



# Cathodic Behavior of Samarium(III) and Sm-Al alloys Preparation in Fluorides Melts



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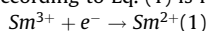
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## ABSTRACT

The electrochemical behavior of samarium ions in LiF-CaF<sub>2</sub> melts at tungsten electrodes is investigated by cyclic voltammetry and square wave voltammetry. The electrochemical reduction of Sm(III) into Sm(II) according to Eq. (1) is reversible within 900 mV/s.



The reduction process for Sm(II) to Sm cannot be observed due to a more negative potential than that of Li(I) ions. Cyclic voltammograms results have proved that Sm and Al ions can be co-reduced from LiF-CaF<sub>2</sub>-AlF<sub>3</sub>-SmF<sub>3</sub> melts. The cathodic product from LiF-CaF<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> (0.15 mol/L)-AlF<sub>3</sub> (8.89 mol/L) melts at -731.4 mA/cm<sup>2</sup> is a thin layer metallic plate mainly composing Al, Al<sub>2</sub>Sm and Al<sub>3</sub>Sm. EDS mapping manifests that Sm-Al alloy exists in the cross-section of the deposit with the molar ratio of Sm/Al of 0.020, smaller than the original value of 0.034. By galvanostatic electrolysis in LiF-CaF<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> (0.225 mol/L)-AlF<sub>3</sub> (0.296 mol/L) with Al (6 mol/L) at -800 mA/cm<sup>2</sup> for 3 h, only small metal particles dispersed in the molten salts are found, giving a lower Sm/Al molar ratio from 0.1 to 0.2 less than the original value of 1.52 in the melts. The results indicate that it is feasible to extract small amounts of Sm with larger amount of Al by codeposition from fluoride melts.

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## 1. Introduction

Currently, metallic samarium is produced by the thermal reduction of metallic La combined with following distillation [1,2]. The Sm production process is discontinuous, and high temperature, high vacuum and complicated equipments are needed. Molten salt electrolysis has shown more advantages in extracting active metals such as Al, Mg and rare-earth metals including La, Ce, Pr, Nd, etc and alloys [3–5]. However, molten salts electrolysis cannot be used to directly electrowin samarium metal due to two stable oxidation states including Sm(II) and Sm(III) ions existing in molten salts, which results in a seriously proportional reaction according to Eq. (2)



However, Sm-Ni alloys could be obtained on the nickel electrode from LiF-CaF<sub>2</sub> media under galvanostatic electrolysis according to Chamelot [6]. Yan reported Al<sub>4</sub>Sm intermetallics are formed by potentiostatic electrolysis at -2.1 V in molten LiCl-KCl-SmCl<sub>3</sub> melts on an Al electrode for 7 h at 773 K [7]. The Sm based

alloys formation has lowered the activity of metallic Sm and make it more stable in the melts. Therefore, it is possible to extract Sm from molten salts by formation of alloys with other metal ions or on an active cathode from molten salts. Direct preparation of Sm-based alloys by molten salts electrolysis is much more simple and cost-efficient than the traditionally directly mixing metallic Sm with other pure metals at high temperature.

On the other hand, electrochemical codeposition of Sm-based alloys can be used to remove Sm ions from the molten salts in the spent nuclear fuel treatment processes according to Castrillejo [8,9].

In fact, a more reasonable method to electrochemically prepare samarium alloys is to apply Sm<sub>2</sub>O<sub>3</sub> as well as alloy oxides/flouride such as Al<sub>2</sub>O<sub>3</sub>/AlF<sub>3</sub> as active components in fluoride system, in which Sm-Al is deposited in cathode and CO/CO<sub>2</sub> are emitted in graphite anode. However, though the electrochemical behavior of samarium ions in LiF-BeF<sub>2</sub> system [10] and LiCl-KCl melt [11–14] were investigated by cyclic voltammetry and chronopotentiometry, there have few reports on the Sm alloys preparation by fluoride-oxide molten salts electrolysis.

So in this paper, first, the electrochemical reduction mechanism of Sm(III) on tungsten electrode in fluoride melts was analyzed by cyclic voltammetry and square wave voltammetry, and the electrons transfer number and diffusion coefficient of Sm(III) ions

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reduction were calculated. The co-reduction process of Sm and Al ions in fluoride melts was further analyzed by electrochemical methods. Then galvanostatic electrolysis in fluoride-oxide system was carried out to examine the possibility of formation Sm-Al alloys.

## 2. Experiments

In the whole experiments, the eutectic composition of LiF-CaF<sub>2</sub> (Aladdin, 99.99%) with 79:21 molar ratio was used as the supporting electrolyte, SmF<sub>3</sub> (Aladdin, 99.99%) or AlF<sub>3</sub> (Macklin, 99.9%) as the active components in the electrochemical measurements, and AlF<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub> as the active components in the galvanostatic electrolysis process. The mixture of LiF-CaF<sub>2</sub> with or without active components was first weighed and located in a graphite crucible in an airtight stainless steel reactor, and heated to 473 K holding for 24 h, then further raised up to 1173 K in a silicon carbide rods heating furnace connected to a programmable device to control the temperature. The electrochemical experiments were carried out in an airtight reactor under pure Ar atmosphere, the electrolysis experiment was in an airtight reactor. The working temperature was measured with a nickel-chromium thermocouple.

During the electrochemical measurements including cyclic voltammetry, square-wave voltammetry and galvanostatic electrolysis, three-electrode system was used, in which W wire (dia. of 1 mm) was used as the working electrodes [15] and the quasi-reference electrode, graphite rod as the counter electrode. In the electrochemical measurements, the potentials are transferred to Li(I)/Li reference electrode according to literature [16]. All the electrodes were polished with emery papers to a mirror finish, washed with distilled water, then dried in a vacuum oven prior to use. The surface area was determined by measuring the immersion depth of the electrode in the melts. The electrochemical measurements were performed using a PAR-STAT2273 (PAR-Ametek Co., Ltd.) with a PowerSuite software package.

After the galvanostatic electrolysis, the cathode products were characterized by X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and scanning electron microscope (SEM).

## 3. Results and discussion

### 3.1. The choice of the molten salts media

According to Al-Sm alloy phase diagrams [7], the eutectic temperatures of Al and Al<sub>3</sub>Sm is below 1073 K. The eutectic temperature of LiF-CaF<sub>2</sub> is about 1000 K close to that of the above Al-Sm alloys [17]. So, the eutectic composition of LiF-CaF<sub>2</sub> with 79:21 molar ratio is used as the supporting electrolyte and the electrolytic temperature is 1173 K.

### 3.2. The electrochemical reduction of SmF<sub>3</sub>

#### 3.2.1. Cyclic voltammetry

Fig. 1a shows a typical cyclic voltammogram obtained on a W electrode in the LiF-CaF<sub>2</sub> melts at 100 mV/s at 1173 K. An obvious reduction current A starting at around 0 V is attributed to the reduction of Li(I) ions and the corresponding anode peak A' is caused by the sequent stripping of Li.

As SmF<sub>3</sub> (0.26 mol/L) is added into the above LiF-CaF<sub>2</sub> melts, a new pair of oxidation/reduction peaks B/B' appears in the cyclic voltammogram in Fig. 1b. The cathode peak B starting from about 0.8 V corresponds to the reduction of Sm(III) to Sm(II) and the anodic peak B' is caused by the oxidation of Sm(II) to Sm(III).

To investigate the reversibility of the redox reaction of Sm(III)/Sm(II), cyclic voltammograms with scan rates from 100 mV/s to

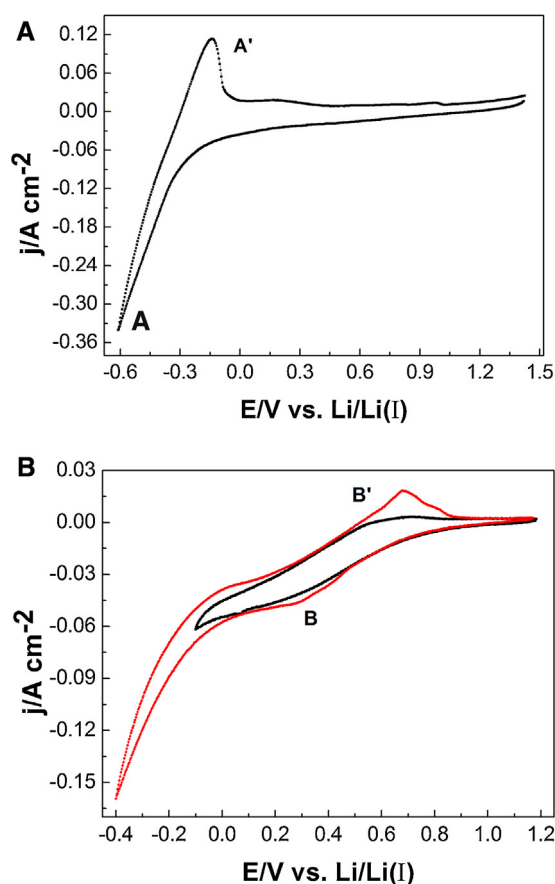


Fig. 1. The cyclic voltammograms recorded on a W electrode ( $S_w = 0.2512 \text{ cm}^2$ ) in (a) LiF-CaF<sub>2</sub> melts. (b) LiF-CaF<sub>2</sub>-SmF<sub>3</sub> (0.26 mol/L) melts with scan rate of 100 mV/s at 1173 K.

2500 mV/s are measured and shown in Fig. 2a. The plot of the peak current for peak B ( $I_p^B$ ) versus the square root of the scan rate ( $v^{1/2}$ ) is shown in Fig. 2b, the line 1 is nearly a linearity passing through the origin within the scan rate of 900 mV/s, while the line 2 is still a linearity without passing through the origin as the scan rate is more than 900 mV/s. The results indicates that the reduction process of Sm(III)/Sm(II) is controlled by diffusion of Sm(III) in the molten salts as the scan rate no larger than 900 mV/s.

The relationship between the cathodic peak potential ( $\log(v)$ ) and logarithmic  $v(\log(v))$  also has shown a good linearity parallel to the X axis independent of logarithmic  $v(\log(v))$  within the scan rate of 900 mV/s, while dependent on logarithmic  $v(\log(v))$  as the scan rate is more than 900 mV/s in Fig. 2c. So when the scan rate is no larger than 900 mV/s, the electrochemical reduction of Sm(III) to Sm(II) is a reversible process. According to previous literatures [18], the redox reaction Sm(III)/Sm(II) is a typical soluble-reversible process.

#### 3.2.2. Electrons transfer number

The relationship between the logarithmic of reduction peak current of peak B and the corresponding potential is shown in Fig. 2d. It is almost a linearity when the scan rate is no larger than 900 mV/s, the number of exchanged electrons can be calculated by Eq. (3).

$$K = \frac{\alpha n F}{2.3 RT} \quad (3)$$

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