Electrodeposition of La–Ni alloy films in a nonaqueous system

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Abstract

The codeposition of La–Ni alloy films in a nonaqueous system was investigated. The effects of several factors including the concentrations of main salts, pH, temperature, current density and substrates on the lanthanum content in the deposit were studied. The results show that the lanthanum content in the deposit can reach 18 wt % by controlling the system composition and deposition conditions. X-ray photoelectron spectrometry, X-ray diffraction and scanning electron microscope were used to characterize the morphology and structure of the deposit. The results show that the majority of lanthanum exists in the form of LaH_2, while the rest exists as metal and its oxide in the deposit, and the structure of the alloy deposited is amorphous.

1. Introduction

Of all the elements in the periodic table only about one-quarter may be electrodeposited from aqueous electrolytes in their elemental form or as alloys suitable for coatings, the rest are of engineering and scientific interest because of their specific properties, and methods of depositing them are desirable. The deposition of certain metals and alloys has been successfully achieved from nonaqueous electrolytes, and they have been used on a commercial scale. However, these electrolytes are often used in the laboratory to obtain deposits and electroforms with characteristics unattainable by other coating methods.

Although the standard electrode potentials of rare earth elements are unknown in nonaqueous systems, the electrodeposition of rare earth elements or their alloys from nonaqueous electrolytes has been recently reported. Bhattacharya has successfully deposited YBaCu superconductor precursor films in DMSO [1] and Yuichi Sato has made a great achievement in electrochemical preparation of Sm–Co magnetic thin films [2]. Co–Gd magnetooptical thin films were also obtained by an electrochemical process [3]. Other rare earth elements or their alloys such as yttrium [4], dysprosium [5] and La–Fe alloy [6] in organic solvents have been successfully deposited. In addition, electrodepositions of Dy–Ba–Cu alloy films [7] and Sm–Te alloy films [8] in an aqueous system and electrodeposition of rare earth elements and their alloys in molten chlorides has been reported [9, 10].

The codepositions of La–Ni alloy films in molten [11] and aqueous system [12] have been reported. The former requires a very high temperature. In the latter, the lanthanum content in the coating is very low, and all lanthanum exists in the oxidized state. Up to now, there has been no report on the codeposition of La–Ni alloy in organic solvents.

The present paper describes the research on the electrodeposition of La–Ni hydrogen storing alloy functional thin films in an organic solvent system. Our primary objective is to increase the La content in the coating because the alloy only has a hydrogen-storing function if the La content is not less than 30%.

2. Experimental details

Analytical grade reagents including lanthanum nitrate [$La(NO_3)_3$], nickel nitrate [$Ni(NO_3)_2$], lanthanum chloride [$LaCl_3$] and nickel chloride [$NiCl_2$] were used. The electrodeposition of La–Ni alloy was studied in the following four solvents: *N,N*-dimethylformamide [DMF], dimethylsulphoxide [DMSO], ethanol, and acetonitrile [AN]. Ethylene diamine tetraacetic acid [EDTA], nitrilotriacetic acid, ammonium bifluoride and triammonium citrate were used as complexing agents. Boric acid was used to adjust the pH of the solution.

Stainless steel, copper, brass and titanium alloy plates with a surface area of 2.5 cm^2 were used as substrates. The surfaces of the substrates were smooth and mirror polished. Two high purity graphite plates were used as the anode. The distance between the anode and the cathode was 1 cm. A closed system was adopted for the plating bath. The electrolysis cell was flushed with dry nitrogen before and during plating. Constant current

electrolysis was carried out by using a potentio-galvanostat. The electrolysis was performed isothermally.

A spectrophotometric method was applied to analyse the lanthanum content in the deposit. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to detect the structure and the morphology of the deposited coating. X-ray photoelectron spectrometry (XPS) was used to test the chemical states of lanthanum and nickel in the deposit.

Because the traditional three-electrode system is inconvenient and aqueous reference electrodes must be avoided in nonaqueous systems, we used a microelectrode technique to determine the voltammograms of the plating solution. The working electrode was a Pt microdisc electrode 30 μm in diameter and the counter electrode was a Pt plate of 1 cm^2 surface area, which also functioned as reference. The scan rate was 100 mV s^{-1}.
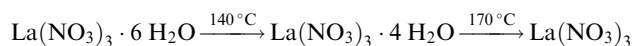
3. Results and discussion

3.1. Electrolysis systems

The solvents used were DMF, DMSO, AN and ethanol, formamide etc. The following conclusions can be obtained by comparison: (i) High content La coating cannot be obtained with DMSO as solvent because of the low solubility of La salt; (ii) codeposition of La and Ni can be obtained only at pH < 1 with formamide as solvent; (iii) coating is relatively coarse and porous with AN as solvent; (iv) the plating bath is unstable with ethanol as solvent due to the high volatility of ethanol. With DMF as solvent, good bath stability, high metal salt solubility and relatively high lanthanum content in the coating are obtained. Therefore, DMF was selected as solvent.

It is well known that the solubility of inorganic salts is generally very low in organic solvents. Improvement of the solubility of the main salts is problematic. Based on complex theory, similarity and compatibility principle, the following salts with different anions were studied: LaCl$_3$, La(NO$_3$)$_3$, (p-CH$_3$C$_6$H$_4$SO$_3$)$_3$La and NiCl$_2$, Ni(NO$_3$)$_2$, (p-CH$_3$C$_6$H$_4$SO$_3$)$_2$Ni. The results show that (p-CH$_3$C$_6$H$_4$SO$_3$)$_3$La and (p-CH$_3$C$_6$H$_4$SO$_3$)$_2$Ni readily dissolve in DMF because of their large anions, whereas the lanthanum content in the deposit was low. The solubilities of LaCl$_3$ and NiCl$_2$ in DMF were low. Adding solubilizer can increase the saturation concen-

tration of NiCl$_2$ in DMF greatly so as to meet the requirement for electrodeposition. The solubility of La(NO$_3$)$_3$ was fairly high due to the formation of a stable complex with DMF. The experimental results show that a fine and closely woven and porous-free deposit with a high lanthanum content can easily be obtained from the system containing La(NO$_3$)$_3$ and NiCl$_2$. Therefore, these were used as the main salts. The preparation process of anhydrous La(NO$_3$)$_3$ was as follows. First, La$_2$O$_3$ was reacted with nitric acid in solution to form La(NO$_3$)$_3$. Then, the solution was dewatered and dried by heating for at least 12 h at 140 °C in order to obtain raw particles. Next, the raw particles were ground into fine particles. Finally, the fine particles were further heated in an oil bath so as to lose crystalline water under reduced pressure at 170 °C. The dehydration process of La(NO$_3$)$_3 \cdot 6$ H$_2$O is

$$\text{La(NO}_3)_3 \cdot 6\,\text{H}_2\text{O} \xrightarrow{140\,°\text{C}} \text{La(NO}_3)_3 \cdot 4\,\text{H}_2\text{O} \xrightarrow{170\,°\text{C}} \text{La(NO}_3)_3$$

The reaction of a complexing agent in a nonaqueous system may be greatly influenced by other ions. The chloride ion functions as a catalyst in the electrodeposition of cobalt in DMF. However, the chloride ion is also an inhibitor if SCN$^-$ is added [13]. Therefore four kinds of complexing agents – ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid, ammonium bifluoride and triammonium citrate – were investigated. The following results were obtained. EDTA and nitrilotriacetic acid not only improved coating quality, but also increased La content. However, their solubility in the plating solution was low. Ammonium bifluoride increased the coating lanthanum content by four to six times, compared with no complexing agent. Even though the solubility of ammonium bifluoride in DMF is poor, fluorine can easily be adsorbed on the cathode and hinder the adsorption of O$_2$ or O$^-$. Therefore, the conductivity of the system can be improved. The fluorine function is similar to a surfactant. In addition, fluorine can greatly increase the solubility of NiCl$_2$ in DMF by functioning as an assistant solubilizer. The coating quality can also be improved by using triammonium citrate. However, it can result in a decrease in La in the coating. By comparison, ammonium bifluoride as complexing agent is the best for increasing La content and for improving the coating quality.

The effects of the five substrates on the electrodeposition of La–Ni alloy are shown in Table 1. It can be seen that the compositions of the coatings and the

Table 1. The effects of substrate on the electrodeposition of La–Ni alloy
($C_{\text{Ni}^{2+}} = 0.05$ mol dm^{-3}, $C_{\text{La}^{3+}} = 0.2$ mol dm^{-3}, pH 4.0, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C)

Substrates	La content/wt %	Current efficiency/%	Surface morphology
Copper	18.0	65.2	brightness
Brass	17.5	60.1	a little dark
Stainless steel	10.4	59.0	very bright
Titanium	12.7	53.4	some black pot on surface
Titanium alloy	20.8	55.3	a little dark

surfaces are obviously different. The current efficiency is different because different substrates are used. When copper is used as the substrate, the La–Ni alloy deposits easily and the current efficiency is highest, while the La content in the coating is relatively high and the coating surface is good.

3.2. Effects of electrodeposition parameters

The surface color and the character of the deposit depend on the current density and La content. If the current density is less than 1.0 A dm^{-2}, the film surface obtained is smooth and bright and has a metallic luster. The effect of current density on the content of lanthanum in the deposit is shown in Figure 1. At 0.6 A dm^{-2}, the La content in the coating reached its highest value,
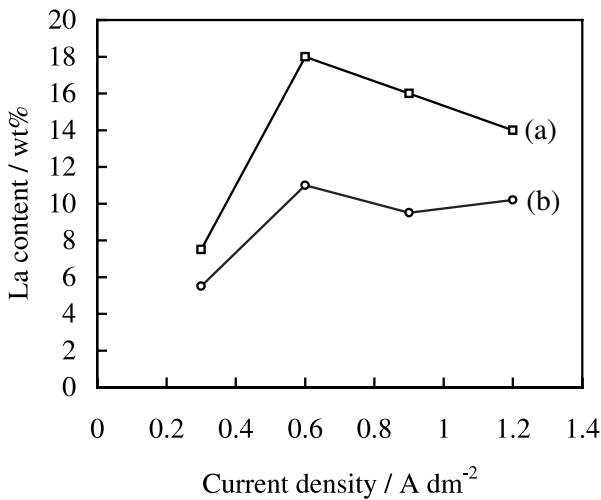
Fig. 1. Effect of current density on La content in the deposit. (a) $T = 50$ °C; (b) $T = 40$ °C ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, $C_{La^{3+}} = 0.2$ mol dm^{-3}, pH 4.0).
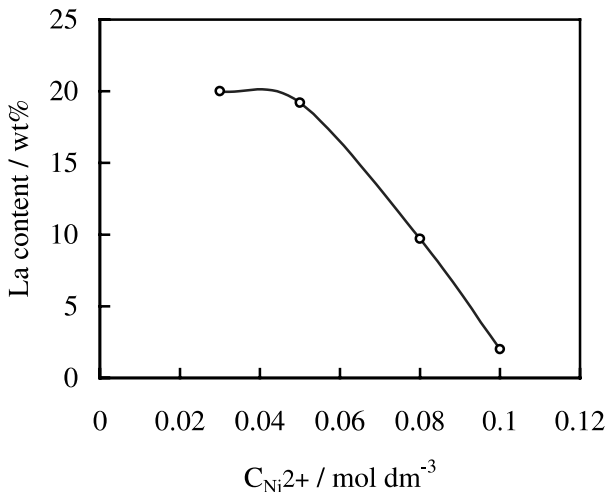
up to 11 wt % ($T = 30$ °C) or 18 wt % ($T = 40$ °C). Figure 2 shows the effect of nickel concentration in the solution on the La content of the deposit. It is obvious that the lower the nickel concentration in the solution, the higher the La content in the deposit. However, the system becomes rather unstable when the nickel concentration in the solution is very low, greatly reducing the rate of deposition. So the nickel concentration in the solution should be maintained in the range 0.05 to 0.06 mol dm^{-3}.

Figure 3 illustrates the effect of La^{3+} concentration in the solution on La content in the deposit. There is a peak at $C_{La^{3+}} = 0.2$ mol dm^{-3}, that is, the La content is the maximum in the deposit at $C_{La^{3+}} = 0.2$ mol dm^{-3} in the solution. Figure 4 shows the cyclic voltammograms of the solutions of the electrolytes containing different concentrations of La^{3+}. The peak current (i_{PC}) decreases with the increasing $C_{La^{3+}}$ in the solution. Experimental results show that the solution becomes gradually colloidal with increase in $C_{La^{3+}}$. The colloidal effect becomes more obvious with increasing $C_{La^{3+}}$ in the solution. Thus the viscosity of the solution increases and the ionic diffusion rate decreases, which results in decrease in i_{PC}. From Figure 4 it can also be seen that the peak potential(E_{PC}) at $C_{La^{3+}} = 0.2$ mol dm^{-3} is more positive than the others. The reason may be that $\varphi_{La^{3+}/La}$ (vs Pt) becomes positive with increase in $C_{La^{3+}}$ when the latter is in the relatively low concentration range. This causes the lanthanum content in the film to increase. However, when $C_{La^{3+}}$ is relatively high, there are some changes in the structure and stability of the complex formed between La(NO$_3$)$_3$ and DMF, which makes La(NO$_3$)$_3$ (DMF)$_n$ (n is an integer from 1 to 6) discharge difficult.

3.3. Performances characterization of the deposits

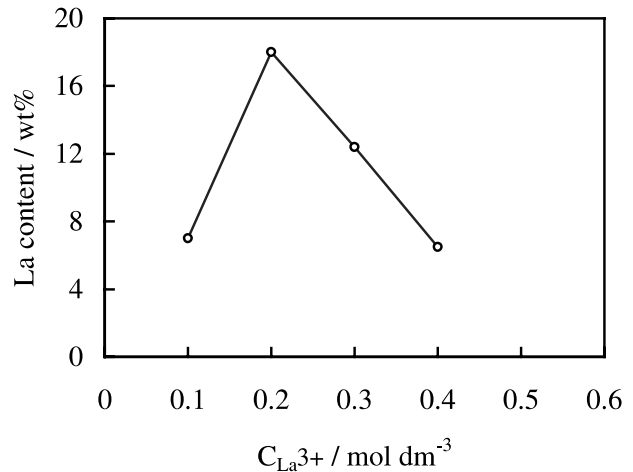The XRD analysis showed that the La–Ni alloy deposit was amorphous because diffraction peaks were not

Fig. 2. Effect of nickel concentration on La content in the deposit ($C_{La^{3+}} = 0.2$ mol dm^{-3}, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C, pH 4.0).

Fig. 3. Effect of La^{3+} concentration on lanthanum content in the deposit ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C, pH 4.0).
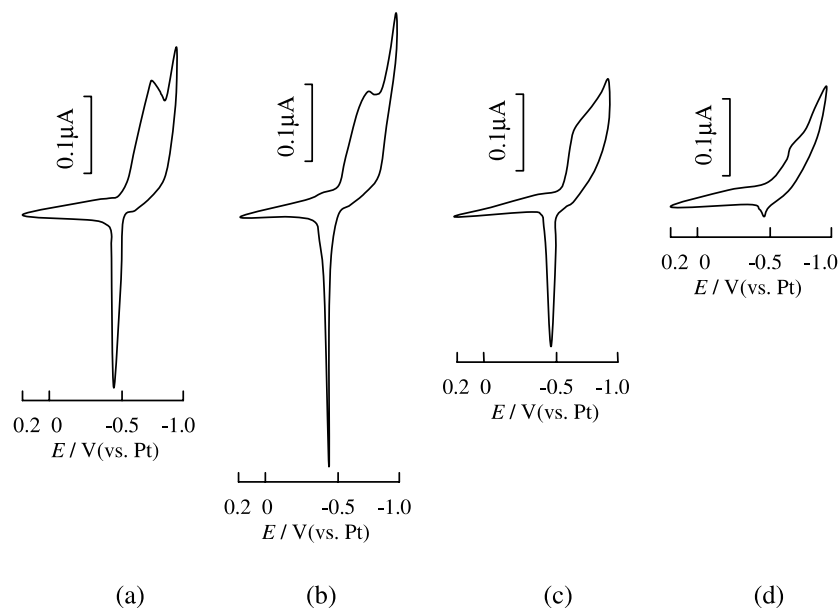
Fig. 4. Cyclic voltammograms of the solutions with x mol dm^{-3} La(NO$_3$)$_3$. (a) $x = 0.1$; (b) $x = 0.2$; (c) $x = 0.3$; (d) $x = 0.4$. ($C_{La^{3+}} = 0.2$ mol dm^{-3}, $T = 50$ °C, pH 4.0, $v = 100$ mV s^{-1}).
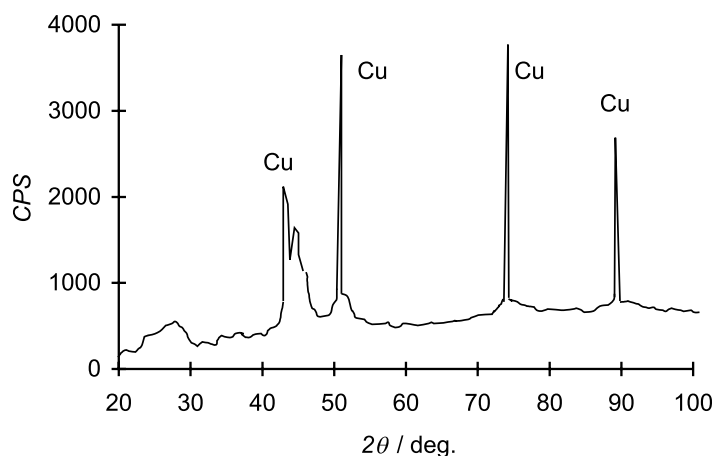
Fig. 5. XRD of La–Ni alloy deposit ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, $C_{La^{3+}} = 0.2$ mol dm^{-3}, pH 4.0, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C, La 18 wt %).

observed (Figure 5), compared with the XRD spectrum of the pure nickel deposit (Figure 6). Although the metals on the surface of the deposit are in their oxidized state, metallic states have been found inside the film by XPS analysis. Figures 7 and 8 show the XPS spectra of lanthanum and nickel in the La–Ni alloy deposit, respectively, after the deposit was etched for 15 min in argon. From Figure 7 it can be seen that the majority of lanthanum is in the form of LaH$_2$, while the rest exists as metal and metal oxide in the deposit. The SEM analysis showed that the La–Ni alloy deposit is much coarser than the pure nickel deposit (Figures 9 and 10). There are many dark dots distributed evenly on the surface of the alloy deposit, which are encircled by a light ring. The energy spectrum analysis of SEM showed that the main composition of the dark dot is lanthanum (up to 94 wt %), and the light ring is almost pure nickel. The reason may be the result of surface bias evolution.

3.4. Mechanism of codeposition

The cyclic voltammograms for the mechanistic study are shown in Figure 11. Comparing Figure 11(a), (b1) and (b2) it can be seen that there are clear reduction currents in Figure 11(a) and (b1). However, only a small current appears in Figure 11(b2). The currents are considered to be due to the reduction of oxygen because oxygen is easier to dissolve in DMF. When the gas phase is air or pure oxygen, the solubilities of oxygen in DMF are 2.2×10^{-3} mol dm^{-3} and 3.1×10^{-3} mol dm^{-3}, respectively. Although nitrogen is added to the system to expel oxygen before deposition, there still exists trace amounts of oxygen as shown in Figure 11(b2). Addition of La(NO$_3$)$_3$ results in a reduction of oxygen in the electric double-layer, which makes the current peak of Figure 11(b1) lower than that of Figure 11(a). Moreover, no lanthanum oxidization takes place in the range of
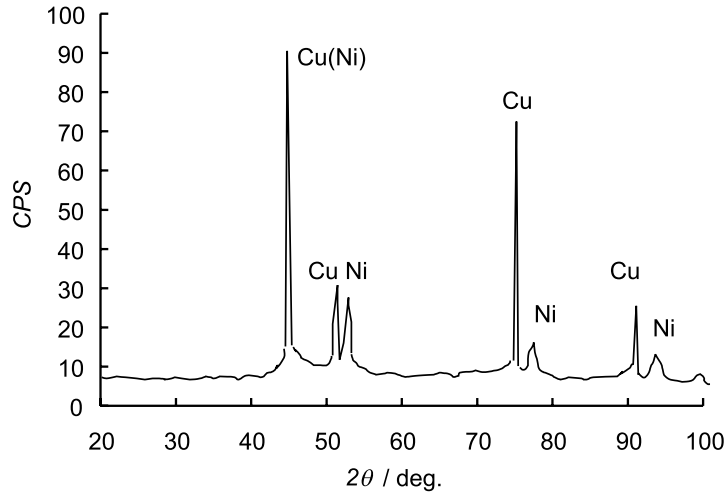
Fig. 6. XRD of pure nickel deposit ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, pH 4.0, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C).

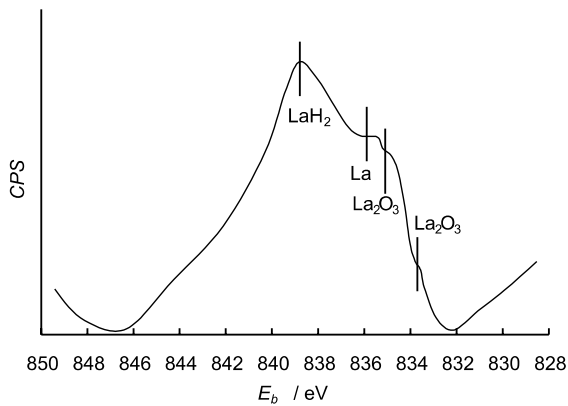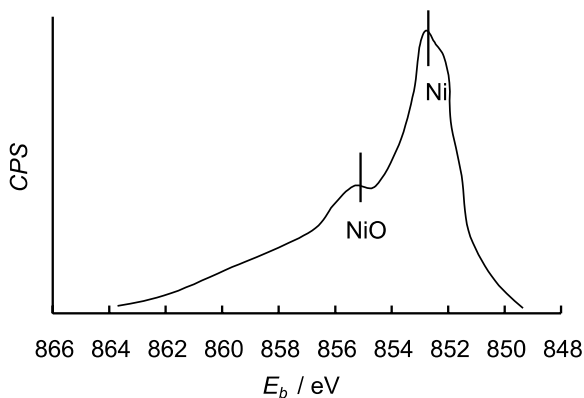Fig. 7. La$_3$d$_{5/2}$ high amplification XPS in La–Ni alloy deposit after being etched by argon for 15 min ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, $C_{La^{3+}} = 0.2$ mol dm^{-3}, pH 4.0, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C, La 18 wt %).

Fig. 9. SEM of La–Ni alloy deposit ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, $C_{La^{3+}} = 0.2$ mol dm^{-3}, pH 4.0, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C, La 18 wt %).

Fig. 8. Ni$_2$p$_{3/2}$ high amplification XPS in La–Ni alloy deposit after being etched by argon for 15 min ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, $C_{La^{3+}} = 0.2$ mol dm^{-3}, pH 4.0, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C, La 18 wt %).

potential scanned in Figure 11(a), (b1) and (b2). There-fore, we can say that there is no La ion discharge at the cathode containing only lanthanum salt in solution.
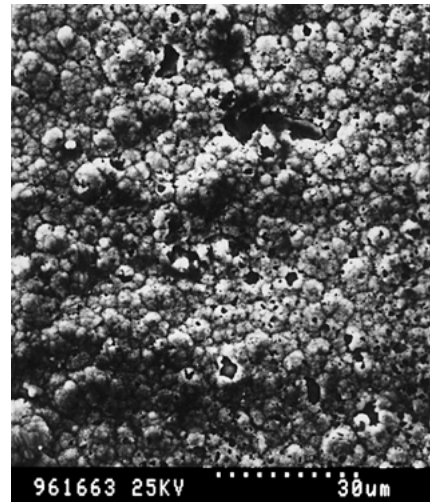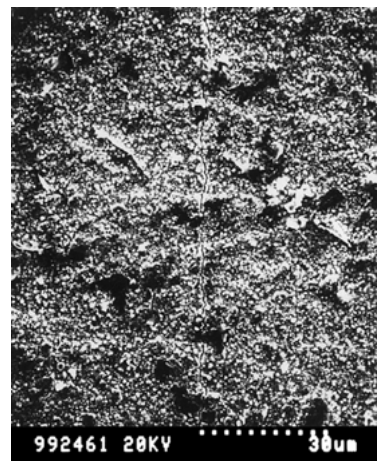

Fig. 10. SEM of pure Ni deposit ($C_{Ni^{2+}} = 0.05$ mol dm^{-3}, pH 4.0, $J_k = 0.6$ A dm^{-2}, $T = 50$ °C).

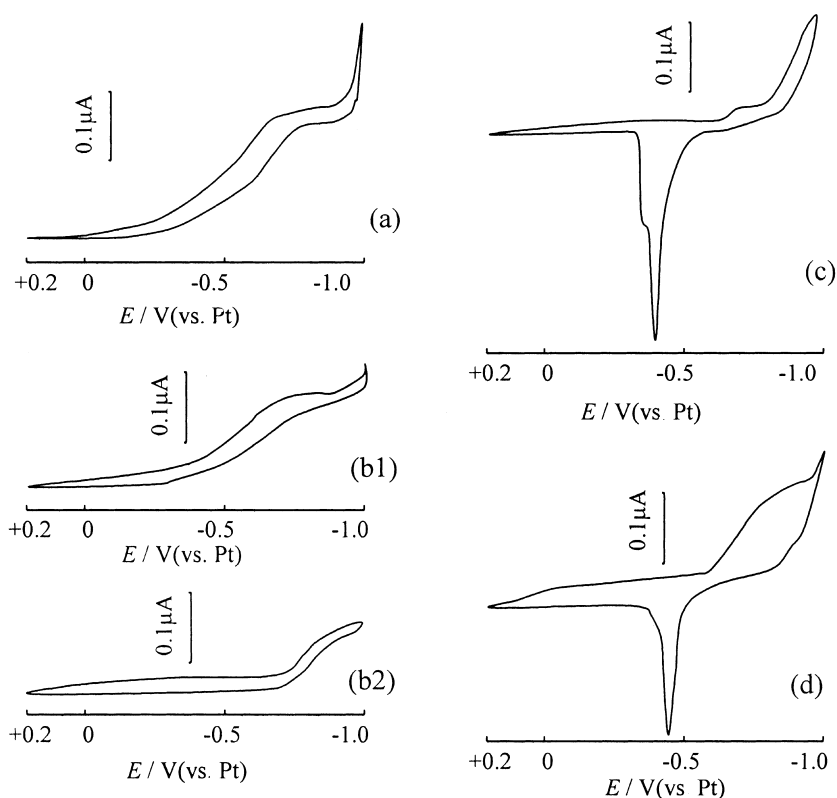*Fig. 11.* Cyclic voltammograms ($v = 100$ mV s^{-1}). (a) Pure DMF; (b1) DMF + 0.2 mol dm^{-3} La(NO$_3$)$_3$; (b2) DMF + 0.2 mol dm^{-3} La(NO$_3$)$_3$ + dry N$_2$; (c) DMF + 0.05 mol dm^{-3} NiCl$_2$ + dry N$_2$; (d) DMF + 0.2 mol dm^{-3} La(NO$_3$)$_3$ + 0.05 mol dm^{-3} NiCl$_2$ + dry N$_2$.

In Figure 11(c) and (d), there is an obviously redox couple. It can be concluded that lanthanum ion cannot deposit solely. However, La^{3+} can deposit after addition of nickel; this is termed induced codeposition.

4. Conclusion

The electrodeposition of La–Ni alloy films from a DMF plating solution can be obtained by using lanthanum nitrate and nickel chloride as the main salts and ammonium bifluoride as the complexing agent. By controlling the composition of the plating solution and deposition condition, La–Ni alloy electrodeposit films containing 18 wt % La can be obtained, in which La and Ni exist in the form of LaH$_2$ and Ni, respectively. The surface of the coating is bright and has a metallic luster. The deposit is amorphous. Therefore, it is possible to use electrodeposition to prepare rare-earth metal-iron group metal amorphous alloy films.

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