

Chemical titration method for Determination of Concentration of REO in Rare Earth Fluoride Melts

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Abstract. In the present study, chemical titration method for determination of concentration of REO in REF₃-LiF-RE₂O₃ melts was investigated. The melts with the composition of 40mol%REF₃-60mol%LiF (RE=La and Nd) was taken as object for illustrating the measurement of concentration and solubility of REO by the chemical titration method. Then the changing of REO concentration in 40mol%REF₃-60mol%LiF melts with electrolytic time in practical electrolysis production was studied. The concentration of REO decreases with the electrolytic time, and rate of the decreasing also declines with the electrolytic time. And the reasonable time interval for REO addition was recommended defining as 1.75 h which is very close to the empirical value 2 h, This would also illustrate the reliability of chemical titration method on determination of concentration of REO in the melts.

1. Introduction

REF₃-LiF-RE₂O₃ is the most important electrolyte for producing rare earth metal and its alloys in modern industry [1-4]. The foundation of developing novel electrolysis technology and equipment are also based on the REF₃-LiF-REO molten salts system. Moreover, REF₃-LiF molten salts are also very significant for their potential use in the extraction lanthanum (RE) elements from molten salts in the general frame of reprocessing nuclear wastes [5-7]. In the electrolysis process, REF₃-LiF acts as the solvent for the oxide, and REO is the actual consumption of the electrolyte. So, REO need to be added continuously. Researches [8-9] found that the current efficiency increases with the increasing of the addition rate of REO. However, the low solubility of REO is the primary cause for forming the precipitation and even the slag at the bottom of the electrolytic cell which is terrible effect on the current efficiency in practical production. So the determination of REO concentration in REF₃-LiF-REO melts is considered as an important process for establishing reasonable RE₂O₃ addition system and the time interval of addition.

In recent years, the solubility of REO in fluoride melts was widely researched [10-21]. It was found that the solubility was relatively low and the melts with high temperature and strong corrosiveness so that there were difficulties for accurate measuring the concentration of REO in fluoride melts. According to the published researches, the specific measurement methods for determining concentration of REO were chemical analysis, thermal analysis. What is more, the surface tension was related to concentration of REO in molten rare earth fluoride melts based on the recent reference on surface tension [22]. So, the determination of concentration of REO can be determined by surface tension and using relationship between surface tension and concentration of REO. In the present study, chemical titration method for determination of concentration of REO in REF₃-LiF-REO melts was discussed.

2. Experimental

All of chemicals were analytical pure (Table 1), REF₃, LiF and REO were dried before being used under the temperature of 150°C for 24 hours so that the moisture could be removed. The crucible, stirring paddle and sampler were all made of high-purity graphite material due to the strongly corrosive of the high temperature molten salts. And the special lid was prepared for preventing the

molten salts from excessive volatilization. The high-purity argon was also needed to be put into the furnace to protect the equipment from oxidation. The furnace system of experiment was shown in Fig.1.

Table 1 Experimental reagents.

| Reagents | Purity (wt%) | Manufacturer |
|--------------------------------|--------------|------------------------------------|
| LaF ₃ | >99.9% | Grirem Advanced Materials Co.,Ltd |
| NdF ₃ | >99.9% | Grirem Advanced Materials Co.,Ltd |
| La ₂ O ₃ | >99.9% | Grirem Advanced Materials Co.,Ltd |
| Nd ₂ O ₃ | >99.9% | Grirem Advanced Materials Co.,Ltd |
| LiF | >99.9% | Sinopharm Chemical Reagent Co.,Ltd |

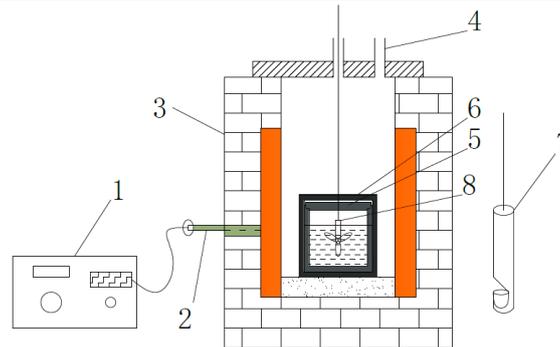


Fig. 1 The furnace system of experiment

1-Temperature controller; 2-Thermocouple for Temperature control; 3-High temperature furnace; 4-Argon inlet; 5-lid; 6-Protective cover; 7-Sampler; 8-Stirring paddle

3. Results and discussion

Chemical titration is one typical laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified analyte. The determination of concentration of REO in RE_F₃-LiF-REO melts usually consists of three steps: preparation of samples for testing, samples dissolving in chemical reagents and chemical titration. However, due to the complex chemical reaction and limited solubility of REO in the RE_F₃-LiF melts, excessively adds REO in melts will lead to the precipitation and even the slag of REOF [23]. So, the supernatant was taken after settling the melts for minutes which can ensure the solid-liquid separation. The samples dissolving in chemical reagents is a process that need to consume nitric acid, perchloric acid and so on. The RE_{wt%} of the supernatant could be calculated by the followed equation.

$$RE_{wt\%} = \frac{T \times V}{W \times 1000} \times 100\% \quad (1)$$

Where *W* is the mass of the sample in g; *T* is the titre of EDTA for La in mg/mL, $T = M \times M_{RE}$, *M* is the molarity of EDTA, *M_{RE}* is the atomic mass of RE; *V* is the consumption of EDTA in mL.

The isothermal and saturated method combining chemical titration has been used by researchers for studying solubility of REO in different rare earth fluoride melts. Wu et al [12] have researched on solubility of mish REO in LiF-BaF₂-REF₃ melts. They found that the solubility of REO was 2% wt-4% wt with the temperature ranged 900-1040°C. Hu [11] has reported the solubility and dissolution rate of Nd₂O₃ in NdF₃-LiF-Nd₂O₃ melts. In present study, the changing law of RE concentration in 40mol%REF₃-60mol%LiF (RE=La and Nd) melts with the continuously added REO was investigated by chemical titration analysis of the supernatant samples, and the results are shown in Fig 2.

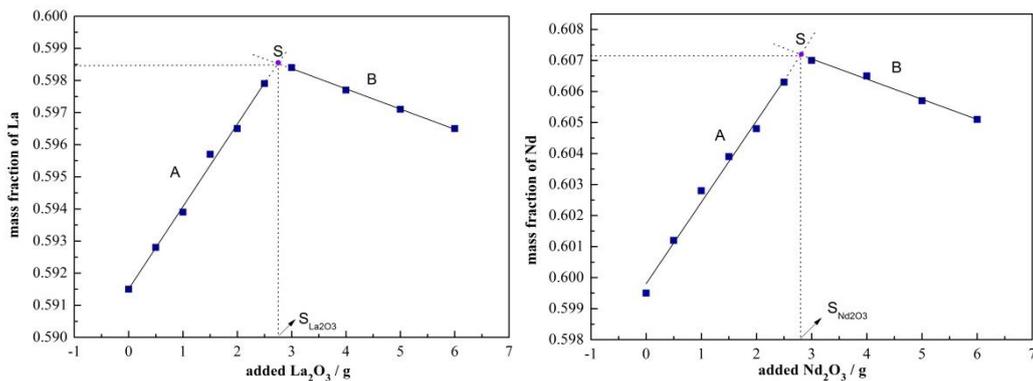


Fig. 2 Relationship between contents of RE and the added REO in the melts

From the Fig 2, one can easily find that the RE concentration linearly increased with the increasing REO and reached the maximum value at the solubility of REO, and then linearly decreased with the continuously adding REO. According to the experimental phenomena and previous references, the changing law was owing to the chemical reaction and relatively low solubility of REO in the melts. On the one hand, when the added RE_2O_3 was lower than solubility, all the added RE_2O_3 chemically reacted with melts to form REOF and then completely dissolved in the melts. On the other hand, when the added RE_2O_3 was higher than solubility, to add RE_2O_3 continuously not only didn't increase the concentration of RE ions but also reduce the content of REF_3 by form of REOF sunk to the bottom according to references [11, 22, 13]. By linear fitting the curves in Fig. 2, one can easily identify that the curves can be thought of as having two sections: the increasing segment A and the decreasing segment B. On the one hand, the fitting parameters of segment A and segment B can be used for calculation and finding intersection S between two line segments. Then, the abscissa value of intersection S represents the saturated solubility of RE_2O_3 in molten system at the definite temperature. On the other hand, the linear fitting of segment A and segment B can be considered as the standard curves and the parameters can be used for calculating REO concentration based on the measured values of RE concentration.

In present study, the REO concentration changing law in the practical electrolysis process of some electrolysis plant was measured by the method discussed above. Then the changing of REO concentration with the electrolytic time was investigated. The composition of the electrolyte was 40mol% REF_3 -60mol%LiF (RE=La and Nd), the cell voltage is 10.5 V, and the electric current is about 4200 A. The measured results are shown in Figs. 3 and 4.

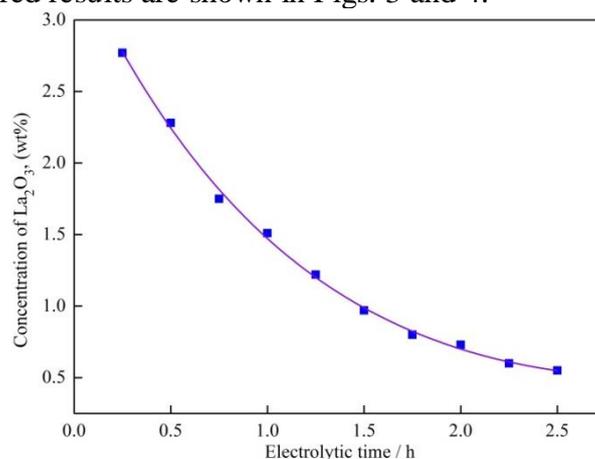


Fig. 3 Relationship between concentration of La2O3 and electrolytic time

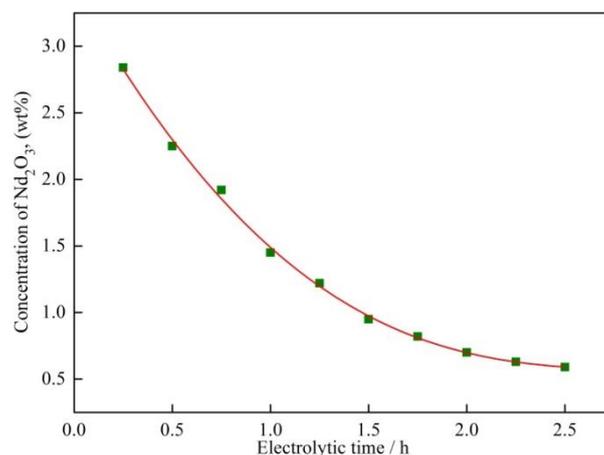


Fig. 4 Relationship between concentration of Nd₂O₃ and electrolytic time

Figs. 3 and 4 show that the concentration of REO decreases with the electrolytic time, and rate of the decreasing also declines with the electrolytic time. According to the references [8-9], the current efficiency increases with the increasing of the addition rate of REO, which can be interpretation of higher REO concentration corresponding to higher current efficiency. So it is benefit of practical production to maintain a higher concentration of REO in the molten salts electrolyte. From the Figs. 3 and 4, it is also found that the REO concentration is relatively low (lower than 1% wt) in the electrolyte when the electrolytic time reaches 1.75 h. And the changing of REO concentration after electrolysis for 1.75 h is relative lower comparing to the values of before 1.75 h. Based on the discussions above, this study recommend that the reasonable time interval of REO addition can define as 1.75 h. At present, the empirical value of time interval of REO addition is usually defined as about 2 h in the practical production, which is close to the recommended value in present study. This would also illustrate the reliability of chemical titration method for determination of concentration of REO in RE₃-LiF-REO melts. The advantage of chemical analysis is that the determined result with high accuracy as well as high reliability. However, due to a great number of chemical reagents need to be consumed in the experimental process, the approach has disadvantages of uneconomic and enviorimentally unfriendly.

4. Conclusion

The melts with the composition of 40mol% RE₃-60mol% LiF (RE=La and Nd) was taken as object for illustrating the measurement of concentration and solubility of REO by the chemical titration method. And then the changing of REO concentration in 40mol% RE₃-60mol% LiF melts with electrolytic time in practical electrolysis production was studied.

1) The concentration and solubility of REO in 40mol% RE₃-60mol% LiF melts is relatively low. The chemical titration method on determination of concentration of REO in the melts is reliability.

2) The concentration of REO decreases with the electrolytic time, and rate of the decreasing also declines with the electrolytic time. And the reasonable time interval for REO addition was recommended defining as 1.75 h which is very close to the empirical value 2 h.

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