Coatings for Use at High Temperatures
Room On Demand - Session A1

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

A1-1 PVD Cr Coatings to Mitigate Corrosion of SiC-SiC$_f$ Composite for LWR Applications*, **Kyle Quillin (quillin@wisc.edu)**, H. Yeom, T. Dabney, J. Lacy, T. Kim,* University of Wisconsin - Madison, USA*; S. Chemerisov,* Argonne National Laboratory, USA*; A. Couet, K. Sridharan,* University of Wisconsin - Madison, USA

SiC-SiC$_f$ composite is being investigated as the fuel cladding material in the next generation of light water reactors (LWRs) based on its high-temperature stability and resistance to irradiation damage. In particular, this composite offers greatly improved safety margins in the event of a loss-of-coolant accident. One challenge in the implementation of this material for cladding applications is the corrosion of SiC under normal LWR operating conditions, where the aqueous environment promotes the conversion of a protective surface silica layer to the water-soluble silicon hydroxide. To mitigate this hydrothermal corrosion of SiC, we are investigating a variety of physical vapor deposition (PVD) processes to deposit Cr coatings 5-7 microns in thickness, including conventional direct current magnetron sputtering (DMCS) and high-power impulse magnetron sputtering (HiPIMS). Coated and uncoated SiC were tested in a pressurized water autoclave at 360 °C and 18.6 MPa for a period of 720 hours. The coatings' microstructure before and after corrosion tests was characterized using scanning and transmission electron microscopy (SEM and TEM). X-ray diffraction (XRD) was used to identify phases and measure stresses in the coatings. Scratch testing using a spheroconical diamond stylus was used to achieve a qualitative assessment of the mechanical performance of the coating-substrate system. The results showed that both DCMS and HiPIMS Cr coatings provided good corrosion resistance and acted as effective barriers for water transport to the underlying SiC composite substrate. The columnar-grained microstructure of the DCMS coating showed some ingress of water along the inter-columnar boundaries as manifested by oxidation in these regions, an effect that was not observed in the more equiaxed and dense HiPIMS coatings. The results of this study and irradiation effects in the coating will be discussed, with the goal of enhancing the viability of coated SiC-SiC$_f$ composites as cladding material for LWR applications.

A1-2 High Temperature Molten Salt Corrosion Behavior of Nickel and Nickel-Molybdenum Coatings for Molten Salt Reactor (MSR)*, **Ketan Kumar Sandhi (ketan.sandhi@usask.ca)**, J. Szpunar,* University of Saskatchewan, Canada

Ni and Ni-Mo coatings were deposited on AISI 304 stainless steel samples using electrochemical deposition technique. Corrosion tests were run in molten FLiNaK (46.5 mol% LiF-11.5 mol% NaF-42 mol% KF) salt environment at 700° C for 100 h under Ar cover gas for coated and uncoated samples. Corrosion was seen to be occurring by Cr depletion from base alloy in uncoated and Ni-Mo coated specimens. Uncoated specimen showed corrosion depth up to 48 µm from the surface of specimen, however Ni-Mo coated specimen had corrosion depth of 100 µm. No significant depletion of Cr was observed from the surface of Ni coated specimen. High resolution Xray photoelectron spectroscopy (XPS) showed the increase in carbide phase at the surface of the corroded samples. Ni-Mo coated specimen showed complete depletion of Mo from the Ni-Mo coating. Results indicated Ni-Mo coated specimen performed worst and Ni coated specimen performed best for corrosion resistance in FLiNaK environment.

A1-3 Laser Cladding NiTi on the Magnesium Alloy Substrate With the Intermediated Aluminum Layer*, C. Zhang, **Yuyun Yang (yangyuyun@hotmail.com)**, X. Cui, G. Jin, W. Zheng,* Harbin Engineering University , China

Magnesium and its alloys are the most promising green engineering structural materials in the 21st century, has the advantage of low density, high damping intensity, etc. While the major obstacle of the magnesium alloy in widespread applications is to overcome the poor corrosion resistance. Laser cladding, an effective surface modification approach, is a kind of high energy beam technology. Nickel-titanium alloy has excellent corrosion resistance and high hardness, which is a favourable coating system of magnesium alloy surface strengthening. The introduction of the intermediated aluminium layer makes it feasible to cladding the NiTi alloy coating on magnesium alloy.

An aluminium intermediated layer was developed on the surface of AZ91D substrate by using laser cladding the pre-set pure aluminium powder on the surface of substrates. Laser power is set as 1,000W at 30mm/s of scanning speed. Then a top layer of NiTi alloy on the intermediated layer is obtained with the laser power of 1300Wat 30mm/s. The microstructure of the coating section morphology was observed by optical microscope and the scanning electron microscope (SEM). X-ray diffraction (XRD) and energy dispersive spectroscope (EDS) are employed to verify the presence of Ti2Ni, NiTi, Ni3Ti, Ni2TiAl and the distribution of the elements. The hardness-depth profile of the layer was measured by a microhardness tester, and the measured hardness value of the NiTi alloy layer is over 7 times of the AZ91D substrate. Weight loss and friction coefficient are evaluated by the tribological wear tester and the result of the test shows that the NiTi alloy layer presents superior wear resistance properties compared with that of magnesium alloys. Corrosion resistance in a simulated seawater environment was tested on an electrochemical workstation and the enhanced corrosion resistance of the NiTi layer is gained on the surface of magnesium alloy substrate.

High energy beam surface modification technology greatly expands the application range of magnesium alloy. With this technology, magnesium alloy will be able to adapt to the worse working environment and higher performance requirements applications, such as aerospace, military aircraft, and car industry, etc.

A1-4 Early Detection and in-situ Monitoring of the Oxidation of an MCrAlY Coating by Thermoreflectometry*, **Maxime Ecochard (maxime.ecochard@mines-albi.fr)**, B. Javaudin, R. Gilblas, D. Texier, T. Sentenac,* ICA, France

Change in oxide formation in thermal barrier coating (TBC) systems is of major interest since the formation of fast-growing oxides instead of the thermally gr own oxide (TGO) could ruin the integrity of TBC systems. Understanding the damage mechanisms associated with the microstructure of surface materials requires a local study of the thermal and oxidation mechanisms of the surface. These mechanochemical phenomena involve local changes in surface reactivity, which is observed in particular by changes in emissivity during a temperature test. An optical monitoring to assess defects in TBC components leading to local thermal variations or change in oxide formation accompanied with a change in emissivity is particularly suitable. Thermoreflectometry is an optical near-infrared (NIR) technique capable to measure both temperature and the emissivity fields of opaque materials (metals, several oxides). The principle is based on the indirect measurement of emissivity through reflectivity (active phase), coupled with a luminance temperature fields measurement (passive phase). The true temperature and emissivity field are calculated from the resolution of a system of equations written for two NIR wavelengths. This method thus allows non-contact measurement of true temperature and emissivity fields on most of the materials with centimetric dimensions subjected to dynamic processes with high thermal gradients [1].

The goal of the present investigation is to capture early local oxidation events that differ from TGO formation at high temperature, e.g. the formation of a Cr_2O_3, NiO, via *in-situ* evaluation of temperature and emissivity by thermoreflectometry.

The approach initially consists of an *ex-situ* and multi-scale analysis of the oxides formed in order to correlate the local optical signature of oxides with their chemical and morphological nature [2]. Such an investigation was possible by tracking change in oxide formation due to breakaway events on ultrathin specimens, leading to a limited content of reactive elements to form the TGO. Once these validations were conducted, an *in-situ* mesoscopic instrumentation approach is developed to monitor the local evolution of the first stages of degradation of oxidized surfaces (local formation of rapidly growing oxides).

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A1-5 Intrinsic and Extrinsic Size Effects on the High Temperature Oxidation of APS and HVOF MCrAlY Coatings*, **Damien Texier (damien.texier@mines-albi.fr)**, M. Ecochard,* ICA, France*; T. Gheno,* ONERA, France*; M. Salem, P. Lours,* ICA, France

MCrAlY coatings are widely used in the manufacturing of high temperature structural components as a protective layer against intermediate and high temperature oxidation and corrosion. They are generally applied with line-of-sight deposition processes such as low-pressure plasma spray (LPPS), air plasma spray (APS), vacuum plasma spray (VPS) or high velocity oxygen fuel (HVOF). Projected coating microstructures typically comprise fine lamellas of melted and resolidified powder particles, un-melted powder particles, pores, and dispersed alumina. The defects present in these complex microstructures act as fast diffusion paths and cause oxide intrusion in the bulk of the coating [1]. In addition, the thickness of overlay coatings can range from tens of micrometers to nearly one hundred of micrometers depending on the application (aeronautical versus marine and versus power plant applications). Aluminum and chromium, which enable the formation of protective oxide scales, are present in limited amounts, and are consumed by both oxidation and interdiffusion with the substrate. Therefore, the coating thickness can be an important factor in the high temperature oxidation behavior of the system. In the present study, 800 µm-thick β-γ NiCoCrAlY coatings were deposited on sacrificial substrates by HVOF and APS. Free-standing NiCoCrAlY specimens were then prepared using a precision Jig and a lapping machine in order to ensure good control over the thickness and surface finish [2]. Freestanding NiCoCrAlY specimens with thicknesses ranging from 9 to 400 µm were oxidized in air at 1150°C for various holding times up to 500 h. Interestingly, the mass gain was found to decrease with decreasing specimen thickness, due to oxide intrusion in the bulk, especially for the HVOF coating. The specific surface is thus increased with the internal defects, as for materials with open porosity. In addition, very thin specimens were found to form different oxide layers as compared to thick specimens, due to complete Al consumption through the specimen thickness (reservoir effect). A progressive mass loss was noticed for high temperature exposures longer than the occurrence of this breakaway phenomenon. The breakaway occurred at longer oxidation time for thicker specimens.

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A1-6 Effects of Temperature and the KCl + K_2SO_4 Load on the Behavior of Several Aluminide Coatings on Ferritic Steels Tested under a Biomass Combustion Atmosphere*, A. Agüero,* ***Marcos Gutiérrez (gutierrezdom@inta.es)***, Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Energy from biomass corresponds to more than 60% of all renewable energy sources in Europe and is currently the most widely used worldwide. However, it has not reached yet the efficiency that can be obtained with fossil fuels, as temperatures cannot be increased due to severe corrosion taking place due to biomass combustion products. New materials and/or coatings are required, and screening laboratory testing is needed to evaluate the high temperature corrosion resistance of these new materials. However, there is no general agreement regarding the methodology to carry out biomass corrosion laboratory tests, which can allow realistic ranking of materials and coatings. In INTA, a laboratory test procedure based data obtained from a thistle-burning pilot plant employing oxy-combustion conditions, was established and the corresponding rig implemented. The present work studies the effect of temperature and the amount of deposits of KCl + K_2SO_4 under an atmosphere containing 60 CO_2, 30 H_2O, 8 O_2, 2 N_2 (v. %), 400 vppm HCl and 2 vppm SO_2.The behaviour of T22 and P92 and as well as of two slurry applied diffusion aluminide coatings with different Al contents was studied. Exposure was performed at 550ºC, 600ºC and 650ºC for more than 600 h and the samples were covered with 0.7 mg/cm^2 of a KCl + K_2SO_4 mixture prior to exposure. In addition, the same substrates and coatings were tested at 550º C employing a salt load of 2.1 mg/cm^2 in order to study the influence of the amount of salt.

Both uncoated substrates exhibited important mass gain/losses indicating a high degree of corrosion as well as of oxide spallation. P92 gained significant weight and there was evidence of spallation based on visual observation of the samples, whereas T22 lost weight after a short weight increase period and even from beginning of the test at 650º C. This indicates that the Cr content (9 wt.% in P92 and 2 in T22) plays a role in developing more protective and adhesive scales. For both alloys the corrosion rates increased with temperature and the higher salt load resulted in earlier and heavier spallation for both substrates.

On the other hand, the coatings exhibited much better behaviour under all conditions and very little variation for the different salt loads. However, at 650º C both coatings exhibited significant degradation but no substrate attack was observed. Microstructure analysis of the tested samples was carried out to study the coatings protection and degradation mechanisms.

A1-7 INVITED TALK: PGM based Diffusion Coatings for Ni-based Superalloys by a Paste Method*, **Hideyuki Murakami (MURAKAMI.Hideyuki@nims.go.jp)***, National Institute for Materials Science (NIMS), Japan*; D. Tue, A. Ishira, L. Honglien,* National Institute for Materials Science (NIMS), Japan **INVITED**

In this study, the new route to develop oxidation resistant coatings on Ni-based single crystal superalloy is introduced. A paste, which contains Pt or Pt-xIr (x = 0-30 at%) alloy nano-powder was sprayed on some Ni-based single crystal superalloys. Then the annealing diffusion treatment at 1100 °C for 1 h in flowing Ar atmosphere was conducted to develop Pt and Pt-Ir coatings. Cyclic oxidation tests were carried out at 1150 °C in still air in order to investigate the thermal stability and oxidation behavior of the coatings and they were compared with electroplated diffusion coatings. It was found that Ir can retard the formation of voids in both the coating and substrate. In addition, by replacing the electroplating method to the paste coating method, the crack problem due to the brittle feature of electroplated Pt-Ir coatings could be solved. Therefore, the Pt-20Ir diffusion coating prepared by the paste-coating method is promising as the bond-coating material due to formation of less voids, no cracks and stable Al_2O_3 on the surface. To further evaluate the pasted Pt and Pt-Ir diffusion coatings, hot corrosion tests and fatigue tests were conducted. Both tests confirmed that Pt-Ir diffusion coatings, developed by the paste method performed promising characteristics.

The Pt-Ir paste diffusion coatings introduced above have several aditioinal advantages: they are easy to recoat, cause less damage to substrates, and offer comparable oxidation resistance. Thus the method can be applicable to the remanufacturing of blades, which may extend the life of components. The future aspect of the paste coating, effect of composite coatings, will also be discussed.

A1-9 Effect of Nickel Percentage on the Morphology, Wear and Corrosion Resistance of Zn-Ni Alloy Coating*, **Ameeq Farooq (ameeq.farooq@gmail.com)**, S. Ahmad,* University of the Punjab, Pakistan*; K. Deen,* University of British Columbia, Canada

The aim of this research work is to develop Zn-Ni alloy electroplating on mild steel substrate in acidic sulphate bath. Different concentration of nickel ions varies from $10gL^{-1}$, $15gL^{-1}$,$20gL^{-1}$ and $25gL^{-1}$ in the electroplating bath effect morphology, mechanical and electrochemical properties of the Zn–Ni alloy coatings. At constant current density of $1.5Adm^{-2}$ for one hour with sulphate containing bath having pH 3 at 35°C with continuous agitation through air purging. The thickness of the coating was measured by microscopic method. Scanning electron microscope along with the Energy dispersive spectroscopy was used to find the surface morphology of the coating along with elemental mapping. Scratch adhesion testing was also conducted on the coated samples at different loads to find the adhesion and wear properties of the coating with the mild steel substrate. The electrochemical behaviour of different coatings was evaluated by using cyclic polarization and electrochemical impedance spectroscopy (EIS) in 3.5% NaCl solution. Salt spray test was also conducted for 96 hours to find the performance of alloy coating in moist saline environment. The results of alloy coating show that Ni content influences the thickness, phase structure, morphology and adhesion of coatings. The thickness decreases with the increase in the concentration of nickel from 38.2 ± 0.5 mm to 20.7± 0.5 mm. Stereomicroscope results shows after scratch test shows that the Zn-Ni alloy resist the propagation of the scratch at all loads independent of the concentration of nickel ions. The free corrosion potential shifted towards the more noble potential with the increase in the nickel ions concentration from -1083 mV $_{\text{vs Ag/AgCl}}$ to -1060 mV $_{\text{vs Ag/AgCl}}$. The electrochemical results showed that Zn-Ni coatings had better corrosion resistance compared to that of the zinc and nickel single layer coating. The Zn-Ni coatings are more pitting resistance in saline environment as compare to nickel coating.

Coatings for Use at High Temperatures
Room On Demand - Session A2

Thermal and Environmental Barrier Coatings

A2-1 Improvement of TBC Coating Resistance to Simultaneous Attacksby Sulfur and Vanadium Compounds*, Jianhong He (Jianhong.He@Oerlikon.com),* Oerlikon Metco , USA*; T. Sharobem, G. Dwivedi,* Oerlikon Metco, USA

Hot corrosion attacks of various TBC systems by sulfur and vanadium compounds have been tested at 1050°C for 2 hours and 4 hours in the presence of 60% V_2O_5 and 40% Na_2SO_4. The results are summarized as follows.

(A) Sulfur and vanadium compounds at high temperature aggressively attacked the conventional 7YSZ TBC, the coating has been damaged at 1050°C for only 2 hours in the presence of 60% V_2O_5 and 40% Na_2SO_4.

(B) High density of coarse YVO_4 crystals are quickly formed on coating surface, removal of Y_2O_3 stabilizer from zirconia leads t'-ZrO_2 to m-ZrO_2 phase transformation and thusdramatic increase in volume. There is no evidence showing fair metallurgical bonds among YVO_4 crystal and YVO_4 crystal, and matrix, therefore, integrity of the coating is totally destroyed by sulfur and vanadium compounds.At the same time, molten salt infiltrate into entire top coat and seal splat boundaries and pores similar to molten silicate deposits to reduce strain tolerance, finally causing top coat delamination.

(C) Hot corrosion resistance of TiO_2 and Y_2O_3 co-stabilized zirconia has doubled compared to a standard 7 YSZ TBC, while single stabilizer TBCs with high Y_2O_3 ratios do not increase hot corrosion resistance in the presence of 60 % V_2O_5 and 40 % Na_2SO_4.

(D) TBC sprayed using mixture of 50% Metco 143 and 50% 48YSZ and Metco143/ A204NS-1/bi-layer TBC had the highest resistance to simultaneous attacks by sulfur and vanadium compounds, although the microstructures on the surface and cross-section of these two TBCs are totally different.

A2-2 High-Temperature Corrosion of Sintered $Er_2Si_2O_7$ With CMAS for Environmental Barrier Coatings*, Seung-Hyeon Kim (kim.seung.hyeon.726@s.kyushu-u.ac.jp),* Kyushu University, Japan*; N. Nagashima, Y. Matsushita,* National Institute for Materials Science, Japan*; B. Jang,* Kyushu University, Japan

Environmental barrier coatings (EBCs) is an element that protects silicon-based ceramic matrix composites (CMCs) from high temperatures. CMCs has high temperature performance and low density, which can greatly improve fuel consumption. CMCs low density can reduce weight by up to 30% compared to Ni-based super alloys. In addition, for the purpose of EBCs, insulation properties are important as the temperature change of the hardware inside the engine occurs at high temperatures. In addition, the demand for thermal protection of CMCs is increasing in higher temperature applications. Research and development are being conducted to investigate the effect of calcium-magnesium-aluminosilicate (CMAS) during high temperature operation. A composition similar to volcanic ash is being studied for the high temperature interaction between CMAS.

EBCs must be resistant to minimize the resistance to decomposition by molten actual volcanic ash (dust and sand) deposits. With increasing high-temperature corrosion requirements, EBCs based on rare earth (RE) monosilicates ($RESi_2O_5$), disilicates ($RE_2Si_2O_7$) and their variants are being developed. Disilicate ($RE_2Si_2O_7$) shows safety because SiC and CTE are better matched than monosilicate ($RESi_2O_5$). The process of preparing a hot corrosion specimen is as follows. The synthesized Er_2O_3-$2SiO_2$ powder was prepared to fabricate a sintered $Er_2Si_2O_7$ by the spark plasma sintering (SPS) at 1400°C for 20 min. CMAS was sprinkled on the sintered $Er_2Si_2O_7$ surface and exposed for 2, 12, and 48 h at 1400°C by isothermal heat treatment.

However, reaction layer for sintered $Er_2Si_2O_7$ by CMAS has not yet been reported. The purpose of the present work is to investigate the influence of CMAS corrosion properties at high temperatures on sintered $Er_2Si_2O_7$ fabricated by SPS. As time increases, it is a phenomenon that appears as $Er_2Si_2O_7$ particles are dissolved in molten CMAS by penetrating into grain boundaries. In addition, it was observed that some crystallization occurred at the boundary of the sintered $Er_2Si_2O_7$ molten CMAS.

Keywords: $Er_2Si_2O_7$; Corrosion behavior; CMAS; Environmental barrier coatings; Spark plasma sintering

A2-3 Experimental and Modelling Analysis of the Driving Force for TBC Damage During Thermal Cycling With Consideration of Temperature Gradients*, Lara Mahfouz (lara.mahfouz@mines-paristech.fr), V. Maurel , V. Guipont, B. Marchand,* Mines ParisTech, PSL Research University, France*; F. Coudon,* Safran Tech, Safran SA, France

The addition of Thermal Barrier systems to hot section components of gas turbines requires understanding of its degradation and failure modes, and its resulting impact on the components' lifetime. The spallation (total or partial) of the top coat will result in thermal protection loss, and hence an important reduction of the component's lifetime. The studied Thermal Barrier system is composed of EB-PDV YSZ ceramic top coat and (Ni, Al)-Pt metallic bond coat deposited on a AM1 substrate, a Ni-based superalloy. A first α-alumina layer is deposited on the substrate and grows in service (TGO).

Different approaches have been developed to asses TBC lifetime [1,2]. The main objective of this study is to provide a robust modeling of the damage and lifetime to spallation of Thermal Barrier systems, for thermo-mechanical stress conditions accounting for thermal gradients. The proposed approach is based on the analysis of the evolution of an interfacial crack. It has been widely observed for such systems, that thermal cycling induces damage at the TC/TGO interface leading to interfacial cracking and finally spallation of the TC. Laser shock test has been used to initiate a crack at the interface. The evolution of the crack is monitored during thermal cycling on a burner rig, with temperature gradients as close as possible to in-service conditions. This technique has been used and analyzed in previous studies [2,3] for furnace cycling tests. A numerical modeling of the energy evolution in a blister under thermal cycling is proposed. It relies on the evaluation of the energy release rate within the system at different cycling stages as the blister propagates. A sensitivity analysis has been achieved considering the influence of components' mechanical behaviors, as well as that of loading, ageing, and geometrical parameters.

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A2-4 Effect of Varying APS Flash Bond Coating Thickness on Furnace Cycle Lifetime*, Michael Lance (lancem@ornl.gov), K. Kane, J. Haynes, B. Pint,* Oak Ridge National Laboratory, USA*; E. Gildersleeve, S. Sampath,* Stony Brook University, USA

The addition of an air plasma sprayed (APS) "flash" bond coating layer on top of a high velocity oxy-fuel (HVOF) bond coating has been found to significantly extend the lifetime of APS yttria stabilized zirconia (YSZ) top coatings on rod and disk specimens. In order to test the hypothesis that the flash coating forms a crack-inhibiting mixed metal-oxide zone and the HVOF layer acts as an Al reservoir, a set of superalloy 247 disks were coated with 0, 25, 50 and 100% APS layers using NiCoCrAlY powder. Groups of five specimens of each coating type were cycled to failure using 1-h cycles in air+10%H_2O at 1100°C. Residual stress in the thermally-grown Al_2O_3 scale was measured using photo-luminescence piezospectroscopy (PLPS) as a function of time for one specimen of each coating variation. Principal component analysis (PCA) of both Raman and x-ray spectroscopy maps were conducted to determine the phases present within the oxide and the bond coating. The results of furnace cycling testing and analysis of the compositions and microstructures will be presented.

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A2-5 Electrodeposited Thin La_2O_3 Based Chromium Barrier Coating for Interconnectors in Solid Oxide Electrolysis, ***Vladislav Kolarik* (*vladislav.kolarik@ict.fraunhofer.de*)**, *M. Juez Lorenzo, E. Walschburger,* Fraunhofer Institute for Chemical Technology ICT, Germany

Solid oxide steam electrolysis (SOE) using electric power from renewable sources is a promising technology to produce hydrogen for energy storage or for industrial purposes. Ferritic stainless steels are used for interconnectors between the SOE cells offering good mechanical properties and forming at high temperatures an electrically conductive Cr_2O_3 scale. In presence of water vapor however, the highly volatile and toxic $CrO_2(OH)_2$ is formed poisoning the SOE cell. To mitigate the Cr(VI) evaporation protective coatings are used.

To reduce the costs of an SOE stack, cost efficient coating processes are required. Electroplating was applied to deposit a $La(OH)_3$ layer on a Crofer 22 APU substrate with a subsequent heat treatment to transform the $La(OH)_3$ to a La_2O_3 coating. The coating thickness and morphology is controlled directly by the electroplating parameters. The electrodeposited layers are well adherent and exhibit thicknesses around 1 µm and a needle-like nano-crystalline structure. With higher layer thickness a network of thin cracks is observed. The heat treatment was followed is situ by high temperature X-ray diffraction both on heating as well as isothermally in order to adjust the parameters.

For investigating the chromium evaporation rate the coated samples as well as an uncoated reference sample were subjected in a closed furnace system to humid air with a mass flow of 2000 ml/min and a water content of 130 g/m^3 at 850°C for 500 h. On the furnace outlet the humid air was cooled to condense the water. The chromium content in the condensed water was detected by a colorimetric quick test as well as by ICP-OES analysis. The evaporation rate as a function of time was determined in time intervals of 24 h. Samples were taken out of the furnace for SEM analysis after 100 h, 200 h, 300 h and 500 h.

Chromium evaporation was found in all time intervals during the whole exposure duration. At the beginning lower chromium evaporation rates were measured with the coated samples than without coating. With longer exposure times the evaporation rate values are closer to those for uncoated steel. Areas with partial coating spallation were observed in the micrographs after longer exposure periods, probably originating from cracks that formed due to the thermal expansion mismatch. An oxide scale consisting of Cr_2O_3 and Cr-Mn-spinel formed beneath the coating as well as in the areas with coating spallation. Electrodeposition is a possible cost efficient method to produce chromium barrier coatings on interconnector steels. The process parameters however, need to be further investigated.

A2-6 Effects of Mo Interlayer on the Oxidation Behaviour and Degradation Mechanism of Amorphous SiAlN Coating at 1000 °C in Steam Environment, ***Zhaohe Gao* (*zhaohe.gao@manchester.ac.uk*)**, The University of Manchester, UK*; J. Malecka, P. Kelly,* Manchester Metropolitan University, UK*; P. Xiao,* The University of Manchester, UK

Loss-of-Coolant Accident (LOCA) in a Light Water Reactor, such as occurred in the Fukushima Daiichi Power Plant, could be potentially mitigated by applying an oxidation-resistant coating onto the surface of the Zr alloy fuel rod as accident tolerant fuel cladding. In this study, 1.1 µm thick SiAlN amorphous coatings, consisting of AlN nanoparticles dispersed in an amorphous Si_3N_4 matrix, have been deposited on Zr alloys with 300 nm or 750 nm Mo interlayers and studied in a steam environment at 1000°C. The SiAlN coating with a 750 nm Mo exhibits excellent oxidation resistance without observable oxide scale after up to 4 hours at 1000°C, while the coating with a 300 nm Mo forms a thin oxide scale in an identical atmosphere after 1 h. The downward diffusion of Si into underlying Zr alloy, followed by relatively faster outward diffusion of N, generates excessive Si and lean N in the outmost surface of SiAlN, thereby resulting in the oxidation of the amorphous coating. A critical composition content of N below which oxidation can happen is predicted and verified. The sluggish effect of Mo on the downward diffusion of Si has also been discussed and this study provides a new insight into the degradation mechanism of this amorphous coating.

A2-7 Laser Processing of Freeze Casted Yttria Stabilized Zirconia / Gadolinia Thermal Barrier Coatings to Mitigate CMAS Attack, ***Said Bakkar* (*SaidBakkar@my.unt.edu*)**, *E. Cairns, M. Vu, M. Young, D. Berman,* University of North Texas, USA*; T. Hossain,* Ceriumlabs, USA*; J. Moldenhauer, E. Steinmiller, W. Flanagan,* University of Dallas, USA*; S. Aouadi,* University of North Texas, USA

Yttria-stabilizedzirconia and Gadolinia blend (YSZ/Gd_2O_3) ceramics with unidirectionally-aligned pore channels were created using the freeze-casting method. Preforms were prepared by freezing 70 wt% YSZ and 30 wt % Gd_2O_3 after ball milling for 15 hours /distilled water/polyvinyl alcohol (PVA) slurry under a freezing temperature of -196 °C. The frozen preform was sublimated using a freeze-drying system in vacuum (0.05 mTorr) at -85 °C. The sublimated preforms were subsequently sintered at 1600°C for 9 h in air. The surface of the sintered samples was modified using a laser process to seal its surface tomitigateCMAS (calcium–magnesium–aluminum–silicon oxide) attack. Scanning electron microscopy (SEM) revealed that the pore channels consisted of columns, which act to decrease the thermal conductivity of the (YSZ/Gd_2O_3) blend. Also, SEM confirmed that the surface treatment successfully sealed the surface. The performance of the different surface treatment systems was compared by conducting CMAS infiltration studies. Deposit of Si_3N_4 as a sacrificial layer on the top of single crystal YSZ provides a perfect seal to cover the defects on the surface.The newly designed fabrication process that combines freeze casting with laser modification and using a sacrificial layer of Si_3N_4 was shown to be a viable technique to significantly reduce CMAS infiltration in porous thermalbarriercoatings.

A2-8 Corrosion Resistance and Fatigue Behavior of Bare and Coated Ni-based Superalloys, ***Sebastien Dryepondt* (*dryepondtsn@ornl.gov*)**, *R. Pillai, J. Kurley,* Oak Ridge National Laboratory, USA

Rising temperature in land-based gas turbines has led to an increase of corrosion degradation of turbine blades operating at ~700-750º C. MCrAlY overlay bond coatings with or without a thermal barrier coatings (TBC) can provide some protection against this type 2 low temperature hot corrosion attack, but the coating impact on the blade mechanical performance needs to be evaluated. Hot corrosion testing in O_2+0.1%SO_2 environment with NA_2SO_4 salt deposition at the sample surface was conducted on bare CM247, Rene 80 and IN738 at 700º C for up to 100h. Systematic image analysis of the corroded specimens revealed a deeper metal loss for the IN738 alloy compared to the CM247 and Rene 80 alloys. Coupons of Rene 80 coated with two different types of MCrAlY coatings or MCrAlY + TBC were also exposed. Significant reduction of mass losses was observed for the MCrAlY coated samples, but the coatings were heavily oxidized after 60h of exposure. On the contrary, the MCrAlY + TBC coating was very protective with very limited corrosion attacks. Finally, low cycle oxidation testing was initiated on bare and coated CM247 specimens at 750º C in air and first results with a total deformation of 0.8% showed no impact of the coating on the number of cycles to failure. The next step is to conduct similar fatigue tests in a corrosive environment.

Coatings for Use at High Temperatures
Room On Demand - Session A3

Materials and Coatings for Solar Power Concentration Plants

A3-1 Biodegradable Polyurethane Antifouling Coating, ***Mohammad Mizanur Rahman* (*mohammadmizanur@gmail.com*)**, King Fahd University of Petroleum and Minerals, Saudi Arabia

Controlled biocide leaching is one of the vital criteria's to consider any polymer as an antifouling coating. Besides the pollution of marine environments using excess toxic biocides is a huge concern worldwide. Almost all of the current commercial antifouling coatings contain toxic biocide. Thus, it is important to use a coating, which can control biocide leaching. Biopolymer can be a good choice in this regard as the biodegradable coating can be degraded easily with proper environment. Unfortunately little research has been done in this respect. Most of the research has been done mainly polycaprolactone based polyol. Xanthangum (Xn) might be a good choice. In this study biopolymer xanthan-poly(N-vinyl imidazole) (Xn-VI)was synthesized. The polymer was used in polyurethane (PU) coating to make a water erodible coating to improve the antifouling properties. Coating hydrophilicity, adhesive strength and erosionall varied with the Xn-VI contents. A good antifouling property for longer time was found in the PU-Xn-VI coating using biocide in the field test.

A3-2 Aluminide Coating for Inconel 625 Prepared by Additive Manufacturing: Investigation of the Surface Reactivity of the Substrate, *N. Ramenatte, L. Portebois, S. Mathieu, L. Aranda,* ***Michel Vilasi* (*michel.vilasi@univ-lorraine.fr*)**, University of Lorraine, France

The project FAIR intends to develop innovative microreactor-exchanger (MR-E) based on 3D printing manufacture in order to intensify the H2 synthesis process. The Ni-based Inco 625 was selected as substrate due to its satisfying high temperature properties. Notably, it can resist against Metal Dusting corrosion provided it is protected by an aluminum reach overlay. The present study made it possible to characterize the coating processes as well as the oxidation behavior of the as-obtained coated substrate in connection with the physicochemical properties of 3D printed alloys (SLM) and in comparison with the conventional melted alloys (CMA).

A. Synthesis of Inco 625 via SLM

This process was conducting using the following main (non-confidential) parameters: alloy powder with a 10µm diameter grain size, melting under Ar atmosphere (P=1bar) and cooling at 10^7 K/s.

The as-obtained substrates are constituted of supersaturated γ grain having the nominal composition of Inco 625 and a textured microstructure showing a grain elongation parallel to the direction of growth.

As expected, the superficial roughness is huge due to the occurrence of fine spherical particles just sealed on the surface.

The wanted mechanical properties are then recovered by applying a heat treatment performed in the conventional conditions.

B. Coating depositions by CVD and slurry processes

Aluminum surface enrichments were performed using two techniques: i) the pack-cementation as CVD technique which is well known and described in the literature and ii) the slurry process also widely implemented for pieces having complex geometry, such as pieces comprising internal small channels. For both techniques, the rate limiting step is the solid state diffusion of metallic elements.

The coating elaborations were carried out on crude SLM and CMA substrates by applying a two steps heat treatment:

- the first one allows the aluminum enrichments through an annealing i) at 640°C during 4h for the packcementation process and ii) at 640°C and then at 700°C during respectively 4h and 1h, for the slurry process.

- The second step allows the NiAl formation by interdiffusion of metallic species which was activated by a high temperature treatment at 980°C during 1h.

Whatever the process, after the first stage of heating treatment, the same coatings were obtained: they are 40 µm thick and are two-phased systems comprising Al3Ni and Al3Ni2. This situation is the consequence of the similar interdiffusion coefficient of metals in SLM and CMA. Moreover, the present experiments evidence obviously that the rate limiting step is effectively the solid state diffusion for both synthesis techniques

A3-3 High-Temperature Protective Coatings against Molten Nitrate Salts for CSP Technology*, **Gustavo García Martín (gustavo.garcia@rep-energysolutions.com)**,* REP-Energy Solutions, Spain*; V. Encinas Sánchez, M. Lasanta Carrasco, T. De Miguel Gamo, F. Pérez Trujillo,* Universidad Complutense de Madrid, Spain

The high demand for energy and its production through the burning of fossil fuel is one of the factors responsible for the impact of climate change on the Planet. This has revealed the need to develop and optimize renewable technologies.

Commercial concentrated solar power plants along with thermal energy storage systems, such as “parabolic trough”, are more attractive than other renewable energies because of their thermal storage capacity, and are used when the resource (sun) is not available

Molten nitrate salts are currently considered ideal candidates for heat transfer and storage applications because of their properties. However, these salts are known for their high corrosiveness, increasing the associated O&M costs and making this technology still expensive compared to other renewable sources. This situation leads to propose solutions for reducing costs in terms of materials for the thermal storage systems (tanks, pipes, valves and heat-exchangers). One of these solutions is the development of high-temperature corrosion-resistant coatings, since they would avoid using expensive alloys (such as Ni-based alloys). The use of high-temperature protective coatings would be a very suitable option for reducing costs in CSP technology, even more if they enable the widespread use of low-cost steels, such as ferritic-martensitic ones. Thus, this solution would allow not only overcoming the corrosion problems, but also reducing the Levelized Cost of Energy, which would have a significant impact on the CSP technology. In this respect, ZrO_2-based sol-gel coatings appear as suitable option both from a technological and economical point of view.

Thus, in this work, sol-gel zirconia-based coatings were deposited on ferritic-martensitic steels and tested in contact with Solar Salt at 500°C, results being compared with the uncoated substrate. Results were also compared to other steels of interest in CSP industry, such as austenitic stainless steels. The study was developed up to 2000 h under static conditions. Samples were characterized via gravimetric, SEM-EDX, and XRD.

Results showed the good behavior of the coated substrates, with very little weight variations after 2000 h of test in comparison with the uncoated ones, which exhibited significant weight gain and spallation. The good behavior of the proposed coatings was also observed by SEM-EDX and XRD, showing a protective diffusion layer of about 5 mm. Furthermore, results also showed the promising behavior when comparing with steels currently used in CSP industry.

Coatings for Use at High Temperatures
Room On Demand - Session AP

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

AP-3 Microstructural Growth and Oxidation Performance of Ti_xSi_y on γ - TiAl*, **Josefina Crespo Villegas (joseffina.crespo@polymtl.ca)**, S. Brown, E. Bousser,* Polytechnique Montreal, Canada*; M. Cavarroc,* Safran Tech, France*; S. Knittel,* Safran Aircraft Engines, France*; L. Martinu, J. Klemberg-Sapieha,* Polytechnique Montreal, Canada

For several decades now Ti-Al intermetallic compounds have been considered attractive materials for structural applications because of their low density and good mechanical characteristics. One area of particular interest is the use of γ-TiAl for low pressure turbine components of aircraft engines, as a replacement for much heavier Ni-based superalloys. Despite this advantage in terms of density, the usage of γ-TiAl is currently limited to the coldest low pressure turbine stages of the engine, due to its oxidation susceptibility above 750°C.

In the current work, we explore the oxidation protection of γ-TiAl using titanium silicide (Ti_xSi_y) coatings which have been shown to have strong temperature stability (melting point > 2000°C), and a relatively good oxidation resistance due to the growth of a protective SiO_2 oxide scale. The Ti_xSi_y coatings are synthesized in a two-step process: silicon is first deposited on γ-TiAl substrates by RF magnetron sputtering, and the coated substrates are then thermally annealed at 950°C in vacuum. The influence of (i) silicon thickness and (ii) thermal annealing time on the growth and the microstructure of the titanium silicides is investigated, with tested values ranging from 3–9.5 µm of silicon and 2-24 hours of thermal annealing. Both of these parameters are shown to directly affect the thickness and composition of the different zones in the γ- TiAl/Ti_xSi_y coating system. In particular, it is noted that beginning with a thicker silicon layer results in more varied compositions of Ti_xSi_y, and that increasing the annealing time improves the uniformity of each individual zone as well as increasing the total thickness of the coating system.

Following annealing, the oxidation performance of the coatings is tested by exposing them to a temperature of 900°C in air for 100 hours. The mass gains during oxidation are recorded, and changes to the chemistry and microstructure of the samples are analyzed. Oxidation of the coated samples is estimated to be parabolic, and all samples show a marked improvement in oxidation resistance, with mass gains 2-3 times lower than those observed for the bare γ-TiAl.

AP-4 Lowering Costs by Improving Efficiencies in Biomass Fueled Boilers: New Materials and Coatings to Reduce Corrosion (BELENUS)*, A. Illana, V. Encinas-Sánchez, M. de Miguel, M. Lasanta, G. García-Martín, **Francisco Javier Pérez Trujillo (fjperez@ucm.es)**,* Universidad Complutense de Madrid, Spain

The primary objective of BELENUS is to lower bioenergy CAPEX and OPEX by an average of 5 and 60% respectively. This will be addressed by preventing or mitigating corrosion as the main limiting factor through a holistic approach to prevent corrosion in the boiler, in particular in superheater (SH) tubes: a) new surface engineering: biomass corrosion highly resistant coatings on creep resistance materials; b) new strategies of welding and bending for coated tubes improving the quality and efficiency of boiler components; and c) new online corrosion monitoring system specifically designed for biomass CHP plants. In addition, the BELENUS solution will impact on other LCOE parameters by improving efficiency in the conversion (up to 42%), increasing a 5% the operational hours of the plant and plant life time (5 years) and reducing the fuel expenditure of the plant by optimising its use and providing flexibility by allowing the use of different types of biomass. Improved performance for high temperature material systems through the technological breakthroughs, will be evaluated and validated an innovative test protocol. Finally, modelling and lifetime prediction tools will be developed and cost analysis and Life Cycle Analysis (LCA) undertaken so the optimum materials and coatings are chosen from the durability, economic and environmental perspectives, maximising the sustainability in economic and environmental terms. BELENUS brings together a multidisciplinary consortium comprising the main stakeholders with leading utilities, steel and tube developers, boiler designer and specialized research institutions from across Europe. This synergy allows a direct transfer of results in TRL5 to be obtained in BELENUS as technical base to go further to higher TRL into commercial biomass electric power plants within less than 5 years.

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