Structure and properties of composite Ni-Co-Mn coatings on metal interconnects by electrodeposition

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Abstract: In order to obtain the high conductivity values and wide spinel stability region for solid oxide fuel cell interconnect, several multilayer Ni, Co and Mn coatings are electroplated and then oxidized in air to form spinel oxide layers. Potentiodynamic polarization curves in different simple solutions are tested to analyze the deposition behavior of Co and Mn. Microstructures and compositions of Ni-Co-Mn multi-layers by adjusting the thickness and deposition parameters are analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that area specific resistance value of sample B-Ni/Co after oxidation at 750°C for 500h is the lowest among the coatings, and the resistance values at 700°C and 800°C are 35.3 and 31.7 mΩ·cm², respectively. When the Ni transition layer in the vicinity of coating/substrate interface is thick, it will lead to the outward diffusion and aggregation of element Fe to form Fe-rich oxide intermediate layer, which will affect the high-temperature performance of the coating. Pure Co and CoMn alloy coatings with a certain thickness can effectively prevent the inward diffusion of oxygen and the outward diffusion of Fe and Cr at high temperature. The thin Ni transition layer combined with the thick Co layer or CoMn layer has the best element diffusion inhibition and high temperature electrical properties during the long-term high-temperature oxidation process.

Keywords: electrodeposition; multilayers; oxidation; Ni-Co-Mn

1 Introduction

With the development of solid oxide fuel cell (SOFC) technology, the operating temperature of SOFC has dropped to 600-800°C, which makes the use of metal interconnects possible. Ferritic stainless steel, which has a low cost and is compatible with thermal expansion coefficient of other components, is considered to be the most promising interconnect material. However, ferritic stainless steels suffer from severe oxidation which leads to an increase in electrical resistance. And the battery performance degrades or even fails because of cathode Cr poisoning due to the formation of volatile Cr-containing medium by the protective Cr_2O_3 film. The conductive oxide coatings prepared on ferritic stainless steel have received extensive attention, especially for Cr-free spinel coatings such as Co-Mn[1-4], Mn-Cu[5,6] and Ni-Co[7,8], because they are relatively simple, effective and low in cost.

Spinel coating has the high conductivity, and its thermal expansion coefficient is matching with ferritic stainless steel. Therefore it shows good application prospects to reduce the growth of Cr_2O_3 film on stainless steel[9-11]. The electroplating method for spinel coatings is to pre-deposit a metal or alloy layer on a stainless steel substrate, and then to form a spinel coating by high temperature oxidation treatment. The relatively dense coatings can be prepared on a complex substrate and the thickness of coating is controllable.

At present, the research mainly focuses on three aspects, namely, the deposition of Ni, Mn and Co metal multi-layer[12], the composite deposition of Co-Mn₃O₄ layer[13] and Ni-Mn₃O₄ layer[7], and Ni-Co-Mn alloy co-deposition[14,15]. Wu[16] successfully prepared Co and Co-Mn alloy layers by direct current and pulse methods. After the on-cell tests the top layer of coated interconnects is mainly (Mn,Co,Fe)₃O₄ spinel. Co and Co-Mn coatings both prevent the diffusion of Cr, but thin pure Co coating accelerates interfacial oxide Cr_2O_3 and (Mn,Cr)₂O₄ growth and Co-Mn coating suppress interfacial oxide growth even if it is thin. Apelt[13] synthesized

composite coatings containing Co and Mn_3O_4 particles using the electrolytic codeposition process. The concentration of Mn_3O_4 particles incorporated into Co matrix will increase to 13 vol.% at high pH values.

However, since the standard potential of Co^{2+}/Co in aqueous solution is much larger than that of Mn^{2+}/Mn at 25°C , it is difficult to achieve Co-Mn alloy co-plating. Karpuz[17] used electrochemical method to prepare Co-Mn co-deposited coating. It is found that Mn concentration of the electrolyte solution, pH value and other parameters have little effect on the Mn content in the deposited Co-Mn coating, and the Mn content was about at 0.5-2 at.%. Zhang[15] obtained Co-Mn alloy coatings with a high Mn content (25 at.%) in a chloride plating solution using EDTA as a complexing agent. Alloy coatings after oxidation transform into the dense and well-bonded MnCo_2O_4 spinel layer. However, as the deposited Mn content increases, Co-Mn alloy coatings are still not uniform enough. The Cr-rich film formed between spinel layer and substrate tends to thicken during oxidation, which will increase the contact resistance.

Therefore, multilayer metallic coatings were electroplated to substitute for Co-Mn co-deposited coatings. Joshi[18] electroplated Ni/Cu/Mn multilayers then oxidized in air at 800°C . The results showed that high conductivity values and wide spinel stability region were obtained for Ni-Cu-Mn-O spinel at the low temperature. Coatings provide good corrosion protection and the thickness of interfacial chromium oxide was less than $1\text{ }\mu\text{m}$ after oxidation. In this study, Ni-Co-Mn multilayers are electroplated in different solutions to analyze the deposition behavior of Co and Mn and to also explore the high temperature behavior of Ni-Co-Mn composite coatings.

2 Materials and methods

The 430 stainless steel is used as the substrate with a size of $15\text{ mm}\times 15\text{ mm}\times 3\text{ mm}$. The chemical composition is 16-18 Cr, 1 Mn, 0.12 C, 0.75 Si, 0.03 S, 0.06 Ni, 0.04 P, and balance Fe (wt. %). The substrate is polished with SiC papers up to 1000 grits, and ultrasonically cleaned in acetone at 60°C for 10 mins, and then stored in a 99.9%

alcohol solution to prevent surface oxidation.

Before plating, 430 SS is placed in a mixed acid solution of 5 wt.% HNO_3 + 25 wt.% HCl at room temperature to remove the surface oxide film, and then activated in a 15 wt.% H_2SO_4 solution at 35°C for 1 min. After 430 SS rinsed with deionized water, A Ni layer is pre-plated on its surface in the electrolyte solution (240 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 320 ml/l HCl) to enhance bonding between the coating and the substrate. The current density of pre-plating Ni is $50 \text{ mA} \cdot \text{cm}^{-2}$ and the deposition time is 2 mins.

A high purity graphite electrode slab is placed in the electroplating system as the anode, and the anode area is twice that of 430 SS specimen in order to reduce the polarization effect. An ITECH-6720 DC source is used as power supply. The bath composition and electroplating parameters for nickel, cobalt and manganese deposition is showed in table 1, which is the same as reference[16,19,20]. The Ni layer is coated firstly, followed by Co, and then by Mn. The different deposition time is carried out for the Ni and Co layers. Samples A, B, C, D and E in table 2 are named by the different electroplating parameters of Ni/Co layers (A,B), Ni/Co/Mn layer (C), Ni/Co/Ni/Co/Mn layer (D) and Ni/CoMn layer (E), respectively. The electrochemical measurements are carried out using CHI600E system (CH Instruments, Shanghai, China) in the electroplating solution with a three-electrode electrochemical cell. Platinum and saturated calomel electrodes (SCE) are employed as the counter electrode and the reference electrode, respectively.

A heat treatment for dehydrogenation in the horizontal tube furnace (Hengli-CHLZG, Luoyang, China) is conducted before the thermal oxidation experiments. After purging the reactor, the Ni/Co/Mn coated substrates are heated up slowly and hold at 650°C for 2h in the high-purity Ar atmosphere, and the Ar flowrate is monitored by using a rotameter.

The high temperature oxidation behavior of coated 430 SS is measured at 750 °C in air for 2h, 100h, 300h, and 500h, respectively. The samples are suspended in the constant temperature zone of a tube furnace, and then are

heated up. After oxidation, samples are taken out from the furnace and directly cooled to room temperature (RT).

The area specific resistance (ASR) measurement of oxide coatings is implemented based on the four-probe DC method at the temperature of 500°C-800°C. Test of details has been described in previous articles[2,21,22].

The surface morphology and cross-section morphology are observed by scanning electron microscopy (SEM) (JSM-5800, JEOL, Tokyo, Japan) and the specimens are embedded into a cold-setting epoxy resin. Energy dispersive X-ray spectroscopy (EDS) (JEOL, Tokyo, Japan) is used to analyze elemental homogeneity in different coatings. Crystallographic information of metal coatings and oxide coatings is examined by X-ray diffraction (XRD) analysis (D/MAX-3B, Rigaku Co., Tokyo, Japan).

3 Results and discussion

3.1 Potentiodynamic polarization

In order to analyze the deposition behavior of Co and Mn, potentiodynamic polarization curves with a scan rate of 5 mV s^{-1} in different solutions are tested (Fig.1). The plateaus in potentiodynamic curves are corresponding to the peak of ion reduction reaction. Fig.1a shows Co^{2+} deposition potential is about -0.79V in CoSO_4 solutions and Mn^{2+} deposition potential is about -1.10V. But the ions reaction starts at about -0.68V in mixed CoSO_4 and MnSO_4 solution, and the composition of deposited coating is almost pure Co based on subsequent component analysis. Fig.1b shows potentiodynamic behaviors in mixed CoSO_4 and MnSO_4 solution with different pH values. As the pH sequentially increases from 2 to 4.5, the potential of each reduction reaction shows an overall trend of shifting in the negative direction. When pH=2, the reduction reaction potential of H^+ rises, accompanied by a large amount of hydrogen bubbles. When the pH value increased to 3, the reduction reaction potential of Co^{2+} is almost unchanged.

Fig.1c shows when the concentrations of sodium gluconate change from 0.1 to 0.7 mol/l, the deposition potentials of the corresponding Co^{2+} ions gradually decrease. There is no limited diffusion current density on the

curves, which is caused by the diffusion of Co^{2+} ions. Gluconate is used as the complex agent to form complex Co^{2+} ions, and the deposition potential of Co^{2+} ions shifts to the negative direction. Gluconate has less effects on the deposition potential of Mn^{2+} ions than that of Co^{2+} ions, when the gluconate concentration is low[23,24]. Gluconate concentration appropriate in mixed solution is beneficial to Co and Mn co-deposition.

3.2 Characteristics of deposited coatings and thermal growth coatings

Fig.2a displays Arrhenius plots of ASR/T vs. $10^3/T$ for alloy coatings after oxidation at 750°C for 100h. The ASR values of all oxide films decrease linearly with temperature increasing, which is consistent with the semiconductor behavior of oxide coatings[25,26]. But there is a slight deviation from the linear law for samples C-Ni/Co/Mn and B-Ni/Co. The electrical conduction of the spinel oxide is concluded to be controlled by the small polaron hopping mechanism[26,27]. When oxide scales are the spinel oxides, the ASR values should be linear with a function of temperature. Obviously, the thermal growth oxides of samples B and C are not simple spinel oxides after oxidations for 100h but composite oxides. So the ASR for 100h deviates from the linear law as a function of temperature. With the extended oxidation time the composite oxides growing uniformly, the ASR values should close to linear law with a function of temperature.

Fig.2b shows the ASR values of oxide films between the temperature 500°C and 800°C . ASR of all coatings is lower than that of 430 SS after oxidation for 100h. ASR of samples E-Ni/CoMn, C-Ni/Co/Mn, and B-Ni/Co is relatively low, especially for sample B-Ni/Co. The ASR values are $25.2 \text{ m}\Omega\cdot\text{cm}^2$ at 600°C , $16.6 \text{ m}\Omega\cdot\text{cm}^2$ at 700°C and $15.2 \text{ m}\Omega\cdot\text{cm}^2$ at 800°C , respectively, which exhibits the best electrical conductivity among coatings in the range of $500\text{--}800^\circ\text{C}$.

ASR is related to electrical conductivity of thermally grown oxide layers, and also related to the thickness of oxide layers. Fig.3 is the average thickness of electrodeposited samples oxidized at 750°C for 0h, 100 h and 500h.

The deposition time of sample A-Ni/Co is 4 mins for Ni layer and 10 mins for Co layer, so it is thinner than other samples. The deposition thickness of sample E-Ni/CoMn is also thin about 3.5 μm , because the Co^{2+} concentration in mixed CoSO_4 and MnSO_4 solution is low and it is difficult for Mn^{2+} ion to electrodeposit in aqueous solution. Sample D possesses the multi-layer plating with the double Ni layers and double Co layers, so it is thick. The thickness of samples B-Ni/Co and C-Ni/Co/Mn increases with the Ni and Co deposition time increasing compared to that of sample A-Ni/Co. After oxidation for 100h and 500h, the average thickness of samples B, C and D is about 20 μm -25 μm .

Fig.4 shows the surface morphology and cross section morphology of the electroplated alloy layers on 430 SS. Samples A and B are both Ni/Co electrodeposited multilayers, in which the deposition parameters of Ni and Co layers are the same except for the deposition time, so there is a thinner Ni layer and a thinner Co layer in the sample A. The surface of samples A and B is relatively smooth with the composition of pure cobalt, and only the local area is convex. The EDS line scan of cross section shows that sample B has a distinct two-layer structure, the inner layer Ni and the outer layer Co, and the thickness of two layers is about 4 μm and 9 μm , respectively. Alloy coatings are compact and excellent adhesion to the stainless steel substrate and no obvious boundary is between the Ni layer and the Co layer.

The sample C-Ni/Co/Mn has a Mn-rich surface layer with a small amount of Co. The Mn content is approximately 95.1 at.%. The surface morphology shows a nano-sheet Mn aggregate structure. Because the Mn layer is relatively thin, the EDS line scan of cross section cannot detect a distinct Ni/Co/Mn three-layer structure but a two-layer structure. Compared with sample B, the alloy layer in the sample C is significantly thinner, which is related to the variation of Ni deposition time. Sample D is a composite multilayer structure and the Mn surface layer is the similar to sample C. Some granular Mn deposits are also found on the surface. The line sweep of cross section shows the double Ni layers and the double Co layers. Sample E-Ni/CoMn is a CoMn co-deposited layer at a

current density of $200 \text{ mA}\cdot\text{cm}^{-2}$, which exhibits a spherical deposition morphology with some microcracks and defects on the surface. The surface composition of sample E is Mn 3.1 at.% and Co 96.9 at.%. The line scan of cross section shows that the outer layer of the coating is mainly a Co metal layer containing a small amount of Mn. Corresponding to Fig.3, sample E is thinner compared to other coatings B, C and D, and sample A is the thinnest.

The surface and cross-sectional morphology of the electrodeposited alloy coatings oxidized at 750°C for 100 h is shown in Fig.5. Sample A-Ni/Co coating mainly produces Co-rich oxide on the surface. Combined with EDS analysis in table 4, the element Fe and Cr contents are 4.7 at.% and 1.6 at.%, respectively. Fig.5(a₂) shows that the oxide film of sample A is very thin, and the average thickness is about $4.5\mu\text{m}$ in combination with Fig.3. A thick Cr-rich oxide layer forms between the oxides and stainless steel, and also some diffusion voids appear in the oxide/substrate interface and the Co-rich oxide layer. According to the results of line scan, the elements Fe and Cr in the substrate diffuse outward and are enriched in the outermost oxides. No Ni-rich oxides are detected in the oxide layer, and the metal Co in the coating diffuses into the stainless steel substrate.

Some micro-pores are evenly distributed in the oxides on sample B-Ni/Co surface after oxidation, which is the typical morphology of Co_3O_4 oxides because element Co diffusion could not keep up with the formation of new scale on the surface [28,29]. EDS analysis in table 4 shows that a small amount of Ni and Fe oxides are found on the surface. The cross-sectional morphology reveals that the interface Cr oxides is significantly thinner than that in the sample A, and the overall thickness of oxides increases. The EDS line scan on cross-section indicates that the outermost oxides are mainly Co oxides. And then the Fe-rich middle layer is detected between the Ni and Co oxide layers, indicating that element Fe in the substrate is mainly concentrated under Co oxides after outward diffusion. The metal Ni in the coating also diffuses into the stainless steel substrate. Sample C-Ni/Co/Mn exhibits a spinel oxide morphology on the surface[6,21] due to the outermost Mn electrodeposited layer. The cross-sectional morphology and line sweep results of sample C are different with that of sample B. The middle layers of dark phase

Fe oxide and light phase Ni oxide are not found.

The spinel oxide morphology is also found on sample E-Ni/CoMn surface. Fig. 5(d₂) shows that the oxide layer is relatively thin and loose with a certain amount of Mn oxide. The Cr-rich oxide intermediate layer of sample E is thicker than that of samples B and C, but thinner than that of sample A.

3.3 Scale composition and area specific resistance for a long oxidation time

X-ray diffraction of coatings on 430 SS after oxidation at 750°C for 2h, 100 h and 500h are showed in Fig.6. Since sample A is relatively thin and elements Fe/Cr in the substrate significantly diffuse outward after oxidation, and sample E is relatively loose, the high temperature performance of these two samples for 500h are not tested here. The surface products of sample B in the initial oxidation stage (2h) are mainly Co₃O₄ and CoO. As the oxidation time is extended to 100h and 500h, the products are only Co₃O₄ oxides. The surface products of sample C in the initial oxidation stage are mainly Mn₃O₄, Co₃O₄ and CoO. With the reaction time increasing to 100h CoO oxides change into Co₃O₄, and Mn₃O₄ concentration decreases. In comparison with the oxidation products for 100h, a small amount of NiFe₂O₄ forms for 500h, which indicates that a part of Fe and Ni outward diffuses. Sample D is similar to sample C after oxidation at 750°C for 0h and 100h. However, after oxidation for 500 h more NiFe₂O₄ spinel phases are detected on the surface of sample D.

Arrhenius plots of ASR/T vs. 10³/T for the three coatings oxidized at 750°C for 500h are showed in Fig.7. Compared with the oxidation for 100h, Arrhenius plots show that the linear deviation of resistance with a function of temperature for samples B, C and D is reduced, and the slope also decreases. The resistance values of sample C increase slightly after 500h oxidation. With the extension of oxidation time, the area specific resistance of sample D significantly increases, especially in the low temperature 500°C. ASR values of sample B are the lowest, and the resistance values at 700°C and 800°C are 35.3 mΩ·cm² and 31.7 mΩ·cm², respectively.

Cross section morphology and EDS analysis of samples B, C and D after oxidation at 750°C for 500h are also showed in Fig.7. The thickness of the oxide layers of samples B, C and D after oxidation for 500h is almost the similar according to Fig. 3. However, the cross-sectional morphology and oxide products are significantly different, which is the reason for the difference in ASR between the three coatings. Figs.7(a₁) and (a₂) show that the oxide layer of sample B-Ni/Co is uniform, compact, and has excellent adhesion to 430SS substrate and only a very thin Cr oxide layer forms on the interface. Figs.7(b₁) and (b₂) reveal that the oxide products of sample D are the multi-layer structure, namely Cr-rich(dark zone), Ni-rich (light zone), Fe-rich(dark zone) and Co-rich oxide layers from the extreme inner part of scale to the outer part. Figs. 7(c₁) and (c₂) show that the oxide layer of sample C is a two-layer structure, a Cr-rich inner layer and a Co-rich outer layer, in which some isolated micro-pores and defects are found. There are no Mn and Ni enrichment zones in the oxide layer, and element Co diffuses into the stainless steel substrate during the oxidation process.

3.4. Discussion

In this study, the various composite coatings of Ni, Co, and Mn are prepared, and the structure and properties of different coatings are studied by adjusting the thickness and deposition parameters. Fig.8 is a schematic diagram of the evolution for the designed coatings during the high temperature process. The interface Ni metal plating can improve the bonding strength between the Co or CoMn layer and substrate, but the thickness control of Ni interface layer will affect the element diffusion and the high temperature performance of the whole coatings.

When the Ni layer and the Co layer in the Ni/Co coatings are both thin, such as sample A, after oxidation for 100h Ni simultaneously diffuses into the substrate and the Co layer, and no Ni-rich oxide layer forms. The thin Co oxide layer is difficult to suppress the inward diffusion of oxygen from the atmosphere, and a thick Cr-rich oxide layer forms at the coating/substrate interface (Fig.8b₁). When the oxidation time is extended, an intermediate oxide

layer of Fe-rich also forms (Fig. 8c₁). The thick Cr₂O₃ and Fe oxide layer will increase ASR of the Ni/Co coatings, which is not conducive to the long-term high temperature service of the coatings.

When the thickness of the Ni and Co deposit layers increases, such as sample B, the thick Co oxides effectively suppress the diffusion of oxygen and the growth of Cr₂O₃. A part of Ni diffuses into the substrate, and a part of Ni forms a Ni-rich oxide layer (Fig. 8b₂). At the same time, element Fe in the substrate diffuses outward and a Fe-rich oxide layer forms between the Ni-rich and Co-rich oxide layers. This indicates that Co oxides are more effective than Ni oxides in suppressing Fe out-diffusion.

When the Ni deposition layer is still thin and only the thickness of the Co deposition layer increases, such as sample C, the formation of thick Co oxides is still effective in inhibiting oxygen diffusion and Cr₂O₃ growth at the interface. The difference is that no Ni-rich oxide layer is detected after the diffusion of the elements at high temperature (Fig. 8b₃), and also no Fe-rich oxide intermediate layer forms. The electrodeposited Mn layer of sample C is relatively thin, so only some oxides containing Mn₃O₄ on the surface is found, and no MnCo spinel forms.

When both the Ni and Co layers are thin, the thickness of coatings increases by repeatedly depositing the Ni and Co layers, as shown in sample D. After oxidation, the composite Ni and Co oxide layers are still thick enough to suppress the Cr₂O₃ growth at the coating/substrate interface. During the oxidation process elements Ni and Co diffuse into the stainless steel substrate, and Fe also forms a Fe-rich intermediate layer in the oxide. After a long period of oxidation, the two Ni layers are combined to form a Ni-rich oxide layer (Fig. 8c₃). The high-temperature behaviors of the electrodeposited Mn layer in sample D are the similar to those in sample C.

When CoMn is co-deposited, it is difficult to obtain the Co and Mn co-deposited layer with a high Mn content because of the large reduction potential difference between the two elements in aqueous solution. The thickness of CoMn alloy layer prepared is slightly thinner than other coatings, such as sample E. The oxidation products are thin and porous, however, thin CoMn composite oxides could better inhibit the growth of Cr₂O₃ at the coating/substrate

interface than thin Ni/Co oxides (sample A).

When the oxide layer remains a double-layer structure after the long-term oxidation (Fig.8c₂), a thin Cr₂O₃ inner layer and a thick Co (Mn) oxide outer layer, the oxide coatings will have the good high temperature conductivity. When the multilayer structure appears in the oxide scales, such as the formation of Ni or Fe oxide layers, the high temperature conductivity of multilayers will decrease.

4 Conclusions

In this study, several composite coatings of Ni, Co and Mn are prepared, and the structure and properties of different coatings at high temperature are studied by adjusting the deposition composition and thickness. The Ni transition layer on the coating/substrate interface effectively increases the adhesion of composite coatings. But if the Ni layer is too thick, it will lead to the outward diffusion and aggregation of element Fe to form Fe-rich oxide intermediate layer, which will affect the high-temperature performance of the coating. Pure Co and CoMn alloy coating with a certain thickness can effectively prevent the inward diffusion of oxygen and the outward diffusion of Fe and Cr at high temperature. Ni/Co coating with multiple deposition layers, although the thickness of the coating increases, the thick Ni oxide layer will lead to the degradation of the oxidation resistance and electrical conductivity of the coating at high temperature. The results show that the thin Ni layer combined with the thick Co or CoMn layer has the best element diffusion inhibition and high temperature electrical properties during the long-term high-temperature oxidation process, and has a good prospect for SOFC application.

Acknowledgements

This work was financially supported by China Scholarship Fund (2017), research fund of Jiangsu University of Science and Technology (1624821607-5) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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Table1 Electroplating parameters for nickel, cobalt and manganese deposition[16,19,20]

conditions	Ni	Co	Mn	Co-Mn
Bath composition, mol/l	0.30NiSO ₄ ,			0.50 MnSO ₄ ,
	0.50Na ₂ SO ₄ ,	0.80CoSO ₄ ,	0.40MnSO ₄ ,	0.10 CoSO ₄ ,
	0.30 NH ₄ Cl,	0.32H ₃ BO ₃ ,	0.10 (NH ₄) ₂ SO ₄ ,	1.0 H ₃ BO ₃ ,
	0.24 H ₃ BO ₃	0.027 Saccharin Sodium	0.03 NH ₂ OH·HCl	0.50 gluconate, 0.1 (NH ₄) ₂ SO ₄
PH	~3.5	~3.5	~3.0	~3.0
Temperature, °C	25	25°C	25°C	25°C
Current density, A·cm ⁻²	25	20	200	200
Deposition time, min	4, 12	8, 10, 20	20	20
Stirring rate, r/min	360	450	400	400

Table 2 Electroplating parameters for samples A-E in in different solutions

Sample	Ni	Co	Ni	Co	Mn
A-Ni/Co	25 mA·cm ⁻² , 4 mins	20 mA·cm ⁻² , 10 mins	-	-	-
B-Ni/Co	25 mA·cm ⁻² , 12 mins	20 mA·cm ⁻² , 20 mins	-	-	-
C-Ni/Co/Mn	25 mA·cm ⁻² , 4 mins	20 mA·cm ⁻² , 20 mins	-	-	200 mA·cm ⁻² , 20 mins
D-Ni/Co/Ni/ Co/Mn	25 mA·cm ⁻² , 4 mins	20 mA·cm ⁻² , 8 mins	25 mA·cm ⁻² , 10 mins	20 mA·cm ⁻² , 8 mins	200 mA·cm ⁻² , 20 mins
E-Ni/CoMn	25 mA·cm ⁻² , 4 mins	Co-Mn co-deposition, 200 mA·cm ⁻² , 20 mins

Fig.1 Potentiodynamic polarization curves in different solutions
 (a) 0.1 mol/l $CoSO_4$, 0.5 mol/l $MnSO_4$ and (0.1 mol/l Co, 0.5 mol/l Mn) SO_4 solutions
 (b) various pH values in (0.1 mol/l Co, 0.5 mol/l Mn) SO_4 solution
 (c) various gluconate concentrations in (0.1 mol/l Co, 0.5 mol/l Mn) SO_4 solution

Fig.2 ASR measurement as a function of temperature for samples after oxidation at 750 $^{\circ}\text{C}$ for 100h

Fig.3 Average thickness for samples by different electroplating parameters oxidized at 750°C for 0h, 100 h and 500h, respectively

Fig.4 Surface morphology and cross section of the electroplated alloy layers on 430 SS

(a₁) (a₂) sample B-Ni/Co, (b₁) (b₂) sample C-Ni/Co/Mn, (c₁) (c₂) sample D-Ni/Co/Ni/Co/Mn, (d₁) (d₂) sample E-Ni/CoMn

Fig.5 Surface morphology and cross section of alloy layers of 430 SS after oxidation at 750°C for 100 h
(a1) (a2) (a3) sample A-Ni/Co, (b1) (b2) (b3) sample B-Ni/Co, (c1) (c2) (c3) sample C-Ni/Co/Mn, (d1) (d2) (d3) sample E-Ni/Co/Mn

Table 3 Elemental composition (at.%) of the surface of samples after oxidation at 750°C for 100 h

elements	Co	Mn	Ni	Fe	Cr	O
A-Ni/Co	38.7	-	-	4.7	1.6	55.0
B-Ni/Co	51.3	-	2.7	1.2	0.6	44.2
C-Ni/Co/Mn	36.4	0.7	3.5	4.0	0.6	54.8
E-Ni/Co/Mn	21.7	18.5	-	3.3	3.9	52.6

Fig.6 X-ray diffraction of alloy layers on 430 SS after oxidation at 750°C for 2h, 100 h and 500h
 (a) sample B-Ni/Co, (b) sample C-Ni/Co/Mn, (c) sample D-Ni/CoNi/Co/Mn

Fig.7 ASR values vs. temperature and SEM morphology for 430 SS and coated-430 SS after oxidation at 750°C for 500 h.

ASR: 1 sample 430 SS, 2 sample D-Ni/Co/Ni/Co/Mn, 3 sample C-Ni/Co/Mn, 4 sample B-Ni/Co

SEM morphology: (a1) (a2) sample B-Ni/Co, (b1) (b2) sample D-Ni/Co/Ni/Co/Mn, (c1) (c2) sample C-Ni/Co/Mn

Fig.8 Schematic drawing of oxidation behavior for the different alloy layers by electrodepositing