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Cathodic behaviour of samarium(III) in LiF–CaF₂ media on molybdenum and nickel electrodes

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Abstract

The electrochemical behaviour of SmF_3 is examined in molten $LiF-CaF_2$ medium on molybdenum and nickel electrodes. A previous thermodynamic analysis suggests that the reduction of SmF_3 into Sm proceeds according to a two-step mechanism:

 $Sm^{III} + e^- = \ Sm^{II}$

 $Sm^{II} + 2e^- = Sm$

The second step occurs at a potential lower than the reduction potential of Li⁺ ions.

Cyclic voltammetry, chronopotentiometry and square-wave voltammetry were used to confirm this mechanism and the results show that it was not possible to produce samarium metal in molten fluorides on an inert cathode (molybdenum) without discharging the solvent. The electrochemical reduction of SmF_3 is limited by the diffusion of SmF_3 in the solution. The diffusion coefficient was calculated at different temperatures and the values obtained obey Arrhenius' law.

For the extraction of the samarium from fluoride media, the use of a reactive cathode made of nickel leading to samarium–nickel alloys is shown to be a pertinent route. Cyclic voltammetry and open-circuit chronopotentiometry were used to identify and to characterise the formation of three alloys: liquid Sm₃Ni and a compact layer made of SmNi₃ and SmNi₂.

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1. Introduction

Partitioning and transmutation (P&T) concepts are acknowledged as efficient ways to reduce the long-term radiotoxicity of nuclear waste by multi-recycling of actinides [1]. Electrochemical based methods (electrorefining, electrolysis) or reductive extraction are used as pyrochemical separation processes. Pyrochemical separation from molten salts (e.g. fluorides or chlorides) is considered as a suitable alternative method to aqueous processes for the separation of minor actinides An (U, Pu, Cm, Am, Np, etc.) from the rest of the fission products containing lanthanides Ln (Ce, Sm, Nd, Eu, Gd, Dy). Success in the process requires reliable data on the electrochemical behaviour and thermodynamic data of actinides and lanthanides in these media.

Samarium is one of the most abundant fission products in nuclear reactors [1]. This work concerns the electrochemical behaviour of this element in molten LiF–CaF₂ in the 810–870 °C temperature range on inert (Mo) and reactive (Ni) electrodes in order to examine the best conditions of samarium extraction.

As far we know in the literature, only LiCl–KCl media have been used for samarium reduction studies at 723 K by Cordoba et al. [2] on an inert cathode and Iida et al. [3,4]

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with a reactive cathode, respectively. These authors found a two-step electrochemical reduction process, but only the first one, which is diffusion controlled, can be observed in molten chloride on a molybdenum electrode:

$$SmCl_3 + 1e^- = SmCl_2 + Cl^-$$
(1)

The reduction of SmCl₂ into Sm metal was not observed by Cordoba because of the prior reduction of Li⁺ ions from the solvent, which hinders the extraction of bulk samarium.

In contrast, Iida et al. [3,4] prepared some nickel–samarium alloys by electrodeposition on a nickel surface in the same temperature range. But these authors found that the composition of the layers obtained depended on the operating conditions (applied potential, temperature).

Borzone et al. [5] and Su et al. [6], using direct calorimetry to calculate the enthalpy of formation of all the samarium–nickel alloys, showed that the alloy which has the most negative enthalpy of formation is $SmNi_2$ at the temperature of 1000 K.

These results in molten chlorides will be compared our own study in molten fluorides. In the first part of this article, the reduction mechanism of SmF_3 will be predicted theoretically, using thermodynamic data of the potential-oxoacidity diagram of samarium species. Then, the second part will detail the electrochemical reduction mechanism, compared with previous works. Finally, the feasibility of samarium extraction by alloying with nickel will be examined.

2. Experimental

• The cell consists of a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled by circulating water [7,8]. The inner part of the walls was protected against fluoride vapours by a graphite liner. The experiments were performed under an inert argon (U-grade: less than 5 ppm O₂) atmosphere, previously dehydrated and deoxygenated using a purification cartridge (Air Liquide). The cell was heated using a programmable furnace and the temperatures were measured using a chromel–alumel thermocouple.

The electrolytic bath consisted of a eutectic LiF/CaF₂ (Merck 99.99%) mixture (77/23 molar ratio). Before use, it was dehydrated by heating under vacuum (10^{-2} mmHg) from ambient temperature up to its melting point (762 °C) for 48 h. Samarium ions were introduced into the bath in the form of samarium fluoride, SmF₃ (Merck 99.99%), powder.

• Electrodes: molybdenum and nickel wires (1 mm diameter) were used as working electrodes. The area of the working electrode was determined after each experiment by measuring the immersion depth in the bath. The auxiliary electrode was a vitreous carbon (V25) rod (3 mm diameter) with a large surface area (2.5 cm²). The potentials were referred to a platinum wire (0.5 mm diameter) immersed in the molten electrolyte, acting as a quasi-reference electrode $Pt/PtO_x/O^{2-}$ [9].

- Electrochemical equipment: all electrochemical studies and electrolysis were performed with an Autolab PG-STAT30 potentiostat/galvanostat controlled by a computer using the research software GPES 4.9.
- Electrochemical techniques: cyclic voltammetry, chronopotentiometry and square-wave voltammetry were the electrochemical techniques used for the investigation of the samarium reduction process.
- Characterisation of reduction products: after the electrolysis runs, the surface of the cathode was examined by Scanning Electron Microscope (LEO 435 VP) with an EDS probe (Oxford INCA 200).

3. Results and discussion

3.1. Analysis of the samarium $E - pO^{2-}$ diagram

The samarium $E - pO^{2-}$ diagram, shown in Fig. 1, exhibits the stability zones of all the samarium species possibly involved in the electrochemical reduction process, as a function of the potential and the oxide content in LiF–CaF₂ bath. This diagram was made using HSC 4.1 software at T = 1100 K, with all soluble species activities equal to 0.1 mol/kg.

First, this diagram shows that SmF₃ should be electrochemically reduced into Sm metal in two steps:

$$Sm^{III} + e^{-} = Sm^{II}$$
⁽²⁾

$$Sm^{II} + 2e^{-} = Sm \tag{3}$$

Secondly, it indicates that at low O^{2-} ion activities, the reduction potential of the second step is more negative than that of Li⁺ (from the LiF–CaF₂). So, according to this diagram, the electrolytic production of samarium metal in fluoride melts seems to be thermodynamically impossible without discharging lithium ions.



Fig. 1. $E - pO^{2-}$ diagram made using HSC 4.1 software at T = 1100 K and all soluble species activities equal to 0.1.

Further information appearing from this diagram is that the oxide content of the bath is a relevant parameter of stability because SmF₃ reacts with oxide ions to form the insoluble oxide species Sm₂O₃ when the O²⁻ ion content is higher than 50×10^{-12} mol/kg.

Thus, the following part of the present article is concerned with the electrochemical study of the SmF_3 reduction process.

3.2. Study of the SmF_3 reduction mechanism

3.2.1. Cyclic voltammetry

Cyclic voltammetry was carried out on a molybdenum electrode in the LiF–CaF₂–SmF₃ melt at 850 °C. Molybdenum was chosen because of its inertness with respect to samarium in the working temperature range according the Mo/Sm binary diagram [10]. The electrochemical window is between the reduction of lithium ions and oxidation of the molybdenum electrode in the cathodic and anodic senses, respectively.

The cyclic voltammogram obtained at 100 mV/s on a Mo electrode is shown in Fig. 2. It exhibits one peak (I_c) in the cathodic run at -1.3 V versus the platinum comparison electrode. The shape of the associated anodic peak (I_a) suggests that the cathodic product is a soluble compound arising from the reduction of Sm^{III} (cf § 3.1). Furthermore, if the SmF₃ concentration in the melt is varied for a given temperature, we observe a linear relationship between the peak current density and the SmF₃ concentration (Fig. 3). So, the cathodic peak is attributed to the reduction of SmF₃, presumably into a divalent species of samarium.

The reduction of Sm^{II} is not observed in this cyclic voltammogram before the solvent reduction, as predicted by the $E - pO^{2-}$ diagram.

Subsequently, the influence of the potential scan rate on the cyclic voltammograms was studied. The cathodic peak intensity is correlated with the potential scanning rate by the following relationship (Randles Sevcik equation) [11], valid



Fig. 2. Typical cyclic voltammogram of the LiF–CaF₂–SmF₃ (5.16×10^{-4} mol/ml) system at 100 mV/s and T=1100 K. Working El.: Mo (S=0.315 cm²); auxiliary El.: vitreous carbon; quasi-reference El.: Pt.



Fig. 3. Linear relationship between the SmF_3 reduction peak current density and the SmF_3 concentration in the melt.

for reversible systems:

$$I_{\rm p} = -0.4463nFSC^{\circ}\sqrt{\frac{nFD}{RT}}\sqrt{v} \tag{4}$$

where *S* is the electrode area (cm²); C° is the solute concentration (mol cm⁻³); *D* is the diffusion coefficient (cm² s⁻¹); *F* is the faraday (96,500 C); *n* is the number of exchanged electrons; *v* is the potential scanning rate (V s⁻¹) and *T* is the absolute temperature (K).

The linearity of I_p versus $v^{1/2}$ is verified in Fig. 4, which indicates that the electrochemical reduction process is controlled by the diffusion of Sm^{III} ions in the solution. The slope of the straight line is:

$$\frac{I_{\rm p}}{\sqrt{v}} = -(0.134 \pm 0.002) \,\mathrm{A \, s^{1/2} \, V^{-1/2}} \tag{5}$$

at $T = 850 \,^{\circ}$ C and $C^{\circ} = 0.515 \times 10^{-3}$ mol/ml.

3.2.2. Chronopotentiometry

In order to confirm the diffusion control of the electrochemical reduction process, several chronopotentiograms were measured on a molybdenum electrode. Fig. 5 shows the evolution of the chronopotentiograms with the applied current density. These curves exhibit a single plateau at about



Fig. 4. Linear relationship of SmF₃ reduction peak current density vs. the square root of the scanning potential rate at T = 1100 K. Working El.: Mo (S = 0.315 cm²); auxiliary El.: vitreous carbon; quasi-reference El.: Pt.



Fig. 5. Typical chronopotentiograms with the intensity of the system LiF–CaF₂–SmF₃ at 1100 K. Working El.: Mo (S = 0.315 cm²); auxiliary El.: vitreous carbon; quasi-reference El.: Pt.

-1.3 V/Pt, corresponding to the reduction potential of Sm^{III} into Sm^{II}. It can also be noted that the transition time (τ) decreases as the applied current density increases. This is in agreement with Sand's law [12]:

$$\frac{I\sqrt{\tau}}{C^{\circ}} = -0.5nFS(\pi D)^{1/2} = \text{constant}$$
(6)

The data plotted in Fig. 6 prove that this equation is verified. These experiments were repeated at various temperatures and confirmed the validity of Eq. (6).

From these data, we obtain, at $850 \degree C$ and $C^{\circ} = 0.515 \times 10^{-3} \text{ mol/ml}$:

$$I\sqrt{\tau} = -(0.083 \pm 0.002) \,\mathrm{A} \,\mathrm{s}^{1/2} \tag{7}$$

Chronopotentiometric measurements confirm the results obtained by cyclic voltammetry: the electrochemical reduction process is limited by the diffusion of Sm^{III} ions in the solution.

The reversal chronopotentiogram, shown in Fig. 7, reveals the formation of a soluble compound, in a reversible system [13], at the Mo electrode during the cathodic run. The cathodic transition time measured τ_{red} ($\tau_{red} = 0.36$ s) is equal to $3\tau_{ox}$ ($\tau_{ox} = 0.12$ s).



Fig. 6. Evolution of $I\tau^{1/2}$ vs. the intensity at 1100 K. Working El.: Mo $(S=0.315 \text{ cm}^2)$; auxiliary El.: vitreous carbon; quasi-reference El.: Pt.



Fig. 7. Reversal chronopotentiogram of SmF₃ (5.15 10^{-4} mol/ml) in LiF–CaF₂, *I*=130 mA/cm² at 1100 K. Working El.: Mo (*S*=0.315 cm²); auxiliary El.: vitreous carbon; quasi-reference El.: Pt.

- 3.2.3. Number of exchanged electrons
- Using the chronopotentiometry and cyclic voltammetry results obtained successively in the same electrolyte, it is possible to determine the number of electrons exchanged. The following relationship can be obtained:

$$\frac{I_{\rm p}/\sqrt{v}}{I\sqrt{\tau}} = 53.85\sqrt{\frac{n}{T}} \tag{8}$$

This procedure allows the incertitude on the electrolyte concentration to be ignored.

In the example of Figs. 4 and 6, 0.99 exchanged electrons are found. The average of electrons exchanged was 0.99 for the results of five experiments. Thus, the conclusion is that one electron is exchanged, proving that the reduction peak observed actually can be attributed to the reaction:

$$Sm^{III} + e^{-} = Sm^{II}$$
⁽²⁾

• Another electrochemical technique allows the number of exchanged electrons to be determined: square-wave voltammetry [14,15]. In this technique, the scanning of potential proceeds stepwise with superimposition, on each step of the staircase, of two potential pulses, direct and reverse, of the same intensity. Plotting the differential intensity measured at each step between the successive pulses versus the potential associated to each electrochemical reaction provides a peak with a Gaussian shape. The mathematical analysis of the peak yields, in the case of a reversible system, a simple equation associating the halfwidth of the peak $W_{1/2}$ and the number of electrons exchanged:

$$W_{1/2} = 3.52 \frac{RT}{nF}$$
(9)

Fig. 8 shows a square-wave voltammogram of SmF₃ in LiF–CaF₂ on a molybdenum electrode at 850 °C. It exhibits a symmetrical single peak at -1.1 V/Pt, corresponding to $E_{p/2}$ for the cyclic voltammogram.

The validity of application of Eq. (9) was verified by plotting the current density of the peak versus the square root of the frequency as reported in previous works [16,17]. In



Fig. 8. Square-wave voltammogram of the LiF–CaF₂–SmF₃ melt. Frequency: 25 Hz, T = 1100 K. Working El.: Mo (S = 0.315 cm²); auxiliary El.: vitreous carbon; quasi-reference El.: Pt.

the present work, a linear relationship was observed in the 9–100 Hz frequency range.

According to Eq. (8), the measurement of $W_{1/2}$ leads to a number of exchanged electrons equal to 1.01 for eight voltammograms. This result confirms that the reduction of SmF₃ in LiF–CaF₂ melts yields a divalent samarium compound.

3.2.4. Diffusion coefficient of Sm^{III} ions

The diffusion coefficient of Sm^{III} ions can be calculated using Eq. (4) and/or (6).

At $T = 850 \degree \text{C}$ and $[\text{SmF}_3] = 1.56 \times 10^{-4} \text{ mol/ml}$, we found the following average result:

$$D_{\rm Sm^{III}} = (3.27 \pm 0.05) \, 10^{-9} \, {\rm m^2/s}$$

The calculation of *D* was repeated at several temperatures. Table 1 reports the value of the diffusion coefficient obtained at different temperatures (830, 850, 870 and 900 $^{\circ}$ C). These results obey the following relationship (Arrehnius' law):

$$D = D^{\circ} \exp\left(-\frac{E_a}{RT}\right) \tag{10}$$

where E_a is the activation energy.

The linearity of the evolution of $\ln D$ versus 1/T is observed in Fig. 9. With these results, the Eq. (10) can be written:

$$\ln D = -3.9237 - \frac{7.1811}{T} \tag{11}$$

where *D* is in cm^2/s and *T* in K.

Table 1

From this relationship, the value of the activation energy is found to be 59.7 kJ/mol.

Evolution of the SmF₂ diffusion coefficient with the temperature

<i>T</i> (°C)	$D imes 10^5 (\mathrm{cm}^2/\mathrm{s})$
830	2.96
850	3.27
870	3.71
900	4.34



Fig. 9. Linear relationship of the logarithm of SmF_3 diffusion coefficient vs. the reciprocal of the absolute temperature.

3.3. Samarium electrodeposition on a reactive cathode (Ni)

3.3.1. Preliminary discussions

The results obtained in the previous paragraph are only related to the reaction $\text{Sm}^{\text{III}} + e^- \rightarrow \text{Sm}^{\text{II}}$. The reduction of Sm^{II} into Sm metal could not be observed because samarium is more reactive than the solvent cations, lithium and probably calcium [18]. Thus, the electrolytic extraction of samarium in these conditions is problematic because it should intervene at a potential where the solvent cations are also discharged.

To have a chance of achieving a successful elimination of samarium ions from the molten salt mixture, the activity of the electrodeposited metal must be lowered. This is feasible if the electroreduction of the samarium ions leads to the formation of an alloy with the cathodic substrate. The methodology was developed in our laboratory [19,20], and in other works [21,22]. In the case where the cathode metal M reacts with the electrodeposited metal N, to form an intermetallic compound MN_x , the equilibrium potential is shifted in the anodic direction; the depolarisation term is equal to the emf of the cell:

$$\frac{MN_x}{solvent}, \frac{N ions}{N}$$
 (12)

Nickel seems to be a good candidate for such a cathode metal, since in previous works, it was shown that alloying nickel with rare-earth metals is particularly easy and rapid at moderate temperatures [23–26].

3.3.2. Nickel-samarium phase diagram

According to the Ni–Sm phase diagram, shown in Fig. 10 [10], samarium can form eight intermetallic compounds with nickel (Sm₃Ni, SmNi, SmNi₂, SmNi₃, Sm₂Ni₇, Sm₅Ni₁₉, SmNi₅, Sm₂Ni₁₇). At the temperature of the experiments, one compound is liquid (Sm₃Ni), and all the others are solid. The identification and the characterization of these compounds in the overall process of electrodeposition of samarium on nickel were carried out by cyclic voltammetry and opencircuit chronopotentiometry.



Fig. 10. Nickel-samarium phase diagram obtained by ASM binary alloys phase diagrams database.

3.3.3. Cyclic voltammetry

Fig. 11 compares the cyclic voltammograms obtained at $850 \,^{\circ}$ C on molybdenum and on nickel electrodes at 100 mV/s. The wave Sm^{III}/Sm^{II} (at $-1.3 \,$ V/Pt) is observed on each substrate. Then, at more cathodic potentials before the solvent limit, we notice a far higher current only in the case of the nickel cathode, with cathodic and anodic peaks not well defined. This current and these peaks are attributed to the formation of nickel–samarium alloys. The current measured in the potential range between the reduction Sm^{III}/Sm^{II} and the



Fig. 11. Comparison of the cyclic voltammograms of the LiF–CaF₂–SmF₃ system on molybdenum and nickel electrodes at 100 mV/s and T=1100 K. Auxiliary El.: vitreous carbon; quasi-reference El.: Pt.

solvent is associated with a reaction of the following kind:

$$Sm^{II} + 2e^{-} + xNi = SmNi_x$$
(13)

where x can take the values given by the binary diagram of Fig. 10.

3.3.4. Open-circuit chronopotentiometry

Cyclic voltammetry cannot be used to identify the intermetallic compounds. A suitable technique is open-circuit chronopotentiometry: after a short cathodic polarisation at a high cathodic overpotential, the open-circuit potential of the electrode is measured versus time. The evolution of the potential consists of successive plateaux, of increasing potential, each plateau being typical of equilibrium in the solid state between two intermetallic compounds. The diffusion of Sm within the substrate explains the increase at potential of the cathode.

An example of an open-circuit chronopotentiogram obtained after polarisation at -300 mA/cm^2 for 15 s is shown in Fig. 12. During this experiment, eight plateaux were observed at about -0.76, -0.89, -1.00, -1.03, -1.25, -1.28, -1.55 and -1.79 V/Pt. The potential is dictated by the difference of the samarium activity in the electrolyte (constant) and at the surface of Sm–Ni alloy (variable). The samarium concentration decreases at the surface of the electrode as it diffuses into the nickel. When a two-phase equilibrium in the solid exists at the surface of the electrode, the samarium



Fig. 12. Open-circuit chronopotentiogram of the LiF–CaF₂–SmF₃ system on nickel electrode at T=1120 K. Auxiliary El.: vitreous carbon; quasi-reference El.: Pt.

activity is equal in each phase and remains constant while the Sm concentration at the surface decreases. This results in a constant potential (plateau) for a given diffusion time. The plateau obtained at -1.79 V/Pt is attributed to Sm₃Ni because it is the compound containing the highest concentration of Sm, and so the last that would be reduced.

3.3.5. Observation and characterisation of the Sm–Ni alloys

In order to characterise the intermetallic compounds obtained, the electrodeposition of samarium–nickel alloys was performed at 200 mA/cm² at 850 °C for 1 h. The cross section of the sample obtained during this run was observed by scanning electron microscopy. The micrograph is presented in Fig. 13. An EDS probe allowed us to determine the composition of each phase present on the micrograph.

Three different alloys were identified:

- (i) The first one was Sm₃Ni located in the micrograph of the solvent layer outside of the electrode. This alloy was obtained during the cooling of the sample. In effect, at 840 °C, according to the phase diagram, only Ni–Sm liquid, falling down in the crucible, was produced. When the sample was cooled, the Ni–Sm liquid produced, at around 660 °C, two compounds: Sm₃Ni and Sm. But Sm is not stable in the bath; it reacts with Li⁺ ions from the solvent, that's why only Sm₃Ni is present on the micrograph.
- (ii) In the magnification in Fig. 13b, the compact layer at the nickel interface exhibits two phases: Ni_3Sm , closer to the nickel boundary and Ni_2Sm further away. This feature could result from the interdiffusion process leading to (a) the compound with the higher Ni content, at the nickel interface and (b) the most thermodynamically stable compound within the layer.

This conclusion is in agreement with the data obtained by Borzone et al. [5] and Su et al. [6] who calculated the free energies of formation of Sm–Ni alloys and determined that SmNi₂ is slightly more stable than Ni₃Sm. By anal-





Fig. 13. (a and b) SEM micrograph of the cross section of a nickel plate after reduction of SmF₃ at -200 mA/cm^2 for 1 h and T = 1120 K.

ogy with Iida et al. [3] who only obtained a Ni_2Sm layer on nickel substrate by reduction of $SmCl_3$ in LiCl–KCl media, we can assume that, when the interdiffusion process was reached equilibrium, only Ni_2Sm will be present in the layer.

The presence of Sm_3Ni in the electrolyte phase confirms that the compound is liquid at this temperature, and is partially removed from the electrode surface. This observation suggests that at higher temperatures, with the same operating current density, only Sm_3Ni would be formed at the nickel surface and would fall down to the bottom of the crucible.

4. Conclusion

The electrochemical behaviour of samarium was studied in the LiF–CaF₂ medium using inert (Mo) and reactive (Ni) electrodes. The results of the electrochemical techniques confirmed that the electrochemical reduction of Sm^{III} occurs in two steps with formation of $\mathrm{Sm}^{\mathrm{II}}$ as an intermediate compound.

$$Sm^{(III)} + 1e^- = Sm^{(II)}$$
 and $Sm^{(II)} + 2e^- = Sm^{(0)}$ (14)

Nevertheless, the second wave was not observed on an inert cathode in the cathodic runs, due to the prior reduction of Li⁺ ions from the solvent.

The diffusion coefficient of the SmF_3 was calculated by cyclic voltammetry and chronopotentiometry and showed a temperature dependence according to Arrhenius' law:

$$\ln D = -7.1811 - \frac{3.9237}{T} \tag{11}$$

Cyclic voltammetry and open-circuit chronopotentiometry results showed that SmF_3 can be reduced on a nickel electrode to form samarium–nickel alloys. Using SEM and EDX analysis, we identified Sm_3Ni and $SmNi_2$. The first compound is liquid at the temperature of the experiments, so it does not stay at the surface of the electrode, and the second one, resulting from intermetallic diffusion, is located at the surface of the nickel.

This article demonstrates that samarium metal cannot be obtained in molten LiF–CaF₂ by electrochemical reduction of SmF_3 on an inert electrode, such as molybdenum. The results open another route for the electrochemical extraction of samarium. Using a reactive cathode made of nickel, it is possible to precipitate this element in the form of an intermetallic compound with nickel, preferentially Sm_3Ni , because, on the one hand, this compound is the richest in samarium, and on the other hand, it is liquid at moderate temperatures.

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