Coatings for Use at High Temperatures
Room Sunrise - Session A2-2

Thermal and Environmental Barrier Coatings

Moderators: Lars-Gunnar Johansson, Chalmers University of Technology, Sweden, Kang Lee, NASA Glenn Research Center, USA

8:00am **A2-2-1 La-Sr-Mn Based Chromium Barrier Coatings for Interconnectors in Pressurized Steam Electrolysis on Exposure to Pure Oxygen and Water Vapor**, ***Vladislav Kolarik***, *M Juez Lorenzo, V Kuchenreuther-Hummel,* Fraunhofer Institute for Chemical Technology ICT, Germany*; M Pötschke, D Schimanke,* Sunfire GmbH, Germany

Power-to-liquids processes converting electric power from renewable energy sources into liquid fuels are of forward-looking interest. For achieving high process efficiency, it is envisaged to run the steam electrolysis under pressures up to 30 bar at temperatures around 850°C. The impact of such severe conditions on the behavior of the interconnector coatings designed to retain evaporating chromium is a crucial issue and needs detailed understanding to ensure a reliable operation.

The commercially available interconnector materials Crofer 22 H, Sanergy HT pre-coated by a thin Co layer and the Mn-free ITM were coated by a La-Sr-Mn based oxidic coating (LSM). The coatings were deposited by thermal spraying and by slurry roll coating. For simulating both opposite extremes of the possible process atmospheres, pure water vapor and pure dry oxygen were selected for the study. The experimentation under a pressure of 30 bar at 850°C was conducted in laboratory test autoclaves from Alloy 602 with exposure times up to 1000 h in water vapor and up to 3000 h in dry oxygen. Post-oxidation analysis was performed by field emission scanning electron microscopy (FE-SEM) with EDX element analysis and XRD.

In water vapor the oxide scales on the interconnector materials with LSM coating are notably thinner than on the uncoated material. However, the coating decomposes with the time to a coarse-grained lanthanum-rich phase in the surface area as well as in vicinity of the oxide scale and to a manganese-rich phase concentrated between them. The thermally sprayed LSM coating is more efficient in oxide scale thickness reduction, probably to its higher density, and it shows a less pronounced decomposition into the two phases.

The effect of reducing the oxide scale thickness on the interconnector alloy is in pure oxygen notable only after 3000 h. The structure of the LSM coating remains homogeneous after exposure to pure oxygen with higher porosity in the case of the slurry roll coating. Chromium is detected in the LSM coating, obviously evaporated from the interconnector alloy. In the case of the slurry roll coated LSM it is equally distributed in the whole coating, whereas with the thermally sprayed LSM a dense Cr-rich phase formed on top, consisting of the semi-conducting $SrCrO_4$.

8:20am **A2-2-2 Investigation of the Adhesion of Glassified Sand/salt Deposits on Thermal Barrier Coatings Exposed to High-temperature Combusted Gas Flows**, ***Michael Walock***, *B Barnett, A Nieto, W Gamble, A Ghoshal, M Murugan,* US Army Research Laboratory, USA*; D Zhu,* National Aeronautics and Space Administration, USA*; J Swab, M Pepi,* US Army Research Laboratory, USA*; R Pegg, C Rowe,* US Navy Naval Air Systems Command, USA*; K Kerner,* US Army Aviation and Missile Research, Development, and Engineering Center, USA

Advanced gas turbines are used in commercial/military aviation, ship propulsion, and industrial power generation. However, degraded environments that contain sand, dust, ash, soot, and/or salt can significantly affect their durability and performance. Specifically, accumulation and infiltration of contaminants, upon melting and subsequent solidification, can significantly reduce the operational life of hot-section components through physical and chemical changes. In this study, standard and advanced thermal barrier coatings (TBCs) were deposited onto engine-relevant substrates, such as Inconel 718 and Rene N5. Prior to molten contaminant exposure, the TBCs are evaluated using non-destructive and destructive techniques, such as scanning acoustic microscopy, scanning electron microscopy, scanning auger electron microscopy, optical microscopy, thermal property testing, erosion testing, and adhesion testing, to elucidate relevant processing-property relationships. After which, the coatings were exposed to sand and salt particle-laden flows (independently and mixed) in a unique hot particulate ingestion rig, under engine-relevant conditions. This environment leads to molten sand/salt particles, enabling the evaluation of melt infiltration and glassy deposit accumulation on TBCs. Post-test evaluations follow the same protocol as the pre-test so as to ascertain the physical and chemical changes that result from sand/salt accumulation and/or infiltration.

8:40am **A2-2-3 Effect of Nanostructure and Composition on the Transient Oxidation Behavior of Nanograined Alloys**, ***Pralav Shetty***, *J Krogstad,* University of Illinois at Urbana-Champaign, USA

Nanograined alloys possess impressive mechanical properties mediated by their high grain boundary density but suffer from poor high temperature stability. To overcome this, alloying has often been used to pin and stabilize the grain boundaries. As the implementation of such alloys in commercial high temperature applications becomes more viable, it is important to understand the effect of grain boundary structure and alloying on their oxidation behavior. In this study, the transient oxidation behavior of far from equilibrium dc magnetron sputtered NiCrAl films has been investigated. Even though the transient oxide forms quickly and makes up a very small volume fraction of the overall scale, it can dictate several key properties like the chemistry, morphology, and growth kinetics. Moreover alloying elements like yttrium (Y) which have a large positive enthalpy of mixing and a higher affinity for oxygen compared to the base element Ni, can have beneficial effects on both the stability and oxidation behavior of the alloy. Through the use of controlled oxidation of free standing sputtered films at 900°C and complimentary scanning transmission electron microscopy elemental analysis, we show an anomalous oxidation behavior compared to previous literature in this system. The columnar sputtered nanostructure seems to enhance the diffusion of preferred species like Cr and Al, to and along the grain boundaries to quickly nucleate a chromia or alumina scale which then proceeds to grow uniformly. Even minute Y additions seems to improve the scale adhesion and density as supported by the oxide growth rate estimated from thermogravimetric analysis. These insights will help in the development of a more complete grain boundary-dominated physics based model of nanograined oxidation and may ultimately influence the way in which oxidation resistant alloys are designed.

9:00am **A2-2-4 CrAlSiYN Coating with AlSiN Intermediate Layers for Enhanced Thermal Stability and Oxidation Resistance at Elevated Temperatures**, *S Liu,* Singapore Institute of Manufacturing Technology, Singapore*; Y Yang,* Data Storage Institute, Singapore*; F Ng,* Singapore Institute of Manufacturing Technology, Singapore*; R Ji,* Data Storage Institute, Singapore*;* ***Xianting Zeng***, Singapore Institute of Manufacturing Technology, Singapore

In this paper, the role of Y and Si doping in the thermal stability and oxidation resistance of CrAlN based coatings are investigated, with the mechanisms of coating oxidation characterized for different temperatures. Y and Si doped CrAlN coatings were deposited in a hybrid HIPIMS and magnetron sputtering disposition system, and their chemical compositions and mechanical properties were studied by EDX and nanoindentation respectively. The as deposited coatings were annealed in Ar and air for 1 hour at a range of temperatures, and the change in coating composition and microstructures were characterized by GIXRD, and cross-sectional FIB/SEM imaging and EDX mapping.

It was found that high level of Y addition is beneficial for the coatings thermal stability, but has a detrimental effect on their oxidation resistance. The enhancement in thermal stability could be attributed to the role of Y in suppressing the diffusional decomposition of CrAlN. However, at the same time, Y doping suppressed the formation of a dense oxide protection layer and facilitated the inward propagation of O_2 due to the low formation of Y_2O_3, giving rise to deteriorated oxidation resistance. In order to achieve concurrent enhancement of coating thermal stability and oxidation resistance, a novel structure of CrAlSiYN coating with AlSiN intermediate layers was developed, which exhibited significant enhancement in both high temperature thermal stability and oxidation resistance, as the presence of AlSiN layers effectively suppressed diffusion processes both within the coating and at its interface with air and the substrate.

9:20am **A2-2-5 Metallic Coatings on Copper for High Heat Flux Application in Rocket Engines**, ***Torben Fiedler***, *J Rösler, M Bäker,* Technische Universität Braunschweig, Germany

The copper wall of regeneratively cooled liquid-fuel rocket combustion-chambers is exposed to high thermomechanical loads. Despite the cooling, surface temperatures of more than 800 °C on the hot-gas side are reached. This results in a high thermal gradient in the copper wall. This gradient leads to thermal stresses which may cause damage of the chamber wall, for example by the so called dog-house effect, where the cooling channels tend to buckle and fracture. To avoid this damage, the temperature in the copper wall can be lowered by applying a thermal barrier coating system. This coating system could also protect the copper surface against oxidation.

Due to the high cooling heat flux in the copper wall, a high thermal gradient and therefore high in-plane stresses as a result of different thermal expansion can be expected. On the hot side of the wall, these stresses are compressive in the heating phase and become tensile after cooling if the compressive stresses relax at high temperatures. To investigate the influence of these loads and to test possible coating systems for the use in rocket engines, laser-cycling experiments were carried out. The laser test facility consists of a 3.3 kW diode laser with a special optics, producing a broad focal point. The laser spot can heat the coating surface up to 1500 °C in less than 0.5 s. The short heating-time leads to a high thermal gradient in the sample, representing the conditions in the rocket combustion-chamber. The temperature is kept constant for a few seconds and the coatings are quenched in water after each laser cycle.

Previously, a coating system consisting of a NiCuCrAl bond-coat and a Ni-superalloy top-coat has been developed. In the laser cycling experiments, three different damage mechanisms were observed:

1. Buckling of the coatings occurs due to the thermal gradient and thus a larger thermal expansion in the hotter coating than in the substrate.

2. Vertical cracks are caused by tensile stresses in the coatings, which form due to relaxation of the compressive stresses at high temperatures after longer heat exposure and subsequent rapid cooling.

3. Coating delamination is caused by the different coefficient of thermal expansion between substrate and bond coat in the roughness profile at the interface.

To gain a better understanding of the damage mechanism and to qualify a coating system for the application in experimental subscale test chambers, finite element simulations were carried out. These simulations may help to identify critical loads in the coatings that may lead to a failure during the laser tests or in the rocket engine and to set up a detailed failure model of the coatings.

9:40am **A2-2-6 Mechanical Properties of ZrO_2-Y_2O_3 Thermal Barrier Coatings by Isothermal Heat Treatment***, **Byung-Koog Jang,*** National Institute for Materials Science, Japan*; K Yasuda,* Tokyo Institute of Technology, Japan*; K Lee,* Kookmin University, Republic of Korea*; S Kim, Y Oh, H Kim,* Korea Institute of Ceramic Engineering and Technology, Republic of Korea

Thermal barrier coatings (TBCs) have received a large attention because they increase the thermal efficiency of gas turbine engines by increasing the gas turbine inlet temperature and reducing the amount of cooling air required for the hot section components. To optimize TBCs for integration into gas turbines,characterization of the relationship between microstructure and thermal-mechanical properties of the coatings is necessary. The purpose of this work is to investigate the influence of the microstructure as well as porosity on mechanical properties of ZrO_2-4mol%Y_2O_3 (YSZ) coatings deposited by air plasma spray (APS) or EB-PVD (electron beam-physical vapor deposition).The mechanical properties of YSZ coatings were evaluated by three-point bending method and nano indentation. The bending strength, Young's modulus and residual stress of plasma sprayed specimens depend on microstructure as well as coating distance. The hardness & Young's modulus of EB-PVD samples show direct proportion to isothermal heat treatment time during 2~100h at 1200°C.

10:00am **A2-2-7 Estimation Of The Mechanical Properties Of Thermal Barrier Coatings With Porous And Dense Vertically Cracked Microstructures By Modified Small Punch Tests***, **Pierre Planques,*** Cirimat - Safran Helicopter Engines, France*; V Vidal, P Lours,* Mines Albi, ICA (Institut Clément Ader), France*; V Proton, F Crabos,* Safran Helicopter Engines, France*; J Huez, B Viguier,* CIRIMAT, France

Cyclic oxidation failure of Atmospheric Plasma Sprayed Thermal Barrier Coatings (APS TBCs), commonly used to insulate hot sections in gas turbines, usually results from the spallation of the ceramic top coat. In order to predict such spalling phenomena, understanding the mechanisms for cracks initiation and propagation in thermal barriers is a major issue for engine-makers. Failure of the TBC is strongly related to the thermal and mechanical properties of each component of the multi-materials system (substrate, bond coat and ceramic) but also to the response of the TBC as a whole. The purpose of the work is to assess the mechanical behaviour of thick TBC using both experimental and computer simulation approaches for two TBC microstructures, i.e. standard lamellar, porous and micro-cracked (classically obtained through APS coatings), and Dense Vertically Cracked (DVC).

The experimental characterisation of the mechanical behaviour of the TBCs and their elementary components is addressed using three points bending (3PB) tests and Small Punch Testing (SPT). For this purpose, a modified instrumented non-standard SPT setup has been designed, allowing mechanical testing of the materials in natural air in the temperature range 25°C-1000°C. This allowed measurements of true material properties, like strength and fracture toughness, of both standard and DVC APS TBCs following various isothermal heat treatments at 1100 °C and 1200 °C. Specifically, the bottom deflexion is measured and specimens are not clamped as usual in the standard configuration of SPT, referred to as "Drawing Punch Test". This last point is crucial for brittle fracture behaviour with little or even no plastic deformation.

The evaluation of strength and stress intensity factors is based on Finite Element (FE) calculations in order to determine the material constitutive parameters by minimizing the difference between simulated and experimental small punch force–displacement curves.

10:20am **A2-2-8 Comparison of Damage Evolution in High Purity Nano and a Conventional YSZ Thermal Barrier Coating during Thermal Cycling***, **Krishna Praveen Jonnalagadda,** R Eriksson,* Linköping University, Sweden*; K Yuan,* Beijing General Research Institute of Mining and Metallurgy, China*; X Li,* Siemens Industrial Turbomachinery, Sweden*; X Ji, Y Yu,* Beijing General Research Institute of Mining and Metallurgy, China*; R Peng,* Linköping University, Sweden

Sintering of the top coat at high temperatures is considered to accelerate the damage development in thermal barrier coatings (TBCs) during thermal cycling. To counter sintering and thus enhance the resistance to thermal cyclic fatigue, a nano structured high purity yttria stabilized zirconia (YSZ) has been developed and in this work, its damage evolution with thermal cycling is studied and compared to that of a conventional YSZ coating. The coatings were deposited by atmospheric plasma spraying (APS). The TBC samples were thermally cycled between 100 °C and 1100 °C with a hold time of 1h at 1100 °C. The results showed that the high purity nano YSZ coating exhibited roughly half the cyclic life compared to the conventional YSZ coating. The difference in the life time is explained with the help of analysis of micro cracking observed on cross sections of the thermally cycled TBC samples. Influence of other factors such as fracture toughness and elastic modulus of the top coats were also studied. Furthermore, finite element modelling was used to understand the crack growth paths in both the materials and their contribution to the final failure.

10:40am **A2-2-9 Non-reactively Sputtered Ultra-High Temperature Hf-C and Ta-C Coatings***, H Lasfargues, T Glechner, C Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; V Paneta, D Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D Holec,* Montanuniversität Leoben, Austria*; **Helmut Riedl**, P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides (TMC) are known for their exceptional thermal stability and mechanical properties, notably governed by the carbon content, degree of crystallinity, and the prevalent vacancies on the non-metallic sublattice. Especially, the binaries Hf-C and Ta-C as well as their ternary mixture Ta-Hf-C are highly attractive due to their ultra-high melting points and their strong tendency to form carbides in the preferred face centered cubic structure. However, when using reactive deposition techniques, the formation of amorphous C-containing phases is often observed.

Therefore, we study in detail the influence of the deposition parameters on the structure and morphology, mechanical properties, as well as thermal stability of non-reactive sputtered Hf-C and Ta-C thin films. The carbon content within the coatings strongly correlates with the target-to-substrate alignment, the deposition temperature, as well as bias voltage applied. For example, in the case of Ta-C maximum values of $TaC_{0.81}$ could be reached applying a $TaC_{0.97}$ target and a substrate temperature of 700 °C combined with a bias potential of -100 V. A further increase could be only achieved through co-sputtering of pure carbon for both systems. Nevertheless, all HfC_y films are single-phase face-centered cubic, whereas the TaC_y films also contain small fractions of the hexagonal Ta_2C phase, which decreases with increasing C contest. The highest hardness and indentation modulus among all coatings studied is obtained for $TaC_{0.78}$ with H = 43.7±0.65 GPa and E = 495.8±8.9 GPa.

Ab initio calculations predict an easy formation of vacancies on the C-sublattice, especially in the Ta-C system, and a temperature driven stabilization of defected structures at high temperatures, with fewer vacancies on the C sublattice for Hf-C than Ta-C. The predicted phase stability is proven up to 2400 °C for both systems by annealing experiments in vacuum, also with stabilization of the hexagonal fraction after 1625 °C in Ta-C films.

11:00am **A2-2-10 Impact of Substrate Surface Morphology on APS Ceramic Coating Adhesion Measured by Laser Shock Test (LASAT)***, H Sapardanis, V Guipont, A Koster,* ***Vincent Maurel****,* Mines ParisTech, France

The aim of this study is to analyze different surface morphology of Haynes 188 Co base superalloys before coating. The surface was alternatively grit blasted, grit blasted and oxidized, processed by electro-discharge machining, or processed by shotpeening. Then pure alumina was deposited using conventional air plasma spray. The use of laser shock adhesion test (LASAT) has shown strong differences in the resulting interfacial toughness of the obtained coating [1-2]. Size of delamination was measured by an original use of infra-red thermography, image analysis and final cross-section analysis. Finally, it has been evidenced that LASAT was able to provide a continuous evolution of the size of the delaminated area as a function of the laser flux with a very high level of results reproducibility. Then a ranking of the quality of the interface could be yielded from this methodology. The combination of the LASAT, in-situ measurement of buckling and finite element analysis of residual stresses is finally used to determine interfacial toughness. The experimental measurement of in-plane displacement field and out-of-plane buckling evolution leads to an accurate description of both boundary condition of FEA and yields to a crosscheck analysis of the interfacial toughness between FEA and experiment.

References

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[2] Sapardanis, H., Maurel, V., Köster, A., Duvinage, S., Borit, F., & Guipont, V. (2016). Influence of macroscopic shear loading on the growth of an interfacial crack initiated from a ceramic blister processed by laser shock. Surface and Coatings Technology, 291, 430-443.

11:20am **A2-2-11 Influence of Pt Concentration on Structure of Aluminized Coatings on a Ni Base Superalloy***, E Pauletti,* ***AnaSofia D'Oliveira****,* Universidade Federal do Paraná, Brazil

">Aluminum diffusion coatings have been processed by chemical vapor deposition techniques. Particularly, pack cementation is a procedure frequently used to process competitive oxidation resistance coatings on Ni based alloys operating at high temperatures. The superior oxidation resistance is associated with the presence of a NiAl layer that supplies Al to maintain an α - Al_2O_3 continue and adherent film at the surface of coatings. Further enhancements on the performance of alloys are gained when a layer of Pt is deposited on the Ni based alloy before pack aluminization. Under these conditions a (Ni,Pt)Al layer forms to act as an efficient diffusion barrier. To achieve high efficiency it is important to understand role of Pt in aluminized coatings. This work assessed the influence of Pt concentration on the structure of aluminized coatings on a precipitation harden Ni alloy. Electroplating was used to deposit Pt layers with different thicknesses (2, 3 and 7 µm) were on a Ni superalloy NI 183. Subsequently, heat treatment at 900 °C for 90min in argon atmosphere was carry out to promote the stress relief of the electroplated Pt layer and to promote the interdiffusion of Pt and the Ni alloy. Aluminization at 1100ºC for 5 hours used out of the pack cementation procedures avoiding direct contact between samples and the pack mixture. X ray diffraction identified phases at the top surface of coatings and scanning electron microscopy analysis showed that aluminized coatings are composed of two main regions a layer of β – NiAl and a interdiffusion zone (IDZ). The aluminide layer is a hipostoichiometric β – NiAl ordered matrix with Pt in solid solution. Pt concentration in this matrix increases the distortion in the ordered crystal structure of NiAl as confirmed by the displacement of XRD peaks towards higher 2θ. Increasing thickness of Pt electroplated layer causes an increase on the total thickness and alters features within the coating. The higher the Pt content the smoother the Al gradient in coatings and the lower the Kirkendall porosity. These features are a consequence of the impact of Pt on vacancy concentration in the NiAl lattice contributing to a higher atomic mobility in the NiAl layer. The concentration of Al in the IDZ followed the Pt thickness and accounts for a change on the alloy solubility hence microstructure. The thinner 2µm Pt layer induced the formation of a $(Ni,Pt)_3Al$ inspite of the processing conditions. Results showed that for the processing parameters tested, oxidation performance at high temperature is improved with Pt electroplated thickness.

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