

Electrodeposition of Fe-Ni alloy coating on ferritic stainless steel

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Received 6 July 2009; accepted 30 December 2009

Abstract: Fe-Ni alloy coatings were electrodeposited on ferritic stainless steel (FSS) in solutions containing FeSO_4 and NiSO_4 . The effects of pH, $[\text{Fe}^{2+}]/[\text{Ni}^{2+}]$ (molar ratio) of electroplating solutions and cathode current density on deposition rate and surface appearances of the coatings were investigated. The results indicated that the deposition rate of the coating in solution with $[\text{Fe}^{2+}]/[\text{Ni}^{2+}]$ of 0.4 slightly increased with increasing pH from 2.5 to 3.5 under the current density of 5.5 mA/cm^2 , and then the deposition rate of the coating in solution with pH 4.0 began to decrease. The deposition rate also slightly increased with pH up to 3.5 under higher cathode current densities of 13.5 and 27 mA/cm^2 . Under 13.5 mA/cm^2 , however, the coating deposited in solution with pH 4 was prone to crack or flake. The deposition rate increased and the surface of coatings became less smooth with increasing cathode current density. The effect of the ratio of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$ on deposition rate was not obvious. With increasing the ratio of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$ in plating solution, the content of Fe in the coatings increased; while the Ni content in the coatings decreased with the increase in the ratio of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$. The deposited coating consisted of Fe-Ni alloy phase.

Key words: Fe-Ni alloy; electroplating; ferritic stainless steel; coating

1 Introduction

Solid oxide fuel cells (SOFCs) are electrochemical conversion devices that produce electricity directly from oxidizing a fuel. SOFCs have a wide variety of applications from use as auxiliary power units in vehicles to stationary power generation due to advantages of SOFCs, including high efficiency, fuel flexibility and low emission[1–2]. Interconnect is a critical component of the planar SOFCs stack that separates the oxidant and fuel gases. It can be either a ceramic or metallic material between each individual cell to connect cells in series, so that the electricity generated by each cell can be combined. Because the interconnect is simultaneously exposed to both the oxidizing side and reducing side of the cell at high temperatures, it must be extremely stable. For this reason, ceramics have been more successful in the long term use than metals as interconnect materials. Nevertheless, these ceramic interconnecting materials are very expensive and difficult to process as compared with metals. Metallic materials are becoming more promising as lower temperature (600–800 °C) SOFCs have been developed[3–5]. The most common metallic materials used today are Cr_2O_3 -forming alloys such as ferritic stainless steel (FSS) that has demonstrated to be

thermally stable at high temperatures and have the ability to match the coefficient of thermal expansion (CTE) of adjacent cell/stack components[6–8]. However, the evaporation of chromia grown thermally on FSS might migrate to and poison the cathode, leading to the degradation of the SOFC stack performance. To solve this problem, different coatings have been developed[9–10]. Thermal expansion behavior of Fe-Ni alloys was similar to that of other SOFC components, and oxide scales formed on them in the environment of SOFC cathode possessed high electrical conductivity[11]. So, Fe-Ni alloy coatings are potential to solve this problem of chromia evaporation. After thermal exposure at the environment of SOFC cathode, the oxide scale of the Fe-Ni alloy coatings was expected to block Cr_2O_3 evaporation.

In this study, the Fe-Ni alloy coatings were electroplated on FSS in the electroplating solutions mainly consisting of NiSO_4 and FeSO_4 . The electroplating solution parameters including pH and ratio of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$ as well as cathode current density were investigated to electroplate the Fe-Ni alloy coating on FSS.

2 Experimental

The specimens of 1.5 cm × 1.0 cm × 1.0 mm in size

cut from the ferritic stainless steel sheet (main composition in mass fraction: 16.4% Cr, 0.28% Si, 0.13% Mn and balance Fe) were ground to 1 000 grit using SiC sand papers and then were ultrasonically cleaned in acetone, followed by rinsing at 60 °C in the solution of 20% NaCO₃ (mass fraction) and 10% H₂SO₄ (mass fraction), respectively. The clean stainless steel sample was used as cathode. Nickel sheet was used as anode. The composition of electroplating solution and the electroplating conditions are listed in Table 1.

Surface morphologies and compositions of the Fe-Ni alloy coatings were examined using scanning electron microscope with an energy dispersive X-ray analyzer (SEM/EDX). The phase structures of the coatings were identified with X-ray diffractometer (XRD).

3 Results and discussion

To study the effect of pH value of plating solution on deposition rate and surface appearance of the Fe-Ni alloy coatings, the pH of plating solution with the ratio of [Fe²⁺] to [Ni²⁺] of 0.4 was adjusted to 4.0, 3.5, 3.0 or 2.5 by adding dilute H₂SO₄. Fig.1 shows the deposition rate of the coating in solutions with different pH values at 60 °C under different cathode current densities. The deposition rate of the coating deposited under 5.5 mA/cm²

slightly increased with pH from 2.5 to 3.5, and then began to decrease. The deposition rate of the coating under higher cathode current densities of 13.5 and 27.0 mA/cm² also slightly increased with increasing pH. However, the coatings deposited in solution with pH 4 began to crack or flake. As shown in Fig.2, the surface of the coating deposited in solution with pH 4 under 5.5 mA/cm² was smooth. Nevertheless, the coating deposited in solution with pH 4 under 13.5 mA/cm² or 27.0 mA/cm² was cracked and peeled. This might be originated

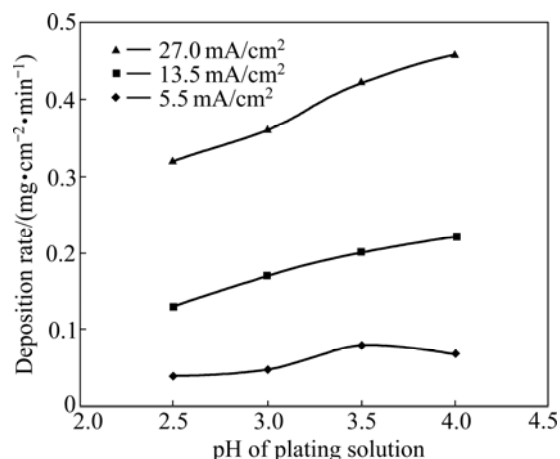


Fig.1 Deposition rate of Fe-Ni alloy coatings electroplated at 60 °C in solution with [Fe²⁺]/[Ni²⁺] of 0.4 under different pH values and different cathode current densities

Table 1 Concentration of chemical reagents and electroplating conditions

Concentration of chemical reagent/(g·L ⁻¹)							Electroplating condition				
Iron() sulfate	Nickel sulfate	Nickel chloride	Boric acid	Sodium citrate	Saccharin	Surfactant	pH	Temperature/°C	Cathode current density/(mA·cm ⁻²)	Ratio of [Fe ²⁺] to [Ni ²⁺]	Time/h
5–20	40	5	10	10	2.5	0.05	2.5, 3.0, 3.5, 4.0	60	5.5, 13.5, 27.0	0.1, 0.2, 0.3, 0.4	1

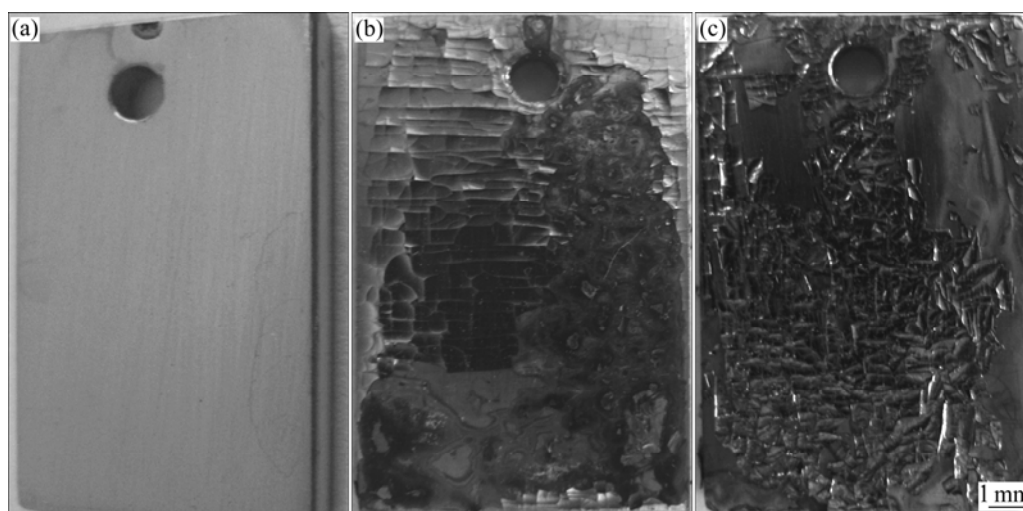


Fig.2 Surface appearances of Fe-Ni coatings deposited at 60 °C in solution with pH 4 and [Fe²⁺]/[Ni²⁺] of 0.4 under different cathode current densities: (a) 5.5 mA/cm²; (b) 13.5 mA/cm²; (c) 27.0 mA/cm²

from higher pH that promoted the formation of $\text{Fe}(\text{OH})_2$ particles on the cathode surface. These particles embedded in the coating subsequently led to the brittlement and cracking/spallation of the coating. Considering quality and deposition rate of the coatings, the electroplating solution with pH 3.5 was chosen.

From Fig.1, it could also be seen that the deposition rate of the coating under higher cathode current density of 13.5 or 27.0 mA/cm^2 was higher than that under lower cathode current density of 5.5 mA/cm^2 . The electro-deposition under further high cathode current density was carried out to study the effect of cathode current density on deposition rate and surface appearances. It could be indicated from Fig.3 that the deposition rate of the coating increased with the increase in cathode current density. However, the surface of the coating deposited under 41 or 57 mA/cm^2 was not as smooth as that deposited under 27 mA/cm^2 . As shown in Fig.4(a), the surface of the coating deposited under 27 mA/cm^2 was very smooth. There were some nodules on the surface (especially on the edges of the samples) of the coatings deposited under 41 mA/cm^2 (Fig.4(b)) and 57 mA/cm^2 (Fig.4(c)). Although the higher cathode current densities accelerated deposition rate, the quality of the coatings became worse due to fast deposition rate. So, the cathode current density of 27 mA/cm^2 was suitable for deposition.

Fig.5 shows the deposition rate of the coatings deposited in solution with different ratios of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$ and pH 3.5 under 27 mA/cm^2 . The deposition rate of the coating in solution with $[\text{Fe}^{2+}]/[\text{Ni}^{2+}]$ of 0.1 was slightly higher than that in the solution with the ratios of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$ of 0.2, 0.3 or 0.4. No obvious differences were found in deposition rate for coatings in solutions

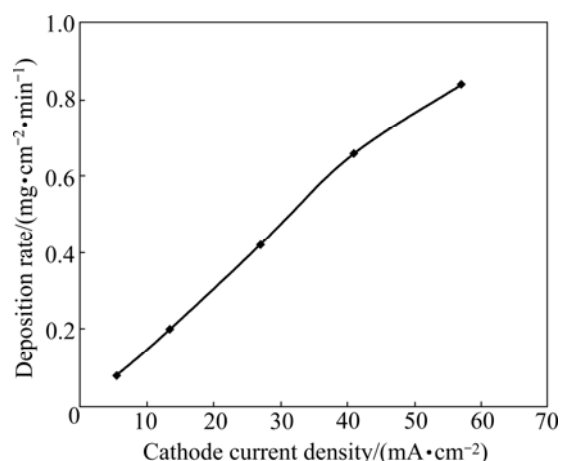


Fig.3 Deposition rates of Fe-Ni coatings deposited at 60 °C in solution with pH 3.5 and $[\text{Fe}^{2+}]/[\text{Ni}^{2+}]$ of 0.4 under different cathode current densities

with $[\text{Fe}^{2+}]/[\text{Ni}^{2+}]$ of 0.2, 0.3 and 0.4. The appearances of the coatings deposited in solutions with different ratios of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$ are similar and smooth. The difference was that the contents of Fe in the coatings increased with increasing the ratio of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$, while Ni contents in the coatings decreased with increase in the ratio of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$. Fig.6 shows Fe and Ni contents detected by EDX in the coatings deposited at 60 °C in pH 3.5 solution with different ratios of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$. When the ratio of $[\text{Fe}^{2+}]$ to $[\text{Ni}^{2+}]$ was 0.4, the composition of the coating was close to Fe-60Ni (mass fraction, %) which was suitable candidate for intermediate temperature solid oxide fuel cell interconnect application among Fe-Ni alloys[11].

Fig.7 shows the XRD patterns of the substrate and the coating deposited at 60 °C in pH 3.5 solution with

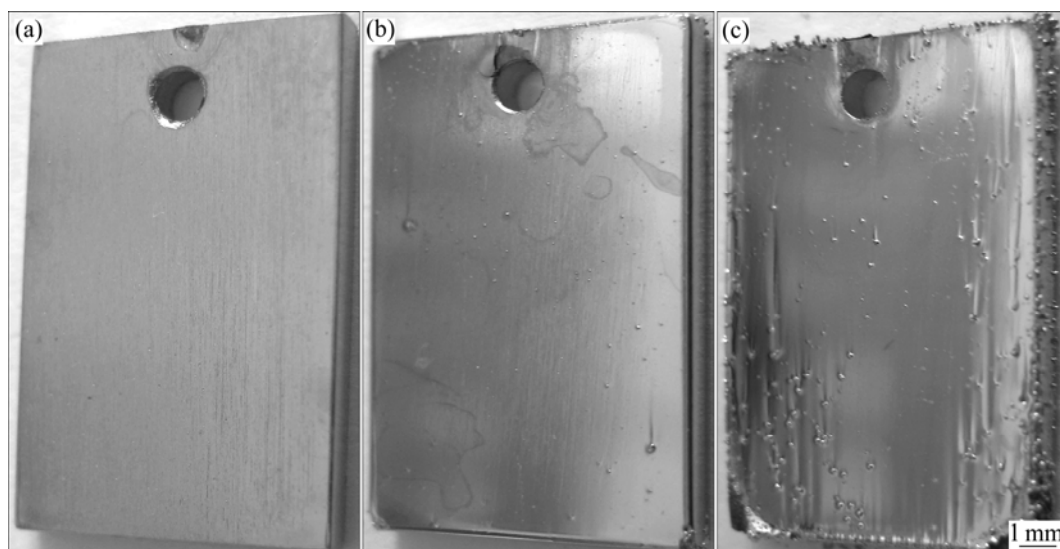


Fig.4 Surface appearances of Fe-Ni coatings deposited at 60 °C in solution with pH 3.5 and $[\text{Fe}^{2+}]/[\text{Ni}^{2+}]$ of 0.4 under different cathode current densities: (a) 27 mA/cm^2 ; (b) 41 mA/cm^2 ; (c) 57 mA/cm^2

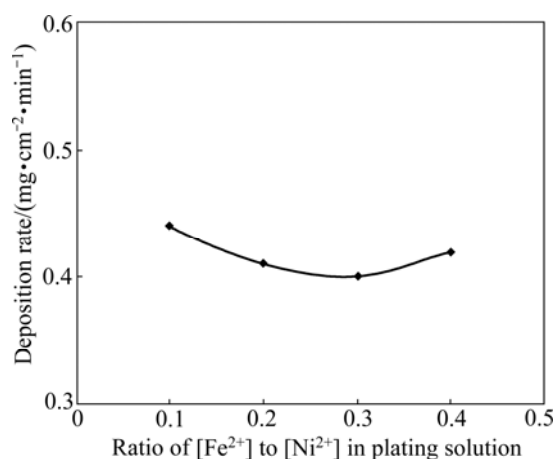


Fig.5 Deposition rate of Fe-Ni coatings at 60 in solution with different ratios of $[Fe^{2+}]$ to $[Ni^{2+}]$ and pH 3.5 under 27 mA/cm^2

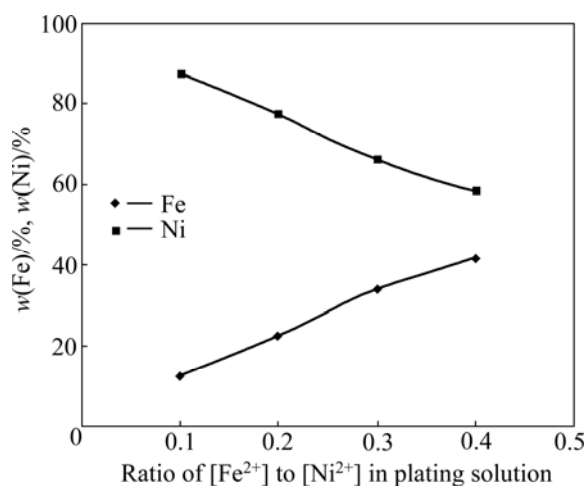


Fig.6 Fe and Ni contents of coatings deposited at 60 in solution with pH 3.5 and different ratios of $[Fe^{2+}]$ to $[Ni^{2+}]$ under 27 mA/cm^2

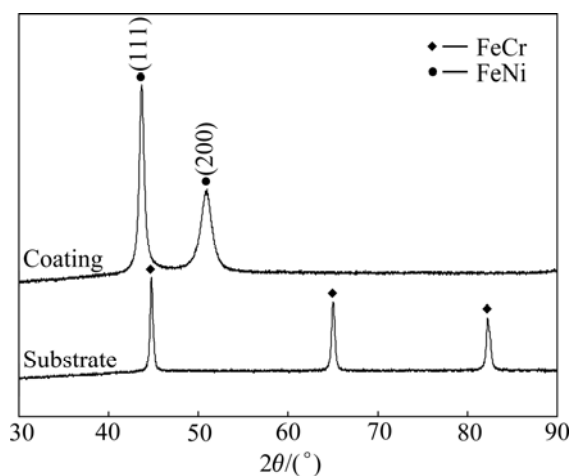


Fig.7 XRD patterns of stainless steel substrate and coating deposited at 60 in pH 3.5 solution with $[Fe^{2+}]/[Ni^{2+}]$ of 0.4 under 27 mA/cm^2

$[Fe^{2+}]/[Ni^{2+}]$ of 0.4. The substrate was composed of Fe-Cr alloy phase and the coating consisted of Fe-Ni alloy phase. A preferred orientations of (111) and (200) were found, which resulted from the addition of saccharin in electroplating solution[12]. The surface morphology of the coating was observed using SEM. As shown in Fig.8, the coating with composition of Fe-60Ni was very dense.

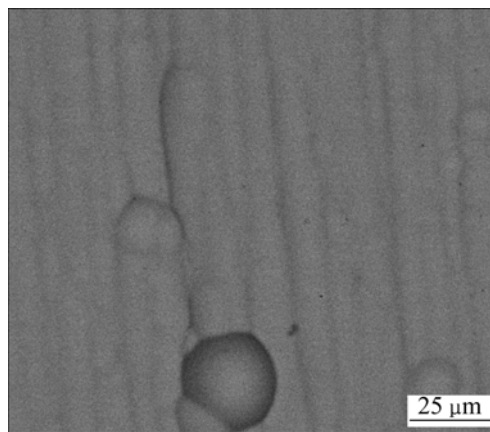


Fig.8 SEM surface morphology of coating deposited at 60 in pH 3.5 solution with $[Fe^{2+}]/[Ni^{2+}]$ of 0.4 under 27 mA/cm^2

4 Conclusions

1) Under 5.5 mA/cm^2 , the deposition rate slightly increased with increasing pH from 2.5 to 3.5. When the pH was 4.0, the deposition rate began to decrease. The deposition rate increased with pH increasing under higher cathode current densities of 13.5 and 27 mA/cm^2 . The coating deposited in solution with pH 4 under 13.5 or 27 mA/cm^2 began to crack and flake.

2) The deposition rate also increased with the increase in cathode current density. However, the surface of the coatings deposited under 41 or 57 mA/cm^2 appeared in nodules.

3) Under 27 mA/cm^2 , there were not obvious differences on deposition rate and surface appearances when the ratio of $[Fe^{2+}]$ to $[Ni^{2+}]$ in pH 3.5 solution was changed from 0.1 to 0.4. As the ratio of $[Fe^{2+}]$ to $[Ni^{2+}]$ increased, the content of Fe in the coatings also increased. The deposited coatings were composed of Fe-Ni alloy.

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(Edited by YANG Bing)