

Special Interest Talk

Room California - Session A1-1

Coatings to Resist High Temperature Oxidation, Corrosion, and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Shigenari Hayashi, Hokkaido University, Sebastien Dryepondt, Oak Ridge National Laboratory, USA

8:00am A1-1-1 Degradation of Protective Coatings at High Temperatures, **Michael Schütze**, DECHEMA-Forschungsinstitut, Germany **INVITED**

The potential of high temperature materials can only fully be exploited if protective surface coatings are being used. These can offer protection against abrasion and wear, and can reduce heat transfer in the form of thermal barrier coatings, but the most widely used function of such coatings is their capacity for high temperature corrosion protection. The life-time and the protective effect of the coatings plays a crucial role for material and component performance, therefore a strong focus has always been directed towards the degradation mechanisms of coatings. These can be of chemical, mechanical and thermomechanical nature and are strongly dependent on the type of coating. The paper aims at giving an overview on the types of high temperature coatings commonly used together with the respective degradation mechanisms that determine their performance. Furthermore, it will be examined in how far quantitative models and assessment procedures exist allowing prediction of coatings behavior. Finally some thoughts will be given to the future needs in research in this area.

8:40am A1-1-3 Development of a New Slurry Coating Design for the Surface Protection of Gas Turbine Components, **Benjamin Grégoire**, **G Bonnet**, **F Pedraza**, University of La Rochelle, France

With the overall increase of the working temperature in gas turbine engines, the colder parts of the turbine (low stages), which used to experience little degradation, start to become sensitive to high-temperature corrosion. Consequently, this broaden the use of protective coatings to these stages to increase the surface stability of gas turbine components (surface engineering). Current industrial processes to produce protective coatings are based upon complex and expensive techniques (e.g. EB-PVD, APS) and put in order hazardous chemicals (e.g. CVD-related techniques). Therefore, cost-effective and environmentally friendly slurry coatings recently came up as a convincing alternative allowing the formation, from Al microparticles, of a complete thermal barrier system in a single step process [1-3].

In this work, a new slurry coating design was developed for the surface protection of nickel-based superalloys (CM-247 LC, DS200 and IN100 superalloys). The addition of Cr microparticles in the water-based slurry compositions was found to decrease the activity of Al upon aluminizing by forming Al_xCr_y phases in the slurry deposit [4]. With further annealing at high temperature (i.e. 1080°C), interdiffusion between the nickel-based substrate and the synthesized Al_xCr_y phases was promoted. The initial contents of Al and of Cr of the slurry deposit allowed to control the coating growth direction (inwardly or outwardly grown coatings as reported for state-of-the-art CVD aluminide coatings). Consequently, different coating microstructures were produced on nickel-based superalloys by adjusting the initial contents of Al and of Cr. It was therefore possible to design, in a single heat treatment, the coating to fight against oxidation and/or hot corrosion.

The present coating design is also expected, in light of the SEM/EDS and XRD characterization, to allow the surface protection of metallic substrates with complex geometry such as gas turbine blades.

References

- [1] F. Pedraza, M. Mollard, B. Rannou, J. Balmain, B. Bouchaud, G. Bonnet, *Materials Chemistry and Physics* **134** (2012), pp. 700-705.
- [2] X. Montero, M.C. Galetz, M. Schütze, *Surface and Coatings Technology* **206** (2011), pp. 1586-1594.
- [3] B. Rannou, B. Bouchaud, J. Balmain, G. Bonnet, F. Pedraza, *Oxidation of Metals* **81** (2014), pp. 139-149.
- [4] B. Grégoire, G. Bonnet, F. Pedraza, *Intermetallics* **81** (2017), pp. 80-89.

9:00am A1-1-4 Slurry Formulation for Industrial Large Scale Aluminum Diffusion Coatings, **M Kimmich**, Fraunhofer ICT, Germany; **Vladislav Kolarik**, Fraunhofer Institute for Chemical Technology ICT, Germany; **J Bermejo Sanz**, **M Juez Lorenzo**, Fraunhofer ICT, Germany

Diffusion aluminide coatings, deposited as Al slurries, are an efficient and economic technique to protect ferritic steels, against oxidation and corrosion at high temperatures. In the international business the transport of liquid Al slurry paint to the application site is often preferred to the transport of high purity Al micro-powders due to legal regulations. The Al slurry paint has to possess appropriate viscosity and rheology, it has to be suitable for storage, transportable and not hazardous for health and environment.

Three slurry formulations were prepared with spherical high purity aluminum particles with an average diameter of 15 μm : formulations SMK1 and SMK2 using a composition of isopropanol and butanol as dissolvent and polyvinylbutyral 30 as binder and slurry formulation SMK3 using acetone and butanol as dissolvent and the commercial Paraloid B72 as binder. Commercially available rheology modifiers were applied to adjust the slurry properties.

To investigate the wet slurry thickness, from which sagging will occur the Anti-Sag-Index was determined according to ASTM 4400-99. Critical wet slurry thicknesses about 200 μm were found for the studied slurry formulations, adjustable by the portion of rheology modifier. Grindometer tests revealed a maximum grain size of 32 μm , which corresponds to the maximum particle size indicating small agglomerates and thus good dispersion and low sedimentation. Plotting shearing stress versus the rate of shearing strain all three formulations exhibit a shear thinning behavior, more pronounced for SMK2 and SMK3.

To simulate the spray process with high shear rates during spraying, the low-high-low shear rate test was applied, measuring the viscosity as a function of time. The slurries show different viscosities in the first low shear rate period. With the high shear rate in the second period the viscosity decreases close to 0 Pa*s for all three formulations. Reducing the shear rate subsequently, it increases to values about 750 Pa*s for SMK1 and SMK2 and to 8000 Pa*s for SMK3. With this behavior SMK3 would be more suitable for a spray process, since it would exhibit a very low viscosity during spraying, which would rapidly increase after deposition and avoid sagging.

The diffusion aluminide coatings prepared with the three slurry formulations showed the same phase structure composed of Fe_2Al_5 and FeAl and a comparable oxidation behavior at 650°C in air. The principal wet slurry thickness notably influences the phase structure of the diffusion aluminide coating and its evolution with the time. An appropriate slurry formulation contributes significantly to adjust a homogeneous wet slurry thickness.

9:20am A1-1-5 Structural Properties of Hybrid Sol-gel Coatings for Corrosion Protection of Low-carbon Steel, **Marie-Joëlle Menu**, CIRIMAT, Université de Toulouse UPS INP CNRS, France; **C Lavollee**, **R Noiville**, **M Gressier**, CIRIMAT, France; **J Garcia**, **J Sobrino**, CETIM, France

This work focuses on the development of hybrid sol-gel coatings for corrosion protection of low-carbon steel. The studied material is a DC04 laminated carbon steel, very sensitive to corrosion and with an uneven topography. Feasibility of the development of an architected hybrid coating prepared by a sol-gel route on the DC04 steel has been demonstrated.

The architecture is based on a gradient of concentration of unloaded and loaded hybrid layers of zirconia nanoparticles imbedded in a hybrid matrix. The resulting coating is adherent, covering, leveling and presents high-performance anticorrosion properties. Architected systems were assessed combining microstructural observations, electrochemical impedance spectroscopy analysis and solid state NMR. ^{13}C , ^{29}Si and ^{27}Al NMR spectroscopies have highlighted the importance of controlling both the inorganic and organic polymerisation reactions to obtain efficient anticorrosion coatings. Moreover, these results demonstrate that the modification of the organic-inorganic hybrid matrix structure allows the insertion of a higher amount of cerium without damage for the anticorrosive properties of the coating.

9:40am A1-1-6 Diffusion Coatings for Corrosion Protection of Ferritic-martensitic Steels for Co-firing Combustion Plants, **Tobias Meissner**, **D Fähsing**, **M Galetz**, DECHEMA-Forschungsinstitut, Germany

In the course of energy transition the use of existing power plants for co-firing with biomass plays a substantial role in terms of base load supply.

While co-firing reduces the CO₂ footprint of the plant, it also leads to higher amounts of corrosive species within the system such as chlorine and sulfur. Consequently, higher corrosion rates and material losses are observed in the firing chamber components. In particular, superheater tubes are subjected to increased corrosive attack and are prone to early replacement. Thus, co-firing is commonly limited to temperatures below 500°C and low biomass-to-coal ratios (10%).

The heat resistant ferritic-martensitic steel X20CrMoV12-1 is of great interest as a material for superheaters because the steel exhibits much better heat transfer behavior and a lower coefficient of thermal expansion, as well as lower costs in comparison to austenitic steels. However, corrosion resistance in the combustion gas atmospheres of biomass power plants is not sufficient.

Therefore, different corrosion protection systems have been developed in order to make ferritic-martensitic steels usable at temperatures above 500°C in such combustion gases. The first step was to apply a thin nickel layer. This interlayer serves as a nickel reservoir for the subsequent diffusion process of potentially protective elements such as Al, Cr and Si.

Coated and uncoated X20 samples as well as austenitic steel DMV 310 N samples were tested in a fireside corrosion atmosphere of N₂-O₂-H₂O-CO₂-SO₂-HCl at 650°C under an ash deposit containing sulfates and chlorides. This paper highlights the improved corrosion behavior of the ferritic-martensitic steel through the coatings even in this very harsh environment.

10:00am A1-1-7 Biomass Corrosion Behavior of Steels and Coatings in Contact with KCl/K₂SO₄ at 550°C: a Screening Laboratory Test, *M Gutiérrez, Alina Agüero Bruna, I Baraibar*, Instituto Nacional de Técnica Aeroespacial (INTA), Spain; *M Hernández*, Instituto Nacional de Técnica Aeroespacial (INTA), Spain; *R Muelas Gamo, S Rodríguez*, Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Increasing the operating temperature in biomass-fueled power plants is a very difficult task when compared to plants operating with traditional fossil fuels in particular under an oxyfuel combustion atmosphere. The corrosion generated by alkaline deposits and chlorine present in biomass will dramatically increase with increasing temperature, and the presence of a higher content of water vapor and SO₂ characteristic of oxycombustion will likely further increase the corrosion rate. The alloys and coatings used until now will have to be modified due to the change in corrosion mechanisms. Due to these aggressive conditions, it is very important to develop a laboratory testing facility which allows to evaluate the viability of using new materials as well as to predict the useful life for those already in used, in particular if the operating parameters change. In the literature, ferritic-martensitic steels and several coatings were studied employing conditions similar to those found in a biomass power plant and it was observed that the presence of chromium in both the substrates and the coatings seems to increase the degradation (*S. Kiamehr, K.V. Dahl, M. Montgomery and M.A. J. Somers, Mater. Corros. 2015, 12, 66*). Aluminum coatings with low chromium content appear to perform better in these alkaline environment. In this work, laboratory testing was carried out to evaluate the effects of salt deposits, as well as the effect of different coating composition and substrates on the corrosion mechanism. Exposure was performed at 550°C for more than 600h in a flowing model biomass oxycombustion atmosphere containing 60%CO₂, 30%H₂O, 8%O₂, 2%N₂ (Vol %), 400 vppm HCl and 2 vppm SO₂. The samples were covered with KCl + K₂SO₄ prior to exposure. The present study compares the corrosion behavior of three steels (P92, T22 and SANICRO28) uncoated and coated in the above described biomass model atmosphere. The coatings include slurry applied diffusion aluminide and Cr aluminide coatings as well as Ni20Cr, Fe50Cr and a modified super hard steel (SHS) deposited by HVOF thermal spray. FESEM and XRD analysis were performed to identify the corrosion products and to determine the mechanism of corrosion. The developed test allows a meaningful ranking of the studied materials. The observed corrosion rate tendency based on the mass variations is as follows:
T22>P92>Ni20Cr»modified SHS»Cr Aluminide>SANICRO28>Fe50Cr>Aluminide.

10:20am A1-1-8 In-situ Post-Annealing of Si-Al Coatings for the Oxidation Protection of γ-TiAl, *K Bobzin, T Brögelmann, C Kalscheuer, Tiancheng Liang*, Surface Engineering Institute - RWTH Aachen University, Germany

Many attempts have been made to extend the service temperatures of lightweight materials based on γ-TiAl alloys due to their insufficient oxidation resistance at T > 850 °C for turbine applications. Among them, deposition of high-temperature oxidation protective coatings has been proved to be a promising approach. The key purpose hereby is the formation of protective oxide scales such as Al₂O₃, Cr₂O₃ and SiO₂, which

offer a barrier against diffusion of oxygen into the bulk material. Besides, a dense microstructure for a suppressed interdiffusion and an adequate coating-substrate adhesion in terms of the chemical compatibility and the similarity of the coefficients of thermal expansion are indispensable.

In the present work, an innovative in-situ plasma-assisted post-annealing combined with pre-oxidation for Si-Al coatings, carried out immediately after the deposition process by high-speed physical vapor deposition (HS-PVD) technology, was developed. The post-annealing aimed at the formation of a protective oxide layer consisting of Al₂O₃ or SiO₂ on the Si-Al coating surface and a refinement of the microstructure for the reduction of interdiffusion, to enable the application of Si-Al coated γ-TiAl in air up to T = 950 °C.

In a first step, three Si-Al coating systems with different Si:Al ratios were deposited on γ-TiAl substrate by HS-PVD, which offers high deposition rates owing to hollow cathode discharge (HCD) and gas flow sputtering (GFS). Subsequently, the coatings were annealed in the coating chamber with different oxygen flow Q_{O2} and bias voltage U_{bias}. Such kind of in-situ post-annealing, combining pre-oxidation and simultaneous argon plasma induced ion bombardment has not been reported elsewhere.

Both, post-annealed and as-deposited coatings were characterized with regards to their coating thickness, morphology, roughness and phase composition. Subsequently, isothermal oxidation tests were carried out at T = 950 °C in air. Weight changes and cross-sections were analyzed at certain annealing time intervals. The results confirm the high oxidation resistance of the post-annealed Si-Al coatings compared to the as-deposited coatings and the uncoated γ-TiAl substrates. Moreover, cross-sectional images and phase analyses of the coating surfaces indicate that the interdiffusion of Ti between coating and substrate can be effectively reduced due to the refined microstructure in the post-annealed coatings. The results of the conducted research reveal a high potential of the post-annealed Si-Al coatings for the oxidation protection of γ-TiAl at T > 850 °C in turbine applications.

10:40am A1-1-9 Fatigue Performance of Bare and Coated 31V Alloy, *Sebastien Dryepont, B Armstrong*, Oak Ridge National Laboratory, USA; *Y Zhang*, Tennessee Technological University, USA; *S Sampath*, Stony Brook University, USA; *J Haynes*, Oak Ridge National Laboratory, USA

Diffusion aluminide and MCrAlY overlay coatings have been used for decades in the gas turbine industry to protect components against oxidation and hot corrosion. Due to increasing temperature in light and heavy duty internal combustion engines, corrosion-resistant coatings might be required to maintain or even improve the in-service lifetime of hot components such as valves. The coating impact on the valve alloy mechanical properties needs, however, to be assessed. ~50um thick slurry and pack aluminized coatings, as well as a NiCoCrAlY overlay coating, were therefore deposited on alloy 31V (57Ni-23Cr-13Fe-2Mo-2.3Ti-1.3Al-0.9Nb) fatigue specimens. The high cycle fatigue (HCF) behavior of the coated specimens at room temperature and 500° C was similar to the fatigue behavior of bare 31V specimens exposed to the coating heat treatments. Cracks in the coating were only observed close to the fracture surface and the cracks did not propagate in the substrate. Optimization of the coating processes to improve the HCF behavior of coated 31V will be discussed.

Author Index

Bold page numbers indicate presenter

— A —

Agüero Bruna, A: A1-1-7, **2**
Armstrong, B: A1-1-9, **2**

— B —

Baraibar, I: A1-1-7, **2**
Bermejo Sanz, J: A1-1-4, **1**
Bobzin, K: A1-1-8, **2**
Bonnet, G: A1-1-3, **1**
Brögelmann, T: A1-1-8, **2**

— D —

Dryepondt, S: A1-1-9, **2**

— F —

Fähsing, D: A1-1-6, **1**

— G —

Galetz, M: A1-1-6, **1**
Garcia, J: A1-1-5, **1**

Grégoire, B: A1-1-3, **1**

Gressier, M: A1-1-5, **1**

Gutiérrez, M: A1-1-7, **2**

— H —

Haynes, J: A1-1-9, **2**
Hernández, M: A1-1-7, **2**

— J —

Juez Lorenzo, M: A1-1-4, **1**

— K —

Kalscheuer, C: A1-1-8, **2**

Kimmich, M: A1-1-4, **1**

Kolarik, V: A1-1-4, **1**

— L —

Lavollee, C: A1-1-5, **1**

Liang, T: A1-1-8, **2**

— M —

Meissner, T: A1-1-6, **1**

Menu, M: A1-1-5, **1**

Muelas Gamo, R: A1-1-7, **2**

— N —

Noiville, R: A1-1-5, **1**

— P —

Pedraza, F: A1-1-3, **1**

— R —

Rodríguez, S: A1-1-7, **2**

— S —

Sampath, S: A1-1-9, **2**

Schütze, M: A1-1-1, **1**

Sobrino, J: A1-1-5, **1**

— Z —

Zhang, Y: A1-1-9, **2**