



Co-reduction behaviors of lanthanum and aluminium ions in LiCl-KCl eutectic



Ya-Lan Liu^{a,b}, Li-Yong Yuan^b, Guo-An Ye^{a,*}, Kui-Liu^b, Lin Zhu^b, Mi-Lin Zhang^c, Zhi-Fang Chai^b, Wei-Qun Shi^{b,*}

^a Department of Radiochemistry, China Institute of Atomic Energy, Beijing, 102413, China

^b Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

^c Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

ARTICLE INFO

Article history:

Received 28 May 2014

Received in revised form 29 August 2014

Accepted 30 August 2014

Available online 18 September 2014

Keywords:

lanthanum
co-reduction
LiCl-KCl eutectic
intermetallic compounds

ABSTRACT

In this work, the co-reduction of La(III) and Al(III) ions on the Mo electrode was investigated in LiCl-KCl eutectic at 723–806 K. Cyclic voltammetry (CV), square wave voltammetry (SWV), and open-circuit chronopotentiometry (OCP) techniques were employed to investigate the electrochemical behaviors of the co-reduction. From the CV and SWV results, the formation signals of five kinds of Al-La intermetallic compounds, which could be attributed to $AlLa_3$, $AlLa$, Al_2La , Al_3La and $Al_{11}La_3$, were observed. The thermodynamic properties of La-Al intermetallic compounds in the temperature range of 723–806 K were estimated by the OCP results. The changes of Gibbs energies, enthalpies and entropies of formation and the apparent standard potentials of La-Al intermetallic compounds were evaluated. Finally, potentiostatic electrolyses at 723 K and galvanostatic electrolyses at 806 K were carried out to confirm the co-reduction process, and the products obtained were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. It was found that the co-reduction products of $Al_{11}La_3$, Al_3La and Al_2La were obtained.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Pyrometallurgical process is one of the most promising options for the reprocessing of advanced nuclear fuels and transmutation blankets which are high burn up and expected to have a high content of Pu and minor actinide [1–5]. In a typical pyrometallurgical process, actinides in chopped spent metal fuels are anodically dissolved into a LiCl-KCl eutectic electrolyte along with the active fission products (FPs). At the same time, uranium is recovered onto a solid steel cathode while uranium, plutonium and minor actinides are recovered together on the liquid cadmium cathode (LCC) [6]. However, some amounts of rare-earth elements can still enter the LCC together with actinides because the redox potentials of rare-earth elements on the LCC are very close to those of actinides [7]. Among these rare-earth elements, lanthanum, which has the closest ionic radius to U(III) among lanthanides, is a typical fission product and difficult to be separated from actinides [8]. To recover and separate lanthanum from actinides, basic

electrochemical properties of lanthanum were studied in recent decades [9,10]. From these investigations, the reduction of La(III) in molten chlorides was found to be a three electron transition step on the inert electrodes, and the electrochemical deposition of lanthanum metal on the inert electrodes was explained in terms of a model involving the instantaneous nucleation with three-dimensional growth of the nuclei [11–14]. Besides the inert electrodes, various kinds of active cathodic materials had been studied to improve the separation efficiency of lanthanum over actinides [7,15–17]. For example, Kato et al. reported the separation of plutonium from lanthanum using saturated liquid cadmium cathode [7], the separation factor (SF) of La against Pu was 0.011. Malmbeck et al. studied the separation of plutonium from lanthanum using molten bismuth cathode in LiCl-KCl eutectic, and found that the potential difference between formation of $PuBi_2$ and $LaBi_2$ was approximately 100 mV [17]. Nevertheless, full separation of lanthanum on the liquid Cd and Bi seemed not possible, because the necessary deposition potential gap should be 200 mV for the separation of trivalent cations [18].

The investigations from ITU (Institute of transuranium) showed that the deposition potential gaps of actinides and lanthanides on the solid Al cathode are bigger than those on other active cathodes,

* Corresponding authors. Tel.: +86-10-88233968; Fax: +86-10-88235294.
E-mail addresses: yeguoan@ciae.ac.cn (G.-A. Ye), shiwq@ihpe.ac.cn (W.-Q. Shi).

therefore the separation of actinides from lanthanides by using a solid Al electrode was more efficient [19,20]. In another context, the electrochemical behaviors of lanthanum on the Al electrode were studied by Nagarajan et al. [14], they found that the reduction of La(III) on a Al cathode occurs at a more anodic potential than that on an inert W electrode, due to the formation of intermetallic compound $\text{Al}_{11}\text{La}_3$. It indicated that the deposition potential, which is highly relevant to the separation efficiency, depends on the formation of intermetallic compounds. The La-Al phase diagram shows the presence of six intermetallic compounds (AlLa_3 , AlLa , Al_2La , Al_xLa , Al_3La , $\text{Al}_{11}\text{La}_3$) [21], but only the formation of $\text{Al}_{11}\text{La}_3$ was observed by Nagarajan et al. Therefore, further investigations on the intermetallic compound formation between La and Al are still necessary for potential technological and industrial applications. Typically, two processes could be employed to obtain Al-La intermetallic compounds: (i) underpotential deposition (UPD) of La(III) ions on a reactive Al cathode; (ii) co-reduction of La(III) ions with aluminium ions using an inert electrode. In our previous work, we found that more kinds of Al-Th, Al-Gd, Al-Er, Al-Sm, Sm-Zn intermetallic compounds were formed by the co-reduction process than that by the UPD process [22–26]. In addition, Gibilaro et al. also observed the formation of more than one kind of Ce-Al and Sm-Al intermetallic compounds through similar depositions. Hence, in the present work, the co-reduction behavior of La(III) and Al(III) on the inert Mo electrode is investigated to get more insights of the La-Al intermetallic compounds. To the best of our knowledge, similar work has not been reported so far.

2. Experimental

2.1. Preparation and purification of the melt

Anhydrous LiCl (Alfa Aesar, AR grade), anhydrous KCl (Alfa Aesar, AR grade), LaCl_3 , AlCl_3 (Alfa Aesar, AR grade), were used for the preparation of the electrolyte. A mixture of 45 g LiCl and 55 g KCl was dried under vacuum for more than 100 h at 473 K to remove the excess water. Then the salt mixture was melted in a 200 cm^3 alumina crucible placed in a quartz cell located in an electric furnace. The temperature of the melt was measured with a nickel-chromium thermocouple sheathed with an alumina tube. When the salt mixture was completely melted, the melt was then pre-electrolysis at -2.2 V (vs. AgCl/Ag) for several hours (usually more than 4 hours) to remove the metal ion impurities. Lanthanum, aluminum elements were introduced into the bath in the form of dehydrated LaCl_3 and AlCl_3 powder, respectively. Due to its volatility, the exact concentration of AlCl_3 in the melts could not be measured. Hence, the concentration of AlCl_3 we present in this work is the concentration of AlCl_3 initially added into the melts. Dehydrated LaCl_3 was prepared from La_2O_3 and NH_4Cl as follows: 3 g La_2O_3 and 6 g NH_4Cl was heated at 573 K for 3 h in a vacuum furnace [27], and the product was confirmed to be LaCl_3 by XRD (Bruker D8).

2.2. Electrodes and electrochemical apparatus

The inert working electrode consisted of 1 mm molybdenum wire (Alfa Aesar 99.99%), and the active electrode surface area was determined after each experiment by measuring the immersion depth of the electrode in the molten salts. A 6 mm diameter graphite rod (Alfa Aesar >99.99%) was used as the counter electrode. The reference electrode is a pyrex tube containing a silver wire (Alfa Aesar, 99.99%, $d=1$ mm) dipped into a solution of 1.0 wt.% AgCl in LiCl-KCl melt. All potentials were referred to the AgCl/Ag reference electrode. PGSTAT302N electrochemical workstation (Autolab, Metrohm) controlled with the Nova 1.9 software package was used to obtain electrochemical data.

2.3. Preparation and characterization of La-Al intermetallic compounds

The samples of La-Al intermetallic compounds were prepared by potentiostatic or galvanostatic electrolysis on a molybdenum electrode, or on an active solid aluminum electrode. The active solid aluminum electrode was an Al plate working electrode (length, 2 cm; width, 1 cm; thickness, 2 mm). After electrolysis, the alloys were extracted from the melt under an argon atmosphere box. All the samples were washed in hexane (99.8% purity) in an ultrasonic bath to remove salts and stored in the glove box. And the samples were washed by 1, 2-ethanediol using ultrasound before analysis. The microstructure and micro-zone chemical analysis of these alloys were measured with SEM (Hitachi S-4800) and the composition of the samples were analyzed by XRD (Bruker D8).

3. Results and Discussion

3.1. Co-reduction behaviors of La(III) and Al(III) on the Mo electrode

Co-reduction means a simultaneous reduction of two or more metallic ions on an inert electrode to form an alloy consisting of at least two metals. The theoretical principles and practical details of a co-reduction process in aqueous media had been described by Brenner [28]. Recently, the co-reduction process in molten salts was also proposed by Taxil et al. and Gibilaro et al. for nuclear wastes reprocessing [1,29]. By the principle of Taxil and Gibilaro, the co-reduction process with Al(III) and La(III) ions can be expressed through the following reactions I, II and III [1,29]:



The overall process can be expressed as:



In this case, the equilibrium potential of the $\text{La}^{3+}/\text{Al}_x\text{La}_y$ system can be described by the following equation:

$$E_{\text{La}^{3+}/\text{Al}_x\text{La}_y} = E_{\text{La}^{3+}/\text{La}}^0 + \frac{RT}{nF} \ln \left[\frac{a_{\text{La}^{3+}}}{a_{\text{La}}(\text{in Al}_x\text{La}_y)} \right] \quad (2)$$

$$E_{\text{La}^{3+}/\text{Al}_x\text{La}_y} = E_{\text{La}^{3+}/\text{La}} - \frac{RT}{nF} \ln [a_{\text{La}}(\text{in Al}_x\text{La}_y)] \quad (3)$$

Where $E_{\text{La}^{3+}/\text{La}}$ is the equilibrium potential of the pure La element, T denotes the absolute temperature in K, n presents the number of exchanged electron, F corresponds the Faraday constant (96485C) and $a_{\text{La}}(\text{in Al}_x\text{La}_y)$ is the activity of La in the Al_xLa_y intermetallic compounds.

To elucidate general information on Al-La intermetallic compounds, the reported La-Al phase diagram is presented in Fig. 1. In the La-Al system, the intermetallic compounds AlLa_3 , AlLa , Al_2La , Al_xLa , Al_3La , $\text{Al}_{11}\text{La}_3$ were treated as stoichiometric phases. The composition of Al_xLa was described as Al_7La_3 [21].

3.1.1. Electrochemical evidence for Al-La intermetallic compounds formation

In order to study the co-reduction behavior of La(III) and Al(III) ions, the experiment was carried out in both LiCl-KCl-LaCl_3 (9.74×10^{-5} mol/ cm^3) and LiCl-KCl-LaCl_3 (9.74×10^{-5})- AlCl_3 (6.04×10^{-5} mol/ cm^3) melts, the recorded voltammograms are displayed in Fig. 2a. The black curve corresponds to the CV obtained in the LiCl-KCl-LaCl_3 melt, a cathodic peak B at around -2.16 V and its corresponding anodic peak B' at about -2.03 V can be observed. It is

Download English Version:

<https://daneshyari.com/en/article/185042>

Download Persian Version:

<https://daneshyari.com/article/185042>

[Daneshyari.com](https://daneshyari.com)