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Investigation of the oxidation behavior of Mn-coated AISI 441 steel for SOFCs interconnect application

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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 manganese was coated 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. Manganese coating during isothermal oxidation caused to the oxidation resistance by limiting the outward diffusion of Cr cation and the inward diffusion of oxygen anion. Results of cyclic oxidation exhibited that the coated substrates demonstrate good resistance against the spallation and cracking.

Keywords: Oxidation, Solid oxide fuel cell, AISI 441 ferritic stainless steel, Interconnect.

1. 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 and pack cementation [10-14].

The objective of the current work was to investigate the oxidation behavior of AISI 441 which was coated in a Mn-base pack mixture by pack cementation method. In order to evaluate the oxidation behavior, isothermal oxidation and cyclic oxidation were accomplished to investigate the role of

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coating during oxidation.

2- Experimental procedure

Samples of AISI 441 stainless steel, measuring 10 mm × 5 mm × 2 mm with chemical composition of 17.8% Cr, 0.25% Mn, 0.54% Si, 0.01% C, 0.02% S, 0.03% P, 0.1 % Ni, 0.1 % Ti, 0.45 % Nb, 0.006% Al with Fe as remaining were used as substrates. Specimens were polished from 320-grit sic paper up to 1200-grit, ultrasonically cleaned in ethanol and dried. In order to deposit manganese onto the substrate, pack cementation method was employed. Mn, Al₂O₃ and NH₄Cl powder were used as powder mixture in average size of 120 μm, 70-80 μm and 240 μm. The optimized conditions for coating of manganese onto the surface of AISI 441 stainless steel by pack cementation were identified : 10% wt. Mn, 2.5% wt. NH₄Cl, 87% wt. Al₂O₃ as powder mixture and annealing at 800 °C for 3 h at presence of Ar gas. After pack cementation treatment, the samples were removed from the pack and ultrasonically cleaned in ethanol to remove any embedded pack material and then weighed using an electronic balance.

The isothermal oxidation was done at 800 °C for 200 hours in static air. The coated and uncoated samples were also subjected to the cyclic oxidation. Each cycle contained 1 h of heating in the furnace at 800 °C and 15 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 the coated specimens were analyzed using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). X-Ray diffraction (XRD) was used to identify the formed phases in the surface layer of as-coated and oxidized specimens with a Philips X'Pert High Score diffractometer using Cu Kα (λ = 1.5405 Å).

3. Results and discussion

3.1. Coating of substrate

Samples of AISI 441 were coated with manganese through the pack cementation method. The coated layer showed complete adherence to the surface and no spalling was observed on cooling and heating, which is attributed to a good thermal match between the scale and the substrate. Fig. 1 shows XRD diffraction pattern of coated specimen. The identified phases include, FeMn₃ and FeMn₄. These phases were also observed in the previous work [15]. There are ferrite and Fe-Cr peaks from the substrate [13-15]. The surface of the coated specimen (Fig. 2) is homogeneous and relatively dense.

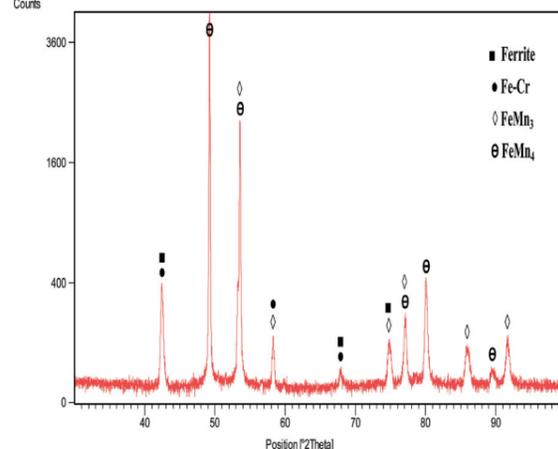


Fig. 1. XRD pattern of as-coated specimen

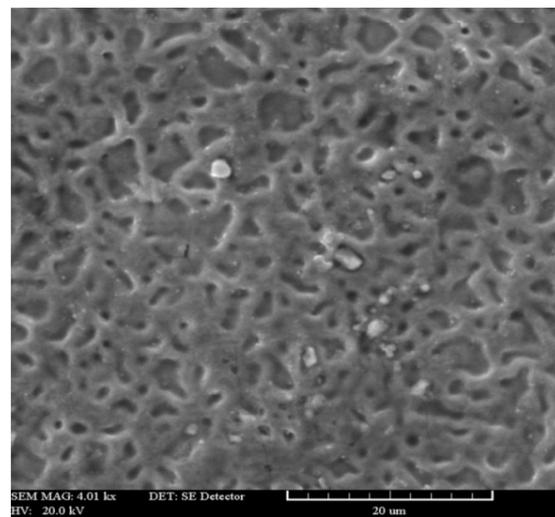


Fig. 2. Surface morphology of coated sample at magnification of 4010.

Some white particles are observed in this micrograph, which are alumina. The presence of Al₂O₃ was believed to be the residue filler (Al₂O₃) material remained after cleaning or the entrapped Al₂O₃ in the coating during the growth of coating layer

3-2-Evaluation of Oxidation Behavior

3-2-1-Isothermal Oxidation Behavior

Isothermal oxidation experiment was performed in static air at 800 °C for 200 h with weight measurement after 5, 10, 20, 40, 60, 80, 100, 120, 150 and 200 h. Fig. 3 illustrates the specific weight gain as a function of time for oxidized uncoated and coated steel coupons.

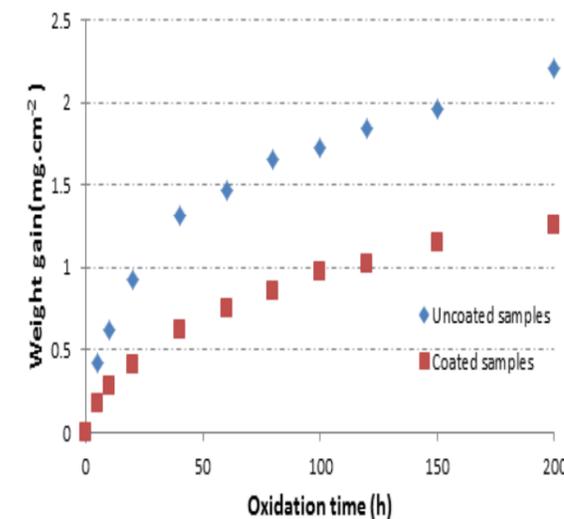


Fig. 3. Specific weight gain for uncoated and coated samples as a function of time during isothermal oxidation.

For the uncoated samples, the initial oxidation rate is higher than the coated ones. This is due to the bare substrate in uncoated samples that oxidizes freely in primary times. In both of samples the weight gain increases parabolically with the isothermal oxidation time, satisfying the parabolic kinetics law described by

$$[\Delta W/A]^2 = k_p t \quad (1)$$

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. 3 is because of chromia scale growth which obeys the parabolic rate law according to Eq. (1) [1]. All the coated samples exhibited smaller mass gain compared with bare substrates in all the times. The bare substrate had weight change of 2.214 mgcm⁻² after 200 h annealing, while the coated samples had the weight change of 1.251 mg cm⁻². It is clearly shown that the coating protect the substrate effectively from the oxidation at high temperatures. After 200 h of 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. 4 shows XRD pattern of uncoated (Fig. 4a) and coated (Fig. 4b) specimens after 200 h of annealing.

The oxide thickness was measured based on the Equation in the previous work, and it was obtained 1.49 μm and 2.64 μm for the Mn-coated and uncoated specimens after 200 h annealing at 800 °C, respectively [15].

As expected from the weight gain and oxide scale thickness, the oxidation rate of the Mn-coated sample reduced after deposition of the coating. A comparison of our results with those of Schuisky et al. [16] reveals that surface coatings were more effective than minor alloying elements in ferritic steels for interconnects in SOFCs. Also, the compare of this research with similar researches reveals that there was a good agreement with our results and the published results [17-19].

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 (Mn,Cr)₃O₄ spinel layer will be formed which is non-protective [20,21]. 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

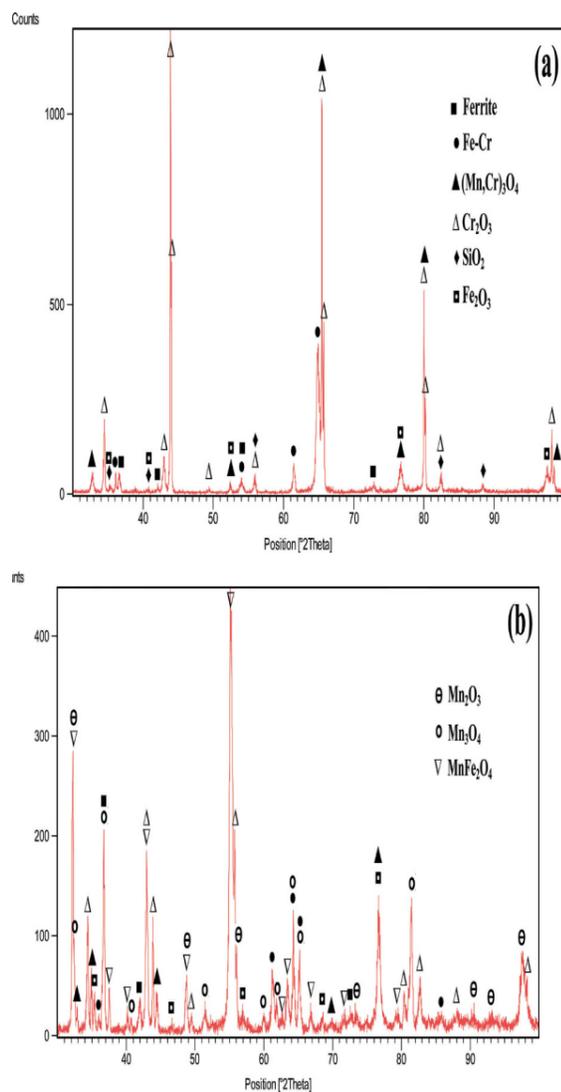


Fig. 4. XRD pattern of (a) uncoated and (b) coated specimens after 200 h isothermal oxidation at 800 °C.

decreases in the order of $D_{Mn} > D_{Fe} > D_{Cr}$ by assuming that these metal ions diffuse via Cr^{3+} lattice sites in Cr_2O_3 [22]. Based on the Cr–Mn–O system phase diagram the $(Mn,Cr)_3O_4$ spinel is thermodynamically favorable even at low Mn concentration [23]. The formation of the $(Mn,Cr)_3O_4$ spinel layer on the oxide scale could reduce significantly the vaporization pressure of gaseous chromium species. Non-protective substrate against oxidation reactions caused to the creation of these phase which decrease the electrical conductivity of interconnects [24]. The formation of manganese spinels (Mn_2O_3 , Mn_3O_4 and

$MnFe_2O_4$) 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 caused to the decrease of weight gain in coated substrates [20].

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 amount 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 [25].

3-2-2-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 1 h of heating and 15 minutes cooling in air. Fig. 5 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 the uncoated ones.

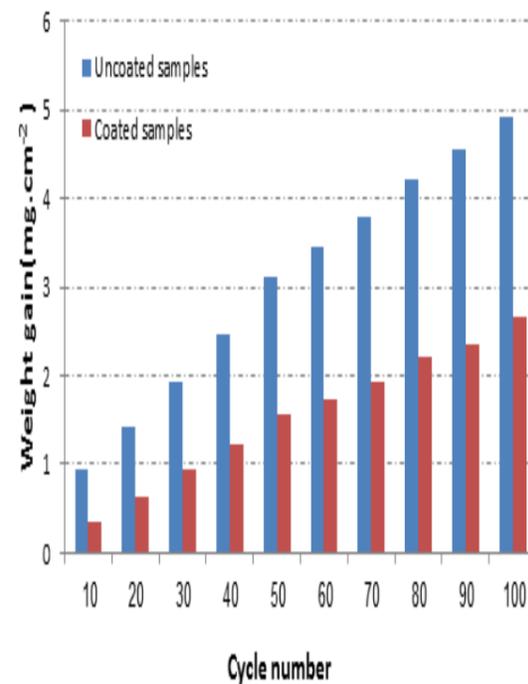


Fig. 5. Specific weight gain as a function of cycle number during cyclic oxidation.

It refers to the protective spinels that limit the oxidation reactions. The mass gain for coated and uncoated specimens was obtained 2.651 mg cm⁻² and 4.932 mg cm⁻² respectively after 100 cycles.

Also the coated substrates demonstrated good resistance against the spallation and cracking. This is because of the thermal expansion coefficient matching of coating layer and substrate [25,26]. The TEC of Mn_3O_4 ($8.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and $MnFe_2O_4$ ($12.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) 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 the thermal expansion coefficient mismatching of oxide or coating layer with substrate [27]. Spalled scale creates diffusion path for cations and anions and therefore through the simple migration of ions the oxide layer grows with higher rate.

4. Conclusion

1. Manganese coating was applied on AISI 441 through the pack cementation method.
2. The formation of manganese spinels (Mn_2O_3 , Mn_3O_4 and $MnFe_2O_4$) during oxidation, decreased the oxide growth by limiting the outward diffusion of Cr cation and inward diffusion of oxygen anion and it caused to the lower weight gain (1.251 mg cm⁻²) compared to the bare samples in isothermal oxidation (2.214 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 caused to the lower values of weight gain (2.651 mg cm⁻²) compared to uncoated samples (4.932 mg cm⁻²) after 100 cycle.

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