ELECTRODEPOSITION OF Ti-Ni

ALLOY IN UREA-NaBr-KBr MELT [①]

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ABSTRACT   The cyclic voltammetry and potential-time curve at current step were used to investigate the electroreduction of Ni(II), Ti(IV) in the urea-NaBr-KBr melt. The electroreduction of Ni(II) to nickel is irreversible in one step. The transfer coefficient and the exchange current density of the reaction Ni(II) + 2e = Ni were determined as 0. 4 and $1. 1 \times 10^{-6} A \cdot cm^{-2}$ at 100 ℃. The Ti(IV) was reduced to Ti(III) and formed alloy with Ni on cathode in urea-NaBr-KBr-NiCl$_2$-TiCl$_4$ melt. The content of Ti in the Ti-Ni alloy changed with the cathode potential and reached 59% (in mole).

Key words   urea-NaBr-KBr melt   electroreduction of Ni(II)   electrodeposition of Ti-Ni alloy

1   INTRODUCTION

Titanium and titanium alloys are well-known for their excellent functions, for example, the Ti-Ni alloy has high corrosion resistance, high heat resistance and shape memory effect[1, 2]. It is difficult to electrolyse TiCl$_4$ in aqueous electrolyte because of its hydrolysis. Titanium and titanium alloy can be electrodeposited in molten salt. But no report about electrodeposition of titanium and titanium alloy at low temperarure melt (~ 100 ℃) was found. The melting point of urea-NaBr-KBr eutectic is 51 ℃[3] and this molten system can be used as the electrolytic medium (background) at about 100 ℃[4, 5]. In this paper, the electroreduction of Ni(II), Ti(IV) and electrodeposition of Ti-Ni alloy in urea-NaBr-KBr at 100 ℃ are investigated.

2   EXPERIMENTAL

Urea, NaBr, KBr, TiCl$_4$, NiCl$_2$·6H$_2$O are analytically pure. The NiCl$_2$·6H$_2$O was dehydrated in vacuum at about 120 ℃ for 3 h. All compounds used here were stored in the desiccator containing P$_2$O$_5$.

The working electrodes were spectrally pure graphite and titanium. The reference electrode was Ag/urea-NaBr-KBr. The mixture of urea and salts in the glass cell was melted at about 100 ℃. The cyclic voltammogram and potential-time curve at current step were made with HD-1A functional generator, HDV-7C potentiostat and 3086 X-Y recorder. The electrochemical measurements proceeded under argon atmosphere. The temperature was controlled by oil-bath thermostat. The composition of electrolytic deposits was analysed by means of EDAX.
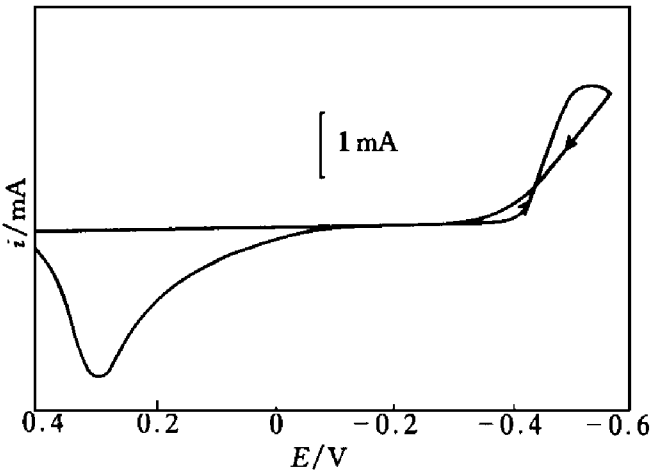
3   RESULTS AND DISCUSSION

3.1   Electroreduction of Ni(II)

Fig. 1 is the cyclic voltammogram (CV) of graphite electrode in the urea-NaBr-KBr-NiCl$_2$ at 100 ℃. The cathodic wave starts at − 0. 41 V. Electrolysis proceeded with copper electrode at − 0. 45 V for 30 min. The deposit was analysed as Ni by means of EDAX, so the cathodic wave corresponds to the reduction of Ni(II) to metallic nickel. The anodic wave with the peak potential of + 0. 3 V is due to stripping of nickel. The anodic wave is very far from the cathodic wave. These results indicate that the electroreduction of Ni(II) in the urea-NaBr-KBr-NiCl$_2$ melt is irreversible in one step.
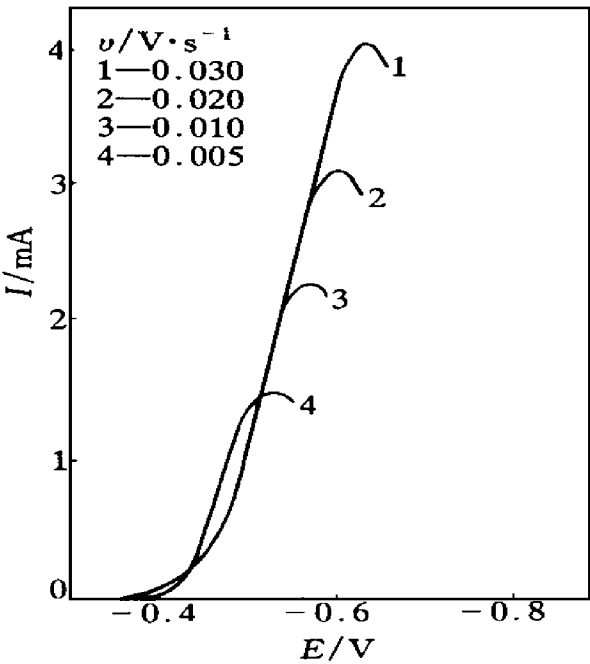
**Fig. 1   CV of graphite electrode (0. 92 cm²)
in urea-NaBr-KBr-NiCl₂ melt**

(C(NiCl₂) = 0. 096 mol/ L,

θ= 100 ℃, υ= 0. 01 V/ s)

For the irreversible charge transfer, the peak potential and half peak potential has the following relation[6]:

$$| E_p - E_{p/2} | = 1.857 RT / \alpha n_a F \qquad (1)$$

From Fig. 1 and equation(1), αn_a is calculated as 0. 75 and α is determined as 0. 38.

The voltammograms of titanium electrode in the urea-NaBr-KBr-NiCl₂ melt at different sweep rates are shown in Fig. 2. From the data of

**Fig. 2   Voltammograms of Ti electrode
(0. 62 cm²) in the melt (as Fig. 1)**

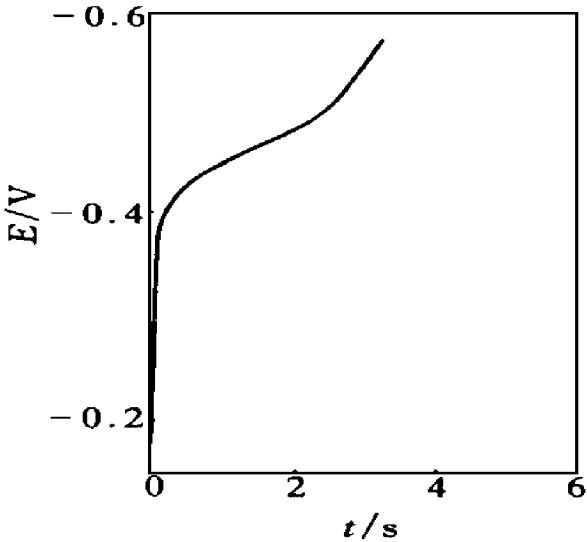(θ= 100 ℃)

$| E_p - E_{p/2} |$ in Fig. 2 and equation (1), the average αn_a is calculated as 0. 90 and the α is determined as 0. 45 (Table 1).

**Table 1   The αn_a and α of
Ni(Ⅱ) + 2e= Ni**

υ/ V·s⁻¹	$| E_p - E_{p/2} |$ / V	αn_a	α
0. 005	0. 061	0. 98	0. 49
0. 010	0. 062	0. 96	0. 48
0. 020	0. 070	0. 87	0. 44
0. 030	0. 076	0. 80	0. 40
	average:	0. 90	0. 45

The potential-time (E-t) curve at current step of titanium electrode in urea-NaBr-KBr-NiCl₂ melt at 100 ℃ is shown in Fig. 3. The plot of E vs ln[1- (t/ τ) $^{1/2}$] is a linear line (Fig. 4), because the electrode reaction is irreversible, so this line accords with the following equation[7]:

$$E = E_e - (RT / \alpha n_a F) \ln(i_k / i_o) + (RT / \alpha n_a F) \ln[1- (t/ \tau)^{1/2}] \qquad (2)$$

From the slope and the intercept of the line in Fig. 4 and equation(2), α and i_o are calculated as 0. 46 and 1. 1 × 10⁻⁶ A·cm⁻².

**Fig. 3 E-t curve of Ti electrode(0. 62 cm²)
in the melt(as Fig. 1)**

(i= 3. 06 mA, θ= 100 ℃)

3. 2   Electroreduction of Ti(Ⅳ)

Fig. 5 is the cyclic voltammogram of graphite electrode in urea-NaBr-KBr-TiCl₄ melt

at 100 ℃. Two cathodic waves start at − 0. 62 V and − 1. 10 V, respectively. The second cathodic wave is due to the decomposition of background[4]. The urea was reduced and the hydrogen evolved[8].
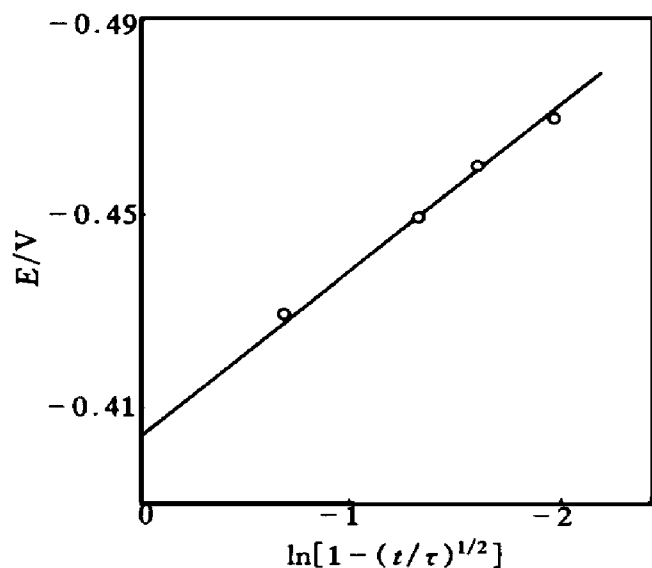

Fig. 4　Plot of E vs ln[1− ($t/$ τ) $^{1/2}$]

Electrolysis proceeded at − 0. 9 V for 30 min, no metallic product was formed on cathode, but the melt around the cathode appeared as blue-purple, which indicates the existance of T i (III) . Hence the first cathodic wave corresponds to the reduction of T i(IV) to T i(III) .
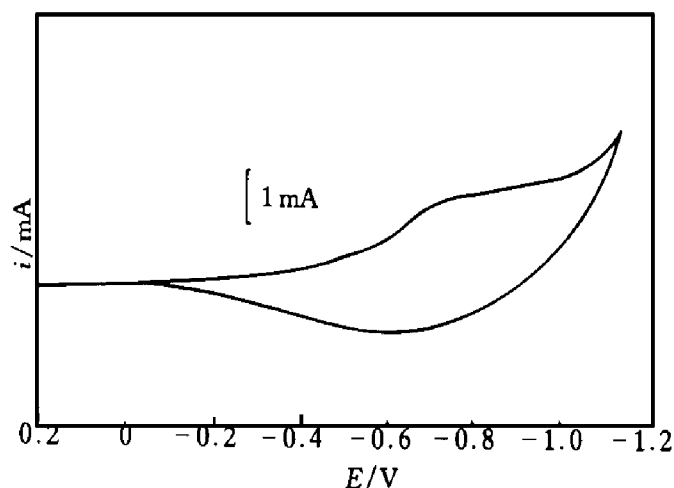

Fig. 5　CV of graphite electrode(0. 92 cm²)
in urea-NaBr-KBr-TiCl₄ melt
(C(T iCl₄) = 0. 064 mol/ L,
θ= 100 ℃, υ= 0. 02 V/ s)

3. 3　Electrodeposition of Ti-Ni alloy

The cyclic voltammogram of graphite elec-

trode in urea-NaBr-KBr-NiCl₂-TiCl₄ melt at 100 ℃ before the cathodic limit of the background is shown in Fig. 6. Two cathodic waves start at − 0. 4 V and − 0. 67 V respectively. Only one anodic wave with the peak potential of + 0. 4 V is found. Electrolysis proceeded with copper electrode at − 0. 50, − 0. 60, − 0. 70, − 0. 80, − 0. 90 and − 1. 0 V respectively for 30 min. The deposits were analysed by means of EDAX and the results are shown in Table 2.
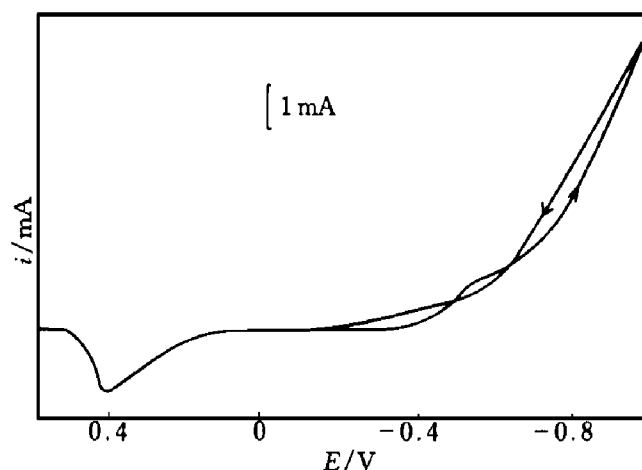

Fig. 6　CV of graphite electrode(0. 92 cm²)
in urea-NaBr-KBr-NiCl₂− TiCl₄ melt
(C(NiCl₂) = 0. 096 mol/ L,
C(TiCl₄) = 0. 064 mol/ L,　θ= 100 ℃,
υ= 0. 02 V/ s)

The data in Table 2 suggest that the first cathodic wave is due to reduction of Ni(II) to nickel, the second wave corresponds to formation of Ti-Ni alloy. The content of Ti in the Ti-Ni alloy increases from the cathode potential of − 0. 7 V to − 0. 9 V.

Table 2　The contents of Ti-Ni alloys
at different cathode potential

E/ V	Mass fraction/ %		Mole fraction/ %	
	Ti	Ni	Ti	Ni
− 0. 50	0	100	0	100
− 0. 60	0	100	0	100
− 0. 70	16. 9	83. 1	19. 9	80. 1
− 0. 80	48. 1	51. 9	53. 2	46. 8
− 0. 90	54. 0	46. 0	59. 0	41. 0
− 1. 00	35. 3	64. 7	45. 5	54. 5

4 CONCLUSIONS

(1) The electroreduction of Ni(II) in urea-NaBr-KBr melt is irreversible in one step and the nickel is deposited on the cathode.

(2) The transfer coefficient of the reaction Ni(II) + 2e= Ni is determined as about 0. 4 and the exchange current density is determined as $1.1 \times 10^{-6} A \cdot cm^{-2}$ at 100 °C.

(3) The electroreduction of Ti(IV) in urea-NaBr-KBr melt before the limit of the background is corresponding to the reaction Ti(IV) + e= Ti(III).

(4) The Ti-Ni alloy can be electrodeposited in the urea-NaBr-KBr-NiCl$_2$-TiCl$_4$ melt. The titanium content changed with the cathode potential and reached 59% (in mole) at − 0. 90 V.

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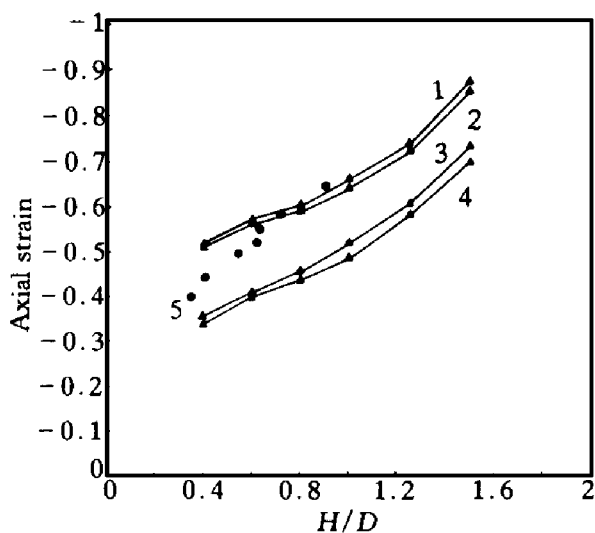~~(Edited by Wu Jiaqunan)~~

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Fig. 6 The critical technological parameters
1 —m= 0. 3, R_0= 0. 85; 2 —m= 0. 3, R_0= 0. 90;
      3 —m= 0. 5, R_0= 0. 85;
  4 —m= 0. 5, R_0= 0. 90; 5 —Experiment

with full account of contact friction boundary conditions, the height to diameter ratio and the initial relative density, in combination with the Lee-Kuhn's fracture criterion. This discussion reveals the effect of height to diameter ratio, friction factor and initial relative density. From the work, the critical technological parameters were obtained, which can lead to choose the suitable technological parameters to avoid the occurence of fracture. It is very important to guide the practical production according to the critical locus.

Of course, for porous materials, if we want to know the details of defects forming, more work should be done.

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