Coatings for Use at High Temperatures
Room Pacific E - Session A1-2-MoA

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

Moderators: Gustavo García-Martín, REP-Energy Solutions, Spain, **Dr. Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

1:40pm **A1-2-MoA-1 Microstructural Changes of Yttria-Containing MMC-Coatings and Their Influence on Hot Corrosion, Wear and Mechanical Behavior***, **Christoph Grimme**, C. Oskay, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

While very high inlet temperatures increase the efficiency of turbines, they lead to the requirement of oxidation resistant bond coats for TBC systems. MCrAlY (M: Ni and/or Co) coatings are used for turbine blades in a broad field of applications. However, their deposition processes by HVOF or EB-PVD are cost-intensive and limited by line-of-sight. Galvanic co-deposition methods can be utilized to apply these types of coatings at lower cost and without line-of-sight limitations. This technique also opens the possibility to incorporate different metallic and ceramic particles alongside with galvanically deposited Ni, Co, and Ni/Co. Coatings for turbine components should not only improve the oxidation resistance of the system, but also increase the hot corrosion resistance to ensure an extended lifetime. One of the most aggressive attack in turbines originates from vanadium present in the fuel to be burned in gas turbines. It forms eutectic ashes with Na_2SO_4 from fuel or air ingestion of NaCl to form low melting V_2O_5/Na_2SO_4 compounds [1].

In this study, a novel galvanic co-deposition method was used to incorporate yttria particles in the Ni-coatings. Thereafter, the pristine Ni/Y_2O_3 coatings were enriched with Al and/or Cr by pack cementation. By the co-depositon of yttria alongside with nickel not only the oxide formation, but also the oxide adherence could be strongly improved due to the reactive element effect [2]. It was proven, that Y_2O_3 is also able to react with V_2O_5 to form high melting YVO_4 and thereby avoiding the formation of highly corrosive, low melting V_2O_5/Na_2SO_4 compounds. The influence of Y_2O_3 on oxidation and hot corrosion, as well as wear and mechanical properties compared to unmodified NiAl coatings was studied.

It was found that additions of nanosized Yttria in the Ni-coating cause a significant grain refinement after the aluminum diffusion process, with the grains being much larger for yttria-free coatings. Hardness measurements revealed an increase of approx. 100 HV1 for MMC NiAlY coatings compared to coatings without dispersed nano–Y_2O_3 particles. Furthermore, significant improvements of the thermocyclic oxidation behavior and hot corrosion resistance were achieved by the incorporation of Y_2O_3 to the metallic coatings.

[1]X. Montero, M. C. Galetz,*Oxid. Met.***2018**, *89*, 499–516.

[2]J. Stringer,*Mater. Sci. Eng. A***1989**, *120*, 129–137.

2:00pm **A1-2-MoA-2 Surface Refinement by Aluminide Diffusion Coatings and Its Effect on the Oxidation Behavior and Creep Strength of Additively Manufactured Fe- and Ni-Based Alloys***, **Ceyhun Oskay**, L. Mengis,* DECHEMA-Forschungsinstitut, Germany*; A. Kulig, H. Daoud,* Neue Materialien Bayreuth GmbH, Germany*; M. Galetz,* DECHEMA-Forschungsinstitut, Germany*; U. Glatzel,* University of Bayreuth, Germany and Neue Materialien Bayreuth GmbH, Germany

Additive manufacturing (AM) has created new possibilities for the rapid production of metallic components and has received considerable interest by a variety of industries such as chemical, energy and transportation, since this form of production of parts and/or spare parts can lead to the independence from supply chains. Furthermore, AM can offer the tailoring the component design, microstructure, and mechanical properties according to the requirements [1]. One of the major drawbacks of the AM is the requirement of a post-processing, since the components in the as-printed condition always possess a significantly high surface roughness and high internal stresses. This leads to a deterioration of their service-relevant properties such as oxidation resistance and fatigue strength. The industrial surface post-processing is usually conducted by grit blasting and heat treatment and is therefore usually difficult to apply for large parts with complex geometries. Even after these post-processing, AM components may still require improvement in their oxidation resistance, as process temperatures steadily increase for higher efficiencies. At higher service temperatures, the enrichment of Al at the surface by diffusion coatings has been shown to be very effective to protect Fe- and Ni-based alloys from oxidation. Such coatings form and maintain a slow-growing and dense alumina scale [2,3].

In this study, pack cementation was utilized to deposit aluminide diffusion coatings on additively manufactured (via Laser Powder Bed Fusion, LPBF) Fe- and Ni-based alloys to chemically modify and refine their surface simultaneously. A significant reduction of the surface roughness as well as sealing of the pores in the vicinity of the surface was observed after the coating deposition. Quasi-isothermal oxidation tests up to 1000 h were conducted at 800°C and 1000°C in laboratory air for aluminized and uncoated LPBF specimens. A significant improvement of the oxidation behavior was observed for the aluminized LPBF alloys compared to uncoated alloys. Creep tests were conducted at 800°C and 1000°C to characterize the performance of LPBF alloys with and without aluminide coatings. These results were compared with aluminized and uncoated wrought samples under the same conditions. Furthermore, load effects on scale formation and re-healing, depletion of the oxide former and crack formation were discussed for the AM alloys.

[1] I.E. Anderson et al., Curr. Opin. Solid State Mater. Sci. 22 (2018) 8-15.

[2] D.K. Das, Prog. Mater. Sci 58 (2013) 151-182

[3] B.L. Bates et al., Surf. Coat. Technol. 204 (2009) 766-770.

2:20pm **A1-2-MoA-3 Influence of High Temperatures on the Friction and Wear of Highly Stressed Exhaust Systems***, **Martin Dienwiebel**,* Institute for Applied Materials IAM - Karlsruhe Institute of Technology, Germany*; T. König,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; T. Kimpel,* Institute for Applied Materials IAM, Karlsruhe Institute of Technology, Germany*; D. Kuerten, A. Kailer,* Fraunhofer Institute for Mechanics of Materials IWM, Germany **INVITED**

We investigated the atmospheric effect of exhaust components on the wear of cast iron against chromium plated steel at temperatures up to 800 °C. Reciprocating wear tests of a cylinder plate configuration were performed in air and a low-oxygen CO_2-N_2-O_2 atmosphere and analyzed afterwards.

At temperatures above 400 °C a tribological induced oxide layer is formed at the interface, a so-called “glaze layer”, which replaces an adhesive regime and leads to a strong decrease of wear. The investigation proves a layered structure out of a porous lower and a highly compacted upper part with different chemical compositions. A change of atmospheres shows low impact on this tribological mechanism above a threshold temperature of 400 °C, assuming sufficient oxidation times of the generated wear particles, which agglomerate, were compacted and sintered due to the tribological stresses and temperatures. Based on this finding, a temperature related sinter or phase transition process is postulated to determine the glaze layer formation independently of comparable small atmospheric differences. At the adhesion dominated regime of lower temperatures a Carbon enriched layer of 400 nm thickness was observed in the CO_2-N_2-O_2 atmosphere and is made responsible for a decrease of wear.

3:00pm **A1-2-MoA-5 Surface Refinement of Additively Manufactured Components: Microstructure and Mechanical Properties***, **Agata Kulig**,* Neue Materialien Bayreuth GmbH, Germany*; C. Oskay, L. Mengis,* DECHEMA-Forschungsinstitut, Germany*; H. Daoud,* Neue Materialien Bayreuth GmbH, Germany*; M. Galetz,* DECHEMA-Forschungsinstitut, Germany*; U. Glatzel,* University of Bayreuth, Neue Materialien Bayreuth GmbH, Germany

Laser Powder Bed Fusion (L-PBF) is already used for manufacturing complex parts with high precision. However, the high cost of surface finishing is still a limiting factor for the spread of L-PBF components in various industries. The high surface roughness and their resulting residual porosity influence the mechanical properties, especially dynamic ones. In this presentation, the pack cementation process will be introduced as a novel method to refine the surface roughness and the microstructure in the surface zone as well as to improve the mechanical behavior of L-PBF parts.

The effect of the pack cementation process on the resulting microstructure in the surface zone of L-PBF specimens was investigated. For this purpose, different Fe- and Ni-Basis alloys were investigated. The surface roughness of as-built and as-modified L-PBF specimens was measured. Finally, the tensile strength as well as the fatigue behavior of both as-built and as-modified specimens will be presented.

3:20pm **A1-2-MoA-6 Oxidation Behavior of Novel Cr-Si Diffusion Coatings Applied by the Slurry Technique***, **Michael Kerbstadt,*** DECHEMA, Germany*; E. White,* DECHEMA, USA*; M. Galetz,* DECHEMA, Germany

Diffusion coatings are widely used in high temperature applications to enhance the oxidation and corrosion resistance of metals and alloys. Commonly Al, Cr, or Si are enriched at the surface in order to form protective oxide scales during exposures at high temperatures. Al, Cr and Si-based diffusion coatings are mostly achieved by pack cementation, where the deposition occurs via a gas diffusion process. For pack cementation the substrates are usually fully embedded into a powder mixture, which is labor-intensive and requires extensive furnace fixturing to be heated-up during each run. For an Al diffusion coating, an alternative slurry process is well established, where the slurry is sprayed onto the metallic surfaces by an air brush. The coating is then established during a subsequent heat treatment by interdiffusion between the metallic particles from the slurry and the substrate. For sufficient diffusion rates during the heat treatment, the existence of a liquid phase at the interface of the substrate surface and the slurry particles is necessary. Because of the high melting point of Cr, the deposition of Cr-based diffusion coatings by the slurry technique has been challenging. Cr-Si slurry coatings have recently been successfully developed at the Dechema-Forschungsinstitut. These newly developed slurry coatings are applied using an aqueous suspension where distilled water is used as the solvent. Higher Cr-activities, due to the partial liquid state, enable higher coating thicknesses when compared to similar coatings applied by pack cementation. This creates a larger reservoir of the protective oxide-forming elements Cr and Si, resulting in longer-lasting protection from the coating.

In this work the oxidation behavior of novel Cr-Si slurry coatings applied on the austenitic steel Sanicro 25 and the Ni-base alloy Inconel 617 are investigated. A Cr and Si enriched diffusion zone of more than 100 µm could be achieved on both materials. Isothermal and cyclic (1h/cycle) oxidation exposures at 900°C for 1000 h in lab air were carried out. To classify the results, samples with coatings applied by pack cementation and also bare substrate materials were exposed under the same conditions. To determine the weight gain samples were removed after 300 h, 700 h and 1000 h. Analysis by XRD, SEM and EPMA was performed to determine the structure and composition of the oxide layers and the degree of oxidative attack. Due to the increased amount of protective elements, the slurry coated samples showed a lower overall mass gain and decreased oxidation attack during the exposures.

3:40pm **A1-2-MoA-7 Use of Machine Learning Algorithms to Optimize and Customize Aluminide Diffusion Coatings***, **Vladislav Kolarik,** M. Juez Lorenzo,* Fraunhofer Institute for Chemical Technology ICT, Germany*; P. Praks,* IT4Innovations National Computing Center, VSB - Technical University of Ostrava, Czechia

Aluminide diffusion coatings are a highly efficient and economic technique to protect steels against corrosion at high temperatures in aggressive media such as molten salts or steam. 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. Machine learning algorithms offer a huge potential for optimization as well as for customization of the coatings to a particular application with different substrate steels and media. The experimental effort can be minimized reducing the costs significantly and accelerating the development. In this context the present work investigates the use of machine learning to determine the coating process parameters that lead to the targeted coating characteristics and properties.

First, the entire coating system and its manufacturing process was fully parametrized considering every single parameter having influence on the coating. Variable input parameters have been defined: green slurry thickness, slurry viscosity, aluminum particle size, curing temperature and time, heat treatment temperature and time. Other input parameters such as the substrate steel, surface roughness, slurry composition, purity of the aluminum particles, slurry deposition method and air as atmosphere were kept constant. Output parameters characterizing the diffusion coating were defined: coating thickness, number of layers and their thicknesses, pores concentrations and FeAl precipitations in the Fe2Al5 layer. Assessment criteria for the targeted properties were defined, such as an overall thickness of 100 to 120µm, three allowed layers (Fe2Al5, FeAl, Fe+FeAl), and a porosity less than 5%. Algorithms from Machine learning such as CatBoost were chosen to undertake the first approaches. Experimental values from former projects were used to train the software for calculating the impact of process parameter variation on the coating properties and to validate the outcome.

4:00pm **A1-2-MoA-8 Self-Healing Aluminide Coatings***, **Fernando Pedraza,** R. Troncy, L. Boccaccini, G. Bonnet,* La Rochelle University, France*; X. Montero,* MTU, Germany*; M. Galetz,* DECHEMA-Forschungsinstitut, Germany

Upon high temperature exposure, the Al reservoir of the aluminium diffusion coatings is lost by oxidation (2-8%) and by interdiffusion (20-35%) [**1**]. This lowers oxidation and mechanical resistance in nickel-based superalloys. Thermodynamically stable γ/γ' $(NiPt)_3Al$-based coatings were thus considered [**2**] but they require appropriate contents of Pt and of Hf to provide adequate oxidation resistance [e.g. **3**]. Since the cost of Pt (and of Hf) is quite high, such stable coatings cannot be applied to the low pressure turbine components that operate at lower temperatures (T<1050°C) where simple aluminide coatings suffice [**4**]. The use of diffusion barriers has been proposed to arrest interdiffusion [e.g. **5**] but such layers can embrittle the whole coating system. In contrast, composite $NiAl\text{-}Al_2O_3$ coatings [**7**] display adequate mechanical properties [**6**] and the high exothermicity between preoxidized Ni powders or coatings and Al [**8,9**] is buffered, hence avoiding projection of molten metal [**10**].

Based on this, this paper investigates the synthesis of self-healing aluminide coatings made of a conventional nickel aluminide matrix where preoxidized Al-rich Ni_xAl_y microreservoirs are embedded [**11**]. The idea is that the oxide shell covering the microreservoirs governs the outward diffusion of the Al-rich intermetallic core whenever the matrix is depleted in Al upon oxidation. For such purpose, Ni_2Al_3 powders were first fabricated by pack aluminizing a Ni plate that was subsequently crushed and milled, preoxidized and then added a nickel-electroplating bath. A final slurry aluminizing process was conducted. The study was conducted on pure Ni as a model of the Ni-based superalloys. Subsequent isothermal oxidation at 1000°C was conducted for 48h in air. The main results show that the Al depletion in conventional simple aluminide coatings ranged between 32 and 45 at% while the ones containing the microreservoirs only lost 11 at% thereby showing the promising character of these coatings. The mechanisms of formation and of degradation of the coatings will be highlighted.

Refs

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5. Bouchaud et al., Mater. Chem. Phys. 143 (2013) 416.
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7. Padmavardhani et al., Intermetallics 6 (1998) 229.
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4:20pm **A1-2-MoA-9 Continuous Al-supply to Cr_2AlC MAX Phase Coatings During Oxidation at High Temperature***, **Clio Azina,** M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; J. Gonzalez-Julian,* Chair of Ceramics, RWTH Aachen University, Germany*; P. Eklund,* Linköping University, IFM, Sweden*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

Phase stability is likely to be one of the most important specifications which determine the lifetime of materials operating in extreme environments. In the case of MAX phases, the weakly bonded A-elements diffuse along the basal planes when a thermal load is applied or when in presence of oxidizing environments. The A element then reacts with the oxidizing environment and forms a protective oxide scale. That is the case of the Cr_2AlC MAX phase in which Al diffuses to the surface and forms an Al_2O_3 scale. However, the Al depletion below the surface causes the local decomposition of the MAX phase into the binary carbide, Cr_7C_3.

In this work, the possibility of continuously supplying Al to Cr2AlC coatings is investigated in order to avoid the formation of the carbide layer. To this end, Cr2AlC substrates with different microstructures were used as substrates. These substrates were then coated with Cr2AlC by magnetron sputtering. The MAXonMAX assemblies were then oxidized in air, at high temperatures and the integrity of the assembly was assessed. Imaging allowed determining whether the different substrates allowed for Al transport across the substrate/coating interface and whether the concept of Al-supply from a MAX phase substrate to a MAX phase coating was viable. It appeared that the substrates played a major role in the oxidation behavior of the coatings as the oxide scale growth was impacted. This was attributed to the microstructure of the substrates which allowed for more or fewer diffusion channels depending on the grain size. Overall, the concept of Al-supply was shown to be successful when using fine-grained substrates but did not yield significant improvement when considering coatings grown on coarse-grained MAX phase substrate compared to those grown on conventional MgO substrates where Al supply does not occur.

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