Study of the Oxidation Resistance of Coated AISI 441 Ferritic Stainless Steel for SOFCs

M. B. Limooei, Hadi Ebrahimifar, and Sh. Hosseini

Abstract—Protective coatings that resist oxide scale growth and decrease chromium evaporation are necessary to make stainless steel interconnect materials for long-term durable operation of solid oxide fuel cells (SOFCs). In this study a layer of cobalt was electroplated on the surface of AISI 441 ferritic stainless steel which is used in solid oxide fuel cells for interconnect applications. The oxidation behavior of coated substrates was studied as a function of time at operating conditions of SOFCs. Cyclic oxidation has been also tested at 800°C for 100 cycles. Cobalt coating during isothermal oxidation caused to the oxide growth resistance by limiting the outward diffusion of Cr cation and the inward diffusion of oxygen anion. Results of cyclic oxidation exhibited that coated substrates demonstrate an excellent resistance against the spallation and cracking.

Keywords—Oxidation resistance, full cell, Cobalt coating, ferritic stainless steel.

I. INTRODUCTION

WITH the decrease of solid oxide fuel cells (SOFC) operation temperatures to 800°C, it is possible to use metallic interconnect materials as interconnects to replace the ceramic, LaCrO₃, which has been commonly used for ca. 950–1000°C technology [1], [2]. Ferritic stainless steels, chromia-formation alloys, are among the most promising alloys given that their coefficient of temperature expansion (CTE) is close to that of others SOFC ceramic components [3], [4]. However, oxidation resistance is limited in these alloys. Excessive growth of chromia and chromium evaporation into the cathode can increase the cell resistance and polarization resistance significantly [5]. One of the most effective approaches to improve the interconnect properties is to apply surface coatings to provide better conductivity, reduced scale growth and Cr volatility. Recent research, however, has concentrated on the application of protective/conductive coatings. Numerous techniques have been developed to apply coatings to ferritic stainless steels. These include slurry coatings [5]-[8], anodic electrodeposition [9], cathodic electrodeposition of particular metals or alloys, followed by annealing/oxidation in air [10]-[13]. The objective of the current work was to investigate the oxidation behavior of AISI 441 which was coated through electroplating method. In order to evaluated the oxidation behavior isothermal oxidation and cyclic oxidation and were accomplished to investigate the role of coating during oxidation samples was rinsed with distilled water and dried, then heat-treated at 900°C for 2h in Ar gas.

The isothermal oxidation was done at 800°C for 200 hours in static air. The coated and uncoated samples were also subjected to cyclic oxidation. Each cycle contained 1h heating in the furnace at 800°C and 30 minutes cooling in free air. After each test the coated and uncoated samples were weighed and weight changes was calculated in order to investigate the role of coating layer during oxidation tests.

Microstructure and chemical composition of cross-section of the coated specimens were analyzed using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). Energy dispersive X-ray (EDX) analyses and X-Ray diffraction (XRD) was used to identify phases formed in the surface layer of as-coated and oxidized specimens with a Philips X’Pert High Score diffractometer using Cu Kα (λ = 1.5405Å).

II. EXPERIMENTAL PROCEDURE

The electroplating solution was made by dissolving 135g of CoSO₄·7H₂O and 33g of CoCl₂·6H₂O in 500g of distilled water and 7g of H₂BO₃ was added to the solution. Samples of AISI 441 stainless steel, with chemical composition of 17.83% Cr, 0.24% Mn, 0.6% Si, 0.01% C, 0.02% S, 0.03% P, 0.1% Ni, 0.1% Ti, 0.5% Nb, 0.006% Al with Fe as remaining were used as substrates. Specimens were ultrasonically cleaned in ethanol and dried and used as the cathode: platinum foil was used as the anode. Cobalt was electroplated on the surface at a current of 25mA cm⁻² for 15 min, resulting in a 30 micron coating.

III. RESULTS AND DISCUSSION

A. Coating of Substrate

Fig. 1 shows SEM micrograph of a coated sample. The surface of the coated specimen is homogeneous, relatively dense, and rough. Some pinholes can be observed, indicating that a high-defect density such as vacancies may be present in the coatings.

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B. Evaluation of Oxidation Behavior

1. Isothermal Oxidation Behavior

Isothermal oxidation experiment was performed in static air at 800ºC for 200h with weight measurement after 10, 20, 40, 60, 80, 100, 120, 150 and 200h. Fig. 2 illustrates the specific weight gain as a function of time for oxidized uncoated and coated steel coupons.

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\left( \frac{\Delta W}{A} \right)^2 = k_p t
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For the coated samples, the initial oxidation rate is higher than the uncoated ones. This is due to the bare substrate in uncoated samples that oxidizes freely in primary times. In both of samples the weight gain increase parabolically with the isothermal oxidation time, satisfying the parabolic kinetics low described by

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alloy is subjected to the temperature range of 650 – 850°C the (Mn,Cr)₃O₄ spinel layer will be formed which is non-protective [16]. Also the chromia which is protective will be formed under the (Mn,Cr)₃O₄ spinel layer [16]. The precipitation of the (Mn,Cr)₃O₄ spinel on the top of the chromia scale can be attributed to the high diffusion coefficients of manganese ions. The metal ion diffusion decreases in the order of $D_{Mn} > D_{Fe} > D_{Cr}$ by assuming that these metal ions diffuse via $Cr^{3+}$-lattice sites in Cr₂O₃ [17].

Based on the Cr–Mn–O system phase diagram the (Mn,Cr)₃O₄ spinel is thermodynamically favorable even at low Mn concentration [18]. The formation of the (Mn,Cr)₃O₄ spinel layer on the oxide scale could reduce significantly the vaporization pressure of gaseous chromium species. Unprotective substrate against oxidation reactions redounded to creation of these phase which decrease the electrical conductivity of interconnects [19]. Cr₂O₃ has been formed on the surface of coated samples but the lower intensity of this phase in XRD pattern confirms that the content of chromia has been considerably decreased. In XRD pattern of bare substrate phase in XRD pattern confirms that the content of chromia has redounded to the precipitation of the (Mn,Cr)₃O₄ spinel layer [16]. Also the chromia which is protective will be grown under the chromia scale [20].

2. Cyclic Oxidation Behavior

The coated and uncoated substrates were submitted to the cyclic oxidation at 800°C. 100 cycles were exerted that each cycle consisted of 1h heating and 15 minutes cooling in air. Fig. 4 shows the mass change of specimens as a function of cycle number after cyclic oxidation the coated samples exhibited a good resistance against spallation and cracking and it redounded to the lower values of weight gain (0.615 mg cm⁻²) compared to bare samples in isothermal oxidation (2.895 mg cm⁻²) after 200 h isothermal oxidation.

3. In cyclic oxidation the coated samples exhibited a good resistance against spallation and cracking and it redounded to the lower values of weight gain (0.615 mg cm⁻²) compared to uncoated samples (3.51mg cm⁻²) after 100 cycle.

REFERENCES