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Electrodeposition of Cobalt and Rare Earth-Cobalt in Urea-NaBr-KBr Melt

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Tab. 3　Contents of rare earth in deposits at different cathodic potentials

deposit	Cathodic potential			
	−0.90 V	−0.95 V	−1.00 V	−1.05 V
La-Co	55.21 wt%	63.75 wt%	72.71 wt%	80.03 wt%
	34.34 at%	42.73 at%	53.06 at%	62.97 at%
Dy-Co	28.53 wt%		57.09 wt%	
	12.65 at%		32.55 at%	
Tm-Co	47.62 wt%		59.19 wt%	
	24.08 at%		33.60 at%	

References

1　Usuzaka N，Yamaguchi H，Watanabe T. Preparation and magnetic properties of Co-Gd amorphous films by electroplating method. *Mater. Sci. Eng.*，1988，99：105

2　Yang Qiqin，Qiu Kairong，Fan Shijuan. Electroreduction of Co(Ⅰ) and La(Ⅲ) in urea melt. *Rare Metals*，1995，14：13

3　Gambino M，Bros J P. Capacite calorifique de l'uree et de quelques melanges eutectiques a base d'uree entre 30 et 140 ℃. *Thermochimica Acta*，1988，127：223

尿素-NaBr-KBr 熔体中钴及稀土-钴的电沉积

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摘要　稀土-钴合金具有许多优异性能，可用于制作磁性、磁光…等功能材料. 日本学者研究了在有机电解液中电沉积Co-Gd 薄膜，未见前人研究低温熔盐体系中电沉积稀土合金的报道. 尿素-(79 mol%)-NaBr(19.5 mol%)-KBr(1.5 mol%)的熔点为51 ℃，可在100 ℃左右下作为电解介质. 在尿素熔体中加入NaOAc，能增加Co^{2+} 还原为 Co 的阴极极化. 因此选择100 ℃的尿素-NaBr-KBr-NaOAc 作为本底熔体，研究Co^{2+} 的电还原，镧、铽、镝、铥各自与钴的电解共沉积. 在所研究的熔体中，Co^{2+} 一步不可逆还原为Co. 测定$Co^{2+}+2e=Co$ 反应的传递系数α为0.45，Co^{2+} 在熔体中的扩散系数为2.5×10^{-6} $cm^2 \cdot s^{-1}$. 稀土离子还原为稀土金属的电位很负，以致在本底熔体分解前未出现阴极波. 但在含$CoCl_2$ 熔体中加入$RECl_3$($LaCl_3$、$TbCl_3$、$DyCl_3$、$TmCl_3$)，使钴的析出电位向正方移动，而且阴极电流增大，因而有可能发生RE(La、Tb、Dy、Tm)与Co 的诱导共沉积. 在尿素-NaBr-KBr-NaOAc-$CoCl_2$-$RECl_3$ 熔体中进行电解，可得到La-Co、Tb-Co、Dy-Co、Tm-Co 沉积物. 沉积物中的稀土含量随阴极电位向负方移动而增加，Dy、Tm 的含量可达50 wt%，La 达到80 wt%. 尿素-NaBr-KBr-NaOAc 低温熔体是电沉积稀土-钴薄膜的新的电解介质，有希望获得稀土含量高的电沉积物. 因此，必须进一步研究影响稀土-钴沉积物的稀土含量和结构的因素.

关键词　稀土-钴合金，电解共沉积，Co^{2+}的电还原，尿素-NaBr-KBr 熔体

Electrodeposition of Cobalt and Rare Earth-Cobalt in Urea-NaBr-KBr Melt[①]

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Films of rare earth-cobalt alloys have many special performances and can be used to make the functional materials (e. g. the magnetic and magneto-optic). Electrodeposition of Gd-Co film in organic solvent electrolyte has been investigated[1]. No electrodeposition of rare earth-cobalt alloy in low temperature molten salt has been reported before we obtained the La-Co alloy electrodeposited from molten urea-metal chlorides at 125 ℃[2]. The m. p. of urea(79 mol%)-NaBr(19. 5 mol%)-KBr(1. 5 mol%) is 51 ℃[3] and can be used at about 100 ℃. The addition of NaOAc into the urea melt, the cathodic polarization of Co^{2+} reduced to Co can be increased[2]. In this paper, electroreduction of Co^{2+}, electrolytic codeposition of cobalt with lanthanum, terbium, dysprosium and thulium respectively in urea-NaBr-KBr-NaOAc melt at 100 ℃ are investigated.

1 Experiment

$CoCl_2$ was obtained by the dehydration of $CoCl_2 \cdot 6H_2O$ in vacuum at about 120 ℃. Anhydrous rare earth chlorides($RECl_3$) were prepared by the reaction of RE_2O_3 and NH_4Cl at 350 ℃. Mixture of urea, NaBr, KBr and NaOAc was melted at 100 ℃ to form the background. The working electrodes are spectral pure graphite and copper. The counter electrodes are spectral pure graphite and cobalt. The reference electrode is Ag/urea-NaBr-KBr. The electrochemical measurements were proceeded at argon atmosphere and the temperature was controlled by oil bath. The composition of the deposit was analysed by EDAX.

2 Results and discussion

2. 1 Cyclic voltammogram

The cyclic voltammogram(CV) of graphite electrode in the background is shown in Fig. 1(a). It shows that the cathodic limit of the background is about —1. 3 V.

Fig. 1(b) is the CV of graphite electrode in the melt contained $CoCl_2$. One cathodic wave started at —0. 72 V. It is due to the reduction of Co^{2+} to Co, because the electrodeposits within the potential

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region of this wave were identified as cobalt by EDAX. The anodic stripping peak of cobalt is very far from the cathodic wave. The peak potential of the cathodic wave is changed with the sweep rate and the plot of I_p vs $v^{1/2}$ is linear (Fig. 2). So, the electrodeposition of cobalt is irreversible. According to the equations:

$$|E_p - E_{p/2}| = 1.857RT/\alpha n_a F$$
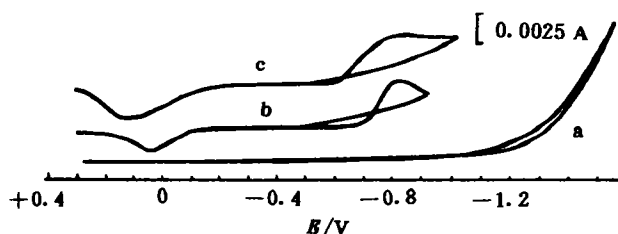$$I_p = 0.459\, 8nFACD^{1/2}$$
$$(\alpha n_a F/RT)^{1/2} v^{1/2}$$

Fig. 1 CV of graphite electrode(0.36 cm²) at 100 ℃ and 0.05 V·s⁻¹

(a) in the background, (b) in the melt contained 0.06 mol·L⁻¹ CoCl₂, (c) in the melt contained 0.06 mol·L⁻¹ CoCl₂ and 0.2 mol·L⁻¹ LaCl₃

and the Fig. 2, the αn_a was calculated as 0.89(Table 1) and the diffusion coefficient of Co^{2+} in the melt was determined as 2.5×10^{-6} cm²·s⁻¹. The transfer coefficient, α was determined as 0.45 because the n_a is 2.
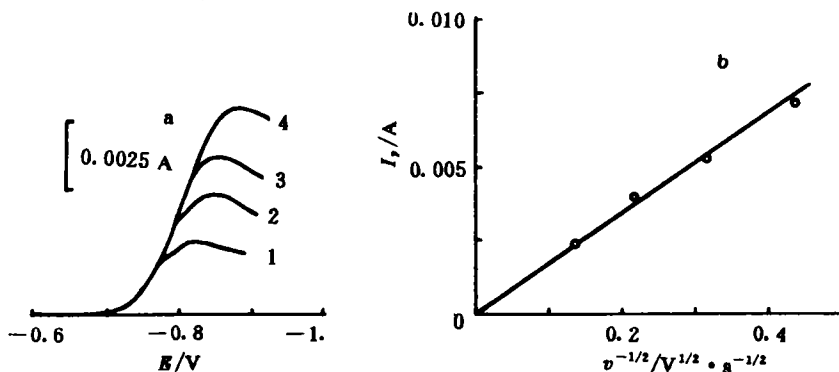

Fig. 2 (a) Voltammograms of graphite electrode(0.36 cm²) in the melt contained 0.06 mol·L⁻¹ CoCl₂ at different sweep rare (V·s⁻¹): 1—0.02, 2—0.05, 3—0.10, 4—0.20 (b) I_p of (a) vs $v^{1/2}$

Reduction potential of RE^{3+} to rare earth metal is so negative that no cathodic wave appeared before the cathodic limit of the background. The CV of graphite electrode in the melt which contained Co^{2+} and La^{3+} is shown in Fig. 1c. The starting potential of the cathodic wave is -0.63 V which is positive compared to that of the melt containing Co^{2+} but no La^{3+}, and the cathodic current is higher. This result indicates that the lanthanum may be inductively codeposited with cobalt. The composition of deposits obtained by potentiostatic electrolysis at -0.8 V was analysed as cobalt and lanthanum by the means of EDAX. Tb^{3+} (or Dy^{3+}, Tm^{3+}) instead of La^{3+}, the CV is similar to the CV of the melt containing CoCl₂ and LaCl₃(Fig. 1c). Hence, we can consider that the terbium, dysprosium, thulium also can be inductively codeposited with cobalt.

2. 2　Electrolytic experiments

The La-Co，Tb-Co，Dy-Co，Tm-Co deposits were obtained on Cu cathode in the urea-NaBr-KBr-NaOAc-CoCl$_2$-RECl$_3$ melt at 100 ℃. The contents of rare earth in the deposits at the cathodic current density of 0. 015 A · cm^{-2} were listed in Tab. 2. The EDAX spectrum of Tb-Co and Tm-Co are shown in Fig. 3.

Tab. 1　Transfer coefficients of Co^{2+} + 2e = Co

v, V · s^{-1}	$\|E_p - E_{p/2}\|$, V	an_a	a
0. 02	0. 060	0. 99	0. 50
0. 05	0. 070	0. 85	0. 43
0. 10	0. 065	0. 92	0. 46
0. 20	0. 075	0. 80	0. 40
	average	0. 89	0. 45

Tab. 2　Contents of rare earth in deposits at 0. 015 A · cm^{-2}

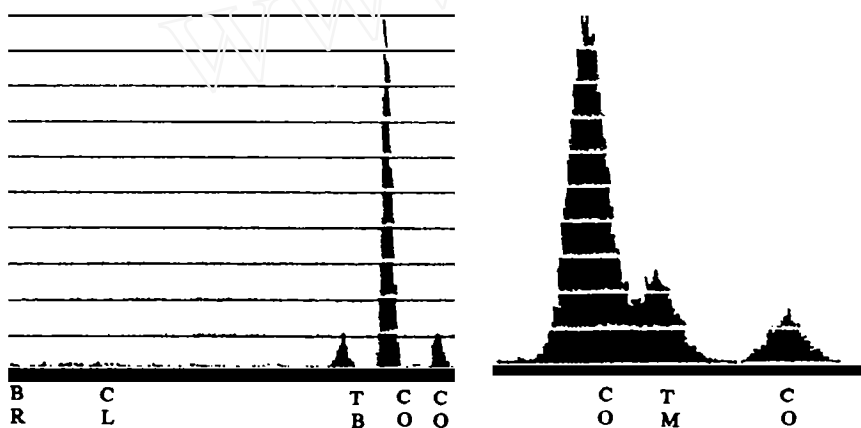| depost	RE, wt%
La-Co	63. 54
Tb-Co	17. 30
Dy-Co	38. 01
Tm-Co	46. 32

Fig. 3　EDAX spectrum of (a) Tb(17. 3 wt%)-Co and (b) Tm(46. 3 wt%)-Co

The contents of rare earth in the deposits are change with the cathodic potential. From the Tab. 3, we can see that the contents of La, Dy, Tm in the deposit are increased with the shift of the cathodic potential to the negative direction and attain over 50 wt%. In particular, the content of La has attained 80 wt%.

Urea-NaBr-KBr-NaOAc low temperature melt is a new and promising electrolyte system for the electrodeposition of rare earth-cobalt films. It is necessary to further investigate the factors influenced on the rare earth content and the structure of the rare earth-cobalt deposits.

Key words　Rare earth-cobalt alloy, Electrolytic codeposition, Electroreduction of Co^{2+}, Urea-NaBr-KBr melt

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关键词　稀土-钴合金，电解共沉积，Co^{2+} 的电还原，尿素-NaBr-KBr 熔体