

[Article ID] 1003 - 6326(2002)06 - 1191 - 04

Preparation of Y-Co alloy film in acetamide-urea-NaBr melt^①

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[Abstract] Electroreduction of Co(II) to Co in acetamide-urea-NaBr melt at 353 K is irreversible in one step. α and D are determined as 0.23 and $2.24 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$. Y(III) is not reduced to Y alone, but can be inductively codeposited with Co(II). The amorphous Y-Co alloy film was obtained by potentiostatic electrolysis. The content of yttrium in the yttrium-cobalt deposits changes with the cathode potential, molar ratio of Y(III)/Co(II) and the electrolysis time, and can reach 83.93%.

[Key words] acetamide-urea-NaBr; electroreduction; inductive codeposition; Y-Co; amorphous alloy;

[CLC number] O 641.4

[Document code] A

1 INTRODUCTION

The rare earth-cobalt alloys have many special properties and can be used to prepare magnetic and magnetooptical components. So far, rare earth alloy films have usually been produced by sputtering or vacuum plating. If such thin films were prepared by electrodeposition, the production process would be simplified and the manufacturing cost would be reduced. Since the rare earth elements are very active, non-aqueous electrolytes are often used. Hence, electroplating of rare earth-cobalt alloy in organic solvent electrolytes was investigated^[1~3], electroplating of rare earth-cobalt alloy films were carried out in amides with alkali metal halides. And it was classified that the amide melting point is low, the melting point of acetamide-urea eutectic amides is 329 K^[4] and will be further lower with addition of NaBr, the systems of amide with some alkali metal salts have lower melting point^[5~6] too and have higher conductivity^[7], the electric conductivity of molten acetamide-urea(27%)-NaBr(12%) is determined as $9 \text{ mS} \cdot \text{cm}^{-1}$ at 353 K, the acetamide-urea-NaBr melt can dissolve $\text{Y}(\text{NO}_3)_3$ and CoCl_2 easily. In addition the electrodeposition of rare earth-cobalt alloy in urea-NaBr or urea-NaBr-KBr melts have been investigated^[8~10]. Therefore in this paper the electrode processes of Y(III) and Co(II) reduced in acetamide-urea-NaBr melt, the electrodeposition of Cobalt with Y, the surface morphology, the structural states of the electrodeposited films, the effects of the cathode potential, the molar ratio of Y(III)/Co(II), and the electrolysis time on the content

of yttrium are investigated in detail.

2 EXPERIMENTAL

CoCl_2 was obtained by dehydration of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in vacuum at 393 K. $\text{Y}(\text{NO}_3)_3$ was prepared by the reaction of Y_2O_3 and HNO_3 and then dehydrated in vacuum at 413 K. Acetamide was dried in vacuum for 2 h at 323 K. All chemical agents were analytical pure.

The mixture of acetamide-urea(27%)-NaBr(12%) was melted at 353 K. The working electrodes were copper(99.9%, 0.180 cm^2). The counter electrode was spectral pure graphite. The Ag|acetamide-urea-NaBr was used as reference electrode. Cyclic voltammograms were made with HDV-7B potentiostat, 3086 X-Y recorder and HD-1A functional generator. Electrochemical measurements were proceeded under argon(99.99%) atmosphere. The experimental temperature was controlled by oil-bath thermostat. The compositions of deposits were analyzed by EDAX(X-ray Energy Dispersive Analysis) with Link-ISIS 300 Energy Dispersive X-ray Spectrometer. The surface morphology and the structural states of deposits were respectively analyzed with S-520 scanning electron microscope and D/MAX-3A X-ray diffractometer.

3 RESULTS AND DISCUSSION

3.1 Electrode processes of Y(III) and Co(II) in acetamide-urea-NaBr melt

Fig. 1 shows the cyclic voltammogram on copper

① **[Foundation item]** Supported by the Visiting Scholar Foundation of Key Laboratory in the Qinghai Normal University

[Received date] 2001-11-22; **[Accepted date]** 2002-03-22

electrode in acetamide-urea-NaBr. The cathodic limit is -1.0 V and the anodic limit is 0.0 V. So the electrochemical window on copper electrode is 1.0 V. The cyclic voltammogram on copper electrode in $Y(NO_3)_3(0.073 \text{ mol} \cdot \text{L}^{-1})$ -acetamide-urea-NaBr shows that Y(III) could not be reduced to Y alone.

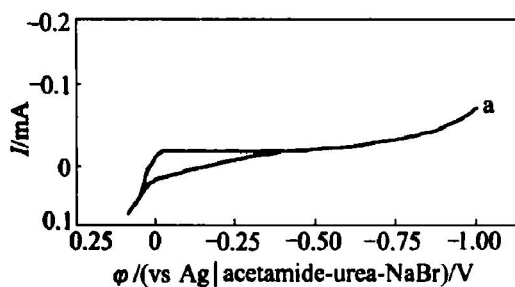


Fig. 1 CV curves of Cu electrode in acetamide-urea-NaBr at 353 K, 100 mV/s

The cyclic voltammogram of copper electrode in $CoCl_2$ -acetamide-urea-NaBr melt is shown in Fig. 2. One cathodic wave starts at -0.32 V. It is due to the reduction of $Co(II)$ to Co , because the electrodeposits within the potential region of this wave were identified as Co by EDAX. Increasing the sweep rate, the peak potential is changed to negative direction. The plot of peak current (I_p) versus sweep rate ($v^{1/2}$) is linear (shown in Fig. 3). These results indicate that the electroreduction of $Co(II)$ to metallic cobalt in acetamide-urea-NaBr melt is irreversible in one step.

According to the equations as

$$|E_p - E_{1/2p}| = 1.857RT/(\alpha n_a F) \quad (1)$$

$$I_p = 0.4958nF(\alpha n_a F D v / RT)^{1/2} AC \quad (2)$$

where α is the transfer coefficient of $Co(II) + 2e^- \rightarrow Co$ and the D is diffusion coefficient of $Co(II)$ in the copper electrode determined as 0.23 and $2.24 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$.

3.2 Codeposition of Y-Co and effect of cathode potential, molar ratio of Y(III)/Co(II) and electrolysis time on content of yttrium

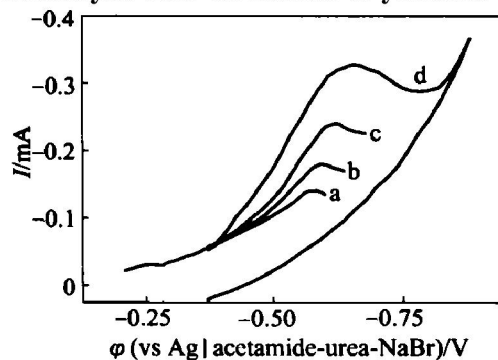


Fig. 2 CV curves of Cu electrode in $CoCl_2(0.03 \text{ mol} \cdot \text{L}^{-1})$ -acetamide-urea-NaBr at 353 K
(a) -10 mV/s ; (b) -20 mV/s ;
(c) -50 mV/s ; (d) -100 mV/s

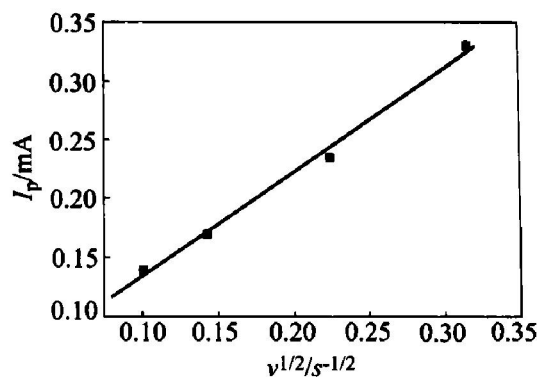


Fig. 3 Plot of I_p vs $v^{0.5}$

Fig. 4 is the polarization curve on copper electrode in acetamide-urea-NaBr- $Y(NO_3)_3(0.073 \text{ mol} \cdot \text{L}^{-1})$ - $CoCl_2$. Cathodic current can be found started at -0.38 V, then the cathodic current is sharply high, which indicates that Y may be inductively codeposited with cobalt. According to Fig. 4, the potentiostatic electrolysis was proceeded on Cu electrode. The deposit film were black and their composition were determined as cobalt and Y by EDAX analysis. This result verifies that Y can be inductively codeposited with cobalt.

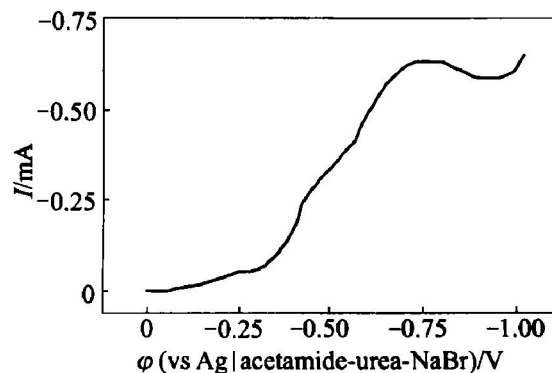


Fig. 4 Polarization curve of copper electrode (0.180 cm^2) in $Y(NO_3)_3(0.073 \text{ mol} \cdot \text{L}^{-1})$ - $CoCl_2(0.03 \text{ mol} \cdot \text{L}^{-1})$ -acetamide-urea-NaBr at 353 K, 100 mV/s

EDAX results of the deposit at different potentials in $Y(NO_3)_3(0.121 \text{ mol} \cdot \text{L}^{-1})$ - $CoCl_2(0.03 \text{ mol} \cdot \text{L}^{-1})$ -acetamide-urea-NaBr are listed in Table 1, the electrolysis time is 25 min. Table 1 shows that the content of yttrium in the deposit increases with the shift of cathode potential to the negative potential. The deposit films are black and the

Table 1 Content of yttrium in Y-Co deposit by potentiostatic electrolysis (25 min)

E/V	$\omega(Y)/\%$	$x(Y)/\%$
-0.65	53.29	43.06
-0.75	63.36	53.41
-0.85	71.73	62.72
-0.90	83.93	77.54

coherence of the deposit on Cu substrate is strong.

The surface of Y-Co alloy film deposited on the Cu substrate was observed by scanning electron microscope (SEM) (shown in Fig. 5). It seems that the deposit is well distributed on the copper substrate. Some cracks of the deposit can also be found distinctly. It was caused by the difference of the expansion coefficient between the Y-Co deposit and the copper substrate when the copper with Y-Co deposit cooled from the melt.

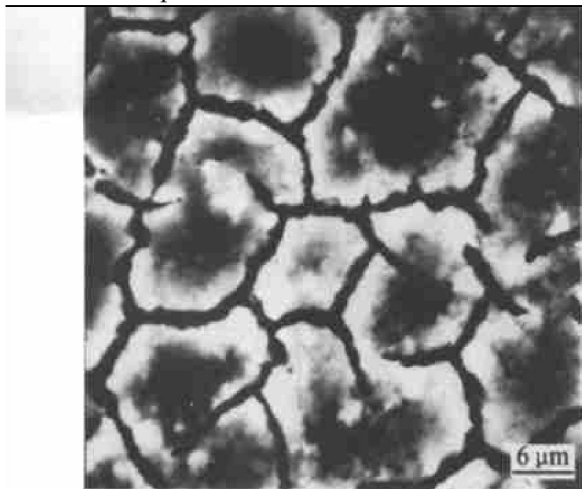


Fig. 5 Surface morphology of Y (53.50%) - Co

EDAX results with different molar ratio of Y (III) / Co (II) are listed in Table 2. The electrolysis time is 25 min. It can also be observed that, the content of yttrium in deposit increases with an increase of the molar ratio of Y (III) / Co (II) in the melt. The higher the molar ratio of Y (III) / Co (II) in the melt, the more the content of Y in the deposits on the copper substrate.

Table 2 Content of yttrium in Y-Co deposit at different molar ratios of Y (III) to Co (II) (– 0.90 V, 25 min)

$n(\text{Y(III)}) / n(\text{Co(II)})$	$c(\text{Y(III)}) / (\text{mol} \cdot \text{L}^{-1})$	$\omega(\text{Y}) / \%$	$x(\text{Y}) / \%$
2.43	0.073	64.10	54.21
3.23	0.097	81.42	74.39
4.03	0.121	83.93	77.54
4.87	0.146	85.01	78.99

At the same time, the electrolysis time also affects the content of yttrium. When the concentration of Y (III) and Co (II) in acetamide-urea-NaBr is $0.121 \text{ mol} \cdot \text{L}^{-1}$ and $0.03 \text{ mol} \cdot \text{L}^{-1}$, deposits obtained at – 0.90 V for 15, 25 and 35 min were analyzed and the contents of the yttrium were 48.79%, 64.10% and 69.63% respectively. Tong^[11] found that the electrolysis time would affect the Gd content of the deposited film Gd-Ni in urea-NaBr melt. It is likely that deposition rate of iron group is slower than rare earth in the amide melt.

3.3 Structural state analysis

The XRD pattern of the Y-Co film obtained by potentiostatic electrodeposit (– 0.90 V, 35 min) in Y (NO₃)₃ ($0.073 \text{ mol} \cdot \text{L}^{-1}$)-CoCl₂ ($0.03 \text{ mol} \cdot \text{L}^{-1}$)-acetamide-urea-NaBr is shown in Fig. 6. The three sharp diffraction peaks ($2\theta = 43.260^\circ$, 50.400° , and 74.080°) belong to the substrate Cu, because the d value of the three sharp diffraction peaks ($d = 2.0896$, 1.8090 and 1.2787) consistent with that of Cu ($d = 2.088$, 1.808 and 1.278). The deposited film is relatively thin. We can not find other obvious sharp diffraction peaks. Hence, the Y-Co film can be considered to be amorphous.

Table 3 Content of yttrium in Y-Co deposit at different electrolysis times (– 0.90 V)

Electrolysis time / min	$\omega(\text{Y}) / \%$	$x(\text{Y}) / \%$
15	48.79	38.71
25	64.10	54.21
35	69.63	60.32

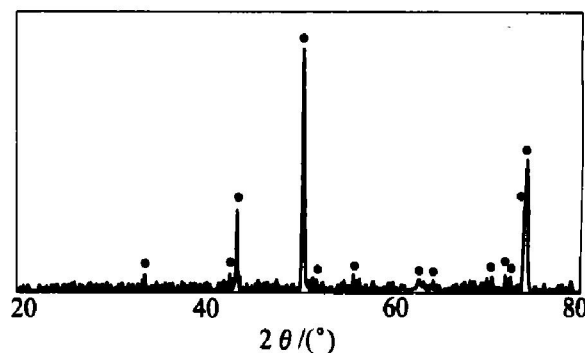


Fig. 6 XRD (Cu K_α radiation) pattern of Y-Co (63.36% Y)

4 CONCLUSIONS

1) Electroreduction of Co (II) to Co is irreversible in one step. The transfer coefficient and the diffusion coefficient at 353 K are determined as 0.23 and $2.24 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$.

2) Y (III) does not reduced to Y alone, but can be inductively codeposited with Co (II) in acetamide-urea-NaBr melt.

3) The content of Y increases with the cathode potential shifts to negative direction, the molar ratio of Y (III) to Co (II) increases and the electrolysis time lengthens. The content of yttrium in deposit reaches as high as 83.93%.

4) The Y-Co alloy film electrodeposited in acetamide-urea-NaBr melt is amorphous.

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(Edited by LONG Huai-zhong)