

# Electrochemical formation of erbium-aluminum alloys from erbia in the chloride melts



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## ABSTRACT

This work presents an electrochemical study of  $\text{Er}^{3+}$  and  $\text{Al}^{3+}$  in the  $\text{LiCl-KCl-AlCl}_3\text{-Er}_2\text{O}_3$  melts at 773 K. Gibbs energy calculation shows that  $\text{AlCl}_3$  can favorably chloridize  $\text{Er}_2\text{O}_3$  and release  $\text{Er}^{3+}$  ions under this condition. Cyclic voltammetry, square wave voltammetry, chronopotentiometry and open-circuit chronopotentiometry were applied using a molybdenum electrode to investigate the reduction behavior of  $\text{Er}^{3+}$  and  $\text{Al}^{3+}$  and to identify the Er-Al alloys. A series of redox signals corresponding to different kinds of Er-Al alloys were revealed. Potentiostatic and galvanostatic electrolysis were both conducted on an aluminium electrode to prepare the Er-Al alloys. The obtained deposits were characterized by SEM-EDS and XRD. A layer of  $\text{ErAl}_3$  was obtained by potentiostatic electrolysis, whereas two kinds of intermetallic compounds of  $\text{ErAl}_3$  and  $\text{ErAl}_2$  were formed by galvanostatic electrolysis.

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## 1. Introduction

Rare earth metals and their alloys have been widely applied as advanced functional materials in numerous industrial fields due to their specific functional properties such as excellent magnetic [1,2] and optical [3,4] properties. They are also used for hydrogen storage [5], and as metallurgical additives to improve mechanical properties of metals [6,7]. Using molten salts as a reaction media, the electro-winning and electrorefining of high purity rare earth metals, as well as for the electrochemical synthesis of rare earth alloys can be fulfilled [8–12].

Another important field involving lanthanides (Ln) and molten salts is the so-called pyrochemical reprocessing of spent nuclear fuels, aiming at the partitioning and transmutation (P&T) strategy, from which the inventory of highly radioactive long-lived minor actinides (MA) and fission products (FP) can be significantly incinerated to reduce their long term risk towards environment. Nevertheless, highly efficient separation of actinides (An) over lanthanides (Ln) is always the essential and challenging issue due to the chemical similarities of trivalent An and Ln [13]. Pyrochemical reprocessing of nuclear fuels using molten salts is

currently considered to be a promising alternative to the traditional hydrometallurgical reprocessing technologies. To some extent, the separations of Ln and An can be achieved through high temperature reductive-extraction and/or electrorefining [14]. On the other hand, it has been reported that aluminum can interact strongly with An to form Al-An alloys which may facilitate the An-Ln separations at a more anodic potential and therefore has attracted considerable interest as a promising dedicated electrode for the separation of actinides and lanthanides in future spent fuel reprocessing [15–17]. The preparations of An-Al alloys such as Al-U [18], Al-Np [19] and Al-Pu [20] alloy have been conducted and a relatively high separation efficiency of An over Ln has been demonstrated when Al was used as the working electrode [21]. Actually, the extractions of Ln by forming Al-Ln intermetallic compounds on the aluminium cathode have been investigated by Catrillejo et al. [22–26]. In addition, Gibilaro et al. [27–29] also explored the co-deposition of Al with Ln on an inert W electrode and found that Ln could be extracted with the good efficiency of more than 99%.

As a typical heavy element among Ln, erbium, has a large resonance in its neutron absorption cross section at 0.47 eV, which was used as a burnable absorber doped to nuclear fuels to more efficiently control the RBMK reactor [30] and also considered to potentially use in the PWR and PTGR to achieve high burn-up of the uranium oxide fuel [31]. Although RBMK reactors are gradually withdrawn from the historical nuclear stage, from

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point of view of the whole nuclear industry, studying molten salt based electrochemical behaviors of erbium is still of importance for understanding the electrochemical properties of lanthanide elements, especially heavy lanthanides. However, to the best of our knowledge, only a few works once concerned about erbium electrochemistry in molten salts. Castrillejo et al. [22] investigated the electrochemical behaviours of erbium in the LiCl–KCl eutectic and concluded that the reduction of  $\text{Er}^{3+}$  to Er metal is a one-step process with 3 electrons exchanged. They also determined the temperature dependence of the diffusion coefficient and obtained the  $\text{ErAl}_3$  intermetallic compound on the Al electrode. The preparation of Al–Li–Er [32] and Mg–Li–Er [33] alloys were performed by co-deposition in the LiCl–KCl– $\text{AlCl}_3$ /MgCl<sub>2</sub> melts. Nevertheless, the redox behavior, the formation mechanism of Er–Al alloys and some other electrochemical properties have not yet been fully clarified, which are of big significance not only to the expansion of the basic knowledge of Er electrochemistry but also to the separation of Er from spent fuels. Hence, in this work, the co-reduction mechanism of  $\text{Er}^{3+}$  and  $\text{Al}^{3+}$  as well as the electro-deposition of Er–Al alloys are specifically demonstrated by employing a series of electrochemical techniques in the LiCl–KCl– $\text{AlCl}_3$ – $\text{Er}_2\text{O}_3$  melts. Our results can provide useful information for the preparation of specific functional materials and the better understanding of extraction and separation of Er from spent fuels in LiCl–KCl molten salts.

## 2. Experimental

### 2.1. Chemicals

All operations of chemicals were carried out in a glove box under inert argon atmosphere in which the concentrations of oxygen and moisture were controlled to be less than 2 ppm. Anhydrous LiCl, KCl,  $\text{AlCl}_3$  (analytical grade) and  $\text{Er}_2\text{O}_3$  (99.999%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The LiCl–KCl eutectic mixture (LiCl: KCl = 58.8: 41.2 mol%) was first dried under vacuum for more than 24 h at 473 K to remove residual water, and then melted under a dry argon atmosphere in an alumina crucible placed in a sealed stainless steel cell inside a programmable electric furnace, the temperature deviation of the furnace can be maintained below  $\pm 2$  K. The working temperature was measured using a nickel–chromium thermocouple protected by an alumina tube inserted into the solution. All of the electrochemical experiments were carried out at 773 K. The anhydrous  $\text{AlCl}_3$  and  $\text{Er}_2\text{O}_3$  powders were directly introduced into the eutectic. Salt samples were collected in the supernatant of the LiCl–KCl– $\text{AlCl}_3$ – $\text{Er}_2\text{O}_3$  melts after a stirring process with argon bubbling. Then samples were dissolved in ultrapure water to determine the initial concentrations of  $\text{Er}^{3+}$  and  $\text{Al}^{3+}$  in the bath by using an inductively coupled plasma atomic emission spectrometer (ICP–AES, Perkin Elmer NEXION 300D).

### 2.2. Electrochemical apparatus and electrodes

All electrochemical measurements were carried out by using an Autolab PGSTAT 302N potentiostat–galvanostat controlled with the Nova 1.9 software package from Metrohm. Transient electrochemical techniques, i.e. cyclic voltammetry, square wave voltammetry and open circuit chronopotentiometry were used to explore the electrochemical properties of erbium in the molten salt systems in this experiment. The reference electrode (RE) was made of a 1 mm silver wire (Alfa, 99.9+%) immersed into the solution of LiCl–KCl–AgCl (1 wt.%) molten salts, which was placed in a closed-end alumina tube with a diameter of 4 mm. A molybdenum wire (Alfa, 99.9+%) with the diameter of 1 mm was polished by sandpaper, washed with alcohol using ultrasound, inserted into a 2 mm

alumina tube, and then was used as the working electrode (WE). Before each measurement, the working electrode was cleaned by galvanostatic anodic polarization. The active electrode surface area was determined after each experiment by measuring the immersion depth of the electrode in the molten salts. As for the counter electrode (CE), a 1 mm molybdenum wire (Alfa, 99.9+%) and a 6 mm graphite rod were used. For the electrolysis, a 1 mm molybdenum wire (Alfa, 99.9+%) and a 2 mm thick aluminum plate (Alfa, 99.999%) were used as cathodes and a 6 mm graphite rod was used as the anode.

### 2.3. Preparation and characterization of cathodic deposits

Erbium electro-deposits were firstly prepared in the LiCl–KCl– $\text{AlCl}_3$ – $\text{Er}_2\text{O}_3$  molten salts on molybdenum and aluminum plates by potentiostatic electrolysis for 4 hours with a cathode potential previously defined by cyclic voltammetry and open circuit chronopotentiometry. Galvanostatic electrolysis was carried out in the molten salt to compare the deposits with those performed at constant potential. Electrodeposits were prepared by applying a constant cathodic current ( $\sim -30$  mA) on the aluminium plate for 2 h. After the electrolysis, the electrodes were removed from the bath and a layer of deposits were found adhering on the surface of the electrodes. Afterward, the aluminum electrode was cut out and washed with ethylene glycol (Sinopharm, 99.8%) by ultrasound to remove residual salt. The deposits on the molybdenum electrode containing many salts were removed and repeatedly washed with ethanol. Then, all the samples were dried and especially stored in a vacuum drying oven before subjected to further analysis. Scanning electron microscopy (SEM) (Hitachi S–4800)–energy dispersive X-ray (EDX) (GENESIS 2000) techniques were employed to analyze the surface morphology and micro composition of Erbium and aluminum deposits. Surface analysis of the samples was also performed by X-ray diffraction (XRD) (Bruker, D8 Advance) to identify the formation of Er–Al intermetallic compounds.

## 3. Results and Discussion

### 3.1. Electrochemical behavior of $\text{Er}_2\text{O}_3$ and $\text{ErCl}_3$ in the LiCl–KCl eutectic

#### 3.1.1. Electrochemical behavior of $\text{Er}_2\text{O}_3$ in the LiCl–KCl eutectic

The cyclic voltammetry (CV) study of erbium oxide was firstly carried out to investigate the probable electrochemical properties of  $\text{Er}_2\text{O}_3$  in the LiCl–KCl eutectic. As shown in Fig. 1, the red dotted curve obtained in the LiCl–KCl– $\text{Er}_2\text{O}_3$  (1.5 wt.%) melts is nearly

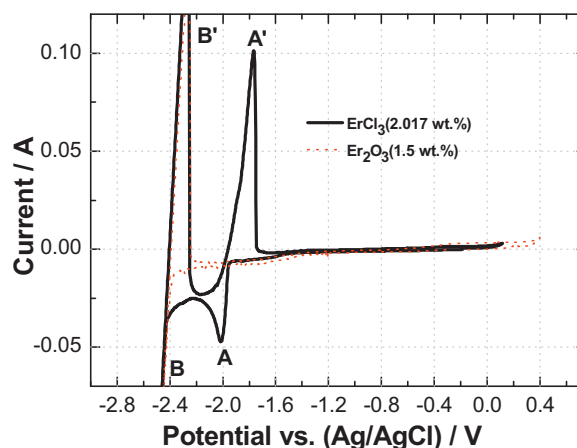


Fig. 1. CV of the  $\text{Er}_2\text{O}_3$  (1.5 wt.%) (red dotted curve) and  $\text{ErCl}_3$  (2.017 wt.%) (black bold curve) in the LiCl–KCl eutectic. Apparent electrode area:  $3.57 \times 10^{-2}$  cm<sup>2</sup>.

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