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, γ-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 γ-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 γ-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/γ-TiAl interface was demonstrated. The oxidation behavior of Ti_xSi_y coated γ-TiAl and uncoated γ-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.

Author Index

Bold page numbers indicate presenter