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ELECTROREDUCTION OF Yb(III) ON NICKEL CATHODE IN MOLTEN CHLORIDE①

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ABSTRACT The cyclic voltammetry, potential-time curve after potentiostatic electrolysis and X-ray diffraction were used to study the electrochemical reaction of Yb(III) in NaCl∶KCl= 1∶1(in mole) mixture on Ni cathode. The reduction of Yb(III) to Yb(II) was realized on Ni electrode at first step and Yb(II) was reduced and alloyed with Ni on electrode surface respectively. The diffusion coefficient of Yb(III) in NaCl-KCl-$YbCl_3$ is $1.25\times10^{-5}cm^2/s$ at 973 K.

Key word Yb(III) electroreduction molten chloride

1 INTRODUCTION

Yb-Ni alloy can be used to manufacture functional materials[1, 2]. It is necessary to study the electrochemical behaviour of Yb(III) on Ni electrode in molten NaCl-KCl-$YbCl_3$. The electroreduction of Yb(III) on the platinum cathode in molten chloride has been reported[3, 4]. The investigation of electrochemical behavior for Ni electrode in melt containing Yb is deficient. In this paper, the electrochemical behavior of Yb(III) reduction on Ni cathode in NaCl-KCl-$YbCl_3$ melt is presented.

2 EXPERIMENTAL

$YbCl_3$ was prepared by the reaction of Yb_2O_3(99.5%) with excess NH_4Cl(A. R. grade) at 573 K, the excess NH_4Cl was removed by raising temperature. NaCl(A. R. grade) and KCl(A. R. grade) were mixed in equi-mol ratio and dehydrated in vacuum at 673 K. The electrochemical measurements were carried out in a quartz cell under Ar atmosphere.

The working electrode was metallic Ni(> 99%), and the counter electrode was spectral pure graphite. The reference electrode was Ag/AgCl(mole fraction of 10%) and NaCl-KCl (equi-mol). All the potential values measured were converted to that versus chlorine electrode according to the data of Flengas[5].

The JH-2B potentiostat, DCD-1 superlow frequency functional generator and 3086 X-Y recorder were used for electrochemical measurements. The temperature was controlled by the WT-722 regulator and KG-6A silicon controlled power unit.

The Yb(III) concentration in melt was analyzed by EDTA titration. The potentiostatically electrolyzed Ni electrode after cleaning was analyzed by X-ray diffraction to determine the surface phase.

3 RESULTS AND DISCUSSION

3.1 Electroreduction of Yb(III) on the Ni cathode

Fig. 1(a) is the cyclic voltammorgram of Ni electrode in molten NaCl-KCl(equi-mol)-$YbCl_3$ (3.0% (in mass)) at 700 ℃. Four cathodic waves start at −1.40, −2.75, −2.90 and −3.10 V respectively. The reduction potential of Na on Ni electrode in molten NaCl-KCl (equi-mol) at 973 K was determined as −3.12 V[6]. Thus one can consider that the last wave in

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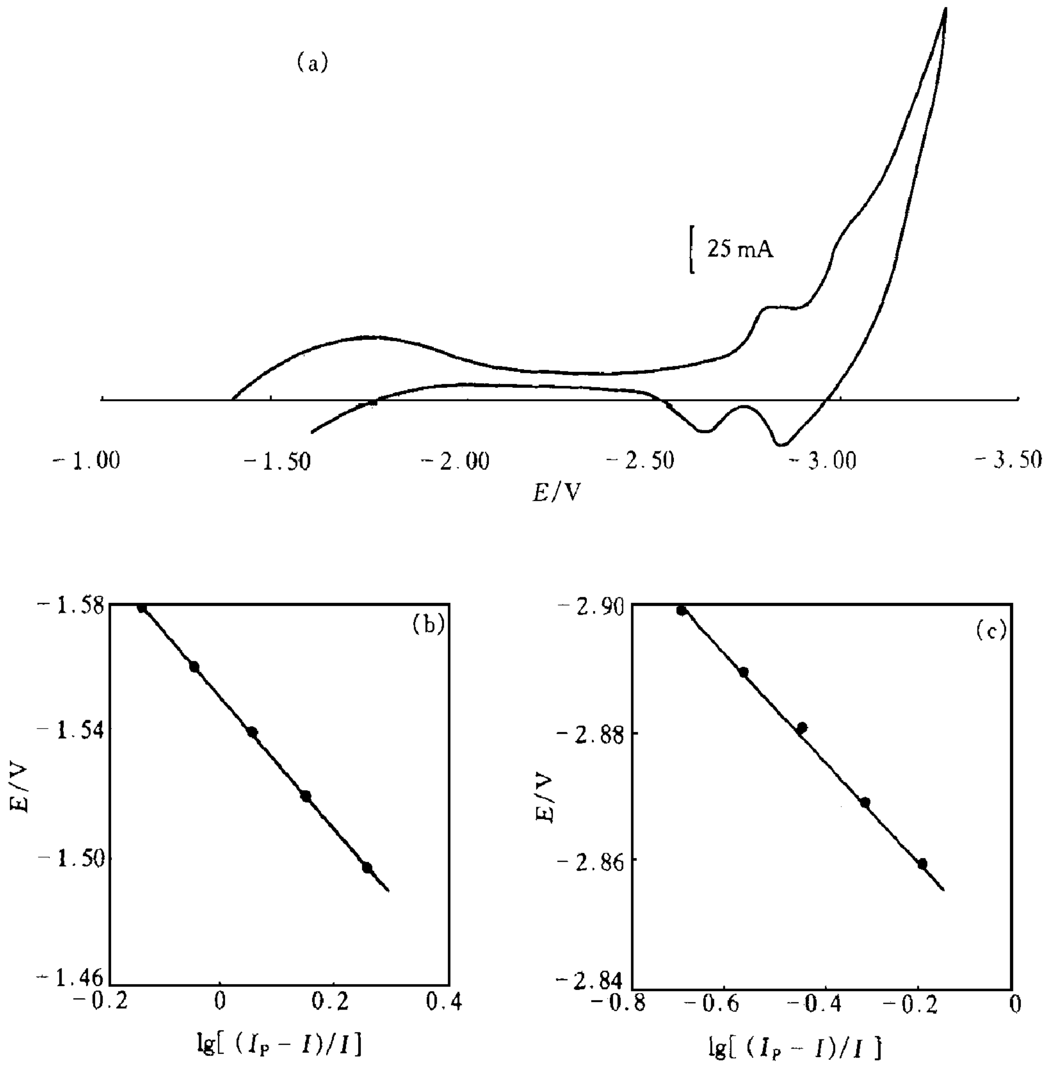

Fig. 1 Cyclic voltammograms for Ni in molten NaCl-KCl(equi-mol) - $YbCl_3$
(a) —973 K, A = 0. 23cm^2, w ($YbCl_3$) = 3. 0%, scanning rate υ= 50mV/ s^{-1};
(b) —E vs lg[(I_p - I)/ I] of peak 1; (c) —E vs lg[(I_p - I)/ I] of peak 2

Fig. 1(a) belongs to the reduction of Na^+ .

For a reversible charge transfer where both reactants and products are soluble, $|E_p - E_{p/2}| = 2.2RT/(nF)$[7] and the plot of E - lg[(I_p - I)/ I] is a straight line with slop $m = 1.72RT/(nF)$[8]. Where E_p, $E_{p/2}$ and I_p are the peak potential, half peak potential and peak current respectively. From $|E_p - E_{p/2}| = 0.21$ V of the first cathodic wave, $n = 0.90$ is calculated. The E vs lg[(I_p - I)/ I] plot for the cyclic voltammogram is linear (Fig. 1(b)) and $n = 0.92$ is obtained. Hence, the electrode reaction of the first cathodic wave of Fig. 1(a) is a single-electron reversible transfer reaction and both the reactants and products are soluble.

From $|E_p - E_{p/2}| = 0.10$ V of the second cathodic wave of Fig. 1(a), $n = 1.90$ is calculated. The E vs lg[(I_p - I)/ I] plot for the cyclic voltammogram is linear (Fig. 1(c)) and $n = 2.2$ is obtained. The starting potential of this wave is about 0. 6V more positive than the reduction potential of Yb(II), indicating an obvious depolarization. Hence, the electrode reaction of the second cathodic wave of Fig. 1(a) is a double-electron reversible transfer reaction and both the reactants and products are soluble. The second cathodic wave corresponds to the formation of Yb-Ni alloy from the experimental results mentioned above.

The electrochemical behavior of Yb(III) reduced on Ni cathode should be:

Yb(III) + e = Yb(II)

Yb(II) + 2e + nNi = YbNi$_n$

Fig. 2 shows the voltammetry curve of the first wave of Fig. 1(a) at different sweep speed. The peak potential E_p doesn't change with increasing sweep speed, it is the characteristic of a reversible charge transfer process. For a reversible charge transfer where both reactants and products are soluble, $I_p = 0.4463 A C_0 (nF)^{3/2} [D\upsilon/(RT)]^{1/2}$[7]. Here A, C_0, D, υ are the area of Ni electrode, the concentration of YbCl$_3$, the diffusion coefficient of Yb(III) and sweep speed respectively. The I_p vs $\upsilon^{1/2}$ plot for the Fig. 2 is linear. So, Yb(III) + e = Yb(II) is the rate-controlling step of the charge transfer process, and $D = 1.25 \times 10^{-5}$ cm^2/s is obtained from the slope of the I_p vs $\upsilon^{1/2}$ straight line.

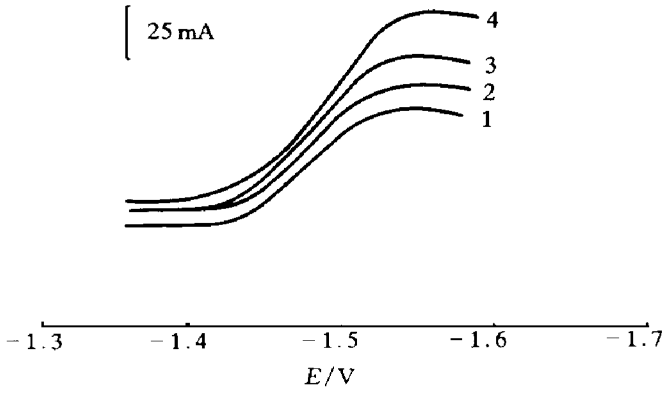

Fig. 2 Voltammetry curve for Ni in NaCl-KCl-YbCl$_3$ at different sweep speeds (υ)
(T = 973 K, A = 0.23 cm^2, w(YbCl$_3$) = 3.0%)
1 — υ_1 = 30 mV·s^{-1}; 2 — υ_2 = 60 mV·s^{-1};
3 — υ_3 = 120 mV·s^{-1}; 4 — υ_4 = 150 mV·s^{-1}

The potential-time curve of Ni electrode in molten NaCl-KCl(equi-mol)-YbCl$_3$ (3.0% (in mass)) after potentiostatic electrolysis at the potential of Yb deposition is shown in Fig. 3. In this figure the curve (the electrolytic time is 30 s in scale interval) has three plateaus appearing at − 2.97 V, − 2.75 V and − 1.50 V. According to the cyclic voltammogram, it is considered that the three plateaus belong to Yb − 2e = Yb(II), YbNi$_n$ − 2e = Yb(II) + nNi and Yb(II) − e = Yb(III), respectively.

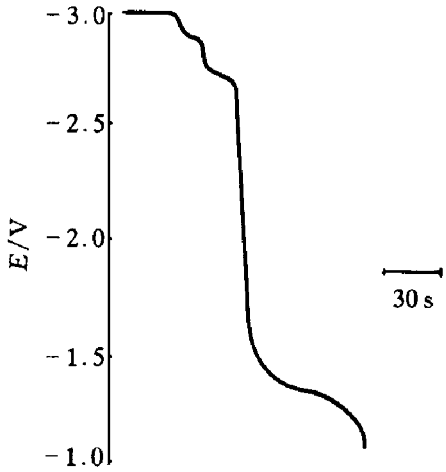

Fig. 3 E vs t curve after potentiostatic electrolysis at − 3.0 V
(T = 973 K, w(YbCl$_3$) = 3.0%, Ni electrode)

3.2 Surface phase of alloyed electrode identified by X-ray diffraction

The potentiostatic electrolysis proceeds in NaCl-KCl (equi-mol)-YbCl$_3$ with Ni electrode at − 3.10 V, T = 973 K for 30 min. The surface of the alloyed electrode after cleaning to remove the salt was analyzed by X-ray diffraction and the pattern is shown in Fig. 4. It can be seen that the electrode surface phases is Yb and Yb-Ni alloy. The surface alloy phases should be Yb$_2$Ni$_{17}$ and YbNi$_5$[9].

4 CONCLUSIONS

The reaction of Yb(III) reducing to Yb(II) in NaCl-KCl equi-mol mixture was realized on Ni electrode at first, and Yb(II) was then reduced and alloyed with Ni on electrode surface. The diffusion coefficient of Yb(III) in molten NaCl-KCl-YbCl$_3$ at 973 K is 1.25×10^{-5} cm^2/s.

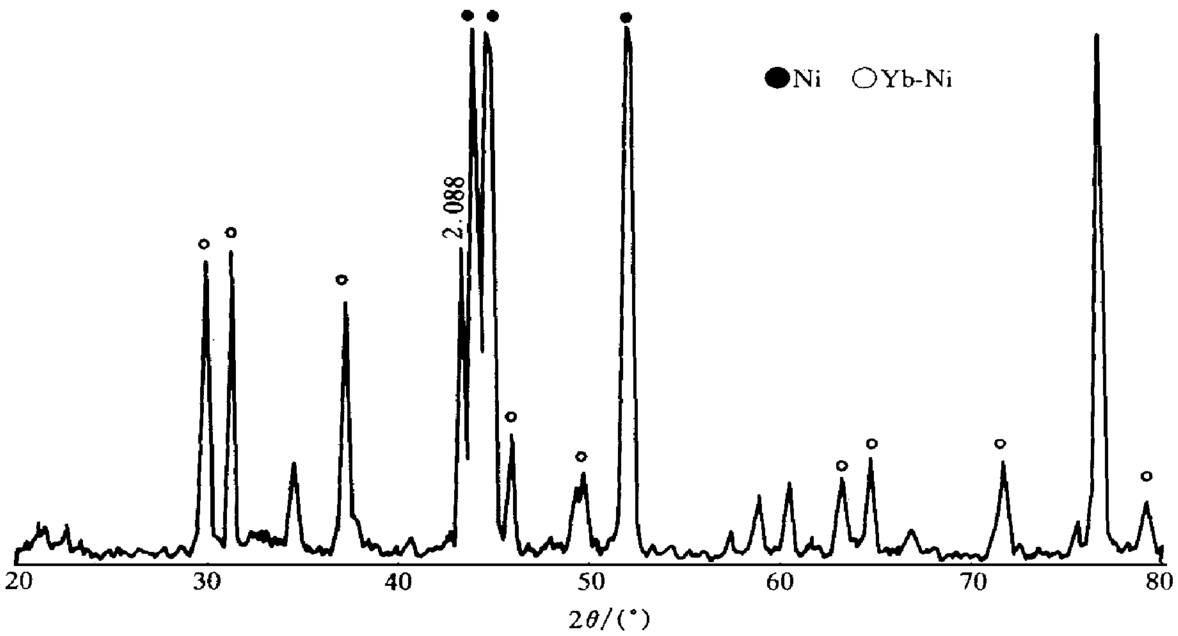

Fig. 4 X-ray diffraction pattern for electrode surface after potentiostatic electrolysis

REFERENCES

1 Liu B X, Ping J R, Zhong H B and Che D Z. Phys Status Solidi A, 1991, 128(1): 103.

2 Yoshio I and Moryoshi H. JP63250429, 1988.

3 Johnson K E and Mackenzie J R. J Electrochem Soc, 1969, 116(12): 1699.

4 Hong H C, Liu G K, Yang Q Q and Zhou T. In: Li W C, Li H, eds. Proceedings of the national symposium on physical chemistry of metallurgy. Guangzhou: Guangdong Metallic Society Publishers, 1994. 349- 354.

5 Flengas S N and Ingraham T R. J Electrochem Soc, 1959, 106(8): 714.

6 Yang Q Q, Liu G K, Tong Y X and Liang G C. Acta Metallurgica Sinica, Series B, 1992, 5(5): 346.

7 Bard A J and Faulkner L R. Electrochemical Methods. New York: John Wiley & Sons, 1980: 218.

8 Mamantov G, Manning D L and Dale J M. J Electroanal Chem, 1965, 9: 253.

9 Palenzana A. J Less-Common, 1973, 33: 361.

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