Coatings for Use at High Temperatures
Room Pacific Salon 2 - Session A3-WeA

Materials and Coatings for Solar Power Concentration Plants

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, **Gustavo García-Martín**, Universidad Complutense de Madrid

2:40pm **A3-WeA-3 Ductility and Creep Rupture Behavior of Diffusion Coatings Deposited on Grade 91 Steel for Concentrated Solar Power Applications***, **Ceyhun Oskay**, T Meissner, C Dobler, M Galetz,* DECHEMA-Forschungsinstitut, Germany

Energy transition aims at the abandoning of fossil-fuel based power generation and shifting to renewable energy technologies. In the course of energy transition concentrated solar power (CSP) technology is qualified as one of the most promising energy generation methods. In CSP systems, solar radiation is concentrated to a receiver via heliostats and molten nitrate salts are employed in the absorber tubes to store and transfer the thermal energy for the consequential generation of electricity via a steam turbine. While offering beneficial thermal and physical properties such as a high heat capacity, thermal conductivity and stability, the utilization of molten nitrate salts, particularly the eutectic mixture of 60 wt.% $NaNO_3$ – 40 wt. KNO_3 (known as the solar salt) is accompanied with an increased corrosion rate and thus limits the selection of structural materials to high-alloyed steels as well as Ni-based alloys due to their high corrosion resistance. As an alternative, cheaper structural materials such as ferritic-martensitic steels can be used by enhancing their molten salt corrosion resistance via the application of diffusion coatings. This can result in a substantial increase in the cost efficiency of the CSP technology and thus improve its competitiveness with respect to other energy generation methods such as photovoltaics.

In this study, three different types of diffusion coatings were deposited on P91 steel substrates by the industrially well-established method of pack cementation. The first two coatings were aimed at Cr and Al enrichment at the surface respectively; whereas the third coating was manufactured by a two-step process involving chromizing followed by aluminizing. Subsequently coated and uncoated specimens were exposed to isothermal oxidation in laboratory air at 650°C for 100, 300 and 1000 h in order to characterize the scaling behavior of coatings by thermogravimetric analysis. Four-point bending tests with in-situ acoustic emission (AE) measurement were conducted to determine the fracture strain at RT, while creep rupture tests at 650°C in laboratory air were undertaken to compare the creep strength of coated specimens with respect to their uncoated counterparts. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were utilized for the phase identification and microstructural characterization. Detailed microstructural analysis enabled the correlation of mechanical behavior with the microstructural degradation of coated and uncoated specimens during exposure.

3:00pm **A3-WeA-4 Long-term Molten Salt Corrosion of Aluminide Coatings for Heat Storage in Concentrated Solar Power Plants***, P Audigié, S Rodríguez, **Alina Agüero**,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Concentrating solar power (CSP) plants represent a valuable technology in terms of baseload and dispatchable renewable energy. However, due to its complicated nature and its difficulty to become an economically viable technology CSP struggle to gain the upper hand over solar photovoltaic and wind power. To overcome the main drawback of intermittency, improving the heat storage system by targeting 15h to 24h storage in the mid- or long-term will bring added-value to CSP. In that sense, advanced molten salts used as heat transfer fluids are investigated but corrosion issues for tubes and tanks materials in contact with them are of concern. To protect base materials with coatings can resolve or moderate corrosion degradation and therefore improve the plant efficiency. This alternative also allows to reduce the capital expenditure when designing a new plant because coatings can be applied on lower cost ferritic-martensitic steels instead of current expensive Ni-base alloys. Slurry aluminide coatings have already demonstrated high corrosion resistance to molten salt after short term exposure (1000h). But the protection mechanism still remains under investigation and long-term exposure is required to confirm the lifetime gain brought by the coatings. This study focuses on the corrosion resistance of slurry aluminide coatings after long-term exposure in contact with the currently employed heat storage system, the so-called Solar Salt (60% $NaNO_3$-40% KNO_3). To do that, slurry applied aluminides to 9 wt.% Cr P91 and 11.5 wt.% Cr VM12-SHC alloys have been deposited, heat treated at high temperature and both systems have been tested at 580ºC in contact with the Solar Salt under static isothermal and cyclic conditions. All the coated systems in all conditions performed much better than the uncoated materials as they exhibited very slight weight variations and formed very thin oxides rich in Na, Al and Fe. Moreover, the coating's morphology and composition were maintained after 5000h with the presence of the same FeAl and Fe_3Al phases than in the initial state suggesting that the Al reservoir is still large enough to protect the underlying metals. On the contrary, both uncoated P91 and VM12-SHC developed a complex, fast growing multilayered oxides rich in Fe, Cr and Na which easily spalled in particular after testing in the more aggressive cyclic conditions. Moreover, as corrosion in molten salt results from the competition between dissolution reactions and corrosion product formation, removing the corrosion products by chemical etching was performed to determine the corrosion kinetics and both substrates experienced parabolic kinetics with significant metal loss.

3:20pm **A3-WeA-5 Burn-in Heat Treatment to Form Aluminide Diffusion Coatings for Industrial Large Scale Application***, **Vladislav Kolarik**, M Juez Lorenzo, J Bermejo Sanz, S Weick,* Fraunhofer Institute for Chemical Technology ICT, Germany

Aluminide diffusion coatings, deposited as Al slurries, are an efficient and economic technique to protect steels against oxidation and corrosion at high temperatures. Moreover, the coating suppresses the evaporation of volatile chromium VI species, which form especially in the presence of water vapor. The typical applications of such coatings are boilers and heat exchangers in all kind of power plants and recently, the application to tubes and storage tanks for molten salt in the up-coming technique of concentrated solar power (CSP) is being investigated.

The diffusion heat treatment, however, is a crucial process step when applied to large scale components, such as a CSP storage tank and even more when aiming at application on-site. Furthermore, the temperature of the heat treatment has to stay below the annealing temperature of the steel for not affecting the microstructure, e.g. 700°C for the ferritic steel P92.

A superficial BURN-IN process was applied to form the aluminide diffusion coating using a heating source with a defined temperature moving with a defined velocity over the slurry coated surface at a defined distance to it. Pre-oxidation forming an alumina scale on top of the coating can be achieved with a proper adjustment of the burn-in process.

A viscosity and rheology adapted slurry formulation was prepared using spherical high purity aluminum particles with an average diameter of 15 µm and was deposited by brushing or spraying on the surface of the ferritic steel P92. A commercially available radiation heating element was used to heat the sample surface. During the burn-in process the temperatures of the heating source, the slurry coating surface as well as the back-side of the sample were recorded as a function of time. Temperatures in the range of 800°C were applied to the slurry coated surface for times up to 5 hours. With these parameters, the back-side temperature of a 3 mm thick sample was around 500°C.

The resulting aluminide diffusion coatings exhibit very low porosity and a very smooth surface forming a two layers-structure, an outer Fe_2Al_5 layer and an inner FeAl layer. Transversal micro-cracks across the aluminide coating are observed locally as it is typical for such coatings. Underneath the diffusion coating the P92 substrate shows an unaffected microstructure as it is found in the case of the conventional heat treatment at 650°C. The superficial burn-in process is a suitable heat treatment for slurry coatings allowing higher temperatures on the surface and applicable to large components.

3:40pm **A3-WeA-6 High-Temperature Coatings For Protection of Steels in Contact with Molten Salt for CSP Technology***, **Gustavo García-Martín**,* REP-Energy Solutions, Spain*; V Encinas Sánchez,* Universidad Complutense de Madrid, Spain*; M Lasanta Carrasco,* Universdad Complutense de Madrid, Spain*; T de Miguel Gamo, F Pérez Trujillo,* Universidad Complutense de Madrid, Spain

The dramatic increase in demand for energy independence has led research groups all over the world to concentrate their investigation on renewable energies. As renewable energy penetration grows, the need for utility-scale renewable generation with storage technology is increasingly important to mitigate intermittency problems, deliver power to peak demand periods and support transmission system reliability. Therefore, concentrated solar power has gained momentum as an attractive technology. Molten nitrate salts are currently considered ideal candidates for heat transfer and storage applications because of their properties. However, this technology is still expensive compared to other renewable sources, which lead to propose solutions for reducing costs. One of these solutions is the development of high-temperature corrosion-resistant coatings, which would avoid the use of expensive alloys. The use of high-temperature corrosion-resistant coatings would be a very suitable option, even more if they were deposited on cheap steels, such as ferritic-martensitic ones. This solution not only would help to overcome the corrosion problems, but also would allow the CSP industry to improve the Levelized Cost of Energy. In this respect, zirconia-based sol-gel coatings seem to be a suitable option, both from an operational and economical point of view.

Thus, in this work, sol-gel zirconia-based coatings were deposited on ferritic-martensitic steels and tested in contact with Solar Salt at 500°C, results being compared with the uncoated substrate. Results were also compared to other steels of interest in CSP industry, such as austenitic stainless steels. The study was developed up to 1000 h under static conditions. Samples were characterized via gravimetric, SEM-EDX, and XRD.

Results showed the good behavior of the coated substrates, with very little weight variations after 1000 h of test in comparison with the uncoated ones, which exhibited significant weight gain and spallation. The good behavior of the proposed coatings was also observed by SEM-EDX and XRD. Furthermore, results also showed the promising behavior when comparing with steels currently used in CSP industry.

Author Index

Bold page numbers indicate presenter

— A —
Agüero, A: A3-WeA-4, **1**
Audigié, P: A3-WeA-4, 1
— B —
Bermejo Sanz, J: A3-WeA-5, 1
— D —
de Miguel Gamo, T: A3-WeA-6, 1
Dobler, C: A3-WeA-3, 1
— E —
Encinas Sánchez, V: A3-WeA-6, 1
— G —
Galetz, M: A3-WeA-3, 1
García-Martín, G: A3-WeA-6, **1**
— J —
Juez Lorenzo, M: A3-WeA-5, 1
— K —
Kolarik, V: A3-WeA-5, **1**
— L —
Lasanta Carrasco, M: A3-WeA-6, 1
— M —
Meissner, T: A3-WeA-3, 1
— O —
Oskay, C: A3-WeA-3, **1**
— P —
Pérez Trujillo, F: A3-WeA-6, 1
— R —
Rodríguez, S: A3-WeA-4, 1
— W —
Weick, S: A3-WeA-5, 1