Electrochemical Reduction of Tm Ions in LiCl-KCl Melt at Liquid Zn Electrodes (Postprint)

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Abstract

The reduction of Tm(III) on a liquid Zn electrode was investigated in a LiCl-KCl melt via cyclic voltammetry, square wave voltammetry, and open circuit chronopotentiometry. On a liquid Zn electrode, the reduction mechanism of Tm(III) ions is through one step with the exchange of three electrons via the formation of a Zn-Tm alloy. This differs from that on an inert electrode, as the reduction is Tm(III) ions were though two consecutive steps. Galvanostatic electrolysis was carried out at a liquid Zn electrode at different current densities in a LiCl-KCl-TmCl3 melt. The Tm2Zn17 intermetallic compound was identified in the deposit, except in the Zn phase, by X-ray Diffraction (XRD).

Full Text

Preamble

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chronopotentiometry. On a liquid Zn electrode, the reduction mechanism of Tm(III) ions occurs in a single step involving the exchange of three electrons through the formation of a Zn-Tm alloy. This differs from the reduction on an inert electrode, where Tm(III) ions are reduced through two consecutive steps. Galvanostatic electrolysis was carried out at a liquid Zn electrode at different current densities in a LiCl-KCl-$TmCl_3$ melt. The Tm_2Zn_{17} intermetallic compound was identified in the deposit, in addition to the Zn phase, by X-ray Diffraction (XRD).

Keywords: Nuclear waste, Electrochemical extraction, Thulium, Molten salt
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Introduction

Nuclear energy has been extensively used for electricity production in many nations. However, the spent fuel reprocessing system of a nuclear power station produces a large quantity of high-level radioactive waste (HLW) each year, which poses a great potential hazard to the environment and future generations. Consequently, the disposal of HLW has attracted significant attention. Partitioning and transmutation (P&T) represents a promising method for HLW disposal, as it can recycle or transform hazardous radionuclides into less hazardous or shorter-lived elements [1–6]. Before transmutation, however, it is necessary to separate minor actinides (MAs) from other fission products (FPs), especially rare earth fission products (RE). Molten salt electrochemical techniques, known as pyrochemical techniques, have been widely studied for decades to investigate the recovery of actinides separated from rare earth elements.

In this paper, the electrochemical behavior of Tm is investigated at a liquid Zn electrode, not only because it is present in small amounts in nuclear waste, but also due to its similar electrochemical behavior to Am in molten salt [7]. However, basic experimental data for Am in molten alkali chlorides are scarce, primarily due to the limited availability of $AmCl_3$ and its intense radioactivity. The similarities between Tm and Am in molten salt are as follows [7–13]: (1) Both have two stable oxidation states, Tm(III)/Tm(II) and Am(III)/Am(II), respectively. (2) The reduction potentials of Tm(II) and Am(II) are more positive than those of common solvent ions such as Li and Na. In contrast, for rare earth elements Sm, Eu, and Yb, their deposition potentials are similar to or more negative than those of Li and Na. (3) The reduction mechanism of Tm(III) and Am(III) depends on the cathode electrode material. On an inert electrode (W), Tm(III) and Am(III) ions are reduced to metallic Tm and Am through two consecutive steps: (i) Tm(III) + e^- Tm(II); (ii) Tm(II) + $2e^-$ Tm(0), and (i) Am(III) + e^- Am(II); (ii) Am(II) + $2e^-$ Am(0). In contrast, for Am in a $CaCl_2$-NaCl melt, when liquid Al is used as a working electrode, Am(III) ions are reduced to Am(0) in a single step involving the exchange of three electrons [13]. For Tm, in LiCl-KCl and NaCl-2CsCl melts, when solid Al is used as a working electrode, Tm(III) ions are reduced to Tm(0) in a single step via the formation of an Al-Tm alloy, with the exchange of three electrons

[7, 8]. Therefore, obtaining basic electrochemical data on Tm in molten salt can help in understanding the extraction process of Am.

Compared with molten fluorides, molten chlorides have a much lower operating temperature. Thus, we propose that Zn is a good cathode material due to its low melting point (approximately 693 K under atmospheric pressure). Moreover, it is much easier to obtain high-purity spongy rare earth elements by reduced-pressure distillation from Zn-Tm alloys.

II. Experimental

A. Preparation and Purification of the Melt

The LiCl-KCl mixture (Sinopharm Chemical Reagent Co., Ltd., analytical grade $\geq$ 99.8% and 99.5%, respectively) was dried under vacuum for more than 72 h at 473 K to remove excess water before use. Tm(III) ions were introduced into the LiCl-KCl melt in the form of anhydrous $TmCl_3$ (Sinopharm Chemical Reagent Co., Ltd., analytical grade $\geq$ 99.9%). Before each experiment, HCl was bubbled into the melt to remove oxide ions, after which Ar gas was bubbled to remove residual HCl, oxygen, and water.

B. Electrochemical Apparatus and Electrodes

Cyclic voltammetry, square wave voltammetry, open circuit chronopotentiometry, and galvanostatic electrolysis were performed using an Autolab PGSTAT 302N potentiostat/galvanostat controlled with the Nova 1.8 software package. The working electrodes were tungsten (d = 1 mm) and liquid Zn placed in an alumina crucible. The cathode crucible for loading Zn (Aladdin Chemical Co., Ltd., analytical grade 99.99%, about 6–8 g) measured 2.2 cm in height and 1.5 cm in diameter. A W wire (d = 1 mm) placed in an alumina sleeve was immersed in the cathode Zn and used as an electrical lead [14]. The surface of W electrodes was polished thoroughly with SiC paper prior to use to remove the oxide film and surface impurities. Moreover, the working electrodes were cleaned by applying anodic polarization between measurements. A graphite rod (d = 6 mm) served as the counter electrode. The reference electrode was the Ag^+/Ag couple consisting of AgCl (1.0 wt.%) in LiCl-KCl molten salt contained in an alundum tube [14].

C. Characterization of Zn-Tm Alloys

Zn-Tm alloys were prepared via galvanostatic electrolysis on liquid Zn electrodes. After electrolysis, the samples were washed with ethylene glycol to remove solidified salts attached to the alloy surface. The samples were then analyzed by X-ray diffraction (XRD) (Rigaku D/max-TTR-III diffractometer) using Cu-Kα radiation at 40 kV and 150 mA. Scanning electron microscopy (SEM) (JSM-6480A; JEOL Co., Ltd.) was used to analyze the microstructure and micro-zone chemical composition of bulk Zn-Tm alloys.

III. Results and Discussion

A. Cyclic Voltammetry

Figure 1 [Figure 1: see original paper] shows cyclic voltammograms obtained in a LiCl-KCl melt containing different concentrations of $TmCl_3$ at a Zn electrode at 723 K. In curve 1, two pairs of signals are present. The signals A/A′ at about −0.63/−0.94 V (vs. Ag/AgCl) correspond to the reduction of Zn(II) ions dissolved from the liquid Zn electrode and the oxidation of Zn, respectively. The cathodic signal C at approximately −2.00 V is ascribed to the deposition of Li(I) on the liquid Zn electrode, forming a Zn-Li alloy. In the reverse scan, the corresponding anodic signal C′ is attributed to the dissolution of the Zn-Li alloy. The electrochemical window of a LiCl-KCl melt on a liquid Zn electrode is limited by the deposition of Zn(II) ions and the formation of a Zn-Li alloy in the cathodic direction. Moreover, the current background of a Zn electrode is larger than that of a solid metal electrode, which is characteristic of liquid metal electrodes [15-17]. After the addition of $TmCl_3$ in curve 2, a new pair of signals B/B′ appears at about −1.55/−1.23 V, which should correspond to the formation/dissolution of a Zn-Tm alloy. The Zn-Tm alloy forms via the underpotential deposition of Tm(III) on the liquid Zn electrode. With increasing $TmCl_3$ concentration in the melt, the deposition potential of Tm(III) ions on the liquid Zn electrode shifts toward more positive values due to changes in the activity of Tm(III) ions in the melt.

B. Square Wave Voltammetry

Square wave voltammetry, which is more sensitive than cyclic voltammetry, was also conducted to investigate the reduction of Tm(III) ions. Figure 2 [Figure 2: see original paper] shows square wave voltammograms obtained in LiCl-KCl-$TmCl_3$ (2 wt.%) at a W electrode (dotted line) and a liquid Zn electrode (solid line). As can be seen, on a W electrode (dotted line), two signals D and E appear at about −1.59 V and −2.15 V. Signal D, characteristic of a soluble-soluble electrochemical exchange, should correspond to the reduction of Tm(III) to Tm(II) [18-20]. Signal E should be related to the deposition of Tm(II) ions on the W electrode. In contrast, on a liquid Zn electrode, only a signal at about −1.43 V is detected, whose potential is slightly more positive than that of Tm(III)/Tm(II) on a W electrode (see signal D). As is known, for a soluble-soluble electrochemical exchange, the reduction is not supposed to be related to electrode materials. Therefore, signal B should not be related to the reduction of Tm(III)/Tm(II), but rather corresponds to the reduction of Tm(III)/Tm(0) on the liquid Zn electrode via the formation of a Zn-Tm alloy.

C. Open Circuit Chronopotentiometry

Open-circuit chronopotentiometry was employed to further investigate the electrochemical formation of Zn-Tm intermetallic compounds. Figure 3 [Figure 3: see original paper] shows open circuit chronopotentiometry curves obtained on a

W electrode (curve 1) and liquid Zn electrodes (curves 2, 3, and 4) in LiCl-KCl-$TmCl_3$ (2 wt.%) melt. On a W electrode, three plateaus (plateaus 1, 2, and 3) are observed at about −2.40 V, −2.05 V, and −1.60 V, corresponding to the deposition of Li(I), deposition of Tm(II)/Tm(0), and reduction of Tm(III)/Tm(II), respectively. When liquid Zn is used as a working electrode, only one plateau (plateau 4) appears at about −1.30 V, which is attributed to the formation of a Zn-Tm alloy. The deposition potential of Tm(III) at a liquid Zn electrode is approximately 0.75 V more positive than that on an inert W electrode.

D. Preparation and Characterization of Zn-Tm Alloys

Based on the above electrochemical analysis, we can conclude that the reduction of Tm(III) ions on a liquid Zn electrode occurs in a single step involving the exchange of three electrons via the formation of Zn-Tm alloys. Extraction of Tm was carried out at a liquid Zn electrode at 723 K via galvanostatic electrolysis at different current densities. Figure 4 [Figure 4: see original paper] shows the XRD patterns of deposits obtained in a LiCl-KCl-$TmCl_3$ (6 wt.%) melt at 723 K at a liquid Zn electrode via galvanostatic electrolysis for 3 h at (a) 200 mA/cm^2 and (b) 300 mA/cm^2, respectively. Zn and Tm_2Zn_{17} phases were detected in the deposits. The Zn phase originates from the liquid Zn electrode, while the Tm_2Zn_{17} phase forms via the underpotential deposition of Tm(III) in liquid Zn.

Figure 5 [Figure 5: see original paper] shows cross-sectional SEM (backscattering image) of Zn-Tm alloys obtained in a LiCl-KCl-$TmCl_3$ (6 wt.%) melt at 723 K at a liquid Zn electrode via galvanostatic electrolysis at (a) 200 mA/cm^2, (b) 300 mA/cm^2, (c) 400 mA/cm^2, and (d) 500 mA/cm^2, respectively. As can be seen, the alloys are composed of two phases: bright and gray zones. According to our previous study [14], the bright zones correspond to Zn-Tm intermetallic compounds. The convex bulges are thought to be Zn-Tm alloy precipitates from the Zn matrix during the cooling period due to the low solubility of Tm in the Zn matrix [14]. The shape of convex bulges in samples a, b, c, and d is irregular, and the size of the convex bulges varies within and between samples, indicating that the distribution of Tm in the deposit and the Tm content in each sample are different.

IV. Conclusion

On an inert W electrode, the reduction of Tm(III) ions occurs through two consecutive steps: (i) Tm(III) + e^- Tm(II); (ii) Tm(II) + $2e^-$ Tm(0). However, on a liquid Zn electrode, the reduction mechanism of Tm(III) ions proceeds in a single step involving the exchange of three electrons via the formation of a Zn-Tm alloy. The Zn-Tm alloy formation was confirmed through cyclic voltammetry, square wave voltammetry, and open circuit chronopotentiometry on liquid Zn electrodes. The Zn-Tm alloy was prepared via galvanostatic electrolysis at different current densities in a LiCl-KCl melt on liquid Zn electrodes. Tm_2Zn_{17} and Zn phases were identified in the deposit by XRD. Cross-sectional

SEM images (backscattering) of the Zn-Tm alloys show that the solubility of Tm in Zn is low.

References

[1] Nishihara K, Nakayama S, Morita Y, et al. Impact of Partitioning and Transmutation on LWR High-Level Waste Disposal. J Nucl Sci Technol, 2008, 1: 84–97. DOI: 10.1080/18811248.2008.9711418
[2] González-Romero E.M. Impact of partitioning and transmutation on the high level waste management. Nucl Eng Des, 2011, 241: 3436–444. DOI: 10.1016/j.nucengdes.2011.03.030
[3] Koch L, Glatz J P, Konings R J M, et al. Partitioning and Transmutation Studies at ITU, ITU Annual Report 1999-(EUR 19054)-Partitioning and Transmutation Studies at ITU.
[4] Usuda S, Wei Y Z, Liu R Q. Challenges to develop single-column MA(III) separation from HLLW using R-BTP type adsorbents. Sci China Chem, 2012, 55: 1732–1738. DOI: 10.1007/s11426-012-4691-x
[5] Wei Y Z, Wang X P, Liu R Q. An advanced partitioning process for key elements separation from high level liquid waste. Sci China Chem, 2012, 55: 1726–1731. DOI: 10.1007/s11426-012-4690-0
[6] Han C Y, Ozawa M, Saito M. Resourceability on nuclear fuel cycle by transmutation approach. Sci China Chem, 2012, 55: 1746–1751. DOI: 10.1007/s11426-012-4697-4
[7] Castrillejo Y, Fernández P, Bermejo M R, et al. Electrochemistry of thulium on inert electrodes and electrochemical formation of a Tm–Al alloy from molten chlorides. Electrochim Acta, 2009, 54: 6212–6222. DOI: 10.1016/j.electacta.2009.05.095
[8] Smolenski V and Novoselova A. Electrochemistry of redox potential of the couple Tm^{3+}/Tm^{2+} and the formation of a Tm–Al alloy in fused NaCl-2CsCl eutectic. Electrochim Acta, 2012, 63: 179–184. DOI: 10.1016/j.electacta.2011.12.089
[9] Novoselova A and Smolenski V. The influence of solvent nature on thermodynamic properties of the reaction Tm(III)+e^- Tm(II) in molten chlorides. J Chem Thermodyn, 2012, 48: 140–144. DOI: 10.1016/j.jct.2011.12.007
[10] Novoselova A and Smolenski V. Thermodynamic properties of thulium and ytterbium in fused NaCl-KCl-CsCl eutectic. J Chem Thermodyn, 2011, 43: 1063–1067. DOI: 10.1016/j.jct.2011.02.015
[11] Novoselova A and Smolenski V. Thermodynamic properties of thulium and ytterbium in molten caesium chloride. J Chem Thermodyn, 2010, 42: 973–977. DOI: 10.1016/j.jct.2010.03.013
[12] Serp J, Chamelot P, Fourcaudot S, et al. Electrochemical behaviour of americium ions in LiCl-KCl eutectic melt. Electrochim Acta, 2006, 51: 4024–4032. DOI: 10.1016/j.electacta.2005.11.016
[13] Córdoba G D, Laplace A, Conocar O. et al. Determination of the activity coefficient of Am in liquid Al by electrochemical methods. J Nucl Mater, 2009, 393: 459–464. DOI: 10.1016/j.jnucmat.2009.07.002

[14] Li X, Yan Y D, Zhang M L, et al. J Electrochem Soc, 2014, 161: D248-D255. DOI: 10.1149/2.061405jes
[15] Castrillejo Y, Bermejo M R, Arocas P D, et al. Electrochemical behaviour of praseodymium (III) in molten chlorides. J Electroanal Chem, 2005, 575: 61-74. DOI: 10.1016/j.jelechem.2004.08.020
[16] Kim S H, Paek S, Kim T J. Electrode reactions of Ce^{3+}/Ce couple in LiCl-KCl solutions containing $CeCl_3$ at solid W and liquid Cd electrodes. Electrochim Acta, 2012, 85: 332-335. DOI: 10.1016/j.electacta.2012.08.084
[17] Córdoba G D, Laplace A, Conocar O. Determination of the activity coefficient of neodymium in liquid aluminium by potentiometric methods. Electrochim Acta, 2008, 54: 280-288. DOI: 10.1016/j.electacta.2008.08.002
[18] Massot L, Chamelot P, Cassayre L, et al. Electrochemical study of the Eu(III)/Eu(II) system in molten fluoride media. Electrochim Acta, 2009, 54: 6361-6366. DOI: 10.1016/j.electacta.2009.06.016
[19] Gibilaro M, Massot L, Chamelot P. Electrochemical extraction of europium from molten fluoride media. Electrochim Acta, 2009, 55: 281-287. DOI: 10.1016/j.electacta.2009.08.052
[20] Castrillejo Y, Fernández P, Medina J, et al. Electrochemical extraction of samarium from molten chlorides in pyrochemical processes. Electrochim Acta, 2011, 56: 8638-8644. DOI: 10.1016/j.electacta.2011.07.059

Note: Figure translations are in progress. See original paper for figures.