Coatings for Use at High Temperatures
Room San Diego - Session A1-2

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

1:30pm **A1-2-1 Pt Effect on Oxidation Resistance and Durability of β-NiAl Coatings : A Coupled *ab initio* and Physics-based Modeling***, **Prakash Patnaik,*** Gas Turbine Laboratory, Aerospace Portfolio, National Research Council, Canada*; K Chen,* Structures, Materials and Manufacturing Laboratory, Aerospace Portfolio, National Research Council, Canada

Possible new mechanisms of the beneficial effect of Pt on oxidation resistance and durability of β-NiAlcoatings were proposed using a coupled *ab initio* calculations and physics-based models combining thermal physical formulae and atomic diffusion theory. First, the beneficial effect of Pt on reducing the β-NiAl/Al_2O_3 interfacial tensile stress was assessed. The coefficients of thermal expansion (CTE) of Pt, β-NiAl and β-NiAl+Pt were calculated using *ab initio* method and thermal physical formulae. The calculated CTE of the β-NiAl, along with the experimentally measured CTE of Al_2O_3, were then incorporated into the interface stress model to evaluate thermal tensile stress at the undulated β-NiAl/Al_2O_3 interface. The results showed that addition of Pt to b-NiAl coating significantly reduced the interfacial tensile stress, thus contributing to the improvement of thermal cyclic durability of the coating. Second, the beneficial effect of Pt on lowering the diffusivity of sulfur in b-NiAl was evaluated. The apparent activation energy and the pre-exponential factor of diffusivity via the next nearest neighbour atom transportation were analyzed, and the bonding characteristics of sulfur with its surrounding atoms were calculated and compared with experimental results to elucidate the diffusion process of sulfur. Addition of Pt in b-NiAl was found to significantly reduce the diffusivity of sulfur, thus supressing the detrimental segregation of sulfur to the β-NiAl coating/a-Al_2O_3 scale interface.

1:50pm **A1-2-2 Synthesis and Characterization of Superalloy Coatings by Cathodic Arc Evaporation***, J Ast,* Laboratory for Mechanics of Materials and Nanostructures, Empa, Switzerland*; M Döbeli,* Ion Beam Physics, ETH Zurich, Switzerland*; A Dommann,* Center for X-ray Analytics, Empa, Switzerland*; M Gindrat,* Oerlikon Metco AG, Switzerland*; X Maeder,* Laboratory for Mechanics of Materials and Nanostructures, Switzerland*; A Neels,* Center for X-ray Analytics, Empa, Switzerland*; P Polcik,* Plansee Composite Materials GmbH, Germany*; **Jürgen Ramm**, H Rudigier,* Oerlikon Surface Solutions AG, Liechtenstein*; K von Allmen,* Center for X-ray Analytics, Empa, Switzerland*; B Widrig,* Oerlikon Surface Solutions AG, Liechtenstein

Superalloy targets were produced from Ni-(Al-C-Co-Cr-Mo-Ta-Ti-W) and Ni-(Al-B-C-Co-Cr-Hf-Mo-Ta-Ti-W-Zr) powders. The crystalline structure of the as produced targets was investigated by XRD analysis and compared with the development of phases resulting from the operation of the cathodic arc at the target (cathode) surface. The targets were utilized to synthesize coatings at different substrate materials from the pure metallic vapour. Deviations in the compositions of the superalloy targets and the synthesized coatings are discussed. The interfaces between coating and different substrate types are investigated by TEM for the as deposited state and after high temperature cycling at 1200°C. In addition to the non-reactive cathodic arc evaporation, the superalloy targets were evaporated in pure oxygen environment and the influence of the oxygen reactive gas is investigated for the processes at the cathode surface and for the synthesized oxygen containing coatings. This has been done for the synthesis of partially as well as fully oxidized coatings. Also for these coatings, high temperature cycling was performed. The diffusion processes in the interface to the different substrates and to the coating surface are investigated by cross-section TEM analysis and a combination of RBS and ERDA analysis. XRD analysis was utilized to demonstrate the differences in the phase formation after high temperature cycling depending on the oxygen content of the coating.

2:10pm **A1-2-3 High Temperature Binary or Doped Nickel Aluminide Coatings on Superalloys: An Industrial Approach***, **Vasileios Papageorgiou**, S Vogiatzis, H Strakov, A Zainal, M Auger,* IHI Ionbond AG, Switzerland

The ongoing demand for remarkably efficient turbine engines for aircraft propulsion and power generation has always been paced by the results of development of higher strength-at-temperature superalloys. However, the compositional requirements for improved high temperature strength and optimum high temperature oxidation and hot corrosion resistance are in general not compatible. A way to solve this problem is to apply coatings which provide adequate protection against oxidation and corrosion, while the composition and microstructure of the substrate are fully optimized for high temperature strength. A modern technique which allows not only the single deposition of such a coating but even the controlled alloying of it with additional elements, by means of various metal halides, is the so-called Chemical Vapor Aluminizing (CVA). Into this work, the industrial CVA technology is used to demonstrate its advantages using tight process deposition control of any binary NiAl coating and to promote various advanced co-deposition processes with addition of different metal elements such as Cr, Si, Co, Zr and Hf to the aluminide coatings. As the major challenge for the development of compatible high temperature coating systems is the coating resistance against spallation induced by thermal cycling, elevated temperature cycling oxidation tests been also performed and presented respectively.

2:30pm **A1-2-4 Corrosion Behavior of Iron Based Alloys Coated with Aluminum Oxide by RF Magnetron Sputtering***, D Melo-Maximo, L Melo-Máximo, A Murillo, O Salas, **Brenda García**,* ITESM-CEM, Mexico*; E Uribe,* ITESM-QRO, Mexico*; J Oseguera,* ITESM-CEM, Mexico

Metal dusting is a common problem in Fe, Ni and Co based alloys exposed to a corrosive environment. Several studies show that the presence of aluminum oxide coatings is a viable alternative to offer protection against this type of corrosion. Based on these studies, the main objective of this work was to evaluate the potential of thin film aluminum oxide coatings as a protective coating for iron based alloys. The coatings were produced by reactive magnetron sputtering with an RF power supply on 304L steel. Coated and uncoated samples were exposed to an atmosphere of CH_4+H_2+residual oxygen at 800°C in a thermobalance. The results indicate that the Al oxide thin films are promising coatings for the protection of ferrous materials in C-rich corrosive atmospheres at high temperature.

2:50pm **A1-2-5 Effect of the Microstructure on Corrosion and Deformation Behavior of Zn-Mg Coatings on Steel Substrate***, **JoungHyun La**, K Bae, S Kim, S Lee, Y Hong,* Korea Aerospace University, Republic of Korea

Zn-Mg alloy is a strong candidate for the protective coating material of steel sheets due to the excellent corrosion resistance of Zn-Mg alloy compared with pure Zn. However, during the PVD process Zn-Mg coatings show the various structures such as amorphous and crystalline depending on the deposition conditions. In this study, the Zn-Mg coatings with various structures were synthesized on the steel substrate using sputtering process and the effect of structure on corrosion and deformation behavior of Zn-Mg coated steel were investigated. The microstructure and the crystal phase of the Zn-Mg coatings were evaluated using the field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). The corrosion and deformation behavior of Zn-Mg coated steel were investigated using the salt spray test (SST) and the punch stretching test (PST). The Zn-Mg coatings synthesized below 50^{o}C showed the amorphous and featureless structure while the porous crystalline Zn-Mg coatings were synthesized above 100^{o}C. The Zn-Mg coated steel with amorphous coating showed the enhanced corrosion resistance compared to that with crystalline Zn-Mg coating. By contrast, during plastic deformation of Zn-Mg coated steel the cracks and the detachments on the amorphous coatings were generated. The featureless microstructure of the amorphous Zn-Mg coatings improved its corrosion resistance by obstructing the direct pathway between a corrosive environment and the substrate, but the intrinsic brittleness of amorphous structure degraded the ductility and formability of coating.

Acknowledgement

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3:10pm **A1-2-6 A Comparative Analysis of Ternary Element Addition on Corrosion Behavior of Aluminide Coatings in Harsh Environmental Conditions***, **Umutcan Erturk**, B Imer,* Middle East Technical University, Turkey

Ni-based super alloys are widely used in industrial gas turbines due to their excellent mechanical strength and creep resistance at high service temperatures. Diffusion coatings including aluminide coatings are widely preferred to improve high temperature oxidation and corrosion resistance of turbine blades. Aluminide coatings form stable oxides that prevent oxygen diffusion to substrate materials. Increasing durability of aluminide coating is an important design criterion to extend life time of turbine blades. It is well-known that addition of reactive and alloying elements have beneficial effect on oxidation behavior of aluminide coatings. Many studies show that addition of hafnium, yttrium, zirconium, chromium, platinum and cobalt improves performance of aluminide coating by increasing oxide adherence and selective oxide formation rate. However, addition of these elements may have adverse effect such as surface rumpling, martensitic transformation and formation of unstable oxides. In this research, effect of ternary elements (Hf, Y, Zr, Y/Zr, Y/Hf) addition on aluminide coating corrosion behavior were investigated. Ternary element addition to aluminide coatings was done by chemical vapor deposition for five different sample set. Accelerated isothermal corrosion tests were conducted under natural gas exhaust. To simulate harsh environmental conditions, Na_2SO_4 and V_2O_5 containing solutions were applied to substrate surface prior to corrosion test. Sampling and weighing was performed in varying periods for each sample set. Mass change data plotted against time to observe oxide formation and spallation behavior of coatings. Microstructural changes and oxide layer thicknesses was analyzed by scanning electron microscopy (SEM). Compositional changes in aluminide coating after corrosion tests was examined by energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS). Formation of metastable oxide phases and undesirable coating phases was analyzed by X-ray crystallography (XRD). Subsequently, effect of ternary element additions on aluminide coating corrosion behavior were analyzed to extend life time of turbine blades.

3:30pm **A1-2-7 Cyclic and Isothermal Corrosion Testing of Aluminide Slurry Coatings in Molten Nitrates for Heat Storage in Concentrated Solar Power Plants***, **Alina Agüero**, S Rodríguez, P Audigié,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

In concentrated solar power plants, thermal energy storage is possible by means of heat transfer fluids (HTF) such as molten nitrate mixtures, which are currently in use in several plants world-wide. Molten nitrates have a high working temperature (» 570 ºC), good thermal and physical properties as well as an excellent capability for thermal energy storage overnight. The molten salt mixture is circulated through steel or Ni based alloy piping in the CSP receiver during the day and held in storage tanks to be used when needed to create superheated steam. This technology is still very expensive as compared with traditional fossil fuels and other renewable sources to produce energy, in particular with photovoltaics which have experienced an important price reduction quite recently. By increasing thermal efficiency, cost reduction can be achieved in concentrated solar plants with molten salt heat storage. Obtaining supercritical steam by increasing pressure and temperature constitute a strategy to achieve this goal. This requires new salt mixtures with higher thermal stability properties as well as understanding the materials corrosion behavior, and finding methods to prevent it or at least mitigate it when using low cost steels instead of expensive Ni based alloys. Coated ferritic or carbon steels are an alternative for the tubing and the storage tanks respectively in solar concentration tower plants. In particular, slurry aluminide coatings are a low cost alternative that allow uniform coating of internal surfaces. Some published work is available regarding the behavior of steels and Ni base alloys under exposure to molten nitrates but little is known of the performance of slurry aluminide. Moreover, the type of oxides formed on steels as well as the mechanisms of formation has not been studied in depth. In this work the comparison of the behavior of coated and uncoated carbon steel A516, and P91 a 9 wt. % Cr ferritic steel, exposed to the molten so called “Solar Salt” (eutectic mixture of 60 % $NaNO_3$ – 40 % KNO_3) at 580º C under both isothermal and cyclic conditions. The coating provides very high resistance to molten nitrate corrosion up to 2000 h both under cyclic and isothermal conditions exhibiting only a very slight weight loss under cyclic corrosion, conditions attributed to losses of the protective oxide. On the other hand the uncoated materials develop thick oxides with a stratified, loosely coherent and little adherent morphology, with oscillating Cr concentration on P91 and under cycling conditions a high degree of spallation was observed.

3:50pm **A1-2-8 Sol-gel ZrO_2-Y_2O_3 Coatings Validated in Molten Salt Environment for CSP Applications***, V Encinas Sánchez, M Lasanta, M de Miguel, G García Martín, **Francisco Javier Pérez Trujillo**,* Complutense University of Madrid, Spain

Material degradation owing to corrosion has been an important subject of study related to molten salts and CSP plants. Ferritic-martensitic steels have been widely used for industrial applications mainly because of their cost, despite of their properties, which are worse in comparison with other materials, such us stainless steel, since they are prone to localize corrosion from severe effects. To prevent this phenomenon occurrence numerous methods can be used, one of them being the use of protective coatings. Numerous methods exist for the preparation and deposition of coatings, sol–gel coatings and dip-coating technique presenting many advantages. On the one hand, frequently, sol-gel protective coatings are formed by oxides. Within them, yttrium-stabilized zirconia seems to be a great option because of its properties. On the other hand, sol-gel solutions can be deposited through various methods (spin-coating, spraying, electro-deposition, dip-coating, etc.) Dip-coating technique is an easy deposition solution that allows the preparation of uniform coatings through an easy control of the withdrawal rate at low cost.

Thus, the aim of this work was to obtain ZrO_2-Y_2O_3 coatings deposited on P92 substrates under various conditions and evaluate their protective behavior against corrosion through static immersions tests in molten salts.

Previously superficially modified coupons of P92 were dip-coated with the prepared sol-gel solution of ZrO_2-Y_2O_3 at the withdrawal rate of 25 $mm \cdot min^{-1}$ and thermally treated at 500ºC. The yttria-doped zirconia solution was synthesized by a previously reported procedure. After characterizating, the samples were tested through isothermal immersion tests in a nitrate molten salt mixture (60 wt.% $NaNO_3$/40 wt.% KNO_3) at 500ºC for 1000 h and evaluated via gravimetric at various times. The study was developed by static tests. The samples were characterized after 500 and 1000 h of testing by SEM and XRD.

The gravimetric results show the good behaviour of the coated substrates in comparison with the uncoated ones. One of the reasons of this behaviour would be probably the high uniformity and compaction obtained at this withdrawal rate, which was selected on the basis of a previous work.

The good behaviour of these coatings is also observed by SEM-EDX and XRD. In SEM-EDX cross-section is observed the compact appearance of the coatings coated at 25 $mm \cdot min^{-1}$. SEM and XRD also show the good behaviour of the coatings after 1000 hours of testing.

From results it is concluded that ZrO_2-Y_2O_3 coatings could be suitable for solar applications. However, it would be interesting to study this system at longer times and using more coating layers.

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