Electrochemical extraction of samarium from molten chlorides in pyrochemical processes

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ABSTRACT

This work concerns the electrochemical extraction of samarium from molten chlorides. In this way, the electrochemical behaviour of samarium ions has been investigated in the eutectic LiCl–KCl at the surface of tungsten, aluminium and aluminium coated tungsten electrodes. On a W inert electrode the electro-reduction of Sm(III) takes place in only one soluble–soluble electrochemical step Sm(III)/Sm(II). The electrochemical system Sm(II)/Sm(0) has not been observed within the electrochemical window, because of the prior reduction of Li(I) ions from the solvent, which inhibits the electro-extraction of Sm species from the salt on such a substrate. Sm metal in contact with the melt react to give Li(0) according to the reaction: $Sm(0) + 2Li(I) \leftrightarrow Sm(II) + 2Li(0)$.

On the contrary, on reactive Al electrodes the electrochemical system Sm(II)/Sm(0) was observed within the electroactive range. The potential shift of the redox couple is caused by the decrease of Sm activity in the metal phase due to the formation of Sm–Al alloys at the interface. The formation mechanism of the intermetallic compounds was studied in a melt containing: (i) both Sm(III) and Al(III) ions, using W and Al coated tungsten electrodes, and (ii) Sm(III) ions using an Al electrode. Analysis of the samples after potentiostatic electrolysis by X-ray diffraction and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), allowed the identification of Al_3Sm and Al_2Sm.

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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, being the strategies for the spent nuclear fuel treatment the following: (i) disposal of spent fuel into deep geological repositories without recycling, (ii) single-recycling of uranium and plutonium by hydrometallurgical methods (PUREX process and its analogue), and (iii) a closed fuel cycle including reprocessing of all actinides [1].

"Partitioning and Transmutation" (P&T) of long-lived fission products and minor actinides represents nowadays a promising alternative to the strategies (i) and (ii), specially for the new types of fuels, which will be probably significantly different from today's commercial fuels. The recycling or destruction (transmutation) of the more hazardous radionuclides in the waste into less hazardous or shorter lived elements would significantly reduce the long-term radiotoxicity and volume of the generated spent nuclear fuel [1]. Consequently, the main objectives for a closed fuel cycle scenario are: (i) to recover all the actinides (Ans) for recycling or destruction, (ii) to ensure sufficient decontamination between Ans and fission products (FPs), (iii) to generate the minimum of ultimate waste flows and (iv) to have suitable confinement of wastes process [2].

In order to achieve these goals, molten salts have been used as reaction media for the mutual separation of Ans from other FPs due to their properties such as their high thermal and radiation stability, which allows a high actinide content, a shorter cooling time for the fuel before reprocessing, a more compact fuel cycle technology and an inherent proliferation resistance. The most developed pyrochemical techniques using molten chlorides or fluorides media, have been electrorefining, electroextraction with reactive cathodes, liquid–liquid metal reductive extraction and oxide precipitation [3–7]. Although fuels proposed for transmutation tolerate small contents of FPs, most of them have to be removed. Special attention must be paid to the Lns not only for their chemical similarity with the Ans, but also because Lns have large neutron capture cross section which spoil the neutron economy of the reactor core [8]. Moreover, upon fuel fabrication, Lns tend to form separate phases, which grow under thermal treatment leading to a heterogeneous material [9]. On the other hand, during the electrochemical separation process the Lns accumulate in the solvent; this fact can modify the characteristics of the electrolyte

and contaminate the final cathodic product. When the Lns concentration exceeds 10 wt% in the melt it must generally be purified or regenerated to avoid affecting the Ans/Lns separation efficiency [10].

Our team has been engaged in a research program in which a two-step process is foreseen in molten chlorides, corresponding to (i) the selective extraction of Ans and (ii) the extraction of Lns for decontamination of the salt. Our studies are devoted to the acquisition of fundamental data of Lns to allow conceptual design and assessment of reprocessing processes involving as separation steps (i) electrolytic extraction using reactive cathodes (Cd, Bi or Al), and (ii) selective dissolution/precipitation of rare earth oxides [11–16].

As a part of the program to look into the Lns series in chloride melts which has impacts for fuel reprocessing, the present work is concerned with the electrochemical behaviour of samarium, one of the most abundant fission products in nuclear reactors [17] on a reactive (Al) electrode. The separation abilities of the electrochemical processes, as well as the efficiency decontamination of the salt by electroextraction of the accumulated Lns, strongly depend on the stability of the formed cathodic products. The work has been focused on the formation of Sm–Al alloys at 723 K and on the characterization of the mechanism and chemical composition of the deposits obtained by electrodeposition of Sm on solid Al electrodes. In order to make clear the mechanism of alloy formation, co-reduction of aluminium and samarium ions has been carried out.

2. Experimental

2.1. General features

Storage of all chemicals and sample preparations were handled in a MBraun glove box in purified Ar atmosphere where the oxygen content and moisture levels were maintained below 1 ppm. The electrolytic bath consisted in a mixture of LiCl:KCl (Sigma Aldrich 99.9% and 99.5% respectively) with the eutectic composition (LiCl:KCl = 58.8:41.2 mol%) and a total amount of salt: ≈80 g, which was introduced in an alumina crucible placed in a cylindrical quartz cell. The electrolyte was initially fused under vacuum in a temperature ramp mode during 8 h and then raised to atmospheric pressure using dry argon (99.999%, Air Liquide). Purification of the melt was carried out by bubbling HCl(g) through the melt for 1 h, and residual HCl was removed by bubbling argon. All electrochemical experiments were done in the purified eutectic mixture under an inert argon atmosphere. The cell was heated using a tubular furnace connected to a West 8100 programmable device, and the working temperature, 723 K, was controlled with a nickel-chromium thermocouple and kept to ±2 K.

Solutions of Sm(III) and Al(III) were prepared by direct additions of anhydrous $SmCl_3$ and $AlCl_3$ (Sigma Aldrich 99.99%).

2.2. Electrodes and instrumentation

As reference electrode the Ag|AgCl system was used. It consisted of a Ag wire of 1 mm diameter dipped into a closed-end Pyrex glass tube, in which the LiCl–KCl eutectic salt containing 0.75 mol kg^{-1} AgCl was placed. Unless stated otherwise, all the potentials are referred to this reference. As working electrodes, tungsten and aluminium wires of 1.0 mm diameter were used as inert and reactive electrodes respectively, for the investigation of the electrochemical behaviour of the system. The counter electrode was a 1.5 mm diameter tungsten wire with a large surface area, in order to ensure uniform distribution of current lines.

In the potentiostatic electrolysis experiments, electrodeposition of Sm_xAl_y alloys, 0.5 mm thick rectangular aluminium foil (Sigma Aldrich, 99.99%) and a graphite rod of 6.0 mm diameter were used as working and counter electrodes, respectively.

The electrochemical measurements were performed with a PAR EG&G Model 273A potentiostat/galvanostat controlled by a computer using the PAR EG&G M270 software package, and a multimeter Fluke 45.

Potentiostatic electrolysis was used to recover Sm onto Al plates, being the experiments performed with an Autolab PGSTAT 320N potentiostat/galvanostat controlled by the research software NOVA. The deposits were analyzed by XRD using a Philips PW1710 X-ray diffractometer. The cross-section of the deposits was characterized by using scanning electron microscopy (SEM, FEI Model Quanta 200F) with energy dispersive spectroscopy (EDAX, SDD Apolo).

3. Results and discussion

3.1. Preliminary discussion

#### 3.1.1. Characterization of Sm electrochemical systems on inert electrodes

The electrochemical window offered by the LiCl–KCl solvent at a tungsten electrode is comprised between the reduction of lithium ions, (the signals (A_c/A_a) in Fig. 1a corresponds to the deposition of liquid lithium and its subsequent reoxidation), and the oxidation of chloride ions (Cl_2 evolution). When $SmCl_3$ is present in the purified melt, another group of signals, I_c/I_a, appear in the voltammogram recorded at 723 K (Fig. 1a), indicating that the electro-reduction of Sm(III) occurs through only one electrochemical step. The shapes of the waves suggest that both the reduction and the oxidation products are soluble, which was corroborated by current reversal chronopotentiometry Fig. 1b ($\tau_{Red} \approx 3\tau_{Ox}$).

On the other hand, the number of electrons involved in the electrochemical step I_c has been determined by square wave voltammetry. Upon the experiments, a single peak with a Gaussian shape was observed (Fig. 1c). The mathematical analysis of the obtained peak yields to a simple equation for a soluble–soluble reversible reaction, associating the width of the half-peak, $W_{1/2}$, and the number of exchanged electrons [18]:

$$W_{1/2} = 3.52\frac{RT}{nF} \tag{1}$$

where n, F, R and T have the usual meaning. The validity of Eq. (1) was verified by plotting the peak current vs. the frequency square root. A linear relationship was observed in the 10–100 Hz frequency range. In addition, it has to be mentioned that the peak potential remains constant in the studied frequency range. According to Eq. (1) a value of 1.0 ± 0.1 electrons was obtained, confirming that the waves I_c/I_a correspond to the electrochemical exchange Sm(III) + 1e ↔ Sm(II). A similar behaviour has been observed by Cordoba et al. [19] and Massot et al. [20] in LiCl–KCl and LiF–CaF$_2$ respectively.

As it is shown in Fig. 1, no other waves attributed to the reduction of the electrogenerated Sm(II) were observed within the electrochemical window of the melt. Indeed, the prior reduction of Li(I) ions from the solvent hinders the reduction of Sm(II) into Sm metal. Therefore, we can conclude that the Sm(II)/Sm(0) couple must be similar or more negative in potential than the Li(I)/Li(0) couple, then Sm metal in contact with the melt could react to give Li(0) according to the reaction:

$$Sm(0) + 2Li(I) \leftrightarrow Sm(II) + 2Li(0) \tag{2}$$
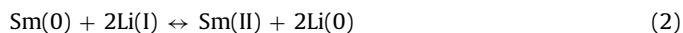
As a result, for molten salt recycling, the electrolytic extraction of samarium from the molten solution is not conceivable on an