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The study of Oxidation Behavior of AISI 439 Steel at the Presence of Manganese Oxides for the Application in Solid Oxide Fuel Cells

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Abstract

Long–term stability and oxidation resistance of AISI 439 ferritic stainless steel used as interconnects in solid oxide fuel cells can be improved by use of a protective coating. In this study the pack cementation method was employed to coat AISI 439 ferritic stainless steel with manganese. Isothermal oxidation was conducted at 800 ºC for 200 hours in static air to investigate the role of coating against oxidation. Cyclic oxidation was also performed for up to 100 cycles at the oxidation temperature of 800 °C. Formation of manganese oxides ($MnFe_2O_4$, Mn_3O_4 and Mn_2O_3) during oxidation tests improved oxidation resistance. The coated samples demonstrated lower mass gain in each test, indicating the coating layer could have act as a mass barrier against the outward diffusion of cations specially Cr.

1. Introduction

Recently, many attempts have been made to reduce the operation temperature of solid oxide fuel cells (SOFCs) from 1273 to 1073K or lower. One advantage of reducing the operation temperature is the application of alloy materials as interconnects, which are expected to provide cost-reduction. Among the candidate alloys, Fe–Cr alloys have attracted much attention for medium operation temperature SOFCs, because of their reasonable price and high mechanical strength. However, at operation temperatures,

oxide scales are always formed on the alloy surface by the reaction with atmospheric gases. The formation of an insulating oxide layer is not favorable, but is needed in order to provide a stable protective layer. To improve the electrical conductivity in the oxide scales, several elements have been added into the Fe–Cr alloys to form Cr_2O_3-based conductive oxide layers [1-7]. However, the application of a protective and conductive oxide coating may be a necessary addition or a good alternative to bulk modification techniques.

Most recent researches, however, have concentrated on the application of protective/ conductive coatings. Numerous techniques have been developed to apply coatings to

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ferritic stainless steels. These include slurry coatings [8-11], Anodic electrodeposition[12], cathodic electrodeposition of particular metals or alloys, followed by annealing/oxidation in air and pack cementation [13-18]. The latter method has been attracting attention due to ease of fabrication, good adhesion between the deposited coating and substrate and extensive application.

The objective of the current work was to investigate the oxidation behavior of AISI 439 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 coating during oxidation.

2. Experimental procedure

Samples of AISI 439 stainless steel, measuring 10mm × 5mm × 2mm were used. The chemical composition of AISI 439 stainless steel is shown in Table 1. Specimens

Table 1. Chemical composition of AISI 439 stainless steel.

Element	Concentration (wt.%)
Fe	Bal
C	0.98
Cr	17.15
Mn	0.7
Si	0.68
Ti	0.64
Nb	0.23
S	0.02
P	0.03

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, Al_2O_3 and NH_4Cl 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 439 stainless steel by pack cementation were identified: 10% wt. Mn, 3% wt. NH_4Cl, 87% wt. Al_2O_3 as powder mixture and annealing at 800 ºC for 3 h at presence of Ar gas. After pack cementation treatment, the samples were removed from the pack. Then the samples ultrasonically cleaned in ethanol to remove any embedded pack material and after that weighed using an electronic balance. The isothermal oxidation was done at 800 ºC for 200 hours in static air. The coated and uncoated samples were also subjected to cyclic oxidation. Each cycle contained of 1 h heating in the furnace at 800 ºC 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 cross-section of the coated specimens were analyzed using scanning electron microscopy (SEM). 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

Figure 1 demonstrates surface morphology of the coated sample. The surface of the coated specimen is homogeneous and relatively dense. Some white particles are observed in this micrograph, which are alumina. The presence of Al_2O_3 was believed to be the residue filler (Al_2O_3) material remained after cleaning or the entrapped Al_2O_3 in the coating during the growth of coating layer. This is a typical feature, suggesting that the coating was formed

via an outward growth process and the out-ward migration of substrate elements, Cr and Fe in particular [13,17].
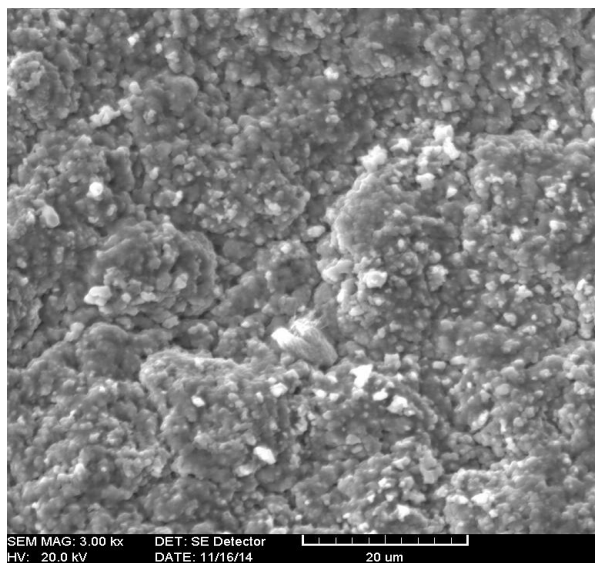

Fig. 1. Surface morphology of coated sample at magnification of 3000.

The coated layer showed complete ad-herence to the surface and no spalling was observed on cooling and heating, which is at-tributed to a good thermal match between the scale and the substrate. Fig. 2 shows XRD dif-fraction pattern of coated specimen. The iden-tified phases include $FeMn_3$ and $FeMn_4$.
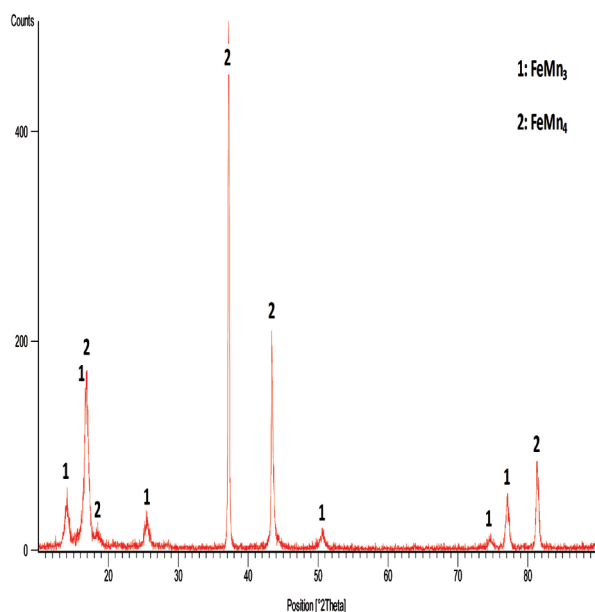
3.2. Evaluation of Oxidation Behavior
3.2.1. Isothermal Oxidation Behavior

In order to evaluated the resistance of samples, the Mn-coated and uncoated specimens were subjected to isothermal oxidation. This experiment was performed in static air at 800 ºC for 200 h. Oxidation weight gain at 800 ºC as a function of exposure time is illustrated in Fig. 3. 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 increase parabolically with the isothermal oxidation time, satisfying the parabolic kinetics low described by

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

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. All the coated samples exhibited smaller mass gain compared with bare substrates in all the times. The bare
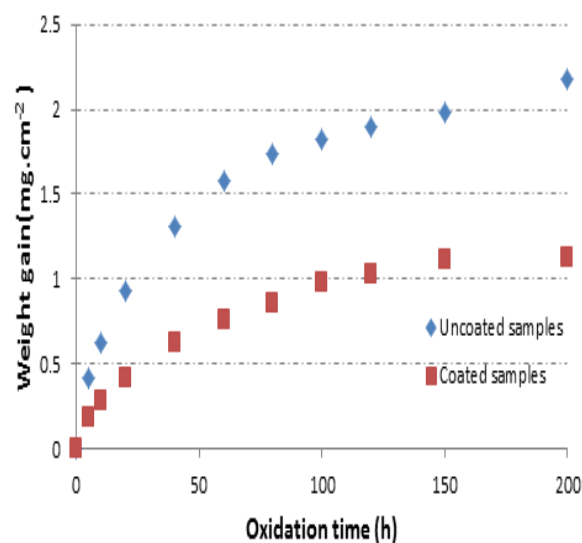

Fig. 2. XRD pattern of as-coated specimen.

Fig. 3. Specific weight gain for uncoated and coated samples as a function of time during isothermal oxidation.
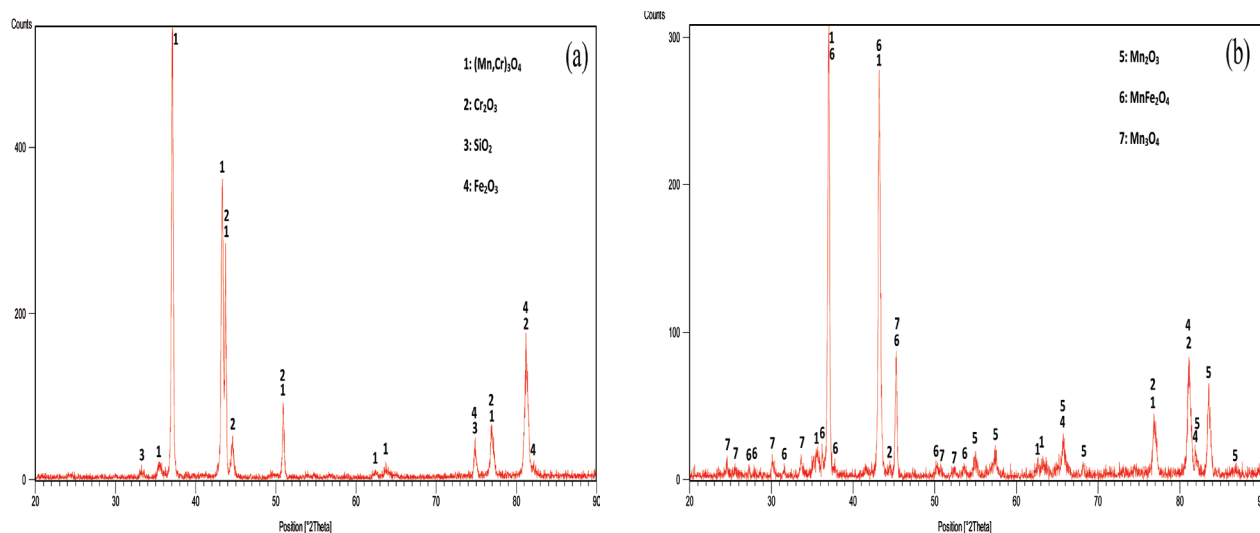
Fig. 4. XRD pattern of (a) uncoated and (b) coated specimens after 200 h isothermal oxidation at 800 ºC.

substrate had weight change of 2.18 mgcm^{-2} after 200 h of oxidation, while the coated samples had the weight change of 1.12 mg cm^{-2}. It is clearly shown that the coating protect the substrate effectively from 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 oxidation.

In XRD pattern of bare substrate $(Mn,Cr)_3O_4$ spinel, chromia, silica and Fe_2O_3 are observed. Presence of $(Mn,Cr)_3O_4$ 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 ºC, the $(Mn,Cr)_3O_4$ spinel layer will be formed which is non-protective [19,20]. The formation of chromia refers to the outward diffusion of chromium and inward diffusion of oxygen. Chromium diffuses primarily along the ferrite grain boundaries along with some bulk diffusion, so that initially more Cr_2O_3 forms at the intersection of the ferrite grain boundaries

with the surface. The precipitation of the $(Mn,Cr)_3O_4$ 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 $D_{Mn} > D_{Fe} > D_{Cr}$ by assuming that these metal ions diffuse via Cr^{3+} lattice sites in Cr_2O_3 [21]. Based on the Cr–Mn–O system phase diagram the $(Mn,Cr)_3O_4$ spinel is thermodynamically favorable even at low Mn concentration [22]. The Formtion of manganese oxides including: Mn_2O_3, Mn_3O_4 and $MnFe_2O_4$; 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 onion, because it caused to decrease the weight gain in coated substrates [23-25].

Cr_2O_3 has been formed on the surface of coated samples but the number of chromia peaks are less in comparison with the number of chromia peaks in bare samples, which specify that the development of Cr_2O_3 has been restricted through the application of coating layer.

Under SOFC operating conditions, chromia-rich scales react with water or

oxygen molecules and form volatile chromium oxyhydroxide ($Cr_2(OH)_2$) and/or Cr(IV) oxide (CrO_3). Volatile Cr species then migrate through the cathode, dissociate and deposit on the cathode/electrolyte interface as chromia and other unwanted compounds like $SrCrO_4$, in the presence of a lanthanum strontium manganite (LSM) cathode. The chromium deposition poisons the cathode's electrochemical activity and drastically deteriorates cell performance. So the application of manganese coating on to the AISI 439 stainless steel will reduce cathode poisoning and therefore the efficiency of the fuel cell will increase.

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 [26]. No silica phase is observed in coated specimens. Mn coating on the coated specimens prevented the growth of silica.

3.2.2. Cyclic Oxidation Behavior

In order to investigate the resistance of coating against the thermal stresses, the uncoated and coated substrates were submitted to the cyclic oxidation at 800 ºC. 100 cycles were exerted that each cycle consisted of 1 h 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 uncoated ones. It refers to the protective spinels that limit the oxidation reactions. The mass gain for coated and uncoated specimens was obtained 2.46 mg cm^{-2} and 4.28 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 [26,27]. The TEC of Mn_3O_4 (8.8×10^{-6} ºC^{-1}) and $MnFe_2O_4$ (12.5×10^{-6} ºC^{-1}) is relatively close to TEC value of ferritic stainless steel (11×10^{-6} ºC^{-1}). Spallation and cracking is due to thermal expansion coefficient mismatching of oxide or coating layer with substrate [28]. Spalled scale creates diffusion path for cations and onions and therefore through the simple migration of ions the oxide layer grows with higher rate.
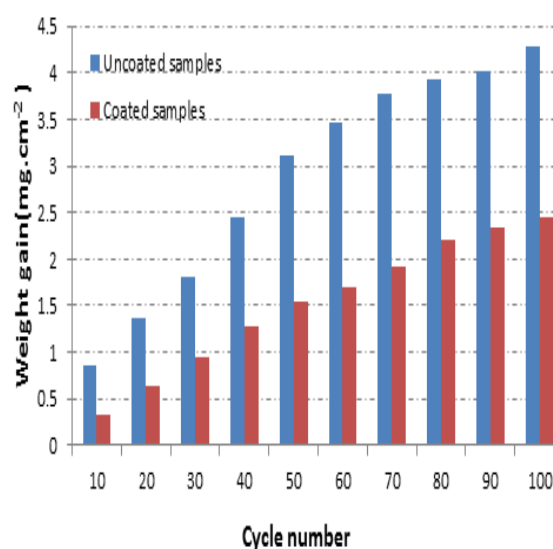
Fig. 5. Specific weight gain as a function of cycle number during cyclic oxidation.

4. Conclusions

1. The application of Mn coating on AISI 439 improved the oxidation resistance.
2. Formation of manganese oxides (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 onion.
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 (2.46 mg cm^{-2}) compared to uncoated samples (4.28 mg cm^{-2}) after 100 cycle.

Acknowledgments

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