Coatings for Use at High Temperatures
Room California - Session A1-2

Coatings to Resist High Temperature Oxidation, Corrosion, and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Shigenari Hayashi, Hokkaido University, Sebastien Dryepondt, Oak Ridge National Laboratory, USA

1:30pm **A1-2-1 Effect of Pre- and Post-Coat Processing on the Fatigue Life of Coated Disk Alloys***, **James Nesbitt**, T Gabb, B Puleo,* NASA Glenn Research Center, USA*; R Miller,* Vantage Partners, USA **INVITED**

Increasing temperatures in aero gas turbines is resulting in oxidation and hot corrosion attack of turbine disks. Since disks are sensitive to low cycle fatigue (LCF), any environmental attack, and especially hot corrosion pitting, can seriously degrade the life of the disk. Application of metallic coatings is one means of protecting disk alloys from this environmental attack. However, since LCF is sensitive to surface conditions, pre- and post-coat processing can have a significant effect on the LCF life of coated bars.

Various pre-and post-coating conditions were examined with a Ni-45wt.% Cr coating applied by High-power impulse magnetron sputtering (HiPiMS) to a Ni-based disk alloy. Initial pre-coat surface conditions examined a grit blasted surface. Later pre-coat surface treatments involved wet blasting, two shot peening levels (8N-200% and 16N-200%) and a highly polished surface. Post-coat treatments involved two shot peening levels (4N-100% and 16N-200%) and a post-coat diffusion anneal in high purity Ar or a low PO_2 environment to encourage chromia scale formation. Half of the coated and uncoated bars were LCF tested at 760°C without further environmental exposure to evaluate the pre- and post-coat treatments. The second half of samples were either oxidized for 500 hours at 760°C in air, hot corroded for 50 hours at 760°C in air using a Na_2SO_4-$MgSO_4$ salt, or subjected to both exposures. Results of the LCF testing and post-test characterization of the various coatings will be presented and future research directions discussed.

2:10pm **A1-2-3 High-temperature Oxidation Resistance of Chromium-based Coatings Deposited by DLI-MOCVD for Enhanced Protection of the Inner Surface of Long Tubes***, **Alexandre Michau**,* CEA, France*; F Maury,* CIRIMAT, France*; F Schuster, J Brachet, E Rouesne, M Le Saux,* CEA, France*; R Boichot, M Pons,* SIMaP, France

For nuclear safety issues, there is an international effort to develop innovative “Enhanced Accident Tolerant Fuels” (EATF) materials. EATF cladding tubes are of particular interest because these components constitute the first barrier against radioactive fission species dispersal in case of accidental scenario such as LOCA (Loss of Coolant Accident). One of the EATF development objectives is thus to improve drastically the high-temperature steam oxidation resistance of the cladding tubes in LOCA situation (temperature up to 1200°C, water steam environment…). Let us recall that the actual nuclear fuel cladding tubes are made from Zr-based alloys (1cm in diameter, 0.6mm thick and more than 4m long).

Several alternatives for outer wall protection have been proposed worldwide but there is currently no solution for the inner wall protection. Upon LOCA transients, the fuel cladding may experience ballooning and burst due to the inner pressure and the high temperature achieved. Then, its internal surface can be exposed to steam environment at high temperature, leading to fast inner oxidation and other secondary degradation effects, which induce significant embrittlement and degradation of the claddings.

In order to resist to this harsh environment, Cr-based coatings deposited by low pressure DLI-MOCVD (Direct Liquid Injection of MetalOrganic precursors) have been investigated. These hard coatings could also be of use in high-temperature oxidative and corrosive environment such as in aeronautics and other industries to protect components with 3D complex geometries.

The process has been optimized to ensure a thickness uniformity along the tube through experimental studies coupled with numerical modeling of the reaction mechanism and the whole deposition reactor. Thanks to a suitable chemistry of the Cr precursor, bis(ethylbenzene)chromium, different coatings were deposited including: metal Cr, chromium carbides Cr_xC_y and mixed carbides $Cr_xSi_zC_y$.

The high-temperature behavior of these Cr-based coatings under oxidative atmospheres has been studied: HT XRD, TGA and various oxidation tests including pure steam environment followed by water quenching at room temperature to be representative of LOCA situations. Amorphous Cr_xC_y coatings showed the most promising properties. The results are discussed in terms of oxidation mechanisms and protection of the fuel claddings inner surface deduced from fine characterizations of the samples before and after the tests.

2:30pm **A1-2-4 A New Process to Produce Localized Chrome Coating and Platinum-Modified Chrome Coating for Protection against Type II Hot Corrosion***, **Zhihong Tang**, J McConnell, K Garing, S Sweeney,* Praxair Surface Technologies, Inc., USA

With increasing operating temperatures and more severe environments in today’s gas turbine engines, there is a need for a localized chromium diffusion coating for protection against type II hot corrosion and stress corrosion cracking. Conventional pack and vapor phase chromizing process have their limitations of applying such a local chrome coating. Masking for these processes is costly and often unsatisfactory. Therefore, pack and vapor phase chromizing process typically coat the entire part surface and then require undesirable post-coating treatment to remove excess chrome coating from locations where it is unwanted.

This presentation will discuss a new slurry based process that produces a localized chromium diffusion coating on the selected regions of gas turbine components in a controlled and accurate manner. No post-chromizing treatments such as machining or chemical treatment are required to remove excess chrome coating in comparison to conventional process. The resultant coating chemistry and microstructure meet the OEMs’ specifications. Other advantages of this new process include capability to coat large parts, and achieve uniform coating on parts having complex geometries such as shank and fir-tree root of turbine blades. This new slurry based process has been in production at Praxair Surface Technologies since 2015 yielding robust consistency in coating thickness and chemistry.

Based on this localized chrome coating technology, a platinum-modified chrome (PtCr) coating is under development. The addition of platinum can further enhance the resistance of chrome coating to type II hot corrosion attack. The PtCr coating process and its compatibility with other coating processes will be discussed.

2:50pm **A1-2-5 Characterization of Films Fabricated on AZ31 Magnesium Alloy by Heat Treatment and Immersion Methods***, **Hyunju Jeong**,* Pohang Iron and Steel Company (POSCO), Republic of Korea

There has been considerable interest in the use of magnesium and magnesium alloys because of their outstanding properties, although their low corrosion resistance inhibits widespread applications. Therefore, many studies have been carried out to investigate the corrosion behavior of magnesium and magnesium alloys. Various coating techniques have also been proposed to improve their surface properties and corrosion resistance.

In the present work,thin films fabricated by immersion in solution, deionized water and NaOH solution were studied on AZ31 magnesium alloy subjected to heat treatment**.** The films were grown by active reactions at the interface of the magnesium alloy and the solution due to the high temperature of the substrate. Surface morphologies showed that the surface of the magnesium substrates was covered by dense films formed in the initial stages of immersion. The results revealed that the surface structures were different from those of films grown by simply immersing in aqueous solution. Cross-sectional results showed that the films formed in NaOH solution with heat treatment were denser than those grown by DI water immersion. X-ray photoelectron spectroscopy results indicated that the films fabricated by immersion in solution with heat treatment were mostly composed of MgO and $Mg(OH)_2$ in both the outer and inner layers. Potentiodynamic polarization measurements revealed that the thin films could improve the surface properties, acting as passive layers.

3:10pm **A1-2-6 Degradation Processes of LSM Based Interconnector Coatings under the Conditions of Pressurized Steam Electrolysis***, **MariadelMar Juez Lorenzo**, V Kolarik, V Kuchenreuther-Hummel,* Fraunhofer ICT, Germany*; M Pötschke, D Schimanke,* Sunfire GmbH, Germany

To ensure energy for mobility in a post-fossil future, power-to-liquids converting electric power from renewable energy sources into liquid fuels is one of the approaches that have attracted attention. The steam electrolysis used to split water to hydrogen and oxygen is run under pressure up to 30 bar at temperatures around 850°C in order to achieve a high efficiency of the process. The impact of such severe conditions on the interconnector materials and coatings designed to retain the evaporating chromium is a crucial issue and needs detailed understanding to ensure a reliable operation.

Coatings of the type La-Sr-Mn oxide (LSM) were deposited on the interconnector material Crofer 22 APU by thermal spraying and by roll coating, the latter as a cost-efficient method. The samples were exposed in laboratory test autoclaves to 850°C and 30 bar in 100% water vapor up to 1000 h and in pure dry oxygen up to 3000 h, both representing the opposite extremes of the possible process atmospheres.

The LSM coating shows in water vapor a grain coarsening after 1000 h as well as a separation of grains with higher La content accumulated in the surface area and grains containing Mn in the interface area. Cr is detected very weakly in the areas with high La contents. In water vapor the oxide scales on the interconnector material with LSM coating are notably thinner than on the uncoated material. However, the LSM coating deposited by roll coating decomposes with the time to a coarse-grained lanthanum-rich phase in the surface area as well as in vicinity of the oxide scale and to a manganese-rich phase concentrated between them. The thermally sprayed LSM coating is more efficient in leading to thinner oxide scales, probably to its higher density. Additionally, it shows a less pronounced separation into the two phases.

After exposure to pure oxygen the LSM coating exhibits a homogeneous morphology with higher porosity in the case of the roll coating than for thermal spraying. Cr stemming from evaporation was found in the whole LSM coating when deposited by rolling and concentrated on the coating surface when thermally sprayed. The phases binding the Cr were identified by X-ray diffraction. After 1000 h the semi-conducting $LaCrO_4$ and $SrCrO_4$ are formed and after 3000 h $CrMn_2O_4$, which exhibits an electrical conductivity an order of magnitude higher than that of Cr_2O_3. The degradation processes influence the electrical conductivity of the chromium barrier coating.

3:30pm **A1-2-7 The Hot Corrosion Resistance of Hot-dip Aluminized Low Carbon Steel with Nickel Interlayer under Static Load***, Huan-Chang Liang, C Wang,* National Taiwan University of Science and Technology, Taiwan

The failure mechanism of hot-dip aluminized (HDA) low carbon steel with nickel interlayer under static loading was studied. The nickel interlayer was plated using electric method with a current density of 1.8 A/cm^2 for 10 minutes in Watts bath, followed by hot-dipped in molten pure aluminum (> 99.5 %) for 10 seconds at 700 ^{o}C. The specimens were smoothly deposited with 2 mg/cm^2 of $NaCl/Na_2SO_4$ salt mixture, with a portion of 50/50 wt. %. The tensile test with hot corrosion, induced by salt mixture, was carried out by applying a static load at 750 ^{o}C. The results show that the intermetallic layer of Ni/Al exhibits great adhesion and formability while the elongation of gauge length rising to 7 percent. Owing to the inter-diffusion between Ni/Al, the intermetallic layer gradually changes to laminar structure with higher nickel content which also contributes to enhance the performance. Meanwhile, hot corrosion induced by salt mixture reduces the amount of aluminum of the outer layer and lowers the thickness of Ni/Al intermetallic layer. As the perpendicular cracks formed, the salt mixture penetrate to the interface between substrate and coating layer causing the oxidation of the carbide and accelerating the phenomenon of break away. Overall, the HDA with nickel interlayer on low carbon steel could increase the lifetime about 5 times compared to bare material.

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