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Direct separation of uranium from lanthanides (La, Nd, Ce, Sm) in oxide mixture in LiCl-KCl eutectic melt

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ABSTRACT

This paper reports the direct separation of U from lanthanides (Ln) in oxide mixtures in LiCl-KCl eutectic, a method that could simplify the pyrometallurgical reprocessing of UO_2-based spent fuels. In the melt, the mixture of UO_2 and lanthanide oxides (Ln_2O_3/LnO_2) was chloridized by $AlCl_3$, and then U was selectively recovered by forming U-Al alloys through the redox reactions of U(IV)/U(III) and U(III)/Al_xU. The results showed that U could be efficiently separated from lanthanides with high separation factors ($SF_{U/La} = 1.1 \times 10^4$, $SF_{U/Ce} = 1.6 \times 10^5$, and $SF_{U/Sm} = 2.5 \times 10^4$). X-ray diffraction analysis indicated the predominant separation products to be Al_3U and Al_4U, whereas the real extraction rate of U was probably affected by trace amounts of O^{2-} in the melt. For the first time, single-cell operation to separate U from Ln in mixed oxides is shown to be feasible by using $AlCl_3$ as chlorination agent followed by electrodeposition.

1. Introduction

Currently, uranium dioxide (UO_2) is a major ceramic nuclear fuel, and thus it comprises the main component of spent fuel that must be reprocessed. In a conventional pyrometallurgical process [1–8], UO_2 in spent fuel is reduced into metallic U [9,10], which is then subjected to further electrorefining in LiCl-KCl melt to remove the impurities [11,12]. Traditionally, the reduction of UO_2 is achieved by reaction with lithium metal, or more preferably by direct electrochemical reduction (DER) because of the fewer unit operations needed. In the DER process, the UO_2-based spent fuel is loaded into a cathode basket in LiCl-Li_2O melt. Then, the oxygen anions are transported through the electrolyte from the cathode to the anode to be removed. To date, although this technology has attracted much attention, some key issues remain challenging, such as basket construction, anode materials [13–15], and scale-up for industrialisation [16]. Besides the DER technology, pyrometallurgical processing of UO_2-based spent fuels itself still faces difficulty in some of its steps. To simplify this process, here we propose a method for the direct separation of UO_2 from Ln_2O_3/LnO_2 by employing $AlCl_3$ as a chlorination agent.

The topic of chlorination has been studied in the last few decades, and several chlorination agents have been tested for UO_2 in molten salt. Kitawaki et al. for example, unsuccessfully tried to chloridize UO_2 and U_3O_8 by a mechanochemical method in the presence of CCl_4 [17]. Sakamura et al. found that UO_2 could be chloridized into UCl_4 by $ZrCl_4$ in LiCl-KCl melt [18], despite the low transformation rate of 37%. The chlorination of UO_2 in molten $MgCl_2$, $CaCl_2$, and $AlCl_3$ [19] was also studied by Dai et al. They found that UO_2 was insoluble in $CaCl_2$ melt, while it gave rise to the uraniumoxychloride complex ($UOCl_2$) in $MgCl_2$ melt. In molten $AlCl_3$, however, the chlorination proceeded very efficiently, and the dissolved species was determined to be UCl_4. Therefore, $AlCl_3$ may be a promising chlorination agent to transform UO_2 into UCl_4. Moreover, we have previously chloridized ThO_2 and Ln_2O_3 (Ln = La, Eu) into $ThCl_4$ and $LnCl_3$ in LiCl-KCl melt, and effectively separated Th from Ln by forming Al-Th alloys [20,21]. Thus, the direct dissolution of UO_2 and lanthanide oxides (Ln_2O_3/LnO_2) using $AlCl_3$ followed by electrodeposition is a potential strategy for U separation.

Furthermore, previous investigations conducted by both the Institute for Transuranium Elements (ITU) [10,16,17] and our laboratory [20] showed that the separation of actinides (An) over Ln was much more efficient by employing an Al electrode, on which Al-An alloys were formed. In light of this, after the chlorination of UO_2 by $AlCl_3$, U could be recovered by electrodeposition on the Al cathode via forming Al-U alloys [22]. As a result, the chlorination of UO_2 and U separation from Ln may be achieved in one single cell, representing a clear opportunity to simplify the traditional

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pyrometallurgical reprocessing of UO_2-based spent fuel.

2. Experimental

2.1. Preparation of electrolyte and electrodes

A mixture of anhydrous LiCl (44.8 g, anhydrous, AR grade, Sinopharm Chemical Reagent Co., Ltd.) and KCl (55.2 g, AR grade, Sinopharm Chemical Reagent Co., Ltd.) was dried under vacuum for more than 100 h at 473 K to remove water, and then melted in a 200-cm^3 alumina crucible to serve as electrolyte.

Both inert and active working electrodes were employed. A tungsten wire ($\Phi = 0.5$ mm, Alfa Aesar, 99.99%) with an electroactive surface area of 0.32 cm^2 was used as the inert working electrode, to investigate the basic electrochemical properties and monitor the concentrations of U and Ln in the melt. Cylinders made of aluminium sheets with a wall thickness of 0.5 mm and diameter of 7 ± 0.5 mm were used as active electrodes to separate U by forming Al-U alloys. The surface area of the active electrode was controlled by the insertion depth (2.5 cm). A graphite rod ($\Phi = 6$ mm, Alfa Aesar, >99.99%) was used as the counter electrode. All the electrodes were polished thoroughly by using SiC paper, and then cleaned in ethanol with the aid of ultrasound. The reference electrode was made from a Pyrex tube containing a silver wire (Alfa Aesar, 99.99%, $\Phi = 1$ mm) dipped into a solution of 1.0 wt% AgCl in LiCl-KCl melt. A PGSTAT302 N electrochemical workstation (Autolab, Metrohm) with the Nova 1.10 software package was used to record the electrochemical data.

2.2. Chlorination of oxide mixture and U separation

After complete melting of LiCl-KCl, a mixture of UO_2 and Ln_2O_3/LnO_2 was added into the melt, then $AlCl_3$ (anhydrous, AR grade, Sinopharm Group Chemical Reagent Co., Ltd.) was incorporated as chlorination agent with Ar gas bubbling. Lanthanide oxides (La_2O_3, CeO_2, Nd_2O_3, and Sm_2O_3) of >99.99% purity were purchased from Baotou Rare-earth Co., Ltd., while UO_2 was purchased from CNNC North Nuclear Fuel Element Co., Ltd. The chlorination reaction of Ln_2O_3/LnO_2 was described in our previous works as follows [20,23]:

$$2Ln_2O_3(s) + 2Al_2Cl_6(l) \rightarrow 2Al_2O_3(s) + 4LnCl_3(l) \quad (1)$$

$$6LnO_2(s) + 4Al_2Cl_6(l) \rightarrow 4Al_2O_3(s) + 6LnCl_3(l) + 3Cl_2(g) \quad (2)$$

Similarly, the reaction of UO_2 with $AlCl_3$ is:

$$3UO_2(s) + 2Al_2Cl_6(l) \rightarrow 2Al_2O_3(s) + 3UCl_4(l) \quad (3)$$

The Gibbs free energy of reaction (3) in the temperature range 273–1273 K was calculated by HSC Chemistry 5.0. The results (Fig. 1 and details presented in Fig. SI1) show that this reaction is thermodynamically favourable with a Gibbs free energy (ΔG^{θ}) of −341 kJ mol^{-1} at 773 K (which was used in the current study).

For the chlorination of UO_2-La_2O_3, UO_2-Nd_2O_3, and UO_2-La_2O_3-CeO_2-Sm_2O_3, the corresponding oxide mixtures and $AlCl_3$ powder (for their compositions see Table 1) were added into the LiCl-KCl melt (100 g), and then stirred continuously for several hours with Ar gas bubbling at 773 K. During the chlorination, the concentrations of U and Ln were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Horiba, JY, 2000-2). The separation of U from Ln was carried out by potentiostatic electrodeposition (at −1.20 V vs. Ag/AgCl) on the Al electrodes, as shown in Fig. 2. After carrying out the separation for a period of time, the electrode with deposited Al-U alloy was taken out and a new electrode was replaced, until all the U in the molten salt was deposited. All the experiments were carried out in a glove box under argon atmosphere, in which the concentrations of O_2 and H_2O were maintained to be less than 1 ppm.

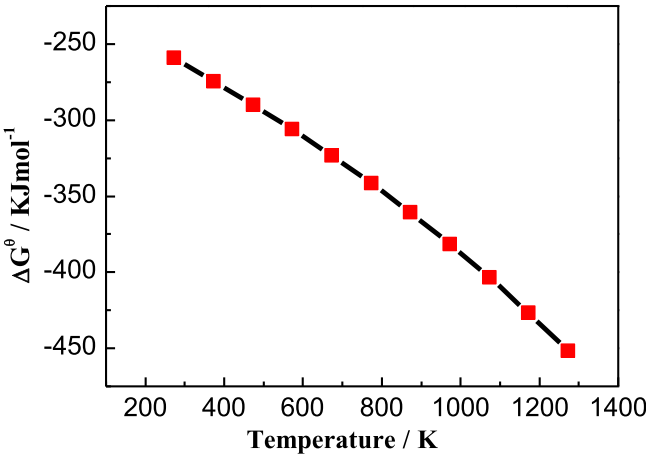

Fig. 1. ΔG^{θ} of reaction (3) at different temperatures.

2.3. Characterisation of the separation products

After cooling, the separation products were washed with ultrapure water in an ultrasonic bath to remove the salts, and then washed with absolute ethyl alcohol. After desiccation in a vacuum oven at room temperature, the final samples were stored in the glove box for further analyses. Scanning electron microscopy (SEM, HitachiS-4800) and energy spectrum analysis (EDS) were employed to observe the microstructure and analyse the surface component of the products, XRD (Bruker D8) was used to characterise the intermetallic compounds. ICP-OES was used to determine the exact composition of the products, after dissolving the samples in a mixture of concentrated HNO_3 and HCl solutions.

3. Results and discussion

3.1. Chlorination of UO_2 and Ln_2O_3/LnO_2

Fig. 3a shows the concentration variation of U(IV) and La(III) in the melt during chlorination of the UO_2-La_2O_3 system. The concentration of La(III) reached 0.335% after 3 h of reaction, and remained almost unchanged afterwards. In contrast, the concentration of U(IV) continuously increased and attained 0.212% at 8 h. The final chlorination rates of La_2O_3 and UO_2 are calculated to be 78.6% and 89.1%, respectively. As shown in Fig. 3b, the chlorination for the UO_2-Nd_2O_3 system gives similar results. Nevertheless, after 8 h of chlorination the concentration of U(IV) was 0.190%, corresponding to a chlorination rate of 79.8%, which is a little lower than that for the UO_2-La_2O_3 system. To further improve the chlorination rate of UO_2, the reaction time was extended to 13 h. The chlorination of UO_2 reached 92.30%, while that of Nd_2O_3 reached 70.2% at the same time. For the UO_2-La_2O_3-CeO_2-Sm_2O_3 system, the chlorination rates of UO_2, La_2O_3, CeO_2, and Sm_2O_3 after 13 h were determined to be 78.54%, 84.70%, 87.33%, and 81.98%, respectively.

In all systems, the melt colour became bright green after chlorination, as shown in Fig. 3b (inset), which is a clear indication of U(IV) in the molten chloride salt [24,25]. It is thus concluded that the chlorination of UO_2 by $AlCl_3$ follows the reaction (3) to form UCl_4 [19].

The results show that all the feeding mixtures of UO_2-Ln_2O_3/LnO_2 can be chloridized by $AlCl_3$ and dissolved in the LiCl-KCl melt. Although the chlorination of UO_2 is slower than that of ThO_2