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Electrochemical studies on La-Co alloy film in acetamide-urea-NaBr melt system^①

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Abstract: The kinetics of La-Co alloy film in acetamide-urea-NaBr molten salt electrolyte at 353 K was investigated. It is shown that the reduction of Co(II) to Co is irreversible reaction with the transfer coefficient of 0.28 and the diffusion coefficient of $7.46 \times 10^{-5} \text{ cm}^2/\text{s}$. While La(III) cannot be reduced to La directly; but can be codeposited with cobalt. The content of La in the uncrystallized La-Co alloy film increases with increasing cathodic overpotential, molar ratio of La^{3+} to Co^{2+} and electrolysis time as well, and reaches the maximum of 66.32%.

Key words: La-Co alloy film; acetamide-urea-NaBr molten salt electrolyte; electroreduction; inductive codeposition; rare earth elements

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1 INTRODUCTION

The magnetic rare earth elements bring significant changes to the magnetic material industry due to their excellent magnetic and magneto-optical properties^[1]. Since La and Co are rich elements in nature, in addition to their relatively cheap prices, it would be very prospective to prepare magnetic functional materials using La-Co alloy. Compared with traditional techniques of spray and vacuum sputtering or sputtering, electrodeposition is an economical method to develop alloy film due to a simple procedure and low expense. Because of the active chemical property of RE and Co, it is difficult to deposit RE-Co alloy in aqueous solution and studies on electrodeposition of RE-Co alloy film in organic electrolytes have been reported^[2-5].

Owing to the lower melting point (up to 315.2 K) and the higher electric conductivity of molten salt electrolyte of acetamide-urea-alkali halide^[6-8] in the certain mixture, the acetamide-urea-NaBr melt was chosen as electrolyte for depositing La and Co from $\text{La}(\text{NO}_3)_3$ and CoCl_2 . In Refs. [8 - 14], the deposition of RE-Co alloy film from urea-NaBr and urea-NaBr-KBr molten salt electrolytes was reported. In this paper, by using cyclic voltammetry, the results related to the reduction behaviors of La(III) and Co(II) in acetamide-urea-NaBr molten salt electrolyte and the relationship between alloy composition and molar ratio of La(III) to Co(II), electrolysis time and electrode potential were discussed. At the same time, the deposited film surface morphology was

studied.

2 EXPERIMENTAL

Water free $\text{La}(\text{NO}_3)_3$ and CoCl_2 were made from A. R. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Shanghai Chemical Co. China) and CoCl_2 (Beijing Red Star Chemical Co. China) by vacuum dehydration. Dried urea (Beijing Chemical Co. China), Acetamide (56%, mass fraction, Beijing Chemical Co. China) and NaBr (7%, mass fraction, Xi'an Chemical Co. China) were uniformly mixed and then put into a cell with three electrodes. All measurements were carried out under the protection of argon gas at 353 K. The reference electrode was Ag/acetamide-urea-NaBr, to which all potentials in this paper were referred. Counter electrode was a platinum plate with high purity of 99.9%. The working electrode was a platinum (99.9%, 0.015 cm^2) and a copper wire (99.9%, 0.35 cm^2). Respectively CV techniques were employed using an Potentiostat HDV-7C and a HD-1A low & ultraslow frequency response analyzer (Sanming Instrumental Co. Fujian, China), and handled by 3086 X-Y data recorder (Sichuan Fourth Instruments, China).

3 RESULTS AND DISCUSSION

3.1 Electrochemical behavior of La(III) in melt of acetamide-urea-NaBr

The experiment is carried out with the melt of acetamide-urea-NaBr as supporting electrolyte and scanning rate is varied in 20, 50, 100 and 200

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mV/s. In order to investigate the electrochemical behavior of the melt of acetamide-urea-NaBr, a cyclic voltammetry is recorded in a wide potential region of $-1.5 \sim 0$ V with a copper wire as working electrode (see Fig. 1(a)). And then $\text{La}(\text{NO}_3)_3$ (324.9 g/mol) is added in the cell and CV curves (Fig. 1(b)) are recorded. Compared with Fig. 1(a), there is an anodic current in Fig. 1(b) at potential of -1.10 V but no evident peak. In the meantime, there is no deposition after electrolysis in the potential range of $-1.10 \sim -1.40$ V, which indicates that $\text{La}(\text{III})$ cannot be reduced to La in the melt and this coincides with McManis's report^[7].

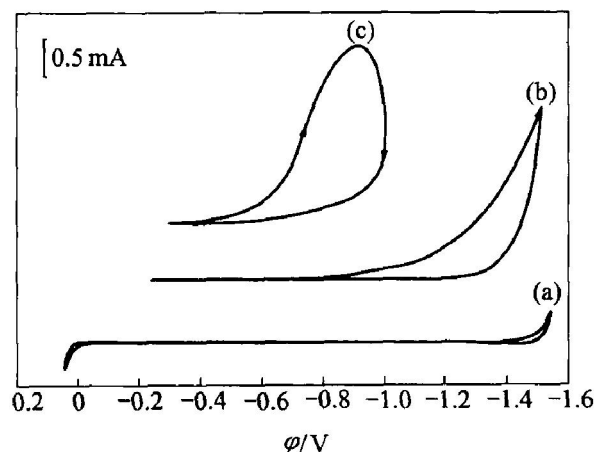


Fig. 1 Cyclic voltammograms of Cu electrode in different solutions
(a) —Melt of acetamide-urea-NaBr;
(b) — $\text{La}(\text{NO}_3)_3$ -acetamide-urea-NaBr;
(c) — CoCl_2 -acetamide-urea-NaBr
(Scanning rate 50 mV/s)

3.2 Electrochemical behavior of Co(II) in melt of acetamide-urea-NaBr

When the previous experiment is repeated in the melt containing 0.06 mol/L CoCl_2 , a peak appears in the negative scanning at -0.82 V (Fig. 1(c)). This peak corresponds to the reduction of Co(II) and it is an irreversible reaction because of no oxidation peak in the backward scanning. After 20 min controlled-potential electrolysis at -0.80 V, a gray color and uniform deposited film appears on the copper plate. Furthermore, the deposit is confirmed to be Co by EDS.

Fig. 2 shows a set of cyclic voltammograms recorded with increasing scanning rate in the region of Co(II) reduction. It is evident that the peak position shifts towards more negative potential values with the increase in scanning rate, indicating that the Co(II) reduction reaction is under diffusion control. In addition, as already discussed above, the Co(II) reduction reaction is shown to be highly irreversible, which can be seen from the linear relationship of peak potential (ϕ_p) and logarithm of scanning rate. By using relation for irreversible

electrochemical reaction at 353 K: $|\phi_{p/2} - \phi_p| = 1.857 RT / (\alpha n F)$, the average transfer coefficient can be calculated as $\alpha = 0.28 (n = 2)$.

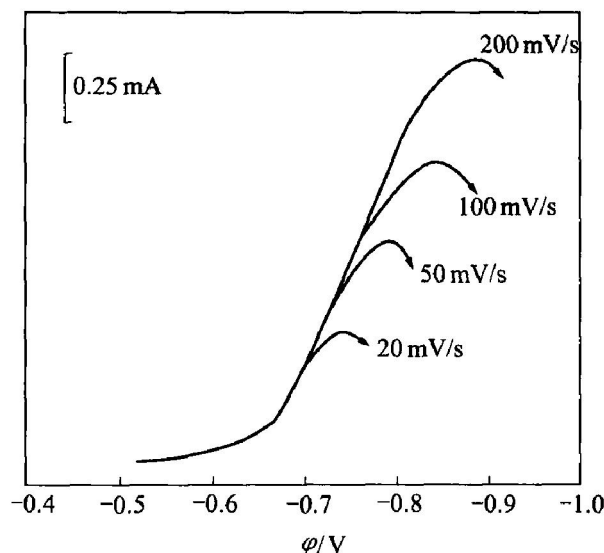


Fig. 2 Cyclic voltammograms of Pt electrode in CoCl_2 -acetamide-urea-NaBr recorded at various scanning rates

In order to calculate the diffusion coefficient, the curve of the peak current (I_p) versus square root of scanning rate is plotted (Fig. 3). By using $I_p = 0.4958 n F (\alpha n F D_0 \nu R T)^{1/2} A c^{[15]}$, the diffusion coefficient is calculated from the slope of line in Fig. 3: $D_0 = 7.46 \times 10^{-5} \text{ cm}^2/\text{s}$ at 353 K and 0.06 mol/L of CoCl_2 . Here A is surface area of electrode, D_0 is diffusion coefficient, and c is concentration.

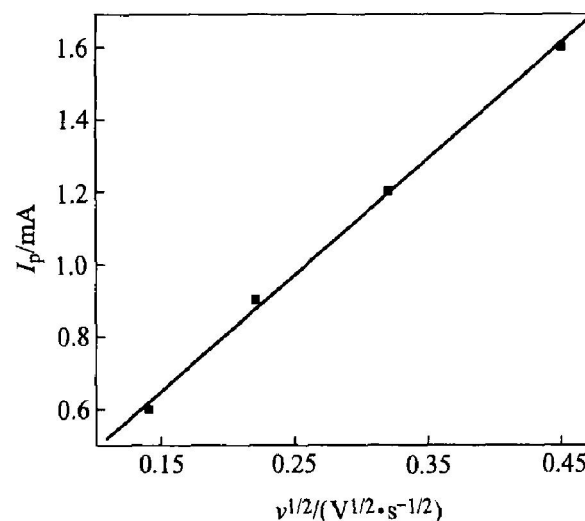


Fig. 3 Dependence of peak current on scanning rate

3.3 Co-deposition of La(III) and Co(II) in melt of acetamide-urea-NaBr

3.3.1 Electrochemical behavior

Fig. 4 shows the cyclic voltammetry curve of $\text{La}(\text{NO}_3)_3$ (0.03 mol/L)- CoCl_2 (0.06 mol/L) in the

melt of acetamide-urea-NaBr on Cu electrode. Compared with Fig. 1(c), the peak potential shifts toward more negative value, and the current increases evidently. It would be an inductive codeposition of Co and La. Under an electrolysis at cathodic potential of -0.8 V , a black deposit on Cu surface is got and it consists of La and Co according to EDS analysis, which further confirms that La(III) can be co-deposited with Co(II) .

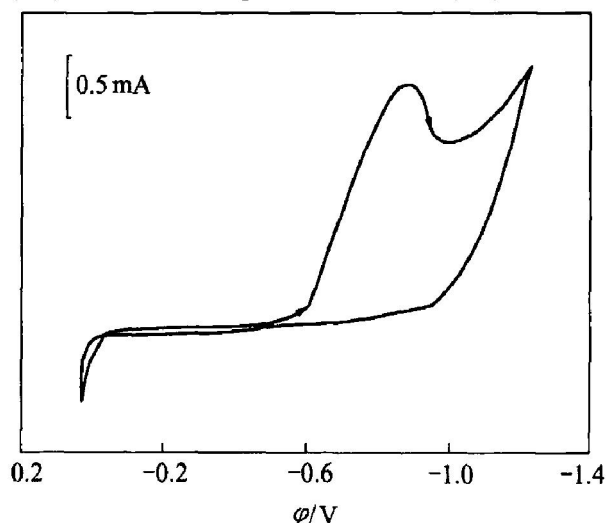


Fig. 4 Cyclic voltammogram of Cu electrode in $\text{La}(\text{NO}_3)_3\text{-CoCl}_2\text{-acetamide-urea-NaBr}$ (Scanning rate 50 mV/s)

3.3.2 Effect of electrodeposition condition on alloy composition

3.3.2.1 Effect of electrode potential

Table 1 shows the content of La-Co alloy film from 20 min controlled potential electrolysis at various potentials when keeping the molar ratio of La(III) to Co(II) at 1:1 in 0.06 mol/L $\text{La}(\text{NO}_3)_3\text{-}0.06\text{ mol/L}$ $\text{CoCl}_2\text{-acetamide-urea-NaBr}$ system. It can be seen that the content of La in alloy film increases with negative shift of cathodic potential and reaches the maximum value of 50.08% at -0.95 V . However, at more negative potential, the content of La decreases, which will be due to the polarization caused by concentration difference under these potentials. Scanning electron microscope (SEM) image of deposited film shows that the film is uniform and well-distributed

Table 1 Content of La in La-Co alloy film at various electrolysis potentials

φ/V	$w(\text{La})/\%$	$x(\text{La})/\%$
-0.75	12.31	5.62
-0.85	33.25	17.45
-0.95	50.08	29.85
-1.05	29.09	14.83
-1.15	26.85	13.47

on the surface of Cu substrate.

3.3.2.2 Effect of molar ratio of La(III) to Co(II)

After the completion of electrolysis at potential of -0.850 V for 20 min, the content of La in the deposited film increases with increasing molar ratio of La(III) to Co(II) (see Table 2). Fig. 5 shows the SEM image of deposited La-Co alloy film.

Table 2 Content of La in La-Co alloy film with different molar ratios of La(III) to Co(II)

$x(\text{La(III)})/x(\text{Co(II)})$	$w(\text{La})/\%$	$x(\text{La})/\%$
0.5:1.0	9.94	4.47
1.0:1.0	33.25	17.45
1.5:1.0	39.36	21.6
2.0:1.0	61.84	40.74

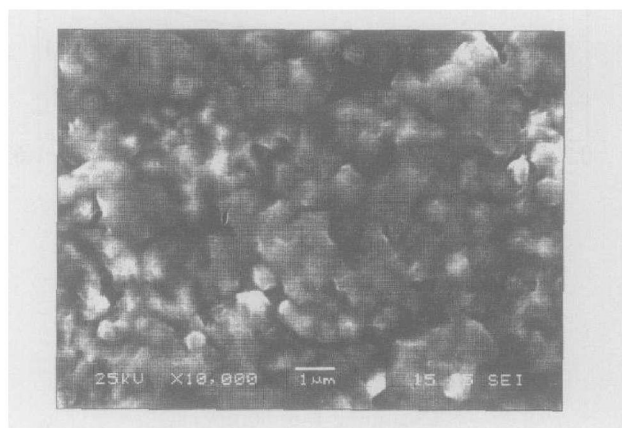


Fig. 5 SEM image of deposited film after heat treatment at $600\text{ }^\circ\text{C}$

3.3.2.3 Effect of time in controlled-potential electrolysis

In order to investigate the relationship between the content of La in deposited alloy film and electrolysis time, the experiment is performed under molar ratio of La(III) to Co(II) of 2:1 and cathodic potential of -0.850 V (Table 3). The results show that the content of La increases at first and then decreases with time. The same trend is also observed from deposition of Gd-Co in melt of acetamide-urea-NaBr, which may be attributed to faster deposition speed of the iron triad elements compared with that of rare earth elements and the increasing extend of rare earth element content decreases with time.

3.3.2.4 Effect of time in controlled-current electrolysis

Table 4 shows that the content of La formed in the melt of $\text{La}(\text{NO}_3)_3(0.12\text{ mol/L})\text{-CoCl}_2(0.06\text{ mol/L})\text{-acetamide-urea-NaBr}$ under cathodic current of 2.50 mA increases at first and then

decreases with time lasting. Moreover, the content of La deposited by controlled-potential electrolysis is much higher than that by controlled-current electrolysis at the same time.

Table 3 Content of La in La-Co alloy film under controlled-potential electrolysis

t/min	$w(\text{La})/\%$	$x(\text{La})/\%$
10	33.51	17.61
20	61.84	40.74
30	6.32	45.51
40	61.11	40.00

Table 4 Content of La in La-Co alloy film under controlled-current electrolysis

t/min	$w(\text{La})/\%$	$x(\text{La})/\%$
10	8.81	3.93
20	16.81	7.89
30	17.42	8.22
40	12.76	5.84

3.4 Analysis of structural image of deposited film

A set of disordered peaks are found in X-ray diffraction pattern of La-Co alloy film obtained from electrolysis in the system of $\text{La}(\text{NO}_3)_3$ (0.12 mol/L)- CoCl_2 (0.06 mol/L)-acetamide-urea-NaBr, which suggests the deposited film is uncrystallized. However after 6 h heat treatment at 600 °C under argon gas protection, only diffraction peaks are observed in XRD pattern, which means that the alloy is crystallized during heat treatment. It can also be confirmed by the scanning electron microscope (SEM) image of La-Co alloy film after heat-treatment at 600 °C (see Fig. 5).

4 CONCLUSIONS

1) $\text{Co}(\text{II})$ can be reduced to Co directly in the melt of acetamide-urea-NaBr and the reduction is an irreversible electrochemical reaction.

2) $\text{La}(\text{III})$ cannot be reduced to La in the melt of acetamide-urea-NaBr, but can be reduced indirectly in the presence of Co.

3) The content of La in La-Co alloy film increases with increasing molar ratio of $\text{La}(\text{III})$ to $\text{Co}(\text{II})$, negative shift of cathodic potential and time lasting as well. The maximum value is 66.32%.

4) La-Co alloy film is uncrystallized when deposition from the melt of acetamide-urea-NaBr, but it becomes crystal after heat treatment.

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