Coatings for Use at High Temperatures
Room San Diego - Session A1-3

Coatings to Resist High Temperature Oxidation, Corrosion and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Prabhakar Mohan, Solar Turbines, USA, Anton Chyrkin, Forschungszentrum Jülich GmbH

8:00am **A1-3-1 Thin Co and Ce/Co Coatings on Ferritic Stainless Steel Interconnects for Solid Oxide Fuel Cells**, ***Hannes Falk-Windisch***, *M Sattari, L Johansson, J Svensson, J Froitzheim,* Chalmers University of Technology, Sweden

The use of Cr_2O_3-forming alloys for Solid Oxide Fuel Cell (SOFC) interconnects is challenged by the volatilization of Cr (VI) species that causes cathode poisoning and by rapid oxide scale growth causing increased electrical resistance. This work investigates the use of Cobalt (Co) and Cerium (Ce) nano coatings to mitigate both degradation mechanisms. The work involves coating the ferritic stainless steel Sanergy HT, which is designed for use as SOFC interconnects, with 640 nm Co and with 10 nm Ce + 640 nm Co using Physical Vapor Deposition (PVD). The materials were exposed in air at 650-850 ˚C for up to 3000 h and chromium volatilization, oxide scale growth and electrical resistance were studied. Mass gain was recorded to follow oxidation kinetics, chromium evaporation was measured using a denuder technique, and Area Specific Resistance (ASR) measurements were carried out on exposed samples. The oxide scale microstructure was characterized using Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM), and Energy Dispersive X-Ray Analysis (EDX). The results show that thin Co coatings effectively mitigated Cr volatilization. Sandwiching a 10 nm Ce layer between the Co coating and the steel greatly improved oxidation resistance, especially at higher temperatures. Also, ASR measurements revealed that the Ce + Co coated material had lower electrical resistance after exposure than the same material coated with only Co. The effect was attributed to the thinner scale formed on the steel coated with Ce + Co. The results imply that the duplex, Co + Ce thin film coating is suitable for ferritic stainless steel interconnects in Solid Oxide Fuel Cells.

8:20am **A1-3-2 Long-term Oxidation of MCrAlY Coatings at 1000 ^{o} C and an Al-activity Based Coating Life Criterion**, ***Pimin Zhang***, *Y Kang, R Lin Peng,* Linköping University, Sweden; *X Li,* Siemens Industrial Turbomachinery AB, Sweden; *S Johansson,* Linköping University, Sweden

MCrAlY type (M=Ni and/or Co) coatings are widely used for the protection of components in the hot sections of gas turbines at high service temperatures by forming a continuous α-alumina. A reliable criterion to estimate the capability to form α-alumina is of great importance to accurately evaluate coating lifetime. However, the traditional Al-concentration based criterion failed to properly predict the formation of a continuous α-alumina. Thus, a new life criterion, namely the critical Al-activity criterion, is proposed.

In this work, critical Al-activity to form a continuous α-alumina is calculated using Thermo-Calc software, based on literature survey of research results of critical Al-concentration to form α-alumina on binary Ni-Al and ternary Ni-Cr-Al system. Long-term oxidation test were performed to support the criterion: IN-792 superalloys coated with five different MCrAlY coatings were oxidized at 1000 ^{o}C for various periods of time up to 10000 hours. The microstructural evolution of MCrAlY coatings were analyzed using Scanning Electron Microscope. The near-surface Al concentration and interdiffusion behavior between substrate and coating were measured using Energy Dispersive X-ray Spectroscopy. The new critical Al-activity criterion has been successfully adopted in α-alumina formation prediction, showing a good agreement with experiment results. Therefore, it can be concluded that the extrapolation of new criterion from binary and ternary systems to multi-alloyed MCrAlY system is reasonable. Furthermore, the partial pressure of oxygen (P_{O2}) in atmosphere has been taken into consideration by combination with Al-activity to calculate the Gibbs energy of formation of α-alumina. The potential applicability of the methodology to predict MCrAlY life is also discussed .

8:40am **A1-3-3 The Preparation of Ti_2AlN MAX Phase Coatings and its Oxidation Mechanism under Different Atmosphere**, ***Zhenyu Wang***, University of Chinese Academy of Sciences, China; *P Ke, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Ti_2AlN belongs to a family of ternary nano-laminate alloys known as the MAX phases, which exhibit a unique combination of metallic and ceramic properties. In the present work, the dense and high-stability Ti_2AlN coating has been successfully prepared on Ti6Al4V (TC4) substrates through combined cathodic arc/sputter deposition method, followed by heat post-treatment. The oxidation of Ti_2AlN coating and the TC4 substrates were investigated in air and in water vapor at 750 °C for 200h. The results indicated that the oxidation processes of both TC4 substrates and the coated samples were accelerated for the presence of steam, resulting in slightly higher mass gains. The oxidation behavior of the bare substrates under different atmosphere exhibited linear kinetics, which indicates a continuous oxidation during its exposure at high temperatures. In contrast, the mass gain was significantly reduced for the coated samples, suggesting that the Ti_2AlN coating can provide an effective protection for the substrates. Moreover, the Ti_2AlN phase can still be found after oxidation in air atmospheres for 200h and the oxide scale showed local Al_2O_3 and rutile TiO_2 growth, namely the oxide did not cover the entire surface of the coating. However, the Ti_2AlN phase disappeared after oxidation in steam condition and double layer scales formed in the water vapor atmospheres, consisting of an outer rich-Al_2O_3 layer and an inner rich-TiO_2 layer. The enhanced oxidation resistance achieved under different condition by the Ti_2AlN MAX phase coatings may satisfy the optimal requirements for many applications in the field of nuclear power plants and aerospace components.

9:00am **A1-3-4 Effect of Coating Architecture on the Corrosion Behavior of Ti-N/Cr-N Multilayer Coatings**, ***Yu-Sen Yang***, National Kaohsiung First University of Science and Technology, Taiwan

Two coating architectures with distinct period number (PN) of Ti-N/Cr-N multilayer coatings were prepared by reactive magnetron sputtering process. Two coating architectures were designed as the multilayers TiN/CrN/…CrN/TiN/Ti/substrate (architecture T) and the CrN/TiN…TiN/CrN/Cr/substrate (architecture C). Four PNs with 1,5,10 and 15 were prepared in architecture T and C, respectively. This study investigates the effect of the coating architectures and PNs on the corrosion behaviors of the coatings. The corrosion rate were tested by immersion the coatings in the 3% HCl solution for 20 hours to measure the weight loss. The results show that the corrosion rate of the coatings were strongly related to the coating architecture and PN. In coating architecture T, the corrosion weight loss is decreased with PN increased. On the contrary, in architecture C, the corrosion weight loss is increased with increasing PN.

9:20am **A1-3-5 Effects of Encapsulating Material and Healing Agent Ratio on Crack Propagation Behavior for Thermal Barrier Coatings**, ***Soo-Hyeok Jeon***, *S Lee, S Jung, H Park, Y Jung,* Changwon National University, Republic of Korea; *J Zhang,* Purdue University, USA

Thermal barrier coatings (TBCs) are important parts to protect metallic substrate in gas turbine engines because turbine inlet temperature is continuously increased to improve fuel efficiency. Recently self-healing TBCs have been proposed to prevent delamination and spalling of TBCs during gas turbine operation. In this study, $MoSi_2$ as the healing agent was coated by three kinds of materials such as tetraethyl orthosilicate (TEOS), sodium methoxide (NaOMe), and their mixture (TEOS + NaOMe) for stabilizing $MoSi_2$ at high temperatures. YSZ and capsulated $MoSi_2$ were mixed with 90:10, 80:20, and 70:30 wt% ratios, respectively. Samples were fabricated by uniaxial compaction at 100 MPa and then sintered at 1300 ^{o}C and 1500 ^{o}C, respectively. Crack propagation behavior was investigated as functions of $MoSi_2$ stabilizing agent, stabilized $MoSi_2$ content, and sintering temperature. Furnace cyclic test (FCT) was performed at 1100 ^{o}C for a dwell time of 40 min, followed by natural air cooling for 20 min at room temperature, after generating artificial cracks in TBC samples by using Vickers indentation. The TBC sample with the $MoSi_2$ of 20 wt% capsulated with the mixture of TEOS and NaOMe and sintered at 1500 ^{o}C showed the best healing effect in FCT test. This study allows us to design reliable TBC systems in operating conditions.

9:40am **A1-3-6 Comparative Study of Monolayer and Multilayer CrAlSiN PVD Coatings Behavior at High Temperature in Steam Atmosphere**, *A Illana, S Mato,* Complutense University of Madrid, Spain*; E Almandoz, G Garcías Fuentes,* Navarra Industry Association, Spain*; F Pérez Trujillo,* ***Maríalsabel Lasanta****,* Complutense University of Madrid, Spain

Technological developments around electric generation power plants aim to increase thermal efficiency of conversion processes in steam turbines, developing materials able to resist ultra-supercritical (USC) vapor conditions at 600-650°C and 35 MPa. Ferritic-martensitic steels, commonly used so far, show very low oxidation resistance at these conditions. The solution is to modify their surface, by means of protective coatings that retard interdiffusion mechanisms which take place at that temperature range and to prolong their service life.

Hard coatings based on nitrides and deposited by PVD have been commonly applied in cutting tools, since possess tribological features that increase their wear and oxidation resistance in aqueous media, mainly alkaline and neutral. CrN coatings have been broadly employed for last decades for this application. The incorporation of Al and/or Si in these films produces an improvement in the mechanical properties, due to hardening for grain refining (Hall-Petch effect), and an increase of thermal resistance against oxidation in comparison to the pure CrN , due to the formation of protective oxides that avoid the migration of oxygen towards the substrate.

In order to contribute to the knowledge on this topic, a monolayer and two multilayers with different periodic thickness of magnetron-sputtered CrAlSiN coatings with similar Cr/Al ratio and Si content were deposited on P92 ferritic-martensitic steel and tested to assess their protection capability under the working conditions of USC steam turbines operation (at 650ºC in 100% steam atmosphere) during 2000 h. Common characterization techniques have been used to achieve this objective, such as: gravimetry analysis in order to study the kinetics of oxidation, x-ray diffraction (XRD) to explored the phases formed during the oxidation process and scanning electron microscopy with energy dispersive detector (SEM-EDX) to evaluate the morphology and semi-quantitative composition of the films.

CrAlSiN coatings have showed a significant improvement to the oxidation resistance of the bare substrate (P92 steel), due to the formation surface oxide layers. Cr_2O_3, SiO_2 and Al_2O_3 resulted more effective against the ionic interdiffusion and with greater compactness, which lead to a reduction of the oxidation rate at isothermal USC vapor conditions. After 2000 h of test, coated samples have shown no diffusion of species from the substrate into the coating and they have presented oxidation kinetics that follow a parabolic trend, typical of the material which has developed a protective oxide on the surface at high temperature.

10:00am **A1-3-7 Material Validation in Molten Salt Environment under Dynamic Conditions Using a Novel Pilot Plant Facility**, *M Lasanta, G García Martín,* ***Víctor Encinas Sánchez****, M de Miguel, F Pérez Trujillo,* Complutense University of Madrid, Spain

Solar thermal plants which concentrate the Sun's energy to produce steam and electricity often use molten salt mixtures as a heat transfer fluid (HTF) and/or as thermal energy storage (TES) medium. The most industrial compound used is an alkali-nitrate mixture composed by 60 wt.% $NaNO_3$/40 wt.% KNO_3 (Solar Salt®). On the other hand, corrosion behavior of materials is a very important issue as regards the molten salts and CSP plants. Up to now, all studies have been carried out through static immersion tests, parameters such as dynamic flow in contact with the substrate, oxidizing gas atmosphere and thermal cycling being dismissed. Thus, the aim of this work was to introduce a novel pilot plant facility and evaluate the corrosion resistance of A516 and 304 steels in Solar Salt in dynamic condition test at 500 ºC using it. The equipment used allows degradation tests of materials in contact with molten mediums simulating thermo-cycling process and keeping the stable conditions during whole studies. These results were compared with the static ones in order to evaluate the effect of the fluid-dynamics.

The isothermal dynamic and static immersion test results were analyzed via gravimetric measurements. Both tests were carried out at 500 ºC. The tested specimens were analyzed after 100 hours of testing and were characterized by SEM-EDX and XRD.

The average weight gain measured in the samples tested by dynamic test was higher than that measured by the static test. Dynamic test approach reproduce the conditions of CSP plants in a better way. Thus, results obtained by dynamic test are considered more reliable for the corrosion prediction behavior of the CSP plants. Furthermore, useful information was extracted from the tested samples after characterizing. The surface appearance of the two samples was quite different, the sample subjected to dynamic test showing more detachments. As expected, the greater thickness of the oxide layer on the sample subjected to the dynamic test was observed in the cross-section micrographs. XRD measurements confirm the observed species in SEM-EDX.

Experiments demonstrated how dynamics tests provokes an increase in corrosion rates, since mass gained is quite greater in samples subjected to dynamic tests than the ones gained through static tests. These results are also confirmed by SEM. This work is a new step forward in the future experimentation for materials and engineering processes for future CSP plants with molten salts.

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