Electrochemical Synthesis of Al-Sm Metal by Coreduction of Sm(III) and Al(III) in a K₃AlF₆ Melt

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Abstract. The electrochemical behaviors of Sm(III) in the molten K₃AlF₆ system were investigated with a tungsten electrode at 1024 K. By electrochemical tests, including cyclic voltammetry and square wave voltammetry, Sm(III) was reduced to Sm(0) in two steps. The diffusion coefficient of Sm(III) was 1.90*10⁻⁵ cm²/s when examined by using cyclic voltammetry in the molten salts. The electrochemical signal of the Al-Sm intermetallic compound was detected at -1.71 V and -2.22 V. AlSm₂ and Al₃Sm were obtained by potentiostatic electrolysis at -2.3 V for 10 h. These intermetallic compounds were characterized by X-ray diffraction analysis (XRD) and scanning electron microscopy with energy.

1. Introduction

The discovered rare-earth reserve within China amounts to 36 million tons, which is mainly distributed in such regions as Inner Mongolia, Jiangxi, and Sichuan. It accounts for approximately 36% of the total rare-earth reserve in the world. Due to their unique physicochemical properties, such as 4f electronic structures, great atomic magnetic moments and potent spin-spin coupling, rare earth elements are extensively applied in many fields, including metallurgy, petrochemicals, agriculture, light textiles, ceramics, permanent magnetic materials, hydrogen-storing materials, luminescent materials, and superconducting materials.

Sm is a valence-varying element in the lanthanoid family; it has a large neutron-absorbing cross-section and can prevent transmuting actinide elements from capturing neutrons, thus reducing the transmutation rate. In recent years, as nuclear energy has become widely used, the treatment of spent fuel has emerged as a key issue limiting the sustainable development of nuclear energy. Separation-transmutation is an important technology for reducing the radioactivity and volume of nuclear waste. Thus, separating and extracting the Sm in rare earths with fused salt electrolysis is of great significance for spent fuel treatment. Many scholars have studied the electrochemical behaviors of Sm(III) on noble electrodes. For example, Ito et al from Japan [1] investigated the electrochemical behaviors of Sm on Mo electrodes at 723 K. Caravaca et al [2], from Spain, analyzed the electrochemical behaviors of Sm ions on Mo electrodes at varying temperatures in a LiCl-KCl fused salt system and found the sable oxidation states for Sm in fused salt to be Sm(III) and Sm(II). Tlenkopachev et al [3] researched the reduction process of Sm ions on different electrodes in KCl-NaCl-CsCl fused salt at 823 K. Novoselova et al [4] focused on the reduction process of Sm in CsCl fused salt at varying temperatures. The findings of the above experiments suggest that the reduction of Sm(III) can only proceed from Sm(III) to Sm(II) but not from Sm(II) to Sm(0) due to the overly negative reduction potential of Sm(II).
The chloride system is largely adopted as the experimental subject for study of the electrochemistry of fused salts, but the electrolysis of rare-earth chlorides is complicated by such problems as the susceptibility of raw materials to moisture, low rare-earth yield, high power consumption, and severe environmental pollution caused by massive chlorine generation. Therefore, such electrolysis was banned by the government in 2010. On the other hand, the fused fluoride system features high current efficiency, low energy consumption, good stability, and low pollution. The research on fused fluoride has received great attention as the energy crisis and environmental challenges have arisen, thus providing an opportunity for the preparation and application of fused fluoride. Tian Zhongliang et al [5] prepared an Al-Sc alloy using Na₃AlF₆-AlF₃ as the elementary electrolyte system and aluminum oxide and Sc-containing compounds as the source materials. Zhang Mingjie et al [6] studied how to prepare an Al-Sc alloy with the nNaF/AlF₃-ScF₃-Sc₂O₃ system. Applying the cyclic voltammetry (CV) approach to the LiF-NdF₃-Nd₂O₃ system research, Stefanidaki et al [7] obtained Nd from the electrodeposition process. In an electrolyte of RE₂O₃-GdF₃-LiF fused salt, Zhang Zhihong et al [8] obtained the RE-Gd alloy. Zhang Milin et al [9] prepared many types of rare-earth alloys through the fluoride-chloride fused salt system. A fluoride-based electrolysis system is currently under development, but few studies have concentrated on preparing Al-Sm alloys with the fluoride system. We previously succeeded in preparing an Al-Sm intermediate alloy with the SmF₃-LiF-Sm₂O₃ fused salt system [10] despite the challenges, such as the high electrolyzing temperature and high fused salt cost. Low-temperature fused fluoride electrolysis represents an important direction for current fused salt electrolysis. As a fused salt, potassium cryolite can achieve low-temperature electrolysis. Therefore, the present paper employs the CV approach and square wave voltammetry (SWV) to unveil the electrochemical behaviors of Sm(III) in the fused potassium cryolite system as well as the mechanism underlying the intermetallic compound preparation.

2. Experimental part

2.1. Reagents and instruments
Potassium cryolite (analytical grade), samarium oxide (analytical grade), platinum wire (Pt, diameter 1 mm, mass fraction 99.99%), tungsten wire (W, diameter 1 mm, mass fraction 99.99%), graphite rod (10 mm diameter, mass fraction 99.999%) and absolute ethanol (analytical grade) were used in the experiment. The electrochemical analysis was carried out using the Autolab AUT302N electrochemical workstation (Swiss Metrohm), and an X-ray diffractometer (Bruker, Germany) was used to analyze all samples. Scanning electron microscopy (SEM, FEI, USA) was used to analyze the microstructure of the Al-Sm intermetallic compounds, and energy dispersive spectrometry (EDS, FEI, USA) was used to analyze the microzone chemical characteristics of the Al-Sm intermetallic compounds.

2.2. Experimental process
The entire experimental procedure was carried out in an electric resistance furnace. The experimental instrument used in the research is shown in Figure 1. K₃AlF₆ was placed in a vacuum drying oven at 473 K for 10 h to remove excess water; then, it was introduced into a graphite crucible placed on refractory brick located in the electric furnace. The electrochemical detections were controlled by Autolab PGSTAT 302N (Metrohm, Ltd.), and the data were processed by NOVA 2.0 software. The K₃AlF₆ molten salt was used in a three-electrode electrochemical cell. A thermocouple was employed to measure the temperature. A Pt wire (1 mm in diameter with a purity of 99.99%) was used to assemble the reference electrode. A graphite rod (10 mm in diameter with a purity of 99.99%) was used as the counter electrode. The electrode was polished using SiC abrasive paper prior to each experiment and then cleaned with deionized water. Tungsten wire (1 mm in diameter with a purity of 99.99%), which was polished by using SiC abrasive paper, acted as the working electrode. Afterwards, the tungsten wire was cleaned ultrasonically with ethanol prior to use. The surface area of the active
electrode was determined after each experiment by gauging the immersion length of the electrode in salts. All the weights were measured using an electronic balance.

The electrochemical reduction behavior of Sm$_2$O$_3$ in the K$_3$AlF$_6$ melt was studied by electrochemical methods such as cyclic voltammetry and square wave voltammetry. Pre-electrolysis of the K$_3$AlF$_6$ melt was performed for 6 h under the conditions of 1024 K and -0.8 V; then, Sm$_2$O$_3$ was added at a constant temperature for 2 h, and the electrochemical data of the molten salt was recorded before and after the addition of Sm$_2$O$_3$. Al-Sm intermetallic compounds were prepared by potentiostatic electrolysis carried out on W electrodes in the K$_3$AlF$_6$-Sm$_2$O$_3$ melt at 1024 K. After electrolysis, all samples were sonicated in ethanol (99.8% purity) in an ultrasonic bath for 15 min for cleaning and stored in a glove box until analysis. Then, the samples were analyzed by XRD (Bruker, Germany), SEM (FEI, USA) and EDS (FEI, USA).

![Figure 1. Schematic diagram of electrolyzer.](image)

3. Results and discussion

3.1. Cyclic voltammetry

Figure 2 shows the CV of the W electrode in the K$_3$AlF$_6$ melt (0.2 V·s$^{-1}$) at 1073 K. The scanning range was -2.5 V~0 V. In the K$_3$AlF$_6$ melt, a pair of cathode/anode signals A/A’ is observed, which correspond to the formation and dissolution of the Al metal, respectively. Signal A at the -0.88 V position corresponds to the reduction of Al(III) to elemental Al, and the anode peak A’ located at approximately -0.48 V is ascribed to the dissolution of Al. The CVs of the K$_3$AlF$_6$-Sm$_2$O$_3$ with scan rates from 0.1 to 0.5 V/s are shown in Figure 3. In the K$_3$AlF$_6$-Sm$_2$O$_3$ melt, a large cathodic and anodic peak, A/A’, was found at approximately -0.74/-0.88 V, which also appears in the CV of the K$_3$AlF$_6$ melt. The A/A’ signals are interpreted as the electrochemical redox reaction of Al(III)/Al(0). Compared with those in Figure 2, three new reduction signals, B, C and D, occur at -0.68 V, -1.71 V and -2.23 V, respectively. Sm is a valence element, and Sm(III) was reduced to Sm(0) in two steps; however, as the reduction potential of Sm is too negative, only the redox reaction of Sm(III)/Sm(II) can be observed. According to other researchers [11], the cathodic electrochemical signal B that occurs at -0.68 V is interpreted as the reduction peak of Sm(III)/Sm(II). In the reverse scan direction, the signal B’ is the corresponding oxidation signal of Sm(III)/Sm(II). In addition, redox couples (C/C’, D/D’) lie behind the aluminum reduction potential, which are attributed to the formation and dissolution of Sm$_x$Al$_y$ intermetallic compounds in the K$_3$AlF$_6$-Sm$_2$O$_3$ melt. Two signals, C and D, occur at approximately -1.71 V and -2.23 V, which correspond to the anodic signals C’ and D’ at approximately -1.68 V and -2.23 V, respectively. As the scanning rate increases, the signals A and B do not shift significantly; it can be concluded that the redox reactions of Al(III)/Al(0) and Sm(III)/Sm(II) are both quasi-reversible.
Figure 2. Cyclic voltammogram in K$_3$AlF$_6$ molten salt. Scan rate: 0.1 V/s, $S_w=0.314$ cm$^2$, $T=1024$ K.

Figure 3. Different scan rate cyclic voltammograms in K$_3$AlF$_6$-Sm$_2$O$_3$ molten salt $S_w=0.314$ cm$^2$, $T=1024$ K.

| $v/V\cdot s^{-1}$ | 0.1  | 0.2  | 0.3  | 0.4  | 0.5  |
|-------------------|------|------|------|------|------|
| $v^{1/2}(V/s)^{1/2}$ | 0.3162 | 0.4472 | 0.5477 | 0.6324 | 0.7071 |
| $E_{p}^c/V$ | -0.6886 | -0.6891 | -0.6996 | -0.6999 | -0.7005 |
| $E_{p}^a/V$ | -0.2945 | -0.2719 | -0.2596 | -0.2554 | -0.2548 |
| $I_{p}^c/A$ | 0.0060 | 0.0013 | 0.0033 | -0.0011 | -0.0020 |
| $I_{p}^a/A$ | 0.3154 | 0.4674 | 0.5805 | 0.9175 | 0.9851 |

Moreover, the relationship between the scan rate and peak potential/current of the cathodic reaction on the tungsten electrode is shown in Table 1; the peak potential of B(Sm$^{3+}$/Sm$^{2+}$) changes very little with the scan rate from 0.1 to 0.5 V/s. The relationship between the square root of the scan rate and the peak current/potential is illustrated in Figure 4(a). The two curves are almost parallel to the x-axis; hence, the reaction of Sm(III)/Sm(II) may be reversible when the scanning rate is lower than 500 mA/s.

Figure 4(b) shows the curve of the cathode peak current $I_p^c$ vs. $v^{1/2}$. The peak current $I_p^c$ has a good linear relationship with $v^{1/2}$, which indicates that the electrode process of Sm(III) in the K$_3$AlF$_6$ molten salt system is controlled by diffusion. Therefore, the diffusion coefficient of Sm(III) in the molten salt system can be calculated by Eq (1)[12].

$$I_p^c=0.61(nF)^{1/2}SC_0D^{1/2}v^{1/2}(RT)^{-1/2}$$

where $S$ is the electrode surface area (cm$^2$); $C_0$ is the molar concentration of Sm(III) ions (mol·cm$^{-3}$); $F$ is the Faraday constant (96485C·mol$^{-1}$); $R$ is the molar gas constant (8.314 J/mol·K); $n$ is the number of exchanged electrons; $V$ is the potential scanning rate (V/s); and $T$ is the thermodynamic temperature (K). The slope of the curve trend line is 0.0197.
3.2. Square wave voltammetry

Square wave voltammetry is a more sensitive transient method than cyclic voltammetry to study the electrochemical behavior of the Sm₂O₃ in the K₃AlF₆ melt (W was used as the working electrode); the square wave voltammetry (SWV) curve obtained for molten K₃AlF₆-Sm₂O₃ at temperatures under 1024 K with a step potential of 5 mV and a frequency of 25 Hz is shown in Figure 5. The cathode scan range was from 0 V to 2.5 V and exhibited four signals having peak potentials of -0.5 V (B), -1.01 V (A), -1.49 V (C), and -2.05 V (D). Peak B corresponds to the reduction of Sm(III) to Sm(II); the potential is slightly positively shifted with cyclic voltammetry. Peak A at -1.01 V corresponds to the reaction of Al(III)/Al(0), which is negatively offset by 0.13 V with the cyclic voltammetry result. Peaks C and D most likely correspond to the formation of Al-Sm intermetallic compounds. The results obtained by square wave voltammetry are consistent with the results of cyclic voltammetry. According to Bard and Faulkner [13], the relationship between the number of electrons transferred (n) and the half-width of the peak (W₁/₂) should be calculated according to Eq. (2) as follows:

\[
W_{1/2} = \frac{3.52RT}{nF}
\]

where, \( W_{1/2} \) —— half width
F —— Faraday constant
R —— gas constant
T —— experimental temperature (Kelvin temperature, K)
N —— Electron transfer number signal of the electrode reaction

The half-widths of peaks A and B are \( W_{1/2}(A) = 0.1109 \) and \( W_{1/2}(B) = 0.2811 \), respectively. The number of transferred electrons at B is 2.8, which is approximately equal to 3. The number of electrons transferred from Sm(III) when it was reduced to Sm(II) was 1.10, which is approximately equal to 1. Consistent with the above results, A and B correspond to the reduction processes of Al(III) and Sm(III), respectively.

3.3. Characterization of the Constant Potential Electrolytic of the Al-Sm Alloy

Based on the results obtained by cyclic voltammetry and square wave voltammetry, to ascertain the type of intermetallic compound, potentiostatic electrolysis was introduced at 1024 K. Electrolysis experiments were conducted using a tungsten wire as the cathode and a spectrum pure graphite rod as the anode. By potentiostatic electrolysis at -2.3 V for 10 h, two types of intermetallic compounds (AlSm₂ and Al₃Sm) were obtained. After electrolysis, the samples were washed by deionized water with the adherent salt eliminated by ultrasound. The samples were characterized by XRD (using Cu Kα radiation at 40 kV and 40 mA). As observed from the patterns in Figure 6, the deposit was composed of Al, AlSm₂ and Al₃Sm.
Figure 7 and Figure 8 show a series of SEM images and the EDS analysis, respectively. As observed from the patterns in Figure 7, there are a large number of white stripes and massive second phases in the black matrix phase, and they are evenly distributed. The EDS spectrum analysis is marked in Figure 7 (b). Figure 8 shows the results of the EDS spectrum analysis, and it reveals that the striped and blocky white areas are Al-Sm alloy phases, and the Sm/Al atomic ratios at mark 2 and mark 3 are less than 1/5. It can be determined that the alloy phase region is composed of AlSm$_2$, Al$_3$Sm, and Al metal, and the black region is an Al matrix without Sm. The Sm content of the bulk alloy portion is significantly higher than that of the strip alloy portion.

![Figure 7. (a) At low magnification SEM image (b) At high magnification SEM image](image)

![Figure 8. EDS spot scanning for al-sm alloy](image)

4. Conclusions
The electrochemical coreduction behavior of Sm(III) and Al(III) ions was investigated in a K$_3$AlF$_6$ melt on a tungsten electrode at 1024 K. The reduction process of Sm(III) in the K$_3$AlF$_6$-Sm$_2$O$_3$ molten salt electrolyte system is quasi-reversible and controlled by the diffusion step, $D_{\text{Sm}^{3+}} = 1.90 \times 10^{-5}$ cm$^2$.s$^{-1}$. Sm(II) cannot be directly electrolytically reduced to Sm; Sm(II) is underpotentially deposited on the predeposited Al at -1.71 V, -2.22 V position. By potentiostatic electrolysis at -2.3 V for 10 h, two intermetallic compounds (AlSm$_2$ and Al$_3$Sm) were obtained on the tungsten electrode, as characterized by XRD, SEM and EDS. The intermetallic compounds were strip-like, massive and evenly distributed.
References

[1] T. Iida, T. Nohira, Y. Ito, Electrochimica Acta, 2001, 46(16): 2537-2544
[2] G. Cordoba, C. Caravaca, Journal of electroanalytical Chemistry, 2004, 572(1): 145 — 151
[3] Kh.B. Kushkhov, M.K. Vindizheva, R.A. Karashaeva, et al., Russian Journal of Electrochemistry, 2010, 46(6): 691-701
[4] A.V. Novoselova, V.A. Khokhlov, V. Yu. Shishkin, Russian Journal of Chemistry, 2001, 74(10): 1672-1677
[5] TIAN Z L, LAI Y Q, YANG S, et al. Method for preparing aluminum-scandium intermediate alloy by molten salt electrolysis: CN104746106A[P]. 2015-07-01
[6] ZHANG M J, LI J L, LIANG J X, Journal of Northeastern University, 2003, 24(04): 358-360
[7] STEFANIDAILI E, HASIOTIS C, KONTOYANNIS C, Electrochimica Acta, 2001, 46: 2665-2670
[8] ZHANG Z H, CHEN G H, YU B, et al, Production of rare earth-gadolinium alloy by codeposition in molten salt bath: CN103924266A. 2014-07-16.
[9] ZHANG M L, HAN W, QIN W Z, Method for separating praseodymium oxide and dysprosium oxide by molten salt electrolysis: CN102134728A[P]. 2011-07-27
[10] LIU H X, YANG G W, ZHEN X, ZHANG X L, Chinese Rare Earths, 2018, 39(1): 11-17
[11] Chen L, Study on Electrochemical Behavior of Sm on Different Cathodes and the Alloys Formation Mechanism in Molten Salt, Harbin Engineering University, Harbin, 2014
[12] A. J. Bard and L. R. Faulkner, Electrochemical Methods: fundamentals and applications, Wiley & Sons Inc, (2011) New York, America
[13] J. Park, S. Choi, S. Sohn, K. Kim and I. S. Hwang, J. Electrochem. Soc., 161 (2014) H97.