第 11 卷 第 11 期 物 理 化 学 学 报 Vol.11, No.11
1995 年 11 月 ACTA PHYSICO - CHIMICA SINICA Nov., 1995

Electrodeposition of Nd-Co, Tb-Co and Yb-Co in Urea-NaBr-KBr Melt*

Yang Qiqin Sa Lichang Qiu Kairong Hong Huichan
(Department of Chemistry, Zhongshan University, Guangzhou 510275)

Keywords: Electrolytic codepostion, Nd-Co, Tb-Co and Yb-Co alloys, Urea-NaBr-KBr melt

Rare earth-cobalt alloys have received much attention because of their functional performances, for example, the magnetic and magneto-optic performances. In the electroplating of rare earth-cobalt (RE-Co) alloys in organic electrolyte, only the Gd-Co and Sm-So films has been reported[1]. Electrodeposition of RE-Co alloys in low temperature molten salt had not been reported before we obtained the La-Co electrodeposited from molten urea-metal chlorides[2]. The melting point of urea (79mol%)-NaBr (19.5mol%)-KBr(1.5mol%) is 51°C[3] and can be used as the electrolytic medium at about 100°C. In this paper, the electrolytic codeposition of cobalt with neodymium, terbium and ytterbium respectively in molten urea-NaBr-KBr medium at 100°C are investigated.

1 Experimental

$CoCl_2$ was obtained by dehydration of $CoCl_2 \cdot 6H_2O$ in vacuum at about 120°C. Anhydrous $NdCl_3$, $TbCl_3$, $YbCl_3$ were prepared by the reaction of Nd_2O_3, Tb_4O_7, Yb_2O_3 repsectively with NH_4Cl at about 350°C. Mixture of urea, NaBr and KBr melted at 100°C 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 under argon atmosphere and the temperature was controlled by oil bath. The composition of deposit was analysed by EDAX(X-ray energy dispersive analysis).

2 Results and discussion

2.1 Cyclic voltammogram

The cyclic voltammogram (CV) of graphite electrode in urea-NaBr-KBr melt is shown in Fig.1a. It shows that the cathodic limit of the background is about −1.3V.

Fig.1b is the CV of graphite electrode in the urea-NaBr-KBr-$CoCl_2$ melt. One cathodic wave starts at −0.57V. It is due to the reduction of Co^{2+} to cobalt, because the

Received 1995-07-30, revised 1995-09-11, Correspondent: Yang Qiqin. * Project by the National Natural Science Foundation

deposits within the potential region of this wave were identified as cobalt by EDAX. The anodic stripping peak of cobalt is very far from the cathodic wave. So, the electrodeposition of cobalt is irreversible.

With the addition of NaOAc into the melt, the CV is shown in Fig.1c. The deposition potential of cobalt is −0.68V which is more negative to that of Fig.1b. The cathodic polarization of Co^{2+} reduced to cobalt can be increased by complex formation of Co^{2+} with acetic radical. It is favourable for smaller grains of deposit to be formed. The deposition potential of cobalt can be changed with the content of NaOAc.

The reduction potential of Tb^{3+} to metallic terbium is so negative that no cathodic wave appeared before the cathodic limit of the background. The CV of graphite electrode in the molten urea-NaBr-KBr-NaOAc-$CoCl_2$-$TbCl_3$ is shown in Fig.1d. The starting potential of the cathodic wave is more positive to that of the melt contained Co^{2+} without Tb^{3+} (Fig.1c) and the cathodic current is higher. This result indicates that the terbium may be inductively codeposited with the cobalt. The composition of the deposit obtained by potentiostatic electrolysis at −0.8V was analysed as cobalt and terbium by means of EDAX.

Nd^{3+} or Yd^{3+} instead of Tb^{3+}, its CV is similar to the CV of the melt contained $CoCl_2$ and $TbCl_3$ (Fig.1d). Hence, we consider that neodymium and ytterbium also can be inductively codeposited with cobalt.

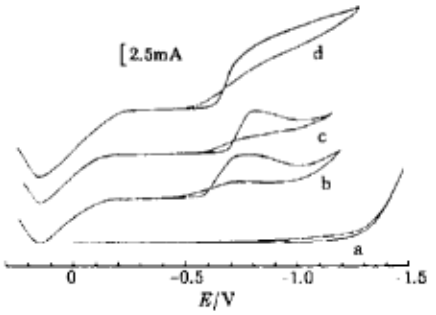

Fig.1 CV of graphite electrode ($0.48cm^2$) at 100°C and $0.05V \cdot s^{-1}$
(a) in the background
(b) in the melt contained 0.06mol $\cdot L^{-1}$ $CoCl_2$
(c) in the melt contained 0.06mol $\cdot L^{-1}$ $CoCl_2$ and NaOAc
(d) in the melt contained 0.06mol $\cdot L^{-1}$ $CoCl_2$, 0.12mol$\cdot L^{-1}$ $TbCl_3$ and NaOAc

2.2 Electrolytic experiments

The Nd-Co, Tb-Co and Yb-Co deposits were obtained on Cu cathode by electrolysis at 100°C. The contents of rare earth in the deposits depend on the cathodic potential (Table 1). It can be seen that the contents of Nd, Tb, Yb in the deposits are increased with the shift of the cathodic potential to the negativ direction. The contents of Tb in Tb-Co or Nd in Nd-Co electrodeposited from urea-NaBr-KBr-NaOAc melt contained $CoCl_2$ and $TbCl_3$ or $NdCl_3$ can be more than over 50 wt%.

The contents of rare earth in rare earth-cobalt deposits will increase when the melt contained no NaOAc. For example, the content of Yb in Yb-Co electrodeposited at −1.0 V from urea-NaBr-KBr-NaOAc-$CoCl_2$-$YbCl_3$ melt is 31 wt%, but the content of Yb in Yb-Co electrodeposited

from urea-NaBr-$CoCl_2$-$YbCl_3$ can be attain able to 55 wt%.

Table 1 Rare earth contents (wt%) in RE-Co deposits

	Cathodic potential(V)			
deposit	−0.80	−0.90	−0.95	−1.00
Tb-Co[a]		32.14	45.05	60.06
Nd-Co[a]	9.43	28.06		54.86
Yb-Co[a]	8.59	20.88		31.53
Yb-Co[b]	20.11	41.35		55.04

[a] Electrodeposited from urea-NaBr-KBr-NaOAc-$CoCl_2$-$RECl_3$ melt

[b] Electrodeposited from urea-NaBr-KBr-$CoCl_2$-$YbCl_3$ melt

References

1 Usuzaka N, Yamaguchi H, Watanabe T. *Mater. Sci. Eng.*, **1988, 99:**105

2 Yang Qiqin, Qiu Kairong, Pan Shijian. *Rare Metals*, **1995, 14:**13

3 Gambino M, Bros J P. *Thermochimica Acta*, **1988, 127:**223

在尿素熔体-NaBr-KBr 中 Nd-Co, Tb-Co 和 Yb-Co 的电沉积

杨绮琴 沙励婿 丘开容 洪惠婵

(中山大学化学系, 广州 510275)

摘要 稀土-钴合金因其具有磁性和磁光性等功能而为人们所关注. 在有机溶剂电解液中, 报道过的稀土-钴合金的电镀只有电镀 Gd-Co 和 Sm-Co 膜. 在我们从尿素-金属氯化物熔体中获得 La-Co 电沉积物以前, 未见在低温熔体中电沉积稀土-钴合金的研究报道. 尿素 (79mol%)-NaBr(19.5mol%)-KBr(1.5mol%) 的熔点为 51°C, 可在 100°C 左右作为本底熔体, 用于电解. 本文研究在 100°C 的尿素-NaBr-KBr 熔体中钴分别与钕、铽、镱的电解共沉积. 测定循环伏安曲线获知 Co^{2+} 还原为 Co 是一步不可逆过程, 加入 NaOAc 使 Co 的析出电位负移, 因而可能有细化沉积物晶粒的作用. NaOAc 的加入量较大时, 还可使体系的熔点降低. Nd^{3+}、Tb^{3+}、Yb^{3+} 还原为金属的电位很负, 因此不能单独析出. 但熔体中存在 Co^{2+} 时, 却可诱导这几个稀土与钴共沉积. 电解结果表明沉积物中 Nd、Tb、Yb 的含量随电位向负方移动而增加. 在熔体中含有 NaOAc, 阴极电位为 −1.0V 时, 电沉积的 Nd-Co 中含 54.86wt%Nd, Tb-Co 中含 60.06wt%Tb, Yb-Co 中含 31.53wt%Yb. 当熔体不含 NaOAc 时, 稀土-钴沉积物的稀土含量增加. 例如阴极电位为 −1.0V 在无 NaOAc 熔体中沉积的 Yb-Co 含 Yb 增加到 55.04wt%. 上述结果未见文献报道.

关键词: 电解共沉积, Nd-Co、Tb-Co 和 Yb-Co 合金, 尿素-NaBr-KBr 熔体