

Coatings for Use at High Temperatures

Room Pacific E - Session A1-1-MoM

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

Moderators: Shigenari Hayashi, Hokkaido University, Japan, Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK

10:00am **A1-1-MoM-1 Performance of Innovative High-Temperature Coatings after Exposure in a Pilot Plant Burning Biomass**, *Alina Agüero Bruna (agueroba@inta.es)*, Instituto Nacional de Técnica Aeroespacial INTA, Spain; *P. Audigié, S. Rodriguez*, Instituto Nacional de Técnica Aeroespacial (INTA), Spain; *M. Gutiérrez*, Instituto Nacional de Técnica Aeroespacial (INTA), Spain; *M. Benito, A. Bahillo*, CIEMAT, Spain **INVITED**

To increase the efficiency of biomass power plants, the operating temperature must be raised with a consequent increase in corrosion rates. New materials and/or coatings are required, and testing is needed to evaluate the corrosion resistance of these new materials under various and very complex atmospheres resulting from the different types of available biomass. However, there is no general agreement regarding the methodology to carry out biomass corrosion tests, which can allow realistic ranking of materials and coatings. A 0.5 kWth simple pilot plant based on fluidised bed combustion was implemented allowing constant feed of biomass pellets. Several alloys with and without coatings were tested at 600-620°C for 1000 h while burning eucalyptus forestry residues pellets. The results were compared to those obtained in a laboratory test carried out under KCl deposits and a model atmosphere containing H₂O, O₂ and N₂. Newly developed Super VM12 ferritic steel was tested with and without coatings, which included slurry aluminides, modified FeCr and NiCr based alloys deposited by HVOF and weld clad IN625. In both the pilot plant and the lab, uncoated Super VM12 showed a very high degree of corrosion, and evidence of a high extent of spallation, whereas all coatings exhibited protective behaviour at different levels. In general, it was observed that the degree of corrosiveness in the plant was similar to that obtained in the lab and in all cases the coatings protected the substrate. For instance, according to the results of both

pilot and lab scale tests, weld clad IN625 (≈700 μm) showed a low degree of corrosion in both environments whereas the best behaved HVOF deposited coating was a 325 μm hard steel alloy modified with Al, that from the initial stages developed an approximately 50 μm corrosion product layer which appears to be protective as no significant thickness variations were observed. On the other hand, the slurry coatings showed non uniform degradation in the pilot plant. Indeed, in some areas typical microstructure changes could be detected due to interdiffusion with the substrate, as well as the development of voids. In addition, some degree of widening of the through thickness cracks originally present in the coating was observed (Figure 1a). These cracks self-healed by forming Al-rich oxides which are protective. The coating exposed in the lab shows a lower amount of voids when comparing with the pilot exposed specimen (Figure 2). Other zones of the coating showed important degradation of the aluminide phases after exposure in the pilot plant (Figure 1b). The causes of the difference in behaviour were analysed and will be discussed.

10:40am **A1-1-MoM-3 Surface Coatings for Improved Corrosion Resistance of Steels in Heavy Liquid Metal Coolants**, *J. Kulczyk-Malecka*, Manchester Metropolitan University, UK; *N. Barron, S. Ortner*, National Nuclear Laboratory Limited, UK; *Peter Kelly (peter.kelly@mmu.ac.uk)*, Manchester Metropolitan University, UK

A key challenge for systems cooled by molten lead is that the cladding materials must resist the harsh environmental conditions that they are exposed to; namely, chemical corrosion by molten lead-based coolant; oxidative corrosion at temperatures above 650°C; and neutron irradiation at doses up to 250 dpa. Austenitic and ferritic-martensitic (FM) steels have been identified as good candidates for cladding materials in molten lead environments. Nevertheless, these steels are susceptible to corrosion in oxidised molten lead and, therefore, their properties need to be improved either by alloying with corrosion protective elements or by depositing a corrosion protective barrier coating on the surface of a steel. The ability of alloying elements, such as aluminium and chromium, to form protective oxides is well known. Thus, the aim of this work was to investigate the deposition of protective barrier layers consisting of Al, Al₂O₃ and FeCrAl on austenitic stainless steel type 316L coupons. The coatings were deposited by mid-frequency pulsed DC unbalanced magnetron

sputtering in reactive (Al₂O₃) and non-reactive modes (Al, FeCrAl). Individual layers were investigated, as well as multi-layer FeCrAl/Al/AlOx coating stacks. Coatings were characterised by SEM and EDX and then subjected to a corrosive environment of molten lead at elevated temperatures (up to 800°C) and varying oxygen contents to investigate and compare the corrosion resistance of the deposited layers to allow the best performing corrosion barrier coatings for HLHC FRs applications to be nominated and further developed.

11:00am **A1-1-MoM-4 Improving the Intermediate Temperature Oxidation Resistance of Refractory Metals and Mo-Based Systems**, *Katharina Beck (katharina.beck@dechema.de)*, A. Ulrich, DECHEMA-Research Institute, Germany; *F. Hinrichs, M. Heilmaier*, Karlsruhe Institut of Technology, Germany; *M. Galetz*, DECHEMA-Research Institute, Germany

Refractory metals and their alloys are interesting materials to be used in high temperature applications. They are characterized by a very high melting point, typically beyond 2000°C, and their good mechanical properties at high temperatures and are therefore promising candidates for novel high-temperature materials. Besides their low oxidation resistance at target temperatures, already at intermediate temperatures, they can be prone to two different attack mechanisms: Pesting and hot corrosion.

Pesting, also referred to as catastrophic oxidation, describes the formation of volatile oxide species at intermediate temperatures and leads to the total disintegration of metal bulk material into powder. Besides pesting another particularly severe corrosion attack is induced by deposits on the surface of compounds, which usually are the result of impurities in combustion atmospheres. In turbine environments sulphates and alkali metal salts are known to induce hot corrosion. To counteract both attack mechanisms, the formation of protective oxide scales is necessary. As α-Al₂O₃ is commonly known to be very resistant in oxidizing as well as hot corrosion environments, this work aims to make the formation of such an oxide scale possible by the application of Al-coatings.

By means of pack cementation, an *in situ* chemical vapor deposition process, Al-coatings (with thicknesses up to 60 μm) were successfully applied on four different refractory metals (Mo, Nb, Ta and W) and two recently developed Mo-Si-Ti alloys (eutectic Mo-20.0Si-52.8Ti and eutectoid Mo-21.0-34.0Ti) [1]. Using thermogravimetric analysis for 100 h in synthetic air at intermediate temperatures (700 °C and 900 °C), the oxide formation was investigated and the improvement of the oxidation behavior correlated to Al₂O₃ scale formation was confirmed. The formation of these scales results in a substantially decreased oxide growth rate in comparison to the uncoated substrates. Post exposure, Al reservoirs (intermetallic phases) were still present below the formed oxide scale, making healing of the scale possible in the case of crack formation. The applied layers, the formed intermetallic phases and the formed oxide scales were analyzed before and after exposure to the oxidizing atmospheres using optical microscopy, XRD, SEM, EDX and EPMA.

[1] Schliephake, Daniel, et al. "Constitution, oxidation and creep of eutectic and eutectoid Mo-Si-Ti alloys." *Intermetallics* 104 (2019): 133-142.

11:20am **A1-1-MoM-5 Arc-Evaporated Ti_{1-x}Al_xN Coatings in Hot-Corrosion Settings**, *Oliver Ernst Hudak (oliver.hudak@tuwien.ac.at)*, A. Scheiber, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *L. Shang, O. Hunold, M. Arndt*, Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein; *S. Kolozsvari*, Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany; *H. Riedl*, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Hot corrosion is a common phenomenon observed in gas turbine engines, coal gasification plants and waste incinerators. It occurs in high-temperature settings, where a sulfur-rich atmosphere reacts with salt impurities such as Na, Mg, Cl or V, and form high-melting sulfate-salts, that then deposit and adhere on machining component surfaces. There, the salt deposit elicits an accelerated degradation of the material through the formation of non-protective porous oxide scales. Depending on the temperature range, two distinctively different corrosion mechanisms can emerge. At temperatures below the melting point of the salt deposit (~600-850 °C), low-temperature hot corrosion dominates as mechanisms, whereas at temperatures above the melting point, high-temperature hot corrosion predominates (~850-950 °C). For all of the above mentioned fields of application, Ni-, Co-, and Fe-based superalloys have proven to be a reliable choice of material, due to their superior mechanical properties at high temperatures, as well as good oxidation resistance in air. However, if

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exposed to hot corrosion conditions, their overall oxidation resistant qualities diminish drastically.

From this perspective, this contribution showcases $Ti_{1-x}Al_xN$ as an interesting candidate as protective PVD coatings for extending the lifetime of highly-stressed material components in hot-corrosion environments. $Ti_{1-x}Al_xN$ coatings with varying metal content ratios were arc-evaporated on Ni-based superalloy substrates and tested in an in-house built hot-corrosion testing rig. By applying a sulphate-salt mixture from the alkali and alkaline earth metal group, the samples were corroded in a SO_x -rich atmosphere for a maximum of 30 h according to the HTHC and LTHC conditions, and subsequently analyzed and evaluated for their applicability using a set of high-resolution characterization techniques.

Keywords: Corrosion Resistance; PVD coatings; Diffusion Pathways; Hot Corrosion; HTHC; LTHC;

11:40am **A1-1-MoM-6 High Temperature Oxidation Behavior of Hafnium Aluminum Diboride Thin Films**, *Samyukta Shrivastav (ss101@illinois.edu)*, D. Yun, C. Romnes, K. Canova, J. Abelson, J. Krogstad, University of Illinois at Urbana Champaign, USA

The integrity of hafnium diboride, a refractory and hard metallic ceramic, is compromised at high temperatures (900-1000°C) when air is present due to oxidation of the boron sublattice to form liquid boron oxide, which evaporates. One potential solution is to deposit a $Hf_{1-x}Al_xB_2$ alloy film, with the expectation that Al can oxidize to form a protective Al_xO_y overcoat.

We use low temperature chemical vapor deposition to deposit the alloys, as described elsewhere in this conference. This approach has the advantage that Al will be distributed throughout the material; by contrast, in conventional hot-pressing of separate HfB_2 and AlB_2 powders the phases may not mix intimately. We previously showed that as-deposited HfB_2 is amorphous and crystallizes upon annealing at temperatures $\geq 600^\circ C$. For the alloy, we hypothesize that excess aluminum will be liberated upon crystallization, and will diffuse to the surface and form a passivating oxide.

We show that the oxidation product is strongly temperature dependent. Upon annealing at $700^\circ C$ for 1 hour, a mixture of hafnium, aluminum, and boron oxides form. But this mixed oxide is not protective, and complete oxidation of films occurs when heated to higher temperatures. At annealing temperatures between $800^\circ C$ and $900^\circ C$, the oxides of boron and aluminum react to form acicular aluminum borate, which is spread uniformly on the surface of the film. TEM cross sections reveal hafnium oxide particles embedded in aluminum borate needles; SEM shows surface roughening; STEM-EDS identifies the composition of the reaction products; and SAED confirms the crystal structures of the products. We conclude that aluminum is not a viable alloying element for the formation of a passivating oxide on diboride thin films. Based on phase diagrams and oxide literature, we suggest using alloying elements like chromium, which forms a passivating oxide but does not react with the oxides of boron and hafnium.

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