

Monday Morning, April 24, 2017

Coatings for Use at High Temperatures

Room San Diego - Session A1-1

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Prabhakar Mohan, Solar Turbines, USA, Anton Chyrkin, Forschungszentrum Jülich GmbH

10:00am **A1-1-1 High-resolution Studies of Phase Transformations in Metal/oxide Composite Films for High-temperature Applications, Gordon Tatlock, M Duffield, K Dawson, University of Liverpool, UK; D Hernandez-Maldonado, SuperSTEM Laboratory, UK; J Lewis, 2DHeat Ltd, UK INVITED**
A novel thick film technology has been developed for the manufacture of electric heating elements from partially oxidised Ni-Cr-Fe alloy powder. The sprayed films were a mixture of metallic alloys and Ni-based oxides and could be sprayed directly onto a substrate to give good thermal efficiency. Electron microscopy and analysis was used to monitor the transformations in the films during subsequent heat treatment. In particular, it was found that homogeneous grains of Cr and Fe doped Ni-based oxides were transformed into NiO grains containing numerous, ordered Ni, Cr and Fe rich spinel particles which grew topotactically within the matrix to give a uniform distribution of particles of about 40nm diameter. High resolution electron microscopy and analysis was used to study these transformations in detail; and the ionic site occupancy of the octahedral and tetrahedral sites in the spinel was determined by electron energy loss spectroscopy at the atomic scale.

10:40am **A1-1-3 High Temperature Corrosion Of Ni-Base Coatings For Boiler Applications - A Microstructural Study, Johan Eklund, J Phother-Simon, Chalmers University of Technology, Sweden; E Sadeghimeresht, University West, Sweden; L Johansson, T Jonsson, Chalmers University of Technology, Sweden; S Joshi, University West, Sweden; J Liske, Chalmers University of Technology, Sweden**

The increasing demand for energy and the urgent need to curb CO₂ emissions are global drivers for introducing new "green" fuels, such as biomass and waste, which can be fired in boilers to generate electricity. However, the resulting boiler environment is much more corrosive compared to power boilers burning fossil fuels. Among the most important corrosive constituents in the boiler environment are alkali chlorides (e.g., KCl). The corrosion problems are especially severe in the steam superheaters due to the relatively high material temperature. To mitigate corrosion so as to avoid unplanned stoppages and reduce maintenance costs, the maximum steam temperature is kept relatively low in these boilers, resulting in poor power efficiency.

To make electricity generation from biomass- and waste-fired boilers more competitive, the power efficiency has to be increased and maintenance costs decreased. This requires solving the fireside corrosion problems, e.g., by using new, more corrosion-resistant materials. However, the new materials must be both affordable and fulfil the stringent mechanical requirements of the application. Both in-plant studies and laboratory experiments mimicking the fireside conditions in boilers show that certain Ni-base alloys tend to be more corrosion resistant than low-alloyed steels and stainless steels in these applications. However, Ni-base alloys are much more expensive than the other materials. The demand for high corrosion resistance at a reasonable price can in principle be fulfilled by applying corrosion resistant coatings on a cheaper substrate material which satisfies the mechanical requirements.

In this work, Ni-base alumina- and chromia- forming coatings are sprayed on a low alloy (16Mo3) substrate using High Velocity Air Fuel (HVAf) technology. The samples are exposed isothermally at 600°C for up to four weeks under well-controlled conditions in the laboratory. The samples are subjected to environments containing alkali chloride + N₂ + O₂ + H₂O. Exposures in N₂ + 5%O₂ + 20%H₂O are used as reference. Coating performance is compared to 304L-type stainless steel and to the FeCrAl alloy Kanthal APMT. The oxidation kinetics are studied and the samples are investigated before and after the corrosion experiment using SEM/EDX of cross sections prepared by focused ion beam (FIB) and broad ion beam (BIB) milling.

11:00am **A1-1-4 Coatings for Oxidation and Hot Corrosion Protection of Disk Alloys, James Nesbitt, T Gabb, S Draper, NASA Glenn Research Center, USA; R Miller, Vantage Partners, LLC, USA; I Locci, University of Toledo, USA; C Sudbrack, NASA Glenn Research Center, USA**

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 potentially seriously degrade the life of the disk. Application of metallic coatings are one means of protecting disk alloys from this environmental attack. However, simply the presence of a metallic coating, even without environmental exposure, can degrade the LCF life of a disk alloy. Therefore, coatings must be designed which are not only resistant to oxidation and corrosion attack, but must not significantly degrade the LCF life of the alloy.

Three different Ni-Cr coating compositions (29, 35.5, 45wt.% Cr) were applied at two thicknesses by Plasma Enhanced Magnetron Sputtering (PEMS) to two similar Ni-based disk alloys. One coating also received a thin ZrO₂ overcoat. The coated samples were also given a short oxidation exposure in a low PO₂ environment to encourage chromia scale formation. Without further environmental exposure, the LCF life of the coated samples, evaluated at 760°C, was less than that of uncoated samples. Hence, application of the coating alone degraded the LCF life of the disk alloy. Since shot peening is commonly employed to improve LCF life, the effect of shot peening the coated and uncoated surface was also evaluated. For all cases, shot peening improved the LCF life of the coated samples. Coated and uncoated samples were shot peened and given environmental exposures consisting of 500 hrs of oxidation followed by 50 hrs of hot corrosion, both at 760°C. The high-Cr coating showed the best LCF life after the environmental exposures. Results of the LCF testing and post-test characterization of the various coatings will be presented and future research directions discussed.

11:20am **A1-1-5 High Temperature Oxidation Protection of γ -Titanium Aluminide using Amorphous (Cr,Al)ON Coatings Deposited by High Speed Physical Vapor Deposition, K Bobzin, T Brögelmann, C Kalscheuer, Tiancheng Liang, Engineering Institute - RWTH Aachen University, Germany**

In recent years great efforts have been made in the development of γ -TiAl alloys for use in aerospace applications such as turbines, where low densities and high temperature strength are required. However, γ -TiAl alloys show poor oxidation resistance at temperatures $T > 850$ °C due to the formation of a non-protective oxide layer consisting of a mixture of TiO₂+Al₂O₃ in air, which is easily spalled off, resulting in a shortened lifetime of the components. One promising way to overcome this problem is the deposition of an oxidation protective coating with low oxygen permeability at high temperatures. However, the interdiffusion between coating and substrate is still challenging even for advanced coatings such as MCrAlY (M = Ni or Co) and Al₂O₃ ceramic coatings, which have made great progress in increasing the oxidation resistance of γ -TiAl. The present work focuses on the (Cr,Al)ON coating system, inspired from its outstanding diffusion barrier properties. Four (Cr,Al)ON coatings with different Cr:Al and N:O ratios were deposited onto γ -TiAl substrate by the innovative high speed physical vapor deposition (HS-PVD) technology, which enables the deposition of oxygen-rich coatings in a stable plasma process without target poisoning. Basing on hollow cathode discharge (HCD) and gas flow sputtering (GFS), the HS-PVD made it possible to deposit (Cr,Al)ON coatings at a deposition rate > 8 $\mu\text{m}/\text{h}$. The amorphous microstructure of the as-deposited coatings was proved by X-ray diffraction (XRD) and investigated by transmission electron microscopy (TEM). The thermal stability of the coatings was evaluated by means of in-situ high temperature X-ray diffraction (HT-XRD) in air. It was confirmed that the amorphous structure even remained up stable to a temperature $T = 1,050$ °C. Moreover, cross-sectional SEM images of the coated samples after the HT-XRD measurements showed neither the formation of oxides at the coating substrate interface nor the interdiffusion of Ti into the coating, indicating a promising performance of the diffusion barrier. Furthermore, cyclic oxidation tests were conducted at $T = 950$ °C in air and the results demonstrated that the oxidation resistance of γ -TiAl has been improved by the (Cr,Al)ON coating significantly. Finally, the mass change Δm of the coated samples in the temperature interval between $T = 25$ °C and $T = 950$ °C was evaluated using thermogravimetric analysis (TGA). The results of the conducted research reveal a high potential of the HS-PVD deposited (Cr,Al)ON coatings for the oxidation protection of γ -TiAl at $T > 850$ °C in turbine applications.

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11:40am **A1-1-6 Cyclic Oxidation and Hot Corrosion Behaviour of Plasma Sprayed CoCrAlY/WC-Co Coating on Turbine Alloys**, *H Nithin, V Desai, Ramesh Matagondanahalli Rangarasaiah*, National Institute of Technology Karnataka, India

Components in energy-production systems suffer a variety of degradation processes as a consequence of complex multicomponent gas environment which include oxidation and molten-salt-induced attack. Coatings provide a composition that will grow the protective scale at high temperature having long term stability. Plasma thermal spraying has been used to deposit CoCrAlY/WC-Co composite coatings on turbine alloys of Hastelloy X and AISI 321(Midhani Grade). Thermo cyclic oxidation behavior of coated alloys was investigated in static air as well as in molten salt (Na_2SO_4 -60% V_2O_5) environment at 700°C for 50 cycles. The thermogravimetric technique was used to approximate the kinetics of oxidation. X-ray diffraction, SEM/EDAX and EPMA techniques were used to characterize the oxide scale formed. The CoCrAlY/WC-Co coatings showed lower oxidation rate in comparison to uncoated alloys. The coatings subjected to oxidation in air show slow scale growth kinetics and oxides of α - Al_2O_3 CoO and Cr_2O_3 were formed on the outermost surface where as accelerated oxidation induced by the molten salt exhibits metastable modification of Al_2O_3 . The preferential oxidation of Al and Cr blocks the transport of oxygen into the coating through pores and voids, thereby making the oxidation rate to reach steady state.

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