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 CO_2 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 600ºC for up to four weeks under well-controlled conditions in the laboratory. The samples are subjected to environments containing alkali chloride + N_2 + O_2 + H_2O. Exposures in N_2 + 5%O_2 + 20%H_2O 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 ZrO_2 overcoat. The coated samples were also given a short oxidation exposure in a low PO_2 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 TiO_2+Al_2O_3 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 Al_2O_3 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 µm/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.

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 Motagondanahalli 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 700ºC 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.

Coatings for Use at High Temperatures
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Coatings to Resist High Temperature Oxidation, Corrosion and Fouling

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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°C showed the amorphous and featureless structure while the porous crystalline Zn-Mg coatings were synthesized above 100°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

This study is financially supported by the Smart Coating Steel Development Center, WPM(World Premier Materials) Program of the Korea Ministry of Knowledge Economy.

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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8:00am **A1-3-1 Thin Co and Ce/Co Coatings on Ferritic Stainless Steel Interconnects for Solid Oxide Fuel Cells***, **Hannes Falk-Windisch**, M Sattari, L Johansson, J Svensson, J Froitzheim,* Chalmers University of Technology, Sweden

The use of Cr_2O_3-forming alloys for Solid Oxide Fuel Cell (SOFC) interconnects is challenged by the volatilization of Cr (VI) species that causes cathode poisoning and by rapid oxide scale growth causing increased electrical resistance. This work investigates the use of Cobalt (Co) and Cerium (Ce) nano coatings to mitigate both degradation mechanisms. The work involves coating the ferritic stainless steel Sanergy HT, which is designed for use as SOFC interconnects, with 640 nm Co and with 10 nm Ce + 640 nm Co using Physical Vapor Deposition (PVD). The materials were exposed in air at 650-850 ˚C for up to 3000 h and chromium volatilization, oxide scale growth and electrical resistance were studied. Mass gain was recorded to follow oxidation kinetics, chromium evaporation was measured using a denuder technique, and Area Specific Resistance (ASR) measurements were carried out on exposed samples. The oxide scale microstructure was characterized using Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM), and Energy Dispersive X-Ray Analysis (EDX). The results show that thin Co coatings effectively mitigated Cr volatilization. Sandwiching a 10 nm Ce layer between the Co coating and the steel greatly improved oxidation resistance, especially at higher temperatures. Also, ASR measurements revealed that the Ce + Co coated material had lower electrical resistance after exposure than the same material coated with only Co. The effect was attributed to the thinner scale formed on the steel coated with Ce + Co. The results imply that the duplex, Co + Ce thin film coating is suitable for ferritic stainless steel interconnects in Solid Oxide Fuel Cells.

8:20am **A1-3-2 Long-term Oxidation of MCrAlY Coatings at 1000 ^{o} C and an Al-activity Based Coating Life Criterion***, **Pimin Zhang**, Y Kang, R Lin Peng,* Linköping University, Sweden*; X Li,* Siemens Industrial Turbomachinery AB, Sweden*; S Johansson,* Linköping University, Sweden

MCrAlY type (M=Ni and/or Co) coatings are widely used for the protection of components in the hot sections of gas turbines at high service temperatures by forming a continuous α-alumina. A reliable criterion to estimate the capability to form α-alumina is of great importance to accurately evaluate coating lifetime. However, the traditional Al-concentration based criterion failed to properly predict the formation of a continuous α-alumina. Thus, a new life criterion, namely the critical Al-activity criterion, is proposed.

In this work, critical Al-activity to form a continuous α-alumina is calculated using Thermo-Calc software, based on literature survey of research results of critical Al-concentration to form α-alumina on binary Ni-Al and ternary Ni-Cr-Al system. Long-term oxidation test were performed to support the criterion: IN-792 superalloys coated with five different MCrAlY coatings were oxidized at 1000 ^{o}C for various periods of time up to 10000 hours. The microstructural evolution of MCrAlY coatings were analyzed using Scanning Electron Microscope. The near-surface Al concentration and interdiffusion behavior between substrate and coating were measured using Energy Dispersive X-ray Spectroscopy. The new critical Al-activity criterion has been successfully adopted in α-alumina formation prediction, showing a good agreement with experiment results. Therefore, it can be concluded that the extrapolation of new criterion from binary and ternary systems to multi-alloyed MCrAlY system is reasonable. Furthermore, the partial pressure of oxygen (P_{O2}) in atmosphere has been taken into consideration by combination with Al-activity to calculate the Gibbs energy of formation of α-alumina. The potential applicability of the methodology to predict MCrAlY life is also discussed .

8:40am **A1-3-3 The Preparation of Ti_2AlN MAX Phase Coatings and its Oxidation Mechanism under Different Atmosphere***, **Zhenyu Wang**,* University of Chinese Academy of Sciences, China*; P Ke, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Ti_2AlN belongs to a family of ternary nano-laminate alloys known as the MAX phases, which exhibit a unique combination of metallic and ceramic properties. In the present work, the dense and high-stability Ti_2AlN coating has been successfully prepared on Ti6Al4V (TC4) substrates through combined cathodic arc/sputter deposition method, followed by heat post-treatment. The oxidation of Ti_2AlN coating and the TC4 substrates were investigated in air and in water vapor at 750 °C for 200h. The results indicated that the oxidation processes of both TC4 substrates and the coated samples were accelerated for the presence of steam, resulting in slightly higher mass gains. The oxidation behavior of the bare substrates under different atmosphere exhibited linear kinetics, which indicates a continuous oxidation during its exposure at high temperatures. In contrast, the mass gain was significantly reduced for the coated samples, suggesting that the Ti_2AlN coating can provide an effective protection for the substrates. Moreover, the Ti_2AlN phase can still be found after oxidation in air atmospheres for 200h and the oxide scale showed local Al_2O_3 and rutile TiO_2 growth, namely the oxide did not cover the entire surface of the coating. However, the Ti_2AlN phase disappeared after oxidation in steam condition and double layer scales formed in the water vapor atmospheres, consisting of an outer rich-Al_2O_3 layer and an inner rich-TiO_2 layer. The enhanced oxidation resistance achieved under different condition by the Ti_2AlN MAX phase coatings may satisfy the optimal requirements for many applications in the field of nuclear power plants and aerospace components.

9:00am **A1-3-4 Effect of Coating Architecture on the Corrosion Behavior of Ti-N/Cr-N Multilayer Coatings***, **Yu-Sen Yang**,* National Kaohsiung First University of Science and Technology, Taiwan

Two coating architectures with distinct period number (PN) of Ti-N/Cr-N multilayer coatings were prepared by reactive magnetron sputtering process. Two coating architectures were designed as the multilayers TiN/CrN/…CrN/TiN/Ti/substrate (architecture T) and the CrN/TiN…TiN/CrN/Cr/substrate (architecture C). Four PNs with 1,5,10 and 15 were prepared in architecture T and C, respectively. This study investigates the effect of the coating architectures and PNs on the corrosion behaviors of the coatings. The corrosion rate were tested by immersion the coatings in the 3% HCl solution for 20 hours to measure the weight loss. The results show that the corrosion rate of the coatings were strongly related to the coating architecture and PN. In coating architecture T, the corrosion weight loss is decreased with PN increased. On the contrary, in architecture C, the corrosion weight loss is increased with increasing PN.

9:20am **A1-3-5 Effects of Encapsulating Material and Healing Agent Ratio on Crack Propagation Behavior for Thermal Barrier Coatings***, **Soo-Hyeok Jeon**, S Lee, S Jung, H Park, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Purdue University, USA

Thermal barrier coatings (TBCs) are important parts to protect metallic substrate in gas turbine engines because turbine inlet temperature is continuously increased to improve fuel efficiency. Recently self-healing TBCs have been proposed to prevent delamination and spalling of TBCs during gas turbine operation. In this study, $MoSi_2$ as the healing agent was coated by three kinds of materials such as tetraethyl orthosilicate (TEOS), sodium methoxide (NaOMe), and their mixture (TEOS + NaOMe) for stabilizing $MoSi_2$ at high temperatures. YSZ and capsulated $MoSi_2$ were mixed with 90:10, 80:20, and 70:30 wt% ratios, respectively. Samples were fabricated by uniaxial compaction at 100 MPa and then sintered at 1300 ^{o}C and 1500 ^{o}C, respectively. Crack propagation behavior was investigated as functions of $MoSi_2$ stabilizing agent, stabilized $MoSi_2$ content, and sintering temperature. Furnace cyclic test (FCT) was performed at 1100 ^{o}C for a dwell time of 40 min, followed by natural air cooling for 20 min at room temperature, after generating artificial cracks in TBC samples by using Vickers indentation. The TBC sample with the $MoSi_2$ of 20 wt% capsulated with the mixture of TEOS and NaOMe and sintered at 1500 ^{o}C showed the best healing effect in FCT test. This study allows us to design reliable TBC systems in operating conditions.

9:40am **A1-3-6 Comparative Study of Monolayer and Multilayer CrAlSiN PVD Coatings Behavior at High Temperature in Steam Atmosphere**, *A Illana, S Mato,* Complutense University of Madrid, Spain*; E Almandoz, G Garcías Fuentes,* Navarra Industry Association, Spain*; F Pérez Trujillo,* ***MaríaIsabel Lasanta****,* Complutense University of Madrid, Spain

Technological developments around electric generation power plants aim to increase thermal efficiency of conversion processes in steam turbines, developing materials able to resist ultra-supercritical (USC) vapor conditions at 600-650°C and 35 MPa. Ferritic-martensitic steels, commonly used so far, show very low oxidation resistance at these conditions. The solution is to modify their surface, by means of protective coatings that retard interdiffusion mechanisms which take place at that temperature range and to prolong their service life.

Hard coatings based on nitrides and deposited by PVD have been commonly applied in cutting tools, since possess tribological features that increase their wear and oxidation resistance in aqueous media, mainly alkaline and neutral. CrN coatings have been broadly employed for last decades for this application. The incorporation of Al and/or Si in these films produces an improvement in the mechanical properties, due to hardening for grain refining (Hall-Petch effect), and an increase of thermal resistance against oxidation in comparison to the pure CrN , due to the formation of protective oxides that avoid the migration of oxygen towards the substrate.

In order to contribute to the knowledge on this topic, a monolayer and two multilayers with different periodic thickness of magnetron-sputtered CrAlSiN coatings with similar Cr/Al ratio and Si content were deposited on P92 ferritic-martensitic steel and tested to assess their protection capability under the working conditions of USC steam turbines operation (at 650ºC in 100% steam atmosphere) during 2000 h. Common characterization techniques have been used to achieve this objective, such as: gravimetry analysis in order to study the kinetics of oxidation, x-ray diffraction (XRD) to explored the phases formed during the oxidation process and scanning electron microscopy with energy dispersive detector (SEM-EDX) to evaluate the morphology and semi-quantitative composition of the films.

CrAlSiN coatings have showed a significant improvement to the oxidation resistance of the bare substrate (P92 steel), due to the formation surface oxide layers. Cr_2O_3, SiO_2 and Al_2O_3 resulted more effective against the ionic interdiffusion and with greater compactness, which lead to a reduction of the oxidation rate at isothermal USC vapor conditions. After 2000 h of test, coated samples have shown no diffusion of species from the substrate into the coating and they have presented oxidation kinetics that follow a parabolic trend, typical of the material which has developed a protective oxide on the surface at high temperature.

10:00am **A1-3-7 Material Validation in Molten Salt Environment under Dynamic Conditions Using a Novel Pilot Plant Facility**, *M Lasanta, G García Martín,* ***Víctor Encinas Sánchez****, M de Miguel, F Pérez Trujillo,* Complutense University of Madrid, Spain

Solar thermal plants which concentrate the Sun's energy to produce steam and electricity often use molten salt mixtures as a heat transfer fluid (HTF) and/or as thermal energy storage (TES) medium. The most industrial compound used is an alkali-nitrate mixture composed by 60 wt.% $NaNO_3$/40 wt.% KNO_3 (Solar Salt®). On the other hand, corrosion behavior of materials is a very important issue as regards the molten salts and CSP plants. Up to now, all studies have been carried out through static immersion tests, parameters such as dynamic flow in contact with the substrate, oxidizing gas atmosphere and thermal cycling being dismissed. Thus, the aim of this work was to introduce a novel pilot plant facility and evaluate the corrosion resistance of A516 and 304 steels in Solar Salt in dynamic condition test at 500 ºC using it. The equipment used allows degradation tests of materials in contact with molten mediums simulating thermo-cycling process and keeping the stable conditions during whole studies. These results were compared with the static ones in order to evaluate the effect of the fluid-dynamics.

The isothermal dynamic and static immersion test results were analyzed via gravimetric measurements. Both tests were carried out at 500 ºC. The tested specimens were analyzed after 100 hours of testing and were characterized by SEM-EDX and XRD.

The average weight gain measured in the samples tested by dynamic test was higher than that measured by the static test. Dynamic test approach reproduce the conditions of CSP plants in a better way. Thus, results obtained by dynamic test are considered more reliable for the corrosion prediction behavior of the CSP plants. Furthermore, useful information was extracted from the tested samples after characterizing. The surface appearance of the two samples was quite different, the sample subjected to dynamic test showing more detachments. As expected, the greater thickness of the oxide layer on the sample subjected to the dynamic test was observed in the cross-section micrographs. XRD measurements confirm the observed species in SEM-EDX.

Experiments demonstrated how dynamics tests provokes an increase in corrosion rates, since mass gained is quite greater in samples subjected to dynamic tests than the ones gained through static tests. These results are also confirmed by SEM. This work is a new step forward in the future experimentation for materials and engineering processes for future CSP plants with molten salts.

Coatings for Use at High Temperatures
Room Sunrise - Session A2-1

Thermal and Environmental Barrier Coatings

Moderators: Lars-Gunnar Johansson, Chalmers University of Technology, Sweden, Kang Lee, NASA Glenn Research Center, USA

2:10pm **A2-1-3 Property Comparisons of Air Plasma Sprayed and Dense Homogeneous Yttrium Disilicate***, **Cory Parker**, R Golden, E Opila,* University of Virginia, USA

Modeling efforts for Rare Earth (RE) silicate Environmental Barrier Coatings (EBCs) typically utilize properties of dense homogeneous materials, yet EBCs are often processed using an Air Plasma Spray (APS) process which results in heterogeneous phase distribution, porosity, and splat microstructures. In this paper, properties of dense homogeneous yttrium disilicate processed by Spark Plasma Sintering (SPS) are compared to those of APS yttrium disilicate. Specifically, phase stability during thermal cycling, thermal expansion, and stability in high temperature steam are compared. Phase changes during repeated temperature cycling were characterized with X-ray diffraction. APS phase mixtures evolved during cycling whereas SPS yttrium disilicates were more phase stable. Thermal expansion of both materials was characterized up to 1400°C using dilatometry. Coefficients of Thermal Expansion (CTE) for APS yttrium disilicate varied significantly without a prior annealing treatment. Once annealed, the CTEs for the SPS material were significantly more consistent than those of the APS material. The silica depletion depth for yttrium disilicate samples was measured after steam-jet exposures at 1200°C for times of 60 to 250 hours and steam velocities between 150-180 m/s. The silica depletion rate was lower in dense homogeneous SPS yttrium disilicate compared to the more porous and heterogeneous APS materials. Cross sectional analysis of APS specimens showed both silica depletion to greater depths at splat boundaries and localized yttria-rich areas with minimal silica depletion. The implications of the heterogeneity of APS RE silicate phases and microstructures for EBC applications will be discussed.

2:30pm **A2-1-4 Performance of Vacuum Plasma Spray Bond Coatings***, **Michael Lance**, A Haynes, B Pint,* Oak Ridge National Laboratory, USA

The effects of composition, temperature and environment on the performance of vacuum plasma sprayed (VPS) NiCoCrAlYHfSi bond coatings (BC) on directionally-solidified (DS) 247 substrates with air plasma sprayed Y_2O_3-stabilized ZrO_2 has been investigated. Four compositions were investigated including the base composition and additions of Ti, B and Ti+B. The addition of B did not improve the average coating lifetime in 1-h cycles at 1100 °C in air with 10% H_2O in either case, however, the addition of Ti caused a decrease in lifetime. Photo-stimulated luminescence spectroscopy was used to map residual stresses in the thermally-grown Al_2O_3 scale. To study performance near the operating temperature of BCs in land-based turbines, the effect of water vapor was studied at 900 °C in laboratory air and air with 10% H_2O for 10-500 h cycles. Water vapor had little effect on the measured parabolic rate constants at 900 °C and a comparison of the oxide microstructures will be reported.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy's Turbine Program.

2:50pm **A2-1-5 Predicting Microstructural Evolution in Aluminide Coatings during Manufacturing and Degradation in Service***, **Rishi Pillai**, A Chyrkin, T Galiullin, W Leng, D Grüner, D Naumenko, W Quadakkers,* Forschungszentrum Jülich GmbH, Germany **INVITED**

Protective metallic nickel aluminide (NiAl) diffusion coatings enhance the oxidation and corrosion resistance of the underlying high temperature materials. Aluminising provides a cost effective alternative and allows coating of complex shaped components. However, the composition of the substrate and the specimen geometry influence the final coating microstructure during the aluminising process and govern the high temperature behaviour of the coating system during subsequent exposure.

The formation of a protective alumina scale and the diffusion from the coating into the substrate result in the loss of Al and thereby the dissolution of the ß-NiAl phase in the coating. The extent of interdiffusion depends on the coating and substrate composition. The compatibility of a given type of a coating with its base material substantially influences the performance of a coated material during service. Potentially detrimental precipitate phases may form especially in the interdiffusion zone (IDZ) during the aluminising process and during subsequent service depending on the composition of the base material. Evaluation of the material's high temperature behaviour requires extensive experimental testing. Computational methods can substantially reduce the extensive experimental efforts required for coating evaluation and qualification.

In the current work, an in-house developed coupled thermodynamic and kinetic computational model was employed to predict the microstructural evolution in nickel aluminide (NiAl) diffusion coatings on Ni-base wrought and cast alloys during the coating (aluminising) process as well as during the subsequent high temperature service. Three Ni-base alloys (602 CA, IN718 and Rene80) were chosen to evaluate the influence of specimen thickness and alloy composition on the performance of nickel aluminide (NiAl) coatings. Specimens of different thicknesses (0.1-2 mm) were coated with nickel aluminide via chemical vapour deposition (CVD) on 602 CA and IN718 and via a slurry coating process on Rene80. The specimens were discontinuously exposed for 1000 h at 1100 °C in laboratory air. Specimens were removed from the furnace at 100, 300 and 1000 h.

Element concentrations and phase distribution were obtained by scanning electron microscopy (SEM). Phases were identified by energy/wavelength dispersive X-ray spectroscopy (EDX/WDX) and electron backscatter diffraction (EBSD). The modelling results were validated with experimental data. The computational approach assists in estimating the lifetime of the coating and provides a tool to predict microstructural changes in coating systems as a function of alloy/coating composition, time and temperature.

3:30pm **A2-1-7 Engineered Architectures of Gadolinium Zirconate/YSZ based TBCs Subjected to Hot Corrosion Test***, **Satyapal Mahade**,* University West, Sweden*; K Jonnalagadda,* Linköping University, Sweden*; N Curry,* Treibacher Industrie AG, Austria*; N Markocsan, P Nylén,* University West, Sweden*; R Peng,* Linköping University, Sweden*; X Li,* Siemens Industrial Turbomachinery AB, Sweden

Gadolinium zirconate (GZ) is considered as a promising top coat candidate for high temperature TBC applications. Suspension plasma spray has shown the capability to generate a wide range of microstructures including the desirable columnar microstructure. In this study, a triple layered TBC comprising a thin YSZ base layer beneath a relatively porous GZ intermediate layer and a denser GZ top layer was deposited by axial SPS process. Additionally, a blend TBC double layered architecture of GZ and YSZ comprising a thin YSZ base layer and GZ+YSZ mixed ceramic top layer was deposited by SPS. SEM analysis of the cross section in both layered and blend architectures revealed a columnar microstructure. The porosity content of the deposited TBCs was measured using image analysis and water intrusion method. The as sprayed TBCs were exposed to corrosive salt environment which comprised of a mixture of vanadium pentoxide and sodium sulphate at 900°C for 8 hours. The top surface and cross section of the TBCs after the hot corrosion test were analyzed by SEM/EDS. The phase content in the as sprayed and corroded TBCs were also analyzed by XRD.

3:50pm **A2-1-8 Thermal Barrier Coatings: The Next Generation***, **Maurice Gell**, E Jordan, R Kumar,* University of Connecticut, USA*; C Jiang, J Wang, B Nair,* HiFunda LLC, USA

Thermal barrier coatings (TBCs) must exhibit a multitude of properties to be successful. Critical properties include: high temperature phase stability, low thermal conductivity, sinter resistance (retention of low thermal conductivity) and thermal cycle durability. It has recently been shown that yttrium aluminum garnet (YAG) TBCs made by the Solution Precursor Plasma Spray (SPPS) process can potentially be used at temperature 200oC higher than state-of-the-art YSZ TBCs. To further improve the properties of SPPS YAG TBCs, emphasis has been given to greater reductions in thermal conductivity by introducing linear arrays of porosity, called inter-pass boundaries (IPBs), and by demonstrating that thicker coatings with adequate durability can be fabricated. This presentation will present the results of these efforts and the associated thermal cycling durability.

4:10pm **A2-1-9 Microstructure of Gas Flow Sputtered Thermal Barrier Coatings***, **Nils Rösemann**,* Institute for Materials, TU Braunschweig, Germany*; K Ortner,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany*; M Bäker,* Institute for Materials, TU Braunschweig, Germany*; J Petersen,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany*; G Bräuer,* Institute of Surface Technology, TU Braunschweig, Germany*; J Rösler,* Institute for Materials, TU Braunschweig, Germany

Thermal barrier coatings (TBC) reduce the thermal load of gas turbine components. State-of-the-art TBCs consist of partially yttria stabilized zirconia (PSZ) and are deposited by thermal spray techniques (e. g. atmospheric plasma spraying) or electron beam physical vapor deposition (EB-PVD). The resulting microstructure is dependent on the process and strongly influences the coating´s properties and time to failure. Columnar structures exhibit a higher lifetime and are thus favored.

This talk investigates an alternative deposition technique (gas flow sputtering - GFS), which also gives rise to columnar microstructures. The aim of this work is to gain a fundamental understanding of the influence of crucial process parameters such as substrate temperature and bias voltage on the microstructure, and the suitability of GFS coatings for the use as TBCs.

PSZ coatings were deposited on polished FeCrAlY-Alloy substrates and described utilizing WDX, SEM, FIB and XRD.

The substrate temperature has been identified to be a crucial parameter. Between 500 and 800 °C, four different types of columnar microstructures are defined based on XRD pattern and morphology. The growth direction of the columns changes from <111> to <100> accompanied by a change in column shape from triangular to four-sided. The principal shape of the columns is furthermore explained using a growth model.

Applying bias voltage at a given substrate temperature does not give rise to a new type of microstructure but alters the microstructure defined by the substrate temperature. While low bias values lead to more regular columns, high bias voltages lead to further densification and compressive stresses, rendering these conditions unsuitable for TBC manufacturing.

Concluding, promising microstructures are presented accompanied by general guidelines for the suitable process parameters.

4:30pm **A2-1-10 Current Environmental Barrier Coatings Research at NASA***, **Kang Lee**, D Waters,* NASA Glenn Research Center, USA

SiC/SiC Ceramic Matrix Composites (CMCs) are a game changer for advanced power generation equipment because of their high temperature capability, oxidation resistance, and light weight that translate to significant reduction in fuel consumption and pollution. Limitations of SiC/SiC CMCs include surface recession and component cracking and associated chemical and physical degradation in the CMC. The solution pursued to mitigate surface recession of SiC/SiC CMCs is the incorporation of coating systems that provide surface protection, which has become known as an Environmental Barrier Coating (EBC). Other key life-limiting EBC degradation modes include oxidation in steam environments, CMAS-EBC reactions, and thermal fatigue. The first and second generation EBCs developed in mid 1990s-early 2000s laid the foundation for current EBCs. Many engine tests have been conducted since late 1990s and a first CMC component entered into service in 2016 in a commercial engine. The introduction of CMCs represents significant challenges as failure of the EBC means rapid reduction in component life. A reliable life model and testing methods relevant to engine conditions to validate life model need to be developed. This paper will discuss the current research activities on EBC development and testing at NASA.

4:50pm **A2-1-11 CMAS Infiltration Prediction for 7YSZ TBCs Deposited by EB-PVD***, **Juan Gomez**,* The University of Texas at El Paso, USA*; R Naraparaju, U Schulz,* German Aerospace Center (DLR), Germany*; R Chintalapalle,* University of Texas at El Paso, USA

The current demand for higher gas turbine engine operating temperatures has brought into attention the hot corrosion attack to thermal barrier coatings (TBCs) due to siliceous debris infiltration into gas turbines. The debris are commonly composed of calcium-magnesium-alumino-silicates (CMAS) which are carried in environmental pollution in the form of sand, fly ash, volcanic ash, among others. Previous studies in standard 7YSZ coatings deposited by EB-PVD techniques have shown a significant relation of coating micro-structure and CMAS infiltration depth. In the previous study a physical model was proposed to estimate CMAS infiltration into EB-PVD coatings by simplifying the micro-structure as a concentric pipe (kernel pipe) with open channels (feather arms) which distribute the CMAS reducing the infiltration time into the TBC. Therefore, it is of highly importance to understand the kinetics of CMAS infiltration since by refining the deposition parameters (deposition pressure, rotation, etc.) CMAS infiltration can be reduced. The current work correlates experimental results obtained for short term CMAS infiltration performed at 5 min. using a synthesized CMAS source with theoretical results using the proposed "concentric pipe model". The calculated results are in good agreement by closely predicting the infiltration time for a given depth when compared with short term infiltration experiments. Additionally, the results were compared with the "open pipe" infiltration model which has been previously used in literature for CMAS infiltration estimation. The results also show a significant error in infiltration prediction for the open pipe model which proved a more realistic approach for CMAS infiltration using the proposed concentric pipe model.

5:10pm **A2-1-12 Oxidation Behavior of CrN, AlCrN, and AlTiN Cathodic Arc PVD Coatings***, **Zuhair Gasem**, A Adesina,* King Fahd University of Petroleum and Minerals, Saudi Arabia

The oxidation behaviors of CrN, AlCrN, and AlTiN *PVD-cathodic-arc* coatings were evaluated isothermally at 800^{o}C, 900^{o}C and 1000^{o}C for a duration of 5hr in ambient atmosphere using 304 stainless steel substrates. A novel substrate design was employed where all substrate edges were chamfered at both faces to coat both surfaces and edges. The oxidation rate measurement of all-surface-coated samples were conducted using *in-situ* thermogravimetric apparatus. The coating composition, morphology, and hardness were analyzed before and after the oxidation test using X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and scanning electron microscope (SEM).

XRD results for CrN revealed the evolution of various temperature-dependent oxides forming within and beneath the coating including Cr_2O_3, Fe_2O_3, and Cr_2O after the oxidation tests. The diffraction peaks for CrN coating (1.8 um in thickness) disappeared entirely after the oxidation test at 1000^{o}C suggesting complete transformation of the CrN layer into mixed oxide layer. The specific weight gain curves showed continuous increase with exposure time at all temperatures examined. The oxidation resistance of AlCrN coating exhibited significant improvement as compared to CrN coating as can be evident by comparing the oxidation kinetic curves of the two coatings owing to the formation of the more protective Al_2O_3 in addition to Cr_2O_3. The coating provided effective protection at 800^{o}C and 900^{o}C as can be inferred from the oxidation rate curves. The thickening of AlCrN layer, the absence of oxidation product at the interface between the coating and the underlying substrate, and the asymptotic oxidation rate behavior suggest persistence of protection of AlCrN coating up to 1000^{o}C.

The major oxidation products of AlTiN coating over 900-1000^{o}C comprised of TiO_2 and Al_2O_3. The oxidation kinetics showed initial rapid growth stage and a delayed linear behavior. The initial stage may be attributed to the formation of porous TiO_2 with non-continuous Al_2O_3. The delayed linear oxidation rate is similar to the oxidation rate of AlCrN coating at 1000^{o}C. This has been explained in terms of the dominance of the growth of continuous Al_2O_3 layer in both coatings at high temperature.

Coatings for Use at High Temperatures
Room Sunrise - Session A2-2

Thermal and Environmental Barrier Coatings

Moderators: Lars-Gunnar Johansson, Chalmers University of Technology, Sweden, Kang Lee, NASA Glenn Research Center, USA

8:00am **A2-2-1 La-Sr-Mn Based Chromium Barrier Coatings for Interconnectors in Pressurized Steam Electrolysis on Exposure to Pure Oxygen and Water Vapor***, **Vladislav Kolarik**, M Juez Lorenzo, V Kuchenreuther-Hummel,* Fraunhofer Institute for Chemical Technology ICT, Germany*; M Pötschke, D Schimanke,* Sunfire GmbH, Germany

Power-to-liquids processes converting electric power from renewable energy sources into liquid fuels are of forward-looking interest. For achieving high process efficiency, it is envisaged to run the steam electrolysis under pressures up to 30 bar at temperatures around 850°C. The impact of such severe conditions on the behavior of the interconnector coatings designed to retain evaporating chromium is a crucial issue and needs detailed understanding to ensure a reliable operation.

The commercially available interconnector materials Crofer 22 H, Sanergy HT pre-coated by a thin Co layer and the Mn-free ITM were coated by a La-Sr-Mn based oxidic coating (LSM). The coatings were deposited by thermal spraying and by slurry roll coating. For simulating both opposite extremes of the possible process atmospheres, pure water vapor and pure dry oxygen were selected for the study. The experimentation under a pressure of 30 bar at 850°C was conducted in laboratory test autoclaves from Alloy 602 with exposure times up to 1000 h in water vapor and up to 3000 h in dry oxygen. Post-oxidation analysis was performed by field emission scanning electron microscopy (FE-SEM) with EDX element analysis and XRD.

In water vapor the oxide scales on the interconnector materials with LSM coating are notably thinner than on the uncoated material. However, the 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 oxide scale thickness reduction, probably to its higher density, and it shows a less pronounced decomposition into the two phases.

The effect of reducing the oxide scale thickness on the interconnector alloy is in pure oxygen notable only after 3000 h. The structure of the LSM coating remains homogeneous after exposure to pure oxygen with higher porosity in the case of the slurry roll coating. Chromium is detected in the LSM coating, obviously evaporated from the interconnector alloy. In the case of the slurry roll coated LSM it is equally distributed in the whole coating, whereas with the thermally sprayed LSM a dense Cr-rich phase formed on top, consisting of the semi-conducting $SrCrO_4$.

8:20am **A2-2-2 Investigation of the Adhesion of Glassified Sand/salt Deposits on Thermal Barrier Coatings Exposed to High-temperature Combusted Gas Flows***, **Michael Walock**, B Barnett, A Nieto, W Gamble, A Ghoshal, M Murugan,* US Army Research Laboratory, USA*; D Zhu,* National Aeronautics and Space Administration, USA*; J Swab, M Pepi,* US Army Research Laboratory, USA*; R Pegg, C Rowe,* US Navy Naval Air Systems Command, USA*; K Kerner,* US Army Aviation and Missile Research, Development, and Engineering Center, USA

Advanced gas turbines are used in commercial/military aviation, ship propulsion, and industrial power generation. However, degraded environments that contain sand, dust, ash, soot, and/or salt can significantly affect their durability and performance. Specifically, accumulation and infiltration of contaminants, upon melting and subsequent solidification, can significantly reduce the operational life of hot-section components through physical and chemical changes. In this study, standard and advanced thermal barrier coatings (TBCs) were deposited onto engine-relevant substrates, such as Inconel 718 and Rene N5. Prior to molten contaminant exposure, the TBCs are evaluated using non-destructive and destructive techniques, such as scanning acoustic microscopy, scanning electron microscopy, scanning auger electron microscopy, optical microscopy, thermal property testing, erosion testing, and adhesion testing, to elucidate relevant processing-property relationships. After which, the coatings were exposed to sand and salt particle-laden flows (independently and mixed) in a unique hot particulate ingestion rig, under engine-relevant conditions. This environment leads to molten sand/salt particles, enabling the evaluation of melt infiltration and glassy deposit accumulation on TBCs. Post-test evaluations follow the same protocol as the pre-test so as to ascertain the physical and chemical changes that result from sand/salt accumulation and/or infiltration.

8:40am **A2-2-3 Effect of Nanostructure and Composition on the Transient Oxidation Behavior of Nanograined Alloys***, **Pralav Shetty**, J Krogstad,* University of Illinois at Urbana-Champaign, USA

Nanograined alloys possess impressive mechanical properties mediated by their high grain boundary density but suffer from poor high temperature stability. To overcome this, alloying has often been used to pin and stabilize the grain boundaries. As the implementation of such alloys in commercial high temperature applications becomes more viable, it is important to understand the effect of grain boundary structure and alloying on their oxidation behavior. In this study, the transient oxidation behavior of far from equilibrium dc magnetron sputtered NiCrAl films has been investigated. Even though the transient oxide forms quickly and makes up a very small volume fraction of the overall scale, it can dictate several key properties like the chemistry, morphology, and growth kinetics. Moreover alloying elements like yttrium (Y) which have a large positive enthalpy of mixing and a higher affinity for oxygen compared to the base element Ni, can have beneficial effects on both the stability and oxidation behavior of the alloy. Through the use of controlled oxidation of free standing sputtered films at 900°C and complimentary scanning transmission electron microscopy elemental analysis, we show an anomalous oxidation behavior compared to previous literature in this system. The columnar sputtered nanostructure seems to enhance the diffusion of preferred species like Cr and Al, to and along the grain boundaries to quickly nucleate a chromia or alumina scale which then proceeds to grow uniformly. Even minute Y additions seems to improve the scale adhesion and density as supported by the oxide growth rate estimated from thermogravimetric analysis. These insights will help in the development of a more complete grain boundary-dominated physics based model of nanograined oxidation and may ultimately influence the way in which oxidation resistant alloys are designed.

9:00am **A2-2-4 CrAlSiYN Coating with AlSiN Intermediate Layers for Enhanced Thermal Stability and Oxidation Resistance at Elevated Temperatures***, S Liu,* Singapore Institute of Manufacturing Technology, Singapore*; Y Yang,* Data Storage Institute, Singapore*; F Ng,* Singapore Institute of Manufacturing Technology, Singapore*; R Ji,* Data Storage Institute, Singapore*; **Xianting Zeng**,* Singapore Institute of Manufacturing Technology, Singapore

In this paper, the role of Y and Si doping in the thermal stability and oxidation resistance of CrAlN based coatings are investigated, with the mechanisms of coating oxidation characterized for different temperatures. Y and Si doped CrAlN coatings were deposited in a hybrid HIPIMS and magnetron sputtering disposition system, and their chemical compositions and mechanical properties were studied by EDX and nanoindentation respectively. The as deposited coatings were annealed in Ar and air for 1 hour at a range of temperatures, and the change in coating composition and microstructures were characterized by GIXRD, and cross-sectional FIB/SEM imaging and EDX mapping.

It was found that high level of Y addition is beneficial for the coatings thermal stability, but has a detrimental effect on their oxidation resistance. The enhancement in thermal stability could be attributed to the role of Y in suppressing the diffusional decomposition of CrAlN. However, at the same time, Y doping suppressed the formation of a dense oxide protection layer and facilitated the inward propagation of O_2 due to the low formation of Y_2O_3, giving rise to deteriorated oxidation resistance. In order to achieve concurrent enhancement of coating thermal stability and oxidation resistance, a novel structure of CrAlSiYN coating with AlSiN intermediate layers was developed, which exhibited significant enhancement in both high temperature thermal stability and oxidation resistance, as the presence of AlSiN layers effectively suppressed diffusion processes both within the coating and at its interface with air and the substrate.

9:20am **A2-2-5 Metallic Coatings on Copper for High Heat Flux Application in Rocket Engines***, **Torben Fiedler**, J Rösler, M Bäker,* Technische Universität Braunschweig, Germany

The copper wall of regeneratively cooled liquid-fuel rocket combustion-chambers is exposed to high thermomechanical loads. Despite the cooling, surface temperatures of more than 800 °C on the hot-gas side are reached. This results in a high thermal gradient in the copper wall. This gradient leads to thermal stresses which may cause damage of the chamber wall, for example by the so called dog-house effect, where the cooling channels tend to buckle and fracture. To avoid this damage, the temperature in the copper wall can be lowered by applying a thermal barrier coating system. This coating system could also protect the copper surface against oxidation.

Due to the high cooling heat flux in the copper wall, a high thermal gradient and therefore high in-plane stresses as a result of different thermal expansion can be expected. On the hot side of the wall, these stresses are compressive in the heating phase and become tensile after cooling if the compressive stresses relax at high temperatures. To investigate the influence of these loads and to test possible coating systems for the use in rocket engines, laser-cycling experiments were carried out. The laser test facility consists of a 3.3 kW diode laser with a special optics, producing a broad focal point. The laser spot can heat the coating surface up to 1500 °C in less than 0.5 s. The short heating-time leads to a high thermal gradient in the sample, representing the conditions in the rocket combustion-chamber. The temperature is kept constant for a few seconds and the coatings are quenched in water after each laser cycle.

Previously, a coating system consisting of a NiCuCrAl bond-coat and a Ni-superalloy top-coat has been developed. In the laser cycling experiments, three different damage mechanisms were observed:

1. Buckling of the coatings occurs due to the thermal gradient and thus a larger thermal expansion in the hotter coating than in the substrate.

2. Vertical cracks are caused by tensile stresses in the coatings, which form due to relaxation of the compressive stresses at high temperatures after longer heat exposure and subsequent rapid cooling.

3. Coating delamination is caused by the different coefficient of thermal expansion between substrate and bond coat in the roughness profile at the interface.

To gain a better understanding of the damage mechanism and to qualify a coating system for the application in experimental subscale test chambers, finite element simulations were carried out. These simulations may help to identify critical loads in the coatings that may lead to a failure during the laser tests or in the rocket engine and to set up a detailed failure model of the coatings.

9:40am **A2-2-6 Mechanical Properties of ZrO_2-Y_2O_3 Thermal Barrier Coatings by Isothermal Heat Treatment***, **Byung-Koog Jang,*** National Institute for Materials Science, Japan*; K Yasuda,* Tokyo Institute of Technology, Japan*; K Lee,* Kookmin University, Republic of Korea*; S Kim, Y Oh, H Kim,* Korea Institute of Ceramic Engineering and Technology, Republic of Korea

Thermal barrier coatings (TBCs) have received a large attention because they increase the thermal efficiency of gas turbine engines by increasing the gas turbine inlet temperature and reducing the amount of cooling air required for the hot section components. To optimize TBCs for integration into gas turbines,characterization of the relationship between microstructure and thermal-mechanical properties of the coatings is necessary. The purpose of this work is to investigate the influence of the microstructure as well as porosity on mechanical properties of ZrO_2-4mol%Y_2O_3 (YSZ) coatings deposited by air plasma spray (APS) or EB-PVD (electron beam-physical vapor deposition).The mechanical properties of YSZ coatings were evaluated by three-point bending method and nano indentation. The bending strength, Young's modulus and residual stress of plasma sprayed specimens depend on microstructure as well as coating distance. The hardness & Young's modulus of EB-PVD samples show direct proportion to isothermal heat treatment time during 2~100h at 1200°C.

10:00am **A2-2-7 Estimation Of The Mechanical Properties Of Thermal Barrier Coatings With Porous And Dense Vertically Cracked Microstructures By Modified Small Punch Tests***, **Pierre Planques,*** Cirimat - Safran Helicopter Engines, France*; V Vidal, P Lours,* Mines Albi, ICA (Institut Clément Ader), France*; V Proton, F Crabos,* Safran Helicopter Engines, France*; J Huez, B Viguier,* CIRIMAT, France

Cyclic oxidation failure of Atmospheric Plasma Sprayed Thermal Barrier Coatings (APS TBCs), commonly used to insulate hot sections in gas turbines, usually results from the spallation of the ceramic top coat. In order to predict such spalling phenomena, understanding the mechanisms for cracks initiation and propagation in thermal barriers is a major issue for engine-makers. Failure of the TBC is strongly related to the thermal and mechanical properties of each component of the multi-materials system (substrate, bond coat and ceramic) but also to the response of the TBC as a whole. The purpose of the work is to assess the mechanical behaviour of thick TBC using both experimental and computer simulation approaches for two TBC microstructures, i.e. standard lamellar, porous and micro-cracked (classically obtained through APS coatings), and Dense Vertically Cracked (DVC).

The experimental characterisation of the mechanical behaviour of the TBCs and their elementary components is addressed using three points bending (3PB) tests and Small Punch Testing (SPT). For this purpose, a modified instrumented non-standard SPT setup has been designed, allowing mechanical testing of the materials in natural air in the temperature range 25°C-1000°C. This allowed measurements of true material properties, like strength and fracture toughness, of both standard and DVC APS TBCs following various isothermal heat treatments at 1100 °C and 1200 °C. Specifically, the bottom deflexion is measured and specimens are not clamped as usual in the standard configuration of SPT, referred to as "Drawing Punch Test". This last point is crucial for brittle fracture behaviour with little or even no plastic deformation.

The evaluation of strength and stress intensity factors is based on Finite Element (FE) calculations in order to determine the material constitutive parameters by minimizing the difference between simulated and experimental small punch force–displacement curves.

10:20am **A2-2-8 Comparison of Damage Evolution in High Purity Nano and a Conventional YSZ Thermal Barrier Coating during Thermal Cycling***, **Krishna Praveen Jonnalagadda,** R Eriksson,* Linköping University, Sweden*; K Yuan,* Beijing General Research Institute of Mining and Metallurgy, China*; X Li,* Siemens Industrial Turbomachinery, Sweden*; X Ji, Y Yu,* Beijing General Research Institute of Mining and Metallurgy, China*; R Peng,* Linköping University, Sweden

Sintering of the top coat at high temperatures is considered to accelerate the damage development in thermal barrier coatings (TBCs) during thermal cycling. To counter sintering and thus enhance the resistance to thermal cyclic fatigue, a nano structured high purity yttria stabilized zirconia (YSZ) has been developed and in this work, its damage evolution with thermal cycling is studied and compared to that of a conventional YSZ coating. The coatings were deposited by atmospheric plasma spraying (APS). The TBC samples were thermally cycled between 100 °C and 1100 °C with a hold time of 1h at 1100 °C. The results showed that the high purity nano YSZ coating exhibited roughly half the cyclic life compared to the conventional YSZ coating. The difference in the life time is explained with the help of analysis of micro cracking observed on cross sections of the thermally cycled TBC samples. Influence of other factors such as fracture toughness and elastic modulus of the top coats were also studied. Furthermore, finite element modelling was used to understand the crack growth paths in both the materials and their contribution to the final failure.

10:40am **A2-2-9 Non-reactively Sputtered Ultra-High Temperature Hf-C and Ta-C Coatings***, H Lasfargues, T Glechner, C Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; V Paneta, D Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D Holec,* Montanuniversität Leoben, Austria*; **Helmut Riedl**, P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides (TMC) are known for their exceptional thermal stability and mechanical properties, notably governed by the carbon content, degree of crystallinity, and the prevalent vacancies on the non-metallic sublattice. Especially, the binaries Hf-C and Ta-C as well as their ternary mixture Ta-Hf-C are highly attractive due to their ultra-high melting points and their strong tendency to form carbides in the preferred face centered cubic structure. However, when using reactive deposition techniques, the formation of amorphous C-containing phases is often observed.

Therefore, we study in detail the influence of the deposition parameters on the structure and morphology, mechanical properties, as well as thermal stability of non-reactive sputtered Hf-C and Ta-C thin films. The carbon content within the coatings strongly correlates with the target-to-substrate alignment, the deposition temperature, as well as bias voltage applied. For example, in the case of Ta-C maximum values of $TaC_{0.81}$ could be reached applying a $TaC_{0.97}$ target and a substrate temperature of 700 °C combined with a bias potential of -100 V. A further increase could be only achieved through co-sputtering of pure carbon for both systems. Nevertheless, all HfC_y films are single-phase face-centered cubic, whereas the TaC_y films also contain small fractions of the hexagonal Ta_2C phase, which decreases with increasing C contest. The highest hardness and indentation modulus among all coatings studied is obtained for $TaC_{0.78}$ with H = 43.7±0.65 GPa and E = 495.8±8.9 GPa.

Ab initio calculations predict an easy formation of vacancies on the C-sublattice, especially in the Ta-C system, and a temperature driven stabilization of defected structures at high temperatures, with fewer vacancies on the C sublattice for Hf-C than Ta-C. The predicted phase stability is proven up to 2400 °C for both systems by annealing experiments in vacuum, also with stabilization of the hexagonal fraction after 1625 °C in Ta-C films.

11:00am **A2-2-10 Impact of Substrate Surface Morphology on APS Ceramic Coating Adhesion Measured by Laser Shock Test (LASAT)***, H Sapardanis, V Guipont, A Koster,* ***Vincent Maurel****,* Mines ParisTech, France

The aim of this study is to analyze different surface morphology of Haynes 188 Co base superalloys before coating. The surface was alternatively grit blasted, grit blasted and oxidized, processed by electro-discharge machining, or processed by shotpeening. Then pure alumina was deposited using conventional air plasma spray. The use of laser shock adhesion test (LASAT) has shown strong differences in the resulting interfacial toughness of the obtained coating [1-2]. Size of delamination was measured by an original use of infra-red thermography, image analysis and final cross-section analysis. Finally, it has been evidenced that LASAT was able to provide a continuous evolution of the size of the delaminated area as a function of the laser flux with a very high level of results reproducibility. Then a ranking of the quality of the interface could be yielded from this methodology. The combination of the LASAT, in-situ measurement of buckling and finite element analysis of residual stresses is finally used to determine interfacial toughness. The experimental measurement of in-plane displacement field and out-of-plane buckling evolution leads to an accurate description of both boundary condition of FEA and yields to a crosscheck analysis of the interfacial toughness between FEA and experiment.

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[2] Sapardanis, H., Maurel, V., Köster, A., Duvinage, S., Borit, F., & Guipont, V. (2016). Influence of macroscopic shear loading on the growth of an interfacial crack initiated from a ceramic blister processed by laser shock. Surface and Coatings Technology, 291, 430-443.

11:20am **A2-2-11 Influence of Pt Concentration on Structure of Aluminized Coatings on a Ni Base Superalloy***, E Pauletti,* ***AnaSofia D'Oliveira****,* Universidade Federal do Paraná, Brazil

">Aluminum diffusion coatings have been processed by chemical vapor deposition techniques. Particularly, pack cementation is a procedure frequently used to process competitive oxidation resistance coatings on Ni based alloys operating at high temperatures. The superior oxidation resistance is associated with the presence of a NiAl layer that supplies Al to maintain an α - Al_2O_3 continue and adherent film at the surface of coatings. Further enhancements on the performance of alloys are gained when a layer of Pt is deposited on the Ni based alloy before pack aluminization. Under these conditions a (Ni,Pt)Al layer forms to act as an efficient diffusion barrier. To achieve high efficiency it is important to understand role of Pt in aluminized coatings. This work assessed the influence of Pt concentration on the structure of aluminized coatings on a precipitation harden Ni alloy. Electroplating was used to deposit Pt layers with different thicknesses (2, 3 and 7 µm) were on a Ni superalloy NI 183. Subsequently, heat treatment at 900 °C for 90min in argon atmosphere was carry out to promote the stress relief of the electroplated Pt layer and to promote the interdiffusion of Pt and the Ni alloy. Aluminization at 1100ºC for 5 hours used out of the pack cementation procedures avoiding direct contact between samples and the pack mixture. X ray diffraction identified phases at the top surface of coatings and scanning electron microscopy analysis showed that aluminized coatings are composed of two main regions a layer of β – NiAl and a interdiffusion zone (IDZ). The aluminide layer is a hipostoichiometric β – NiAl ordered matrix with Pt in solid solution. Pt concentration in this matrix increases the distortion in the ordered crystal structure of NiAl as confirmed by the displacement of XRD peaks towards higher 2θ. Increasing thickness of Pt electroplated layer causes an increase on the total thickness and alters features within the coating. The higher the Pt content the smoother the Al gradient in coatings and the lower the Kirkendall porosity. These features are a consequence of the impact of Pt on vacancy concentration in the NiAl lattice contributing to a higher atomic mobility in the NiAl layer. The concentration of Al in the IDZ followed the Pt thickness and accounts for a change on the alloy solubility hence microstructure. The thinner 2µm Pt layer induced the formation of a $(Ni,Pt)_3Al$ inspite of the processing conditions. Results showed that for the processing parameters tested, oxidation performance at high temperature is improved with Pt electroplated thickness.

Coatings for Use at High Temperatures
Room Grand Exhibit Hall - Session AP

Symposium A Poster Session

AP-2 Fracture Behavior and Thermal Durability of Lanthanum Zirconate Based Thermal Barrier Coatings with Buffer Layer in Thermally Graded Mechanical Fatigue Environments*, **BongGu Kim**, G Lyu, S Jung, S Lee, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Purdue University, USA

The effects of buffer layer on the fracture behavior and lifetime performance of lanthanum zirconate ($La_2Zr_2O_7$; LZO)-based thermal barrier coatings (TBCs) were investigated through thermally graded mechanical fatigue (TGMF) tests, which is designed to simulate the operating conditions of rotation parts in gas turbines. To improve the thermal durability of LZO-based TBCs, composite top coats, consisting of two feedstock powders of LZO and 8 wt% yttria-doped stabilized zirconia (8YSZ), were prepared by mixing in different volume ratios (50:50 and 25:75, respectively). In addition, buffer layers were introduced in layered LZO-based TBCs deposited using an air-plasma spray method. The TGMF tests with a tensile load of 60 MPa were performed until 2000 cycles at a surface temperature of 1100°C for a dwell time of 10 min, and then the samples were cooled at room temperature for 10 min in each cycle. For the single layer TBCs, the thermal durability was enhanced by controlling the LZO:8YSZ ratio as 25:75 vol.%. The TBC with the double buffer layer showed the best thermal cycle performance among all samples, suggesting the buffer layer was efficient in improving lifetime performance. It is noted that failure modes were different in TBC samples. Delamination and/or cracks were created at the interface between the bond and top coats or above the interface in the single-layer TBCs, but the TBCs with the buffer layer was delaminated and/or cracked at the interface between the buffer layer and the top coat, independent of buffer layer species. This study allows us to further understand the LZO-based TBC's failure mechanisms in operating conditions, especially in the thermal and mechanical environments, in order to design reliable TBC systems.

AP-3 Correlation of Thermal Characteristics and Microstructure of 7YSZ/$La_2Zr_2O_7$ and 7YSZ/$Gd_2Zr_2O_7$ Quadruple Layer EB-PVD Thermal Barrier Coatings*, K Bobzin, T Brögelmann, C Kalscheuer, **Tiancheng Liang**, M Welters,* Surface Engineering Institute - RWTH Aachen University, Germany

Referring to the increasing amount of aviation until the year 2030, energy and fuel efficiency as well as the emission of harmful gases are of prime importance to the technological and ecological evaluation of aircraft engines. Minimizing fuel consumption and improving energy efficiency of jet engines can be reached by increased turbine entry temperatures. However, the permitted combustion temperatures are restricted by material-dependent maximum operating temperatures. Nowadays, yttria stabilized zirconia (YSZ) is commonly used as thermal barrier coating (TBC). YSZ generally withstand a permanent surface temperature of T = 1,200 °C, which is limited due to thermally induced phase transformation. Therefore, lanthanum zirconate ($La_2Zr_2O_7$) and gadolinium zirconate ($Gd_2Zr_2O_7$) with their exceptional properties concerning thermal conductivities, melting points and phase stabilities, get into the focus. However, the mismatch of thermal expansion coefficient α of the new ceramic layers and the bond coats or substrates can lead to delamination under thermal load. In recent years, research projects have shown that multilayer systems might be a solution to combine the advantages of different ceramic layers, avoiding detrimental effects such as delamination. In order to assess this potential of multilayer systems, quadruple multilayer systems consisting of 7wt.% YSZ and $La_2Zr_2O_7$ or 7wt.% YSZ and $Gd_2Zr_2O_7$ were deposited on Inconel 600 by electron beam-physical vapor deposition (EB-PVD). To evaluate the long term behavior under thermal cycling and isothermal load, extended thermal cycling tests were conducted at temperatures of T = 1,200 °C and T = 1,300 °C for n = 1,000 cycles as well as isothermal oxidation tests were performed at a temperatures of T = 1,100 °C for t = 50 h. Furthermore, different analyses regarding the basic characteristics of TBC such as thermal conductivity via laser flash method, phase analyses via X-ray diffraction, microstructure analyses via scanning electron microscope and element analyses by means of X-ray spectroscopy were conducted and correlated with each other. The results of the quadruple TBC were compared to those of mono and double layer TBC. These investigations showed a systematic relationship between porosity and thermal conductivity. Moreover, the thermal cycling tests highlight the great advantages of multilayer systems regarding the thermal expansion properties, compared to the monolayer. In this manner, the multilayer systems illustrated the potential of an adapted coating architecture, which leads to an improved TBC lifetimeunder alternating thermal and isothermal load.

AP-5 Oxidation Behavior of Nb–Si–N Coatings*, **Yung-I Chen**, Y Gao,* National Taiwan Ocean University, Taiwan*; L Chang,* Ming Chi University of Technology, Taiwan

Nb–Si–N coatings were fabricated using reactive direct current magnetron cosputtering on Si substrates. The N contents of Nb–Si–N coatings ranged from 39 to 48 at.% as varying the sputter powers for Nb and Si targets. The Nb–Si–N coatings with a Si content less than 13 at.% exhibited a face centered cubic phase, whereas the coatings with a Si content higher than 17 at.% exhibited near-amorphous. The nanohardness increased from 22.8 GPa for Nb–N coatings to 25.4 GPa for the coating with a 4 at.% Si, and then decreased continuously to 13.3 GPa as increasing the Si content to 23 at.%. The oxidation experiments of Nb–Si–N coatings were conducted at 600 °C in a 1% O_2–99% Ar atmosphere. The results indicated that crystalline Nb–Si–N coatings was oxidized to form Nb_2O_5 after they were annealed for 4 h, whereas no evident oxide scale was observed for the near-amorphous $Nb_{32}Si_{23}N_{45}$ coatings after annealing up to 24 h.

AP-6 Corrosion Behavior of Amorphous and Crystalline Zn-Mg Coating in NaCl Solution*, **JoungHyun La**, K Bae, S Kim, S Lee, Y Hong,* Korea Aerospace University, Republic of Korea

Recently, Zn-Mg coatings have been studied extensively for the protective coatings of steel sheets due to the excellent corrosion resistance of Zn-Mg coatings compared with pure Zn coatings. However, the structure of Zn-Mg coatings changed with deposition conditions such as power density, pressure, and temperature. In this study, the amorphous and crystalline Zn-Mg coatings were synthesized on the steel substrates using sputtering process at various temperatures. The microstructure, the crystal phase, and corrosion resistance of the Zn-Mg coatings were investigated using the field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and salt spray test (SST), respectively. The synthesized Zn-Mg coatings at low temperature below 50°C showed the amorphous and featureless microstructure. By contrast, the porous crystalline Zn-Mg coatings were synthesized at the temperature above 100°C. The amorphous Zn-Mg coatings showed the enhanced corrosion resistance in NaCl solution compared to the crystalline Zn-Mg coatings. 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 as well as inhibiting localized corrosion.

Acknowledgement

This study is financially supported by the Smart Coating Steel Development Center, WPM(World Premier Materials) Program of the Korea Ministry of Knowledge Economy.

AP-7 Nanocomposite Multilayered Coatings with High Thermal Stability and Oxidation Resistance*, **Dmitry Shtansky**, K Kuptsov, M Golizadeh, P Kiryukhantsev-Korneev,* National University of Science and Technology "MISiS", Russian Federation

High thermal stability and oxidation resistance are important properties for various high-temperature applications. Superhard TiAlSiCN coatings with "comb"-like nanocomposite structure, in which fine (Ti,Al)(C,N) columnar grains were separated by well-developed amorphous SiCN interlayers, recently developed in our group, exhibited the highest thermal stability reported to date for nanocomposite coatings. The main drawback of the TiAlSiCN coating is a relatively large difference in temperatures between its thermal stability (1300 °C) and oxidation resistance (1000 °C), which limits their use at high temperatures.

In this work we applied a multi-layering approach to close the gap between thermal stability and oxidation resistance. The coatings were deposited on Al_2O_3 substrate by reactive DC magnetron sputtering of TiAlSiCN target and ion sputtering of SiBC or Al_2O_3 targets in a gaseous mixture of Ar + 15% N_2. The coatings were annealed in vacuum at 1000, 1300 and 1400°C as well as in air at 1000, 1100 and 1200°C for 1 hour to investigate thermal stability and oxidation resistance. XRD, SEM and EDX studies showed that TiAlSiCN/Al_2O_3 coating mostly lost its multilayer structure already after annealing at 1300°C and experienced significant grain growth, while TiAlSiCN/SiBCN coating maintained its multilayer structure with negligible grain growth. Annealing at 1400°C led to a partial recrystallization of top layers of TiAlSiCN/SiBCN coating, while most of the coating remained its structure. After annealing at 1100°C in air, TiAlSiCN/Al_2O_3 coatings were only partly oxidized due to the formation of a dense Al_2O_3 top layer, while TiAlSiCN monolayer and TiAlSiCN /SiBCN coatings were almost completely oxidized. However, incorporated amorphous Al_2O_3 layers in TiAlSiCN/Al_2O_3 coating were crystallized to a certain degree, which shortened initial and transient stages of oxidation by providing preferred nucleation sites and facilitating lateral growth of the oxide.

AP-10 Structure, Mechanical, Tribological, And Chemical Properties Of Mo-Si-B And Mo-Al-Si-B Coatings*, Philipp Kiryukhantsev-Korneev, A Sheveyko, A Bondarev,* National University of Science and Technology "MISiS", Russian Federation*; K Kuptsov,* National University of Science and Technology "MISIS", Russian Federation*; E Levashov, D Shtansky,* National University of Science and Technology "MISiS", Russian Federation

Mo-Si-B and Mo-Al-Si-B coatings were deposited by DC magnetron sputtering and ion implantation assisted magnetron sputtering (IIAMS) of the MoSiB and MoAlSiB composite targets fabricated by the self-propagating high-temperature synthesis method. The structure, element and phase composition of coatings were studied by means of scanning and transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, energy-dispersive spectroscopy, and glow discharge optical emission spectroscopy. The mechanical properties of the coatings were measured using nanoindentation. The tribological properties were evaluated in air using impact-tester and high-temperature ball-on-disc tribometer. To evaluate oxidation resistance, the coatings were annealed in air in the temperature range of 1200-1700 °C during different time slots between 10 min and 5 h. The results obtained demonstrate that the Mo-Si-B coatings possess higher hardness, improved oxidation resistance and better thermal stability compared with their Mo-Al-Si-B counterparts. The 7-mm thick Mo-Si-B coatings were shown to withstand successfully oxidation during short-time exposure for 10 min at temperature as high as 1700 °C due to the formation of protective silica scale. The oxidation of Mo-Al-Si-B coatings was accompanied by the diffusion of aluminum to the coating surfaces and the formation of a single Al_2O_3 layer at 1200-1300 °C and a double Al_2O_3-SiO_2 layer at 1500 °C which were less protective against oxidation. The surface oxidation processes were also accompanied by phase transformations inside the oxygen-free part of both Mo-Si-B and Mo-Al-Si-B coatings with the formation of MoB and Mo_5Si_3 phases.

AP-11 Oxidation Resistance of Ta–Si–N Coatings*, Y Chen,* ***Yu-Xiang Gao,*** National Taiwan Ocean University, Taiwan*; L Chang,* Ming Chi University of Technology, Taiwan

Ta–Si–N coatings with a high Si content of 18–21 at.% were fabricated using reactive direct current magnetron cosputtering as the sputter power was set at 100W for each target, and these coatings exhibited near-amorphous in the as-deposited state. The N contents of Ta–Si–N coatings increased from 31 to 47 at.% as varying the nitrogen flow ratio from 0.1 to 0.4, accompanied with decrease trends of nanohardness from 20 to 14 GPa and Young's modulus from 220 to 196 GPa. By contrast, Ta–Si–N coatings prepared using substrate-holder rotating speeds of 1–30 rpm and a nitrogen flow ratio of 0.4 exhibited a similar chemical composition, accompanied with a nanohardness of 12–14 GPa and a Young's modulus of 187–199 GPa. The oxidation resistance of Ta–Si–N coatings was evaluated by performing annealing at 800 °C in ambient air, which showed notably oxidation resistance related to TaN coatings because the oxide scales formed with restricted thicknesses. The oxidation behavior of near-amorphous Ta–Si–N coatings was examined using transmission electron microscopy and X-ray photoelectron spectroscopy.

AP-12 Effect of Hot-dip Aluminum Coating on Dissimilar Weldment between Low Carbon Steel and 304 Stainless Steel in NaCl/Na_2SO_4 Mixture Salts Induced Hot Corrosion*, **Huan-Chang Liang**, K Tsai, C Wnag,* National Taiwan University of Science and Technology, Taiwan

The effect of hot-dip aluminum (HDA) coating on the hot-corrosion behavior of dissimilar weldment was studied. The dissimilar weldment of low carbon steel and 304 stainless steel (SS 304) was joined by gas tungsten arc welding, using 309L stainless steel (SS 309L) filler. Weldment was coated by hot-dipping into pure molten aluminum for 60 and 120 seconds respectively. Prior to hot corrosion of as-welded and aluminized specimens in static air at 750 °C, specimens were coated with 2 mg/cm^2 of a various portions of NaCl and Na_2SO_4 salt mixtures. The results of as-welded specimens show that the intergranular corrosion took place in both SS 304 and SS 309 L, also especially in the heat-affected zone (HAZ) of SS 304 due to chromium depletion as a results of sensitization. In addition, the interface between low carbon steel and SS 309L was under severe corrosion attributed to difference in chemical composition. The results of HDA for 60 seconds show that there was no intergranular corrosion observed in each zone of stainless steel. Results also show that the low carbon steel/SS 309L interface was protected by aluminide, which eliminate the compositional effect on the surface. Same phenomenon was also observed for HDA 120 seconds, however, more cracks were observed in the aluminide layer on the interface of low carbon steel/SS 309L. It therefore shows that HDA processing on dissimilar weldment performed better hot-corrosion resistance with less difference of chemical composition.

AP-13 Influence of Arc Power and Spray Distance on Mechanical Properties of ZrO_2-10%Y_2O_3-18%TiO_2 Coatings Produced by Plasma Spray*, **Sugehis Liscano**, L Gil,* Universidad Nacional Politecnica UNEXPO, Venezuela (Bolivarian Republic of)*; A Portoles,* Universidad Politecnica de Madrid, Spain*; K Silva,* Universidad Nacional Central de Venezuela, Venezuela (Bolivarian Republic of)

Torch Power and spraying distance during the deposition have been referred as important factors in the coating microstructure and properties. ZrO_2-10%Y_2O_3-18%TiO_2 coatings were prepared on NiCrAlCoYO bond coat and metal substrate by atmospheric plasma spraying (APS) to evaluate the effect of these parameters on the mechanicals properties. The microstructures of the coatings were characterized using scanning electron microscopy (SEM) technique coupled with X-Ray microanalysis (EDS). The coatings microhardness and adhesion strength were determined using ASTM E384-2010 for Vickers microhardness and ASTM-C633 for adhesion test. The results corroborate that torch power and spraying distance have significant influence on the mechanical properties in the range evaluate. The adhesion strength of the prepared coatings was between 7 - 14 MPa, while the microhardness measurement was more between 251 - 942 $HV_{(0,5)}$. It was concluded that the best coatings properties, for the level of the variables studied in this work, could be obtained if the torch power is maintained at 34 KW and the spraying distance in 100 mm.

AP-14 A Parametric Study for Minimizing Thermal Stress of a Thermal Barrier Coating System*, **JangGyun Lim**, M Kim,* Sungkyunkwan University, Republic of Korea

1. Introduction

Thermal barrier coating (TBC) is presently used as thermal insulating coating to protect hot component of gas turbines. Commonly, TBC system consists of four layers; a substrate, an aluminum containing metallic bond-coat, a thermally grown oxide (TGO), and a thermally insulating ceramic layer called top-coat. However, its full usage is limited by unexpected pre-failure mainly caused by thermal stress. Temperature change in an operation cycle induces thermal stress on TBC due to mismatch of material properties. Additionally, growth and wavy deformation of TGO, creep, delamination complicate this failure mechanism. Despite of intensive research on pre-failure for several decades, it is difficult to predict the lifetime because of the variety of specifications, operating conditions, and the emergence of new materials. Therefore, it is necessary to understand the influence of the design parameters of the TBC system on the thermal stress, including the properties and specifications, in consideration of interplays.

2. Modeling and conditions

We constructed a 2D rectangular unit cell model in the axis symmetry and periodic conditions. The topological features of TGO and depletion region were figured out by a microstructural analysis so that TGO was represented by sinusoidal wave. In addition, temperature-dependent-properties were assigned to elasto-plastic deformation and the creep behavior was also considered by power-law creep strain rate. Particularly, nano-indentation was conducted on aluminum depletion area in bond-coat to measure elastic modulus. After constructing a model considering interplays, heat transfer analysis and thermal stress analysis are sequentially conducted. Based on the proposed model, an intensive parameter study with 144 different cases was conducted to investigate the effects of various design parameters on thermal stress. They are elastic modulus, thermal expansion coefficient of the top-coat, and thickness of both bond-coat and top-coat.

3. Results and discussion

As a result, it is observed that elastic modulus is the most influential parameter to thermal stress and thermal expansion coefficient, top-coat thickness, and bond-coat thickness follow. Also, the smaller mismatch of thermal expansion coefficient between bond-coat and TGO is in favor of thermal stress reduction. This parametric study will play an important role in an optimal design of TBC system.

AP-15 Investigation of the Influence of Subcoating on Thermal Shock and Corrosion Resistance in the Liquid Zinc of APS ZrO_2 Coating Doped with MgO*, Aleksander Iwaniak,* Silesian University of Technology, Poland*; A Moscicki,* Jolanta Mzyk Silesian University of Technology, Poland*; G Wieclaw,* Krzysztof Rosner Certech, Poland

Liquid zinc is an aggressive corrosive medium and poses a considerable problem for steels that come into contact with it. In the paper, the thermal shock and corrosion resistance of APS coating ZrO_2-24MgO to the action of molten zinc was examined. Various types of bond coats were used: Ni-Cr single-layer and layer with different contents of NiCr and ZrO_2-24MgO. The tests of thermal shock and corrosion resistance involved cyclical exposure of coated specimens in a molten zinc bath for one hour and subsequently, their rapid cooling in water. The coatings were subjected to structural examination (SEM, EPMA, XRD, 3D topography of surface) before and after the test. Macroscopic evaluation of the condition of coatings' surfaces after thermal shock test in liquid zinc, in comparison with their original state after spraying, showed the following changes in their image: surface discoloration, spots, and local fractures in case of ground coating. It was noticed that sectional view of all tested samples was reduced after corrosion resistance test (cyclic exposure to liquid zinc). It was connected with coating thickness decrease. Structural tests proved formation of zinc and zinc oxide on samples' surfaces. Coating thickness decrease after the test was caused by dissolution of ZrO2-24MgO coating in liquid zinc. Strong relation between the kind of subcoating and fractures formation in ZrO2-24MgO coating was not noticed. Only in case of a single subcoating sample, a slight flake in the upper section of ZrO2-24MgO coating was noticed after corrosion resistance test.

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