Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A1-1-TuM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderators: Justyna Kulczyk-Malecka, Manchester Metropolitan University, **Lars-Gunnar Johansson**, Chalmers University of Technology, Sweden, **Shigenari Hayashi**, Hokkaido University

8:00am **A1-1-TuM-1 Modeling the Influence of Heat Treatment and Base Alloy Composition on the Performance of Aluminide Coatings for High Performance Engine Valve Alloys***, **Rishi Pillai**, S Dryepondt, B Armstrong, Q Guo, K Unocic, G Muralidharan,* Oak Ridge National Laboratory, USA

Ni-based alloys are currently being used for engine valves in internal combustion engines.The currently employed valve alloys have reached their operational limit and the need to increase engine efficiency and hence operating temperatures combined with the added challenge of low component cost tolerance makes high temperature materials selection for durability and cost a primary concern since there are fewer lower-cost materials which possess sufficient oxidation, creep and fatigue resistance.

Protective metallic nickel aluminide (NiAl) diffusion coatings enhance the oxidation and corrosion resistance of the underlying high temperature materials.However, the substrate composition and specimen geometry influence the final coating microstructure during the aluminising process and govern the high temperature behavior of the coating system during subsequent exposure.Potentially detrimental phases may form in the interdiffusion zone (IDZ) during the aluminizing process.The formation of a protective alumina scale and the diffusion from the coating into the substrate during subsequent service result in the loss of Al and thereby the dissolution of the ß-NiAl phase in the coating.The compatibility of a given type of a coating with its base material substantially influences the performance of a coated material during service.Evaluation of the coating's high temperature behavior requires extensive experimental testing, but computational methods can substantially reduce these efforts required for coating evaluation and qualification.

In the current work,a coupled thermodynamic and kinetic computational model was employed to predict the microstructural evolution in nickel aluminide (NiAl) diffusion coatings on the Ni-base 31V alloy (UNS NO7032) and new recently developed high strength alloys during the coating (aluminising) process.Various heat treatment procedures were assessed to optimize the coating microstructure.The model was also used to predict the microstructural evolution of coated 31V coupons exposed at 800ºC for up to 5,000h.

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 model predicted the formation of sigma phase and carbides of the MC-type in the IDZ of the coating on 31V which was in agreement with experimental observations. The computational approach provides a general approach in predicting the IDZ microstructure during manufacturing and estimating the extent of microstructural changes in the coating as a function of alloy/coating composition, time and temperature.

8:20am **A1-1-TuM-2 Fabrication, Characterisation and Testing of Cr Coated Zr Alloy Nuclear Fuel Cladding for Enhanced Accident Tolerance***, A Evans,* Manchester Metropolitan University, UK*; D Goddard,* National Nuclear Laboratory, UK*; A Cole-Baker,* Wood plc, UK*; G Obasi, M Preuss,* Manchester University, UK*; E Vernon,* National Nuclear Laboratory, UK*;* ***Peter Kelly****,* Manchester Metropolitan University, UK

The deposition of an oxidation resistant Cr coating on Zr alloy nuclear fuel cladding is an advanced concept for deployment of an accident tolerant fuel, which is attracting considerable interest in the market. Improvements have been shown relative to uncoated Zr alloys in both operational conditions and when subjected to high temperature steam. Initial irradiation testing of this concept is also in progress. In the UK, a collaborative programme of research is investigating Cr deposition using magnetron sputtering. This research is examining how the integrity and microstructure of the coating is affected by deposition conditions and coating thickness for both flat coupons and short lengths of Zr alloy tube. Test coatings have been subjected to static autoclave tests under standard PWR operating conditions, as well as accelerated tests in air at 900ºC and in 400°C steam. The as-deposited and post-testing coatings have been characterised using SEM/EDX and XRD to determine structure, texture and residual stress and, in the latter case, damage arising from testing. Initial results have shown significant differences in the stress condition in the coatings as a function of deposition parameters. Furthermore, selected coatings have successfully undergone accelerated oxidation tests with little or no discernible detrimental effects.

8:40am **A1-1-TuM-3 High-temperature Oxidation Resistance and Self-healing Capability of HiPIMS Cr-Al-C Coating on Zr-based Alloy***, **Michaël Ougier**, A Michau, F Lomello,* CEA, Université Paris-Saclay, France*; F Schuster,* CEA Cross-Cutting Program on Materials and Processes Skills, France*; H Maskrot, M Schlegel,* CEA, Université Paris-Saclay, France

The development of nuclear accident-tolerant fuels (ATF) claddings has gained new momentum since Fukushima Daiichi accident. The primary goal of this study is to develop alternative fuel claddings which are more resilient to high-temperature steam oxidation to reduce hydrogen generation during loss-of-coolant-accident (LOCA). A promising solution is to protect the claddings by metallic or ceramic coatings, such as MAX phases. In order to resist such accidental conditions, the oxide coatings need to be physically and chemically stable in normal operating conditions and accidental (steam) situations; also, they should act as protectives barrier against oxygen diffusion. Al-containing MAX phases, as Cr_2AlC, possess excellent high-temperature oxidation resistance both in air and in humid atmosphere due to the formation of a dense and adherent alumina scale. In this work, Cr-Al-C thin films were synthesized as coatings on Zr-based alloy from a Cr_2AlC compound target by high-power magnetron sputtering (HiPIMS) and subsequent thermal annealing. The crystal structure, microstructure and oxidation behavior of these films were investigated in air. As-deposited coatings are dense and amorphous regardless the deposition temperature (between 25 to 450°C). The effect of the annealing post-treatment was studied by *in situ* X-ray diffraction from 550 to 650°C in helium for up to 12 h. In such conditions, HRTEM analysis demonstrated that the amorphous coating partially crystallized into Cr_2AlC nanocrystals above 600°C. Microcracks also appear on the surface for very thick films, due to the release of residual stresses originating from both the mismatch in thermal expansion coefficients of the coating and the substrate, and from internal stresses. Oxidation at temperatures up to 1200°C in air reveals no significant oxidation of the substrate thanks to the growth of a dense and protective Al_2O_3 layer fully covering residual Cr carbides. Voids also formed at the interface between oxide and Cr carbides. The relative weight gain of coated samples typically decreases by 80% compared with uncoated Zr-based alloy. Furthermore, coatings also possess a self-healing capability due to the formation of alumina within microcracks. In addition, water quenching tests prove that coatings demonstrate high adherence and thermal-shock resistance. As a comparison, the oxidation behavior of the crystalline film is also conducted. Results indicate that Cr-Al-C thin films grown by HiPIMS process are promising candidates for ATF cladding coatings.

Keywords : Accident-Tolerant Fuels, MAX phase coating, physical vapor deposition, oxidation resistance, self-healing

9:00am **A1-1-TuM-4 Ceramic Coatings for Protection of Ti and Zr Alloys at High Temperature***, **Ping Xiao**, Z Gao, X Zhang, H Liu,* University of Manchester, UK*; J Kulczyk-Malecka, P Kelly,* Manchester Metropolitan University, UK*; Z Zhang,* University of Manchester, UK **INVITED**

SiAlN coating have been produced with use of magnetron sputtering on both Ti and Zr alloy substrates for protection from oxidation in both air and steam environments. The coatings have demonstrated excellent oxidation resistance tested in both air and steam and the strong coating/substrate bonding, measured with use of scratch testing. Electron microscopy has been used to understand the oxidation mechanisms and the mechanisms controlling the coating/substrate adhesion. The study has presented that the coatings are very promising for protection of Ti and Zr alloys from oxidation in air and steam at high temperature.

9:40am **A1-1-TuM-6 Multi-functional AlZr-TiO_2 Bilayer Coatings Combining Anticorrosion and Antifouling Properties***, **Caroline Villardi de Oliveira**,* ICD-LASMIS, Université de Technologie de Troyes, France, Françe*; A Alhussein,* University of Technology of Troyes (UTT), France*; C Jiménez,* Univ. Grenoble Alpes, CNRS, France*; Z Dong,* School of Materials Science and Engineering, Nanyang Technological University, Singapore*; F Schuster,* CEA, PTCMP, France*; S Narasimalu,* School of Materials Science and Engineering, Nanyang Technological University, Singapore*; M Schlegel,* CEA, Université Paris-Saclay, France*; F Sanchette,* Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France

Fouling in marine environment is a costly problem and can be described by the development of biofilms containing various types of micro and macro-organisms, which can enhance the processes and rates of steel corrosion in saline seawater. TiO_2 coating shows photocatalytic activity and hydrophilic behavior which can promote antifouling properties in order to minimize the biofouling process in the marine structures. Photocatalytic oxidation is a non-toxicity low cost promising technology to control fouling in submerged surfaces by generation of reactive oxygen species [1]. In this work we present a multi-functional coating made by an anticorrosion Al-Zr interlayer covered by an antibiofouling TiO_2 top layer. Al-Zr film is proposed as a potential candidate for affording sacrificial corrosion resistance of steels since it presents a good compromise between the mechanical reinforcement and the electrochemical properties[2].

Steel substrates were initially coated by magnetron sputtering with Al-Zr alloy (3 µm thick films) containing 5 at.% Zr. TiO_2 films were deposited on the top of the Al-Zr layer by atmospheric pressure Aerosol-Chemical Vapor Deposition (AACVD). The structure and morphology of the multi-functional coatings were analyzed by XRD and SEM. Photocatalytic activity using Orange G under UV light and electrochemical tests in saline solution were performed. The biofouling behavior and performance in natural seawater were also tested by in situ immersion tests.

Keywords: Al-Zr alloys, magnetron sputtering, steel protection, biofouling, TiO_2, AACVD, Photocatalysis.

References

[1]Liu, H., Raza, A., Aili, A., Lu, J., AlGhaferi, A., & Zhang, T. (2016). Sunlight-sensitive anti-fouling nanostructured TiO 2 coated Cu meshes for ultrafast oily water treatment. *Scientific reports*, *6*, 25414.

[2] Sanchette, F. & Billard, A. Main features of magnetron sputtered aluminium transition metal alloy coatings. *Surf. Coatings Technol.* 218–224 (2001).

10:00am **A1-1-TuM-7 The Oxidation Behavior of ZrO_2-Coated Zircaloy-4 with ZrN Interlayer***, **I-Sheng Ting**, J Huang,* National Tsing Hua University, Taiwan

The purposes of this study were to investigate the oxidation behavior of ZrO_2-coated Zircaloy-4 (Zry-4) with different crystal structure and evaluate the effect of ZrN interlayer. Oxidation is a crucial problem for the Zry-4 fuel cladding in light water nuclear reactor. In general, when reacting with water, Zry-4 will naturally form a surface oxide layer that is composed of both tetragonal and monoclinic ZrO_2. Although ZrO_2 is a well-known protective material, the naturally formed oxide layer is only several nanometers, which is insufficient to protect the Zry-4 substrate from the severe water-corrosion environment in nuclear reactor. Several transition metal nitride coatings (TMeN), such as CrN, TiN, and TiAlN have been proposed to improve the oxidation resistance of Zry-4. Owing to the excellent thermal and chemical stability, TMeN can act as a diffusion barrier and prevent the substrate from further oxidation. In addition, TMeN possess superior mechanical properties that may enhance the service time of the Zry-4 claddings. Therefore, this study aimed to investigate the oxidation behavior of ZrO_2-coated Zry-4 with tetragonal, monoclinic, and yttria-stabilized cubic crystal structure, and evaluate whether the ZrN interlayer can act as an efficient diffusion barrier. ZrO_2 thin films with three different crystal structure and ZrN interlayer were deposited on both sides of the Zry-4 plate by unbalanced magnetron sputtering (UBMS). After the deposition of ZrO_2 thin films, the crystal structure was characterized by X-ray diffraction (XRD), and the chemical composition was measured using X-ray photoelectron spectroscopy (XPS). Thermogravimetric analysis (TGA) was carried out at 700, 800 and 900°C in argon atmosphere for 1 h. After the TGA oxidation, the uniformity of the multi-phases ZrO_2 oxide layer was examined using azimuthal $\cos^2\alpha\sin^2\psi$ technique, which combines $\cos^2\alpha\sin^2\psi$ XRD method [1] with average X-ray strain (AXS) method [2]. The surface morphology of the ZrO_2 thin films and the precipitation of nonuniform surface oxides after TGA oxidation were observed by SEM equipped with EDX.

[1] C. H. Ma, J. H. Huang, H. Chen, Thin Solid Films 418 (2002) 73-78.

[2] A.N. Wang, C.P. Chuang, G.P. Yu, J.H. Huang, Surf. Coat. Technol. 262 (2015) 40-47.

10:20am **A1-1-TuM-8 Novel HIPIMS Deposited Nanostructured CrN/NbN Coatings for Environmental Protection of Steam Turbine Components.***,* ***Papken Hovsepian****, A Ehiasarian, Y Purandare,* Sheffield Hallam University, UK*; P Mayr, K Abstoss,* Technische Universitat Chemnitz, Germany*; M Mosquera, W Schulz, A Kranzmann,* Federal Institute for Materials Research and Testing, Germany*; M Lasanta Carrasco, J Trujillo,* Universdad Complutense de Madrid, Spain

A significant reduction of CO_2 emissions is expected by increasing the efficiencies of the steam turbines to $\eta > 50\%$ which can be achieved by moving from subcritical low pressure/ low temperatures, to high pressure/high temperature, ultra-supercritical regime of operation. The main challenges faced by different steel components of the power plant with this approach however, consist of material failure due to high temperature oxidation, and phenomenon such as creep, erosion and descaling after a stipulated period of time.

In the current work, 4 µm thick CrN/NbN coating utilising nanoscale multilayer structure with bi-layer thickness of Δ = 3.4 nm has been used to protect low Cr content P92 steel widely used in steam power plants. The novel High Power Impulse Magnetron Sputtering (HIPIMS) deposition technology has been used to deposit CrN/NbN with enhanced adhesion (critical scratch adhesion value of Lc= 80N) and very dense microstructure as demonstrated by XTEM imaging.

P92 coated samples were oxidised at 600°C in 100% high pressure, 50 bar steam atmosphere up to 1500 h. The gas-flow velocity through the reaction zone of the test rig was 0.0133 m/s. In these conditions CrN/NbN provided reliable protection of the P92 steel.

This research also revealed that unlike other state-of -the-art PVD technologies, HIPIMS does not have an adverse effect on the mechanical properties of the substrate material, which is of paramount importance in case of turbine blade applications. In high temperature (650°C) tensile strength test uncoated P92 steel showed Ultimate Tensile Strength (UTS) values of 229 MPa and Yield Strength, (YS) values of 222 MPa compared to UTS = 307 MPa and YS = 291 MPa measured for CrN/NbN coated P92 steel. Similarly in strain controlled, (0.4% strain) Low Cycle Fatigue tests at 650°C both uncoated and coated specimens failed after similar number of cycles, N_f = 1700 and N_f= 1712 respectively and showed similar half-life stress drop of -37% and -43% respectively. Finally high temperature creep tests at 650°C, tensile stress of 120 MPa revealed that the HIPIMS coating improved the creep lifetime by almost factor of two from 564 hours to 908 hours whereas the creep rate was decreased from 17.6 10^{-6} s^{-1} to 13.5 10^{-6} s^{-1}.

The protection properties of the coating against water droplet erosion attack were tested using specialized test rig. The coating shows high resistance against water droplet erosion. After $2.4E^6$ impacts no measurable weight loss was detected.

10:40am **A1-1-TuM-9 NiAl Coatings Deposited on Inconel 600 by Using an Arc Ion Plating Process***, **Yinan Li**,* University of Manchester, UK*; Y Hung,* Feng Chia University, Taiwan*; M Lin, A Matthews,* University of Manchester, UK*; J He,* Feng Chia University, Taiwan

To protect against the most demanding environments in gas turbines, thermal barrier coatings (TBCs) made of a ceramic top coat and an intermetallic bond coat are applied throughout the hot sections. In a TBC system, a top coat of partially yttria stabilized zirconia (PYSZ) presently offers the main thermal insulation, whilst a bond coat of Ni(Pt),Al or MCrAlY provides the vital oxidation resistance. Currently, these coatings are typically deposited by electron beam physical vapour deposition (EB-PVD). A potential alternative processing route is to deposit both top coat and bond coat by an arc PVD method in a single coating cycle. Little work has been carried out on arc PVD NiAl and PYSZ coatings, which may offer benefits (e.g. in the degree of ionisation achieved, and therefore coating structure and uniformity improvements) compared to other methods.

In this study, the arc ion plating (AIP) method is used to deposit NiAl films on nickel-based alloy (Inconel 600) and AISI 304 stainless steel substrates. The composition of the cathode target is $Ni_{50}Al_{50}$. In order to study the influence of processing conditions on microstructure and phase composition, the parameters of substrate bias voltage and current, target pulse current and working pressure are controlled during the deposition. Thermal cyclic oxidation testing is carried out to evaluate the cyclic oxidation resistance. The results demonstrate the benefits of the process in terms of improved morphology and performance.

Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A1-2-TuA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II

Moderators: Lars-Gunnar Johansson, Chalmers University of Technology, Sweden, **Shigenari Hayashi**, Hokkaido University, **Justyna Kulczyk-Malecka**, Manchester Metropolitan University

1:40pm **A1-2-TuA-1 Nano Coatings To Achieve Cost Effective And Long Lifetime SOFC Interconnects***, **Jan-Erik Svensson**,* Chalmers University of Technology, Sweden **INVITED**

Ferritic stainless steel interconnects are widely used in solid oxide fuel cells (SOFC) due to a combination of low cost, compatible thermal expansion properties and ease of manufacturing. Nonetheless, their viability is hindered by several key technical hurdles. Most stainless steels suggested for SOFC applications rely on the formation of a fairly protective chromium oxide scale. However, in air side environments Cr species evaporation leads to material failure and insufficient lifetimes. Additionally even a protective oxide scale grows with time and since chromium oxide is only a moderate electronic conductor, this results in an increase of Area Specific Resistance (ASR). This work investigates nano coatings to mitigate both degradation mechanisms. FeCr steels have been coated with Co and/or Ce using Physical Vapor Deposition (PVD). The materials were exposed in air at 600-850 °C for up to 3000 h and oxide scale growth, chromium evaporation and electrical resistance were studied using mass gain data, the Cr-evaporation denuder technique and ASR measurements respectively. The effect of dual atmosphere exposure are also investigated. Exposed samples were additionally examined by Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX) analysis. The results show that thin Co coatings effectively mitigate Cr volatilization. By adding Ce to the coating the performance was further improved as the oxidation rate was significantly reduced, thus resulting in substantially reduced ASR values. These results imply that the duplex, Co + Ce thin film coating is suitable for ferritic stainless steel interconnects in SOFCs.

2:20pm **A1-2-TuA-3 Influence of Ta Content on Properties of TiAlTaN Films***, **Hongfei Shang**, T Shao,* State Key Laboratory of Tribology, Tsinghua University, China

Binary and ternary nitrides of transition metal elements, such as Ti, Cr, Zr, V, Nb, or Ta, exhibit outstanding mechanical, chemical, and thermal properties, and are utilized as protective coatings in machining, automobile and other industrial areas. Recently, alloying titanium aluminium nitride (TiAlN) with tantalum can improve cutting performance. Titanium aluminium tantalum nitride (TiAlTaN) films have been reported on improved mechanical and tribological properties.

In this work, a series of TiAlTaN films with different Ta contents were deposited using an ion beam assisted deposition. Microstructure of the as-deposited films was characterized by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). Mechanical properties of the TiAlTaN films were also tested. Tribological behavior and corrosion performance of the TiAlTaN films were analyzed and compared to that of the TiAlN film. Results show that the TiAlTaN films demonstrated better mechanical properties, tribological behavior and corrosion resistance than the TiAlN film. Ta content has a great influence on the properties of the TiAlTaN films.

2:40pm **A1-2-TuA-4 Cr-Al-Si-N Quaternary Coating Applied on Zirconium Alloy: Combining Superior Resistance of High-temperature Steam Oxidation and Improved Mechanical Properties***, **Fangfang Ge**, H Zhu, F Huang,* Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, China

Accident tolerant fuel claddings are extremely urgent to increase the safety margin of light water reactors. Cr-Al-Si-N quaternary coatings were proposed to increase mechanical properties and high-temperature steam oxidation resistance of Zr-based alloy. $(Cr_{60}Al_{30}Si_{10})_xN_{1-x}$ coatings with three kinds of microstructure, were prepared on Zr coupons, followed by evaluation of their mechanical properties and oxidation resistance under high-temperature steams. Moreover, to reveal the anti-oxidation mechanism, much examination was performed on the microstructure the oxidized samples. Compared to the “dense & columnar” coating, the “dense & featureless” coating exhibits a combination of the best mechanical properties and the highest oxidation resistance. It increases the H and the E^* of the uncoated Zr coupon by ~4 times has a and ~twice, respectively. After coated on the “dense & featureless” coating with the thickness of ~5 µm, the oxidation of the Zr coupon was completely suppressed in the 1000 °C steam for 15 min, and the thickness of the α-Zr(O) layer deceased by 40% - 92% in the 1200 °C steam for 30 min. Furthermore, a ~10 µm thick “dense & featureless” coating can prevent the Zr coupon from oxidizing in the 1200 °C steam for >1 h. By contrast, the “porous & columnar” coating can hardly provide any protection for the undeath Zr substrate in the high-tempeature steam. It demonstrates that the densely fine-grained or amorphous microstructure could effectively suppress the inner-diffusioin of O and favor the formation of a dense and coherent scale on surface, which would be highly desirable for the protection coatings of Zr claddings.

4:00pm **A1-2-TuA-8 Polyurethane Protective Coating with Self Polishing Property***, **Mohammad Mizanur Rahman**,* King Fahd University of Petroleum and Minerals, Saudi Arabia

Waterborne Polyurethane (WBPU) coatings are widely used to protect metals from corrosion and fouling. Owing to restrictions on using toxic materials scientists are attempting to develop new, more environmentally-friendly coatings that maintain their performance over extended periods. Unfortunately, these coatings are inadequate to prevent metal corrosion and fouling under adverse conditions especially marine condition. Self-polishing coatings (SPC) are considered to be among the most effective technologies. Self-polishing coatings facilitate the continuous renewal of the surface and the release of active compound via a hydrolysis reaction or an ion exchange reaction with seawater. In this study, WBPU coatings were synthesized by in-situ polymerization. Synthesis and properties of coatings were investigated by Fourier transform-infrared spectrometer, proton-nuclear magnetic resonance and dynamic light scattering. The polishing rate of coating was determined from the reduction in dry film thickness after artificial seawater immersion under a dynamic condition. The corrosion and fouling resistance of coatings were also considered after certain interval.

4:20pm **A1-2-TuA-9 Production of a Zinc Impregnated Stainless Steel Surface Utilizing Cathodic Plasma Electrolytic Deposition (CPED) for Retardation of Cobalt Ion Deposition in High Temperature Aqueous Conditions***, **Ciara Fox**, F Scenini, A Yerokhin, N Laugel,* University of Manchester, UK*; R Wain,* Rolls-Royce, UK

The majority of the radiation field present in light water nuclear reactors is the result of the build-up of radioactive cobalt species on structural components and this can lead to occupational radiation exposure to personnel during maintenance and inspections. However, it has been shown that zinc added to the high temperature coolant water hinders the deposition of aqueous cobalt cations onto the surface of stainless steel because it is preferentially incorporated into the inner spinel corrosion layer on stainless steel surfaces over cobalt. This work looks at the feasibility of preconditioning the stainless steel surface with zinc to remove the need for zinc additions into the coolant water.

In this work the surface modification of a 316 stainless steel to promote superficial zinc enrichment is explored. The modified alloy is created utilised Cathodic Plasma Electrolytic Deposition (CPED). The stainless steel work piece is used as the cathode in an aqueous electrolyte bath containing zinc cations and a voltage between 110V – 150V is applied to generate plasma discharges at the surface of the cathode. The superficial layer was characterised by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), grazing angle X-ray diffraction (G-XRD) and glow discharge optical emission spectroscopy (GDOES) to identify the phases present on the treated samples.

The high surface temperatures generated during plasma discharges were shown to promote the diffusion of zinc which has been detected up to 3 micrometres in depth into the stainless steel substrate. In addition to zinc penetration into the stainless steel matrix, zinc is also deposited on the surface as a rough and porous zinc oxide coating which can be mechanically removed from the stainless steel surface. The effect of process parameters on zinc diffusion into the substrate as well as the treatment time and composition of the electrolyte, are discussed.

Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A1-3-WeM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling III

Moderators: Justyna Kulczyk-Malecka, Manchester Metropolitan University, **Lars-Gunnar Johansson**, Chalmers University of Technology, Sweden, **Shigenari Hayashi**, Hokkaido University

8:20am **A1-3-WeM-2 Corrosion Monitoring Of High-Temperature Protective Coatings Under Molten Salts Environments For CSP Applications**, ***Francisco Javier Pérez Trujillo***, *V Encinas Sánchez, T de Miguel Gamo,* Universidad Complutense de Madrid, Spain; *M Lasanta Carrasco,* Universdad Complutense de Madrid, Spain; *G García-Martín,* Universidad Complutense de Madrid, Spain

In recent years there has been a substantial increase in interest in renewable energy, this being particularly high in the field of concentrated solar power (CSP). Commercial CSP plants usually use molten salt mixtures as thermal energy storage medium. The currently used industrial compound is an alkali-nitrate mixture composed of 60 wt.% $NaNO_3$/40 wt.% KNO_3. One of the main drawbacks of this medium consists in the severe corrosion problems to which its composition and high temperature lead. Thus, the development of protective coatings for steels could be an economical alternative for increasing the lifetime of pipes and tanks in CSP plants against molten salt corrosion. This solution would allow CSP plants to reduce the Levelized cost of electricity (LCOE), which is one of the major objectives currently set.

The conventional methods used for assessing the corrosion in molten salt environments are not the optimal methods when monitoring the real-time corrosion process. A better understanding of the process requires a monitoring system that allows recording corrosion rates in real-time. In this respect, electrochemical impedance spectroscopy (EIS) is a powerful technique for monitoring corrosion processes that take place in steels under molten salt environments.

Thus, this work aimed at developing sol-gel protective coatings on low alloyed steels and monitoring the protective behavior in contact with molten salts by employing EIS technique. To this end, electrochemical sensors, patented under the reference code WO2017046427, were employed. Corrosion tests were performed at 500ºC up to 2000 h and EIS results were supported by gravimetric and microstructural characterizations. All results were compared to the uncoated steels.

Results showed the good behavior of the coated substrates. Corrosion monitoring system showed the protective behavior of the coatings, these being compared with the uncoated samples, where widespread corrosion was determined. Results were supported by gravimetric analyses, with very little weight variations after 2000 h of test in comparison to uncoated samples.

8:40am **A1-3-WeM-3 Development of a Ti_xSi_y Protective Layer on TiAl48-2Cr-2Nb for Increased Oxidation Resistance**, ***Josefina Crespo Villegas***, *S Loquai, É Bousser,* École Polytechnique de Montréal, Canada; *M Cavarroc,* SAFRAN Tech, France; *S Knittel,* SAFRAN Aircraft Engines, France; *L Martinu, J Klemberg-Sapieha,* École Polytechnique de Montréal, Canada

Given the extreme and wide range of operational conditions of jet engines, the aircraft industry has been a driving force in the development of high performance materials. There is a well-known need for lowered fuel consumption and greenhouse gas emission. Weight reduction of the aircraft engine is essential to meet these needs. In this context, ɣ-TiAl alloys have been extensively studied to be used as a replacement for Nickel-based alloys, due to their well-balanced ratio of density and mechanical properties. In fact, these alloys have recently been introduced as a material candidate for low-pressure turbine blades by several engine manufacturers. However, their application is limited by a maximum operating temperature around 750°C due to their limited oxidation resistance. Indeed, the formation of an outer mixed oxide scale (Al_2O_3 - TiO_2) and oxygen inward diffusion, due to the high affinity for oxygen, lead to material degradation and embrittlement of the component.

To increase the thermal stability of ɣ-TiAl alloys over 750°C, the development of coatings that promote stable and slow growing protective oxide scales is one of the preferred methods. Consequently, this work presents a study on the growth of Ti_xSi_y layers on a ɣ-TiAl alloy by Si deposition using RF magnetron sputtering and subsequent vacuum thermal annealing at 900°C. The composition and microstructural evolution of the coating are investigated by X-Ray Diffraction (XRD), Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM-EDS). To evaluate the efficiency of the Ti_xSi_y coatings, the oxidation resistance of the coating is investigated by isothermal measurements at 900°C.

The deposition of Si and the subsequent thermal annealing step resulted in the formation of a continuous coating of mixed Ti_xSi_y compounds. A significant dependence of the coating microstructure on the diffusion process conditions at the Ti_xSi_y coating/ɣ-TiAl interface was demonstrated. The oxidation behavior of Ti_xSi_y coated ɣ-TiAl and uncoated ɣ-TiAl were compared and the protective behavior of the Ti_xSi_y coating was confirmed. The chemical composition remained stable, no delamination was observed, and only a thin external layer of mainly protective SiO_2 was formed. Finally, the effect of the diffusion process of Ti_xSi_y promoted by the thermal annealing conditions is discussed.

9:00am **A1-3-WeM-4 The Impact of Aluminide and MCrAlY Coatings on the Fatigue Properties of Ni-based Valve Alloys**, ***Sebastien Dryepondt***, *B Armstrong, G Muralidharan,* Oak Ridge National Laboratory, USA

Increasing temperature in light and heavy-duty internal combustion engines offers a straightforward solution for increasing engine efficiency. Development of new Ni-based high temperature alloys is, however, burdensome due to the need for both high strength and high oxidation resistance. One solution is to apply corrosion-resistant coatings to high strength materials, but the coating must not affect the alloy mechanical properties. The impact of diffusion aluminides and MCrAlY overlay coatings on the high cycle fatigue (HCF) properties of alloy 31V ((57Ni-23Cr-13Fe-2Mo-2.3Ti-1.3Al-0.9Nb) was evaluated at 20, 500 and 800º C. At all temperatures, the numbers of cycles to failure for the bare and coated specimens were similar, as long as the specimen heat treatments were identical. A 3h at 1100º C heat treatment was initially used to fabricate a ~50um thick slurry aluminide coating but it was shown that a similar coating thickness can be achieved at temperature as low as 850º C. For the slurry and pack aluminide coatings, cracks initiated in the interdiffusion zone, whereas cracks initiated at the substrate/coating interface for the NiCoCrAlY-coated specimens. Initial characterization of aluminide and MCrAlY coatings deposited on advanced high strength Ni-based alloys will also be presented. This research was sponsored by the U.S. Department of Energy's (DOE), Vehicle Technologies Office, Propulsion Materials Program

9:20am **A1-3-WeM-5 High Temperature Oxidation of γ-TiAl Produced by Additive Manufacturing**, ***Radoslaw Swadzba***, Institute for Ferrous Metallurgy, Poland; *B Mendala, L Swadzba, B Witala, J Tracz,* Silesian University of Technology, Poland; *L Pyclik, K Marugi, S Sabbadini,* Avio Aero A GE Aviation Business, Poland

Recently γ-TiAl intermetallics have been successfully applied on low pressure turbine blades mostly due to their low density, high specific strength and creep resistance, all of which make them excellent alternatives for Ni-based superalloys. The paper presents the results of analytical TEM and STEM investigations on the microstructure and scale growth on γ-TiAl 48-2-2 alloy produced by EBM (Electron Beam Melting) in the range of 750 – 900 °C during short term experiments in air and pure oxygen. Moreover, the results of research works performed on Si-modified aluminide coatings for γ-TiAl are presented. The coatings were produced using pack cementation method with varying content of Si and Al in the pack. Total of five different pack chemistries were utilized to obtain coatings of different microstructure and high temperature oxidation performance. Moreover, a comparison of the high temperature oxidation behavior of 48-2-2 alloy produced by Additive Manufacturing and cast TNB-V5 alloy is presented. The samples were thermally cycled at 850 °C in 23 h cycles to a total of over 3000 hours in order to obtain mass change curves. The results of cyclic oxidation tests were related to the microstructure of the as-deposited coatings. Special effort has been done in order to perform a detailed investigation of the growth of protective oxide scales using high resolution Scanning Transmission Electron Microscopy (STEM), energy filtered TEM (EFTEM) and EELS (Electron Energy Loss Spectroscopy).

11:00am **A1-3-WeM-10 High Temperature Oxidation Protection of Gamma-based TiAl by Sputtered Al-O-F Films**, ***Florence Bergeron***, *S Loquai, É Bousser,* École Polytechnique de Montréal, Canada; *M Cavarroc,* SAFRAN Tech, France; *S Knittel,* SAFRAN Aircraft Engines, France; *L Martinu, J Klemberg-Sapieha,* École Polytechnique de Montréal, Canada

γ-based TiAl alloys are considered for major components of aircraft engines. Indeed, their excellent mechanical properties and relative light weight make them good candidates to replace nickel-based alloys for blades and vanes in the low-pressure stages of the turbine. However, the use of TiAl for other engine parts is limited by its high sensitivity to oxidation phenomena at temperatures above 750°C. The presence of TiO_2

in the generated oxide scale is an issue, as it grows faster than Al_2O_3 and hinders the formation of a continuous protective Al_2O_3 oxide scale. Indeed, alumina is a slow growing oxide, and offers good protection against oxygen diffusion.

Therefore, a solution to protect gamma-based TiAl is to form an α-Al_2O_3 layer at its surface, for which the halogen effect can be very effective approach. The addition of a halogen on the surface or the subsurface of TiAl promotes the growth of alumina by preferentially forming gaseous aluminum halides instead of titanium halides. Specifically, fluorine has been shown to offer excellent performance during high-temperature oxidation, as aluminum fluorides react with oxygen to form Al_2O_3. Fluorination of TiAl can be performed using either F ion implantation or fluorocarbon overlay coatings applied by spraying, painting, dipping, etc.

In the present work, we propose a new approach to deposit Al-O-F coatings based on low-pressure RF reactive magnetron sputtering of Al in an atmosphere composed of an O_2 and fluorocarbon mixture. The resulting coating microstructure was characterized by Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-Ray Spectroscopy (EDS) and Rutherford Backscattering Spectrometry (RBS) chemical analysis. Their oxidation performance was then tested using isothermal oxidation at 850°C in laboratory air. The fluorine content of the coatings varied between 50 and 70 at.% and it was found that the Al-O-F coatings protect TiAl against damaging oxidation. The resulting outer oxide scale at the surface was thin and was composed of a continuous Al_2O_3 layer at the interface, covered by a mixed TiO_2 and Al_2O_3 oxide layer.

In parallel, the discharge was studied using mass spectrometry and the relationships between gaseous precursor concentrations, power, pressure and the plasma's chemistry and coating composition are discussed.

11:20am **A1-3-WeM-11 Corrosion Behavior and Durability of Microstructure of Stainless Steel Rebars in Simulated Concrete Pore Solution Containing Chloride with Different Ph**, ***Dhruba Babu Subedi,*** Chinese Academy of Sciences, China

Corrosion is a problem of science and technology. It cannot eliminate completely although the corrosion control is becoming more practical and achievable to decrease its rate. Nowadays, the corrosion control method of metals and alloys using various types of eco-friendly coating to save passive film on metal surface is becoming a fundamental academic and research concerns corrosion scientists.

All the experiments were conducted under static or dynamic flow conditions at room temperature. The corrosion rate evaluations were implemented by electrochemical measurements (open circuit potential, linear polarization, potentiodynamic polarization, and electrochemical impedance spectroscopy), while surface analytical techniques (SEM/EDS, XRD and XPS) were employed to examine and characterize the compositions, microstructure of alloys and the corrosion product films.

Fig1;Nyquist plot, 1-28day Austenitic Stainless Steel Fig1; Nyquist plot of three Stainless Steel

The corrosion resistance performance of the different stainless steel, 304ss, 410ss and 2304ss

Ware evaluated in different chloride condition at 9.3 pH comparing with microstructure and mechanism of passivation film formation. EIS results of both accelerated corrosion tests showed the corrosion resistance performanceof different alloys

Fig; Phase and Bode plot of Austenitic stainless steel for 1- 28day

The results of a study examining the Cl_ induced corrosion resistance of austenitic,duplex, and ferritic high-strength stainless steels in simulated alkaline and carbonated concretesolutions during exposed to carbonated solutions, corrosion resistancewas reduced and only duplex grades 2304SS exhibited high corrosion resistance.

Fig; surface srtructure of duplex stainless steel after 14 days

A strong correlation between microstructural defects and corrosion damage was observed by the help of morphology of SEM picture and optical observations. The pitting corrosion behavior of 304ss, 2304ss and 410ss in 3.5% NaCl solution has been investigated by electrochemical noise M-S Curve and the experimental data was analyzed based on stochastic theory. The change in the pit initiation site and the outstanding repassivation ability of 2304ss thin film determined that metastable pit events occurred more frequently and the probability of stable pits developing from metastable pits was lower than that of 304ss and 410ss, which improved the pit corrosion resistance of duplex thin film.he difference between growth mechanisms of stable pits on two materials led to different corrosion resistance, thus enhancing the pit corrosion resistance of duplex thin film compare to other two alloys.

11:40am **A1-3-WeM-12 High-temperature Sulfidation of Hot-dip Aluminized 9Cr-1Mo Steel**, ***Muhammad Ali Abro,*** Mehran University of Engineering and Technology, Pakistan*; D Lee,* Sungkyunkwan University, Republic of Korea

The 9Cr-1Mo ferritic steel is used frequently in petroleum refining, petrochemical units, and coal power plants due to its good combination of weldability, ductility and high-temperature creep resistance. However, it could suffer serious corrosion in the H_2S gas that is produced as the byproduct during processing in plants. The H_2S gas could accelerate the corrosion and structural deterioration through forming the nonprotective FeS scale and causing the hydrogen dissolution. Hence, the Al hot-dipping was performed in order to protect this steel from the serious H_2S gas corrosion. Aluminum hot-dipped coatings behavior applied on 9Cr-1Mo steels have been studied under N_2/0.1%H_2S gas corrosion for up to 50 h at 800 and 900 ºC, which suffered little general corrosion on the exterior, due to the frequent incorporation and dissolution of foreign ions such as S to a certain extent. The results have shown that initially, the coating forms by outward growth possibly due to the dissolution of the Fe and matrix elements in molten aluminum. At a later stage, during exposure to N_2/0.1%H_2S at 800-900 ºC, aluminum diffuses inward and Fe diffuses outward resulting in the progressive development of Kirkendall voids. A protective aluminum oxide scale (α-Al_2O_3) forms on the surface which remains homogenous, continuous and non-adherent to the alloy layer, but constitutes a protective behavior against sulfurized corrosion attack to a certain extent. The corrosion resistance of hot-dipped steels was much better than that without hot-dipping was largely attributed to its Cr, Mo and Si content in the matrix and Al-rich alloy layer formed at the oxide scale/substrate interface.

The samples without were also sulfidized at similar conditions for comparison purposes and in order to find the diffusion mechanism using Pd marker testing. The samples were inspected using SEM equipped with an EDS, an EPMA and a high-power X-ray diffractometer with Cu-Kα radiation at 40 kV and 300 mA. The microstructures of the aluminized layer and the steel substrate were etched using Keller's reagent and Vilella's reagent, respectively. Vickers microhardness was measured using a microhardness tester.

Acknowledgment. This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017R1D1A1B03028792). Authors are also thankful to HEC Pakistan to provide the travel grant.

Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A3-WeA

Materials and Coatings for Solar Power Concentration Plants

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, **Gustavo García-Martín**, Universidad Complutense de Madrid

2:40pm **A3-WeA-3 Ductility and Creep Rupture Behavior of Diffusion Coatings Deposited on Grade 91 Steel for Concentrated Solar Power Applications***, **Ceyhun Oskay**, T Meissner, C Dobler, M Galetz,* DECHEMA-Forschungsinstitut, Germany

Energy transition aims at the abandoning of fossil-fuel based power generation and shifting to renewable energy technologies. In the course of energy transition concentrated solar power (CSP) technology is qualified as one of the most promising energy generation methods. In CSP systems, solar radiation is concentrated to a receiver via heliostats and molten nitrate salts are employed in the absorber tubes to store and transfer the thermal energy for the consequential generation of electricity via a steam turbine. While offering beneficial thermal and physical properties such as a high heat capacity, thermal conductivity and stability, the utilization of molten nitrate salts, particularly the eutectic mixture of 60 wt.% $NaNO_3$ – 40 wt. KNO_3 (known as the solar salt) is accompanied with an increased corrosion rate and thus limits the selection of structural materials to high-alloyed steels as well as Ni-based alloys due to their high corrosion resistance. As an alternative, cheaper structural materials such as ferritic-martensitic steels can be used by enhancing their molten salt corrosion resistance via the application of diffusion coatings. This can result in a substantial increase in the cost efficiency of the CSP technology and thus improve its competitiveness with respect to other energy generation methods such as photovoltaics.

In this study, three different types of diffusion coatings were deposited on P91 steel substrates by the industrially well-established method of pack cementation. The first two coatings were aimed at Cr and Al enrichment at the surface respectively; whereas the third coating was manufactured by a two-step process involving chromizing followed by aluminizing. Subsequently coated and uncoated specimens were exposed to isothermal oxidation in laboratory air at 650°C for 100, 300 and 1000 h in order to characterize the scaling behavior of coatings by thermogravimetric analysis. Four-point bending tests with in-situ acoustic emission (AE) measurement were conducted to determine the fracture strain at RT, while creep rupture tests at 650°C in laboratory air were undertaken to compare the creep strength of coated specimens with respect to their uncoated counterparts. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were utilized for the phase identification and microstructural characterization. Detailed microstructural analysis enabled the correlation of mechanical behavior with the microstructural degradation of coated and uncoated specimens during exposure.

3:00pm **A3-WeA-4 Long-term Molten Salt Corrosion of Aluminide Coatings for Heat Storage in Concentrated Solar Power Plants***, P Audigié, S Rodríguez, **Alina Agüero**,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Concentrating solar power (CSP) plants represent a valuable technology in terms of baseload and dispatchable renewable energy. However, due to its complicated nature and its difficulty to become an economically viable technology CSP struggle to gain the upper hand over solar photovoltaic and wind power. To overcome the main drawback of intermittency, improving the heat storage system by targeting 15h to 24h storage in the mid- or long-term will bring added-value to CSP. In that sense, advanced molten salts used as heat transfer fluids are investigated but corrosion issues for tubes and tanks materials in contact with them are of concern. To protect base materials with coatings can resolve or moderate corrosion degradation and therefore improve the plant efficiency. This alternative also allows to reduce the capital expenditure when designing a new plant because coatings can be applied on lower cost ferritic-martensitic steels instead of current expensive Ni-base alloys. Slurry aluminide coatings have already demonstrated high corrosion resistance to molten salt after short term exposure (1000h). But the protection mechanism still remains under investigation and long-term exposure is required to confirm the lifetime gain brought by the coatings. This study focuses on the corrosion resistance of slurry aluminide coatings after long-term exposure in contact with the currently employed heat storage system, the so-called Solar Salt (60% $NaNO_3$-40% KNO_3). To do that, slurry applied aluminides to 9 wt.% Cr P91 and 11.5 wt.% Cr VM12-SHC alloys have been deposited, heat treated at high temperature and both systems have been tested at 580ºC in contact with the Solar Salt under static isothermal and cyclic conditions. All the coated systems in all conditions performed much better than the uncoated materials as they exhibited very slight weight variations and formed very thin oxides rich in Na, Al and Fe. Moreover, the coating's morphology and composition were maintained after 5000h with the presence of the same FeAl and Fe_3Al phases than in the initial state suggesting that the Al reservoir is still large enough to protect the underlying metals. On the contrary, both uncoated P91 and VM12-SHC developed a complex, fast growing multilayered oxides rich in Fe, Cr and Na which easily spalled in particular after testing in the more aggressive cyclic conditions. Moreover, as corrosion in molten salt results from the competition between dissolution reactions and corrosion product formation, removing the corrosion products by chemical etching was performed to determine the corrosion kinetics and both substrates experienced parabolic kinetics with significant metal loss.

3:20pm **A3-WeA-5 Burn-in Heat Treatment to Form Aluminide Diffusion Coatings for Industrial Large Scale Application***, **Vladislav Kolarik**, M Juez Lorenzo, J Bermejo Sanz, S Weick,* Fraunhofer Institute for Chemical Technology ICT, Germany

Aluminide diffusion coatings, deposited as Al slurries, are an efficient and economic technique to protect steels against oxidation and corrosion at high temperatures. Moreover, the coating suppresses the evaporation of volatile chromium VI species, which form especially in the presence of water vapor. The typical applications of such coatings are boilers and heat exchangers in all kind of power plants and recently, the application to tubes and storage tanks for molten salt in the up-coming technique of concentrated solar power (CSP) is being investigated.

The diffusion heat treatment, however, is a crucial process step when applied to large scale components, such as a CSP storage tank and even more when aiming at application on-site. Furthermore, the temperature of the heat treatment has to stay below the annealing temperature of the steel for not affecting the microstructure, e.g. 700°C for the ferritic steel P92.

A superficial BURN-IN process was applied to form the aluminide diffusion coating using a heating source with a defined temperature moving with a defined velocity over the slurry coated surface at a defined distance to it. Pre-oxidation forming an alumina scale on top of the coating can be achieved with a proper adjustment of the burn-in process.

A viscosity and rheology adapted slurry formulation was prepared using spherical high purity aluminum particles with an average diameter of 15 µm and was deposited by brushing or spraying on the surface of the ferritic steel P92. A commercially available radiation heating element was used to heat the sample surface. During the burn-in process the temperatures of the heating source, the slurry coating surface as well as the back-side of the sample were recorded as a function of time. Temperatures in the range of 800°C were applied to the slurry coated surface for times up to 5 hours. With these parameters, the back-side temperature of a 3 mm thick sample was around 500°C.

The resulting aluminide diffusion coatings exhibit very low porosity and a very smooth surface forming a two layers-structure, an outer Fe_2Al_5 layer and an inner FeAl layer. Transversal micro-cracks across the aluminide coating are observed locally as it is typical for such coatings. Underneath the diffusion coating the P92 substrate shows an unaffected microstructure as it is found in the case of the conventional heat treatment at 650°C. The superficial burn-in process is a suitable heat treatment for slurry coatings allowing higher temperatures on the surface and applicable to large components.

3:40pm **A3-WeA-6 High-Temperature Coatings For Protection of Steels in Contact with Molten Salt for CSP Technology***, **Gustavo García-Martín**,* REP-Energy Solutions, Spain*; V Encinas Sánchez,* Universidad Complutense de Madrid, Spain*; M Lasanta Carrasco,* Universdad Complutense de Madrid, Spain*; T de Miguel Gamo, F Pérez Trujillo,* Universidad Complutense de Madrid, Spain

The dramatic increase in demand for energy independence has led research groups all over the world to concentrate their investigation on renewable energies. As renewable energy penetration grows, the need for utility-scale renewable generation with storage technology is increasingly important to mitigate intermittency problems, deliver power to peak demand periods and support transmission system reliability. Therefore, concentrated solar power has gained momentum as an attractive technology. Molten nitrate salts are currently considered ideal candidates for heat transfer and storage applications because of their properties. However, this technology is still expensive compared to other renewable sources, which lead to propose solutions for reducing costs. One of these solutions is the development of high-temperature corrosion-resistant coatings, which would avoid the use of expensive alloys. The use of high-temperature corrosion-resistant coatings would be a very suitable option, even more if they were deposited on cheap steels, such as ferritic-martensitic ones. This solution not only would help to overcome the corrosion problems, but also would allow the CSP industry to improve the Levelized Cost of Energy. In this respect, zirconia-based sol-gel coatings seem to be a suitable option, both from an operational and economical point of view.

Thus, in this work, sol-gel zirconia-based coatings were deposited on ferritic-martensitic steels and tested in contact with Solar Salt at 500°C, results being compared with the uncoated substrate. Results were also compared to other steels of interest in CSP industry, such as austenitic stainless steels. The study was developed up to 1000 h under static conditions. Samples were characterized via gravimetric, SEM-EDX, and XRD.

Results showed the good behavior of the coated substrates, with very little weight variations after 1000 h of test in comparison with the uncoated ones, which exhibited significant weight gain and spallation. The good behavior of the proposed coatings was also observed by SEM-EDX and XRD. Furthermore, results also showed the promising behavior when comparing with steels currently used in CSP industry.

Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A2-1-ThM

Thermal and Environmental Barrier Coatings I

Moderators: Sabine Faulhaber, University of California, San Diego, USA, **Kang N. Lee**, NASA Glenn Research Center, USA, **Pantcho Stoyanov**, Pratt & Whitney, USA

8:00am **A2-1-ThM-1 Mechanical Characterization and Modelling Issues for Thermal Barrier Coating Lifetime Assessment**, ***Vincent Maurel**, V Guipont,* Mines-ParisTech, France **INVITED**

One of the major challenges for protective coatings is to determine the time to failure of ceramic layer during ageing for both TBC and EBC. For TBC, scenarii of damage have been well established from decades, based on microstructure to damage analysis with an increase use of 3D measurement tools (synchrotron tomography, FIB). The aim of this paper is to review some experiments to modeling issues.

Firstly, the characterization of adhesion is a key factor in the evaluation of time to failure. The measurement of adhesion should be addressed including the analysis of scatter induced by both the methodology of measurement and the "natural" scatter associated to TBC process. Recently, the use of LAser Shock Adhesion Test (LASAT) has shown its capability for both ranking different coating solutions and evaluating the evolution of a given coating as a function of aging [1-2], limiting the scatter associated to measurement. Besides, the laser shock could be used to introduce a defect, an interfacial delaminated area, known in size and location. Thus, local adhesion properties could be determined [2].

Secondly, dealing with modeling of lifetime, different strategies have been discussed in the literature taking into consideration a typical multi-scaled problem. Local analysis of failure has shown its efficiency to model the link to microstructure and aging to local failure. However, for the time being, only macroscopic analysis enables to derive lifetime at the scale-length of a typical component (eg turbine blade). We develop macroscopic lifetime model based on adhesion testing [3,5]. Finally, the robustness of this kind of models has been analyzed through sensitivity analysis based on large numerical sampling. As a conclusion, the propagation of scatter from measurement to life modeling is evaluated and guidelines for experimental focus points have been derived.

References

[1] Guipont, et al (2010). Journal of Biomedical Materials Research Part A, 95(4), 1096-1104.

[2] Guipont, et al. "Interfacial toughness evolution under thermal cycling by laser shock and mechanical testing of an EB-PVD coating system." (2018). http://dc.engconfintl.org/cgi/viewcontent.cgi?article=1033&context=tbcv

[3] Courcier, C et al (2011). Interfacial damage based life model for EB-PVD thermal barrier coating. Surface and Coatings Technology, 205(13-14), 3763-3773.

[4] Dennstedt, et al (2018). Crack Morphology in a Columnar Thermal Barrier Coating System. https://opus4.kobv.de/opus4-zib/files/6938/3DMS2018_AnneDennstedt.pdf

[5] Theveneau, M. (2018). Internal report, Mines-ParisTech.

8:40am **A2-1-ThM-3 The Effect of Bond Coat Asperity Removal on the Lifetime of Atmospheric Plasma Sprayed Thermal Barrier Coatings**, ***Kenneth Kane***, Oak Ridge National Laboratory, USA; *M Sweet,* Praxair, USA; *M Lance, B Pint,* Oak Ridge National Laboratory, USA

Atmospheric plasma sprayed (APS) MCrAlY (M = Co, Ni) bond coats are inherently rough, typically being comprised of a mixture of convex and concave regions. Initially the roughness provides a high surface area platform for mechanical interlocking of a yttria stabilized zirconia (YSZ) top coat however after high temperature oxidation the convex asperities of the bond coat are prone to form multiphasic, nonhomogeneous thermally grown oxide (TGO). Non-uniform TGO growth is generally thought to have a deleterious effect on top coat adhesion and the removal of these regions should impact coating performance. In the presented work, CoNiCrAlY APS bond coats deposited onto Hastelloy-X substrates were modified to varying degrees (unmodified, lightly modified, and heavily modified) prior to YSZ deposition. The modifications resulted in large asperities being replaced with flat regions, leaving intact concavities and smaller asperities. Samples were isothermally exposed at 1100°C for 100 h to evaluate the effect modification has on TGO formation. Furnace cycle testing (FCT) at 1100°C/1-h was used to gauge the effect modification has on coating lifetime. BS-SEM and EDS analysis of TGO formation and cracking behavior was used to elucidate the changes in FCT lifetime due to modification.

9:00am **A2-1-ThM-4 Effect of Superalloy Substrate on the Lifetime of Electron Beam Physical Vapour Deposited Thermal Barrier Coatings**, ***Chen Liu**, Y Chen, P Xiao,* University of Manchester, UK

Previous studies have reported that the cyclic oxidation lifetime of thermal barrier coatings (TBCs) is affected by the composition of superalloy substrates [1-3]. The presence of titanium (Ti) in CMSX-4 has been reported to be detrimental to TBC lifetime because the Ti-rich oxides can degrade the thermally grown oxide (TGO)/bond coat interface adherence [4]. However, the mechanism of how the chemical composition of the substrate affect the lifetime of TBCs is still not fully understood. To further elucidate the effect of substrates on TBCs, the CMSX-4 and René N5 single crystal superalloys have been used as substrates for TBCs with Pt-diffused γ/γ' bond coats and electron beam-physical vapour deposited (EBPVD) yttria-stabilized zirconia (YSZ) top coats. The cyclic oxidation (1 h holding time at 1200°C) test has been carried out on TBCs with different substrates. It was found that TBC deposited on the CMSX-4 substrate exhibited an average lifetime 20% higher than that deposited on the René N5 substrate. Specifically, spallation of TBC occurred mainly along the bond coat/TGO interface for TBC with the René N5 substrate whereas, for TBC with the CMSX-4 substrate, failure occurred mostly along the TGO/YSZ interface and sometimes within the TGO. This suggests that the bond coat/TGO interface for TBC with the René N5 substrate might be degrade by the chemical composition diffused from the substrate into the coating. To confirm this, transmission electron microscope (TEM) with STEM (scanning transmission electron microscope)/EDX (energy-dispersive X-ray) detector was used to examine the TGO/coating interface of TBCs. Segregation of sulfur has been found at the bond coat/TGO interface of TBC with the René N5 substrate, while no impurity segregation was observed at the bond coat/TGO interface of TBC with CMSX-4 substrate. In addition, no Ti-rich oxides was found in the TGO on the CMSX-4 substrate, indicating that the lifetime of this TBC system is not affected by the presence of Ti in the substrate.

Reference

[1] Pint BA, Haynes JA, Zhang Y. Surf Coat Tech 2010;205:1236-40.

[2] Bouhanek K, Adesanya OA, Stott FH, Skeldon P, Lees DG, Wood GC. High Temperature Corrosion and Protection of Materials 5, Pts 1 and 2 2001;369-3:615-22.

[3] Tawancy HM, Al-Hadhrami LM. J Eng Gas Turb Power 2011;133.

[4] Tawancy HM, Mohamed AI, Abbas NM, Jones RE, Rickerby DS. J Mater Sci 2003;38:3797-807.

9:20am **A2-1-ThM-5 Self-Healing Thermal Barrier Coatings Produced by Laser Processing**, ***Bowen Wei**, J Gu, S Joshi, T Huang, N Dahotre, S Aouadi,* University of North Texas, USA

Thermal barrier coatings (TBCs) are widely applied to protect superalloy blades in gas turbines and jet engines that are subjected to high temperatures and corrosive environments. However, the dissimilarities between the coefficients of thermal expansion of the ceramic coatings and metallic substrates will cause thermal stresses and lead to the generation and growth of cracks. This will facilitate oxygen diffusion through the TBC, and a thermally grown oxide (TGO) will be generated between the TBC and the bond coat, which will ultimately lead to failure. A potential effective solution to overcoming this challenge is to grow a self-healing layer on the TBC. In this work, YSZ/Al2O3/SiC and YSZ/Al2O3/TiC self-healing model systems were produced by laser processing with the premise that the healing process occurs as a result of the oxidation of the carbide phase. The formation of the healing oxide phase was observed using X-Ray diffraction and its formation in the crack site was confirmed using cross-sectional scanning electron microscopy. The optimum process parameters to create a self-healing composite were determined. Finally, the impact of the self-healing overlayer on deformation and failure resistance as well as corrosion resistance at elevated temperatures was investigated.

9:40am **A2-1-ThM-6 Influence of Heat Treatment on Thermal Cyclic Fatigue Lifetime of TBC System**, ***Jianhong He**, T Sharobem,* Oerlikon Metco, USA

Heat treatment of a component with TBC coating in vacuum is a common industrial practice. However, there is no systematic investigation on its cause. This paper tested thermal cyclic fatigue lifetime of TBC systems heat treated in different levels of vacuum (as sprayed, heat treated in atmosphere, 0.5 mbar and 6.67 x 10 -4 mbar) and found there are significant difference in thermal cyclic fatigue lifetime. Detailed TGO examinations on cross section and EDS analysis indicate that TGO configurations in samples heat treated in different levels of vacuum is rationale of the differences in thermal cyclic fatigue lifetime.

10:20am **A2-1-ThM-8 Effects of Chemical Modification on Bond Coat Oxidation and Internal Stresses in $Yb_2Si_2O_7$ Environmental Barrier Coatings*, Benjamin Herren,*** California Institute of Technology, USA*; J Almer,* Argonne National Laboratory, USA*; K Lee,* NASA Glenn Research Center, USA*; K Faber,* California Institute of Technology, USA

A key failure mode of environmental barrier coatings in steam environments is spallation, often caused by a thermally grown oxide (TGO) resulting from oxidation of the bond coat. Safeguarding against this failure mode can increase the usable lifespan of EBCs, with one approach focused on limiting oxide growth rate. This study examines the effects of topcoat compositional modification on oxide growth rate and internal stresses, by addition of Al_2O_3 or Al_2O_3-containing compounds, e.g., mullite and yttrium-aluminum-garnet, of a current state-of-the-art EBC ($Si/Yb_2Si_2O_7$). Cyclic steam oxidation tests of these EBC systems and post-exposure analyses were used to study the effects of oxide additions on TGO growth rate and microstructure; after 1000-hour exposures to high-temperature steam conditions, some modified EBC compositions showed significant reductions to TGO growth – in certain cases, larger than 80 percent. (K. N. Lee, J. Am. Ceram. Soc., doi: 10.1111/jace.15978). X-ray scattering of these same EBC systems at the Advanced Photon Source at Argonne National Laboratory was used to evaluate strain in the multilayer systems as steam oxidation progressed. Strain and the associated internal stresses for modified EBCs were evaluated with respect to TGO thickness and chemistry and compared to the baseline EBC composition for the same exposure conditions.

10:40am **A2-1-ThM-9 Thermal Shock and CMAS Resistant Tunable Self-Healing Thermal Barrier Coatings*, Jingjing Gu,*** *B Wei, T Huang, S Bakkar, D Berman, R Reidy, S Aouadi,* University of North Texas, USA

Thermal barrier coatings (TBCs) are used to protect gas turbine blades from oxidation and corrosion. Commercial TBCs often exposed to sand, dust, ash, and other particulates in addition to elevated temperatures. Found in desert sands and volcanic ash, calcia-magnesia-alumina-silicate(CMAS) particles can degrade TBCs through chemical attack, and coating delamination and spallation, thus, limiting the durability of gas turbines in these environments. In this work, laser cladding was used to create a self-healing protective overlayer on TBC coatings to improve chemical and thermal resistance. Self-healing coatings were applied onto traditional yttria-stabilized zirconia (YSZ) layers. $YSZ/Al_2O_3/SiC$ and $YSZ/Al_2O_3/TiC$ overlayer coatings were deposited using a Nd:YAG laser. Within the overlayer, the carbide phase oxidizes and seals the porosity in the TBCs. After thermal cycling and CMAS tests, resulting phases were identified X-Ray diffraction. In addition, cross-sectional scanning electron microscopy was used to investigate the subsurface and interlayer damage and CMAS penetration occurring resulting from thermal cycling. The performance of these overlayered TBC was compared to the traditional TBCs.

11:00am **A2-1-ThM-10 Variables Affecting Steam Oxidation Kinetics of Environmental Barrier Coatings*, Kang N. Lee,*** NASA Glenn Research Center, USA

Increased fuel efficiency is obtained through increased thermal efficiency of turbine engines by increasing the overall pressure ratio (OPR). Increased OPR requires increased turbine inlet temperature, which is paced by advances in turbine hot section materials. SiC/SiC Ceramic Matrix Composites (CMCs) are the most promising materials to enable a quantum leap in temperature capability. Environmental Barrier Coatings (EBCs) are an enabling technology for CMCs by protecting them from water vapor-induced recession. Spallation of EBC induced by thermally grown oxide (TGO) resulting from steam oxidation is a key EBC failure mode. A logical approach to improve EBC life, therefore, is to reduce TGO growth rates. A study was undertaken to investigate the effect of two variables, EBC chemistry and CMC substrate, on TGO growth rates. Using Si/Yb2Si2O7 as the baseline, various oxides were added in Yb2Si2O7 to investigate the former, while various CMC substrates were used to investigate the latter. EBC was processed using air plasma spraying. Oxidation kinetics was determined using steam cycling test in 90% H2O + 10% O2. Correlations between oxidation kinetics, chemistry, phase, and microstructure are used to explain the effect of EBC chemistry and CMC substrate on TGO growth rates.

11:20am **A2-1-ThM-11 High Temperature Investigations of Thermochemistry and Phase Stability in the ZrO_2-Y_2O_3-Ta_2O_5 System*, Maren Lepple,*** DECHEMA Forschungsinstitut, Technische Universität Darmstadt, Germany*; S Ushakov, K Lilova,* University of California, Davis, USA*; C Macauley, C Levi,* University of California, Santa Barbara, USA*; A Navrotsky,* University of California, Davis, USA

Compositions in the ZrO_2-Y_2O_3-Ta_2O_5 system are of interest for new high performance thermal barrier coating applications due to their promising high-temperature properties. Alongside an extended tetragonal phase field stable to temperatures at least up to 1500 °C obtained by equimolar co-doping of Y^{3+} and Ta^{5+}, the $YTaO_4$ phase field recently attracted attention. Both phase fields of interest lie on the ZrO_2-$YTaO_4$ quasibinary investigated in this work.

For high temperature applications, it is essential to understand phase stabilities and relations as well as energies and driving forces of the stable and metastable phases. Experimental and computational thermodynamics using the method CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) gives a self-consistent description of the materials system, facilitating materials development. In this work, the energetics and phase stabilities of several compounds in the ZrO_2-Y_2O_3-Ta_2O_5 system were investigated experimentally. The enthalpies of formation of different phases as a function of composition were determined using high-temperature oxide melt solution calorimetry. Transition temperatures and enthalpies and phase stabilities were explored by differential thermal analysis (DTA) up to 2400 °C and in-situ high temperature synchrotron X-ray diffraction. The very high melting temperatures of the refractory oxides were investigated by measurement of cooling traces using laser melting. The enthalpy of fusion of $YTaO_4$ was determined using drop calorimetry on a laser heated aerodynamically levitated samples. The results will be used for CALPHAD modeling to obtain a comprehensive understanding of the thermochemistry of the quasibinary.

Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A2-2-ThA

Thermal and Environmental Barrier Coatings II

Moderators: Sabine Faulhaber, University of California, San Diego, USA, **Kang N. Lee**, NASA Glenn Research Center, USA, **Pantcho Stoyanov**, Pratt & Whitney, USA

1:20pm **A2-2-ThA-1 Design of Multiphase Environmental Barrier Coatings: Toward Multifunctional Molten Deposit Resistance***, David Poerschke,* University of Minnesota, USA **INVITED**

The ceramic thermal and environmental barrier coatings (T/EBC) employed to protect SiC-based composited in gas turbine engines must satisfy multiple interrelated performance requirements including phase stability, tolerance to thermal strains, and resistance to environmental degradation (e.g., via molten deposits or foreign object impact). It is increasingly evident that rare earth disilicate coatings, which offer good phase stability and minimize the coefficient of thermal expansion (CTE) mismatch with SiC, are not sufficiently resistant to degradation caused by silicate deposits. Reactions between the coatings and deposits progressively consume the coating and produce phases with increased CTE mismatch. Upon thermal cycling, the penetration of channel cracks originating in the reaction layer through the remaining coating and into the composite accelerates the failure of both the coating and the underlying component. Due to the limited number of materials satisfying all of the design requirements, achieving improved performance likely requires multiphase coating systems. This presentation presents a multi-pronged approach to new develop new coating materials. The effort combines new understanding of the thermochemistry of the coating-deposit interactions in order to identify material combinations that minimize the coating recession depth upon exposure to various deposits while developing composite materials with precisely tunes CTEs to manage thermal strains over a wide range of operating conditions.

2:00pm **A2-2-ThA-3 Comparison of Oxidation Procedures of MCrAlY Coatings Deposited by PVD Cathodic Arc Evaporation***, X Maeder, J Ast,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Polyakov,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Döbeli,* ETH Zürich, Switzerland*; A Neels, A Dommann,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; B Widrig, **Oliver Hunold**, J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Development of superalloys which can sustain higher operating temperatures is necessary to increase efficiency of land-based and areo turbines. This requires enhanced surface stability of the components with respect to oxidation and corrosion. The coatings applied to superalloys substrates need therefore to form a well adherent and stable interface towards the substrate by diffusion process and create a protective oxide at their surface. We will show here the capability of depositing MCrAlY coatings by cathodic arc evaporation on Ni-based superalloy substrates. MCrAlY targets where produced by spark plasma sintering and processed in non-reactive mode and in mix non-reactive and reactive modes on directional solidified CM247 and single crystalline PWA1483 substrates. The phases, microstructure and composition of the targets and synthesized coatings are characterized by TEM, transmission EBSD, X-ray diffraction and RBS analyses and discussed. The interface between the MCrAlY coatings and the different Ni-based superalloy substrates before and after annealing is investigated and different approaches to form an oxide scale on top of the MCrAlY coating are discussed.

2:20pm **A2-2-ThA-4 Effect of APS Flash Bond Coatings and Curvature on Furnace Cycle Lifetime of Rods***, **Michael Lance**, J Haynes, B Pint,* Oak Ridge National Laboratory, USA*; E Gildersleeve, S Sampath,* Stony Brook University, USA

The addition of an air plasma sprayed (APS) "flash" bond coating layer on top of a high velocity oxy-fuel (HVOF) bond coating significantly extended the lifetime of APS yttria stabilized zirconia (YSZ) top coatings on rod specimens of superalloy 247 tested using 100-h cycles in air+10%H_2O at 1100°C. The flash coatings of both NiCoCrAlY and NiCoCrAlYHfSi powder were compared to an HVOF-only and a vacuum plasma sprayed (VPS) NiCoCrAlYHfSi bond coating. The flash coatings appear to form a mixed oxide-metal zone that appeared to inhibit crack formation and extend lifetime compared to conventional bond coatings. The underlying HVOF layer acted as a source of Al for this intermixed zone and prevented the oxide from penetrating deeper. Residual stress in the thermally grown Al_2O_3 scale was measured using photo-luminescence piezospectroscopy (PLPS) as a function of time for each coating variation, including a comparison of concave and convex surfaces.

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

2:40pm **A2-2-ThA-5 Investigation of Thermally Grown Oxide Stress in Plasma-spray Physical Vapor Deposition and Electron-beam Physical Vapor Deposition Thermal Barrier Coatings via Photoluminescence Spectroscopy***, **Linda Rossmann**, M Northam,* University of Central Florida, USA*; V Viswanathan,* Praxair Surface Technologies, USA*; B Harder,* NASA Glenn Research Center, USA*; S Raghavan,* University of Central Florida, USA

Gas turbine engines for aircraft propulsion require thermal barrier coatings (TBCs) to protect metallic components in the hot section from the extreme temperatures of operation, which may exceed 1200 °C. These coatings are typically 6-8% yttria-stabilized zirconia (YSZ), and the standard methods of coating deposition are air plasma spray (APS) and electron-beam physical vapor deposition (EB-PVD). EB-PVD produces a higher-quality coating than APS due to its resulting columnar microstructure that increases the strain tolerance of the coating. Plasma-spray physical vapor deposition (PS-PVD) is a promising technique that offers several advantages over EB-PVD, including lower cost, shorter coating time, customizability of microstructure by varying processing parameters, and possibility of non-line-of-sight coating. However, the effect of this process on the resulting microstructure, properties, and performance is not fully understood. In this work, TBCs manufactured by both EB-PVD and PS-PVD were investigated via photoluminescence spectroscopy after varying amounts of thermal cycling, to investigate the effect of deposition process on the stress state of the thermally grown oxide (TGO) layer.

This work investigates the residual stress in the TGO of samples made by EB-PVD and PS-PVD, thermally cycled in the same way at multiple lifetimes (as-deposited, 300 cycles, and 600 cycles), to evaluate the effects of deposition method. As-deposited PS-PVD samples were given a 1-hour heat treatment, during which they developed a TGO. This was found to be in compression on the order of 2-3 GPa, consistent with published data on EB-PVD TBCs. Other PS-PVD samples were cycled for 300 and 600 hours, and these exhibited stress relaxation compared to the 1-h heat treated, suggesting some stress relief from damage. The findings from these investigations will be presented in the paper.

In this study, we compare the TGO residual stress evolution in PS-PVD and EB-PVD TBCs to shed light on their respective responses to thermal cycling. These results contribute to understanding how the PS-PVD process compares to the EB-PVD process with respect to coating life and durability.

3:00pm **A2-2-ThA-6 Thermally Conductive and Electrically Insulating Epoxy Nanocomposites with Intercalation of Aluminum Nitride Nanoparticles into Exfoliated Graphite***, **Che Juei Wu**,* National Cheng Kung University, Taiwan

In this study, the enhancement of thermal conductive of epoxy-based nanocomposites without scarifying electrical insulating were demonstrated. This was done by introducing intercalated aluminum nitride (AlN) into expanded graphite in the nanocomposite. Intercalation of AlN nanoparticles into adjacent exfoliated graphite were firstly prepared via solution mixing with supercritical fluid CO_2 ($SCCO_2$). $SCCO_2$'s low surface tension and viscosity lead to greater penetration into porous solid. Epoxy composites with an intercalated of AlN nanoparticles into exfoliated graphite were fabricated using a three roll mills machine. Scanning electron microscopy images reveal that intercalation of AlN into exfoliated graphite structures were formed and were uniformly dispersed in the epoxy matrix. The in-plane and through-plane electrical and thermal conductivities of thin thermal interface layers of epoxy composites were discussed. Compare to epoxy composites with only exfoliated graphite, epoxy composites with intercalation of AlN nanoparticles into exfoliated graphite not only maintain epoxy's electrically insulation but also enhance through-plane thermal conductivity, which make this material an attractive candidate for electronic field applications especially thermal interface materials (TIMs).

3:20pm **A2-2-ThA-7 Effect of Feedstock Species on Thermal Durability of Thermal Barrier Coatings***, **Sangwon Myoung**, B Yang, I Kim,* Doosan Heavy Industries and Construction, Republic of Korea*; Y Jung,* Changwon National University, Republic of Korea

Thermal durability and stability of thermal barrier coatings (TBCs) are closely related with its microstructure and feedstock species. Numerous factors, besides the thermal and mechanical properties, have to be considered in practical applications of TBCs. There is therefore a need to the reliability and lifetime performance of the plasma sprayed TBC system.

In this study, the microstructures in the top and bond coats of TBCs have been deposited different plasma spray process. The TBC system with the thicknesses of 500 and 200 mm in the top and bond coats, respectively, were prepared with the air plasma sprayed (APS) coating system using ZrO_2–8wt% Y_2O_3 powders for the top coats and vacuum-plasma sprayed coating system using Ni-based metallic powders for the bond coats . In order to investigate the improvement of thermal durability, the furnace cyclic test (FCT) was performed for the TBC samples at a temperature of 1100°C with a dwell time of 1 h for 1000 cycles. Porosity and pore size distribution were measured with the FCT, and the effects of feedstock species in the TBC on mechanical properties such as hardness and toughness were observed, including the adhesive strength before and after the FCT. The nominal pore size of as-prepared TBC system is dramatically reduced with increasing thermal exposed cycle. The harness and toughness values are increased to 1000 cycles. The influence of feedstock species on the microstructural evolution and thermal durability of TBC is discussed.

3:40pm **A2-2-ThA-8 Development of Environmental Barrier Coatings for SiC/SiC Ceramic Matrix Composites via CVD***, **Till König**, M Galetz,* DECHEMA-Forschungsinstitut, Germany

With increasing combustion temperature of turbine engines the commonly used nickel-based superalloys are getting closer to their melting point and excessive cooling along with thermal barrier coatings are used to maintain the properties at the desired level. The substitution of these alloys by Ceramic Matrix Composites (CMC) for applications in the high temperature region of turbines is widely discussed and first parts are in service. Due to their mechanical properties at high temperatures especially SiC/SiC-CMC are investigated. Their advantages include a low density, high specific strength and a low creep rate even at very high temperatures. Therefore the efficiency of the turbines can be increased by using higher combustion temperatures, the abandonment of cooling and reducing the mass. In oxidizing atmospheres these materials form silica scales, which are generally considered protective. But the presence of water vapor, which forms during the combustion process, results in the volatilization of the silica scale by the formation of hydroxides. The simultaneous process of oxidation and evaporation follows paralinear kinetics and makes it necessary to apply coatings that reduce the evaporation and result at best in parabolic kinetics. Under investigation are multi layered environmental barrier coatings (EBC) that reduce the silica activity by mixed oxides (e.g. rare earth silicates) or by forming oxides not prone to evaporation (e.g. Al_2O_3).

In this study the chemical vapor deposition process (CVD) was used instead of or in addition to the commonly used thermal spraying with the aim to apply coatings that show a better adherence and cover the whole surface (line of sight). A layered chromium aluminide, chromium silicide coating was applied by chromizing and subsequent aluminizing in a second step, both via pack cementation. Aluminum nitride was applied by a two-step process consisting of aluminizing via pack cementation and subsequent nitriding as well as by direct deposition via high temperature CVD. The evaporation of these coatings was tested in comparison to the uncoated CMC in water vapor containing atmospheres. The adherence was investigated in synthetic air under thermal cycling conditions to test the influence of possible thermal expansion mismatches. To identify the phases and the microstructure X-ray diffraction (XRD), scanning electron microscope (SEM) and electron probe microanalysis (EPMA) were used.

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

Coatings for Use at High Temperatures (Symposium A) Poster Session

AP-ThP-2 High Temperature Performance of CrAlN Coating on Stainless Steel Substrates in Simulated Diesel Exhaust Environment*, S Yang,* Miba Coating Group. Teer Coatings Ltd., UK*; V Vishnyakov,* Institute for Materials Science, University of Huddersfield, UK*; P Navabpour,* Miba Coating Group. Teer Coatings Ltd., UK*; J Allport,* Institute for Materials Science, University of Huddersfield, UK*; **Hai Lin Sun**,* Miba Coating Group. Teer Coatings Ltd., UK

CrAlN coatings on stainless steels were subjected to temperature cycling up to 750 ^{0}C in air, simulated diesel engine exhaust composition and actual diesel engine exhaust. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and glow discharge optical emission spectrometry (GDOES) were used to study the surface morphology, phase microstructures and composition coating depth profiles. It was found that high temperature corrosion on the coating surface induced formation of passive oxides, which provided a barrier function to further corrosion. The microstructure of the coatings did not change significantly in ambient air at temperature of 750 ℃ . The results show that CrAlN coatings have high hardness, thermal stability, corrosion and erosion resistance. The coatings have potential for applications to protect surface of mechanical components in diesel exhaust systems.

Key words: Thermal stability, high temperature, oxidation, corrosion, erosion.

AP-ThP-3 e-Poster Presentation: Improvement of the Robustness of Time to Failure Assessment in Tbc System*, M Theveneau, B Marchand, V Guipont,* Mines ParisTech, PSL Research University, MAT - Centre des Matériaux, France*; F Coudon,* SAFRAN Tech, France*; **Vincent Maurel**,* Mines ParisTech, PSL Research University, MAT - Centre des Matériaux, France

One of the major challenges for TBC system is to determine the time to failure of ceramic layer during ageing. The aim of this paper is to propose new methodologies for both experimental assessment of adhesion and for analyzing the robustness of model of lifetime to spallation.

Recently, the use of LAser Shock Adhesion Test (LASAT) has shown its capability for both ranking different coating solutions and evaluating the evolution of a given coating as a function of aging [1-2]. The methodology developed in this study is based on the evaluation of interfacial crack propagation from a defect introduced by laser shock, an interfacial delaminated area, known in size and location. The evolution of interfacial delamination during thermal cycling was shown to be consistent with measured interfacial delamination measured by cross-sectioning. Thus, the influence of dwell time at high temperature has been clearly established, confirming that short dwell time was very detrimental as compared to long dwell at high temperature [3-4]. Moreover, this new method has shown a very small scatter as compared to other adhesion testing [2].

On the other hand, some lifetime to spallation models have been tested, focusing on two mains aspects. Firstly, the ability of existing models to reproduce the influence of loading parameters has been tested (e.g. the influence of dwell time at high temperature or the influence of maximum temperature) [3-5]. Secondly, the robustness of this kind of models has been analyzed through sensitivity analysis based on large numerical sampling. As a conclusion, the propagation of scatter from measurement to life modeling has been evaluated and guidelines for experimental focus points have been derived.

References

[1] Guipont, et al (2010). Journal of Biomedical Materials Research Part A, 95(4), 1096-1104.

[2] Guipont, et al. "Interfacial toughness evolution under thermal cycling by laser shock and mechanical testing of an EB-PVD coating system." (2018). http://dc.engconfintl.org/cgi/viewcontent.cgi?article=1033&context=tbcv

[3] Courcier, C et al (2011). Interfacial damage based life model for EB-PVD thermal barrier coating. Surface and Coatings Technology, 205(13-14), 3763-3773.

[4] Soulignac, Romain, et al. "Cohesive zone modelling of thermal barrier coatings interfacial properties based on three-dimensional observations and mechanical testing." Surface and Coatings Technology 237 (2013): 95-104.

[5] Chaboche, J. L., et al "Lifetime assessment tools for thermal barrier systems" in "Thermal Barrier Coatings IV",Eds, ECI Symposium Series, (2015). http://dc.engconfintl.org/thermal_barrier_iv/34

AP-ThP-5 Wear Resistance Performance of AlCrN and TiAlN Coated H13 Tools during Friction Stir Welding of A2124/SiC Composite*, **Akeem Adesina**, F Al-Badour, Z Gasem,* King Fahd University of Petroleum and Minerals, Saudi Arabia

Tool wear during friction stir welding (FSW) of hard particulate reinforced aluminum metal matrix composites

(Al MMCs) are more prominent due to the tool interaction with the particulates at high strain rate. Considering

the excellent mechanical and wear resistance properties of cathodic arc PVD coatings, they are expected to abate

the wear of tools during FSW of Al MMCs. Hence, it is the aim of this study to investigate the contribution of

cathodic arc PVD deposited AlCrN and TiAlN coatings in alleviating tool wear during FSW of Al MMCs. AlCrN

and TiAlN coated H13 FSW tools were used to butt weld 8 mm thick aluminum alloy 2124 reinforced with 17 vol

% SiC of 3 µm particle size. Interestingly, the coated tools exhibited significant improvement in wear resistance

of about 92 and 80%, respectively, over the bare H13 tool. Over 97% reduction in the wear of the FSW tool was

recorded during the plunging stage with the use of the coated tools. Additionally, AlCrN and TiAlN coated tools

considerably improved the surface finish of the welded Al MMC. The coated tools demonstrated superior wear

resistance due to the improved scratch crack resistance, high mechanical and oxidation resistance properties of

the coatings. Dominant wear mechanisms on AlCrN and TiAlN coated tools were abrasive erosion and chipping

off by sharp and hard SiC particles while severe striation and oxidation characterized the wear mechanism of the

bare tool. The use of these coatings did not deteriorate the weld properties, rather somewhat improvement in the

hardness of the nugget zone was observed due to the characteristic dynamic stirring and refinement of the Al

matrix and SiC particles.

AP-ThP-6 Diffusion Model for Estimating the Iron Boride Layer Thicknesses*, **Oscar Armando Gómez-Vargas**,* Instituto Tecnológico de Tlalnepantla, México*; M Ortiz-Domínguez,* Universidad Autónoma del Estado de Hidalgo, México*; J Solis-Romero,* Instituto Tecnológico de Tlalnepantla, México*; M Flores-Rentería, I Morgado-Gonzalez, E Cardoso-Legorreta,* Universidad Autónoma del Estado de Hidalgo, México*; M Elias-Espinosa,* Tecnológico de Monterrey, México*; A Cruz Avilés,* Universidad Autónoma del Estado de Hidalgo, México

Surface hardening, a process that includes a wide variety of techniques (Carburizing, Nitriding, Nitrocarburizing, Boriding, and Thermal diffusion process), is used to improve the wear resistance of parts without affecting the more soft, tough interior of the part. In particular, resistant layers of borides are produced in ferrous and no-ferrous materials though the well-developed process of boriding. In the present work, the AISI 9840 steel was pack-borided in the temperature range 1123-1273 K for 2- 8 h to form a compact layer of Fe_2B at the material surface. A recent kinetic approach, based on the integral method, was proposed to estimate the boron diffusion coefficients in the Fe_2B layers formed on AISI 9840 steel in the temperature range 1123-1273 K. In the present model, the boron profile concentration in the Fe_2B layer is described by a polynomial form based on the Goodman's method. As a main result, the value of activation energy for boron diffusion in AISI 9840 steel was estimated as 193.08 $kJmol^{-1}$ by the integral method and compared with the values available in the literature. Three extra boriding conditions were used to extend the validity of the kinetic model based on the integral method as well as other diffusion models. An experimental validation was made by comparing the values of Fe_2B layers' thicknesses with those predicted by different diffusion models. Finally, an iso-thickness diagram was proposed for describing the evolution of Fe_2B layer thickness as a function of boriding parameters.

AP-ThP-7 STEM Investigations of Oxide Scales formed during Pre-oxidation of γ-TiAl, ***Radoslaw Swadzba,*** Institute for Ferrous Metallurgy, Poland

The paper presents results of pre-oxidation experiments of ɣ-TiAl alloy with Si-modified aluminide coatings intended for application as bondcoatings for Thermal Barrier Coatings. The goal of this work was to provide insight into the effect of different oxidation atmospheres and temperatures on the initial stages of oxide scale formation on bare and coated ɣ-TiAl. It is assumed that the formation of a thin (several hundreds of nanometers) and slow growing TGO consisting of α-alumina will enhance the adherence and lifetime of the TBCs on ɣ-TiAl.

The coatings were produced by pack cementation method applying a mixture consisting of Si and Al-containing powders and NH_4Cl activator. The additional surface modification by pre-oxidation under various atmospheres was performed to foster the formation of oxide scales characterized by various thicknesses as well as phase and chemical compositions. The pre-oxidation experiments were performed in various gases including a mixture of Ar and O_2 (from 0.01 to 10 %) as well as pure O_2 at 900 °C for 0.5, 2 and 4 hours. After the pre-oxidation experiments systematic studies were performed using Scanning Transmission Electron Microscopy (STEM) method in order to characterize the phenomena at the metal-scale interface and study the phase and chemical compositions as well as the microstructures of the formed oxide scales.

AP-ThP-9 Microstructure of MCrAlY Coatings Deposited Using HVOF after Heat Treatment and Aluminizing, *L Swadzba,* ***Aleksander Iwaniak,*** *R Swadzba, B Witala, B Mendala,* Silesian University of Technology, Poland*; G Wieclaw, P Lubaszka,* Certech Sp. z o.o., Poland

Effective oxidation and corrosion protection of turbine blades in aircraft engines used at high temperature in the atmosphere of exhaust gases is still a major technological challenge and is the subject of intensive research. In this work, the microstructure of coatings deposited on Inconel 738 alloy used for turbine blades was investigated. In the first stage of the research work MCrAlYHfSi (M=Ni) coatings made of Amperit 405.001 material with granulation +22-45 μm were deposited using HVOF method. The coatings were applied with variable process parameters by HVOF method using the Thermico system and the CJS K5.2-N burner. Then thermal treatment of the sprayed coatings was performed at 1050°C for 4 hours in argon atmosphere. After the heat treatment vapor phase aluminizing using the "out-of-pack" method was carried out at 1050°C for 5 hours. After each treatment thickness of the coatings was measured, the microstructures were investigated using SEM and chemical composition analysis (EDS) and their surface topography and roughness were determined using 3D profilometry.

AP-ThP-10 Effect of Vanadium Content on the High-temperature Tribo-mechanical Properties of Cr-Al-V-N Coatings Deposited by DC UBMS, *H Kim,* ***In-Wook Park,*** Korea Institute of Industrial Technology (KITECH), Republic of Korea

Quaternary Cr-Al-V-N coatings with vanadium content ranging from 0 to 13 at.% were deposited on WC-Co alloy substrates by an d.c. unbalanced magnetron sputtering using Cr-Al composite targets and pure vanadium target in an N_2/(Ar+N_2) gas mixture for applications of the high-strength steel and aluminum alloys entails increasing demands on the surfaces of tools used for forming processes. The microstructure, mechanical, wear, tribological properties of the coatings were investigated by XRD, XPS, FESEM, HRTEM, surface 3D profiler, nano-indentation, scratch tester, and ball-on-disc tribo-meter. As the vanadium content increased, the nanohardness of the Cr-Al-V-N coatings showed higher hardness values (~30GPa) than that of CrAlN coating (~25GPa). Ball-on-disc tri-tests were used to assess the friction at 700^{o}C, the friction coefficient of the Cr-Al-V-N coatings drastically decreased from 0.6 to 0.35 with increasing vanadium content up to 7 at.% in the coatings due to the formation of a tribolayer containing the lubricious oxide V_2O_5 as evidenced by XPS. Moreover, it was found that the improved friction coefficient and nanohardness with incorporated small amount of the vanadium contents contributed to excellent wear resistance of the coatings.

AP-ThP-11 Tensile Behavior of Air Plasma Spray MCrAlY Coatings: Role of High Temperature Aging and Process Defects, *C Cadet,* Mines ParisTech, PSL Research University, France*;* ***Thomas Straub,*** Fraunhofer Institute for Mechanics of Materials IWM, Germany*; D Texier,* Mines Albi, ISAE-SUPAERO, France*; C Eberl,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; V Maurel,* Mines ParisTech, PSL Research University, France

MCrAlY coatings are used as a protection layer against high temperature oxidation and corrosion for components working in an aggressive environment. In order to predict both coating and substrate lifetime, the characterization of thermomechanical properties of the coating is a challenging issue [1-3]. As these coatings are only a few hundreds of micrometers thick, their properties should be investigated with experimental tests adapted at this small scale [1-4].

In the present study, the mechanical properties of a free-standing MCrAlY coating and their evolution were scrutinized when it is aged in air for a large range of time and temperature. Free-standing micro-tensile specimens were prepared [1] and tested after different time/temperature ageing [4]. Based on digital image correlation to derive the strain evolution during loading, the stress-strain behavior has been identified. Thus a crucial effect of intrusive oxidation from deposition process defects and surface oxidation has been evidenced to drive both the ductility and the fracture mechanism of the tested material. For coarse intrusive oxidation, a loss of ductility has been identified, whereas metallic phase transformation (from b to g) increases the ductility of the material from 0.5 up to 3%. This composite effect will be analyzed through systematic microstructure and homogenization analyses. This methodology could be straightforward to determine the coupling between coating cracking and substrate failure under thermo-mechanical fatigue conditions [5].

References

[1] D. Texier, D. Monceau, J. C. Salabura, R. Mainguy, E. Andrieu, *Materials at High Temperatures*, 33 (2016) 325–337.

[2] D. Texier, D. Monceau, Z. Hervier, E. Andrieu, *Surface and Coatings Technology*, 307 (2017) 81–90

[3] Alam, M.Z., Satyanarayana, D.V.V., Chatterjee, D., Sarkar, R., Das, D. K., *Materials Science and Engineering: A*, 641 (2015) 84-95.

[4] Straub, T., Baumert, E.K., Eberl, C., Pierron, O.N., *Thin Solid Films*, 526 (2012) 176–182.

[5] Esin, V.A., Maurel, V., Breton, P., Köster, A., Selezneff, S., *Acta Materialia*, 105 (2016) 505–518.

AP-ThP-13 Influence of Si-Al Coating on Mechanical Properties of EBMed TiAl Alloy, ***Lukasz Pyclik,*** Avio Aero A GE Aviation Business, Poland*; L Swadzba, B Mendala, B Witala, J Tracz, R Swadzba,* Silesian University of Technology, Poland*; K Marugi,* Avio Aero A GE Aviation Business, Poland

The paper presents the results of investigations concerning the effect of silicon modified aluminide coatings on EBMed Ti-48Al-2Cr-2Nb (48-2-2) alloy. The study was performed on specimens machined from EBMed rods. The rods were printed by Avio Aero Cameri, Italy, and met heat treatment by hipping and solutioning. The specimens were manufactured by Silesian University of Technology, Poland, for coating or heat treatment. The anti-oxidation coating was applied on pre-machined specimens by a pack cementation process. The test results revealed difference between specimens in three conditions: bare, coated and heat treated corresponding to coating deposition process. The mechanical tests ensure environments as close as possible to current application in commercial novel engine, GE9X, where EBMed blades are applied on last stages of Low-Pressure Turbine designed by Avio Aero. All tests covered work at elevated temperatures at and above 1500F. All tests shown impact of coating on mechanical properties.

Author Index

Bold page numbers indicate presenter