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Effect of various lanthanum sol–gel coatings on the 330Cb (Fe–35Ni–18Cr–1Nb–2Si) oxidation at 900 °C

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ABSTRACT

The influence of a lanthanum sol–gel coating on the oxide scale adherence has been studied during the 330Cb (Fe–35Ni–18Cr–1Nb–2Si) oxidation at 900 °C, in air. The alloy oxidation is performed in order to generate a protective chromia scale acting as a good barrier against carburization. Argon annealing of lanthanum sol–gel coatings have been performed at various temperatures in order to find the best conditions to insure the scale adherence. Kinetic results show that lanthanum sol–gel coatings lead to a lower oxidation rate compared to blank specimens. Thermal cycling tests on lanthanum the sol–gel coated specimen show that the oxide scale formed at 900 °C, in air, is adherent.

1. Introduction

Corrosion and carburization are the main reasons of conveyor units degradation due to a quick alloy weakening. In order to improve the alloys carburization resistance it is assumed that the presence of an adherent oxide scale acts as a carbon diffusion barrier. In the literature, a Fe–35Ni–18Cr–2Si (niobium free) alloy has been studied in the 1000 and 1300 °C temperature range as a resistance heating-element material [1]. It is proposed that chromia Cr_2O_3 is the protective oxide scale formed at high temperature. Stevens shows that at temperatures higher than 1100 °C the chromium oxide CrO_3 evaporation occurs. In this case chromium depletion is observed in the oxide scale and in the alloy. The concentration of elements in the protective oxide was found to be both temperature and time dependent. Chromia is stable at low temperature (<1100 °C) and was found to evaporate at higher temperatures and longer oxidation time, thereby increasing nickel and iron concentrations. On the basis of changes in the chemical composition of the oxide film, together with scaling, the failure of heating-element wire by the development of hot spots can be explained. At failure both long-term (low temperature < 1000 °C) and shorter-term tests (temperature > 1000 °C) were found to have oxidized to the same depth. This can be explained on the basis of a depletion of chromium, which occurred at the oxide–alloy interface, and becomes insufficient for a healing process. Another study has shown that in the 800–1000 °C temperature range, the 330Cb oxidation leads to a chromia scale acting as a good diffusion barrier under isothermal conditions [2]. The external manganese chromite subscale has no influence on the diffusion properties of the main chromia scale. It is expected that the manganese chromite can limit the chromia scale evaporation at temperatures higher than 1000 °C [3].

Nevertheless, after oxidation and cooling to room temperature, important scale spallation occurred [2]. At 900 °C, spallation only appeared on the niobium and silicon rich areas. At 1000 °C, scale spallation is present on the entire specimen surface indicating that this temperature is too high to obtain an adherent chromia scale on the alloy surface. The comparisons between the 48 and 160 h oxidation duration have shown that at 800 and 900 °C a short oxidation duration (46 h) is favourable to the oxide scale adherence. It then appeared that the chromia scale never shows a perfect adherence on the alloy under the tested conditions.

In order to improve the chromia scale adherence previous works have proposed to introduce lanthanum as an alloying element [4] or on the alloy surface as a La_2O_3 coating [5–9].

Gleeson demonstrated the significant effects of alloy composition on long-term, cyclic-oxidation resistance. Each of the alloys exhibited scale spallation; however, the manner by which

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spallation occurred varied between the alloys [4]. The 230 alloy, which contains 0.02 wt.% La, exhibited partial scale spallation, thus allowing for the easier formation of a protective Cr_2O_3-rich scale during subsequent oxidation. The HR-160 alloy exhibited complete spallation owing largely to its relatively high silicon content (2.75 wt.%). However, the silicon was also beneficial in promoting protective scale formation when the exposed alloy was subsequently oxidized. The HR-120 alloy showed the poorest cyclic-oxidation resistance, due in part to poor scale adhesion and the tendency of the iron in this alloy (33 wt.%) to eventually oxidize and result in the formation of a less-protective scale. All of the alloys underwent internal attack in the form of internal oxidation and void formation. In most cases, the extent of internal attack was significantly greater than that of metal loss.

Fontana shows that Crofer 22 APU, AL 453 and Haynes 230 alloys seem particularly suitable as interconnect in SOFC devices [5]. The beneficial effects of reactive elements on oxidation behaviour were clearly visible. However, the conductivity of oxide scales was sometimes higher than that of uncoated samples. The coatings composed of a thin reactive element oxide such as, La_2O_3, Nd_2O_3 and Y_2O_3 resulted in an important improvement in the high temperature oxidation resistance; the oxide growth rate decreased, the adhesion between alloy and oxide scale is improved. The MOCVD method showed good reproducibility and excellent efficiency to obtain nanometric layers on the interconnect surface. The first objective of these coatings was to form perovskite oxide with the chromia growing layer because perovskite present better conductivities than chromia, especially when they are doped with iron.

Fernandes explained that sols of La_2O_3, were prepared as aqueous dispersions with nitric acid and a non-ionic surfactant, heated to 80 °C for 1 h to form a sol, the RE oxide sol then sprayed on specimens of the two alloys to form a coat and finally the specimens heated to 150 °C to form a 10 μm thick surface layer of RE oxide gel [6]. These specimens were isothermally oxidized at 1000 °C for about 400 min in a thermogravimetric balance to obtain mass gain per unit area versus time curves. This article presents the influence of surface additions of nanocrystalline rare earth (RE) oxide La_2O_3 and CeO_2, on the isothermal oxidation behaviour of Fe20Cr and Fe20Cr5Al at 1000 °C. Thermogravimetric studies revealed parabolic kinetics in all cases and the scale thickness on specimen surfaces varied with the nature of RE oxide. The oxidation resistance of specimens coated with two RE oxides was significantly higher than those coated with either one of the two oxides. The marked increase in the oxidation resistance of the alloys coated with two RE oxides is due to optimization of RE ion radius and RE oxide grain size/shape.

Under similar conditions, Ramanathan proposed that in extended cyclic oxidation tests that were carried out from peak temperatures of 900 °C, 1000 °C and 1100 °C to room temperature at cooling rates of 300 °C/s and 1000 °C/s, the La_2O_3 coating increased cyclic oxidation resistance of the Fe20Cr alloy significantly more than the Pr_2O_3 coating [7]. The cyclic oxidation resistance of reactive element oxide coated Fe20Cr alloy was significantly higher than that of the uncoated alloy. The thickness of the chromia layer on reactive element oxide coated Fe20Cr alloy varied with the reactive element oxide. Spalling of the chromia scale occurred when mass gain due to scale formation reached a limiting value of $1.25–1.5\ \mathrm{mg\,cm^{-2}}$. Evidence of a direct correlation between RE ion radius and oxidation resistance of reactive element oxide coated Fe–20Cr alloy has been observed.

Yoon indicates that solid oxide fuel cells typically operate at temperatures of about 1000 °C [8]. At these temperatures only ceramic interconnects such as $LaCrO_3$ can be employed. The development of intermediate-temperature solid oxide fuel cells (IT-SOFCs) can potentially bring about reduced manufacturing costs as it makes possible the use of an inexpensive ferritic stainless steel interconnector. However, this ferritic stainless steel suffers from Cr_2O_3 scale formation and a peeling-off phenomenon at the IT-SOFC operating temperature in an oxidizing atmosphere. Application of an oxidation protective coating is an effective means of providing oxidation resistance. In its study, he coated an oxidation protective layer on ferritic stainless steel using a precursor solution prepared from lanthanum nitrate, ethylene glycol, and nitric acid. Heating the precursor solution at 80 °C yielded a spinable solution for coating. A gel film was coated on a ferritic stainless steel substrate by a dip coating technique. At the early stage of the heat-treatment, lanthanum-containing oxides such as La_2O_3 and La_2CrO_6 formed at temperatures lower than 600 °C. As the heat-treatment temperature was increased over 700 °C, an oxidation protective perovskite-type $LaCrO_3$ layer was produced by the reaction between the lanthanum-containing oxide and the Cr_2O_3 scale on the substrate. As the concentration of La-containing precursor solution was increased, the amount of La_2O_3 and La_2CrO_6 phases was gradually increased. The coating layer, which was prepared from a precursor solution of 0.8 M, was composed of $LaCrO_3$ and small amounts of $(Mn,Cr)_3O_4$ spinel. A relatively dense coating layer without pin-holes was obtained by heating the gel coating layer at 1073 K for 2 h. A La-based gel film was successfully coated on a STS444 substrate by a dip coating technique and $LaCrO_3$ perovskite phase was formed by heat-treating the gel film at 500–800 °C.

Transient phases such as La_2O_3 and La_2CrO_6, which were formed at lower temperature, reacted with Cr_2O_3 to produce $LaCrO_3$ perovskite. It is believed that control over the reaction between La_2O_3 or La_2CrO_6 and Cr_2O_3 by modification of the precursor solution and heat-treatment temperature is an effective means of producing a dense and thick $LaCrO_3$ coating layer on the STS substrate. Higher viscosity resulted in a thicker gel coating layer. In order to increase the film thickness, the precursor solution should be further modified. During oxidation $(Mn,Cr)_3O_4$ spinel and Cr_2O_3 phases were formed on STS444. The spinel and Cr_2O_3 might result from outward diffusion of Mn and inward diffusion of oxygen, respectively. As a consequence, large spinel grains were produced at the top surface while growth of a Cr_2O_3 layer occurred between the $LaCrO_3$ coating layer and the alloy. Compared with non-coated specimens, the oxidation resistance of $LaCrO_3$-coated STS444 was significantly improved.

Zhao exposed the effects of La_2O_3 laser-clad on AISI 1115 steel substrates. The oxidation kinetic of the coatings was studied by testing the weight gain [9]. Cyclic oxidation tests were performed to determine the eventual weight loss due to spallation. The experimental results showed that Cr_2O_3 was formed on all coatings after oxidation. The coatings with La_2O_3 exhibited excellent high-temperature oxidation behaviour including low oxidation rates and high resistance to spallation. In addition, the effect of La_2O_3 was discussed. This included the change of transport mechanism in the oxide scales, the increase in the nucleation rate of the oxide, the release of stresses in the oxide scales by refining the oxide grains and the improvement of the adhesion of the oxide scales to the coatings by changing the scale growth mechanisms.

The present work will focus on the effect of a lanthanum sol–gel coating applied on the specimen surface before oxidation. The sol–gel coating argon annealing as been tested on the 330Cb chromia forming alloy because previous works have already indicated that the argon annealing during 2 h could improve the effect of the coating on the oxide scale adherence [10–12].

2. Experimental

The 330Cb alloy is an austenitic stainless steel. Table 1 gives the 330Cb composition in wt.%. 1.5 mm thick cylindrical specimens of