Coatings for Use at High Temperatures
Room Pacific E - Session A1-1-MoM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderators: Shigenari Hayashi, Hokkaido University, Japan, **Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

10:00am **A1-1-MoM-1 Performance of Innovative High-Temperature Coatings after Exposure in a Pilot Plant Burning Biomass***, **Alina Agüero Bruna (agueroba@inta.es)**,* Instituto Nacional de Técnica Aeroespacial INTA, Spain*; P. Audigié, S. Rodriguez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; M. Gutiérrez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; M. Benito, A. Bahillo,* CIEMAT, Spain **INVITED**

To increase the efficiency of biomass power plants, the operating temperature must be raised with a consequent increase in corrosion rates. New materials and/or coatings are required, and testing is needed to evaluate the corrosion resistance of these new materials under various and very complex atmospheres resulting from the different types of available biomass. However, there is no general agreement regarding the methodology to carry out biomass corrosion tests, which can allow realistic ranking of materials and coatings. A 0.5 kWth simple pilot plant based on fluidised bed combustion was implemented allowing constant fed of biomass pellets. Several alloys with and without coatings were tested at 600-620º C for 1000 h while burning eucalyptus forestry residues pellets. The results were compared to those obtained in a laboratory test carried out under KCl deposits and a model atmosphere containing H2O, O2 and N2. Newly developed Super VM12 ferritic steel was tested with and without coatings, which included slurry aluminides, modified FeCr and NiCr based alloys deposited by HVOF and weld cladded IN625. In both the pilot plant and the lab, uncoated Super VM12 showed a very high degree of corrosion, and evidence of a high extent of spallation, whereas all coatings exhibited protective behaviour at different levels. In general, it was observed that the degree of corrosiveness in the plant was similar to that obtained in the lab and in all cases the coatings protected the substrate. For instance, according to the results of both pilot and lab scale tests, weld cladded IN625 (⍰700 µm) showed a low degree of corrosion in both environments whereas the best behaved HVOF deposited coating was a 325 µm hard steel alloy modified with Al, that from the initial stages developed an approximately 50 µm corrosion product layer which appears to be protective as no significant thickness variations were observed. On the other hand, the slurry coatings showed non uniform degradation in the pilot plant. Indeed, in some areas typical microstructure changes could be detected due to interdiffusion with the substrate, as well as the development of voids. In addition, some degree of widening of the through thickness cracks originally present in the coating was observed (Figure 1a). These cracks self-healed by forming Al-rich oxides which are protective. The coating exposed in the lab shows a lower amount of voids when comparing with the pilot exposed specimen (Figure 2). Other zones of the coating showed important degradation of the aluminide phases after exposure in the pilot plant (Figure 1b). The causes of the difference in behaviour were analysed and will be discussed.

10:40am **A1-1-MoM-3 Surface Coatings for Improved Corrosion Resistance of Steels in Heavy Liquid Metal Coolants***, J. Kulczyk-Malecka,* Manchester Metropolitan University, UK*; N. Barron, S. Ortner,* National Nuclear Laboratory Limited, UK*; **Peter Kelly (peter.kelly@mmu.ac.uk)**,* Manchester Metropolitan University, UK

A key challenge for systems cooled by molten lead is that the cladding materials must resist the harsh environmental conditions that they are exposed to; namely, chemical corrosion by molten lead-based coolant; oxidative corrosion at temperatures above 650°C; and neutron irradiation at doses up to 250 dpa. Austenitic and ferritic-martensitic (FM) steels have been identified as good candidates for cladding materials in molten lead environments. Nevertheless, these steels are susceptible to corrosion in oxidised molten lead and, therefore, their properties need to be improvedeither by alloying with corrosion protective elements or by depositing a corrosion protective barrier coating on the surface of a steel. The ability of alloying elements, such as aluminium and chromium, to form protective oxides is well known. Thus, the aim of this work was to investigate the deposition of protective barrier layers consisting of Al, Al_2O_3 and FeCrAl on austenitic stainless steel type 316L coupons. The coatings were deposited by mid-frequency pulsed DC unbalanced magnetron sputtering in reactive (Al_2O_3) and non-reactive modes (Al, FeCrAl). Individual layers were investigated, as well as multi-layer FeCrAl/Al/AlOx coating stacks. Coatings were characterised by SEM and EDX and then subjected to a corrosive environment of molten lead at elevated temperatures (up to 800ºC) and varying oxygen contents to investigate and compare the corrosion resistance of the deposited layers to allow the best performing corrosion barrier coatings for HLMC FRs applications to be nominated and further developed.

11:00am **A1-1-MoM-4 Improving the Intermediate Temperature Oxidation Resistance of Refractory Metals and Mo-Based Systems***, **Katharina Beck (katharina.beck@dechema.de)**, A. Ulrich,* DECHEMA-Research Institute, Germany*; F. Hinrichs, M. Heilmaier,* Karlsruhe Institut of Technology, Germany*; M. Galetz,* DECHEMA-Research Institute, Germany

Refractory metals and their alloys are interesting materials to be used in high temperature applications. They are characterized by a very high melting point, typically beyond 2000°C, and their good mechanical properties at high temperatures and are therefore promising candidates for novel high-temperature materials. Besides their low oxidation resistance at target temperatures, already at intermediate temperatures, they can be prone to two different attack mechanisms: Pesting and hot corrosion.

Pesting, also referred to as catastrophic oxidation, describes the formation of volatile oxide species at intermediate temperatures and leads to the total disintegration of metal bulk material into powder. Besides pesting another particularly severe corrosion attack is induced by deposits on the surface of compounds, which usually are the result of impurities in combustion atmospheres. In turbine environments sulphates and alkali metal saltsare known to induce hot corrosion.To counteract both attack mechanisms, the formation of protective oxide scales is necessary. As α-Al_2O_3 is commonly known to be very resistant in oxidizing as well as hot corrosion environments, this work aims to make the formation of such an oxide scale possible by the application of Al-coatings.

By means of pack cementation, an *in situ* chemical vapor deposition process, Al-coatings (with thicknesses up to 60 µm) were successfully applied on four different refractory metals (Mo, Nb, Ta and W) and two recently developed Mo-Si-Ti alloys (eutectic Mo-20.0Si-52.8Ti and eutectoid Mo-21.0-34.0Ti) [1]. Using thermogravimetric analysis for 100 h in synthetic air at intermediate temperatures (700 °C and 900 °C), the oxide formation was investigated and the improvement of the oxidation behavior correlated to Al_2O_3 scale formation was confirmed. The formation of these scales results in a substantially decreased oxide growth rate in comparison to the uncoated substrates. Post exposure, Al reservoirs (intermetallic phases) were still present below the formed oxide scale, making healing of the scale possible in the case of crack formation. The applied layers, the formed intermetallic phases and the formed oxide scales were analyzed before and after exposure to the oxidizing atmospheres using optical microscopy, XRD, SEM, EDX and EPMA.

[1] Schliephake, Daniel, et al. "Constitution, oxidation and creep of eutectic and eutectoid Mo-Si-Ti alloys." Intermetallics 104 (2019): 133-142.

11:20am **A1-1-MoM-5 Arc-Evaporated $Ti_{1-x}Al_xN$ Coatings in Hot-Corrosion Settings***, **Oliver Ernst Hudak (oliver.hudak@tuwien.ac.at)**, A. Scheiber,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; L. Shang, O. Hunold, M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; S. Kolozsvari,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Hot corrosion is a common phenomenon observed in gas turbine engines, coal gasification plants and waste incinerators. It occurs in high-temperature settings, where a sulfur-rich atmosphere reacts with salt impurities such as Na, Mg, Cl or V, and form high-melting sulfate-salts, that then deposit and adhere on machining component surfaces. There, the salt deposit elicits an accelerated degradation of the material through the formation of non-protective porous oxide scales. Depending on the temperature range, two distinctively different corrosion mechanisms can emerge. At temperatures below the melting point of the salt deposit (~600-850 °C), low-temperature hot corrosion dominates as mechanisms, whereas at temperatures above the melting point, high-temperature hot corrosion predominates (~850-950 °C). For all of the above mentioned fields of application, Ni-, Co-, and Fe-based superalloys have proven to be a reliable choice of material, due to their superior mechanical properties at high temperatures, as well as good oxidation resistance in air. However, if exposed to hot corrosion conditions, their overall oxidation resistant qualities diminish drastically.

From this perspective, this contribution showcases $Ti_{1-x}Al_xN$ as an interesting candidate as protective PVD coatings for extending the lifetime of highly-stressed material components in hot-corrosion environments. $Ti_{1-x}Al_xN$ coatings with varying metal content ratios were arc-evaporated on Ni-based superalloy substrates and tested in an in-house built hot-corrosion testing rig. By applying a sulphate-salt mixture from the alkali and alkaline earth metal group, the samples were corroded in a SO_x-rich atmosphere for a maximum of 30 h according to the HTHC and LTHC conditions, and subsequently analyzed and evaluated for their applicability using a set of high-resolution characterization techniques.

Keywords: Corrosion Resistance; PVD coatings; Diffusion Pathways; Hot Corrosion; HTHC; LTHC;

11:40am **A1-1-MoM-6 High Temperature Oxidation Behavior of Hafnium Aluminum Diboride Thin Films***, **Samyukta Shrivastav (ss101@illinois.edu)**, D. Yun, C. Romnes, K. Canova, J. Abelson, J. Krogstad,* University of Illinois at Urbana Champaign, USA

The integrity of hafnium diboride, a refractory and hard metallic ceramic, is compromised at high temperatures (900-1000°C) when air is present due to oxidation of the boron sublattice to form liquid boron oxide, which evaporates. One potential solution is to deposit a $Hf_{1-x}Al_xB_2$ alloy film, with the expectation that Al can oxidize to form a protective Al_xO_y overcoat.

We use low temperature chemical vapor deposition to deposit the alloys, as described elsewhere in this conference. This approach has the advantage that Al will be distributed throughout the material; by contrast, in conventional hot-pressing of separate HfB_2 and AlB_2 powders the phases may not mix intimately. We previously showed that as-deposited HfB_2 is amorphous and crystallizes upon annealing at temperatures ≥ 600°C. For the alloy, we hypothesize that excess aluminum will be liberated upon crystallization, and will diffuse to the surface and form a passivating oxide.

We show that the oxidation product is strongly temperature dependent. Upon annealing at 700°C for 1 hour, a mixture of hafnium, aluminum, and boron oxides form. But this mixed oxide is not protective, and complete oxidation of films occurs when heated to higher temperatures. At annealing temperatures between 800°C and 900°C, the oxides of boron and aluminum react to form acicular aluminum borate, which is spread uniformly on the surface of the film. TEM cross sections reveal hafnium oxide particles embedded in aluminum borate needles; SEM shows surface roughening; STEM-EDS identifies the composition of the reaction products; and SAED confirms the crystal structures of the products. We conclude that aluminum is not a viable alloying element for the formation of a passivating oxide on diboride thin films. Based on phase diagrams and oxide literature, we suggest using alloying elements like chromium, which forms a passivating oxide but does not react with the oxides of boron and hafnium.

Coatings for Use at High Temperatures
Room Town & Country D - Session A1-2-MoA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II

Moderators: Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK, **Gustavo Garcia Martin**, REP Energy Solutions, Spain

3:00pm **A1-2-MoA-5 Influence of Dispersed Nano-Y_2O_3 Particles in NiAlY and NiCrAlY MMC Coatings on Microstructure, Oxidation and Wear***, **Christoph Grimme (christoph.grimme@dechema.de)**, R. Kupec, F. Schulze, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

State of the art MCrAlY coatings are known to protect structural materials against oxidation and corrosion and are part of TBC systems. Due to their mechanical properties at high temperature, they are commonly applied in the hottest sections of turbine engines and other high temperature environments. High costs for the thermal spraying process of MCrAlY coatings drive forwards cost saving alternatives such as galvanic co-deposition of particles. Co-deposition of particles is influenced by numerous factors, such as particle size, kinetic effects, current density, pH related zeta potential or chemical stability of the particles [1]. In this study, nano-Y_2O_3 particles are co–deposited galvanically alongside with nickel and subsequently pack chromized and aluminized. Y_2O_3 is known to improve both oxide scale formation and oxide scale adherence. Another promising effect of Yttria is the reaction with low melting V_2O_5 to form high melting YVO_4, which reduces the aggressiveness and of corrosive salt deposits and thereby reduces corrosion attack [2].

Subsequent chromium and/or aluminum enrichment(s) after co-deposition using a pack cementation process is shown to lead to microstructural refinement compared to coatings without particles and are able to decrease wear up to high temperature. Additional microhardness measurements revealed an increase of approx. 100 HV1 for MMC NiAlY coatings compared to coatings without dispersed nano–Y_2O_3 particles. Depending on the activity of the pack cementation method to be used, differences in the distribution of dispersed particles are observed and discussed. Besides wear, the oxidation resistance as well as corrosion resistance of the manufactured coatings against molten V_2O_5/Na_2SO_4 salt mixtures at 700 °C in 0.1 SO_2/air gas are tested and compared against bare IN617 alloy.

[1]L. Besra, M. Liu,*Progress in Materials Science***2007**, *52*, 1–61.

[2]N. S. Bornstein,*Vanadium Corrosion Studies***1993**.

3:20pm **A1-2-MoA-6 Reactive Magnetron Sputtering of Al-O-F for High-Temperature Oxidation Protection of γ-TiAl via the Halogen Effect***, **Stephen Brown (stephen.brown@polymtl.ca)**, F. Bergeron,* Polytechnique Montréal, Canada*; M. Cavarroc,* SAFRAN Tech, France*; S. Knittel,* SAFRAN Aircraft Engines, France*; L. Martinu, J. Klemberg-Sapieha,* Polytechnique Montréal, Canada

The implementation of γ-based TiAl alloys in aircraft engines is motivated by their low weight and high specific strength at high temperatures compared to conventional nickel alloys. Their mechanical properties, such as yield strength and elastic modulus, match those of Ni-based alloys already employed in aircrafts engines, while their density is significantly lower than current solutions, allowing for the manufacture of lighter turbines and increased thrust-to-weight ratios. Their use, however, is restricted to low-pressure turbines due to the growth of a mixed Al_2O_3/TiO_2 oxide scale at temperatures greater than 750°C. While the dense Al_2O_3 is protective against further oxidation, the porous TiO_2 allows oxygen diffusion to the substrate, voiding the alumina's protective properties.

Of great interest for the protection of TiAl is a surface treatment based on the halogen effect, where a halogen, such as chlorine or fluorine, is used to promote the growth of a protective alumina scale. Aluminum halides are formed at the surface of TiAl and are transported through the oxide scale, where oxygen partial pressure is high enough to lead to the oxidation of these halides, promoting the formation of a protective Al_2O_3 scale.

This work demonstrates the possibility of exploiting the halogen effect through the deposition of Al-O-F films on γ-based Ti-Al48-Cr2-Nb2 substrates via reactive magnetron sputtering. The plasma chemistry of Al sputtered in an Ar, O_2, and CF_4 atmosphere was first measured by mass spectroscopy, and coated samples were deposited under a range of sputtering conditions. Coating microstructure was characterized by Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-Ray Spectroscopy (EDS), while Rutherford Backscattering Spectrometry (RBS) was used to determine coating composition. A subset of deposited coatings was oxidized at temperatures up to 875°C. Analysis by EDX and X-ray Photoelectron Spectroscopy (XPS) confirmed the transformation from Al-O-F to Al_2O_3 after oxidation, and the coated samples showed mass gains up to 10 times lower than the uncoated TiAl.

3:40pm **A1-2-MoA-7 Development of a New Coating Against High-Temperature Erosion-Corrosion in Fluidized Bed Biomass Boiler Condition***, **Suzue Yoneda (s-yoneda@eng.hokudai.ac.jp)**, S. Tanaka,* Hokkaido University, Japan*; Y. Miyakoshi,* Hokkaido Research Organization, Japan*; T. Kogin,* Dai-ichi High Frequency Co., Ltd., Japan*; E. Ishikawa,* EBARA Environmental Plant Co., Ltd., Japan*; M. Noguchi,* EBARA Corporation, Japan*; S. Hayashi,* Hokkaido University, Japan **INVITED**

High-temperature Erosion-Corrosion (E-C) is one of the critical issues for the heat exchanger used in a fluidized bed biomass boiler plant. E-C occurs by not only erosion due to impact of sand particles but also high-temperature corrosion in chlorine containing atmospheres. Current coatings widely used for boiler tubes in fluidized boiler plants are Ni-based protective coating (Japan Industrial Standard: JIS SFNi4 and/or SFNi5). However, E-C resistance of those coatings is still not sufficient. Thus, development of coating which have good E-C resistance is strongly required. SFNi4 contains a lot of alloying elements (Cr, B, Si, C, Fe, Co, Mo and Cu). In this study, effect of Mo, Si, Cr and Fe on E-C resistance was evaluated by using model alloys in order to optimize the Fe content. Mo and Si were found to be detrimental for E-C and Fe addition significantly improve E-C resistance. After E-C, oxide scale consisted of thinner NiO on the alloy without Fe, but thicker Fe-rich oxide on the alloy with Fe. Erosion resistance of Fe-rich oxide could be higher than that of NiO, resulting in higher E-C resistance in the alloy with Fe. Based on the results obtained from E-C test, the new coating which is higher Fe content and lower Mo and Si content was proposed and it was confirmed that E-C resistance of this coating was higher than previous coating in the actual plant.

4:20pm **A1-2-MoA-9 Introduction of Methodologies from Artificial Intelligence Into Slurry Coating Development***, **Vladislav Kolarik (vladislav.kolarik@ict.fraunhofer.de)**, M. Juez Lorenzo, W. Becker,* Fraunhofer Institute for Chemical Technology ICT, Germany

Aluminum slurry coatings are a high-impact and economic technique to protect steels against corrosion at high temperatures and in aggressive media. They are easy to apply using different methods of deposition such as spraying or brushing with a subsequent heat treatment to form the diffusion coating. For optimization as well as for customization to particular applications with different substrate steels and media further development is needed. The use of methodologies and algorithms from artificial intelligence (AI) can significantly accelerate the development and reduce the costs by minimizing the experimental effort. For an AI supported approach the entire system has to be considered and digitalized integrating all components, all process parameters at all processing steps including the models for the different mechanisms such as diffusion.

To digitalize the aluminum slurry coating the entire coating system and its manufacturing process was fully parametrized considering every single parameter having influence. In doing so the coating process was divided into three sections: slurry formulation, slurry deposition and the heat treatment to form the aluminide diffusion layer including the substrate steel data. The parameters comprise the particle size and slurry components, spray characteristics such as distance, particle velocity or angle and heat treatment temperature, time and atmosphere.

The parameters were formatted in computer readable formats: (i) numerical values (numbers x, y, z, …) when specific values can be assigned such as the heat treatment temperature in degree Celsius; (ii) groups of values (x to y), e.g. small, medium, large aluminum particles within a range of µm and (iii) categories with I/0 decision, where specific values or ranges of values are not applicable, e.g. slurry deposition by spraying (yes/no). Target values were defined for the parameters describing the targeted coating properties as well as assessment criteria for their achievement. Algorithms from the field of Design of Experiments were chosen for the first approach elaborating a parameter matrix for a slurry coating system. A set of experimental values from former projects was filled in to train the software for calculating the impact of process parameter variation on the coating properties.

4:40pm **A1-2-MoA-10 Slurry Coatings for Heat Exchangers of Particle Receivers of Solar Towers***, **Michael Kerbstadt (michael.kerbstadt@dechema.de)**, A. Ulrich, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

Diffusion coatings are widely used in high temperature applications to enhance oxidation and corrosion resistance of metals and alloys. Metallic elements (commonly Al, Cr, or Si) are enriched at the surface to form protective oxide scales during exposures at high temperatures. Al, Cr and Si-based diffusion coatings are mostly accomplished by pack cementation, where the deposition occurs via a gas diffusion process. For the pack cementation process the substrates usually have to be fully embedded into a powder mixture, which is laborious and requires a lot of furnace furniture to be heated up. For Al an alternative slurry process is well established, where the slurry is sprayed on the metallic surfaces by air brush. This simple deposition leads to economic advantages compared to other diffusion coating techniques and also to the possibility to coat large technical parts, weldings or to do local repair works. The target application of this work focuses on a new generation of solar power plants, where bauxite particles are used as receiver and heat storage medium instead of the state of the art tubes with molten nitride salts. In this case the coating on the outside of the heat transfer tubes, which are in contact with the particles not only has to withstand oxidizing environments at high temperatures but also abrasion due to the impact of the heat carrying particles. For this application Cr- and Si-rich coatings are very interesting, e.g. because of the hard silicide phases, which are more oxidation resistant than the respective Cr-carbides at the target temperatures.

Due to the higher melting points and limited phase formation, the development of Si- or Cr-based diffusion coatings via the slurry process is more complicated, e.g. the use of Cr-Al pre-alloyed powder leads only to Al diffusion.

In this work novel slurry coatings are presented applied by a water-based slurry. The subsequent heat treatment is conducted in an inert Ar atmosphere at temperatures up to 1200° C. The application of such slurry coatings is demonstrated on Inconel 740 (Ni-base) and Sanicro 25 (austenitic stainless steel). Therefore, different slurry compositions and heat treatment parameters are tested. The coating thicknesses achieved are up to 10 µm on the Inconel 740 and up to 300 µm on the Sanicro 25. For phase determination and microstructural characterization X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) are used. Oxidation exposures in synthetic air at 900°C show the formation of a protective scale and indicate an improved oxidation behavior by the applied coatings of the two investigated substrates.

5:00pm **A1-2-MoA-11 Low Emissivity Thin Films Coatings to Reduce Thermal Emittance of SSA for Evacuated Solar Collectors***, **Antonio Caldarelli (antonio.caldarelli@na.isasi.cnr.it)**, C. D'Alessandro, D. De Maio, D. De Luca, E. Gaudino, M. Musto, E. Di Gennaro,* University of Napoli “Federico II”, Italy*; R. Russo,* National Research Council of Italy, Napoli Unit, Institute of Applied Sciences and Intelligent Systems, Italy

Solar energy is the ideal energy source to provide heat at medium temperatures with the aim of transitioning to clean, renewable energy sources. Evacuated flat plate solar collectors (EFPCs) are able to convert solar energy directly into heat with high efficiency. Thanks to the high vacuum insulation, the main mechanism of loss in EFPCs is represented only by the radiative losses from the selective solar absorber (SSA). Thermal emittance plays a more important role than solar absorbance for the efficiency of SSA used in EFPCs working at medium temperature [1].

Once the SSA has been optimized for a maximum efficiency [2,3], further improvement can be obtained by reducing the substrate emissivity. We therefore deposited by electron beam low emissive Cu or Ag thin film on an Aluminium bulk substrate to improve the coating performances by reducing its thermal emittance, keeping the economic advantages of using a substrate as cheap and light as Aluminium. The low emissive coating can be used to reduce the thermal emittance of both the selective coating side and the substrate side of SSA. The thermal emittance was measured as a function of temperature through a calorimetric approach [4]. The thermal stability of the coating and the use of thin films of Cr_2O_3 as a diffusion barrier were also investigated.

[1] F. Cao, K. McEnaney, G. Chen and Z. Ren, Energy Environ. Sci. 7 (2014) 1615-28.

[2] D. De Maio, C. D'Alessandro, A. Caldarelli, D. De Luca, E. Di Gennaro, M. Casalino, M. Iodice, M. Gioffre, R. Russo, M. Musto, Multilayers for efficient thermal energy conversion in high vacuum flat solar thermal panels, Thin Solid Films, 735, 138869, (2021).

[3] D. De Maio, C. D'Alessandro, A. Caldarelli, D. De Luca, E. Di Gennaro, R. Russo, M. Musto, A Selective Solar Absorber for Unconcentrated Solar Thermal Panels, Energies, 14(4), 900, (2021).

[4] R. Russo, M. Monti, F. Di Giamberardino, and V. G. Palmieri, Characterization of selective solar absorber under high vacuum, Opt. Express, 26, (10), A480-A486, (2018).

Coatings for Use at High Temperatures
Room Pacific E - Session A1-3-TuM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling III

Moderators: Gustavo García-Martín, REP-Energy Solutions, Spain, **Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

9:00am **A1-3-TuM-4 Protective Sol-Gel Coatings for Steels Against Corrosion of Molten Carbonates for Concentrated Solar Power Plants***,* ***Gustavo García Martín (gusgarci@ucm.es)****,* Universidad Complutense de Madrid, Spain*; T. de miguel Gamo,* Universidad Complutense de Madrid , Spain*; I. Lasanta Carrasco, M. Lambrecht, F. Pérez Trujillo, N. Garcia, C. Gómez de Castro,* Universidad Complutense de Madrid, Spain

In the last few years, the interest in renewable energies has suffered a significant increase, representing the Concentrated Solar Power (CSP) technology in the present and the future of the electric energy obtained from the sun on large scale. Commercial CSP plants usually use molten salt mixtures as thermal energy storage mediums. The currently used industrial compound is an alkali-nitrate mixture composed of 60 wt.% NaNO3/40 wt.% KNO3. However, the development of new molten salt mixtures with higher thermal stabilities that allow increasing the working temperature has received great interest in the last few years. In this respect, many authors have recently proposed the replacement of molten nitrate salts by molten carbonate salts, making possible an increase in the operational temperature beyond 700 °C. However, one of the main drawbacks of this medium consists in the severe corrosion problems to which its composition and high temperature lead. Thus, the development of protective coatings for steels could be an interesting alternative, both from a technological and economical point of view, for increasing the lifetime of pipes and tanks in contact with molten carbonates. In both cases, the levelized cost of electricity (LCoE) would suffer a substantial reduction, which is one of the major objectives currently set in CSP technology. Thus, this work aimed at developing zirconia-based sol-gel protective coatings (on stainless steels and monitoring the protective behaviour in contact with a eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3. Corrosion tests were performed at 700°C up to 1000 h results were supported by gravimetric and microstructural characterizations. All results were compared to the uncoated steels. Results showed the promising behaviour of the coated substrates. The corrosion monitoring system showed the protective behaviour of the coatings, these improving the behaviour of the uncoated samples, where detachments and high weight variations were observed.

9:20am **A1-3-TuM-5 Experimental Study on Steam Oxidation Resistance at 600ºC of Inconel 625 Coatings Deposited by HVOF and Laser Cladding***,* ***Francisco Javier Pérez Trujillo (fjperez@ucm.es)****,* *G. García Martín, A. Illana Sánchez, T. De Miguel Gamo,* Universidad Complutense de Madrid, Spain*; F. Gonçalves , M. Sousa,* Tecnologia e Engenharia de Materiais , Portugal

Technological developments around electric generation power plants aim to increase the thermal efficiency of conversion processes in steam turbines, developing materials able to resist ultra-supercritical (USC) conditions (600-620°C and 20-30 MPa). 9-12 %Cr ferritic-martensitic steels, commonly used for that application, tend to develop thick and non-protective iron-rich oxide scales. Therefore, partial or complete spallation of these oxide scales may cause serious consequences for the lifetime and safe operation of the components in contact with the steam and even the own plant. The solution to prolong their service life is to modify their surface, by means of protective coatings that retard interdiffusion mechanisms that take place at that temperature range.

Inconel 625 is used for its high strength, excellent fabricability (including joining), and oxidation resistance up to 982°C, so has been considered as one possible candidate for A-USC power plants (up to 700°C and 35 MPa).

In this research Inconel 625 coatings were deposited by High Velocity Oxy-fuel (HVOF) and laser cladding (LC) processes on a 12%Cr steel to improve its oxidation resistance. A high-temperature oxidation test under isothermal conditions up to 500 h was performed on uncoated and coated steel in a pure steam atmosphere at 600°C. The specimens were weighed monitoring at different times during the testsand characterized before and after oxidation tests by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). The results have shown that the application of Inconel 625 coatings reduces the weight gain of the steel by more than 50%. In addition, after 500 h of oxidation both coatings deposited by HVOF and LC exhibited an excellent oxidation resistance at 600°C in pure steam due to the formation of thin layers of protective Cr_2O_3 and $NiCr_2O_4$ oxides on the external surface of the coatings.

9:40am **A1-3-TuM-6 Oxidation Kinetics of γ-TiAl Based Coating Materials***,* ***Paul Mayrhofer (paul.mayrhofer@tuwien.ac.at)****,* *S. Kagerer, O. Hudak,* TU Wien, Austria*; M. Schloffer,* MTU Aero Engines, Muenchen, Germany*; H. Riedl,* TU Wien, Austria

The reduction of carbon emissions as well as the improving of fuel efficiencies tied to modern aerospace and aviation have heavily invested in the development of lighter and more durable high temperatures materials. γ-TiAl bulk materials, with their low density and distinguished creep resistance, fulfill all these tasks till 780°C. Above 780°C, oxidation protection of γ-TiAl based alloys is a challenging task for the aero- and automotive industry. Here, especially thin films rise the possibility to protect these alloys while not affecting other material properties. Typically, ceramic like thin films are applied to defend the bulk materials against oxidation and corrosion attacks. Within this study, we applied a different approach utilizing metallic coating materials deposited by PVD.

Therefore, we grow Al-rich γ-TiAl based coatings onto well-established TNM bulk alloys using a semi-industrial scaled unbalanced magnetron sputtering system. To study the oxide scale formation and its kinetics, also on a long-term view, all coatings were oxidized at 850 °C up to 1000 h in ambient air. The scale formation and accompanying diffusion processes have been investigated methodically by various electron imaging techniques (SEM and HR-TEM) as well as structural and chemical analysis. The prevalent diffusion process was separated in two dominating effects: *(i)* oxygen inward diffusion and outermost scale formation as well as *(ii)* Al interdiffusion between the coating and bulk interface. The so obtained diffusion lengths were used to estimate diffusion coefficients by the parabolic growth rate of the TGO and the oxygen inward diffusion by a logarithmic rate law. In a further step, morphological changes due phase transformation based on Al diffusion processes was investigated in detail. The highly dense, thermally grown oxide (alumina based scale) reaches a thickness up to maximum of 4 µm depending on the coating thickness (> 10 µm) leading to superior protection of the bulk material. In summary, the application of γ-TiAl based coating materials to enhance the oxidation resistance of TNM bulk alloys is an interesting alternative to ceramic like coatings, also on a long-term perspective.

10:00am **A1-3-TuM-7 The Impact of Aluminide Slurry Coatings on the Oxidation and Fatigue Resistance of High-Strength Ni-Based Valve Alloys***,* ***Sebastien Dryepondt (dryepondtsn@ornl.gov)****,* *R. Pillai , B. Armstrong, M. Lance, G. Muralidharan,* ORNL, USA

Increasing temperature in light and heavy-duty internal combustion engines offers a straightforward solution for increasing engine efficiency and reducing CO_2 emission. Development of new Ni-based high temperature alloys is, however, burdensome due to the need for both high strength and high oxidation resistance. One solution is to apply corrosion-resistant coatings to high strength materials. A slurry aluminide coating was, therefore, deposited on commercial (alloy 31V) and ORNL-developed high strength gamma prime Ni-based superalloys. A significant improvement of the alloy cyclic oxidation resistance at 900°C and 950°C in air + 10%H_2O was observed for both alloys due to coating application. The coated ORNL sample exhibited more rapid oxidation rates than the 31V coated sample due to the higher Ti concentration in the former alloy leading to the formation of Ti-rich nonprotective oxides. High cycle fatigue testing was also conducted on bare and coated specimens to assess the coating impact on the alloy fatigue resistance at 800-900°C. Similar cycles to rupture were measured for the bare and coated samples, confirming that the coated ORNL alloy is a viable option for valve application up to ~900°C. Further optimization of the substrate/coating couple could allow for even higher valve operating temperature.

This research was sponsored by the U.S. Department of Energy, Energy Efficiency & Renewable Energy, Vehicle Technologies Office, Powertrain Materials Core Program.

Coatings for Use at High Temperatures
Room Town & Country D - Session A2-1-TuA

Thermal and Environmental Barrier Coatings I

Moderators: Sabine Faulhaber, University of California, San Diego, USA, **Pantcho Stoyanov**, Concordia University, Canada

1:40pm **A2-1-TuA-1 Mechanisms of CMAS Attack on Aero-Engine Components***, **Elisa Zaleski (elisa.zaleski@pw.utc.com)**,* Pratt & Whitney, USA **INVITED**

Gas turbine engines operating in hot, sandy environments ingest siliceous debris termed CMAS for calcium magnesium aluminosilicate (CMAS). This siliceous material deposits on the surface of hot section components leading to premature degradation of these materials. As engine temperatures rise, CMAS-induced failures accelerate, leading to the need for more robust, capable mitigation strategies. This talk will focus on the aspects and mechanisms of CMAS attack most relevant to gas turbine engines.

2:20pm **A2-1-TuA-3 A New Approach to Protect Thermal Barrier Coatings (TBCs) Using Air Plasma Spray (APS)/High-Velocity Oxygen Fuel (HVOF) Coating of Si_3N_4***, **Said Bakkar (sbakkar@udallas.edu)**, E. Zucha, J. Moldenhauer, E. Steinmiller,* University of Dallas, USA*; T. Hossain,* Ceriumlab , USA*; W. Flanagan,* University of Dallas, USA

Gas Turbine Engines (GTEs) operate at high temperatures, submersed in a high-density gas. Thermal barrier coatings (TBCs) are widely used to protect the engine superalloys from oxidation and other degradation. TBC is a compound of Yttrium stabilized zirconia (YSZ). These TBCs are vulnerable to Calcium–Magnesium–Alumino–Silicate (CMAS) deposits and volcanic ash penetration. A new approach of protecting the topcoat of the TBC from the infiltration of molten CMAS was explored using various thicknesses of silicon nitride Si_3N_4 to work as a sacrificial/Impermeable layer. The High-Velocity Oxygen Fuel (HVOF) and Air Plasma Spray (APS) coating techniques were used and the CMAS test was performed using torch and furnace techniques at 1250 °C. The blocked CMAS infiltration in this approach was investigated using XRD, SEM, TEM techniques.

2:40pm **A2-1-TuA-4 Development of a Low Power Plasma Reactor for the Local Deposition of YSZ Thermal Barrier Coatings at Atmospheric Pressure***, **Sandra Segondy (sandra.segondy@chimieparistech.psl.eu)**,* Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), France*; C. Rio, S. Landais,* ONERA, DMAS, Université Paris-Saclay, France*; C. Guyon, F. Rousseau,* Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), France

Repair methods are of great interest for the aeronautic industry, especially for gas turbines. Deposition techniques that can quickly and easily repair small and localized damaged areas of Thermal Barrier Coatings (TBCs) located on combustion chambers could be economically interesting. In a first approach, a Low-Power Plasma Reactor (LPPR) working at low pressure (< 1000 Pa, 240 W) and using solution precursors was tested to locally deposit performant Yttria Stabilized Zirconia (YSZ) as TBC. Highly porous TBCs exhibiting low thermal conductivity were deposited, however, vacuum conditions were difficult to implement at an industrial scale. For this reason, a new version of LPPR working at atmospheric pressure with solution precursors was investigated.

The plasma torch (AcXys Plasma Technologies) based on a non-thermal rotating arc technology was mounted on a 3-axis motorized table (**Fig. 1**). The plasma discharge was generated in the reactor by AC electrical power with a frequency of 80 kHz. Operating power ranged between 600 – 1000 W using air as the discharge gas (gas flow rate: 35 slpm). The precursors were composed of zirconium and yttrium salts in aqueous solution. The liquid precursors were injected (solution feed rate: 1 mL/min) in the plasma afterglow to be sprayed and deposited onto superalloy substrates (with or without a MCrAlY bond coat) to form a TBC. Because the afterglow temperature was colder than in the case of thermal spray processes (T < 1000 °C), the spray distance was lower than 10 mm. Therefore, the YSZ deposition could be done locally in hard-to-reach regions through this low power plasma.

FTIR analysis was used to evaluate the ratio of produced oxides over the remaining precursors. The coating microstructural characteristics and the porosity were assessed by SEM observations. The composition and crystalline structure were determined by EDX and XRD respectively. The YSZ coatings exhibited the expected stoichiometry, a precursor conversion of 98 mol%, a tetragonal structure (**Fig. 2**), a good adherence to the substrate and a porosity evaluated around 30 vol%. In addition, the thickness of the YSZ coating could be higher than 100 µm in less than 1 hour (**Fig. 3**). The coating morphology seemed to exhibit two different microstructures depending on the deposition conditions: a more porous morphology closer to a columnar structure and a denser and granular microstructure (**Fig. 4**). The impact of the coating deposition conditions explaining these two different microstructures is currently under investigation.

3:00pm **A2-1-TuA-5 Oxidation Behaviour and Mechanical Properties of Sputter-Deposited $TMSi_2$ Coatings (TM = Mo, Nb, Ta)***, **Ahmed Bahr (ahmed.bahr@tuwien.ac.at)**,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; S. Richter, T. Glechner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; J. Ramm,* Oerlikon Surface Solutions AG, Liechtenstein*; O. Hunold,* Oerlikon Surface Solutions AG , Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

High temperature environments not only involve materials with excellent creep properties, but also highest oxidation resistance and chemical inertness. Transition-metal disilicides ($TMSi_2$) based thin films are suggested as promising candidates for novel protective coating materials used in various high temperature applications. $TMSi_2$ exhibit an attractive mix of highest phase stability, reasonable mechanical properties and outstanding oxidation resistance.

In this study, we investigated the role of Si on the phase formation and oxidation kinetics of sputter-deposited $TMSi_2$ (TM = Mo, Ta, Nb) films. The coatings were analyzed in terms of chemical composition, phase constitution, and mechanical properties (i.e. H and K_{IC}) using diverse high-resolution characterization techniques. Moreover, the oxidation kinetics were systematically studied for all three systems at different temperature regimes up to 1400 °C. These analyses were supported by a detailed structural and morphological characterization of oxide scales formed.

4:00pm **A2-1-TuA-8 New Hydrogen Barrier Coatings***, **Akram ALHUSSEIN (akram.alhussein@utt.fr)**, I. LAKDHAR,* University of Technology of Troyes , France*; J. CREUS,* La Rochelle University , France

The interaction of hydrogen with different metallic materials was reported and discussed in the literature. It has been found that hydrogen affects significantly the mechanical properties. This smallest chemical element penetrates into the metallic structure and reduces its ductility and loading capacity [1].

Coatings present a great solution to protect a material and give it multifunctional properties. Coatings are widely considered as a good solution to design hydrogen barriers in order to trap the adsorbed hydrogen and avoid its diffusion towards the substrate through the interface.

The objective of our work is the development of new generation of hydrogen barrier coatings to protect metallic components used in hydrogen atmosphere. After three years of working on this research project, we successfully developed a new AlTiW thin film deposited by magnetron sputtering technique [2]. The deposition rate was controlled to obtain 4 µm as an uniform film thickness.

The functional properties of coating such as corrosion properties and thermal stability as well as its protective performance for steels in a hydrogen environment were investigated. The influence of tungsten content on the microstructure, thermal stability, mechanical properties, corrosion resistance and hydrogen permeation inhibition of the coating was analyzed.

XRD, DSC and TEM analyses were carried out to check the amorphous state of the coating and to determine the glass transition and crystallization temperatures. These later were increased with the increase of W concentration up to 17 at%. On the other side, the corrosion resistance in a saline solution was decreased. The addition of W led to increase the coating mechanical properties (hardness and Young's modulus).

Chemical and electrochemical hydrogen charging methods were carried out to expose coated steels to hydrogen. The tungsten incorporation in the binary AlTi coatings highly improved their resistance to hydrogen absorption. The results obtained confirm that the $Al_{45}Ti_{38}W_{17}$ coating presents the best hydrogen barrier behavior.

In the near future, we will focus on the enhancement of the coating efficiency and the development of other nanostructured coatings for using in different real conditions.

References:

[1] A. Alhussein, J. Capelle, J. Gilgert, S. Dominiak, Z. Azari, Int J Hydrogen Energy 36 (2011) 2291.

[2] I. Lakdhar, A. Alhussein, J. Capelle, J. Creus, Applied Surface Science 567 (2021) 150786.

4:20pm **A2-1-TuA-9 Dual–Layer PVD Coating System With Integrated Diffusion Barrier for Oxidation Protection of γ–Tial Based Alloys***, **Peter-Philipp Bauer (peter-philipp.bauer@dlr.de)**,* German Aerospace Center, Germany*; R. Swadźba,* Łukasiewicz Research Network - Institute for Ferrous Metallurgy, Poland*; L. Klamann, N. Laska,* German Aerospace Center, Germany

Titanium aluminides are used as structural materials for turbine blades in jet engines due to their low density and the resulting weight reduction. However, their application is limited to service temperatures below 800 °C due to insufficient oxidation resistance. A feasible way to increase the service temperature is the application of Al-rich oxidation protective coatings to ensure the formation of a thermally grown alumina layer. Nevertheless, interdiffusion processes, especially of Al, between the intermetallic coatings and the TiAl-based substrate materials have detrimental effects on the coating as well as on the substrate alloy. Therefore, the interdiffusion processes should be suppressed or at least reduced.

In the present work, the properties of a 1 µm thick layer of the Ti_5Si_3 phase as a potential diffusion barrier for an afterwards applied oxidation resistant Al–Ti coating was investigated. For this purpose, DC magnetron sputtering was used to deposit a coating of partially crystalline Ti_5Si_3 phase prior to the deposition of an Al_2O_3 forming Al-30Ti (in at.%) top layer. The deposition was performed as a one-batch process in an industrial scale multisource sputter coater. This allowed depositing the Ti_5Si_3 interlayer from pure Ti and Si targets. Afterwards, the Al-30Ti top layer was deposited in the same sputter process by changing the substrate position and using Ti and Al targets.

Cyclic oxidation tests at 900 °C for 1000 cycles (1 h each) combined with thermogravimetric analysis were performed in laboratory air in order to study the oxidation behavior of the coating systems. The morphologies of the coating systems and the microstructural development during the oxidation tests were investigated by scanning electron microscopy and high-resolution transmission electron microscopy. The intermetallic phases and the phase evolution were monitored by in–situ high temperature x-ray diffraction as well as standard x–ray diffraction.

The results show that the Ti_5Si_3 phase could effectively slow down the Al depletion in the Al-30Ti at.% coating due to minor Al inwards diffusion into the γ–TiAl substrates. As a result, the dual–layer coating system provided a high oxidation resistance due to the long-term stable formation of thermally grown alumina on the surface. The stability of the interlayer of the Ti_5Si_3 phase was excellent and it was still present even after 1000 1-h-cycles of oxidation at 900 °C without any changes in thickness. In contrast, the single layer coating of Al-30Ti suffered from breakaway oxidation after already 800 cycles of exposure to 900°C in air.

Coatings for Use at High Temperatures
Room Pacific E - Session A2-2-WeM

Thermal and Environmental Barrier Coatings II

Moderators: Sabine Faulhaber, University of California, San Diego, USA, **Kang Lee**, NASA Glenn Research Center, USA

8:00am **A2-2-WeM-1 Design of Multi-Component Rare Earth Silicate EBCs for Property Optimization***, M. Ridley, C. Miller, R. Webster, H. Olson, A. Salanova, K. Tomko, J. Tomko, J. Ihlefeld,* University of Virginia, USA*; C. Toher,* Duke University, USA*; P. Hopkins,* ***Elizabeth Opila (ejo4n@virginia.edu)****,* University of Virginia, USA **INVITED**

Environmental barrier coatings (EBCs) are required for application of SiC-based ceramic matrix composites in hot section turbine engine applications. State of the art EBCs are composed of ytterbium silicates. Multicomponent rare earth (RE) silicates offer the opportunity to simultaneously optimize a multitude of coating properties, including thermal conductivity, steam resistance, calcium magnesium aluminosilicate (CMAS) resistance, and thermal expansion coefficient. Design criteria for RE cation selection in multicomponent RE silicates can be formulated. Thermal conductivity of the EBCs can be reduced via phonon scattering mechanisms attributed to a wide range of RE mass and size. Large RE cations favor formation of an apatite barrier layer limiting further CMAS reactions. Small RE cations favor the beta-phase disilicate and X2 monosilicate with more favorable steam resistance and thermal expansion coefficients. Preliminary results for multicomponent rare earth silicate EBC thermal and thermochemical property optimization will be presented.

8:40am **A2-2-WeM-3 Cyclic Steam Oxidation of Single Layer Ytterbium Disilicate-Based Environmental Barrier Coatings Deposited onto Enhanced Roughness Silicon Carbide***, K. Kane,* Oak Ridge National Laboratory, USA*; E. Garcia,* Center for Thermal Spray Research, Stony Brook University, USA*; C. Parker, M. Lance, B. Pint,* ***Mackenzie Ridley (ridleymj@ornl.gov)****,* Oak Ridge National Laboratory, USA **INVITED**

Environmental barrier coatings (EBCs) are used to protect SiC-based structural components from water vapor induced recession in gas-turbine environments. The current generation of EBCs are typically comprised of a ytterbium disilicate (YbDS) top coat deposited onto a Si bond coat with atmospheric plasma spray. While having already achieved commercial success in the aviation sector, these EBCs are inherently temperature limited by the melting temperature of Si, 1414°C. Increasing EBC application temperatures therefore necessitates the removal of the Si bond coat. In this study, single layer ytterbium disilicate/monosilicate EBCs were deposited directly onto SiC manufactured with enhanced roughness to increase single layer adhesion. 1-h cyclic steam testing was conducted at 1350° and 1425°C, and several variations of ytterbium disilicate based EBCs were tested on several variations of enhanced roughness to investigate the relationship between EBC composition and underlying SiC geometry on both thermally grown oxide formation and coating spallation. This research was funded by the Advanced Turbine Program, Office of Fossil Energy, Department of Energy.

9:20am **A2-2-WeM-5 Raman Spectroscopic Identification of Ytterbium Silicate and Thermally Grown Oxide Silica Phases in Environmental Barrier Coatings***,* ***Michael Lance (lancem@ornl.gov)****, K. Kance, B. Pint,* Oak Ridge National Laboratory, USA

To accurately model the long-term durability of multilayered (bond coat/ top coat) environmental barrier coatings (EBCs), a more complete understanding of the phase composition and transformations of the silica thermally grown oxide (TGO) is desired.For the top coating, mixed Y/Yb silicate EBCs have been proposed as a dual-function thermal/environmental barrier coating that may also offer several other advantages over solely Yb-silicate EBCs. For the TGO formed during thermal cycling in steam, cristobalite formation and subsequent ß- to α-cristobalite transformation has been identified as a potentially life limiting parameter. In this study, Raman micro-spectroscopy was used to both compare top coating phase evolution of mixed Y/Yb- and Yb-silicate EBCs, and to quantify cristobalite formation on a thermally sprayed Si bond coating. This research was funded by the Advanced Turbine Program, Office of Fossil Energy, Department of Energy.

9:40am **A2-2-WeM-6 The Behavior Of Suspension Plasma Sprayed 8YSZ Thermal Barrier Coating With Laser Microtextured Bond Coat Under High Temperature Testing***,* ***Pawel Sokolowski (pawel.sokolowski@pwr.edu.pl)****, T. Kielczawa, M. Nowakowska,* Wroclaw University of Science and Technology, Poland*; R. Musalek, T. Tesar,* Institute of Plasma Physics of the Czech Academy of Sciences, Czechia

Despite intensive development, the Thermal Barrier Coating technology still relies on the idea of oxidation resistant metallic bond coat and thermally insulating ceramic top coat. The interface between these two layers plays a crucial role in how the structure of the TBC system behaves during high-temperature operation. In this work, laser microtexturing is proposed as a method for controlling that interface.

The 80 to 100 µm thick NiCrAlY layer was deposited by Atmospheric Plasma Spraying over the nickel-based super alloy substrate. Then, the infrared fiber nanosecond laser was used for shaping the topography of the bond coat prior to the top coat deposition. The surface geometry was controlled by the laser set-up operational conditions, mainly: (i) laser power, (ii) frequency, (iii) scanning velocity, and (iv) inter-pass spacing. The two groove-based patterns were finally selected for further work together with one as-sprayed bond coat, as a reference. The 8 wt.% yttria stabilized zirconia (8YSZ) was deposited by means of Suspension Plasma Spraying over all three types of bond coats. The samples were then subjected to isothermal oxidation and thermal cyclic fatigue testing to study the influence of bond coat topography on the overall behavior of coatings under high-temperature conditions. Microstructural studies revealed that the tailored bond coat topography may promote the obtaining of a homogeneous, columnar-like top coat. On the other hand, the grooves seem to promote locally the oxidation of the bond coat and the substrate. This means that the microtexture depth plays a crucial role and should be very precisely controlled in order to prolong the TBC lifetime.

11:00am **A2-2-WeM-10 Oxidation and Failure in Environmental Barrier Coatings***,* ***Bryan Harder (bryan.harder@nasa.gov)****, K. Lee, M. Presby,* NASA Glenn Research Center, USA*; J. Setlock,* University of Toledo, USA **INVITED**

The use of silicon carbide (SiC) ceramic matrix composites (CMCs) in turbine engines enables increased operating temperatures and reduced cooling demands, which can reduce cost, increase efficiency, and lower emissions.However, due to reactions with the turbine environment that can cause rapid oxidation and recession of components, SiC/SiC CMCs require a protective barrier called an environmental barrier coating (EBC).Although the EBC provides protection from recession via the gas stream, oxidation of the bond coat or substrate occurs with prolonged exposure during operation.The thermally grown oxide (TGO) layer that forms between the EBC and the bond coat or the substrate is a weak interface that can cause failure of the coating system.In this work, we evaluate the influence of the TGO on coating failure in state-of-the-art and advanced EBC systems.The change in the bond strength with a growing TGO layer is discussed as well as the effect of calcium-magnesium-aluminosilicate (CMAS) glass exposure on TGO kinetics and coating adhesion.

11:40am **A2-2-WeM-12 Impact of Surface Degradation on the Radiative Heat Transfer in Thermal Barrier Coatings***,* ***Francis Blanchard (francis.blanchard@polymtl.ca)****, B. Baloukas, M. Azzi, M. Kadi, J. Sapieha, L. Martinu,* Polytechnique Montreal, Canada

As aircraft engine operating temperatures increase, so must the thermal insulation capabilities of the thermal barrier coatings (TBCs) used to shield metallic components in the combustion chamber and high-temperature turbine areas. Heat transfer from the hot gases to the engine components occurs through two main mechanisms: conduction and radiation. Considerable efforts have been deployed over the years to ensure TBCs have low thermal conductivity, thanks to a porous microstructure generally achieved by thermal spray or EB-PVD techniques. The radiative component of heat transfer, however, has been comparatively largely ignored in TBC design. This issue is compounded by the exponential increase in radiative heat for higher gas temperature.While TBCs are naturally reflective to radiative heat due to scattering, this property is vulnerable to degradation, even more so than their low thermal conductivity.

The two main degradation phenomena threatening TBCs over their lifetime are (1) morphological changes due to high heat exposure (sintering, phase transition, etc…) and (2) chemical attack by CMAS (Calcium-Magnesium-Alumino-Silicate). Fundamental understanding of these two mechanisms is an important aspect in the design and development of high performance TBCs. In this work, the effects of high temperature cycling and CMAS infiltration on the optical performance of Yttria-stabilized zirconia (YSZ) coatings prepared by APS were systematically investigated. Absorption and scattering coefficients have been extracted from spectrophotometry measurements in a novel way via the inverse adding-doubling (IAD) method. The microstructure was analysed using scanning electron microscopy (SEM) and mercury infiltration porosimetry (MIP) in an attempt to establish a relationship between the evolving microstructure and the optical properties. Both were found to have a significant impact on performance, with CMAS infiltration having the biggest impact. A finite-difference time-domain (FDTD) model was developed in order to predict the optical performance of TBCs before and after degradation with good agreement with experimental data. This model could be used to investigate ways to mitigate the effect of this degradation.

12:00pm **A2-2-WeM-13 Development and Characterization of an Environmental Barrier Coating System for Novel Mo-Si-Ti Alloys Using Magnetron Sputtering***, **Ronja Anton (ronja.anton@dlr.de)**, N. Laska, U. Schulz,* German Aerospace Center (DLR), Germany

Mo-Si-Ti-based alloys are promising candidates for future high temperature applications beyond-Ni-based superalloys in turbine engines. Mo-Si-Ti-based alloys have a density of about 7.7 g/cm^3 to 7.0 g/cm^3 depending on the Ti content, which makes them lighter than Ni-based superalloys. Moreover, a better creep resistance at high temperature favors the application. Unfortunately, due to their insufficient oxidation and corrosion behavior especially at intermediate (pest oxidation) and partially at high temperature, the necessity of a protective coating becomes inevitable to perform in an oxidizing and water vapor containing atmosphere. In the present work, a multisource sputter coater was used for the deposition of a four-layer EBC system. The oxidation protection was provided by a dual layer coating system, containing a graded Mo-Si interlayer in order to compensate differences in the coefficient of thermal expansion (CTE) and a top layer of pure Si for the development of the desired thermally grown oxide layer of SiO_2. Coatings were applied by DC magnetron sputtering using pure elemental targets of Mo and Si. Regarding a sufficient water vapor resistance, ytterbium monosilicate (YbMS) is well-known and provides a CTE close to the Mo-based substrate alloys. Consequently, to reinsure the thermodynamic equilibrium between the oxidation protective Si layer and the YbMS, a further intermediate layer of ytterbium disilicate (YbDS) was deposited. The manufacturing of the Yb-based silicate coatings was done by reactive magnetron sputtering using oxygen and pure elemental targets of Yb and Si. Since the Yb target is highly reactive and leans towards poisoning, a parameter study with varying pressures, O_2 flows and target currents was performed to find the optimal operating point and the most stable process window to ensure the required coating composition. Finally, the entire EBC system consists of four different layers.

In this study, the multilayer coating system has been applied by magnetron sputtering on two novel Mo-Si-Ti alloys with a chemical composition of Mo21Si34Ti0.5B and Mo12.5Si8.5B27.5Ti2Fe (in at.%). The produced EBC system on the different alloys was tested at 800 °C and 1200 °C in laboratory air as well as in a streaming water vapor test rig. The emphasis was put on the chemical reactions and diffusion processes within the interfaces of the coating system and that were analyzed by scanning and transmission electron microscopy equipped with EDS respectively. In addition, the phase formation was evaluated using high temperature X-ray diffraction techniques.

Coatings for Use at High Temperatures
Room Golden State Ballroom - Session AP-ThP

Coatings for Use at High Temperatures (Symposium A) Poster Session

AP-ThP-2 Corrosion Induced Diffusion Pathways in Pvd $Al_{1-x}Cr_xN$ Coatings Investigated by Atom Probe Tomography*, Oliver Ernst Hudak (oliver.hudak@tuwien.ac.at),* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; V. Dalbauer,* Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; L. Shang, M. Arndt, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; P. Felfer,* Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Corrosion processes are common phenomena in fields of engineering and there is nearly never an instance, where a material is totally inert to its environment. Therefore, corrosion and corrosion-resistance are essential variables that play a pivotal role in the development of protective coatings. Ingenuity of next generation PVD coatings has given rise to a wide range of material concepts set out to withstand all kinds of corrosive attacks (e.g. NaCl, HCl, SO_3 and O_2). While their performance is mostly assessed on descriptors such as mass change, impairment of mechanical properties, or variance in electrochemical surface potential, little work has been dedicated to understand corrosion driven diffusion pathways, specifically on an atomic scale.

Particularly the production of metallic-spits or “droplets” during PVD processes poses a significant drawback in light of the coating’s corrosion resistive capabilities. In many regards, embedded macro particles, logged within the deposited coating matrix, serve a beneficial cause, when it comes to improved mechanical properties, such as hardness, fatigue resistance and fracture toughness. However, in light of corrosion behavior, macro-particles provide formations of voids and rugged grain boundaries that allow for fast-track diffusion of corrosive media to the substrate-coating interface.

This study showcases a systematic approach on highlighting preferred diffusion pathways of corrosive NaCl-rich media in PVD thin films. Intended as a model system, arc-evaporated- as well as sputtered AlCrN coatings were deposited on low alloy steel substrates and electrochemically investigated using a three-electrode set-up. With a Ag/AgCl reference electrode (RE), a Pt-counter electrode (CE) and the coated-steel sample as working electrode (WE), linear potentiodynamic polarization experiments were conducted in a 1M NaCl solution.

Next to SEM investigations, high resolution analytical techniques such as APT and TEM were consulted to help identify preferential diffusion paths, and highlight differences in the corrosion behavior of arced- and sputtered coatings.

Keywords: Corrosion Resistance; PVD coatings; Diffusion Pathways; Atom Probe Tomography

AP-ThP-8 Microstructure and Oxidation Behaviour of $MoSi_2$ Thin Films Grown by DCMS and HiPIMS*, Ahmed Bahr (ahmed.bahr@tuwien.ac.at),* *S. Richter, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Refractory transition-metal disilicides ($TMSi_2$) can be considered as promising candidates to be applied as protective coatings in high temperature applications as they have attractive combined properties such as high melting point, acceptable mechanical properties and especially high oxidation resistance in air.$MoSi_2$ exhibits an attractive mix of good mechanical properties and outstanding high temperature oxidation resistance due to the formation of a protective silicon-based oxide.

In our study, we employed direct current magnetron sputtering (DCMS) and High-power magnetron sputtering (HiPIMS) techniques to synthesize $MoSi_2$ thin films. We investigated the influence of the deposition parameters on the phase formation and the mechanical properties of the films. Moreover, the oxidation kinetics were analyzed at different temperature regimes up to 1500 °C. The coatings were characterized in terms of chemical composition, phase constitution, and mechanical properties using high-resolution characterization techniques.

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