Cyclic oxidation of Ni-Fe$_2$O$_3$ composite coating electrodeposited on AISI 304 stainless steel

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Abstract

Protective coatings can be applied to enhance the performance of interconnects in solid oxide fuel cells (SOFCs). In this study, AISI 304 steel was coated with a Ni-Fe$_2$O$_3$ composite from a modified Watt’s type electrolyte by the conventional electro co-deposition (CECD) method. The characterization of the coatings before and after cyclic oxidation was done by scanning electron microscopy (SEM) and X-ray diffraction (XRD). In order to evaluate the oxidation behavior, thermal cycling was carried out in a furnace at 850°C. Results indicated that the coated steel had better oxidation resistance in comparison to the uncoated steel. After 60 cycles of oxidation, the Ni-Fe$_2$O$_3$ composite coating was converted to FeNi$_2$O$_4$, NiCrO$_4$, MnFe$_2$O$_4$ and Fe$_2$NiO$_4$. The Fe$_2$O$_3$ / NiFe$_2$O$_4$ composite coating reduced the outward migration of chromium and the growth rate of the Cr$_2$O$_3$ layer.

Key words: Oxidation, Electrodeposition, Composite coating, AISI 304 stainless steel, Microstructure, X-ray diffraction.
1. Introduction

The performance of metallic interconnects is important for the operation of solid oxide fuel cells (SOFCs). For example, lowering the operating temperature to 600–800 °C allows the use of stainless steel interconnects. This is notable because it is generally agreed that stainless steel is considered a useful oxide scale \(^1\), \(^2\). On the other hand, when stainless steel is used in SOFCs, several problems will occur. The biggest problem is chromia poisoning. Stresses produced in the oxide scale lead to spallation and cracking. Due to the easy migration of chromium through these defects, degradation of the cathode will occur \(^3\), \(^4\).

Hence, composite coatings have been deposited on stainless steel, particularly on the cathode side of the SOFC \(^5\). Recently, in order to enhance wear resistance \(^6\), \(^7\), oxidation resistance \(^7\)-\(^10\), and corrosion resistance \(^11\), \(^12\) of steels, various studies have been carried out. Nickel has been employed as a matrix metal by many researchers. For example, deposition of nickel matrix composite coatings reinforced with Al\(_2\)O\(_3\) \(^13\), \(^14\), SiC \(^14\), \(^15\), CeO\(_2\) \(^16\), TiO\(_2\) \(^17\), \(^18\) and Fe\(_2\)O\(_3\) \(^19\)-\(^21\) particles have been investigated. Electroplating was one of the most successful techniques to produce a composite coating. The most widely used coating technique was conventional electro co-deposition. Electrodes are positioned vertically in the plating cell in the CECD technique \(^22\), \(^23\).

Cyclic oxidation of micro-crystalline 304 SS coating has been evaluated at 900 °C by Zhang and et al. \(^24\). The micro-crystalline steel slowly gained weight in the first 25 cycles of oxidation and after 40 cycles of oxidation, spallation was observed. Surface analysis by XRD showed the formation of Fe\(_2\)O\(_3\) and FeCr\(_2\)O\(_4\). \(^24\). Stanisłowski and et al. \(^25\) indicated that metallic coatings of cobalt, nickel or copper could reduce outward migration of chromium. The metallic coatings and their oxides considerably decreased the oxide scale growth. Ferritic stainless steel oxidation with Fe-Co-Ni coating has been investigated by Geng and et al. \(^26\). After thermal exposure in air at
800°C, the Fe-Co-Ni coating was changed into a (Fe,Co,Ni)₃O₄ spinel layer. This spinel not only prevented outward migration of Cr, but also decreased the growth rate of the inner layer of chromia. Also, Jeng and et al. ²⁰ investigated the oxidation behavior of a Ni-Fe₂O₃ composite coating. They found that the oxidation rate for coated steel was lower than uncoated AISI 304 steel. During oxidation, a double layer oxide formed on the surface of Ni-Fe₂O₃ composite coating. This layer was composed of an inner layer of chromia and an outer layer of (Ni,Fe)₃O₄/NiO.

Currently, no research exists concerning the influence of thermal stresses during the operation of SOFCs on Ni-Fe₂O₃-coated interconnects.

Ni-Fe₂O₃ composite coating on steel substrate due to the dispersion of Fe₂O₃ particles in the nickel matrix improves oxidation resistance at high temperatures, corrosion resistance and mechanical properties. Composite coatings containing metal nickel and a small amount of Fe₂O₃ particles were deposited on Ferrites 430 by Geng ²⁰.

Austenitic stainless steels are widely used in high temperature conditions, including solid oxide fuel cell connections and boiler tubes. Application in these places, they are exposed to severe thermal cycles, so protecting them at high temperatures is essential. For this purpose, composite and ceramic coatings have been considered for oxidation to increase the life of these components ²⁷,²⁸.

The aim of this research was therefore to fabricate a Ni-Fe₂O₃ composite coating on AISI 304 stainless steel. Based on the real working conditions of the SOFCs, cyclic oxidation that produced thermal stresses was done. The cyclic oxidation resistance of Ni-Fe₂O₃-coated and uncoated specimens were then studied. In addition, we investigated the surface scale structure of the Ni-Fe₂O₃ composite coating and the uncoated AISI 304 steel before and after cyclic oxidation.
2. Experimental procedure

Samples with dimensions of 10mm×10mm×2mm were cut from an AISI 304 stainless steel plate with a chemical composition in wt % of: C 0.08%, Mn 1.6%, Cr 19.1%, Si 1%, Ni 8.2% and Fe for the balance. Nickel and an AISI 304 steel plate were used as the anode and cathode, respectively. A small-scale laboratory test was done to achieve the best quality and efficiency. Before the coatings were applied, the 304 steel substrates were polished from 400-grit SiC paper up to 1200-grit and then cleaned with acetone in an ultrasonic bath. Based on previous studies, the composition of the plating bath for the electrodeposition of nickel coatings was chosen as follows in g/L: 240 NiSO$_4$·6H$_2$O, 45 NiCl$_2$·6H$_2$O, 30 H$_3$BO$_3$, 5 – 30 Fe$_2$O$_3$ powder and 0.2 Sodium dodecyl sulfate (SDS) as the surfactant.

All chemicals were analytic grade reagents from Merck. Contents of the electrolyte bath were sonicated for about 15 minutes in order to break down any agglomeration. Next, agglomeration of any particles was further prevented by a magnetic stirrer. The electrolyte temperature was adjusted to 55 °C and pH value was set at 3.8-4.8, per previous studies. The Taguchi method was then applied to obtain the best (optimum) coating, and the optimum pH was found to be 4.8.

For pH adjustment, either 0.1 M/L sulfuric acid or sodium hydroxide was used. Deposition was carried out following the CECD technique with the vertical electrode configuration. The DC power supply was turned on and a current density of 15-35 mA/cm$^2$ was applied for 5 minutes. This current density range was chosen based on previous studies and was used by the Taguchi method for determining the best (optimum) coating. The optimum current density was found to be 20 mA.cm$^{-2}$. 
The electrolyte bath was agitated with a magnetic stirrer during electrodeposition. After electrodeposition, the applied current was turned off and the substrate was removed from the electrolyte bath. In order to remove the loosely bound extraneous material from the coated surface, it was washed with distilled water in the ultrasonicator. After rinsing, the coated steel was dried in air and then weighed using an electronic balance.

Coated and uncoated specimens were then subjected to cyclic oxidation, similar to previous studies \(^{33-36}\). The selection of the cyclic oxidation parameters was based on the real working conditions of SOFCs. In real conditions, the SOFC stack is turned off and on so thermal stresses develop on the coated interconnects. Therefore, the coating should be stable during operation.

Coated and uncoated samples (3 of each) were placed simultaneously in the furnace on a refractory ceramic for cyclic oxidation. The temperature of furnace was set at 850°C. After each 45-minute oxidation cycle, they were removed from the furnace and placed in free air for 15 minutes. Again, the samples were placed in the furnace 850°C. This cycle was repeated for 60 times. After each cycle, the uncoated and Ni-Fe\(_2\)O\(_3\) composite coated specimens were weighed to within 0.0001 g. Microstructure, cross-section and chemical composition data for the Ni-Fe\(_2\)O\(_3\) composite coated samples before and after oxidation tests were studied using scanning electron microscopy (SEM) (Oxford, model 7431) with energy dispersive spectroscopy (EDS). X-Ray diffraction (XRD) was used to determine the crystallographic phases in the surface layer of the Ni-Fe\(_2\)O\(_3\) coated and oxidized specimens. A Philips X’Pert High Score diffractometer was used with Cu K\(_\alpha\) radiation (\(\lambda = 1.5405\) A), a step angle of 0.02° and time step of 1 sec/degree in all the measurements.
3. Results and discussion

3.1. Coating of the substrate

The experimental parameters used during the coating process significantly impacted the properties of the resulting coatings, as has been explained in other studies. The best adhesion, homogeneous distribution of particles and maximum amount of Fe₂O₃ was achieved from the plating bath containing 20 g/L Fe₂O₃ particles, a pH value of 4.8, an electrodeposition time of 5 minutes, a current density of 20 mA/cm² and a minute SDS addition.

During the precipitating process of nickel, nickel ions are deposited on the substrate and the nickel layer is formed. Subsequently, nickel ions and ceramic particles simultaneously precipitate on a growing metal background. The process of nickel deposition of Watts baths involves a multi-stage reaction.

The reactions carried out during the sedimentation process are shown by Equations 1 to 3.

\[
\begin{align*}
\text{Ni}^{+2} + \text{H}_2\text{O} & = \text{Ni} (\text{OH})^+ + \text{H}^+ \\
\text{Ni} (\text{OH})^+ + e^- & = \text{Ni OH}_(\text{ads}) \\
\text{Ni} (\text{OH})^+ + \text{Ni OH}_(\text{ads}) + 3 e^- & = 2 \text{Ni} + 2\text{OH}^-
\end{align*}
\]

During the plating, secondary particles are absorbed into the electrolyte by Ni⁺. These particles migrate with the adsorbed cations toward the growing nickel base. The presence of these particles prevents the excessive growth of nickel grains. These particles increase the amount of nucleation points and delay the growth of nickel grains. Therefore, the final coating shows better properties than pure nickel coating.
Figure 1(a) shows the SEM cross-section of Ni-Fe$_2$O$_3$ composite coated steel. The thickness of the coating was determined to be approximately 25 µm, uniform, dense and adhering well to the substrate. Also, the concentration profiles of Ni, Fe, Mn, O and Cr in the Ni-Fe$_2$O$_3$ composite coating layers and EDX analysis of the coating layer are shown in Figure 1(b) and 1(c), respectively.

Figure 1(b) demonstrates the distribution of elements across the Ni-Fe$_2$O$_3$ composite coating layer. The profiles verified that both Ni and Fe$_2$O$_3$ elements were deposited onto the substrate, which led to the creation of a uniform and Ni-rich layer. The Ni concentration changed from about 82 at. % at the surface of the Ni-Fe$_2$O$_3$ composite coating to about 75 at. % at the depth of approximately 24 µm. Then the nickel concentration rapidly reduced to approximately 8 at. % at the depth of 26 µm. The concentration of Fe is approximately 7 at. % just below the surface, then suddenly increases at the depth of 26 µm to 70 at.%. The concentration of O in the coating layer is about 12 at. %, which is because of the deposition of Fe$_2$O$_3$.

The EDX spectrum from the cross section of the Ni-Fe$_2$O$_3$ composite coated sample (Figure 1(a)) confirms the formation of Fe$_2$O$_3$ (Figure 1(c)). The EDX spectrum demonstrates that the coating mainly consists of Ni and small amount of Fe and O.

Figure 2 shows the XRD pattern of the as-coated specimen. In this pattern, Ni (JCPDS, Card No. 01-1260) and FeNi (JCPDS, Card No. 03-1175) phases were distinguished from the Ni-Fe$_2$O$_3$ composite coated steel. The SEM image of Ni-Fe$_2$O$_3$ composite is shown in Figure 3. It is clear that the surface of the Ni-Fe$_2$O$_3$ composite coated 304 steel was continuous as no porosity or cracks were observed on the coated surface.
3.2. Study of oxidation resistance

3.2.1 Study of parabolic rate constant

The uncoated and Ni-Fe$_2$O$_3$ composite coated specimens were subjected to 60 cycles of oxidation. Each cycle of oxidation included 45 minutes of heating at 850 °C and 15 minutes of cooling out of the furnace. In order to minimize the error associated with the cyclic oxidation experiment, 3 coated and 3 uncoated specimens were exposed to oxidation and the average mass gain was calculated. The mass gain of uncoated and Ni-Fe$_2$O$_3$ composite coated specimens as a function of cycle number is shown in Figure 4. The uncoated specimens had less mass gain compared with coated ones during all of the cycles. The coated steel had mass gain of 0.5963 mg.cm$^{-2}$ after 60 cycles of oxidation. After 60 cycles of oxidation, the mass gain of Ni-Fe$_2$O$_3$ coated steel was low, which is consistent with similar work.$^{20}$ The uncoated steel had mass gain of 1.4124 mg.cm$^{-2}$ after 60 cycles of oxidation. The parabolic rate constant in cyclic oxidation was calculated by converting the number of cycles to the oxidation time by Equation 4:

$$t = \frac{\text{Cycle number} \times \text{Oxidation time}}{60} \quad (4)$$

$k_p$ can then be obtained by Equation 5

$$\left( \frac{\Delta W}{A} \right)^2 = k_p t \quad (5)$$

Where $\Delta W$ is the mass gain, $A$ is the surface area of sample, $K_p$ is the parabolic rate constant and $t$ is the time of oxidation. The slope demonstrates the parabolic rate constant $K_p$ and is used to measure oxidation resistance. The parabolic rate constant is an inherent characteristic of an oxidation-resistant alloy. The calculated value of $K_p$ for the coated steel was $1.111 \times 10^{-12}$ g$^2$cm$^{-4}$s$^{-1}$, which is in agreement with a previous study.$^{37}$
Figure 5 shows the square of mass gain of the uncoated AISI 304 stainless steel and Ni-Fe$_2$O$_3$ coated steel as a function of time for cyclic oxidation in air at 850 °C. The square of mass gain increases linearly with the time of cyclic oxidation. This increase of the parabolic kinetics law was explained by 37, 38.

Three stages of oxidation were observed for the uncoated specimen. During the first stage, the rate of oxidation occurred according to the parabolic law 38, and was about $K_p = 3.39 \times 10^{-12}$ g$^2$cm$^{-4}$s$^{-1}$. According to the kinetics of oxidation, a protective oxide scale should be thermally formed between the non-protective oxide scale which developed during the initially fast oxidation stage and the substrate 20. During the second stage, a high oxidation rate was observed. The calculated value of $K_p$ for this stage was $K_p = 1.744 \times 10^{-11}$ g$^2$cm$^{-4}$s$^{-1}$. Based on the laboratory observation after 30 cycles, some spallation and cracks were seen on the surface of Ni-Fe$_2$O$_3$ coated samples. The cracks on the surface of the bare steel are likely related to stresses which originated from the mismatch in thermal expansion coefficient (TEC) between the created oxides on the surface and the substrate. The TEC of iron oxides is larger than that of the stainless steel, which results in tensile stresses in the oxide scale during cooling 39. The cracked and spalled scale then produces diffusion paths for anions and cations and as a result of the easy transfer of ions, the oxide layer develops with a higher rate.

After 50 cycles of oxidation, the oxidation rate decreased significantly. At this stage, the oxide grew with the rate of about $K_p = 3.66 \times 10^{-12}$ g$^2$cm$^{-4}$s$^{-1}$. The decrease in the oxidation rate was because of the thickening of the oxide scale during which the outward diffusion of ions and inward diffusion of oxygen ions was retarded. Therefore, the growth of oxide scale was limited.
3.2.2. Study of morphology and microstructure

Figures 6(a) and 6(b) display the surface morphology of uncoated and Ni-Fe$_2$O$_3$ composite coated steel after 60 cycles of oxidation in air at 850$^\circ$C, respectively.

After 60 cycles of oxidation, the uncoated sample surface cracked and spalled in some areas as shown in Figure 6(a), while the Ni-Fe$_2$O$_3$ composite coated sample surface demonstrated good resistance against cracking and spallation, as shown in Figure 6(b).

The mass gain of the Ni-Fe$_2$O$_3$ composite-coated specimen at all times was lower than the bare sample. Lower mass gain shows that the Ni-Fe$_2$O$_3$ composite coating has acted as a protective layer against the diffusion of ions (corrosive elements), and has resulted in less mass gain and therefore, better oxidation resistance. After 50 cycles of oxidation, the uncoated samples cracked and spalled from the surface (Fig. 6a), while no cracks or spallation was seen in the Ni-Fe$_2$O$_3$ composite-coated samples (Fig. 6b). This indicates that the thermal expansion coefficient (TEC) match of the Ni-Fe$_2$O$_3$ composite coating with the AISI 304 substrate $^{40-44}$. Cracking and spallation are the consequences of the TEC mismatching of the coating layer or oxide scale with the steel substrate. The TEC of the nickel oxides is comparatively matched to the TEC value of AISI 304 stainless steel. Cracking and spallation introduce easy diffusion routes for corrosive elements (cations and anions), and throughout the easy routes movement for ions, the oxide scale develops at a higher rate. In coated coupons, the nickel oxides create complicated diffusion routes and therefore, the movement of oxygen anions and chromium cations would be extremely restricted. In fact, nickel oxides are effective in reducing the diffusion rate of ions, especially O anions and Cr cations $^{42-44,45}$.

Figure 7 demonstrates higher magnification SEM morphologies of uncoated and Ni-Fe$_2$O$_3$ composite coated samples after 60 cycles of oxidation. Large cracks and spallation were seen on
the oxidized surface of the uncoated steel as shown in Figure 7(a). The surface of Ni-Fe$_2$O$_3$ coated steel was covered with dense and uniform oxide scale as shown in Figure 7(b), but small cracks were observed in this micrograph.

Figure 8 shows the cross section and EDS line scan from the oxide scale formed on the uncoated steel after 60 cycles of oxidation in air at 850 °C. A double-layer oxide structure was developed on the bare steel. The double-layer oxide with an outer Fe-rich layer and an inner Cr-rich layer was continuous and uniform. The outer Fe-rich layer is probably Fe$_2$O$_3$ and Cr-rich layer is probably Cr$_2$O$_3$. Due to the outward diffusion of chromium, the inner layer was Cr-rich$^{38,46}$. It is clear that Cr has an outward diffusion by comparison to other elements. Consequently, it is necessary to limit the migration of chromium and therefore limiting the growth of Cr-rich layer. So, with this purpose in mind, the Ni-Fe$_2$O$_3$ composite coating was electrodeposited on the bare steel.

Figure 9 shows the cross section and the EDS line scan of elements in the formed oxide scale on the Ni-Fe$_2$O$_3$ coated steel after 60 cycles of oxidation in air at 850 °C. In Ni-Fe$_2$O$_3$ coated steel, a triple oxide layer formed. This triple oxide layer consists of an outer Fe-rich layer, a middle Ni-rich layer and an inner Cr-rich layer. Hence, the outer and middle layers of the oxide scale were verified to be Fe and Ni-rich, and no Cr was identified. It is clear that the thickness of Cr-rich layer in the Ni-Fe$_2$O$_3$ composite coated layer is less than for the uncoated sample. Consequently, the growth of Cr-rich layer was prevented in the Ni-Fe$_2$O$_3$ composite coating after cyclic oxidation. This result indicated that Ni-Fe$_2$O$_3$ composite coating operates as a useful obstacle against inward diffusion of the oxygen onion and outward diffusion of the Cr cation$^{26,38}$. 
The Ni-Fe$_2$O$_3$ composite coating after oxidation transfers into a nickel oxide layer. Nickel oxides prevent the penetration of chromium and also improve adhesion of the composite coating to the substrate.

Several factors can contribute to the improved oxidation resistance and limitation of chromium diffusion for the Ni-Fe$_2$O$_3$ composite coated steels over uncoated AISI 304 steel. These include the higher oxidation resistance of the scale consisting of nickel compositions, improved adhesion of the scale to the substrate and elimination of scale spallation. The increase in the thickness of the middle layer, which is Ni-rich, also suggests that there is an outward diffusion of Ni through the Cr$_2$O$_3$-rich inner layer. Therefore, the Cr$_2$O$_3$-rich subscale is not adequately protective against the outward diffusion of Ni $^{47}$.

Some cracks were observed between Cr$_2$O$_3$ layer and the oxidized Ni-Fe$_2$O$_3$ coating layer. The creation of these cracks was related to the presence of Cr$_2$O$_3$ oxide at the interface, and the different TEC values. Steel alloys which contain Si in amounts greater than 0.5 wt %, can result in an insulating, continuous or network-like film of silica that can grow under the chromia scale $^{48}$. The TEC of SiO$_2$ (0.55×10$^{-6}$ °C$^{-1}$) is significantly lower than the TEC value of Cr$_2$O$_3$ (9.6×10$^{-6}$ °C$^{-1}$) $^{40,41}$ and of Fe$_2$O$_3$ (11×10$^{-6}$ °C$^{-1}$) $^{49}$. Also, AISI 304 austenitic stainless steel has a TEC of ~19×10$^{-6}$ °C$^{-1}$, which is higher than silica, chromia and hematite $^{50-52}$. Another reason for the cracking of oxide scales is the formation of chromia and hematite. Chromia and hematite are P-type oxides which grow through the outward diffusion of chromium and iron cations. During the long oxidation time, cationic vacancies moved inward and aggregated at the interface of oxide-metal. This led to the formation of porosity and reduced the adherence of oxide scale to the substrate and coating $^{53}$. 


3.2.3. XRD patterns

Figure 10 contains the XRD patterns of the formed oxide scale on uncoated steel after 60 cycles of oxidation in air at 850 °C. The oxide scale on the bare steel surface consisted of MnCr$_2$O$_4$ (JCPDS, Card No. 75-1614), MnFe$_2$O$_4$ (JCPDS, Card No. 74-2403), Fe$_2$O$_3$ (JCPDS, Card No. 73-0603), Cr$_2$O$_3$ (JCPDS, Card No. 76-0147) and Mn$_2$CrO$_4$ (JCPDS, Card No. 36-0546) spinel. The XRD pattern of the bare steel and EDS analysis obtained from the cross section of the uncoated steel shown in Figure 8(b) confirm the formation of MnCr$_2$O$_4$, MnFe$_2$O$_4$, Fe$_2$O$_3$, Cr$_2$O$_3$ and Mn$_2$CrO$_4$ spinel. According to the XRD pattern and cross section EDS line scan of elements from the uncoated steel after 60 cycles of oxidation, a double oxide layer with an outer layer of Fe$_2$O$_3$ and Cr$_2$O$_3$ and an inner layer of Cr$_2$O$_3$ with MnCr$_2$O$_4$, MnFe$_2$O$_4$ and Mn$_2$CrO$_4$ spinel were developed, which is consistent with SEM observations shown in Figure 8(a).

The formation of Cr$_2$O$_3$ is due to the inward diffusion of oxygen ions and outward diffusion of chromium ions. Also, the formation of Fe$_2$O$_3$ is due to the inward diffusion of oxygen ions and outward diffusion of iron ions. Fe$_2$O$_3$ was also seen in the oxide scale of uncoated Fe-Cr alloys, in previous studies $^{54-59}$, where a sub layer of Cr$_2$O$_3$ and a (Mn, Cr)$_3$O$_4$ layer were formed.

In our prior study, Cr$_2$O$_3$ and Fe$_2$O$_3$ overlapped with each other $^{36}$. The Cr$_2$O$_3$–Fe$_2$O$_3$ phase diagram points out that Cr$_2$O$_3$ and Fe$_2$O$_3$ are mutually soluble $^{60}$. Both phases of Cr$_2$O$_3$ and Fe$_2$O$_3$ have the same crystal structure (hexagonal) and analogous lattice parameters: a=0.4959 nm and c=0.1.3594 nm for Cr$_2$O$_3$, whereas a=0.5036 nm and c=1.3749 nm for Fe$_2$O$_3$ $^{45}$. Therefore, Cr$_2$O$_3$ and Fe$_2$O$_3$ can overlap with each other.
The formation of MnFe$_2$O$_4$ spinel refers to the diffusion of Mn$^{2+}$ and Fe$^{3+}$ cations. Once a continuous layer of Cr$_2$O$_3$ is created, Fe and Mn ions diffuse through the Cr$_2$O$_3$ scale and react at the surface to form the MnFe$_2$O$_4$ phase.

The formation of Mn-Cr spinels is related to the stainless steel alloys that contain low amounts of manganese. When the steel is placed to the temperature range of 650 – 850 ºC, the (Mn,Cr)$_3$O$_4$ spinel layer will be created which is not protective.

Figure 11 demonstrates XRD patterns of the oxide scale formed on Ni-Fe$_2$O$_3$ composite coated steel after cyclic oxidation for 60 cycles in air. The oxide scale on the Ni-Fe$_2$O$_3$ coated steel surface included FeNi$_2$O$_4$ (JCPDS, Card No. 88-0385), NiCrO$_4$ (JCPDS, Card No. 21-0596), MnFe$_2$O$_4$ (JCPDS, Card No. 74-2403), Fe$_2$NiO$_4$ (JCPDS, Card No. 74-1913) and Cr$_2$O$_3$ (JCPDS, Card No. 76-0147). These phases are consistent with EDS element line scan shown in Figure 9(b).

Schematics describing the structures of the surface oxide layers created on the uncoated and Ni-Fe$_2$O$_3$ composite-coated AISI 304 steel are illustrated in Figure 12 (a) and (b), based on the above results from the XRD and EDS analyses. Based on SEM micrographs from the cross section of coated and uncoated specimens (Figures 8 and 9), the Cr$_2$O$_3$ oxide layer exists in both samples but the thickness of chromia layer in coated sample (~ 5 μm) is significantly lower in compared with the bare sample (~ 40 μm). Also, based on the XRD pattern from the coated and uncoated specimens, the intensity of chromia for the Ni-Fe$_2$O$_3$ coated steel is lower in comparison with bare steel. Based on the XRD analysis (Figure 11), some scattered (Mn,Cr)$_3$O$_4$ spinels are shown for Ni-Fe$_2$O$_3$ composite-coated in Fig. 12b. The intensity of this phase for the Ni-Fe$_2$O$_3$ composite-coated specimens in the XRD analysis is low and in the SEM micrograph of coated samples, (Mn,Cr)$_3$O$_4$ spinels were not observed. Based on this reasoning, scattered Cr-Mn
spinels are shown in Figure 12 (b). The formation of (Mn,Cr)$_3$O$_4$ spinels on the surface of the Ni-Fe$_2$O$_3$ composite-coated specimens is related to the formation of chromia. The chromia growth creates stresses and then creates some cracks in the Ni-Fe$_2$O$_3$ composite coating, which leads to the chromium or manganese migration to the surface $^{61}$.

This schematic graph (Figure 12) shows the effectiveness of Ni-Fe$_2$O$_3$ composite coating in decreasing outward diffusion of chromium (Figure 10). The thickness of Cr$_2$O$_3$ oxide layer in Ni-Fe$_2$O$_3$ composite-coated AISI 304 (Fig. 9a) is less than the uncoated AISI 304 steel (Fig. 8a) because the coating layer restricted chromium diffusion.

For the formation of chromia, oxygen dissolves in the base metal and diffuses inwards through the metal matrix. The critical forming energy, for the precipitation of Cr$_2$O$_3$ is based on the reactions on the top of the surface by the outward diffusion of the Cr element and the inward diffusion of the O element. The nucleation and precipitation of the Cr$_2$O$_3$ oxide takes place and the Cr$_2$O$_3$ grows $^{61}$. The schematic growth of the Cr$_2$O$_3$ and the reactions based on the above mechanism are illustrated in Figure 13.

Ni-Fe$_2$O$_3$ composite coating consisted of spinel compositions. Cubic spinel has the general formula of AB$_2$O$_4$ with A and B as divalent, trivalent and quadrivalent cations in octahedral and tetrahedral sites and oxygen anions on the face centred cubic (FCC) lattice sites. Figure 14 shows a Schematic describing the structure of spinel composition. Spinels containing Ni and Fe can be good electronic conductors and show excellent CTE match with the steel substrate and other cell components, including the anode and cathode. Spinel coatings (FeNi$_2$O$_4$, NiFe$_2$O$_4$ and MnFe$_2$O$_4$) have shown excellent capability for absorbing Cr species that migrate from the chromia-rich scale to the scale surface and cause Cr poisoning $^{40,62}$. 
It is clear that the coating layer prevented the outward diffusion of oxygen, which limited the growth rate of the \( \text{Cr}_2\text{O}_3 \) layer. Consequently, the \( \text{Fe}_2\text{O}_3/\text{NiFe}_2\text{O}_4 \) layer was developed on an inner \( \text{Cr}_2\text{O}_3 \) layer, and prevented the Cr volatilization. Previous works \(^{36}\) illustrated that metallic coatings include of cobalt, copper and nickel on Crofer 22 APU with a thickness of approximately 10 \( \mu \text{m} \) demonstrated good retention of Cr volatilization.

4. Conclusions

A Ni-\( \text{Fe}_2\text{O}_3 \) composite coating was electrodeposited on AISI 304 austenitic stainless steel. The optimum coating was achieved from the plating bath containing 20 g/L \( \text{Fe}_2\text{O}_3 \) particles, pH value of 4.8, electrodeposition time of 15 minutes and with a current density of 20 mA/cm\(^2\). The Ni-\( \text{Fe}_2\text{O}_3 \) composite coating improved cyclic oxidation resistance. The formed oxide scale on the uncoated steel mainly consisted of \( \text{Cr}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \). The coated AISI 304 SS after 60 cycles consisted of \( \text{FeNi}_2\text{O}_4 \), \( \text{NiCrO}_4 \), \( \text{MnFe}_2\text{O}_4 \) and \( \text{Fe}_2\text{NiO}_4 \) phases. These compositions limited the outward diffusion of chromium ions and inward diffusion of oxygen anions.
References


Figure Captions

Fig. 1. SEM cross section image of coating (a), EDS line scan (b) and EDX analysis of the coating layer (c).

Fig. 2. XRD patterns of Ni-Fe$_2$O$_3$ composite coating.

Fig. 3. Surface morphology of Ni-Fe$_2$O$_3$ coated steel.

Fig. 4. The mass gain of uncoated and coated specimens as a function of cycle number for cyclic oxidation in air at 850 °C.

Fig. 5. The square of mass gain as a function of oxidation time for the uncoated AISI 304 stainless steel and coated steel in air at 850 °C.

Fig. 6. Surface morphology after 60 cycles of oxidation in air at 850°C: (a) uncoated steel, (b) coated steel.

Fig. 7. Surface morphology under high magnification: (a) uncoated steel, (b) coated steel.

Fig. 8. The cross section (a) and the EDS elements line scan of the oxide scale (b) formed on the bare steel after 60 cycles of oxidation.

Fig. 9. The cross section (a) and the EDS elements line scan of the oxide scale (b) formed on the coated steel after 60 cycles of oxidation.

Fig. 10. XRD patterns of the oxide scale formed on uncoated steel after cyclic oxidation in air at 850 °C.

Fig. 11. XRD patterns of the oxide scale formed on coated steel after cyclic oxidation in air at 850 °C.
Fig. 12. Schematic structure of thermal grown oxide layers on AISI 304 (a) uncoated and (b) Ni-Fe₂O₃ coated after 60 cycles of oxidation at 850 °C.

Fig. 13. Schematic growth of Cr₂O₃ during cyclic oxidation.

Fig. 14. Schematic structure of spinel composition.
Coating layer  Substrate

SEM MAG: 1.02 kx  DET: BSE Detector
HV: 20.0 kV
Figure 1b: Graph showing atomic percentage as a function of distance from the surface (micron). The graph displays the atomic percentage of Fe, Ni, O, Cr, and Mn over the distance from the surface.
Figure 7a: Spallation

SEM MAG: 1.08 kx DET: SE Detector
HV: 20.0 kV 100 μm
Spallation
Figure 8a: SEM image showing the oxide scale and substrate. 

- **SEM MAG:** 995 x 
- **HV:** 20.0 kV 
- **DET:** BSE Detector 
- **Scale:** 100 μm
Counts

Position [°2Theta]

1: FeNi$_2$O$_4$
2: NiCrO$_4$
3: MnFe$_2$O$_4$
4: Fe$_2$NiO$_4$
5: Cr$_2$O$_3$
(a)

(Mn, Cr)$_3$O$_4$

Fe$_2$O$_3$ + Cr$_2$O$_3$

Substrate
Substrate

\[
\begin{align*}
\text{Cr}^{+3} & \quad \text{O}_2 \\
O^{-2} & \\
e^- & \\
\end{align*}
\]

\[
2\text{Cr} = 2\text{Cr}^{+3} + 6e^- \\
\text{or} \\
2\text{Cr}^{+3} + 6e^- + 3/2\text{O}_2 = \text{Cr}_2\text{O}_3 \\
\text{or} \\
2\text{Cr} + 3\text{O}^{2-} = \text{Cr}_2\text{O}_3 + 6e^- \\
3/2\text{O}_2 + 6e^- = 3\text{O}^{2-}
\]

Overall reaction: \(2\text{Cr} + 3/2\text{O}_2 = \text{Cr}_2\text{O}_3\)
Oxygen

Cation in octahedral site: Fe, Ni, Mn

Cation in tetrahedral site: Ni, Fe

Octahedral intersice (32 per unit cell)

Tetrahedral intersice (64 per unit cell)