Preparation of Gd-Co alloy film in acetamide-urea-NaBr melt①

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[Abstract] Electroreduction of Co(II) to metallic Co in acetamide-urea-NaBr melt at 353 K is irreversible in one step. Gd(III) is not reduced to Gd alone, but can be inductively codeposited with Co(II). The amorphous Gd-Co alloy films were obtained by potentiostatic electrolysis. With the cathode potential shifting to negative direction, the content of gadolinium in the alloy increases and can get to 65.89% (mass fraction). The additive of Na₂EDTA can make the diameter of the particles of crystalline alloy smaller and change the shape of particles.

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

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1 INTRODUCTION

Films of rare earth-cobalt alloy have many special performances and can be used to make functional materials, for example, Gd-Co alloy film has good magneto-optic effect and can be used to prepare magnetic and magneto-optical 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 alloy in organic solvent electrolytes has been investigated[1].

The follows were clear that the melting point of amide is low and that of the acetamide-urea eutectic amides is 329 K[2], the systems of amide with some alkali metal salts can lower melting point[3, 4] and have higher conductivity[5], the electric conductivity of molten acetamide-urea(27%, mass fraction)-NaBr (12%, mass fraction) was 0.9 S/m at 353 K, the acetamide-urea-NaBr melt can dissolve GdCl₃ and CoCl₂ easily, electrodeposition of rare earth-cobalt alloy in urea-NaBr or urea-NaBr-KBr melts have been prepared[6~8]. So, in this paper, the electrode processes of Gd(III) and Co(II) reduced in acetamide-urea-NaBr melt, electrodeposition of Cobalt with gadolinium, the surface morphology and the structural states of the electrodeposited films, and the influence of the additive of Na₂EDTA on the diameter of particles of the alloy are investigated.

2 EXPERIMENTAL

CoCl₂ was obtained by dehydration of CoCl₂·6H₂O in vacuum at 393 K. GdCl₃ was prepared by the reaction of Gd₂O₃ and NH₄Cl at about 623 K. Acetamidemide was dried in vacuum for 2 h at 323 K. All chemical agents were analytical pure.

The mixture of acetamide-urea-NaBr was melted at 353 K. The working electrodes were platinum(99.9%) and copper (99.9%). 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 Gd(III) and Co(II) in acetamide-urea-NaBr melt

Fig. 1 shows the cyclic voltammogram of platinum electrode in acetamide-urea-NaBr melt(353 K). The cathodic limit is − 0.68 V and the anodic limit is + 0.75 V. So the electrochemical window on platinum electrode is 1.43 V.

The cyclic voltammogram of platinum electrode in acetamide-urea-NaBr-GdCl₃ melt is shown in Fig. 2. One cathodic wave starts at − 0.25 V. It is different from the reduction process of Gd(III) in urea-NaBr melt. Gd(III) have no cathodic wave appearing before the cathodic limit of the background in urea-NaBr melt[9]. It may be the effect of acetamide[10].

But the Gd could not electrodeposite within the potential region of this wave in acetamide-urea-NaBr-GdCl₃ melt.

　　Fig. 3 shows the cyclic voltammogram of platinum electrode in acetamide-urea-NaBr-CoCl₂. One cathodic wave started at − 0. 20 V. It is due to the
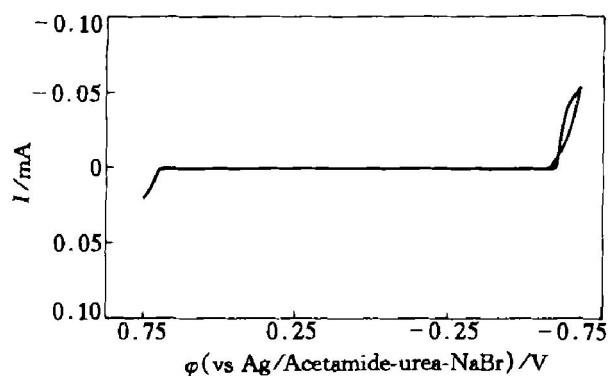

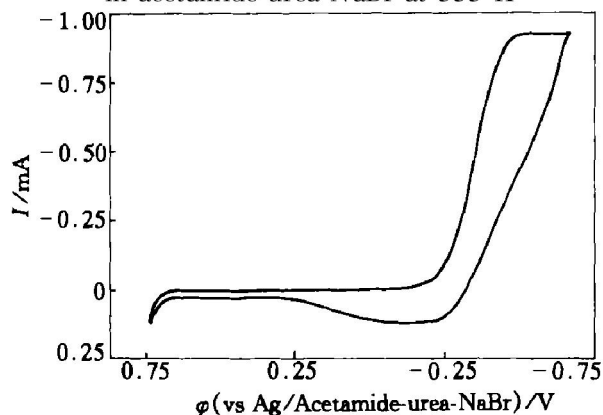**Fig. 1**　Cyclic voltammogram of platinum electrode
in acetamide-urea-NaBr at 353 K

Fig. 2　Cyclic voltammogram of platinum
electrode in acetamide-urea-
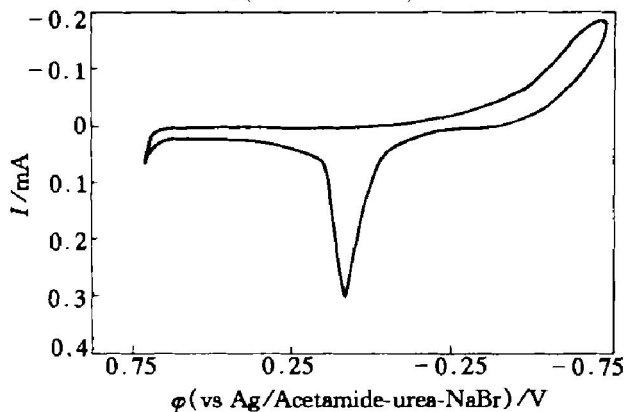NaBr-GdCl₃(0. 13 mol/ L) at 353 K

Fig. 3　Cyclic voltammogram of platinum
electrode in acetamide-urea-
NaBr-CoCl₃(0. 03 mol/ L) at 353 K

reduction of Co(II) to Co, because the electrodeposite within the potential region of this wave were identified as Co by EDAX. The potential of the anodic stripping peak is at about + 0. 08 V, which is much positive to the potential of the cathodic peak. The plot of I_p versus $v^{0.5}$ (I_p —peak current, v —sweep rate) is linear. These results indicate that the reduction of Co(II) to metallic cobalt is irreversible in one step.

　　According to the following equations,

$$| E_p - E_{0.5p} | = 1.857 RT / (\alpha n_a F) ,$$

$$I_p = 0.4958 nF (\alpha n_a FDv / RT)^{0.5} A C$$

the α(transfer coefficient) of Co(II) $+ 2e \rightarrow$ Co and the D (diffusion coefficient) of Co(II) were determined as 0. 26 and 2.83×10^{-7} cm²/ s.

3. 2　Codeposition of Gd-Co and influence of Na₂EDTA on surface morphology of alloy

　　The cyclic voltammogram of platinum electrode in acetamide-urea-NaBr-GdCl₃-CoCl₂ is shown in Fig. 4. From it, one cathodic wave can be found, the potential of the cathodic stripping peak is about − 0. 45 V, and the cathodic current increases sharply. One anodic stripping peak can be found at about 0 V, which is more negative and the anodic current increases to be higher compared to that in melt only contained Co (II) also. Above results indicate that the gadolinium may be inductively codeposited with cobalt.
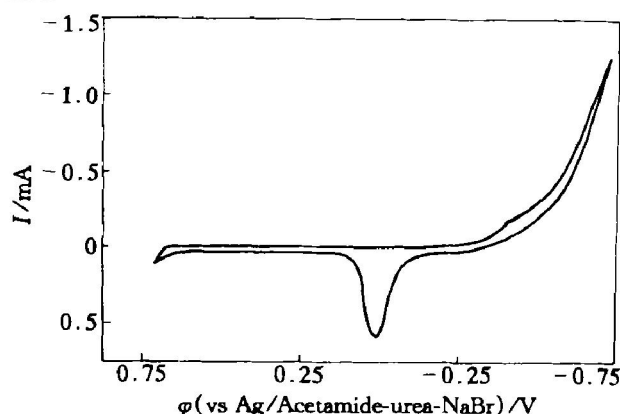

Fig. 4　Cyclic voltammogram of platinum
electrode in acetamide-urea-NaBr-GdCl₃
(0. 13 mol/ L)-CoCl₂(0. 03 mol/ L) at 353 K

　　Fig. 5(a) and (b) show the polarization curve of copper electrode in acetamide-urea-NaBr and acetamide-urea-NaBr-GdCl₃-CoCl₂, respectively. According to Fig. 5(b), the potentiostatic electrolysis was proceeded on Cu electrode as cathode. The deposit film was grey black and its composition was determined as cobalt and gadolinium by EDAX analysis. This result verifies that the gadolinium can be inductively codeposited with cobalt.

　　EDAX results of deposit with different potentials are listed in Table 1. The electrolysis time is 20 min.
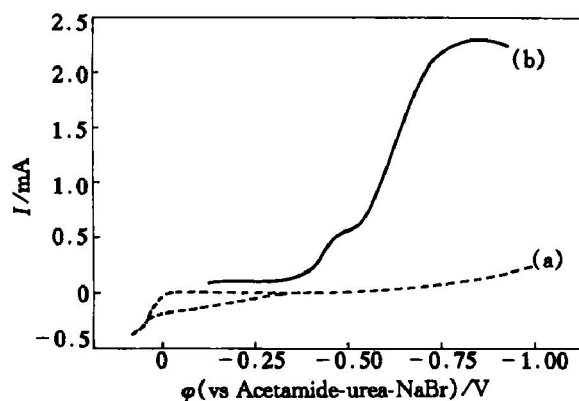
Fig. 5 Cyclic voltammogram of copper electrode
in acetamide-urea-NaBr (a) and acetamide-
urea-NaBr-GdCl₃(0. 13 mol/ L)-CoCl₂
(0. 03 mol/ L) (b) at 353 K

Table 1 shows that with the shift of cathode potential
to negative direction, the content of gadolinium in-
creases. The polarization curve of copper electrode of
acetamide-urea-NaBr-CoCl₂-GdCl₃(as shown in Fig. 5
(b)) can explain that. Two cathodic waves can be
found, and the potential of the first cathodic stripping
peak is about − 0. 50 V, which is corresponded to the
reduction of Co(II) to metallic cobalt. Then the ca-
thodic current increases sharply. The potential of the
second cathodic stripping peak is about − 0. 78 V,
which is corresponded to the reduction of Gd(III) to
Gd with Co(II) to Co. When the electrolytic poten-
tial is very negative, the coherence of the deposit on
Cu substrate is the weakest and the color turns dark-
er.

Table 1   Content of gadolinium in Gd-Co deposit

φ/ V	w / %	x / %
− 0. 60	1. 08	0. 41
− 0. 65	2. 04	0. 78
− 0. 70	28. 50	11. 28
− 0. 75	53. 50	24. 57
− 0. 85	65. 89	41. 99

The surfaces of Gd-Co alloy films deposited on
the Cu substrate were observed by Scanning Electron
Microscope (SEM) (as shown in Fig. 6 and Fig. 7).
Fig. 6 is the Gd (53. 50%, mass fraction)-Co deposit
obtained by potentiostatic electrodeposit at − 0. 75 V
in   acetamide-urea-NaBr-GdCl₃ (0. 13   mol/ L)-CoCl₂
(0. 03 mol/ L). Fig. 7 is the Gd(46. 03%, mass frac-
tion)-Co deposit obtained by potentiostatic electrode-
posit at − 0. 75 V in acetamide-urea-NaBr-GdCl₃(0.
13 mol/ L)-CoCl₂ (0. 03 mol/ L)-Na₂EDTA (0. 06
mol/ L). In Fig. 6 the particles is needle shape. In
Fig. 7 the diameter of the particles is smaller. We can
consider that the additive of Na₂EDTA can make the
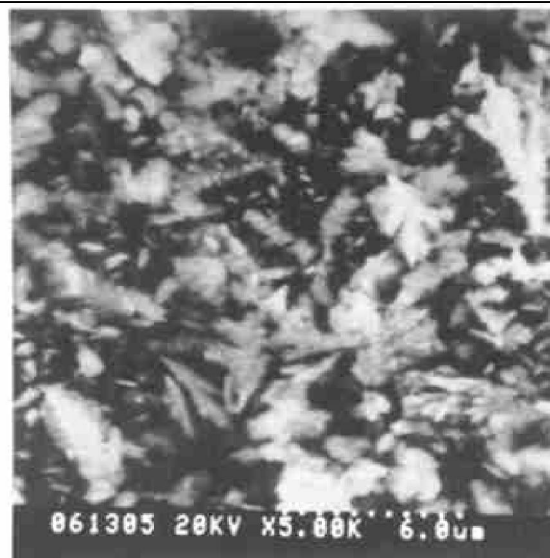diameter of the particles smaller and change the shape
of the particles.

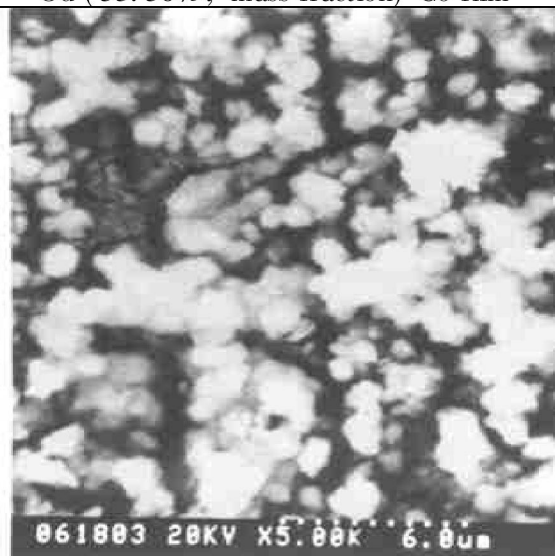**Fig. 6** Surface morphology of
Gd (53. 50%, mass fraction)-Co film

Fig. 7 Surface morphology of
Gd (46. 03%, mass fraction)-Co film

3. 3 Structural state analysis

The XRD pattern of the Gd-Co deposit obtained by
potentiostatic electrodeposit (− 0. 75 V, 60 min) is
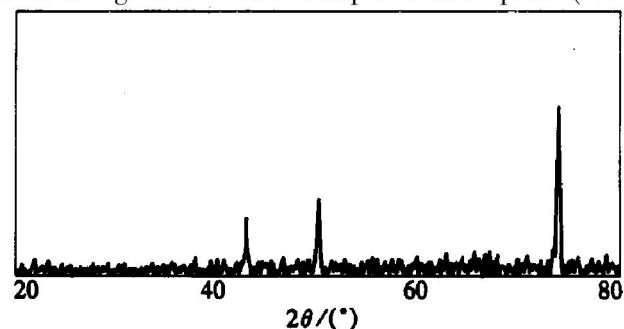shown in Fig. 8. The three sharp diffraction peaks (2θ

Fig. 8 XRD pattern of Gd-Co deposit obtained by
potentiostatic electrodeposit(− 0. 75 V, 60 min)

= 43. 160°, 50. 320°, 73. 980°) belong to Cu, because the d value of the three sharp diffraction peaks (d = 2. 0 942, 1. 811 7 and 1. 280 2) consistent with that of Cu(d = 2. 088, 1. 808 and 1. 278). Hence, the Gd-Co film can be considered to be amorphous.

4　CONCLUSIONS

1) Electroreductions of Co (II) to Co in acetamide-urea-NaBr melt at 353 K is irreversible in one step.

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

3) The content of Gd increases with the shift of cathode potential to negative direction.

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

5) The additive of Na$_2$EDTA can make the diameter of particles of crystalline alloy smaller and change the shape of particles.

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