Evaluation of electrical resistance activation energy for cobalt-coated interconnects

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The oxidation resistance and the electrical conductivity of solid oxide fuel cells (SOFCs) interconnects can be improved with a protective/conductive coating layer. In this study AISI 441 ferritic stainless steel is coated by pack cementation method in a Co-base pack mixture. The microstructure of the samples is then examined by SEM and EDS, and phases are identified by XRD. In order to evaluate the area specific resistance (ASR) isothermal oxidation is applied at 800ºC for 300 h. Also oxidation at different temperatures (500-1000ºC) is carried out to evaluate electrical resistance activation energy. Results show the formation of cobalt spinels during oxidation caused to the reduction of electrical resistance (ASR for coated substrates: 12.3 mΩ cm$^2$ and for uncoated substrates: 40.1 mΩ cm$^2$). Also electrical resistance activation energy for coated samples is lower compared to uncoated ones.

Keywords: Interconnect, Solid oxide fuel cell, Activation energy, AISI 441 ferritic stainless steel

The interconnect is an individual part of solid oxide fuel cell (SOFC) stack that physically divides the oxidant and fuel gases, shares out the gases to electrodes and supplies electrical connections between single cells\textsuperscript{1-3}. In intermediate-temperature SOFCs operating in the typical range 600-800°C, the material of selection for interconnects are ferritic stainless steel grades. The principal reasons for this material choice are sufficient high temperature mechanical and chemical properties, coefficient of thermal expansion matching the other fuel cell stack components and cost-effectiveness\textsuperscript{4}. Nevertheless, the employ of this material is not devoid of drawbacks. Specifically, (i) the high Cr content have a tendency to lead to the creation of volatile Cr compounds that finish poisoning the catalysts and (ii) oxides forming on the bare ferritic stainless steel have a relatively low electrical conductivity, resulting in a build-up of series ohmic resistance at each contact. Interconnect durability issues are currently believed to be the single most critical source of cell degradation, limiting the lifetime of planar SOFC systems implementing metallic interconnects\textsuperscript{5,6}.

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. Many coating have been investigated but Mn-Co coatings are the best candidates for the application of interconnects\textsuperscript{7,12}. Petric and Ling\textsuperscript{13} reviewed and studied the thermal andelectrical properties of a vast variety of binary spinels. It was found that spinels containing Mn-Co oxides and Co oxides have a good oxidation resistance and high electrical conductivity\textsuperscript{13}. These types of coatings can limit the growth of Cr$_2$O$_3$ scale which leads to the higher electrical conductivity and higher efficiency.

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\textsuperscript{7-10}, anodic electrodeposition\textsuperscript{11}, cathodic electrodeposition of particular metals or alloys, followed by annealing/oxidation in air and pack cementation\textsuperscript{12,14-17}. The latter method has been attracting attention due to its low cost, ease of fabrication, good adhesion between the deposited coating and substrate and extensive application.

The objective of the current work is to obtain the area specific resistance (ASR) as a function of time at 800ºC and then obtain the electrical resistance activation energy of coated specimens which are coated in a Co-base pack mixture by pack cementation method to investigate the coated layer electrical conductivity on the substrate.

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**Experimental Procedure**

Coupons of AISI 441 stainless steel, measuring 10 mm × 5 mm × 2 mm with chemical composition of 17.65% Cr, 0.82% Mn, 0.54% Si, 0.31% Ni, 0.11% C, 0.02% S, 0.03% P 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 cobalt onto the substrate, pack cementation method was employed. Co, Al₂O₃ and NH₄Cl powder were used as powder mixture in average size of 1 μm, 70-80 μm and 240 μm. All the powders have been prepared from Merck with above 99.99% purity. The optimized conditions for coating of cobalt onto the AISI 441 stainless steel by pack cementation were identified: 10 wt% Co, 1 wt% NH₄Cl, 89 wt% Al₂O₃ as powder mixture and heating at 800ºC for 4 h in argon gas.

The substrate samples and pack materials were placed in an stainless steel crucible, which was closed with a stainless steel lid using high-temperature cement. The crucible was placed into an electric tube furnace, which was heated to 200ºC and held at this temperature for 1.5 h to remove moisture from the pack. The furnace was circulated with argon, and the temperature was raised to a final coating depositing temperature and held there for the required time. The furnace was then cooled to room temperature at its natural rate by switching off the power supply while maintaining the argon gas flow. After pack cementation, the samples were removed from the pack and ultrasonically cleaned in ethanol to remove any embedded pack material.

In order to measure the area specific resistance (ASR) of the oxidized samples, the set-up shown in Fig. 1 was employed. Platinum wires were spot welded to one side of two identical non-oxidized samples to provide electrical connections. To avoid alloy-to-alloy adhesion and erroneous results, platinum wire welded coupons were pre-oxidized for 24 h at 800ºC. No conductive paste, which may affect the oxidation mechanism, was applied between the two samples. A constant current density of 500 mAcm⁻² was applied and the voltage was recorded every 30 min. 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 441 coupon and the resulting resistance was subtracted from the original test results. ASR was measured as a function of time at 800ºC for 300 h and as a function of different temperatures (from 500ºC to 1000ºC). All the above-mentioned tests were run at an electric box furnace and static air.

**Results and Discussion**

**Microstructure of the coated steel**

Cobalt coating was applied onto the surface of AISI 441 steel, using the pack cementation method. Figure 2 shows a secondary electron (SE) cross-section image and an elemental distribution of the coated sample at 800ºC for 4 h in argon gas.
sectional SEM image (Fig. 2a) of an as-coated specimen. As shown, the thickness of the coating layer is approximately 55 µm. Good adherence between the deposited layer and the substrate, with no void, pore, or discontinuity, is seen. The elemental distribution across the coating layer was determined using an EDX analyzer, which is shown in Fig. 2b. Figure 3 shows an XRD diffraction pattern of the coated specimen. The identified phases include, Co₇Fe₃, CoFe and CoCr. Pack cementation coatings are formed through the diffusion of atoms. Outward diffusion of Fe and Cr elements from the substrate toward the coating layer, caused to the formation of Co₇Fe₃, CoFe and CoCr phases. It was discussed in earlier reported work.

Electrical properties of the coated steel

The ASR for coated and uncoated AISI 441 stainless steel, as a function of time were plotted in Fig. 4. ASR values for uncoated substrates increase rapidly with oxidation time and approach a value of 40.1 mΩcm² after 300 h oxidation at 800ºC. Coated specimens however, exhibited a very low resistance (12.3 mΩcm²) after 300 h oxidation.

In an XRD pattern of a bare substrate (Fig. 5a), (Mn,Cr)₃O₄, spinel, Fe₂O₃, chromia and silica are observed. In ferritic stainless steels, when the alloy is subjected to the temperature range of 650-850ºC, the (Mn,Cr)₃O₄ spinel layer will form, which is non-protective. Fe₂O₃ was also observed in the oxide scale of non-coated Fe-Cr alloy in earlier studies where a dense sub-layer of Cr₂O₃ and a (Mn,Cr)₂O₄ layer, were formed. Also, the chromia, which is protective, was formed.

Fe₂O₃ and Cr₂O₃ has formed on the surface of the coated samples (Fig. 5b), but the reduced intensity of this phase in the XRD patterns confirms that the growth of chromia was considerably decreased. In an XRD pattern of a bare substrate (Fig. 5a), the silica phase was observed. In the steels that contain Si in amounts greater than 0.5wt%, insulating, continuous or network-like films of silica can also grown under the chromia scale.

Figure 5b shows the XRD pattern of coated specimens after 300 h oxidation. Coating layer on coated substrates has converted to Co₃O₄, CoFe₂O₄ and CoCr₂O₄ spinels during isothermal oxidation.

Figures 6 and 7 show SEM images of a cross-section of uncoated and cobalt coated samples after oxidation at 800ºC for 300 h, respectively. On the surface of uncoated samples (Fig. 6a) one oxide scale layer is seen. Two layers can be seen for the cobalt coated sample that consist of the coating layer and
Cr₂O₃ scale layer. The thickness of chromium oxide scale layer for cobalt coated sample is lower than the uncoated one, therefore the diffusion of Cr cations and oxygen anions has been decreased.

The elemental distribution across the oxidized uncoated and cobalt coated samples using an EDX analyzer, are shown in Figs 6b and 7b, respectively.

Several factors can contribute to the improved electrical conductivity for the coated substrate over uncoated ones. These include the higher electronic conductivity of the scale consisting of spinel layers, the absence of silica phase, improved adhesion of oxide scale and elimination of spallation and cracking⁰²⁻¹⁰²².

Evaluation of electrical resistance activation energy

To evaluate the effect of temperature on the area specific resistance (ASR), the ASR was measured at different temperatures (from 500ºC temperature to 1000ºC) for coated and uncoated samples. The ASR of the oxidized alloy is dependent on the thickness and electrical conductivity of the oxide scale because the resistance of the oxide is much greater than that of the alloy.

ASR values are defined as:

\[ ASR = \frac{l_o}{\sigma_o} \]  \hspace{1cm} \ldots (1)

where \( l_o \) is the thickness of the oxide layer and \( \sigma_o \) is the electrical conductivity of the oxide. The thickness of the oxide layer obeys Wagner's oxidation theory, which states that the oxide thickness is directly proportional to the square root of time at a constant temperature, as follows ²³⁻²⁸:

Fig. 6—(a) Cross-sectional SEM micrographs of the uncoated sample oxidized at 800ºC for up to 300 h and (b) concentration profile of major elements in the coating layer

Fig. 7—(a) Cross-sectional SEM micrographs of the Co-coated sample oxidized at 800ºC for up to 300 h and (b) concentration profile of major elements in the coating layer
\[ I_o^2 = K_p t \quad \ldots \ (2) \]

Where \( K_p \) is the oxidation rate constant and \( t \) is time.

\( K_p \) is dependent on the activation energy for diffusion of oxidation rate-limiting species and has an Arrhenius relation as follows:

\[ K_p = K^* \exp \left( \frac{-E_o}{kT} \right) \quad \ldots \ (3) \]

where \( K^* \) is pre-exponent constant, \( E_o \) is activation energy for oxidation, \( k \) is Boltzmann constant, and \( T \) is temperature.

In the same manner, the electrical conduction at the oxide is affected by the polaron hopping process through the connection structure of electron holes.

\[ \sigma_o = \sigma^* T \exp \left( \frac{-E_c}{kT} \right) \quad \ldots \ (4) \]

where \( \sigma^* \) is pre-exponent constant and \( E_c \) is activation energy for conduction.

Accordingly, Eq. (5) can be rewritten by combining Eqs (2)-(4) as:

\[ \begin{align*} 
ASR &= 2 \frac{K^* t}{\sigma^*} T \exp \left( \frac{-1(1/2)E_o + E_c}{kT} \right) \\
&= ASR T \exp \left( \frac{E_o}{kT} \right) \quad \ldots \ (5)
\end{align*} \]

Activation energy \( (E_a) \) of electrical resistance simultaneously includes both the oxidation rate and conduction of oxide scale. \( E_a \) can be obtained from the directly proportional relationship between \( \log(ASR/T) \) and \( 1/T \) from Eq. (5) (Fig. 8).

Electrical resistance activation energy of uncoated and coated samples was obtained in order 0.91 eV and 0.69 eV. The lower electrical resistance activation energy of coated samples resulted to the higher electrical conductivity with respect to uncoated ones and this lower value is because of spinel compositions existence on the coated substrates (Co\(_3\)O\(_4\), CoFe\(_2\)O\(_4\) and CoCr\(_2\)O\(_4\) spinels).

Lee and Bae\(^{28}\) investigated the activation energy \( (E_a) \) of electrical resistance of coated and uncoated SS 430. There is a good match between the reported data in the author’s work and their work\(^{28}\).

Electrical resistance activation energy is a barrier for conduction. By increasing the electrical resistance activation energy, the conductivity decreases. One of the most important factors that causes to the decrease of electrical conductivity, is the growth of chromia layer. By increase of temperature, the thickness of chromia layer increases therefore the conductivity decreases. The decrease of conductivity leads to the higher electrical resistance activation energy.

The local activation energies of the ASRs decreased as temperature decreased and the decreasing rates of those gradually decreased. This may be because the thickness of the oxide scale affects ASR and the growth rate of the oxide scale decreases as temperature decreases, based on the assumption that stable phases of the oxide scale are not changed significantly even by changing temperature\(^{28,29}\).

For both cases (i.e. cobalt coated and uncoated samples), the square of the weight gain increased linearly with the isothermal oxidation duration, satisfying the parabolic kinetics law. The parabolic rate constant is an intrinsic property of an oxidation-resistant alloy and is, typically, used for measuring its oxidation resistance. The \( k_p \) value obtained for the coated AISI 441 alloy was \( 2.244 \times 10^{-13} \text{g}^2\text{cm}^{-4}\text{s}^{-1} \), after a 300 h oxidation, which is lower than that of the uncoated sample \( (k_p = 5.142 \times 10^{-12} \text{g}^2\text{cm}^{-4}\text{s}^{-1}, \) after a 300 h oxidation.

Activation energies for oxidation were calculated as 103 mol\(^{-1}\) for the uncoated specimens and activation energy was 91 kJ mol\(^{-1}\), for the cobalt coated samples. The activation energy for the coated samples is lower than the value for the uncoated steel, which would imply that oxide formation is easier. This is an interesting result, which imply that the oxides on the coated samples are thinner than the oxides on the uncoated AISI 441 samples. The activation energy for oxidation of the cobalt coated

Fig. 8—ASR values as a function of temperature for uncoated and coated samples
samples is relatively close to that for the oxidation of the uncoated samples. It is, thus, possible that oxidation of the coated samples, at these temperatures in air, is essentially controlled by the same mechanism that control the oxidation of the cobalt coated samples.

Conclusions

From this study, the following conclusion can be drawn:

(i) Metallic phases in cobalt coating transformed to cobalt spinels (Co$_3$O$_4$, CoFe$_2$O$_4$ and CoCr$_2$O$_4$) during isothermal oxidation.

(ii) Cobalt spinels resulted to the improvement of high temperature electrical conductivity of AISI 441 ferritic stainless steel which is used for SOFC interconnects.

(iii) The ASR was obtained 40.1 m$\Omega$cm$^2$ for uncoated samples and 12.3 m$\Omega$cm$^2$ for coated samples after 300 h of isothermal oxidation in static air at 800°C.

(iv) The electrical resistance activation energy was obtained 0.91 eV for uncoated samples and 0.69 eV for coated samples.

(v) The lower electrical resistance activation energy of coated samples is because of high electrical conductivity of spinel compositions with respect to chromia scale on the surface of uncoated samples.

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