

Oxidation behavior and electrical Characteristics of used interconnects in solid oxide fuel cells at presence of Mn_3O_4 and $MnFe_2O_4$ coatings

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Abstract

In order to enhance the performance of interconnects which are used in solid oxide fuel cells (SOFCs), a protective/conductive coating can be applied. In this research AISI 430 ferritic stainless steel was coated in a Mn-base pack mixture by pack cementation method. In order to evaluate the oxidation behavior, isothermal oxidation was accomplished for 200 h at 800 °C. Electrical behavior was also investigated as a function of temperature and time. In isothermal oxidation unprotected substrate exhibited more weight gain in comparison with coated sample. The formation of Mn_3O_4 and $MnFe_2O_4$ spinels during isothermal oxidation redounded to the decrease in area specific resistance (ASR) for coated specimens. The ASR was obtained 17.4 mΩ cm² for coated samples and 36.1 mΩcm² for uncoated samples after 200 h annealing in static air at 800 °C.

Keywords: AISI 430 ferritic stainless steel, solid oxide fuel cell (SOFC), Isothermal oxidation, area specific resistance (ASR), spinel.

1. Introduction

Interconnector is a part of solid oxide fuel cells (SOFCs) used to separate the fuel-side anode and the air-side cathode of multiple cells when stacked as a series. It also allows transport of electrons from one cell to another and to the external circuit. For conventional SOFCs working at around 1000 °C, ceramic materials such as doped lanthanum chromite have been proposed as interconnectors. However, the attempt is made nowadays to decrease the working temperature of SOFCs to 650–800 °C¹⁾. At these working temperatures, stainless steels are considered as promising materials to be applied as interconnectors^{2,3)}, primarily due to their gas-tight property and high electrical conductivity. Amongst the stainless steels, ferritic stainless steels are preferred because of low cost and excellent formability, good thermal conductivity and thermal expansion coefficient compatibility with other cell components⁴⁾.

The relatively high-operating temperatures of SOFCs and the presence of oxygen and fuel, however, result in oxidation of stainless steel interconnects. Stainless steels are chromia-forming alloys. The scale that forms during high-temperature oxidation usually consists of two layers, a chromia subscale and a Mn–Cr spinel outer layer⁵⁾.

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The formation of a chromia subscale causes serious problems leading to premature degradation of the SOFC stack^{6,7)}. One approach to overcome these problems is through the application of a protective coating on the stainless steel interconnect. The materials for a protective coating ought to have high electrical conductivity and low chromium cation and oxygen anion diffusivity at the operating temperatures⁸⁾. Recently, ferritic stainless steel was aluminized in order to enhance the oxidation resistance of interconnects used in solid oxide fuel cells⁹⁾. Bateni et al. deposited Co-Mn and Cu-Mn spinels by electroplating. The formed spinel layer had good adherence and it exhibited good electrical conductivity¹⁰⁾.

The objective of the current work was to investigate the oxidation resistance and area specific resistance (ASR) of coated specimens coated in a Mn-base pack mixture by pack cementation method.

2. Experimental procedure

Coupons of AISI 430 stainless steel, measuring 10 mm × 5 mm × 2 mm were used as substrates. The composition of AISI 430 stainless steel is listed in Table 1. 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 powders were used as powder mixture in average size of 150 μm, 70–80 μm and 240 μm, respectively. The optimized conditions for coating of manganese onto the AISI 430 stainless steel by pack cementation in the previous work¹¹⁾ were identified : 10% w.t. Mn, 3% w.t. NH₄Cl, 87% w.t. Al₂O₃ as powder mixture and annealing at 800 °C

for 3 h at presence of Ar gas. After the pack cementation treatment, samples were removed from the pack and ultrasonically cleaned in ethanol to remove any embedded pack material, and then weighed using an electronic balance. In order to evaluate the oxidation behavior, isothermal oxidation was accomplished at 800 °C. This test was performed in static air at 800 °C for 200 h by employing 10 uncoated and 10 coated samples with weight measurement after 5, 10, 20, 40, 60, 80, 100, 120, 150 and 200 h.

Area specific resistance (ASR) measurement of the oxidized samples was accomplished. Platinum wires were spot welded to one side of two identical polished samples to provide electrical connections. In order to prevent alloy-to-alloy adhesion and local melting due to the oxidation, which lead to erroneous results^{12,13}, platinum wire welded specimens were pre-oxidized for 24 h at 800 °C. No conductive paste, which may affect the oxidation mechanism, was applied between the two samples. A constant current density of 500 mA cm⁻² was applied and the voltage was recorded every 30 minutes. An ammeter and a voltmeter were employed for this purpose.

The data were used to calculate the resistance according to Ohm's law and the ASR as a product of the resistance and surface area. In order to measure the resistance contribution from the junctions, wires and the alloy, two platinum wires were spot welded to the sides of a single AISI 430 specimen and the resulting resistance was subtracted from the original test results. ASR values were measured as a function of temperature and time. All the above-mentioned tests, including ASR and oxidation tests, were run at an electric box furnace and static air.

Cross-section microstructure and chemical composition of coated specimens were analyzed using scanning electron microscopy (SEM) (Camscan MV2300) 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 K α ($\lambda = 1.5405 \text{ \AA}$).

Table 1. Chemical composition of AISI 430 stainless steel.

Element	C	Cr	Si	Mn	Fe
Concentration (wt.%)	0.12	17.14	0.85	0.92	80.97

3. Results and discussion

3.1. coating of substrate

Fig. 1 shows cross-sectional SEM image and EDS line scan of a coated sample. The deposited layer has good contact to the substrate with no void, pore and discontinuity. The identified phases included CrMn₃, alpha-Mn and FeMn₄¹¹.

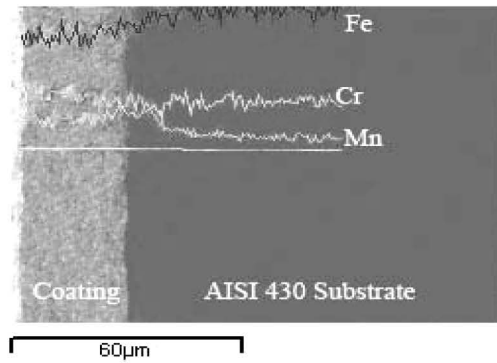


Fig. 1. SEM cross section image of coating and EDS line scan.

3.2. Evaluation of Oxidation Behavior

Fig. 2 illustrates the specific weight gain as a function of time for oxidized uncoated and coated steel coupons.

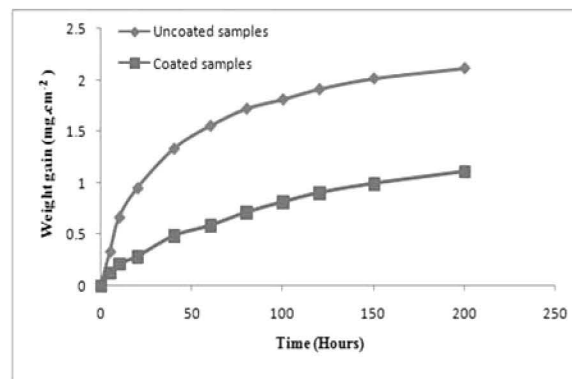


Fig. 2. Specific weight gain for uncoated and coated samples as a function of time during isothermal oxidation.

As shown in both samples, the weight gain increases 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 Eq. (1)². The coated sample exhibited lower mass gain compared to bare substrate at different oxidation times. For the coated samples, the initial oxidation rate is remarkably higher than the uncoated one. This is due to the fact that the bare substrate oxidizes freely in primary times. Afterwards, the growth of spinel and chromia layers

limit the diffusion rate of ions, and this results in less weight gains.

As can be seen in Fig. 2, the weight change of bare sample, which is annealed for the period of 200 h is 2.115 mg.cm^{-2} , while the weight change of coated sample is 1.112 mg cm^{-2} after the same period. This can be due to the fact that the coating protects the substrate effectively from the oxidation at high temperatures. Fig. 3 shows XRD pattern of uncoated (Fig. 3a) and coated (Fig. 3b) specimens after 200 h annealing. In XRD pattern of bare substrate, $(\text{Mn,Cr})_3\text{O}_4$ and chromia are observed. Presence of $(\text{Mn,Cr})_3\text{O}_4$ spinel on the surface of bare substrate refers to ferritic stainless steels that normally contain small levels of Mn. When the alloy is subjected to the temperature range of $650 - 850 \text{ }^\circ\text{C}$, $(\text{Mn,Cr})_3\text{O}_4$ spinel layer will be formed which is non-protective¹⁴⁾. In the coated sample chromia, Mn_2O_3 , Mn_3O_4 and MnFe_2O_4 are observed. The lower weight gain of the coated sample after 200 h of oxidation revealed that the formation of Mn_3O_4 and MnFe_2O_4 spinels during oxidation improved the oxidation resistance. As can be seen, the oxidation resistance of unprotected substrate redounded to more weight gain in comparison to the coated one. The spalled surface and the probable existence of cavities in the bare substrate led to more weight gain which was observed by other researchers¹²⁾.

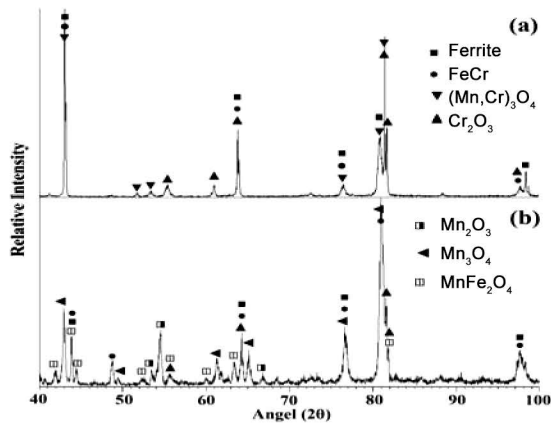


Fig. 3. XRD pattern of (a) uncoated and (b) coated specimens after 200 h isothermal oxidation at $800 \text{ }^\circ\text{C}$.

3.3. Evaluation of area specific resistance (ASR)

In order to investigate the effect of temperature on the area specific resistance (ASR), the ASR was measured at different temperatures (from room temperature to $800 \text{ }^\circ\text{C}$) for uncoated and coated samples after pre-heating at $800 \text{ }^\circ\text{C}$ for 24 h. Fig. 4 illustrates the ASRs as a function of temperature after 1 h oxidation at different temperatures. As shown, by increasing the temperature, the ASR increases. The ASR of uncoated and coated samples was obtained $28 \text{ m}\Omega\text{cm}^2$ and $14.2 \text{ m}\Omega\text{cm}^2$ at $800 \text{ }^\circ\text{C}$, respectively.

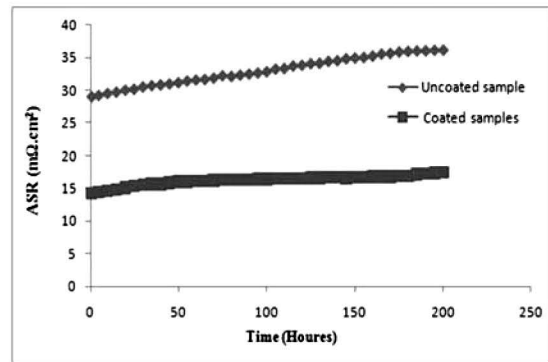


Fig. 4. ASR values as a function of temperature for uncoated and coated samples at $800 \text{ }^\circ\text{C}$ for 200 h.

The ASRs for coated and uncoated AISI 430 stainless steel at $800 \text{ }^\circ\text{C}$, as a function of time were plotted in Fig. 5. As illustrated in the graph, ASR values for uncoated substrate increases rapidly with oxidation time and approaches $36.1 \text{ m}\Omega\text{cm}^2$ after 200 h isothermal oxidation. Coated specimens, however, exhibited a very low resistance ($17.4 \text{ m}\Omega\text{cm}^2$) after 200 h.

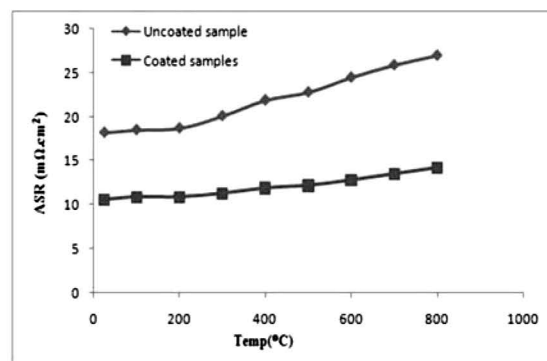


Fig. 5. ASR values as a function of time for uncoated and coated samples during isothermal oxidation at $800 \text{ }^\circ\text{C}$ for 200 h.

There are several factors which can contribute to the enhancement of resistance for uncoated sample. The primary factor is the growth of the chromia scale. The conductivity of chromia is considerably lower in comparison to the metallic substrate¹⁵⁾. An increase in the thickness of the oxide scale proportionally increases the ASR. There are also other contributions to the increase in ASR that are related to the metal/oxide scale interface. Interfacial imperfections, including voids and cavities as well as impurity segregation, reduce the scale-to-metal adhesion and actual surface area of intimate contact between the metal and oxide scale and, consequently, increase the interconnect ASR¹⁶⁾. The formation of Mn_3O_4 and MnFe_2O_4 spinels

during oxidation improved the electrical conductivity. Which is remarkably higher than chromia¹⁷⁾. Cr₂O₃ is also formed on the surface of coated sample, but the low intensity of this phase in XRD pattern after oxidation, indicating that the amount of chromia is decreased in comparison to the uncoated sample. Several factors can contribute to the improved electrical conductivity for the coated substrate over uncoated one. These include the higher electronic conductivity of the scale consisting of spinels layer and improved adhesion of oxide scale. The spalled surface and the probable existence of cavities in the bare substrate reduced the actual contact surface area between the alloy and scale^{12,17)}. This redounded to the higher ASR value, which is the product of resistance and the nominal contact surface area of the scale and alloy.

4. Conclusion

- The weight change of bare sample, which was annealed for the period of 200 h at 800 °C was 2.115 mgcm⁻², while the weight change for coated samples was 1.112 mg cm⁻² after the same period and temperature. This can be due to the fact that Mn₃O₄ and MnFe₂O₄ phases protect the substrate effectively from the oxidation at high temperatures.
- The formation of chromia during oxidation on the surface of AISI 430 bare sample redounded to the higher values of ASR in comparison to the coated sample. This is due to higher electrical conductivity of Mn₃O₄ and MnFe₂O₄ spinels.
- The application of Mn₃O₄ and MnFe₂O₄ spinels, increased the high temperature electrical conductivity of AISI 430 ferritic stainless steel used for SOFC interconnects.
- The ASR of uncoated sample, which was oxidized in static air at 800 °C for the period of 200 h was 36.1 mΩ cm², while the ASR of coated sample was 17.4 mΩcm² after the same conditions.

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