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).

[1] R. Gilblas, T. Sentenac, D. Hernandez, and Y. Le Maoult, "Quantitative temperature field measurements on a non-gray multi-materials scene by thermoreflectometry," *Infrared Phys. Technol.*, 2014.

[2] W. Brandl, D. Toma, J. Krüger, H. J. Grabke, and G. Matthäus, "The oxidation behaviour of HVOF thermal-sprayed MCrAlY coatings," *Surf. Coatings Technol.*, 1997.

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.

[1] D. Texier, C. Cadet, et. al, Metall. Tensile behavior of Air Plasma Spray MCrAlY coatings : role of high temperature agings and process defects, *Mater. Trans. A* (2019) submitted.

[2] D. Texier, D. Monceau, et al., Micromechanical testing of ultrathin layered material specimens at elevated temperature, *Mater. High Temp.* 33 (2016) 325–337. doi:10.1080/09603409.2016.1182250

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 $_{vs\ Ag/AgCl}$ to -1060 mV $_{vs\ Ag/AgCl}$. 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.

Author Index

Bold page numbers indicate presenter