Films***, **Aparna Saksena**, Y Chien, K Chang, P Kuemmerl, M Hans,* RWTH Aachen University, Germany*; B Völker,* Max-Planck-Institut für Eisenforschung GmbH, Austria*; J Schneider,* RWTH Aachen University, Germany

The dependence of phase formation and mechanical properties on the chemical composition has been investigated for Pt-Ir and Pt-Au combinatorial thin films. Composition spreads are deposited at substrate temperatures ranging from room temperature to 950°C and are subsequently characterized using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning transmission electron microscopy (STEM), atom probe tomography (APT) and nanoindentation. The formation of a single, metastable Pt-Ir solid solution phase has been observed for all experimentally probed compositions and growth temperatures. Upon Ir addition to Pt the experimentally determined changes in lattice parameter and Young's modulus display the expected rule of mixture behavior which is in very good agreement with our *ab initio* data. Whereas, in the Pt-Au system, the single metastable solid solution phase is seen to decompose into two solid solution phases as the growth temperature is raised to ≥ 600°C. The lattice parameters of the single metastable phase grown at temperatures < 600°C increase linearly as Au is added, showing rule of mixture behavior in good agreement with *ab initio* predictions. However, the lattice parameters of the phases in the dual phase region are independent of chemical composition displaying phase formation behavior consistent with the CALPHAD results. The substrate temperature and chemical composition dependent phase formation in Pt-Ir and Pt-Au thin films can be rationalized based on CALPHAD calculations combined with estimations of the activation energy required for surface diffusion: The metastable phase formation during film growth is caused by kinetic limitations, where Ir atoms (in Pt-Ir) need to overcome an up to factor 6 higher activation energy barrier than Au (in Pt-Au) to enable surface diffusion.

3:30pm **TS4-7 From Plasmas Towards Surfaces: How Plasma Simulation Supports Materials Development***, Mark J. Kushner,* University of Michigan, USA **INVITED**

New materials development and fabrication often have the goals of new functionality or smaller dimensions. In many cases, thermal or equilibrium processes are challenged to achieve this functionality. The inherent non-equilibrium reactivity available from low-temperature plasma materials processing addresses both the prospect of new functionality, by enabling new structures to be fabricated, and smaller dimensions, due to the precision available to plasma produced fluxes to surfaces. An example of achieving both new functionality and finer precision is plasma enabled atomic layer deposition (ALD) and atomic layer etching (ALE). The broad parameter space available to plasma enhanced materials processing has motivated integrated plasma-materials modeling to help narrow the scope. In this talk, contributions of modeling of plasmas and plasma-surface-interactions to the development of new functionality and greater precision will be discussed. Examples will be shared from the low pressure, modeling enhanced development of new plasma excitation schemes with the goal of customizing fluxes; and feature scale modeling for ALE and high aspect ratio processes. Modeling enabled insights to atmospheric pressure plasma functionalization of surfaces will also be discussed.

4:10pm **TS4-9 Numerical Estimation of Intrinsic Stress in Physical Vapor Deposited Thin-Films***, **Anurag Chakraborty**, R Anderson, J Ash,* South Dakota School of Mines and Technology, USA*; F Kustas,* Arbegast Materials Processing and Joining Laboratory (AMP), USA*; S Ahrenkiel,* South Dakota School of Mines and Technology, USA

A method of numerically quantifying the intrinsic stress estimates has been developed for physical vapor deposited thin-film coatings prepared at 250°C. This method involved constructing a prototype of a dedicated optical setup for measuring the curvatures of thinly coated samples with a film thickness ranging from 3-5 microns. A portable fixture was made which was clamped onto the translation stage of an optical microscope and this could be potentially usable with any commercial microscope that has 40 mm or more of vertical stage travel. Characterizations were performed on the optical instrument to enhance the sensitivity of detecting curvature changes over a given range of radii for the samples. The optical setup is compatible with reverse-mounted thin-film samples across a range of radii and it was modeled in Autodesk Inventor. A finite element model was developed in Abaqus where the deformation due to the residual stress in the thin-film sample was modeled as a pure thermal load. Subsequently, the initial stress state parameter was incorporated into the original model and systematically varied until the finite element model showed a deflection and a curvature which was in the range of 1-3% of the actual values obtained from the optical setup. The difference in the S11 and S22 principal stress values generated by the two models could be considered as equivalent to the actual intrinsic contribution to the eventual residual film stress in the coating responsible for the physical deflection. A test model with fixed constraints in Abaqus was also developed to capture the pre-deformed state of stress. Finally, this method was used to observe the intrinsic stress variations across 20 samples which were placed in a rectangular array formation over an 8" by 6" area of an aluminum supporting plate as a function of their separation distance from the target material. All 20 coatings were developed in a single deposition run to eliminate the process variables from having a non-uniform impact on the intrinsic stress development.

4:30pm **TS4-10 Modeling of UHMWPE Surface Texture for Reducing Wear on a Knee Prosthesis***, **Tomas De la Mora Ramírez**,* Universidad Autónoma Metropolitana, Mexico*; I Hilerio Cruz,* Universidad Autónoma Metropolitana- Azcapotzalco, Mexico*; M Doñu Ruiz,* Universidad Politécnica del Valle de Mexico, Mexico*; N Lopez Perrusquia,* Universidad Politecnica Del Valle De Mexico, Mexico*; E García Bustos,* Universidad de Guadalajara, CUCEI, Mexico, México*; D Maldonado Onofre,* Tecnológico de Estudios Superiores de Jocotitlán, Mexico

The objective of the research is to improve tribological properties of UHMWPE through the morphological modification of its surface texture with the analysis of stress distribution, contact stress, volume loss and coefficient of friction. Test specimens were made through 3D printing to produce hexagonal geometric textures at depths of 18, 25, 36 and 50 micrometers at different geometric densities with respect to a uniform distribution on the surface of the specimen of 5, 10, 20 and 40%. Microabrasion tests were performed using a UHMWPE specimen and a ball of 52100 steel material one inch in diameter. Throughout 3D perfolometry the wear rate and the wear constant of the test specimens with and without texture were obtained. A dynamic simulation was performed by finite element analysis of the tribometer microabrasion test using a subroutine in fortran language linked to Abaqus V6.12 finite element software. With the simulation a rate of wear is obtained; comparing with the experimental results. With the experimental results and the simulation the subroutine was applied to predict its lifetime.

4:50pm **TS4-11 Perturbation Analysis Of Glassy Alloy Film Formation***, **Rahul Basu**,* Adarsha Insitute of Technology, VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated incorporating surface convective effects. These equations which are non linear due to the moving interface are linearised and decoupled. Effects of the Biot, Fourier and Stefan numbers are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for several alloys in various groups of the Periodic Table. Earlier work by Duwez (1) and Spaepen & Turnbull (2) is analysed in light of the present analysis.

References:

1) P. Duwez, Annual Review of Materials Science, 1976

2) F Spaepen and D Turnbull, Scripta Met, 8,563, 1974

5:10pm **TS4-12 First Principles Study of the Nb-Al Intermetallic System***, **David Holec**,* Montanuniversität Leoben, Austria*; N Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; K Preininger, S Zoehrer, R Franz,* Montanuniversität Leoben, Austria

Physical-vapour-deposited materials exhibit a variety of interesting and useful properties. Often, however, the actual behaviour strongly depends on the specific synthesis method and conditions. For revealing such synthesis-property relationships, understanding of the deposition process, which in turn is influenced by the target material used for the deposition, is critical.

In this contribution we will use first principles calculations to assess the stability of phases in a model binary intermetallic Nb-Al system. The convex hull constructed using the USPEX code yields Al_3Nb and $AlNb_2$ as the stable phases along with $AlNb_3$ being slightly metastable. These phases appear in published phase diagrams, in which the $AlNb_3$ is nevertheless a stable phase. Surprisingly, the reported compositional window for $AlNb_3$ does not contain the nominal x=0.75 composition.

Cohesive energies are calculated as representatives for the bonding strength and hence ease of the evaporation during an arc evaporation process. Additionally, we propose to use vacancy formation energies instead of cohesive energies as they provide species-specific information as well as their temperature dependence can be estimated. The vacancy formation energies are further on studied as a function of distance from the surface as well as the surface orientation. A correlation with experimental measurements of cathodic arc behaviour is attempted.

Topical Symposia
Room Royal Palm 1-3 - Session TS5

Anti- and De-icing Surface Engineering

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

1:30pm **TS5-1 Multi-step Modification of TI-Alloy and Stainless Steel Surfaces for Icephobic Applications***, **Stephen Brown**, J Lengaigne, A Riera, L Martinu, J Klemberg-Sapieha,* Polytechnique Montreal, Canada

In-flight component icing is a major issue in aerospace as it can lead to component failure or even cause aircraft to crash. While active solutions to icing such as heating and pneumatic boots do exist, a passive solution is desirable to avoid the additional weight and energy requirements of these systems. Superhydrophobic surfaces have been shown to reduce ice adhesion compared to bare metal surfaces; as such there is much interest in the modification of components to render them superhydrophobic.

In the present study, we look at a technique to modify the surfaces of Ti-6Al-4V and stainless steel substrates, to give them the hierarchical micro- and nano-scale roughness required for superhydrophobicity without invoking complex and costly processes such as photolithography. The desired morphology is obtained through a two-step process: samples are first sandblasted with alumina particles, and are subsequently etched in SF_6 plasma with a stainless-steel mesh placed directly on the sample to serve as a mask. The sandblast step induces a micro-scale roughness on the sample surface; the etching step adds more organized micro-scale features in the form of consistently sized and spaced pits, as well giving the surface nano-scale features. Mesh sizes as well as etching times are taken into consideration. Surface roughness remains relatively low after etching, with $R_a < 5\mu m$, and $R_z < 30$ µm. After coating with a fluorocarbon by thermal evaporation, the surfaces are rendered superhydrophobic with static water contact angles up to 170° and contact angle hysteresis as low as 6°.

1:50pm **TS5-2 Design and Characterization of Super-low Ice Adhesion Surfaces***, **Zhiliang Zhang**,* Norwegian University of Science and Technology (NTNU), Norway

Preventing the formation and accretion of ice on exposed surfaces is of great importance for Arctic operation, renewable energy, electrical transmission cables in air and shipping. While studies on suppressing ice nucleation by surface structuring and local confinement are highly desired, a realistic roadmap to icephobicity for many practical applications is perhaps to live with ice, but with the lowest possible ice adhesion. From the viewpoint of fracture mechanics, the key to lower ice adhesion is to maximize the ice-substrate interface-crack driving forces at multiple length scales. Herein, we present a novel macro-crack initiator mechanism in addition to the nano-crack and micro-crack initiator mechanisms, and demonstrate a new strategy to design super-low ice adhesion surfaces by introducing ordered sub-structures into smooth durable PDMS coatings to ultimately weaken ice-substrate interface [1]. Our results show that PDMS (weight ratio 10:10) thin films with 1 mm inner holes in two layers approach an ice adhesion strength of 5.7 kPa. The introduction of sub-structures into PDMS thin films promotes macro-crack initiators, and is able to further reduce ice adhesion strength by ~50% compared with that of PDMS thin films without sub-structures, regardless of layer thickness, curing temperature, weight ratio and the size of inner hole. Therefore, rationalizing the three crack-initiator mechanisms and their interactions at multi-length scales may provide an effective strategy towards designing super-low ice adhesion surfaces.

Reference:

[1] Zhiwei He, Senbo Xiao, Huajian Gao, Jianying He and Zhiliang Zhang, Multiscale crack initiator promoted super-low ice adhesion surfaces, *Soft Matter*, (2017) 13, 6562-6568.

2:10pm **TS5-3 Icephobic Nanocomposites for Aeronautics***, F Martín, **Silvia Larumbe**, M Monteserin, G Garcia Fuentes,* Asociación de Industria Navarra, Spain*; J Mora Nogues, P García Gallego, A Agüero Bruna, R Atienza,* INTA, Spain

Ice Protection Systems (IPS) are remarkable and essential parts of aircrafts since the formation of ice undergone in extremely hard conditions could give rise to the lack of the controllability of the aircraft. Traditional deicing systems suppose expensive and complicated systems that demand a very careful maintenance [1]. Moreover, the complexity of some of these systems makes them difficult to accommodate in small-medium aircraft. The need of seeking new systems with advantages like costs, low power consumption, reparability and lightness entails a relevant challenge.

In this regard, different coatings based on nanocomposites have been developed as passive systems against ice formation [2]. The basis of these coatings is the additivation of a hydrophobic matrix (silicones) with inorganic nanoparticles creating a controlled microroughness in the surface responsible of the icephobic behavior of the final coating. The main features to control during the process are on one side, the dispersion of the inorganic nanoparticles and on the second hand the final roughness. For the first aim, the inorganic particles were dispersed ultrasonically using high surface particles to improve the final dispersability in the organic matrix and also the final concentration was adjusted to obtain an enough microroughness for the accomplishment of a superhydrophobic coating keeping a good final adherence of the coating.

Several coatings based on nanocomposites with silicone and fluorosilicone reinforced with high surface alumina nanoparticles were prepared onto Al6061 substrates with different concentration of particles. The final adherence was optimized through different chemical and physical approaches obtaining as result a better adherence after the imprimation of the bare substrate and the subsequent use of an anchoring coating. The measurement of contact angle, roughness, ice formation, ice adherence and resistance to erosion were some of the characterization measurements carried out for the different coatings. Good adherence, contact angles within the range of 110-150° were obtained depending on the final additive concentration, improvement of the erosion resistance and lower ice formation comparing with other hydrophobic materials were some of the features of the developed materials, revealing these coatings as a promising alternative to other conventional IPS.

Acknowledgements

The authors thank financial support from the Spanish Ministry of Economy, Industry and Competitiveness (MINECO) through the project TRA2013-48603-C4-3-R.

References

F.T. Lynch et al, *Progress in Aerospace Sciences* **37,** 669 (2001).

H. Wang et al, *Applied Surface Science***349,** 724 (2015).

2:30pm **TS5-4 Development of Hydrophobic/icephobic Poly (Dimethylsiloxane) Based Composite Coating for Application in Ice Protection***, **Junpeng Liu**, J Wang,* University of Nottingham, UK*; H Memon,* University of nottingham, UK*; T Barman, B Turnbull, K Choi, X Hou,* University of Nottingham, UK

Accretion of ice on the surfaces of various engineering products under severe temperature condition is known to cause adverse socio-economic impacts and may lead to disasters. Development on hydrophobic/icephobic coatings has attracted increasing attention in many industrial areas, especially in aerospace. Aiming for reducing energy consumption for ice protection, poly(dimethylsiloxane) (PDMS) based composite coating had been developed. Particulate phase was integrated into the coating to improve the hydrophobicity and de-icing performance of the coating, and to reduce the overall energy consumption on ice protection. Ice adhesion tests were performed using a centrifuge method with a glaze ice block frozen on the studied coating in an environment chamber with temperature of -5 °C, with un-coated aluminium plates as references. The durability of the coatings was evaluated by erosion test under pressurized water droplet impinging. The composite coating demonstrated a typical water contact angle of 153° indicating good hydrophobicity. The ice adhesion test results showed an average ice adhesion strength of 5.8 kPa between the ice block and the coatings which is much lower than that of aluminium references (152.7 kPa). The de-icing test result indicated that PDMS-based composite coatings would effectively remove the ice and had great potential for application in ice protection.

Acknowledgement:

This work was supported by CleanSky II EU initiative GAINS (Grant Agreement No: 671398). The work forms a part of the project to develop a suitable hydrophobic and icephobic coating on aircraft wing surfaces.

2:50pm **TS5-5 Correlation Between Room Temperature Characteristics and Ice Adhesion***, **Jianying He**,* Norwegian University of Science and Technology (NTNU), Norway

Ice adhesion strength is dependent on the surface properties, and surface wettability is often correlated with ice adhesion strength. However, these established correlations are limited to high ice adhesion and become invalid when the ice adhesion strength is low. In this work we carried out an experimental study to explore the relationships between low ice adhesion strength and room temperature surface properties [1]. A variety of room temperature properties of hydrophilic and hydrophobic samples consisting of both low and high ice adhesion surfaces were analysed. The properties investigated include water adhesion force, water wettability, roughness, elastic modulus and hardness. Our results show that low ice adhesion strength does not correlate well with water contact angle and its variants, surface roughness and hardness. Low elastic modulus does not guarantee low ice adhesion though surfaces with low ice adhesion always show low elastic modulus. Low ice adhesion (below 60 kPa) of tested surfaces may be determinative of small water adhesion force (from 180 to 270 µN). Therefore, measurement of water adhesion force may provide an effective strategy for screening anti-icing or icephobic surfaces, and surfaces within specific values of water adhesion force will possibly lead to a low ice adhesion.

Reference:

[1] Zhiwei He, Elisabeth T. Vågenes, Chrisrosemarie Delabahan, Jianying He & Zhiliang Zhang, Room Temperature Characteristics of Polymer-Based Low Ice Adhesion Surfaces, *Scientific Reports* (2017) 7:42181.

3:10pm **TS5-6 Impact Dynamics and Icing Behavior of Supercooled Water Microdroplets on Surfaces of Different Wettabilities Ranging from Superhydrophilic to Superhydrophobic***, **Jacques Lengaigne**,* Polytechnique Montreal, Canada*; E Bousser,* Polytechnique Montreal, UK*; A Riera,* Polytechnique Montreal, Canada*; D Batory,* Lodz University of Technology, Poland*; S Brown,* Polytechnique Montreal, Canada*; A Dolatabadi,* Concordia University, Canada*; L Martinu, J Klemberg-Sapieha,* Polytechnique Montreal, Canada

Atmospheric icing on aircraft is a significant danger during flight and leads to high additional costs for operators. Icing occurs when supercooled micrometric water droplets (SWD), impact surfaces and freeze. Icephobic coatings based on superhydrophobic surfaces are the most promising avenue to replace current energy intensive techniques such as heaters and de-icing fluids. However, their wetting behavior under SWD icing is not well explored.

In this work, we investigate the influence of wettability on the impact dynamics of supercooled microdroplets. Four surface types with different wettabilities (characterized by their water contact angle, θ) were studied: superhydrophilic θ=10°, hydrophilic θ=70°, hydrophobic θ=107° and superhydrophobic θ=173° . Realistic atmospheric conditions, leading to supercooled microdroplet freezing, were simulated in an icing wind-tunnel with a wind speed of 10 m/s, subzero temperatures (down to minus 18° C) and a mean droplet diameter of 40 µm. High speed imaging was used to capture the impact sequence of droplets on the different surfaces.

Impact dynamics show transition from wetting to bouncing when the surface becomes hydrophobic. However, in icing conditions the repelling behavior is only maintained for the superhydrophobic coating whereas droplets freeze on the other surfaces. Limitations of superhydrophobic coatings under SWD icing are also explored.

3:30pm **TS5-7 Quasicrytalline Coatings by HVOF to Improve the Ice Accretion and Durability in Aerostructures Components***, R Muelas Gamo, **Julio Mora Nogues**, P García Gallego, A Agüero Bruna,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Weather hazards, in particular icing conditions, are an important contributing factor in aviation accidents and incidents world-wide. Further advancements in mitigation of in-flight performance degradation are necessary. This problem is being studied following two strategies: active systems or de-icing once the ice has formed, and passive or anti-icing systems to prevent or retard accretion. Many different anti-icing strategies are currently being explored to find suitable long-lasting solutions such as surface engineering which can provide a better alternative by reducing or eliminating ice accumulation.

Quasicrystals (QCs) are metallic materials in nature but with similar properties to those of ceramic materials, such as low thermal and electrical conductivities, and high hardness. These materials exhibit five and seven fold rotational symmetries, which were forbidden according to the rules of classical crystallography. In particular, those that have low surface energy are good candidates to be employed as icephobic coatings. These types of coatings are used commercially instead of Teflon on frying pans as they do not scratch easily.

Al based QCs have been applied by High Velocity Oxyfuel (HVOF) thermal spray on typically used aeronautic materials such as Ti and Al alloys as well as steels. The coatings have been characterized and evaluated (adhesion, hardness, wetting angle and ice accretion in an Icing Wind Tunnel. Moreover surface modifications of the coating have been carried out by laser and machining in order to study the effect of the surface roughness and morphology on the ice accretion properties. The QC coating has been compared with an anti-icing commercial paint, and the result indicate a significant reduction of the ice accretion behaviour. Since the coatings are hard ($HV_{0.3}$: 550), a durable behaviour is expected.

The proposed solution is and will help eliminate the need for frequent on-ground de-icing procedures. This in turn will contribute to the reduction of cost, pollution and flight delay.

Topical Symposia
Room Sunrise - Session TS3
Coating of Synthetic Materials – Engineering for the Future
Moderators: Klaus Böbel, Bosch GmbH, Fred Fietzke, Fraunhofer FEP

8:00am **TS3-1 Development of PVD Coatings by R2R on Basis of TI/AG, TI/ZN and TI/AG/ZN on Textile Fabrics***, **Martin Fenker**, H Kappl,* FEM Forschungsinstitut Edelmetalle & Metallchemie, Germany

Silver and zinc coatings are interesting materials in the biomedical field as they possess antimicrobial properties. Therefore, PVD coatings on the basis of Ti/Ag, Ti/Zn and Ti/Ag/Zn have been deposited by non-reactive DC magnetron sputtering on textile fabrics like polypropylene (PP), polyvinylidene fluoride (PVDF) et cetera. These polymers are used for example as implant material or for wound bandage. A roll-to-roll (R2R) unit was constructed and installed in our semi-industrial PVD machine and tests have been performed with elemental targets as well as with compound targets. Coating thickness was measured on coated glass samples. Ageing test were performed by ultrasonic agitation of the coated fabrics. Light optical microscopy and scanning electron microscopy were used for visual inspection of the as-deposited as well as the sonicated samples. Delamination of the coating occurred for some samples and will be discussed.

8:20am **TS3-2 Coating of Plastic Components by Electron-beam Evaporation***, **Fred Fietzke**, H Klostermann, J Heinß,* Fraunhofer FEP, Germany

Vacuum coating of plastic components as an alternative to electroplating already has a long tradition in industrial practice. The applications range from metallization of headlamp reflectors over decorative controls and instruments up to EMC shielding of electronic devices. Predominantly used methods are magnetron sputtering and thermal evaporation.

A particular challenge is the low thermal stability of many engineering plastics in conjunction with the high energy input of PVD processes and the limited possibilities of substrate cooling in vacuum. Furthermore, for most plastics a sufficient adhesion of PVD coatings directly on the substrate material still cannot be achieved, so that primers or lacquers have to be used as sublayers.

A new approach for PVD direct metallization is taken by Fraunhofer FEP. Here, a short-cycle system for the coating of components by high-rate electron beam evaporation is used to coat components made of polycarbonate (PC) and PC/ABS (acrylonitrile butadiene styrene copolymer) blend. After a short treatment in oxygen plasma the parts are coated with an aluminum layer of some microns thickness in less than one minute, without showing thermal deformations or film delamination.

The key to meet these challenges lies in a high evaporation rate already at low power input in combination with a substrate movement adapted to the component geometry. Possibilities and limitations of the method are explained, properties of coated parts are analyzed in comparison with the current state of the art, and further possible applications are discussed.

8:40am **TS3-3 Aspects of Coatings on Plastic products for Decorative and automotive parts.***, **Roel Tietema**,* IHI Hauzer Techno Coating BV, Netherlands*; D Doerwald, C Trivedi, I Kolev, J Landsbergen,* IHI Hauzer Techno Coating B.V., Netherlands **INVITED**

Plastic products are playing an ever bigger role in our daily life and they draw more and more attention of the market. Reasons for this trend are low cost, ease of producibility, large freedom of design and low weight.

Coatings on plastic products have mainly been produced by electroplating and lacquers.

Since the 1980's PVD coatings have been used for decorative applications in the watch industry. Nowadays decorative coatings are applied on watches, faucets, door handles, spectacles (both frames and glasses) and mobile phones.

In recent years a new market has emerged for PVD-coatings on plastics driven by the requirement to reduce weight. This occurs because on one side the expectations of a growing market share for electrical cars exists as well as on the other side CO_2 emissions and fuel consumption can be reduced by weight reduction. The consequence is that the use of plastics in the automotive industry as light weight base material for both interior and exterior parts will have an increasing share. Until now electroplating is the major applied technology, but PVD will get an increasing share in this market due to the requirement for replacement of electroplated chromium. Electroplating is a technology requiring the use of carcinogenic hexavalent chromium (in form of trichromate) during several steps of the plating process. This material is on the list of SVHC's (Substances of Very High Concern) and imposes severe health dangers on personnel working with the plating lines. Besides this plating technology requires intensive efforts to dispose waste materials.

As replacement for electroplating in-line processes where plastic parts are coated with UV-cured lacquer and a subsequent chromium PVD layer have been developed and are available on the market. Mass production for automotive plastic products is already applied.

In this presentation the developments will be discussed beginning from initial applications on watches and faucets by sputter and arc technology in the 1990's. In the early 2000's coatings have been introduced on mobile phones, whereas finally in the last decade the application of coatings on plastic parts by hybrid lacquer/PVD-PECVD processes have been developed.

Different aspects of the requirements for coated products and the related processes will be discussed from the point of view of technologies, productivity, performance and sustainability.

9:20am **TS3-5 Combined Impact and Sliding Testing for Evaluation of Surfaces on Different Materials***, **Claus Rebholz**,* University of Cyprus, Cyprus **INVITED**

Light-weight materials such as polymers and magnesium alloys exhibit tremendous challenges for surface engineering, not only in terms of selecting appropriate coating architectures and processes, and therefore reducing or avoiding issues that can result in premature coating failure at relatively low stress levels compared to more rigid substrates, but also for the development of sophisticated testing methods for quality evaluation and inspection.

Several well established testing methods (e.g. impact, pin-on-disk, scratch) have been widely used to evaluate the properties of coatings on various substrates. However, many of these existing techniques have limitations, since they mainly focus on a single mode of loading and wear (e.g. only impact or sliding). Here, a combined impact and sliding test for the tribo-mechanical evaluation of surfaces under complex loading conditions is presented, where materials are simultaneously subjected to sliding and impact loading. Such modes exist in many critical applications, from biomedical (e.g. hip/knee implants) to automotive applications (e.g. diesel injectors, engine valves, cam shafts), in cutting tools, general machine parts and systems, etc. The proposed testing set-up offers a feasible way for fast, economical and reliable evaluation of complex coating/tribo systems. Benefits include the time and cost effective evaluation of various surfaces (testing time usually less than a minute) and the better understanding of their properties such multi-mode loading conditions. Some of the unique characteristics of this new instrument (e.g. combined impact and sliding, wear area in a single small "point", etc.) are discussed and examples of evaluated metallic bulk materials/coatings are presented.

10:00am **TS3-7 Interfacial Stability of the Aluminium-Polyimide Interface Against Thermal Treatments***, **Barbara Putz**,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; G Milassin, Y Butenko,* European Space Research and Technology Centre, Netherlands*; B Völker, C Gammer,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; C Semprimoschnig,* European Space Research and Technology Centre, Netherlands*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Monanuniversität Leoben, Austria

Metal-polymer systems are usable for innovative high-tech applications, including flexible and rigid microelectronics or spacecraft and satellite insulation. The metal-polymer interfaces, which have to bridge the distinct physical and chemical properties of the adjacent materials, are critical elements determining the overall reliability of the composite. A thorough understanding of the thermal stability of these interfaces is essential for reliable devices, considering the inevitable thermal treatments such as annealing or cycling which typically occur during manufacturing or operation. Considering the low homologous temperature of polymers combined with the difference in thermal expansion coefficients (factor 2-3) between the two components thermal treatments are likely to cause interfacial degradation and need to be critically investigated. In this study the interfacial stability of Aluminum-Polyimide (Al-PI), used as multilayer insulation blankets on satellites, is investigated as a function of thermal cycling (±150°C) and thermal annealing treatments (150-300°C). Mechanical adhesion measurements are combined with X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy

(TEM) in order to relate the interface strength to the interface chemistry and structure. The interfacial adhesion energy was measured using tensile induced delamination. In order to assess the chemistry of the interface, a 180° peel test was used to provide access to the metal side and the polymer side of the interface without additional etching or sputtering steps that would alter the interface chemistry. XPS survey and high resolution core level scans were recorded on both sides of the peeled interfaces to identify and understand relevant interfacial bonding and distinguish between adhesive failure of the interface and cohesive failure in the substrate during peeling. TEM cross-sections were used to examine the interface microstructure and morphology. It was determined that the Al-PI interface, which initially shows very good adhesion, is resistant to thermal cycling of +/-150°C up to 200 thermal cycles. After thermal annealing, however, small mutations in the interface chemistry and structure were detected and identified starting at 225°C. Mutations were invisible to mechanical adhesion measurements and include the thickness increase of an amorphous interlayer between Al and PI of about 2nm and a change in the failure mechanism during the peeling. Being able to trace and identify subcritical mutations with the presented experimental approach before they become fatal is essential to predict the reliability and improve the design of metal-polymer composites.

Topical Symposia
Room Royal Palm 4-6 - Session TS1
Thermal and Kinetic Spray Deposition

Moderators: Andrew Vackel, Sandia National Laboratories, USA, Charles Kay, ASB Industries, Inc., USA

8:00am **TS1-1 Latest Developments for Turbomachinery Coatings*, Kirsten Bobzin*, *L Zhao, F Linke, S Wiesner, B Yildirim, T Liang, M Welters,* Surface Engineering Institute - RWTH Aachen University, Germany **INVITED**

In accordance with the key objectives -higher efficiencies and lower emissions- components of modern turbomachinery systems, i.e. stationary and rotating blades, are subject to very high demands, which need to be fulfilled among others with innovative coating solutions. Protective coatings are, therefore, the state of art to ensure functionality of turbomachinery components with prolonged life times.

In this presentation, some of research work of Surface Engineering Institute of RWTH Aachen University on the above-mentioned coating solutions is introduced summarily. Firstly, an erosion resistant coating based on nanocomposite nitride (Ti,Al,Si)N applied by means of high speed physical vapor deposition (HS-PVD) for protection of gas turbine compressor blades and a thick erosion resistant Ni-based composite coating applied by deposition brazing for protection of steam turbine blades will be presented. Subsequently, EB-PVD thermal barrier coatings (TBC) based on different pyrochlore zirconates with multilayer coating architecture will be demonstrated. Furthermore, a highly porous, plasma sprayed TBC, based on Gd_2O_3- Yb_2O_3 co-doped ytrria-stabilized zirkonia (YSZ), will be introduced. Finally, two oxidation protective coatings for γ-TiAl substrates will be subjected. The first one is an amorphous (Al,Cr)ON coating deposited by means of HS-PVD. The second one is a plasma sprayed coating with a Ti-diffusion barrier interlayer. All of the coatings show promising results with respect to their intended functions.

8:40am **TS1-3 Repair of Nickel Base Superalloys by Cold Spray*, Robert Vaßen*, *R Singh, T Kalfhaus, G Mauer, O Guillon,* Forschungszentrum Jülich GmbH, Germany*; J Gibmeier,* Karlsruhe Institute of Technology (KIT), Germany **INVITED**

In the cold spray process, deposition of particles takes place through intensive plastic deformation upon impact in a solid state at temperatures well below their melting point. The high particle impact velocities and corresponding peening effects can lead to high compressive residual stresses in cold spray coatings. This can be advantageous with regard to mechanical properties as fatigue life and hence, cold spray seems to be an ideal process for repair applications. In this study, Inconel 718 powder particles were cold-sprayed on Inconel 718 substrates by using nitrogen gas for an application as a repair tool for aero engine components. First, velocities of the cold sprayed particles have been determined as a function of process conditions and particle size. Critical velocities have been determined considering the deposition efficiencies.

Furthermore, the magnitude of the residual stress and its distribution through the thickness of the cold-sprayed coatings were measured by using the hole-drilling and the bending methods. Mainly compressive residual stresses were observed in cold-sprayed Inconel 718 coatings. Accumulation of residual stresses in the coatings is highly affected by peening during deposition and it decreases with increase in thickness. It has been observed that the bond--strengths of cold-sprayed Inconel 718 coatings are highly influenced by coating thickness and residual stress states of the coating/substrate system. A detailed discussion will be given.

In addition, also further results on cold spraying different Ni base superalloys on CMSX 4 type substrates will be presented and discussed. Especially the influence of substrate temperature will be highlighted.

9:20am **TS1-5 Multi-layer Metallization of Polymer Materials via Thermal Spray*, Andrew Vackel*, *M Smith, A Miller,* Sandia National Laboratories, USA*; B Peter, B Post,* Oak Ridge National Laboratories, USA

With the emerging prevalence of 3D printed polymer materials for rapid prototyping, there is an increasing demand for a similar ease and quickness in producing metallic and multi-material components. One such approach is through the metallization of printed polymer parts using thermal spray, where thick deposits can be quickly and economically deposited. However, technical challenges include management of residual stress of the deposit, assessing the adhesion strength of sprayed metal onto polymers, and potential thermal degradation of polymer substrates from molten droplet impingement during spraying.

This presentation will discuss the methodologies used to accomplish successful metallization of polymer substrates (e.g., ABS, HDPE) including *in-situ* measurements of substrate deflection for calculation of residual stress, mechanisms and quantification of adhesion between polymers and sprayed metal, and optimization of spray processing and material layering.

9:40am **TS1-6 Dielectric Ceramic Thick Films produced via Aerosol Deposition*, EricA. Patterson*, ASEE Postdoc, US Naval Research Lab, USA*; S Johnson, E Gorzkowski,* U.S. Naval Research Laboratory, USA

The aerosol deposition (AD) method is a thick-film deposition process that uses ~500 nm particle size oxide powders to produce 95% dense films, up to several hundred micrometers thick with nanometer sized grains. The deposition can be performed on a variety of substrates because bonding and densification between the film/substrate interface are thought to be facilitated by local temperature rise, high pressure, particle fracture, and chemical bonding during deposition, which leads to the nano-grained microstructures created at room temperature. In this work, we present film characterization results of depositing dielectric and ferroelectric materials using aerosol deposition. Film properties will be compared when adjusting process parameters such as varying flow gas rate, gas type, and substrate material. Further characterization will be performed by changing annealing conditions, and electrode application.

10:00am **TS1-7 Tribological Properties of Cold Sprayed Metal Matrix Composite Coatings*, Richard Chromik*, McGill University, Canada **INVITED**

Metal matrix composites (MMCs) provide a significant advantage for their tribological properties compared to pure metals. There is a long history of metal-ceramic composites for enhancement of load carrying capacity and solid lubricating composites for friction reduction. Both type of composites will generate 'tribofilms' that help to reduce wear and control friction. One may also engineer MMCs with both hard phase and solid lubricants.

There are many methods of manufacture for MMCs in bulk form and a few options for manufacturing them as coatings. Cold spray is one such coating deposition technique that has received increased attention in recent years. Researchers have developed a wide range of MMC coatings by cold spray, typically basing materials selection on metal-ceramic or metal-solid lubricant MMCs made by traditional methods. Recent work from our group has included cold spray coatings of Al-Al_2O_3, Ti-TiC, Cu-MoS_2 and Ni-WC.

In this presentation, cold sprayed MMCs will be discussed in terms of their 'sprayability' and, for successful coating systems, their tribological properties. Coatings are tested in sliding wear and sometimes fretting wear test conditions. For both cases, post-characterization of cross-sectioned wear scars reveals microstructural evolution near surface leading to formation of tribofilms that provide wear resistance and friction control. Structure and properties of the tribofilms are determined with SEM, TEM, EDS, Raman spectroscopy and nanoindentation. Tribofilms are found to be mixtures of the two components in the MMC, but with finer microstructure and some level of oxidation that leads to higher hardness. The tribological performance of cold sprayed MMC coatings, similar to MMCs made by other methods of manufacture, depends significantly on the nature of the third bodies formed by the wear process. However, due to the cold-worked nature of cold sprayed metals and the lack of full metallurgical bonding in some coatings, some differences were observed and will be discussed.

10:40am **TS1-9 Assessment of Magnetic Orientation of Barium Hexaferrite Thick Films Deposited by Aerosol Deposition with *in situ* Magnetic Field*, ScooterD. Johnson*, Naval Research Laboratory, USA*; D Park,* Korean Institute of Material Science, Korea*; A Hauser, S Ranjit, K Law,* University of Alabama, USA*; H Newman, S Shin, S Qadri, E Gorzkowski,* Naval Research Laboratory, USA

Devices utilizing magnetic materials such as frequency selective limiters, circulators, inductors, and filters are critical components in many of today's electronics [1]. The need for ferromagnetic materials in these devices poses many difficulties for minimizing device size, weight, and cost. One issue that hampers integration of ferromagnetic materials is the high-melting temperature of the ferrite compared with the low-melting temperature component structure [2]. Furthermore, the need for low-loss and narrow bandwidth operation adds another significant barrier to the advancement of integration of ferromagnetic materials into these device structures.

The high-frequency operation regime and strong uniaxial anisotropy of barium hexaferrite ($BaFe_{12}O_{19}$, BaM) makes this material particularly interesting to utilize as an oriented film for microwave components. In this study, we characterize BaM films deposited onto sapphire substrates by a room-temperature thick-film growth technique called aerosol deposition.

We perfomed alternating gradient magnetometry depth studies on a series of as-deposited films that show a variation in magnetization with depth. Cross-sectional SEM images indicate laterally uniform film density. Electron dispersive spectroscopy of the interfacial region suggest significant Al_2O_3 mixing into the film volume. Fe XPS spectra indicate a change in peak weighting as a function of thickness, possibly indicative of modified structure or oxygen incorporation due to Al incorporation.

To explore the possibility of magnetically orienting the films we deposited additional films in the presence of a 4 kOe static magnetic field. We report VSM, FMR, and XRD results of these films as-deposited and after post-deposition sintering at temperatures from 700C to 1000C.

The films deposited in the field show an increased saturation magnetization and remanence compared to the films deposited with no applied field. XRD results of all of the films in this study suggest good crystallinity. Rietveld refinement of the data also suggests that the films deposited in the field presence have a smaller unit cell volume compared to films deposited without the applied field. Post-growth sintering increases the crystallite size from about 10 nm to 25 nm. Annealing improves the overall properties of the films further increasing the magentic orientation and saturation.

[1] Adams, J., Davis, L., Dionne, G., Schloemann, E., and Stitzer, S., IEEE Transactions on Microwave Theory and Technology, **50** (2002), No. 3, pp.721.

[2] Johnson, S., Newman, H., Glaser, E., Cheng, S.-F., Tadjer, M., Kub, F., and Eddy, C., IEEE Trans. on Magnetics, **51**, (2015), No. 5, pp. 2200206.

11:00am **TS1-10 Development of Repair Methods for Nickel Based Super Alloys using Cold Gas Spray**, ***Tobias Kalfhaus***, *R Vaßen,* Forschungszentrum Jülich GmbH, Germany

The hot section parts in aviation engines and stationary gas turbines are exposed to extreme environments, where high temperatures and eroding atmospheres lead to oxidation, corrosion and fatigue damage of the inserted parts. As the manufacture of the nickel based superalloys for those high temperature applications is expensive, the repair of worn or damaged parts is from an economic viewpoint desirable, however, usually difficult due to the poor weldability of these alloys.

The coating technology Cold Gas Spray has been tested to repair such worn parts and reduce the maintenance cost. In this process heated and pressurized gas is expanded through a Laval-Nozzle. This leads to a high-speed gas jet and accelerates the powder to supersonic velocities. The operating temperature is relatively low compared to the melting point of the used alloys. The particles hit the substrate, deform and are bonded to the substrate by mechanical clamping and formation of intermixing zones. An oxide free and dense coating is formed. With an increasing coating thickness the stored elastic energy in the coating increases and can lead the delamination of the coating at a critical thickness.

In this study the alloys CMSX-4, Rene 80, Inconel 625, Inconel 713 and Inconel 738 are deposited on single crystalline substrates that are similar to CMSX-4 and polycrystalline Inconel 738 substrates. All used powders are spherical and have a diameter between 5-45 µm. To show different residual stresses that evolve during the coating process curvature measurements were performed on round Inconel 738 samples. Each powder shows different adhesion to the substrate. To characterize the differences adhesion tests were performed.

To reduce residual stresses and increase the critical thickness of the coating a heated stage is tested to investigate the influence of a heated substrate. Additional heat treatments were performed to investigate the change of porosity and microstructure within the coating and at the interface between the substrate and the coating. The evolving microstructures were examined using scanning electron microscopy (SEM) and Electron Backscatter diffraction (EBSD).

11:20am **TS1-11 Microstructure-scale Simulations of High-rate Loading of Porous, Thermally-sprayed Metal Coatings**, ***Corbett Battaile***, *N Moore, S Owen,* Sandia National Laboratories, USA

The properties of most engineering materials depend on the characteristics of internal microstructures and defects. In metals, these features can include grains in the polycrystalline aggregate, impurities, multiple phases, and in the case of thermally sprayed coatings, significant levels of porosity. The microscopic details of the interactions between these internal defects, and the propagation of applied loads through the body, act in concert to dictate macro-observable properties like strength, conductivity, spall, etc. In order to achieve a comprehensive understanding and control of a material's high-rate properties, the relevant structure-properties relationships must be understood. In this work, we used Sandia's Alegra finite element software [1] to simulate the high-rate loading of metal coatings manufactured by thermal plasma spraying. These simulations include a direct representation of the microstructural details of the material, such that internal features like second phases and pores are represented and meshed explicitly as individual entities in the computational domain. We will discuss the dependence of the high-rate mechanical properties of these materials on microstructural characteristics such as the shapes, sizes, and volume fractions of the second phases and pores. We will also examine the effects of pore collapse on high-rate response, and how the details of the microstructural representation affect the microscopic material response to the applied load. In particular, we will discuss the effects of using “stairstep” (on a cubic finite-element “grid”) versus comformal (smooth) interfaces created via Sandia's SCULPT capability in CUBIT [3].

1. <http://www.cs.sandia.gov/ALEGRA/Alegra_Home.html>

2. <http://www.sandia.gov/mst/pdf/LENS.pdf>

3. <https://cubit.sandia.gov/>

11:40am **TS1-12 Simulation and Visualization of the Aerosol Deposition Process**, ***EdwardP. Gorzkowski***, *S Johnson, T Martin, R Saunders,* U.S. Naval Research Laboratory, USA*; A Borgdorff,* U.S. Naval Academy, USA*; D Schwer,* U.S. Naval Research Laboratory, USA*; E Patterson,* ASEE Postdoc, U.S. Naval Research Laboratory, USA

Aerosol deposition (AD) is a thick-film deposition process that can produce layers up to several hundred micrometers thick with densities greater than 95% of the bulk. Though this process has been used for two decades the precise mechanisms of bonding and densification is still debatable. Therefore, we have used a combination of computational fluid dynamics (CFD) and finite element (FE) modelling and high speed videography to help understand the flight of the particles as well as the interaction of the particle and the substrate. The CFD model results show the flight of particles from the nozzle to just before the substrate. At the point just before impact, the velocity and direction is collected and used to inform the FE model of the flight of the particle. Initially the FE model is run with the parameters obtained from the CFD model but the work is extended to include variations in particle size, velocity, and material to show their effects on the deposition process. The model is developed as full 3-D implementation with symmetric boundary conditions applied when/where appropriate. The particle and substrate materials are independent and each is varied between Al_2O_3, SiC, and float glass. Each material is simulated using a Johnson-Cook constitutive model, which includes plasticity, damage initiation and evolution, and failure. The mechanical properties of each material are taken from bulk properties. The particle velocity is varied from 100 m/s to 300 m/s with sizes between 0.5 µm and 1.5 µm. The bounds were informed by the results of the CFD analysis. High-speed videography will help validate this model and to better understand the process as a whole.

Topical Symposia
Room Grand Hall - Session TSP
Symposium TS Poster Session

TSP-1 Enhanced Hardening and Damage-tolerance Nanotwinned Medium Entropy Alloy CoCrNi Coatings Deposited by Magnetron Sputtering*, Fuyang Cao,* *P Munroe,* University of New South Wales, Australia*; Z Zhou,* City University of Hong Kong, China, Hong Kong*; Z Xie,* University of Adelaide, Australia

High entropy alloys (HEA) are defined as alloys consisting of at least five or more equiatomic elements, such as FeNiCoCrMn, commonly with a single FCC (or BCC) crystal structure. HEAs are reported to have promising mechanical properties, high thermodynamic stability, as well as excellent fracture toughness at cryogenic temperature. Herein we have investigated a series of equiatomic medium entropy alloy coatings, containing only three elements, Co, Cr, Ni. These coatings were deposited onto M2 steel substrates using a DC magnetron sputtering system with a CoCrNi alloy target (1:1:1 at.%). The microstructure and mechanical properties were examined by a number of techniques, including transmission electron microscopy (TEM) and nanoindentation. TEM results showed that the coatings were composed of elongated grains containing fcc {111} nanotwins. Such coatings exhibited a very high hardness, ~10 GPa as well as exceptional damage-tolerance under contact loading. It is believed that the nanotwinned structure is responsible for the high hardness and damage tolerance in these coatings.

TSP-4 Hvof Coatings Modified With Polymers To Reduce Ice Accretion For Use In Aerostructures Components*, Raúl Muelas Gamo,* *A Agüero Bruna, J Mora Nogues, P García Gallego,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Accretion of ice on aerostructures affects airplanes as well as rotorcraft as it constitutes a severe security issue and requires certified anti-icing technologies. Moreover, icing increases the aerodynamic drag on an aircraft and thus increase fuel burn. Most ice protection technologies presently in use have inherent negative effects such as high energy consumption, increased weight, a negative environmental impact, and the need for frequent reapplication among others.

Surface engineering can contribute to reduce ice accumulation in a durable manner. An attractive approach to this issue is the development of hard icephobic coatings applied by thermal spray in particular High Velocity Oxyfuel (HVOF), using highly resistant coatings to the different atmospheric aggressions and doping them with polymers particles, which can provide the icephobic properties necessary to complete the demanded functionality.

The inclusion of the polymer in the high resistance coating improves the hydrophobicity and the ice accretion behavior without affecting its structural properties. This polymer-doped cermet coating has been tested on an ice wind tunnel and compared with an anti-icing commercial paint, and has improved the properties in terms of ice accretion behavior.

The proposed solution is environment-friendly, will contribute to the reduction of energy consumption, and will help eliminate the need for frequent on-ground de-icing procedures. This in turn will contribute to the reduction of cost, pollution and flight delay.

TSP-5 The Electro-Mechanical Properties of Cathodic Arc Deposited High Entropy Alloy Thin Films on Polymer Substrates*, A Xia,* Montanuniversität Leoben, Austria*; O Glushko, M Cordill,* Erich Schmid Institute of Materials Science, Austria*; **Robert Franz**,* Montanuniversität Leoben, Austria

In recent years a new class of materials has emerged in the field of metallurgy: high entropy alloys (HEAs). These 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 strength, ductility, corrosion resistance, wear resistance, hardness, diffusion and thermal conductivity. While research on bulk high entropy alloys has seen quite a boost over the past years, investigations on thin films are still a relatively unexplored area.

The focus of this report lies on the cathodic arc deposition (CAD) of two different HEA thin films and the characterization of their electro-mechanical properties, in particular their fracture behavior. The MoNbTaVW and AlCuCrTaTi thin films were synthesized by CAD with an Ar pressure of 4.9 Pa and a current of 120 A to a thickness of 200 nm on polyimide foils and silicon substrates. While the MoNbTaVW film revealed a smooth surface with columnar microstructure, the AlCuCrTaTi film showed a high number of droplets on the surface and a coarse microstructure. In-situ characterization techniques were used to examine the mechanical and electrical properties of the films, while the adhesion energies were calculated using the geometry of buckles formed due to the presence of compressive stresses. The films were exposed to uniaxial tensile straining, while simultaneously measuring the change in electrical resistance. Additionally, the crack formation during straining was investigated with optical microscopy. The results showed that both films remained electrically conductive up to 3% strain. At higher strains MoNbTaVW revealed brittle behavior as seen by straight through thickness cracks and an abrupt increase in resistivity, whereas AlCuCrTaTi showed a more ductile fracture and a less steep resistivity increase.

TSP-6 Synthesis and Characterization of Multicomponent Nitrides in the Al-Cr-Nb-Y-Zr System*, **Kristina Johansson**,* Uppsala University, Sweden*; P Soucek,* Masaryk University, Czech Republic*; A Srinath, D Rehnlund, E Lewin,* Uppsala University, Sweden

Nitride based thin films are commonly used as protective coatings for e.g. cutting tool applications due to their excellent properties regarding high hardness, thermal stability as well as corrosion and oxidation resistance. Recently, multicomponent nitrides with five or more principal elements have attracted a lot of attention due to their interesting material properties. In this regard they can outperform their respective binary nitrides. Multicomponent nitrides are based on the high entropy concept, where the high entropy of mixing caused by including at least five elements will favor the formation of a solid solution. Whereas binary nitride materials, such as Cr-N, Nb-N, Zr-N and Cr-Al-N, have been widely studied for their high hardness and corrosion resistance, multicomponent nitrides have not been studied to the same extent. Also, by addition of yttrium corrosion and oxidation resistance can be improved as previously studied for the Cr-Al-Y-N and Ti-Cr-Al-Y-N systems [1-2]. In this study, multicomponent nitride thin films of the Al-Cr-Nb-Y-Zr system were deposited in order to study their mechanical and electrochemical properties. The films were synthesized by dc magnetron reactive sputtering using elemental targets of the respective elements and a gas flow of Ar and reactive N_2. Both the substrate temperature and the target powers were varied to study their effect on the structure and the material properties.

All films were found to have a nitrogen content of about 40 at.%, indicating substoichiometric films with respect to N. From XRD it was found that all coatings were of single solid solution phase with NaCl-type structure. The lattice parameter ranged between 4.29 to 4.38 Å depending on both the composition and the substrate temperature, where is it was found that the unit cell size decreased with increased temperature and also increased with increased Nb and Zr content. SEM cross section images revealed a columnar microstructure, which became finer with increased temperature and with decreased Al and Cr content. The hardness increased from 17 GPa up to 27 GPa with increased substrate temperature and with decreased Al and Cr content. Corrosion resistance, studied by polarization measurements between -0.2 V to +1.5 V in a 1.0 M HCl aqueous electrolyte, showed improved corrosion resistance for all the studied samples, i.e. increased corrosion potential and lower current densities, compared to an industrial stainless steel reference sample. Thus, this material system shows a potential for the use as hard and corrosion resistant coating.

References

1. F. Rovere et al., Surf. Coat. Technol. 202 (2008)

2. L.A. Donohue et al., Vacuum, 55 (1999)

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.

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