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Pr(III)离子在LiCl-KCl熔体中Bi膜W电极上的电化学行为

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摘要: 采用循环伏安、方波伏安、计时电位和开路计时电位等电化学方法研究了Pr(III)离子在LiCl-KCl-BiCl₃熔体中W电极上的电化学行为。循环伏安和方波伏安的研究表明, Pr在预先沉积的Bi膜电极上发生欠电位沉积是由于生成了Pr-Bi金属间化合物, 导致Pr(III)在Bi膜电极上的还原电位比在W电极上还原电位更正。从开路计时电位曲线可以观察到两相共存的Pr-Bi金属间化合物的两个平台。利用开路计时电位计算了723–873 K温度范围内Pr在Pr-Bi合金中的活度和偏摩尔Gibbs自由能以及Pr-Bi金属间化合物的生成Gibbs自由能。通过恒电位电解, 在液态Bi电极上得到了Pr-Bi合金, 并采用X射线衍射(XRD)和扫描电子显微镜(SEM)附带能量分散谱(EDS)对样品进行了表征, 结果表明所得到的Pr-Bi金属间化合物为PrBi₂和PrBi。

关键词: 电化学行为; Pr-Bi金属间化合物; 欠电位沉积; 热力学性质; 恒电位电解
中图分类号: O646

Electrochemical Behavior of Pr(III) Ions on a Bi-Coated W Electrode in LiCl-KCl Melts

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Abstract: The electrochemical behavior of Pr(III) ions was studied on a Bi-coated W electrode in LiCl-KCl melts by a series of techniques, such as cyclic voltammetry, square wave voltammetry, and open circuit chronopotentiometry. From the cyclic voltammogram and square wave voltammogram, the underpotential deposition of Pr(III) on pre-deposited Bi (i.e., a Bi-coated W electrode) occurs, owing to the formation of Pr-Bi intermetallic compounds, resulting in the electrochemical reduction of Pr(III) at less cathodic potentials than that on an inert W electrode. Using the open circuit chronopotentiometry technique, two plateaus, corresponding to the co-existence of two phases of Pr-Bi intermetallic compound, were observed. Thermodynamic properties, such as the activities and relative partial molar Gibbs energies of Pr in the Pr-Bi alloys as well as Gibbs energies of the formation for the Pr-Bi intermetallic compounds, were estimated from the open circuit potential measurement in the temperature range of 723–873 K. Pr-Bi alloys were produced on the liquid Bi pool electrode by potentiostatic electrolysis, and were characterized by X-ray diffraction (XRD) and scanning electronic microscopy with energy-dispersive spectrometry (SEM-EDS). The results indicated that the intermetallic

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compounds, PrBi_2 and PrBi , were obtained.

Key Words: Electrochemical behavior; Pr-Bi intermetallic compound; Underpotential deposition; Thermodynamic property; Potentiostatic electrolysis

1 Introduction

Managing spent nuclear fuel in a safe, economic, and proliferation resistant manner represents one of the most important issues connected to the sustainable development of nuclear energy. Pyrochemical technique using molten salt media is one of the most promising options for extracting lanthanides (Lns) and actinides from the fission products^{1–4}. The most developed pyrochemical processes include electrorefining, electroextraction with reactive cathodes, liquid-liquid metal reductive extraction and oxide precipitation^{5–8}. The electrochemical extracting Lns from molten salt (chlorides or fluorides) was extensively researched using reactive cathodes, such as $\text{Al}^{9–11}$, $\text{Ni}^{12–14}$, $\text{Mg}^{15,16}$, $\text{Cd}^{17,18}$, and $\text{Bi}^{18–20}$.

For liquid Bi electrode, Castrillejo *et al.*^{18,19} investigated electrochemical behavior of Ce(III) and Pr(III) in LiCl-KCl melts by electrochemical techniques. They determined the thermodynamic properties of Ce-Bi and Pr-Bi intermetallic compounds in LiCl-KCl melts in the temperature range of 673–823 K using electromotive force (emf) measurements.

Praseodymium is a typical fission product and difficult to be separated from actinides. Therefore, the separation and extraction of Pr from molten salt have been extensively studied on different electrode materials, like W²¹, Al^{21} , $\text{Ni}^{22–26}$, $\text{Mg}^{16,27}$, liquid Cd¹⁸, and liquid Bi¹⁸.

However, electrochemical extracting Pr(III) in LiCl-KCl melts on Bi-coated W electrode has not been investigated. In order to acquire the basic electrochemical and thermodynamic information on Pr(III) in LiCl-KCl-BiCl₃ system, we explored the electrochemical behavior of Pr(III) on Bi coated W electrode, and the thermodynamic properties for Pr-Bi intermetallic compounds were determined by means of emf.

2 Experimental

2.1 Preparation and purification of the salts

A mixture of anhydrous LiCl (44.8 g, Sinopharm Chemical Reagent Co. Ltd., AR grade) and KCl (55.2 g, Sinopharm Chemical Reagent Co. Ltd., AR grade) was dried under vacuum for more than 60 h at 523 K to remove the excess water. Then the salt mixture was melted in an alumina crucible located in an electric furnace. The temperature of the molten salt was measured with a nickel chromium-nickel aluminium thermocouple sheathed with an alumina tube. The impurities in the melts were removed by pre-electrolysis at -2.0 V (vs Ag/AgCl) for 4 h. Anhydrous PrCl_3 (99.9%, High Purity Chemical Co. Ltd.) and BiCl_3 (Sinopharm Chemical Reagent Co. Ltd., AR grade) were added directly to the molten salt as Pr(III) and Bi(III) ion sources, respectively.

2.2 Electrochemical apparatus and electrodes

Cyclic voltammetry, square wave voltammetry (SWV), and open circuit chronopotentiometry were performed using an Au-

tolab PGSTAT 302N (Metrohm, Ltd.) with Nova 1.8 software. A silver wire ($d = 1$ mm) dipped into a solution of AgCl 1.0% (w, mass fraction) in the LiCl-KCl melts contained in a Pyrex tube was used as the reference electrode. All potentials were referred to this Ag/AgCl couple. The counter electrode was a spectral pure graphite rod ($d = 6$ mm). The inert electrode was a W wire ($d = 1$ mm; 99.99%), which was polished thoroughly using SiC paper, and then cleaned ultrasonically with dilute hydrochloric acid and ethanol prior to use. The Bi-coated W electrode was prepared by deposition a layer of fresh Bi film on the surface of W electrode at -0.2 V for 1 s before each electrochemical measurement. The active electrode surface area was determined by measuring the immersion depth of the electrode in the molten salts after each experiment. Some granules of Bi (99.99%) added in a J shaped Pyrex tube, which was immersed in the LiCl-KCl melts, was used as liquid Bi pool electrode. An electric lead was a W wire ($d = 1$ mm) placed in the liquid Bi phase through the Pyrex tube.

2.3 Molten salts electrolysis and characterization of deposits

The samples of Pr-Bi alloy were prepared by potentiostatic electrolysis in LiCl-KCl- PrCl_3 melts on liquid Bi electrode. After electrolysis, all samples were washed in hexane (99.8%) in an ultrasonic bath to remove salts, and then stored in a glove box for analysis. These specimens were analyzed by X-ray diffraction (XRD, X'Pert Pro; Philips Co., Ltd., Netherlands) using $\text{Cu } K_\alpha$ radiation at 40 kV and 40 mA. The microstructure and micro-zone chemical analyses were measured using scanning electron microscopy and energy dispersive spectrometer (SEM-EDS; JSM-6480A, JEOL Co., Ltd., Japan).

3 Results and discussion

3.1 Electrochemical behavior of Pr(III) in LiCl-KCl-BiCl₃ melts on W electrode

3.1.1 Cyclic voltammetry

Fig.1 shows the typical cyclic voltammograms (CVs) obtained in LiCl-KCl melts before and after the addition of PrCl_3 2.4% (w) on W electrode. In the dotted curve (curve 1), only a cathodic signal A is observed at about -2.44 V, which is ascribed to the deposition of lithium, and the corresponding anodic signal A' at around -2.29 V is associated with the dissolution of lithium. In the solid curve (curve 2) in Fig.1, prior to the A/A', a pair of new peaks, B/B' at about -2.08 V/ -1.89 V, correspond to the reduction/reoxidation of Pr after the addition of PrCl_3 2.4% (w) in LiCl-KCl melts on W electrode, which indicates that the electro-reduction of Pr(III) in LiCl-KCl melts proceeds in a one-step process involving three electrons^{16,21,26,27}.

The CVs of LiCl-KCl-BiCl₃ 0.24% (w) melts before and after the addition of PrCl_3 2.4% (w) are presented in Fig.2a. In the LiCl-

Fig.1 CVs obtained on W electrode ($S = 0.628 \text{ cm}^2$) in LiCl-KCl melts before (curve 1) and after (curve 2) the addition of PrCl_3 at 773 K

S : electrode area; scan rate: $0.08 \text{ V} \cdot \text{s}^{-1}$

KCl-BiCl_3 , 0.24% (w) melts (dotted curve), except for the peaks A/A', corresponding to the reduction/re-oxidation of Li, two pairs of peaks, C/C' and F/F', are observed. Cathodic peak F at around 0.12 V and its corresponding anodic peak F' at about 0.24 V should be ascribed to the deposition and dissolution of Bi metal, respectively. The experimental results are consistent with our previous study²⁰. Signals C/C', between signals of A/A' and F/F', correspond to the formation of Li-Bi intermetallic by underpotential deposition of Li on the pre-deposition Bi which already

covered the W electrode, i.e. Bi coated W electrode.

After the addition of PrCl_3 , 2.4% (w) in LiCl-KCl- BiCl_3 melts, the CV is more complex than the one obtained LiCl-KCl- BiCl_3 melts. In addition to the peaks A/A', C/C', and F/F', peaks D/D' can be ascribed to the formation/dissolution of Pr-Bi intermetallic compound. Since the Pr metal can react with pre-deposition Bi to form Pr-Bi intermetallic compounds after deposition, reduction potential of Pr(III)/Pr was observed at less negative potential values than that on W electrode.

In order to associate the dissolution anodic peaks with their corresponding cathodic formation, the voltammograms were registered at different inversion cathodic potentials, and the results are shown in Fig.2b. It can be seen that two new anodic peaks, D' and E' correspond to the formation of two Pr-Bi intermetallic compounds, respectively. Since reduction peak potentials of D and E are very close, the two cathodic peaks overlap each other. We cannot distinguish the two cathodic peaks.

3.1.2 Square wave voltammetry

Square wave voltammetry is more sensitive and has a higher resolution than cyclic voltammetry. Thus, it was performed to investigate the electrochemical behavior of Pr(III) in LiCl-KCl- BiCl_3 melts. Fig.3a presents square wave voltammograms (SWVs)

Fig.2 (a) CVs obtained in KCl-LiCl- BiCl_3 , 0.24% (w) after the addition of PrCl_3 , 2.4% (w) melts; (b) CVs obtained in KCl-LiCl- BiCl_3 , 0.24% (w)- PrCl_3 , 2.4% (w) melts at different inversion potentials

scan rate: $0.1 \text{ V} \cdot \text{s}^{-1}$; electrode: W; $S = 0.628 \text{ cm}^2$

Fig.3 (a) SWVs obtained in LiCl-KCl- BiCl_3 , 0.24% (w) before and after the addition of PrCl_3 , 2.4% (w) melts on W electrode ($S = 0.628 \text{ cm}^2$) at 773 K; (b) SWV obtained in LiCl-KCl- BiCl_3 , 0.24% (w)- PrCl_3 , 2.4% (w) melts on W electrode ($S = 0.628 \text{ cm}^2$) at 773 K

(a) potential step: 1 mV, frequency: 20 Hz;

(b) potential step: 1 mV, frequency: 5 Hz

obtained in LiCl-KCl-BiCl₃ melts before and after the addition of PrCl₃ on Bi-coated W electrode at a step potential of 1 mV and frequency of 20 Hz at 773 K. According to the reduction potentials of Pr(III) and Li(I) on Bi coated W electrode in Fig.2, the attribution of these reduction peaks could be confirmed. In the dotted curve (curve 1) in Fig.3a, except for the peaks, A and F, corresponding to the reduction of Li(I) and Bi(III), respectively, the peak C, at about -1.79 V, is ascribed to the formation of Li-Bi alloy compound. In the red solid curve (curve 2), compared with curve 1, two new pairs of reduction signals, B and D, are observed. In addition to the signal B corresponding to the reduction of Pr(III), the signal D should be attributed to the deposition of Pr-Bi alloy.

In order to investigate the peak D splitting, square wave voltammetry was conducted on W electrode at a step potential of 1 mV and frequency of 5 Hz in LiCl-KCl-BiCl₃-PrCl₃ melts from 0.5 to -1.6 V. We can observe from Fig.3b that two reduction peaks D and E occur. The two peaks D and E, identified at -1.33 and -1.27 V, correspond to the formation of two different Pr-Bi intermetallic compounds, respectively, which are consistent with those obtained from CVs in Fig.2.

3.1.3 Chronopotentiometry

Fig.4 presents a group of chronopotentiograms measured on Bi-coated W electrode ($S = 0.628 \text{ cm}^2$) in the LiCl-KCl-BiCl₃ 0.24% (w)-PrCl₃ 2.4% (w) melts at different currents. When the cathodic current reaches -25 mA, only one potential plateau (E) observed belong to the formation of Pr-Bi intermetallic compound. While the cathodic current more positive than -50 mA, the curve exhibits another new potential plateau (D) corresponding to the formation of another Pr-Bi intermetallic compound. At the current of -200 mA, a third plateau C, associated with the formation of Li-Bi intermetallic compound. While the cathodic current is more negative than -205 mA, the curve exhibits another two new potential plateaus (A and B) which are ascribed to the formation of pure lithium and praseodymium metals, respectively. It is obvious that the potential ranges for deposition of Pr and Bi are the same as those observed in the cyclic voltammograms (in Fig.2).

3.1.4 Open circuit chronopotentiometry

Open circuit chronopotentiometry is a suitable technique to

Fig.4 Chronopotentiograms obtained at different currents on W electrode ($S = 0.628 \text{ cm}^2$) in LiCl-KCl-BiCl₃ 0.24% (w)-PrCl₃ 2.4% (w) melts at 773 K

investigate the formation of Pr-Bi intermetallic compounds. The measurements were performed as follows: after cathodic polarization at -2.5 V (vs Ag/AgCl) for 20 s at 773 K, the polarization was stopped and the electrode was kept in the melts. During this currentless step, where only intermetallic diffusion occurs, the open-circuit potential was recorded vs. time; meanwhile the electrode potential was shifted towards more positive values. During this process, a potential plateau is observed when a composition of the electrode surface is within a range of two phases coexisting state.

Fig.5 displays the open circuit chronopotentiograms measured on W electrode in LiCl-KCl-PrCl₃, LiCl-KCl-BiCl₃ and LiCl-KCl-BiCl₃-PrCl₃ melts, respectively. Six plateaus, A, B, C, D, E, and F, are observed at -2.34, -1.91, -1.66, -1.18, -1.12, and 0.19 V, respectively. It is obvious that the first plateau A is considered to correspond to the equilibrium of Li(I)/Li(0). The second plateau B is ascribed to the equilibrium of Pr(III)/Pr(0). After that, three plateaus C, D, and E are correlated to the coexisting states of Li-Bi and Pr-Bi intermetallic compounds, respectively. According to our previous results²⁰, the plateau C should be related to the coexisting states of Li₃Bi and Bi. The last plateau F is ascribed to the equilibrium of Bi(III)/Bi(0). According to the following results of XRD and SEM-EDS in potentiostatic electrolysis experiments, we speculated that the potential plateaus in Fig.5 could be ascribed to the following reactions:

The emf corresponding to the chemical composition of the alloy is related to the activity and the relative partial molar Gibbs energy of Pr, by the expression:

$$\Delta \bar{G}_{\text{Pr}} = -3F\Delta E = RT \ln a_{\text{Pr}} \quad (9)$$

where a_{Pr} is the activity of Pr in the Pr-Bi alloy, taking pure Pr as the standard state; $\Delta \bar{G}_{\text{Pr}}$ is the relative partial molar Gibbs energy

Fig.5 Open circuit chronopotentiograms obtained in the LiCl-KCl-PrCl₃ 2.4% (w), LiCl-KCl-BiCl₃ 0.24% (w), and LiCl-KCl-BiCl₃ 0.24% (w)-PrCl₃ 2.4% (w) melts on W electrode ($S = 0.628 \text{ cm}^2$) after deposition at -2.5 V for 20 s at 773 K

Table 1 Thermodynamic properties of Pr for Pr-Bi intermetallic compounds in two-phase coexisting states at different temperatures

Plateau	<i>T</i> /K	<i>E</i> _{eq} /V (vs Ag/AgCl)	Δ <i>E</i> /V (vs P(III)/Pr)	Δ <i>G</i> _B ⁰ /(kJ·mol ⁻¹)	Δ <i>G</i> _B ⁰ /(kJ·mol ⁻¹) ¹⁸	<i>a</i> _{Pr}	<i>a</i> _{Pr} ¹⁸
B	723	-1.933					
	773	-1.897					
	823	-1.869					
	873	-1.855					
D	723	-1.199	0.734	-212.49 ± 0.29	-213.9 ± 1.00 ¹⁸	-4.44 × 10 ⁻¹⁶	(-3.53 ± 0.50) × 10 ⁻¹⁶
	773	-1.171	0.726	-210.18 ± 0.58		-2.63 × 10 ⁻¹⁵	
	823	-1.153	0.716	-207.28 ± 0.87	-213.0 ± 0.40	-6.97 × 10 ⁻¹⁴	(-3.01 ± 0.20) × 10 ⁻¹⁴
	873	-1.149	0.706	-204.39 ± 0.58		-5.89 × 10 ⁻¹³	
E	723	-1.194	0.769	-222.63 ± 0.58	-214.5 ± 0.20	-8.23 × 10 ⁻¹⁷	(-6.00 ± 0.20) × 10 ⁻¹⁷
	773	-1.140	0.757	-219.15 ± 0.87		-1.55 × 10 ⁻¹⁵	
	823	-1.123	0.746	-215.97 ± 0.29	-219.3 ± 0.80	-1.96 × 10 ⁻¹⁴	(-1.20 ± 0.10) × 10 ⁻¹⁴
	873	-1.119	0.733	-212.20 ± 0.87		-2.01 × 10 ⁻¹³	

of Pr in the Pr-Bi alloy. The thermodynamic properties obtained at different temperatures are listed in Table 1. Compared with the values of activities and relative partial molar Gibbs energies of Pr in Pr-Bi alloy obtained by Castrillejo *et al.*¹⁸, their values are consistent with our results.

The standard Gibbs energies (Δ*G*_f⁰) of formation for PrBi and PrBi₂ are calculated by the equation presented in Table 2. We can see from Table 2 that the values of Gibbs energy of formation for PrBi and PrBi₂ at 723 and 823 K are very close to the results obtained by Castrillejo *et al.*¹⁸. Fig.6 shows the variation of the energy of formation for the different intermetallic compounds with the temperatures. We can find that the linear dependence of the

energy of formation for PrBi₂ and PrBi with the temperatures, which is formulated as follows:

$$\Delta G_{\text{PrBi}_2}^0 = -277.53 - 0.0749T \quad (10)$$

$$\Delta G_{\text{PrBi}}^0 = -262.73 - 0.0622T \quad (11)$$

3.2 Electrochemical formation of Pr-Bi alloys in LiCl-KCl-BiCl₃-PrCl₃ melts

Based on the results obtained by cyclic voltammetry, square wave voltammetry, chronopotentiometry, and open circuit chronopotentiometry, the potentiostatic electrolysis was carried out in LiCl-KCl-BiCl₃ 0.24% (w)-PrCl₃ 5.5% (w) melts on Bi-coated W electrode. To avoid the formation of Li-Bi intermetallic com-

Table 2 Standard molar Gibbs energies of formation for Pr-Bi intermetallic compounds

Intermetallic compound	Equation	<i>T</i> /K	Δ <i>G</i> _f ⁰ /(kJ·mol ⁻¹)	Δ <i>G</i> _f ⁰ /(kJ·mol ⁻¹) ¹⁸
PrBi ₂	Δ <i>G</i> _f ⁰ (PrBi ₂) = -3 <i>F</i> Δ <i>E</i> ₁	723	-222.63 ± 0.58	-224.6 ± 0.4
		773	-219.15 ± 0.87	
		823	-215.97 ± 0.29	-219.4 ± 0.8
		873	-212.20 ± 0.87	
PrBi	Δ <i>G</i> _f ⁰ (PrBi) = $\frac{1}{2}[\Delta G_f^0(\text{PrBi}_2) - 3F\Delta E_2]$	723	-217.66 ± 0.44	-219.3 ± 0.1
		773	-214.67 ± 0.73	
		823	-211.63 ± 0.58	-216.2 ± 0.2
		873	-208.30 ± 0.73

Fig.6 Variation of the Gibbs energy of formation for Pr-Bi intermetallic compounds with temperature in LiCl-KCl melts

Fig.7 XRD pattern of deposits obtained on liquid Bi electrode (*S* = 0.2 cm²) in LiCl-KCl-PrCl₃ 5.5% (w) melts by potentiostatic electrolysis at -1.6 V for 4 h

Fig.8 SEM and EDS analyses of sample obtained by potentiostatic electrolysis at -1.6 V (vs Ag/AgCl) for 4 h on liquid Bi electrode ($S = 0.2$ cm²) in LiCl-KCl-PrCl₃ 5.5% (w) melts
(a) SEM; (b, c) EDS analyses of zones 1 and 2 in Fig.8a.

pounds, the deposition potential was controlled to be more positive than -1.7 V for the potentiostatic electrolysis. However, the Pr-Bi alloys prepared were always residue-shaped in molten salts, whether at low or high temperature. We could not collect the Pr-Bi alloys. Therefore, potentiostatic electrolysis was conducted on a liquid Bi pool electrode in the LiCl-KCl-PrCl₃ melts.

Fig.7 presents the XRD pattern of sample obtained in LiCl-KCl-PrCl₃ 5.5% (w) melts by potentiostatic electrolysis at -1.6 V for 4 h. According to the Pr-Bi phase diagram²⁸, there are five Pr-Bi intermetallic compounds, PrBi₂, PrBi, Pr₃Bi₃, Pr₅Bi₃, and Pr₇Bi₃. Since JADE 5.0 software only provides the XRD source data of PrBi, we can observe from Fig.7 that the formation of Pr-Bi intermetallic compound, PrBi, when the applied potential at -1.6 V. Fig.8 displays a group of SEM micrograph and EDS analyses of the Pr-Bi alloy sample obtained by potentiostatic electrolysis at -1.6 V. The SEM image of the sample shows that different sizes of grey areas discretionarily distribute on the surface. To further investigate the distribution of the element Pr, EDS quantitative analysis was performed (Fig.8(b, c)). The EDS results of the zones labeled 1 and 2 taken from two represented zones in Fig.8a indicate that ratios of Pr to Bi are about 2 : 5 and 2 : 3, respectively. XRD pattern confirms the existence of PrBi intermetallic compound, based on the results of EDS analysis, we could infer the formation of PrBi₂ in Pr-Bi alloy.

4 Conclusions

The results of cyclic voltammetry, square wave voltammetry, chronopotentiometry, and open circuit chronopotentiometry proved that Pr(III) ions in the LiCl-KCl-BiCl₃-PrCl₃ melts could be reduced on the Bi coated W electrode by forming Pr-Bi intermetallic compounds. Emf measurements for the Pr-Bi intermetallic compounds in two-phase coexisting states were carried out in the temperature range of 723–873 K. From the results of emf, the activities and relative partial molar Gibbs energies of Pr in the Pr-Bi alloys were calculated. Moreover, the formation Gibbs energies as well as the overall formation constant of each Pr-Bi intermetallic compound were also obtained. Potentiostatic electrolysis was performed to confirm the deposition of Pr on liquid Bi electrode. XRD pattern and SEM-EDS analysis revealed the formation of PrBi and PrBi₂ intermetallic compounds.

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