

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 evaluate 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 K α ($\lambda = 1.5405\text{\AA}$).

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 H₃BO₃ 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, 0.55% 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 800°C 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.

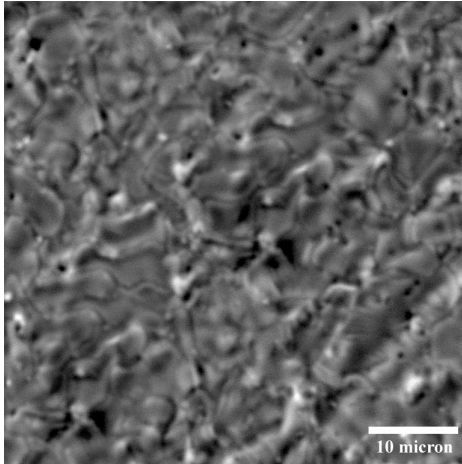


Fig. 1 SEM micrograph of a coated AISI 441

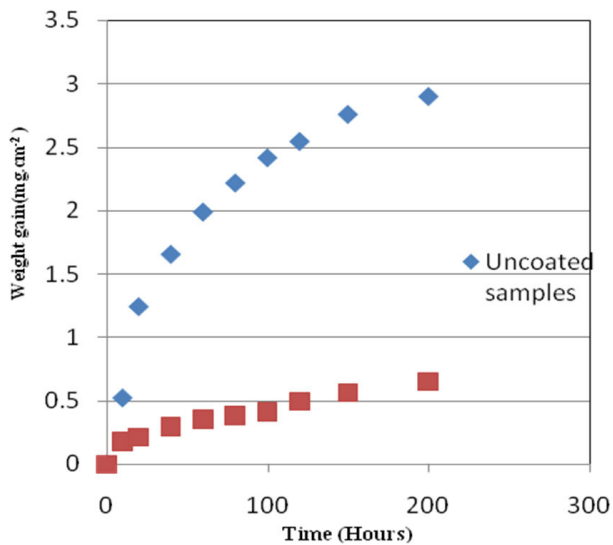


Fig. 2 Specific weight gain for uncoated and coated samples as a function of time during isothermal oxidation

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 law described by

$$\left(\frac{\Delta W}{A}\right)^2 = k_p t \quad (1)$$

where ΔW is the weight gain, A is the sample surface area, k_p is the parabolic rate constant and t is the oxidation time. Parabolic behavior in Fig. 2 is because of chromia scale growth which obeys the parabolic rate law according to (1) [14]. All the coated samples exhibited smaller mass gain compared with bare substrates in all the times. The bare substrate had weight change of 2.895mg cm⁻² after 200h annealing, while the coated samples had the weight change of 0.652mg cm⁻². It is clearly shown that the coating protect the substrate effectively from oxidation at high temperatures. After 200h isothermal oxidization, the uncoated sample grew a black oxide scale which spalled from the surface in some areas, while the coated sample exhibited a grey, shiny surface. Fig. 3 shows XRD pattern of uncoated (Fig. 3 (a)) and coated (Fig. 3(b)) specimens after 200 h annealing. Formed spinels (Co_3O_4 and Co_2CrO_4) during oxidation improved the oxidation resistance. The results of weight changes illustrate that this scale acts as an effective barrier against outward diffusion of Cr cation and inward diffusion of oxygen anion, because it rounded to decrease the weight gain in coated substrates [15].

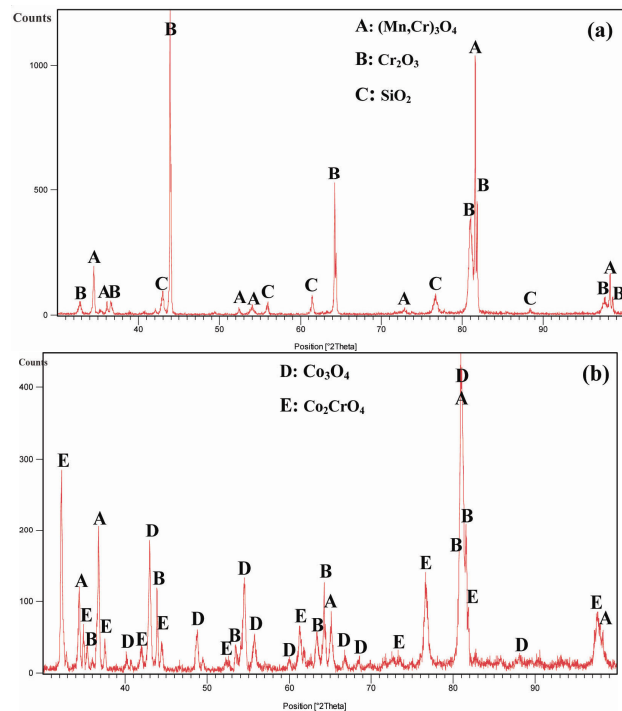


Fig. 3 XRD pattern of (a) uncoated and (b) coated specimens after 200h isothermal oxidation at 800°C

In XRD pattern of bare substrate (Mn,Cr)₃O₄ spinel, chromia and silica are observed. Presence of (Mn,Cr)₃O₄ spinel on the surface of bare substrate refers to ferritic stainless steels that normally containing small levels of Mn. When the

alloy is subjected to the temperature range of 650 – 850°C the $(\text{Mn,Cr})_3\text{O}_4$ spinel layer will be formed which is non-protective [16]. Also the chromia which is protective will be formed under the $(\text{Mn,Cr})_3\text{O}_4$ spinel layer [16]. The precipitation of the $(\text{Mn,Cr})_3\text{O}_4$ 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 $D_{\text{Mn}} > D_{\text{Fe}} > D_{\text{Cr}}$ by assuming that these metal ions diffuse via Cr^{3+} -lattice sites in Cr_2O_3 [17]. Based on the Cr–Mn–O system phase diagram the $(\text{Mn,Cr})_3\text{O}_4$ spinel is thermodynamically favorable even at low Mn concentration [18]. The formation of the $(\text{Mn,Cr})_3\text{O}_4$ spinel layer on the oxide scale could reduce significantly the vaporization pressure of gaseous chromium species. Un protective substrate against oxidation reactions redounded to creation of these phase which decrease the electrical conductivity of interconnects [19]. Cr_2O_3 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 silica phase is observed. The steels which contains Si in amounts greater than 0.5 wt%, insulating, continuous or network-like films of silica can also 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. In all of the cycles the coated specimens had less mass gain compared with uncoated ones. It refers to the protective spinels that limit the oxidation reactions. The mass gain for coated and uncoated specimens was obtained 0.615 mg cm^{-2} and 3.51 mg cm^{-2} respectively after 100 cycles.

Also the coated substrates demonstrated an excellent resistance against the spallation and cracking. This is because of the thermal expansion coefficient matching of coating layer and substrate [20], [21]. The TEC of Co_3O_4 ($9.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and CoCr_2O_4 ($7.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) is relatively close to TEC value of ferritic stainless steel ($11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$). Spallation and cracking is due to thermal expansion coefficient mismatching of oxide or coating layer with substrate [22]. Spalled scale creates diffusion path for cations and anions and therefore through the simple migration of ions the oxide layer grows with higher rate.

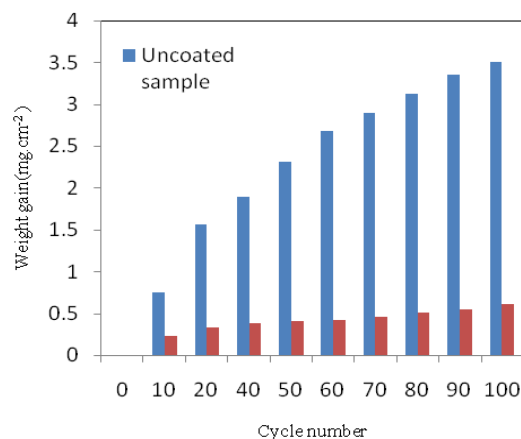


Fig. 4 Specific weight gain as a function of cycle number after cyclic oxidation

IV. CONCLUSIONS

1. The lower value of weight gain during oxidation tests is because of the more oxidation resistance.
2. Spinels forming (Co_3O_4 and Co_2CrO_4) during oxidation decrease the oxide growth by limiting the outward diffusion of Cr cation and inward diffusion of oxygen anion and it redounded to lower weight gain (0.652 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 (3.51 mg cm^{-2}) after 100 cycle.

REFERENCES

- [1] W. Z. Zhu and S. C. Deevi, 2003, *Materials Science and Engineering A*, 348, pp. 227.
- [2] W. J. Quadackers, J. P. Abellan, V. Shemet and L. Singheiser., 2003, *Materials at High Temperatures*, 20, pp. 115.
- [3] X. Chen, P. Y. Hou, C. P. Jacobson, S.J. Visko and L.C. De Jonghe., 2005, *Solid State Ionics.*, 176, pp. 425.
- [4] H. Kurokawa, C. P. Jacobson, L. C. DeJonghe and S. J. Visko, 2007, *Solid State Ionics*, 178, pp. 287.
- [5] X. Chen, P. Y. Hou, C. P. Jacobson, S. J. Visko and L. C. De Jonghe., 2005, *Solid State Ionics*. 176, pp. 425.
- [6] Z. Yang, G. Xia, S. P. Simner and J.W. Stevenson., 2005, *Journal of the Electrochemical Society*, 152, pp. 1896.
- [7] Z. Yang, G. Xia, X. Li and J.W. Stevenson., 2007, *International Journal of Hydrogen Energy*, 32, pp. 3648.
- [8] Z. Yang, G. Xia and J. W. Stevenson., 2005, *Electrochemical and Solid-State Letters.*, 8, pp. A168.
- [9] W. Wei, W. Chen and D.G. Ivey., 2007, *Chemistry of Materials*, 19, pp. 2816.
- [10] M.R. Bateni, P. Wei, X. Deng and A. Petric., 2007, *Surface & Coating Technology.*, 201, pp. 4677.
- [11] P. Wei, X. Deng, M.R. Bateni and A. Petric., 2007, *Corrosion* 63, pp. 529.
- [12] X. Deng, P. Wei, M.R. Bateni and A. Petric., 2006, *Journal of Power Sources* 160, pp. 1225.
- [13] Y.S. Chou, J.W. Stevenson and P. Singh., 2008, *Journal of Power Sources*, 185, pp. 1001.
- [14] W.J. Quadackers, J. Piron-Abellan, V. Shemet and L. Singheiser, 2003, *Materials at High Temperatures*, 20, pp. 115.

- [15] N. Shaigan, D.G. Ivey and W. Chen., 2008, J. power sources, 185, pp. 331.
- [16] L. Cooper, S. Benhaddad, A. Wood and D.G. Ivey., 2008, J. power sources, 184, pp. 220.
- [17] M.G.C. Cox, B. Mcenaney and V.D. Scott, 1972, Phil Mag., 26, pp. 839.
- [18] H. Kurokawa, K. Kawamura and T. Maruyama, 2004, Solid State Ionics, 168, pp. 13.
- [19] Z.G. Yang, 2008, International Materials Reviews, 53, pp. 39.
- [20] E. N'Dah, S. Tsipas, M.P. Hierro and F.J. Pérez, 2007, Corrosion Science, 49, pp. 3850.
- [21] S. Molin, B. Kusz, M. Gazda and P. Jasinski, 2008, J. power sources, 181, pp. 31.
- [22] A. Petric and H. Ling, 2007, J. Am. Ceram. Soc. 90, pp. 1515.