Preparation of Gd-Ni alloy film in urea-NaBr melt[①]

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[Abstract] Electroreduction of Ni(II) to metallic Ni in urea-NaBr melt at 373 K is irreversible in one step. Gd(III) is not reduced to Gd alone, but can be inductively codeposited with Ni(II). The amorphous Gd-Ni alloy films were obtained by potentiostatic electrolysis and galvanostatic electrolysis. With the cathode potential shift to negative direction and the increase of current density, the content of gadolinium in the alloy increases first, and then drops down gradually. The molar ratio of Gd(III) to Ni(II) and the time also influence the content of Gd. Crystalline GdNi₃ alloy was obtained after heat treatment of the deposit.

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

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1　INTRODUCTION

Gd in 4f lanthanoid has ferromagnetic-paramagnetism transform temperature (Curie point), and the highest magnetic thermal entropy changes at room temperature. So far, it is still the best magnetic refrigeration working substance material at room temperature. Now rare earth alloy films are produced by sputtering or vacuum plating, while electrodeposition of rare earth metals and their alloys in aqueous solution are very difficult. Hence, electroplating of rare earth alloy in organic solvent electrolytes has been investigated[1].

The systems of urea with some alkali metal salts have lower melting point (301~ 389 K)[2]. The metal halides have greater solubility and higher conductivity[3]. Golubchik et al[4] investigated the surface metallizing of aluminum with indium, indicated that the oxide film on aluminum substrate and water impurity could be removed in urea melt. We had ever prepared some rare earth-cobalt, rare earth-iron alloys and Ti-Ni in urea-NaCl, urea-NaBr-KBr or urea-NaBr melts[5~ 11]. In this paper, the electrode processes of Ni(II) reduced in urea-NaBr melt, electrodeposition of nickel with gadolinium, the surface morphology and the structural states of the electrodeposited films and the heat treated films have been investigated.

2　EXPERIMENTAL

NiCl₂ was obtained by dehydration of NiCl₂ · 6H₂O in vacuum at 393 K. GdCl₃ was prepared by the reaction of Gd₂O₃ and NH₄Cl at about 623 K. All chemical agents are analytical pure.

The mixture of urea and salts was melted at temperature of about 373 K. The working electrodes were platinum (99. 9%) and copper (99. 9%). The counter electrode was spectral pure graphite or platinum sheet. The Ag | urea-NaBr(20%, mass fraction) 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 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 and deposits after heat treatment 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 Ni(II) in urea-NaBr melt

Reduction potential of Gd(III) in the urea melt is so negative that no cathodic wave appears before the cathodic limit of the background, as shown in Fig. 1. Hence the Gd(III) can not deposite in urea melt alone.

Fig. 2. is the Cyclic voltammogram of platinum electrode in the melt containing NiCl₂. One cathodic wave started at - 0. 22 V is due to the reduction of Ni (II) to Ni, and electrodeposits within the potential region of this wave has been identified as nickel by EDAX. The potential of the anodic stripping peak is
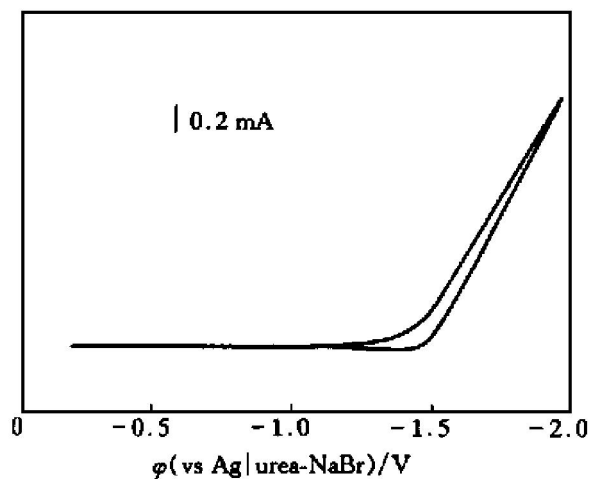
Fig. 1　Cyclic voltammogram of platinum electrode (0. 091 cm^2) in urea-NaBr-GdCl$_3$(0. 18 mol•L^{-1}) at 373 K,　100 mV•s^{-1}
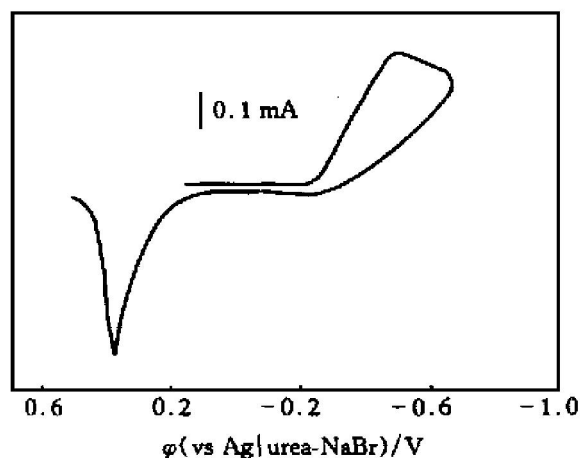
Fig. 2　Cyclic voltammogram of platinum electrode (0. 091 cm^2) in urea-NaBr-NiCl$_2$(0. 036 mol•L^{-1}) at 373 K,　100 mV•s^{-1}

at about + 0. 38 V, which is much positive than that of the cathodic peak. So, we can consider that the reduction of Ni(II) to metallic nickel is irreversible.

3. 2　Codeposition of nickel and gadolinium

The cyclic voltammogram of platinum electrode in the melt, which contained Ni(II) and Gd(III), is shown in Fig. 3. Only one cathodic wave can be found, and the starting potential of the cathodic wave is − 0. 15 V, which is positive compared to the melt contained Ni(II) alone, and the cathodic current is sharply higher. This result indicates that the gadolinium may be inductively codeposited with nickel.

According to the voltammogram of copper electrode in urea-NaBr-NiCl$_2$-GdCl$_3$ melt (shown in Fig. 4), potentiostatic electrolysis was proceeded on Cu electrode as cathode. The deposit film was grey black and its composition was determined as nickel and gadolinium by EDAX analysis. This result verifies that the gadolinium can be inductively codeposited
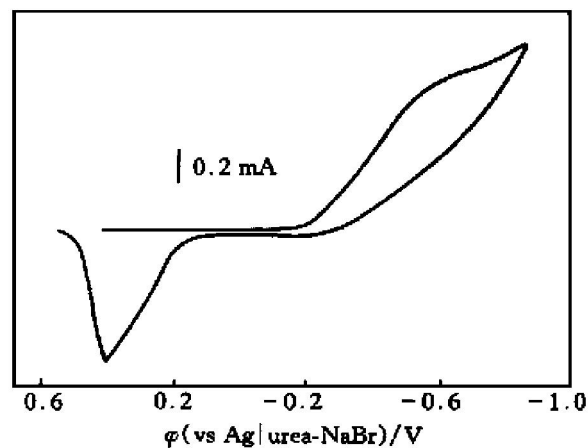

Fig. 3　Cyclic voltammogram of platinum electrode (0. 091 cm^2) in urea-NaBr-NiCl$_2$(0. 036 mol•L^{-1})-GdCl$_3$(0. 18 mol•L^{-1}) at 373 K,　100 mV•s^{-1}
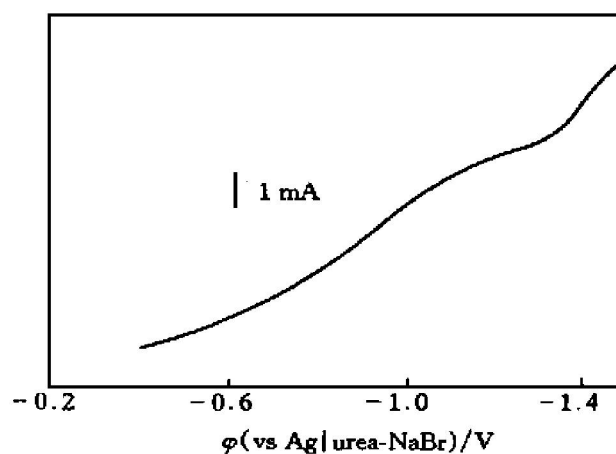
Fig. 4　Voltammogram of copper electrode (0. 85 cm^2) in urea-NaBr-NiCl$_2$(0. 036 mol•L^{-1})-GdCl$_3$(0. 18 mol•L^{-1}) at 373 K,　20 mV•s^{-1}

with nickel.

3. 3　Factors influencing composition of electrodeposited Gd-Ni film

EDAX results of the deposit with different molar ratios of Gd(III) to Ni(II) are listed in Table 1. At the potential of − 1. 0 V and molar ratio of 6. 1: 1, the content of gadolinium is the highest. When the electrolytic current is very high, the coherence of the deposit on Cu substrate is the weakest. When increasing content of gadolinium in Gd-Ni, color turns darker. Table 1 shows that with the shift of cathode potential to negative direction, the content of gadolinium increases first, and then drops down gradually. It can also be observed that, in the range of the molar ratios of Gd(III) to Ni(II) we chose, the content of gadolinium in the deposit increases with the rise of molar ratio in the solution.

At the same time, electrodepositing time also affects the Gd content. When the molar ratio of Gd (III) to Ni(II) was 4. 9: 1, the deposits obtained at

Table 1 Mass fractions of gadolinium in
Gd-Ni deposit at different potentials（ % ）

Molar ratio of Gd(III) to Ni(II)	Cathode potential/ V				
	− 0. 85	− 0. 90	− 0. 95	− 1. 00	− 1. 10
4. 9: 1	0. 25	0. 45	5. 48	1. 32	
6. 1: 1		0	0. 68	29. 6	10. 7

− 0. 90 V for 15 min and 30 min, contents were ana-
lyzed respectively with 0. 48% and 1. 07% Gd re-
spectively. The coating gets thicker with time
longer. Frequently the agent nickel is near the copper
substrate, with black outermost layer-Gd, so it is
likely that the deposition rate of nickel is faster than
that of gadolinium. The fact that the content of Gd
increases with time can also verify it.

Table 2 lists the composition of Gd-Ni deposits
obtained by galvanostatic electrodeposit. When in-
creasing current density, the content of gadolinium
increases first, and then drops down gradually.

Table 2 Mass fraction of gadolinium in
Gd-Ni deposit at different current densities
and molar ratio of Gd(III) to Ni(II) at 4. 1: 1

$J/ (mA•cm^{-2})$	7. 69	12. 30	16. 67	20. 00
$w (Gd) / \%$	0. 10	0. 93	34. 02	30. 09

### 3. 4　Structural analysis of deposit
3. 4. 1　XRD analysis of Gd-Ni deposit

The XRD pattern of the Gd (30. 09%)-Ni de-
posit obtained by potentiostatic electrodeposit is
shown in Fig. 5, and the results are the same with
galvanostatic electrodeposit. The two sharp diffrac-
tion peaks ($2\theta= 43. 10°$, $2\theta= 50. 24°$) belong to the
Cu substrate, because the d value of the two sharp
diffraction peaks ($d = 2. 096$ Å and $d = 1. 811$ Å)
consistent with that of Cu ($d = 2. 088$ Å and $d =
1. 808$ Å), and the deposit is likely relatively thin.
The XRD pattern of an amorphous film shows broad
diffraction peak, so much as the diffraction peak dis-
appeared. Hence, the Gd-Ni film can be considered to
be amorphous.

3. 4. 2　XRD pattern of Gd-Ni deposit after heat
　　　treatment
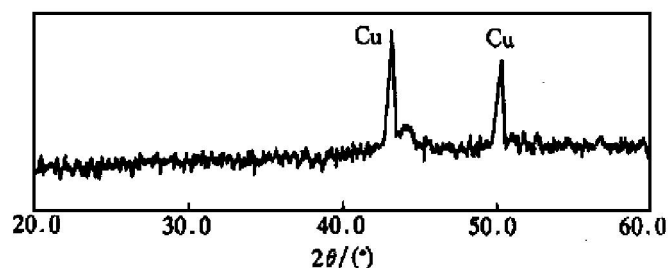
Fig. 5 XRD (CuK$_\alpha$ radiation) pattern of
Gd (34. 02%)-Ni deposit

The XRD pattern of the Gd (30. 28%)-Ni de-
posit film after heat treatment is shown in Fig. 6.
Two sharp diffraction peaks corresponding to $2\theta=
42. 40°$ and $2\theta= 49. 56°$ can be found. We consider
they belong to GdNi$_3$, because in the range of the
possible substances, only the d value of GdNi$_3$($d =
2. 130$ Å and $d = 1. 838$ Å) is close to the diffraction
peak in Fig. 6 ($d = 2. 130$ Å and $d = 1. 841$ Å). It
shows that the alloying process of gadolinium and
nickel in the deposit occurred, and the GdNi$_3$ phase
was formed after heat treatment. Hence, the amor-
phous deposited Gd-Ni film can be considered to be
crystalline.
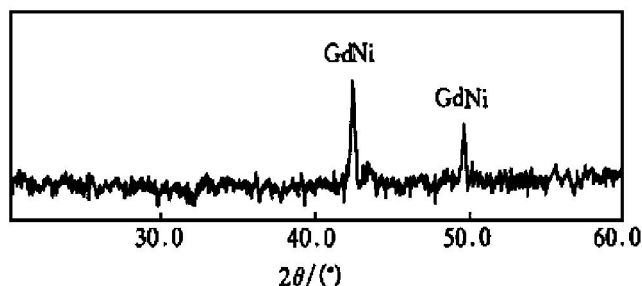
Fig. 6 XRD (CuK$_\alpha$ radiation) pattern of
Gd(30. 28%)-Ni deposit after heat
treatment at 873 K for 1 h

The surface of the Gd-Ni deposit on the Cu sub-
strate after heat treatment was observed by Scanning
Electron Microscope (shown in Fig. 7). The crys-
talline particles appear clearly in the photo. Some
cracks of the deposit can also be found distinctly. It
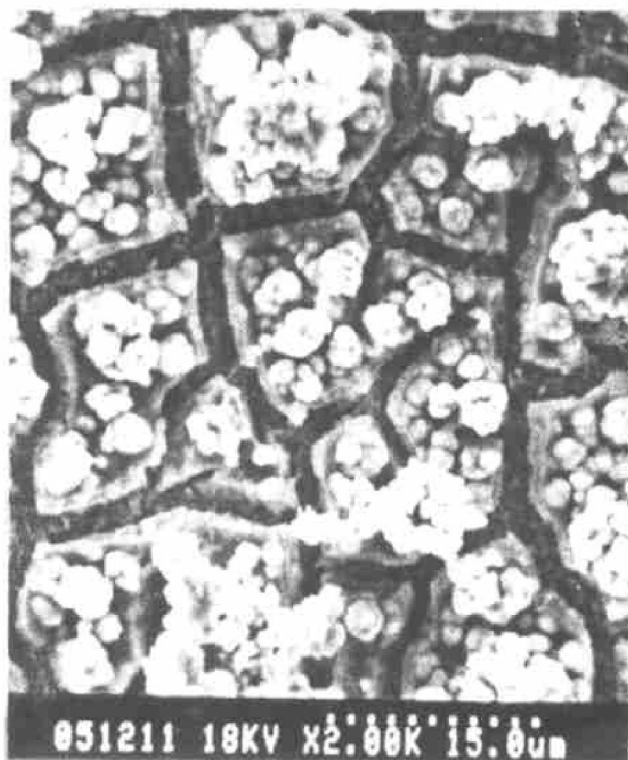
Fig. 7 Surface morphology of Gd(30. 28%)-Ni
after heat treatment at 873 K

was caused by the difference of the expansion coefficient between the Gd-Ni deposit and the copper substrate at high temperature.

4 CONCLUSIONS

1) Electroreduction of Ni(II) to Ni in urea-NaBr melt at 373 K is irreversible.

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

3) With the shift of cathode potential to negative direction and with current density being raised, content of Gd increases first, and then drops down gradually. The molar ratio of Gd(III) to Ni(II) and electrodepositing and time all influence the content of Gd.

4) The Gd-Ni film electrodeposited in urea-NaBr melt is amorphous. After heat treatment, $GdNi_3$ phase was formed and the morphology of the deposit changed to crystalline.

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