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Properties of electrodeposited Ni-S(La) coatings ①

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[Abstract] Ni-S(La) coatings were obtained by electrodeposition in a typical Watt bath by adding $CS(NH_2)_2$ and $LaCl_3$. The minimum HER overpotential is 75 mV. The corresponding electrochemical parameters (Tafel slope b, exchanging current density J_0) were obtained by measuring the steady-state polarization curves. The content of S, La in the coating and its structure were measured by EPMA and XRD. The results show that there is no lanthanum in such coating and its structure is amorphous. From the anodic polarization curves, it is shown that the corrosion resistance of coating is very good. Based on the cathodic polarization curves during electrodeposition, it is found that $LaCl_3$ is benefit for amorphous coating structure to form.

[Key words] rare earth; electrodeposition; Ni-S alloy; HER
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1 INTRODUCTION

Electrolysis in alkaline solution is an ideal technique to produce hydrogen. However, the high hydrogen overpotential (h. o. v.) of cathode often limits the application in large scale. At present, the cathodes applied in industry for hydrogen evolution reaction (HER) are ferrous (h. o. v. 380 mV) and electrodeposited nickel coating (h. o. v. 480 mV) which results in consuming large quantities of electrical energy[1]. During the past twenty years, electrodeposited Ni-S coating, produced by adding NH_2CSNH_2 (TU)[2~4], KSCN[5], NaSCN[6] or $Na_2S_2O_3$[7] into a typical Watt bath, was explored to replace the electrodes described above in view of its excellent electrocatalytic property for HER (the minimum h. o. v. is 90 mV under industrial conditions). But there exist some disadvantages, such as the loss of sulphur during electrolysis, the decrease of adhesion of coating with substrate, which influence its service life.

It has been proposed that, because there exists a special composition of electronic shell in rare earth (RE), the RE ion can adsorb on the surface of electrode though it never electrodeposits in aqueous solutions. So the course of electrodeposition must be influenced to some extent[8]. In present research work, $LaCl_3$ is added in Ni-S electroplating bath to improve the properties of Ni-S coating.

2 EXPERIMENTAL

The composition of the bath determined by orthogonal experiments was described as follows: $NiSO_4 \cdot 7H_2O$ (AR) 200 g/L, $NiCl_2 \cdot 6H_2O$ (AR) 40 g/L, H_3BO_3 (AR) 35 g/L, $CS(NH_2)_2$ (AR) 100 g/L, $LaCl_3$ (99.99%, calculated as La_2O_3) 1 g/L, pH = 4.6. The Ni-S(La) alloy was obtained at 308 K and the electrodeposited current density was 200 A/m^2. The mild steel and copper used for X-ray diffraction measurement were taken as substrate.

The components of Ni-S(La) layer and its composition were tested by EPMA and XRD. Polarization curves at different temperatures were obtained by steady-state polarization experiments. The anodic polarization curves were measured by means of linear polarization. All the above-mentioned electrochemical experiments were carried out through Model 173 potentiostat/galvanostat. The working electrodes were Ni-S(La) alloys while a large platinum foil acted as counter electrode. A $Hg/HgO/OH^-$ electrode was used as reference electrode. The electrolyte was 28% (mass fraction) NaOH solution, held at 353 K. As for the polarization curves obtained in bath, an HP 34401A multimeter was used to measure the cathodic potential at various current.

3 RESULTS AND DISCUSSION

3.1 Composition and components of Ni-S(La) layers

Fig. 1 shows that the Ni-S(La) layer obtained at optimum electrodeposited condition is amorphous. As shown in Table 1, the sulphur content decreases significantly in comparison with traditional amorphous Ni-S alloy (19% ~ 20%)[4], and its distribution is homogeneous. Since the standard potential of reaction $La^{3+} + 3e \longrightarrow La$ is more negative than that of reaction $H^+ + e \longrightarrow H$, no lanthanum was found in

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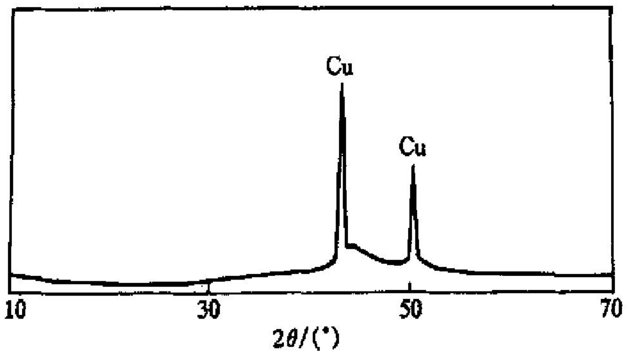

Fig. 1 XRD pattern for Ni-S(La) layer

Ni-S(La) layer (Table 1). According to Wen's opinion, $CS(NH_2)_2$ exists in the form of $Ni(TU)^{2+}$ and $Ni(TU)_2^{2+}$ complexing ions in the electrodeposited solution[4]. Since the radii of La^{3+} and the complexing ions are larger than that of Ni^{2+}, the adsorption of $Ni(TU)^{2+}$ and $Ni(TU)_2^{2+}$ on the electrode will be influenced by the adsorption of La^{3+} while the effect of Ni^{2+} ion is relatively low. Thus the sulphur content reduces.

Table 1 Composition of Ni-S(La) alloy obtained at optimum electrodeposition condition

Location	Content of S (mass fraction)/%	Content of La (mass fraction)/%
1	15.232	0
2	14.820	0
3	15.199	0
4	15.603	0

3.2 Electrochemical property and corrosion resistance of Ni-S(La) alloy

The influence of temperature on HER of Ni-S (La) electrodes is significant in alkaline solution by measuring the Tafel curves at various temperatures (Fig. 2). With increasing temperature, the h. o. v. (η) decreases and the Tafel slope reduces gradually. It means that HER electrocatalytic property rises which is shown by the exchange current density (Table 2).

Table 2 Electrochemical parameters of Ni-S(La) electrodes at various temperatures

Temperature /K	η_{150} /mV	$b/(mV\cdot dec^{-1})$ At low η	$b/(mV\cdot dec^{-1})$ At high η	$J_0/(A\cdot m^{-2})$ At low η	$J_0/(A\cdot m^{-2})$ At high η
308	135	95.89	275.8	43.5	486
323	112	83.73	232.6	46.9	495
338	96	72.65	197.7	49.7	516
353	75	58.23	162.9	52.3	542

Under industrial conditions, i. e, 353 K, 28% (mass fraction) NaOH and electrolysis current density being 1 500 A/m², the electrocatalytic property of Ni-S (La) electrodes for HER, whose h. o. v. is 75 mV, is much higher than that of mild steel (380 mV) and electroplated Ni (480 mV).

Fig. 3 shows the anodic polarization curves of ferrous, Ni-S and Ni-S(La) electrodes in the same electrolyte. The dissolved current of ferrous electrode is relatively large while a passivating area exists between − 0.1 V and 0.7 V (vs $Hg/HgO/OH^-$). As for Ni-S and Ni-S(La) electrode, the current increases slightly and proportionally with promoting potential in the course of anodic polarization. It means that the Ni-S and Ni-S(La) coatings are passivated under open-circuit, i. e, self-passivation. Their compositions are very homogeneous and keep stable during the anodic polarization. Therefore the conclusion can be obtained that the corrosion resistance of Ni-S(La) alloy is equal to traditional Ni-S coating and much better than ferrous electrode applied in industry.

3.3 Polarization curves in course of electrodeposition

In order to explain the improved property of Ni-S(La) alloy, polarization curves of Ni-S and Ni-S(La) coatings in bath were obtained. Fig. 4 shows that cathodic polarization increases significantly with adding of $LaCl_3$. The result indicates that $LaCl_3$ is

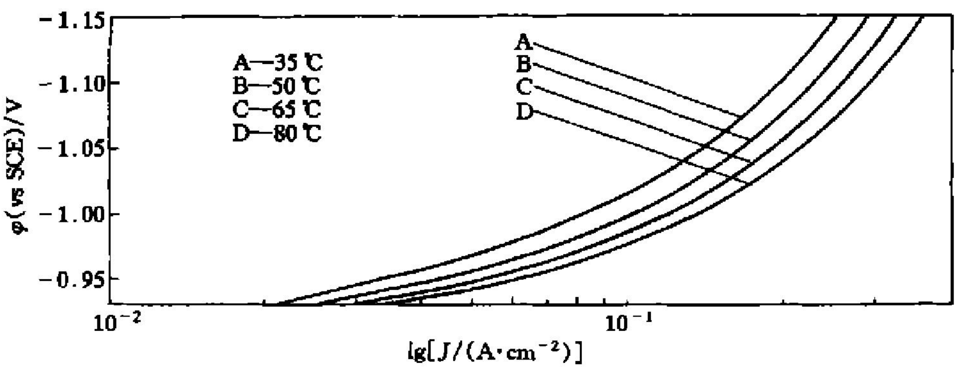

Fig. 2 Polarization curves of Ni-S(La) electrodes at various temperatures

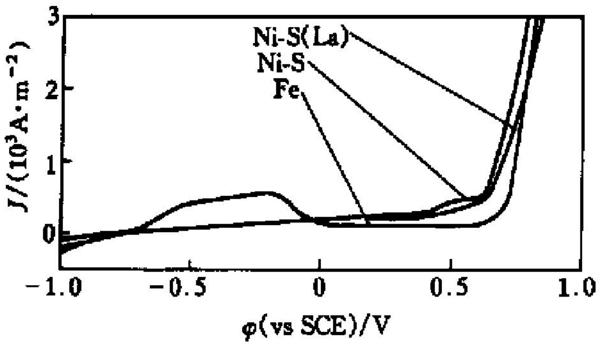

Fig. 3 Anodic polarization curves of various electrodes

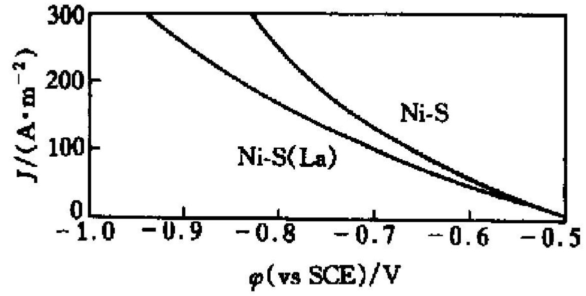

Fig. 4 Polarization curves of Ni-S and Ni-S(La) coatings in electroplating baths

helpful to form amorphous composition by means of altering double-layer which affects the electrodeposited rule of Ni and S atoms on the substrate. The specific mechanism should be studied further.

4 CONCLUSIONS

1) The Ni-S(La) alloy obtained under optimum condition is amorphous by means of XRD measurement; there exists no lanthanum and the distribution of sulphur is homogeneous in such amorphous alloy determined by EPMA.

2) The HER activity of Ni-S(La) electrode increases with promoting temperature, which can be proved by the polarization curves at various temperatures. The h. o. v. as low as 75 mV was obtained under industrial condition by using Ni-S(La) electrode.

3) Much better corrosion resistance of Ni-S(La) alloy can be determined by comparing anodic polarization curves with that of ferrous one.

4) In view of the cathodic curves obtained in eletrodeposited baths, the electrodeposition is influenced significantly by adding La^{3+} ion so that the composition of Ni-S coating is altered. That is the main reason why the electrochemical property increases for Ni-S(La) alloy.

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