APPLICATION OF UREA–NaBr–KBr MELT TO ELECTRODEPOSITION OF METALS AND ALLOYS

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The electric conductivity of urea-NaBr-KBr melt is measured as 19 mS cm⁻¹ at 100 °C. Electroreduction of Fe²⁺, Co²⁺ and Ni²⁺ to corresponding metal in urea–NaBr–KBr melt is irreversible in one step. The diffusion coefficients of Fe²⁺, Co²⁺ and Ni²⁺ and the transfer coefficients of the electroreduction reaction were determined. The rare earth(RE) can be inductively codeposited with iron group element to form alloy. Over ten rare earth–iron group alloys were obtained. The content of rare earth in the deposits changed with the cathode potential, current density, molar ratio of RE⁷⁺/M²⁺ in melt.

INTRODUCTION

The systems of urea with some alkali metal salts have lower melting points (28 — 116 °C) and the melts of these systems can be used as nonaqueous electrolytic medium below 150 °C. Samavskii et al. obtained an adherent plate of nickel on titanium and stainless steel substrates by electroplating in urea–NiCl₂–sodium benzoate melt at 115 °C. Details of the electrode process were not reported. The melting point of urea(79.0 mol%)-NaBr(19.5 mol%)-KBr(1.5 mol%) eutectic is 51 °C which may be used as electrolytic medium at about 100 °C. In this paper, some properties of urea–NaBr–KBr system were determined. The electroreduction of Fe²⁺, Co²⁺, Ni²⁺ and electrolytic codeposition of iron group–rare earth alloys are investigated.

EXPERIMENTAL

FeCl₂·4H₂O, CoCl₂·6H₂O and NiCl₂·6H₂O were dehydrated in vacuum at 120 °C to obtain FeCl₂, CoCl₂ and NiCl₂. RECl₃ was prepared by the reaction of RE₂O₃ and NH₄Cl at about 350 °C. All chemical agents are analytical pure. The mixture of urea and salts was melted at a temperature of about 100 °C. The temperature of the melt was controlled by an oil-bath thermostat.
The density of melt was determined by the Westphal balance. The electric conductivity of melt was determined by the conductance cell with two platinized platinum electrodes and the DF-881 digital conductivity apparatus.

The working electrodes were spectral graphite, titanium and copper. The counter electrode was spectral graphite. The Ag/urea–NaBr–KBr eutectic was used as reference electrode. Cyclic voltammogram and chronopotentiogram were made with HDV-7C potentiostat, 3086 X-Y recorder and HD-1A functional generator. Electrochemical measurements proceeded under argon atmosphere. The composition and phase of deposits were analyzed by X-ray energy dispersive analysis(EDAX), scanning electron microscope(SEM) and X-ray diffraction(XRD).

RESULTS AND DISCUSSION

Some properties of urea–NaBr–KBr system

The densities of urea–NaBr–KBr melt at different temperatures were determined. The plot of density versus temperature is a straight line (Fig 1). The relation between density and temperature was obtained as Eq.1.

\[ d = 1.576 - 0.0007937T \]  

The electric conductivities of urea–NaBr–KBr melt at different temperatures were determined. The plot of electric conductivity versus temperature is a straight line (Fig 2). The relation between conductivity and temperature was given by Eq.2.

\[ \kappa = -27.12 + 0.4667T \]  

The conductivity of this melt at 100 °C is 18.96 mS cm\(^{-1}\). This value is higher than the conductivity of 0.1 mol L\(^{-1}\) KCl aqueous solution at 35 °C(15.39 mS cm\(^{-1}\)).

Golubchik investigated the surface metalliding of aluminum with indium, indicated that the oxide film on an aluminum substrate and water impurity can be removed in the urea melt\(^{[9]}\). With addition of 1.0 g H\(_2\)O into the urea–NaBr–KBr melt (10 g), one cathodic wave appeared at -0.7V before the cathodic limit of the background in the cyclic voltammogram. The temperature of the melt was raised to 125 °C for two hours and then the cyclic voltammogram was measured again. The cathodic wave disappeared which indicates that the water was removed from the melt.

The urea melt can dissolve many inorganic salts easily and the electric conductance of the molten urea–inorganic salt is increased. The electrochemical window of urea–NaBr–KBr melt is about 2.3V, from +1.0V to -1.3V vs a silver reference electrode.
From these properties, we can conclude that the urea–NaBr–KBr melt is a stable electrolyte for the electrodeposition of iron group metals and their alloys.

**Electroreduction of Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\)**

Fig 3 is the cyclic voltammogram of graphite electrode in urea–NaBr–KBr–MC\(_12\) (M= Fe, Co, Ni) at 100 °C. One cathodic wave and one anodic wave appear in the cyclic voltammogram. Electrolysis was performed with a copper electrode at the potential of the cathodic wave. A lustrous layer was obtained and was analyzed as iron group element by means of EDAX. The anodic wave is very far from the cathodic wave. These results indicate that the electroreduction of M\(^{2+}\) to metallic M in urea–NaBr–KBr–MC\(_12\) melt is irreversible in one step.

According to the following equations\(^1\ 4\ 1\), the transfer coefficients for the reaction of M\(^{2+}\) + 2e \(\rightarrow\) M and the diffusion coefficients of M\(^{2+}\) were determined (Table I).

\[
|E_r - E_{p/2}| = 1.857RT/an_F \quad [3]
\]

\[
I_r = 0.4958nF(\alpha n_FFDv/RT)^{1/2}Ac \quad [4]
\]

In Eq.4 and Eq.5, \(E_r\) and \(E_{p/2}\) represent the peak potential and the half peak potential, \(I_r\) represents the peak current, \(\alpha\) and \(D\) represent the transfer coefficient and the diffusion coefficient.

| Table I Diffusion coefficients and transfer coefficients at 100 °C |
|-----------------|-------------------|-----------------|--------|
| \(M^{2+}\)      | \(D/cm^2 s^{-1}\) | \(M^{2+} + 2e \rightarrow M\) | \(\alpha\) |
| Fe\(^{2+}\)     | \(1.18 \times 10^6\) | Fe\(^{2+}\) + 2e \(\rightarrow\) Fe | 0.35   |
| Co\(^{2+}\)     | \(2.31 \times 10^6\) | Co\(^{3+}\) + 2e \(\rightarrow\) Co | 0.46   |
| Ni\(^{2+}\)     | \(1.01 \times 10^6\) | Ni\(^{3+}\) + 2e \(\rightarrow\) Ni | 0.43   |

The potential-time curves at current step were shown in Fig 4. The plots of \(E\) versus \(\ln(1-\phi/\phi_0)^{1/2}\) are linear (Fig 5). According to the following equation\(^5\):  

\[
E = E_\circ - \left(\frac{RT}{an_F}\right)\ln(i/i_0) + \left(\frac{RT}{an_F}\right)\ln[1-\left(\phi/\phi_0\right)^{1/2}] \quad [5]
\]

the exchange current density, \(i_0\) at 100 °C is calculated as follows:

- Fe\(^{2+}\) + 2e = Fe \(2.89 \times 10^5\) A cm\(^{-2}\)
- Co\(^{2+}\) + 2e = Co \(5.54 \times 10^5\) A cm\(^{-2}\)
- Ni\(^{2+}\) + 2e = Ni \(1.81 \times 10^6\) A cm\(^{-2}\)
Electrodeposition of rare earth–iron group alloys

The reduction potential of rare earth ion to metallic rare earth is so negative that no cathodic wave appears before the cathodic limit of the melt. For example, the cyclic voltammogram of Cu electrode in urea–NaBr–KBr–NdCl₃ melt (Fig 6.2) is similar to the cyclic voltammogram of the background (Fig 6.1). Hence the rare earth metal can not be deposited alone in the urea melt.

The cyclic voltammogram of Cu electrode in urea–NaBr–KBr–NdCl₃–FeCl₃ melt is shown in Fig 6.4. The starting potential of the cathodic wave is more positive to that of the melt containing FeCl₂ but not NdCl₃ (Fig 6.3), and the cathodic current is higher. This result indicates that the neodymium may be inductively codeposited with iron. Other RECl₃ containing melts have cyclic voltammograms which are similar to that in Fig 6.4. Therefore, the other rare earth metals also can be inductively codeposited with iron group elements.

The rare earth–iron group alloy deposits were obtained on copper cathode by electrolyzing in the urea–NaBr–KBr–MCl₂–RECl₃ melt at 100 °C. The contents of rare earth in some rare earth–iron group alloy deposits are listed in Table II. The contents of rare earth in these deposits at the cathode potential of -1.0V ranged from 55 wt% to 86 wt%.

The appearance of the deposited film is related to its rare earth content. The appearance is good in the condition of low rare earth content. For example, the La(1 wt%)-Fe deposited film is smooth and resistant to corrosion. With an increased La content, the color of deposited film is changed from white-gray to gray and to black. The adhesion of the deposit to the substrate will diminish when the La content is larger than 20 wt%.

Table II  Codeposition of rare earth–iron group alloys

| RE-M  | La-Fe | La-Co | La-Ni | Nd-Fe | Nd-Co | Gd-Co |
|-------|-------|-------|-------|-------|-------|-------|
| at%   | 67.21 | 62.97 | 48.49 | 71.90 | 64.78 | 41.30 |
| wt%   | 83.60 | 80.03 | 69.02 | 86.86 | 81.83 | 65.19 |
| RE-M  | Tb-Co | Dy-Co | Ho-Co | Er-Co | Tm-Co | Yb-Co |
| wt%   | 38.71 | 37.58 | 36.95 | 28.55 | 33.60 | 29.43 |
| at%   | 63.11 | 62.41 | 62.12 | 53.13 | 59.19 | 55.04 |

The content of rare earth in the deposits is altered by the cathode potential, current density and molar ratio of RE⁺/M²⁺ in the melt. The experimental results are
as follows (e.g. Table III):

1. The content of rare earth in deposit increases with the shift of cathode potential to the negative in suitable potential range.
2. The content of rare earth in deposit increases with an increase of current density in suitable potential range.
3. The content of rare earth in deposit increases with an increase of the molar ratio of $\text{RE}^{3+}/\text{M}^{2+}$ in the melt.

Table III Rare earth contents in some rare earth–iron group alloys

| Alloy  | Influenced factor | Nd–Fe   | La–Co   | Tb–Co  |
|-------|------------------|---------|---------|--------|
|       | $E/N$            | -0.80   | -0.90   | 1.2    |
|       | Nd wt%           | 38.80   | 58.89   | 49.28  |
|       |                   | 78.67   | 61.62   | 49.28  |
|       |                   | 86.86   | 58.85   | (at -1.0V) |
|Nd–Fe | $i$/mA cm$^2$    | 2.8     | 4.3     | 5.7    |
|       | La wt%           | 9.27    | 31.91   | 61.62  |
|       |                   | 16.74   | 61.62   | 58.85  |

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