Coatings for Use at High Temperatures
Room Town & Country D - Session A1-2-MoA

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

Moderators: Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK, **Gustavo Garcia Martin**, REP Energy Solutions, Spain

3:00pm **A1-2-MoA-5 Influence of Dispersed Nano-Y_2O_3 Particles in NiAlY and NiCrAlY MMC Coatings on Microstructure, Oxidation and Wear***, **Christoph Grimme (christoph.grimme@dechema.de)**, R. Kupec, F. Schulze, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

State of the art MCrAlY coatings are known to protect structural materials against oxidation and corrosion and are part of TBC systems. Due to their mechanical properties at high temperature, they are commonly applied in the hottest sections of turbine engines and other high temperature environments. High costs for the thermal spraying process of MCrAlY coatings drive forwards cost saving alternatives such as galvanic co-deposition of particles. Co-deposition of particles is influenced by numerous factors, such as particle size, kinetic effects, current density, pH related zeta potential or chemical stability of the particles [1]. In this study, nano-Y_2O_3 particles are co–deposited galvanically alongside with nickel and subsequently pack chromized and aluminized. Y_2O_3 is known to improve both oxide scale formation and oxide scale adherence. Another promising effect of Yttria is the reaction with low melting V_2O_5 to form high melting YVO_4, which reduces the aggressiveness and of corrosive salt deposits and thereby reduces corrosion attack [2].

Subsequent chromium and/or aluminum enrichment(s) after co-deposition using a pack cementation process is shown to lead to microstructural refinement compared to coatings without particles and are able to decrease wear up to high temperature. Additional microhardness measurements revealed an increase of approx. 100 HV1 for MMC NiAlY coatings compared to coatings without dispersed nano–Y_2O_3 particles. Depending on the activity of the pack cementation method to be used, differences in the distribution of dispersed particles are observed and discussed. Besides wear, the oxidation resistance as well as corrosion resistance of the manufactured coatings against molten V_2O_5/Na_2SO_4 salt mixtures at 700 °C in 0.1 SO_2/air gas are tested and compared against bare IN617 alloy.

[1]L. Besra, M. Liu,*Progress in Materials Science***2007**, *52*, 1–61.

[2]N. S. Bornstein,*Vanadium Corrosion Studies***1993**.

3:20pm **A1-2-MoA-6 Reactive Magnetron Sputtering of Al-O-F for High-Temperature Oxidation Protection of γ-TiAl via the Halogen Effect***, **Stephen Brown (stephen.brown@polymtl.ca)**, F. Bergeron,* Polytechnique Montréal, Canada*; M. Cavarroc,* SAFRAN Tech, France*; S. Knittel,* SAFRAN Aircraft Engines, France*; L. Martinu, J. Klemberg-Sapieha,* Polytechnique Montréal, Canada

The implementation of γ-based TiAl alloys in aircraft engines is motivated by their low weight and high specific strength at high temperatures compared to conventional nickel alloys. Their mechanical properties, such as yield strength and elastic modulus, match those of Ni-based alloys already employed in aircrafts engines, while their density is significantly lower than current solutions, allowing for the manufacture of lighter turbines and increased thrust-to-weight ratios. Their use, however, is restricted to low-pressure turbines due to the growth of a mixed Al_2O_3/TiO_2 oxide scale at temperatures greater than 750°C. While the dense Al_2O_3 is protective against further oxidation, the porous TiO_2 allows oxygen diffusion to the substrate, voiding the alumina's protective properties.

Of great interest for the protection of TiAl is a surface treatment based on the halogen effect, where a halogen, such as chlorine or fluorine, is used to promote the growth of a protective alumina scale. Aluminum halides are formed at the surface of TiAl and are transported through the oxide scale, where oxygen partial pressure is high enough to lead to the oxidation of these halides, promoting the formation of a protective Al_2O_3 scale.

This work demonstrates the possibility of exploiting the halogen effect through the deposition of Al-O-F films on γ-based Ti-Al48-Cr2-Nb2 substrates via reactive magnetron sputtering. The plasma chemistry of Al sputtered in an Ar, O_2, and CF_4 atmosphere was first measured by mass spectroscopy, and coated samples were deposited under a range of sputtering conditions. Coating microstructure was characterized by Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-Ray Spectroscopy (EDS), while Rutherford Backscattering Spectrometry (RBS) was used to determine coating composition. A subset of deposited coatings was oxidized at temperatures up to 875°C. Analysis by EDX and X-ray Photoelectron Spectroscopy (XPS) confirmed the transformation from Al-O-F to Al_2O_3 after oxidation, and the coated samples showed mass gains up to 10 times lower than the uncoated TiAl.

3:40pm **A1-2-MoA-7 Development of a New Coating Against High-Temperature Erosion-Corrosion in Fluidized Bed Biomass Boiler Condition***, **Suzue Yoneda (s-yoneda@eng.hokudai.ac.jp)**, S. Tanaka,* Hokkaido University, Japan*; Y. Miyakoshi,* Hokkaido Research Organization, Japan*; T. Kogin,* Dai-ichi High Frequency Co., Ltd., Japan*; E. Ishikawa,* EBARA Environmental Plant Co., Ltd., Japan*; M. Noguchi,* EBARA Corporation, Japan*; S. Hayashi,* Hokkaido University, Japan **INVITED**

High-temperature Erosion-Corrosion (E-C) is one of the critical issues for the heat exchanger used in a fluidized bed biomass boiler plant. E-C occurs by not only erosion due to impact of sand particles but also high-temperature corrosion in chlorine containing atmospheres. Current coatings widely used for boiler tubes in fluidized boiler plants are Ni-based protective coating (Japan Industrial Standard: JIS SFNi4 and/or SFNi5). However, E-C resistance of those coatings is still not sufficient. Thus, development of coating which have good E-C resistance is strongly required. SFNi4 contains a lot of alloying elements (Cr, B, Si, C, Fe, Co, Mo and Cu). In this study, effect of Mo, Si, Cr and Fe on E-C resistance was evaluated by using model alloys in order to optimize the Fe content. Mo and Si were found to be detrimental for E-C and Fe addition significantly improve E-C resistance. After E-C, oxide scale consisted of thinner NiO on the alloy without Fe, but thicker Fe-rich oxide on the alloy with Fe. Erosion resistance of Fe-rich oxide could be higher than that of NiO, resulting in higher E-C resistance in the alloy with Fe. Based on the results obtained from E-C test, the new coating which is higher Fe content and lower Mo and Si content was proposed and it was confirmed that E-C resistance of this coating was higher than previous coating in the actual plant.

4:20pm **A1-2-MoA-9 Introduction of Methodologies from Artificial Intelligence Into Slurry Coating Development***, **Vladislav Kolarik (vladislav.kolarik@ict.fraunhofer.de)**, M. Juez Lorenzo, W. Becker,* Fraunhofer Institute for Chemical Technology ICT, Germany

Aluminum slurry coatings are a high-impact and economic technique to protect steels against corrosion at high temperatures and in aggressive media. They are easy to apply using different methods of deposition such as spraying or brushing with a subsequent heat treatment to form the diffusion coating. For optimization as well as for customization to particular applications with different substrate steels and media further development is needed. The use of methodologies and algorithms from artificial intelligence (AI) can significantly accelerate the development and reduce the costs by minimizing the experimental effort. For an AI supported approach the entire system has to be considered and digitalized integrating all components, all process parameters at all processing steps including the models for the different mechanisms such as diffusion.

To digitalize the aluminum slurry coating the entire coating system and its manufacturing process was fully parametrized considering every single parameter having influence. In doing so the coating process was divided into three sections: slurry formulation, slurry deposition and the heat treatment to form the aluminide diffusion layer including the substrate steel data. The parameters comprise the particle size and slurry components, spray characteristics such as distance, particle velocity or angle and heat treatment temperature, time and atmosphere.

The parameters were formatted in computer readable formats: (i) numerical values (numbers x, y, z, …) when specific values can be assigned such as the heat treatment temperature in degree Celsius; (ii) groups of values (x to y), e.g. small, medium, large aluminum particles within a range of µm and (iii) categories with I/0 decision, where specific values or ranges of values are not applicable, e.g. slurry deposition by spraying (yes/no). Target values were defined for the parameters describing the targeted coating properties as well as assessment criteria for their achievement. Algorithms from the field of Design of Experiments were chosen for the first approach elaborating a parameter matrix for a slurry coating system. A set of experimental values from former projects was filled in to train the software for calculating the impact of process parameter variation on the coating properties.

4:40pm **A1-2-MoA-10 Slurry Coatings for Heat Exchangers of Particle Receivers of Solar Towers***, Michael Kerbstadt* ***(michael.kerbstadt@dechema.de)****, A. Ulrich, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

Diffusion coatings are widely used in high temperature applications to enhance oxidation and corrosion resistance of metals and alloys. Metallic elements (commonly Al, Cr, or Si) are enriched at the surface to form protective oxide scales during exposures at high temperatures.

Al, Cr and Si-based diffusion coatings are mostly accomplished by pack cementation, where the deposition occurs via a gas diffusion process. For the pack cementation process the substrates usually have to be fully embedded into a powder mixture, which is laborious and requires a lot of furnace furniture to be heated up. For Al an alternative slurry process is well established, where the slurry is sprayed on the metallic surfaces by air brush. This simple deposition leads to economic advantages compared to other diffusion coating techniques and also to the possibility to coat large technical parts, weldings or to do local repair works.

The target application of this work focuses on a new generation of solar power plants, where bauxite particles are used as receiver and heat storage medium instead of the state of the art tubes with molten nitride salts. In this case the coating on the outside of the heat transfer tubes, which are in contact with the particles not only has to withstand oxidizing environments at high temperatures but also abrasion due to the impact of the heat carrying particles. For this application Cr- and Si-rich coatings are very interesting, e.g. because of the hard silicide phases, which are more oxidation resistant than the respective Cr-carbides at the target temperatures.

Due to the higher melting points and limited phase formation, the development of Si- or Cr-based diffusion coatings via the slurry process is more complicated, e.g. the use of Cr-Al pre-alloyed powder leads only to Al diffusion.

In this work novel slurry coatings are presented applied by a water-based slurry. The subsequent heat treatment is conducted in an inert Ar atmosphere at temperatures up to 1200° C.

The application of such slurry coatings is demonstrated on Inconel 740 (Ni-base) and Sanicro 25 (austenitic stainless steel). Therefore, different slurry compositions and heat treatment parameters are tested. The coating thicknesses achieved are up to 10 µm on the Inconel 740 and up to 300 µm on the Sanicro 25.

For phase determination and microstructural characterization X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) are used.

Oxidation exposures in synthetic air at 900°C show the formation of a protective scale and indicate an improved oxidation behavior by the applied coatings of the two investigated substrates.

5:00pm **A1-2-MoA-11 Low Emissivity Thin Films Coatings to Reduce Thermal Emittance of SSA for Evacuated Solar Collectors***, Antonio Caldarelli* ***(antonio.caldarelli@na.isasi.cnr.it)****, C. D'Alessandro, D. De Maio, D. De Luca, E. Gaudino, M. Musto, E. Di Gennaro,* University of Napoli “Federico II”, Italy*; R. Russo,* National Research Council of Italy, Napoli Unit, Institute of Applied Sciences and Intelligent Systems, Italy

Solar energy is the ideal energy source to provide heat at medium temperatures with the aim of transitioning to clean, renewable energy sources. Evacuated flat plate solar collectors (EFPCs) are able to convert solar energy directly into heat with high efficiency. Thanks to the high vacuum insulation, the main mechanism of loss in EFPCs is represented only by the radiative losses from the selective solar absorber (SSA). Thermal emittance plays a more important role than solar absorbance for the efficiency of SSA used in EFPCs working at medium temperature [1].

Once the SSA has been optimized for a maximum efficiency [2,3], further improvement can be obtained by reducing the substrate emissivity. We therefore deposited by electron beam low emissive Cu or Ag thin film on an Aluminium bulk substrate to improve the coating performances by reducing its thermal emittance, keeping the economic advantages of using a substrate as cheap and light as Aluminium. The low emissive coating can be used to reduce the thermal emittance of both the selective coating side and the substrate side of SSA. The thermal emittance was measured as a function of temperature through a calorimetric approach [4]. The thermal stability of the coating and the use of thin films of Cr2O3 as a diffusion barrier were also investigated.

[1] F. Cao, K. McEnaney, G. Chen and Z. Ren, Energy Environ. Sci. 7 (2014) 1615-28.

[2] D. De Maio, C. D'Alessandro, A. Caldarelli, D. De Luca, E. Di Gennaro, M. Casalino, M. Iodice, M. Gioffre, R. Russo, M. Musto, Multilayers for efficient thermal energy conversion in high vacuum flat solar thermal panels, Thin Solid Films, 735, 138869, (2021).

[3] D. De Maio, C. D'Alessandro, A. Caldarelli, D. De Luca, E. Di Gennaro, R. Russo, M. Musto, A Selective Solar Absorber for Unconcentrated Solar Thermal Panels, Energies, 14(4), 900, (2021).

[4] R. Russo, M. Monti, F. Di Giamberardino, and V. G. Palmieri, Characterization of selective solar absorber under high vacuum, Opt. Express, 26, (10), A480-A486, (2018).

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