

## Electrochemical formation of holmium-copper alloys on copper cathode in molten KCl-HoCl<sub>3</sub>

SU Yu-zhi(苏育志)<sup>1</sup>, YANG Qi-qin(杨绮琴)<sup>2</sup>, LIU Guan-kun(刘冠昆)<sup>2</sup>

1. School of Chemistry and Chemical Engineering, Guangzhou University,  
Guangzhou 510006, China;

2. School of Chemistry and Chemical Engineering, Zhongshan University,  
Guangzhou 510275, China

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**Abstract:** Cyclic voltammetry, open circuit potential–time curve after potentiostatic electrolysis and potential step chronoamperometry were used to investigate the electrochemical formation processes of holmium-copper alloys on copper cathode in molten HoCl<sub>3</sub>-KCl. Intermetallic compounds HoCu<sub>5</sub>, HoCu<sub>4</sub>, HoCu<sub>2</sub> and HoCu are formed in sequence and then the metallic Ho is deposited when Ho<sup>3+</sup> is reduced on copper electrode in molten KCl-HoCl<sub>3</sub> at 1 066 K. The first charge-transfer reaction is reversible. The structure of holmium-copper alloy film deposited on copper electrode by potentiostatic electrolysis was characterized by X-ray diffraction. The standard free energies of formation for the intermetallic compounds HoCu<sub>5</sub>, HoCu<sub>4</sub>, HoCu<sub>2</sub> and HoCu are –95.5, –92.6, –73.8 and –44.0 kJ/mol, respectively. The diffusion coefficient and diffusion activation energy of Ho atom in the alloy are estimated to be 10<sup>–10</sup>–10<sup>–11</sup> cm<sup>2</sup>/s and 75.35 kJ/mol, respectively, from the chronoamperometry data.

**Key words:** holmium-copper alloy; electrochemical formation; free energy of formation; diffusion coefficient

## 1 Introduction

Alloys of rare earth Ho with other metals (Fe, Co, Ni, Cu, etc) possess electrical, magnetic and other properties important for modern technology[1–4]. LI and ZHU[5] proposed a new processing technology for high property permanent magnets. Holmium is an active element and can not be deposited from aqueous solution, but it can be prepared by molten salt electrolysis at high temperature. If Ho-alloy is deposited in molten salts on a consumable cathode, the operation temperature may be decreased. Codeposition process of Ho and Co was recently investigated in organic solvent by WANG et al[6].

In this work, we study the electrode process of Ho<sup>3+</sup> reduction on copper electrode in molten chlorides. The free energies of formation for the intermetallic compounds of Ho-Cu systems, the diffusion coefficients and the diffusion activation energy of Ho in the alloy are determined.

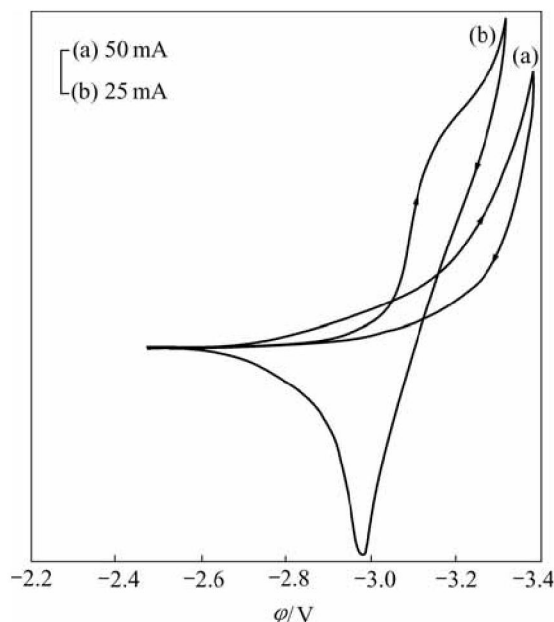
## 2 Experimental

Dehydrated HoCl<sub>3</sub> was obtained by the reaction of Ho<sub>2</sub>O<sub>3</sub> (99.99%) with NH<sub>4</sub>Cl (A.R.) at 623 K. KCl was dehydrated in vacuum at 673 K. A molten mixture of the dehydrated KCl and HoCl<sub>3</sub> was used as electrolyte. The working electrode was a copper or tungsten electrode, the auxiliary electrode was a glass carbon electrode, and the reference electrode was Ag/AgCl (x=0.1) electrode. All potentials measured in this paper are converted to the values versus the Cl<sub>2</sub>/Cl<sup>–</sup> electrode[7]. The electrochemical measurements were carried out in a quartz electrolytic cell under argon atmosphere by using a potentiostat (HDV-7B), a functional generator (DCD-3) and an x-y recorder (3086x-y). The silicon-controlled power unit (KG-6A) and the temperature regulator (WT-710) were used to control the temperature. The concentration of HoCl<sub>3</sub> in molten salts was analyzed by EDTA complexometry. The phase of surface alloy layer on working electrode was analyzed by XRD.

### 3 Results and discussion

#### 3.1 Electrode processes

The cyclic voltammogram of a tungsten electrode in molten KCl is shown in Fig.1(a). The potassium deposition is at about  $-3.15$  V. Addition of  $\text{HoCl}_3$  to the molten KCl is resulted in Fig.1(b), in which two reduction peaks start at  $-3.01$  and  $-3.16$  V, respectively. The first reduction peak is due to the reduction of  $\text{Ho}^{3+}$  to Ho metal and the second reduction peak corresponds to the deposition of potassium metal.

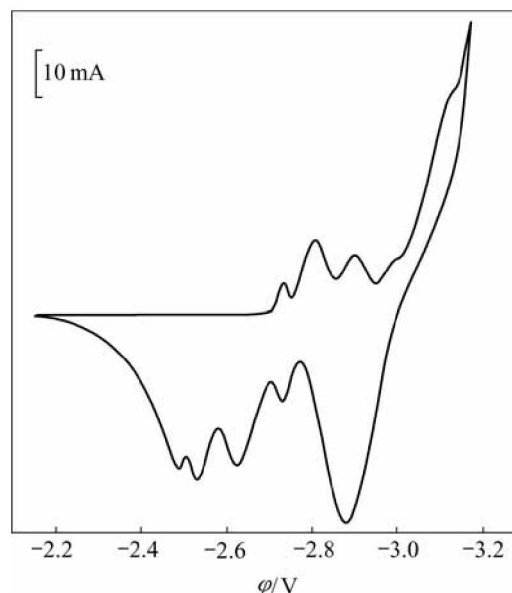


**Fig.1** Cyclic voltammogram of tungsten electrode ( $0.31 \text{ cm}^2$ ) at 1 063 K, 60 mV/s in KCl (a) and KCl- $\text{HoCl}_3$  (2.44 %, mole fraction) (b)

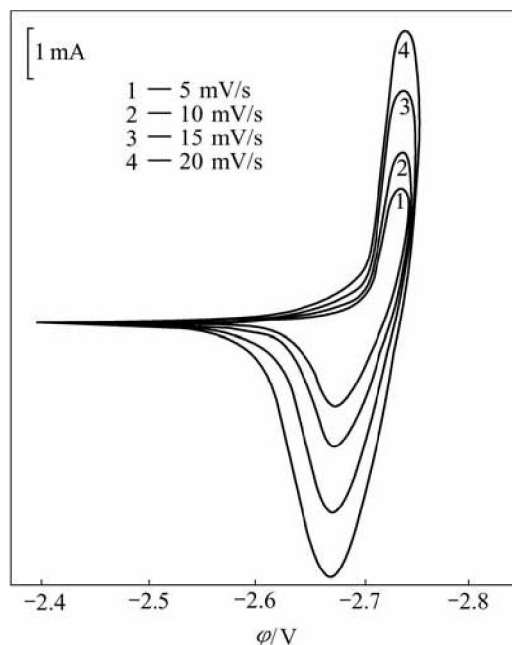
The cyclic voltammogram of copper electrode in the molten KCl- $\text{HoCl}_3$  at 1 066 K is shown in Fig.2. Six reduction peaks which start at  $-2.70$ ,  $-2.75$ ,  $-2.85$ ,  $-2.95$ ,  $-3.02$  and  $-3.14$  V are observed. In contrast to the first reduction peak in Fig.1(b), it can be found that the last two reduction peaks in Fig.2 corresponds to the deposition of pure metallic holmium and potassium, respectively [8]. Fig.3 corresponds to the voltammograms of the first reduction peak in Fig.2 at different scan rates. The reduction peak potentials  $\varphi_{p,c}$  and the oxidation peak potentials  $\varphi_{p,a}$  are almost independent on the scan rate. These results indicate that the first reduction reaction is reversible. Furthermore, from the average value of  $|\varphi_{p,c} - \varphi_{p,a}|$ , 0.066 V, the electron transfer number is obtained as  $n=3.2$ , according to  $|\varphi_{p,c} - \varphi_{p,a}| = 2.3RT/nF$  [9]. These results indicate that the electrode reaction of the first reduction peak is three-electron transfer reaction. Furthermore, the starting potential evidently is more positive than the potential of  $\text{Ho}^{3+}/\text{Ho}$ , owing to the existence of

depolarization [10]. It is inferred that the first reduction peak starting at about  $-2.70$  V is caused by the formation of the intermetallic compound of Ho-Cu,  $\text{Ho}^{3+} + 3e + n\text{Cu} = \text{HoCu}_n$ , and the 2nd, 3rd, 4th and 5th reduction peaks, which start at about  $-2.75$ ,  $-2.85$ ,  $-2.95$  V and  $-3.02$  V, respectively, may be related to the formation of Ho-Cu intermetallic compounds too. Thus four intermetallic compounds are formed before  $\text{Ho}^{3+}$  ions are reduced to pure Ho metal.

The open current potential—time curve shown in

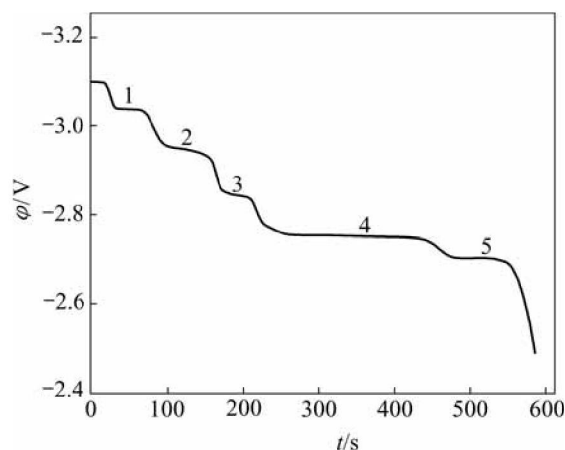


**Fig.2** Cyclic voltammogram of Cu electrode ( $0.47 \text{ cm}^2$ ) in KCl- $\text{HoCl}_3$  (2.16 % mole fraction, scan rate 10 mV/s,  $T=1\ 066$  K)



**Fig.3** Cyclic voltammograms of first reduction peak in Fig. 2 at different scan rates ( $T=1\ 066$  K)

Fig.4 is obtained after electrolysis at a constant potential of  $-3.10$  V for 30 s at 1 066 K. Compared with cyclic voltammogram of Fig.2, it can be found that five plateaus at  $-2.70$ ,  $-2.75$ ,  $-2.84$ ,  $-2.94$  and  $-3.03$  V in Fig.4 correspond to the five peaks starting at  $-2.70$ ,  $-2.75$ ,  $-2.85$ ,  $-2.95$  and  $-3.02$  V, respectively, in Fig. 2.

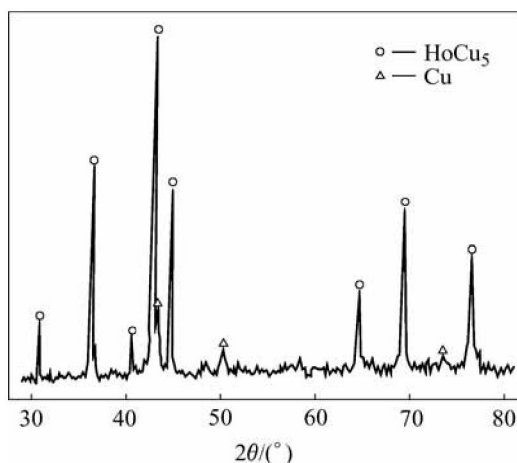


**Fig.4** Potential—time curve of KCl-HoCl<sub>3</sub> (2.16%, mole fraction) on copper electrode (0.47 cm<sup>2</sup>) after electrolysis at constant potential of  $-3.10$  V for 30 s ( $T=1\ 066$  K)

### 3.2 Alloy phase analysis of surface layer

There are four intermetallic compounds in the Ho-Cu system, which are HoCu<sub>5</sub>, HoCu<sub>4</sub>, HoCu<sub>2</sub> and HoCu. In order to determine the composition of copper electrode surface alloy, controlled potential electrolysis is carried out on copper cathode at  $-2.74$  V (the first reduction peak) at 1 114 K for 30 min in molten KCl-HoCl<sub>3</sub>. After removing the salts, the copper electrode is analyzed by XRD and the result is shown in Fig.5, which indicates that the phase of the electrode surface alloy is HoCu<sub>5</sub>.

The overall process of Ho<sup>3+</sup> reduced on the electrode to form the intermetallic compounds includes



**Fig.5** XRD patterns of Cu electrode surface after electrolysis at  $-2.74$  V for 30 min at 1 114 K

the following steps: diffusion of Ho<sup>3+</sup> to the surface of copper cathode, reduction of Ho<sup>3+</sup> to Ho, diffusion of Ho into the copper cathode and formation of intermetallic compounds with copper. The higher the Ho content in the compound, the lower the reduced potential necessary to reduce Ho<sup>3+</sup>.

At first HoCu<sub>5</sub> is formed, and then HoCu<sub>4</sub> is formed when Ho<sup>3+</sup> is reduced on copper cathode. From the results of cyclic voltammetry, open circuit potential—time curve after potentiostatic electrolysis and XRD, it is concluded that five reduction peaks at  $-2.70$ ,  $-2.75$ ,  $-2.85$ ,  $-2.95$  and  $-3.02$  V in Fig.2 are related to HoCu<sub>5</sub>, HoCu<sub>4</sub>, HoCu<sub>2</sub>, HoCu and Ho, respectively.

### 3.3 Free energies of formation for Ho-Cu intermetallic compounds

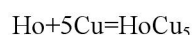
Five plateaus at  $-2.70$ ,  $-2.75$ ,  $-2.85$ ,  $-2.95$  and  $-3.02$  V in Fig.4 correspond to HoCu<sub>5</sub>, HoCu<sub>4</sub>, HoCu<sub>2</sub>, HoCu and Ho, respectively. These plateaus are due to the formation of Ho-Cu intermetallic compounds and the diffusion of Ho deposited on copper electrode surface into the copper electrode. The potential difference between the first plateau and the fifth plateau is related to the electromotive force of the cell as follows:



The electrode reaction is



The cell reaction is



This is the reaction of HoCu<sub>5</sub> formation, and for the above cell:

$$\Delta_f G_{m,1} = -nF\varphi_1 = -nF[\varphi_1^\ominus - (RT/nF)\ln(a_{\text{HoCu}_5} - a_{\text{Ho}}a_{\text{Cu}}^5)] \quad (1)$$

where  $\Delta_f G_{m,1}$  is the free energy of formation for HoCu<sub>5</sub>,  $n$  is the number of electrons transferred in the reaction:  $\text{Ho} + 5\text{Cu} = \text{HoCu}_5$ ,  $F$  and  $R$  are Faraday constant and universal gas constant respectively,  $\varphi_1$  and  $\varphi_1^\ominus$  are the potential difference and the standard potential difference for above cell respectively,  $a_{\text{HoCu}_5}$ ,  $a_{\text{Ho}}$  and  $a_{\text{Cu}}$  are the activities of HoCu<sub>5</sub>, Ho and Cu respectively.

HoCu<sub>5</sub>, Ho and Cu are all solid and have unit activity, so

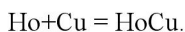
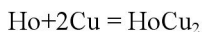
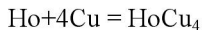
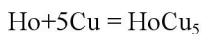
$$\Delta_f G_{m,1} = -nF\varphi_1^\ominus = \Delta_f G_{m,1}^\ominus \quad (2)$$

where  $\Delta_f G_{m,1}^\ominus$  is the standard free energy of formation for HoCu<sub>5</sub>. The potential differences between other plateaus and the first plateau responded to the

electromotive force of the cells are listed respectively as follows:



The cell reactions listed are respectively as follows:



The standard free energies of formation for  $\text{HoCu}_5$ ,  $\text{HoCu}_4$ ,  $\text{HoCu}_2$  and  $\text{HoCu}$  are shown in Table 1.

**Table 1** Standard free energies of formation for Ho-Cu alloys (1 114 K)

Ho-Cu alloys	$\text{HoCu}_5$	$\text{HoCu}_4$	$\text{HoCu}_2$	$\text{HoCu}$
$\Delta_f G / (\text{kJ} \cdot \text{mol}^{-1})$	-95.5	-92.6	-73.8	-44.0

### 3.4 Diffusion coefficients and diffusion activation energy of Ho in $\text{HoCu}_5$

Fig.6 shows the current-response curve at different potential steps from steady potential to  $-2.74$  V, at which  $\text{HoCu}_5$  is formed on copper electrode in molten  $\text{KCl-HoCl}_3$ . The diffusion coefficients of Ho into  $\text{HoCu}_5$  can be calculated from the current-time curve in Fig.7 according to the Eqn.(3)[11]:

$$D = (1/2\tau)(Q_e M / x_n F A \rho)^2 \quad (3)$$

where  $M$  and  $\rho$  are molecular mass and density, respectively, of a intermetallic compound,  $x_n$  is the number of electrons transferred in the reaction:  $\text{Ho}^{3+} + 3e + 5\text{Cu} = \text{HoCu}_5$ ,  $F$  is Faraday constant,  $A$  is electrode area,  $Q_e$  is electric quantity consumed to get a steady state for the formation of intermetallic compounds and  $\tau$  is time for a steady state. The diffusion coefficients  $D$  of Ho atoms into  $\text{HoCu}_5$  are shown in Table 2. The relationship between  $\ln D$  and  $(1/T)$  is approximately linear. It is inferred from the slope of the linear plot of  $\ln D$  against  $(1/T)$  that the temperature dependence of diffusion coefficient can be expressed as

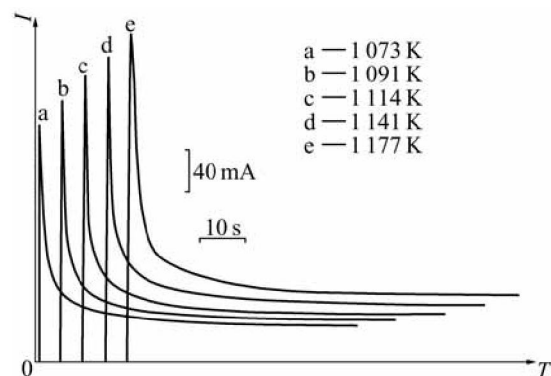
$$D = 2.37 \times 10^{-6} \exp(-9062/T) \quad (4)$$

or

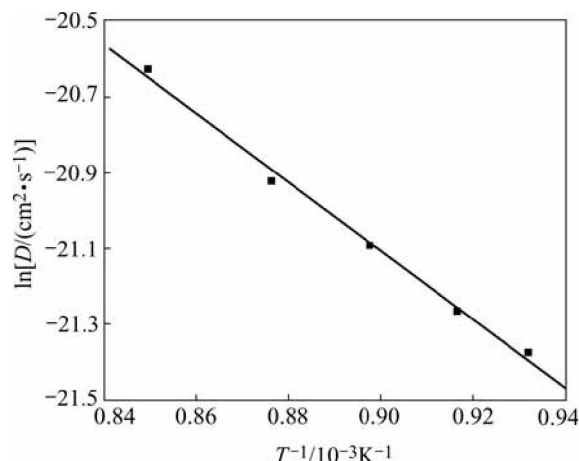
$$D = 2.37 \times 10^{-6} \exp(-75.34 \times 10^3/RT) \quad (5)$$

where the diffusion activation energy of Ho in  $\text{HoCu}_5$  is 75.34 kJ/mol.

From previous and present investigation[12-14], we note that the overall processes of  $\text{Ho}^{3+}$  reduction on a cathode to form alloys include the following steps:



**Fig.6** Potential-step current-time curves of Cu electrode ( $0.35 \text{ cm}^2$ ) in molten  $\text{KCl-HoCl}_3$  (1.86% mole fraction) at different temperatures



**Fig.7** Plot of relation of  $\ln D$  and  $1/T$

**Table 2** Diffusion coefficients of Ho in  $\text{HoCu}_5$

$T/\text{K}$	$t/\text{s}$	$Q_e/C$	$D/(\text{cm}^2 \cdot \text{s}^{-1})$
1 073	60	0.545	$5.2 \times 10^{-10}$
1 091	65	0.600	$5.8 \times 10^{-10}$
1 114	70	0.681	$6.9 \times 10^{-10}$
1 141	75	0.769	$8.2 \times 10^{-10}$
1 177	85	0.931	$1.1 \times 10^{-9}$

diffusion of  $\text{Ho}^{3+}$  ions in molten  $\text{KCl-HoCl}_3$  to the surface of the cathode, reduction of  $\text{Ho}^{3+}$  to Ho, diffusion of Ho atoms into copper cathode and formation of a intermetallic compounds. When the process of formation of the intermetallic compound is the rate determining step, there exists a linear relation between current and potential[15]. But we do not find this feature. The diffusion coefficient of  $\text{Ho}^{3+}$  in molten  $\text{KCl-HoCl}_3$  at 1 071 K is  $0.92 \times 10^{-5} \text{ cm}^2/\text{s}$ [8], however, the diffusion coefficients of  $\text{Ho}^{3+}$  into  $\text{HoCu}_5$  are in the range from  $10^{-10}$  to  $10^{-11} \text{ cm}^2/\text{s}$  which are several orders of magnitude smaller than that of  $\text{Ho}^{3+}$  in molten  $\text{KCl-HoCl}_3$  at the same temperature range. Hence, the diffusion step of Ho atom into cathode may be the

rate-determining step of the electrode process.

## 4 Conclusions

Intermetallic compounds  $\text{HoCu}_5$ ,  $\text{HoCu}_4$ ,  $\text{HoCu}_2$  and  $\text{HoCu}$  are formed in sequence and then the metallic Ho is deposited when  $\text{Ho}^{3+}$  is reduced on copper electrode in molten  $\text{KCl-HoCl}_3$  at 1 066 K. The first charge-transfer reaction is reversible. The diffusion of Ho atoms into the cathode is the rate-determining step of the cathodic process. The standard free energies, diffusion coefficients and diffusion activation energy of Ho atom in the alloy phase are determined.

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