Quantitative Study on Dissolution Behavior of Nd$_2$O$_3$ in Fluoride Melts

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1. INTRODUCTION

As its principal application, over 75% of neodymium is used in the magnet industry. Since their discovery in 1984, NdFeB magnets have been outperforming all other materials with respect to magnetic flux density. They have been applied to many advanced technologies, such as miniature high-capacity hard disk drives, compact industrial motors, electric vehicles, and wind turbines. In 2015, the total amount of rare earth metals (REMs) used in NdFeB magnets was around 25 to 30 kt. This accounts for 20% of the total rare earth consumption (calculated based on rare earth oxides). It is estimated that the global demand for rare earth metals in permanent magnets will increase to 40 kt in 2020, which means that annual growth of 7% is foreseen. Therefore, neodymium is categorized in the most critical raw materials, having the highest supply risk in the commission communication on the 2017 List of Critical Raw Materials for the European Union.

Nowadays, oxide-fluoride electrolysis is the dominant technique for the commercial production of neodymium and its alloys from neodymium oxide in both primary and secondary (recycling) production. In the process, neodymium oxide is reduced to metal at the cathode. A mixture of fluorides, mostly containing rare earth fluoride (REF), alkali metal fluoride (AF), and possibly small amounts of alkali earth metal fluorides (AEF), serves as both a solvent for neodymium oxide and an electrolyte for the electrolysis. The electrolysis conditions were found to have significant effects on the process and the current efficiency. One of the critical factors is the feeding rate of neodymium oxide, which needs to be well controlled to ensure smooth production. On the other hand, the deficiency of oxide can lead to the generation of fluorocarbon, covering the graphite anode and inhibiting the electrolysis process. On the other hand, overfeeding can cause a sludge of excess oxide at the bottom of the cell, which is detrimental to the quality of the final products.

A systematic study on the dissolution behavior of Nd$_2$O$_3$ in molten fluorides can lead to an improved understanding of its dissolution mechanisms and a quantitative description of the dissolution rate, which would provide crucial theoretical support for feeding control in the industrial production. However, research on the interaction between rare earth oxides and molten salts is almost blank. Stefanidaki et al. and Hu studied the products of the interaction between Nd$_2$O$_3$ and fluoride melt with Raman spectroscopy and found the formation of M−O−F (M = metal) complex anions during Nd$_2$O$_3$ dissolution. A previous study investigated the interactions of Nd$_2$O$_3$ with molten CaCl$_2$ and CaF$_2$−LiF. It is found that Nd$_2$O$_3$ reacted vigorously with CaCl$_2$ to form NdOCl, while Nd$_2$O$_3$ gradually dissolved in molten CaF$_2$−LiF. However, a quantitative discussion of the dissolution process was missing. In the present study, the dissolution of Nd$_2$O$_3$ particles in molten fluorides is investigated with confocal scanning laser microscopy (CSLM), which provides in situ observation of the dissolution process. This research focuses on understanding the dissolution mechanisms, examining both qualitatively and quantitatively the influencing factors, i.e., temperature, salt type, and composition, and...
providing a method for predicting the dissolution rate of Nd₂O₃ in LiF-NdF₃.

2. EXPERIMENTAL PROCEDURES

2.1. Materials. The chemicals used in the CSLM experiments are produced by Alfa Aesar with a purity of 99.95 wt % (more than 250 K/min) and cooling rate (more than 500 K/min). Each test began with melting the master salt pieces in a molybdenum crucible. After cooling down, a flat surface was formed. The depth of the melt was about 5 mm, which means that the whole particle can be immersed in the melt during dissolution as its density is higher than the melt, and it should be settled on the bottom of the crucible. The melts used in this study are transparent, which allows easy observation of the particle underneath. Therefore, there is no limitation on the depth of the melt as long as the whole particle can be immersed in it. After melting the master salt in the crucible, a Nd₂O₃ particle was placed on the surface. This started the in situ observation of the dissolution process. The observed images were recorded by a camera at a rate of one frame per second for analysis.

Frequently, the particles made in-house were not perfectly spherical as seen in Figure 1. However, the study on particles with irregular shapes that can be approximated to distorted spheres showed that this imperfection would not significantly alter the dissolution curve, and the total dissolution time is the same as the spherical particles with equivalent radii. Therefore, the equivalent radius was applied in postanalysis. The dissolution curve, and the total dissolution time is the same as the spherical particles with equivalent radii. Therefore, the equivalent radius was applied in postanalysis. It was calculated based on the measured 2D area using an image processing software, ImageJ, with which a border was drawn around the particle, as shown in Figure 2. To minimize the systematic errors in generating the borders, an average was taken from three repeats was used in the kinetic study.

Figure 2 is a series of CSLM images taken from the experiments, showing the dissolution of a Nd₂O₃ particle in KF-23NdF₃ at 1141 K. The dashed lines indicate the border of the particle. The shrinkage of the particle can be clearly seen in the images. The equivalent radius of the particle can then be estimated according to the area enclosed by the lines. The left-up corner of the CSLM images shows the time from experiment beginning and the measured temperature. The starting of the dissolution process is when the set temperature is reached. The particle size changing with time can be extracted from 50 to 100 CSLM images with specific time intervals. This relationship will be further analyzed to reveal the dissolution mechanisms and related kinetic parameters.

2.2. Experimental Apparatus and Procedures. The in situ observations of the dissolution were conducted with a CSLM-IIF microscope (Lasertec, 1LM21M-SVF17SP). A detailed description of the equipment was given in our previous work. The heating profile was programmed with HiTOS software and controlled by a REX-P300 controller. The heating component is a halogen lamp located at the lower focal point of the elliptical chamber. It can offer a very high heating rate (more than 250 K/min) and cooling rate (more than 500 K/min). A sample holder is placed at the upper focal point of the chamber. The temperature of samples is measured by a B-type thermocouple welded at the bottom of the holder. The experiment temperature was calibrated by measuring the melting points of four standard pure metals, i.e., copper, nickel, palladium, and iron. The actual temperature of the sample was found to be 18 K higher than the measured value in the temperature range of this study. The temperatures indicated in this paper are the actual values.

The CSLM tests were performed under argon (purity >99.99%) atmosphere. The chamber was evacuated and refilled with high purity argon three times to ensure a low oxygen level. Each test began with melting the master salt pieces in a molybdenum crucible. After cooling down, a flat surface was formed. The depth of the melt was about 5 mm, which means that the whole particle can be immersed in the melt during dissolution as its density is higher than the melt, and it should be settled on the bottom of the crucible. The melts used in this study are transparent, which allows easy observation of the particle underneath. Therefore, there is no limitation on the depth of the melt as long as the whole particle can be immersed in it. After melting the master salt in the crucible, a Nd₂O₃ particle was placed on the surface. This started the in situ observation of the dissolution process. The observed images were recorded by a camera at a rate of one frame per second for analysis.

Figure 1 is a series of CSLM images taken from the experiments, showing the dissolution of a Nd₂O₃ particle in KF-23NdF₃ at 1141 K. The dashed lines indicate the border of the particle. The shrinkage of the particle can be clearly seen in the images. The equivalent radius of the particle can then be estimated according to the area enclosed by the lines. The left-up corner of the CSLM images shows the time from experiment beginning and the measured temperature. The starting of the dissolution process is when the set temperature is reached. The particle size changing with time can be extracted from 50 to 100 CSLM images with specific time intervals. This relationship will be further analyzed to reveal the dissolution mechanisms and related kinetic parameters.
3. RESULTS AND DISCUSSION

3.1. CSLM in Situ Observations. The dissolution of Nd₂O₃ in other melts studied in this paper was very similar to that shown in Figure 2. The dissolution was gradual, and no severe reaction was observed. No solid product was formed outside the particle during dissolution. In some cases, a change of particle shape was noticed, possibly due to differences in dissolution rate at spots with different curvature. Qualitatively, it is evident that the dissolution from convex areas is more efficient than from concave ones, resulting in the spheroidization of particles. Simulation on the shape change of a 4-fold symmetrical precipitate during dissolution confirmed the existence of the spheroidization. With the experimental results published in the same paper, the author also demonstrated that the theory could be extrapolated to three dimensions and irregular shapes. The total dissolution time of a 4-fold symmetrical precipitate is the same as that of a circular one with the same amount of solute. Therefore, the equivalent radius is calculated and applied to determine the dissolution mechanisms and related parameters.

During the dissolution, the generation of bubbles was observed, as indicated in Figure 3. The bubbles probably result from the release of trapped air in the particle. This sometimes triggered the rotation of the particle during the dissolution. To make sure that the experimental conditions are fulfilled with the requirements of the physical model for the kinetic study, the experiments were selected so as to exclude those, in which the movement triggered by the release of bubbles was visually significant. The other reason why the movement is considered
to be insignificant in this research will be discussed in the following section.

3.2. Dissolution Mechanisms. In the literature, the fluid is usually assumed to be stagnant when convection is significantly depressed. In this research, stagnant fluid is assumed because of the following reasons: 1) the particle movement is observed to be minor; 2) the sample size is relatively small to ensure insignificant temperature gradient in the fluid; 3) the heating source with a high power and a low sample amount enables high heating and cooling rates with almost negligible temperature turbulence once a set temperature is reached. Therefore, it is appropriate to assume that the fluid is stagnant as shown in related references for this type of research.\(^{16}\)

For the dissolution without solid products in a stagnant fluid, the process involves (i) the chemical reaction that transfers atoms or molecules across the phase interface and (ii) the diffusion of solute in the melt.\(^{17}\) These two steps determine the dissolution rate. In two limiting cases, the process can be reaction-controlled or diffusion-controlled.

Under the assumption of the chemical reaction controlling the dissolution process, the relationship between the radius and dissolution time is obtained as\(^{18}\)

$$\frac{r}{r_0} = 1 - \frac{t}{\tau} \quad (1)$$

where \(r\) and \(r_0\) are the actual and original particle radius in m, respectively, and \(t\) and \(\tau\) are the actual time and total dissolution time in s, respectively. The rate of dissolution \((dr/dt)\) is constant in this case and equal to \(-r_0/\tau\).\(^{16}\)

For diffusion-controlled dissolution that follows Fick’s second law, the exact solution for spheres is not available.\(^{19}\) Approximate solutions are alternatives for solving related problems. To select an appropriate approximation,\(^{20}\) the supersaturation index \(k\) is a crucial physicochemical parameter, expressing the supersaturation ratio, defined as\(^{19}\)

$$k \equiv \frac{2(C_M - C_0)}{C_p - C_f} \quad (2)$$

where \(C_M\) is the far-field concentration of the solute in the solution in mol/L, \(C_p\) is the composition of the particle in mol/L, which is taken as a constant in this study, and \(C_f\) is the equilibrium concentration of the solute at the interface in mol/L.

\(C_M\) equals the original composition of the melt. As the melt did not contain any Nd\(_2\)O\(_3\) at the beginning, \(C_M\) is zero under the experimental conditions.

\(C_p\) represents the density of the solute in the particle. If the particle contains the solute purely, \(C_p\) can be calculated directly from the particle density, which is 6.8 g/cm\(^3\) in this study.

$$C_p = \frac{6.8 \text{ g/cm}^3}{M_{Nd_2O_3} \text{ (g/mol)}} = \frac{6.8 \text{ g/cm}^3 \times 1000 \text{ cm}^3/\text{L}}{336.5 \text{ g/mol}} = 20 \text{ mol/L} \quad (3)$$

For Nd\(_2\)O\(_3\)-fluoride systems, the equilibrium concentration can be calculated via

$$C_f = \frac{5Nd_{2O_3}}{V_m} \quad (4)$$

where \(5Nd_{2O_3}\) is the solubility of Nd\(_2\)O\(_3\) in the melt in mol %, and \(V_m\) is the molar volume of the specific mixture in L/mol. The Nd\(_2\)O\(_3\) solubility in molten fluorides is low (see Table 2),\(^{21}\) which means that

$$C_f \ll C_p \quad (5)$$

### Table 2. Nd\(_2\)O\(_3\) Solubility in LiF-23NdF\(_3\)

| Parameter | Values |
|-----------|--------|
| Temperature (K) | 868 918 968 1018 |
| Solubility (mol %) | 0.24 0.28 0.33 0.38 |

The definition of \(k\) can be approximated to

$$k \approx \frac{2C_f}{C_p} \quad (6)$$

The values of \(k\) for the systems studied in this paper are listed in Table 3. Due to the lack of solubility data for other binary systems, only the \(k\) values for LiF-23NdF\(_3\) are available. It can be seen that the \(k\) values in the systems are always small, and the dissolution in such systems is governed by the concentration profile in a steady state, which is the same in one system and determined by \(C_p\), \(C_M\), and \(C_f\).\(^{20}\) This also suggests that the influence of the transition period before steady state is negligible. When a small disturbance occurs, the influence of the interruption before the establishment of a new stable concentration field is considered to be insignificant. The dissolution would continue as that before the disturbance. Screening the experiments with obvious movement, it is acceptable to hypothesize that the dissolution takes place in a stagnant fluid and the particle position is fixed.

The \(k\) values are in the range of 0.018–0.022, in which the invariance-field (IF) approximation is a good choice considering its accuracy to describe a diffusion-controlled process.\(^{20}\) In the IF approximation, the relationship between particle radius and time is described by

$$\frac{r}{r_0} = \left(1 - \frac{t}{\tau}\right)^{1/2} \quad (7)$$

The theoretical dissolution curves of interface reaction (IR) control (eq 1) and of diffusion control (eq 7) are shown in Figure 4. Comparing the experimental data with theoretical curves can reveal the rate-limiting step(s) of the dissolution.
Some representative data from the CSLM experiments are selected and shown in Figure 4. It shows that the shrinkage of the Nd2O3 particle follows the trend of the diffusion-controlled process. This confirms that the dissolution of a Nd2O3 particle in molten fluorides is diffusion-controlled, and the IF approximation can be employed to describe the dissolution process.

3.3. Diffusion Coefficient of Nd2O3 in LiF-NdF3. The total dissolution time in the case of diffusion control can be calculated by

$$\tau = \frac{r_0}{kD}$$

(8)

In this paper, the Nd2O3-fluoride system is treated as a quasibinary system of a solute (Nd2O3) and a solvent (the binary melt). The diffusion coefficient D represents the effective diffusion of Nd2O3 in the melt.

With the experimental data, including the total dissolution time, original particle radius, and k values, it is possible to calculate the diffusion coefficients (see Table 3 and Figure 5). Expectedly, the diffusion coefficients increase with temperature, indicating enhanced diffusion at high temperature. The diffusion coefficient correlates with temperature, following the Arrhenius equation

$$D = D_0 \exp \left( -\frac{E_A}{RT} \right)$$

(9)

where $D_0$ is the pre-exponential factor in m²/s, R is the universal gas constant, and $E_A$ is the activation energy for diffusion in J/mol. The fit of eq 9 to the experimental data in Figure 5 yields an activation energy of 68 kJ/mol for diffusion and a pre-exponential factor $D_0 = 3.2 \times 10^{-6}$ m²/s. Thus, in LiF-23NdF₃, the diffusion coefficient of Nd₂O₃ can be calculated via

$$D_{Nd_2O_3} = 3.2 \times 10^{-6} \text{ m}^2/\text{s} \times \exp \left( -\frac{6.8 \times 10^4 \text{ J/mol}}{RT} \right)$$

(10)

With the k values and eq 10, it is possible to estimate the total dissolution time of Nd₂O₃ particles in LiF-23NdF₃ in the temperature range of 1141–1291 K. These parameters are also essential for the numerical simulations of more complex processes, for instance, the dissolution of feed materials in an industrial electrolytic cell with forced mixing effects introduced by generated CO and CO₂ bubbles at the anodes during electrolysis.

For dilute solutions, the diffusion coefficient is often viewed as a parameter independent of composition. The Nd₂O₃ solubility in LiF-NdF₃ is quite low, and it is, therefore, reasonable to assume that the diffusion coefficient remains unchanged in LiF-NdF₃ melts with different NdF₃ concentrations. To validate this hypothesis, the Nd₂O₃ solubility is calculated, assuming that the diffusion coefficient is independent of salt composition. The results are listed in Table 3 and shown in Figure 6. Assuming a linear relationship of the solubility to NdF₃ concentration yields a rather good fitting ($R^2 = 0.97$). The gap between the second point and the fitted line suggests that this is a bad datum, and the experiment needs repeating. As other data have already demonstrated the

![Image](image_url)

Table 3. Summary of Experimental Conditions and Related Parameters

| melt         | T (K) | $C_i$ (mol/L) | $C_m$ (mol/L) | $C_F$ (mol/L) | $k$     | $r_0$ (μm) | $\tau$ (s) | $kD$ ($10^{-6}$m²/s) | $D$ ($10^{-6}$m²/s) |
|--------------|-------|---------------|---------------|---------------|---------|------------|------------|----------------------|---------------------|
| LiF-23NdF₃  | 1141  | 0.18          | 0             | 20            | 0.017   | 233        | 1210       | 0.45                 | 26                  |
| LiF-23NdF₃  | 1191  | 0.20          | 0             | 20            | 0.019   | 312        | 1486       | 0.65                 | 34                  |
| LiF-23NdF₃  | 1241  | 0.21          | 0             | 20            | 0.021   | 309        | 902        | 1.1                  | 49                  |
| LiF-23NdF₃  | 1291  | 0.22          | 0             | 20            | 0.023   | 338        | 851        | 1.3                  | 59                  |
| LiF-20NdF₃  | 1241  | 0.20          | 0             | 20            | 0.021   | 279        | 772        | 1.01                 | 49                  |
| LiF-15NdF₃  | 1241  | 0.15          | 0             | 20            | 0.015   | 258        | 900        | 0.74                 | 49                  |
| LiF-10NdF₃  | 1241  | 0.14          | 0             | 20            | 0.014   | 265        | 1026       | 0.68                 | 49                  |
| LiF-5NdF₃   | 1241  | 0.03          | 0             | 20            | 0.003   | 235        | 3439       | 0.16                 | 49                  |
| NaF-23NdF₃  | 1141  | 0             | 0             | 20            | 0.00   | 240        | 1827       | 0.32                 |                     |
| KF-23NdF₃   | 1141  | 0             | 0             | 20            | 0.00    | 243        | 5338       | 0.11                 |                     |

“*The solubility was obtained from ref 22, and the density of the melt was calculated according to the data from ref 9. The solubility to NdF₃ concentration yields a rather good fitting ($R^2 = 0.97$). The gap between the second point and the fitted line suggests that this is a bad datum, and the experiment needs repeating. As other data have already demonstrated the
Figure 6. Solubility of Nd₂O₃ in LiF-NdF₃ at 1241 K.

Figure 7. Product KD determining Nd₂O₃ dissolution in LiF-23NdF₃, as a function of temperature.

linearity, the bad datum can be ignored in this paper. This linear relationship agrees well with the conclusion from ref 21, which confirms that a composition-independent diffusion coefficient is a valid assumption. With this conclusion, it is possible to extend the application of the diffusion coefficient obtained previously. This means that eq 10 can be applied to estimate the diffusion coefficient of Nd₂O₃ in LiF-NdF₃ melt with 5–23 mol % NdF₃ at 1141–1291 K.

3.4. Influencing Factors. 3.4.1. Temperature. According to eq 8, the total dissolution time is inversely proportional to the value of KD, suggesting that Nd₂O₃ particles dissolve faster in the melts with higher KD values. The factors that influence the diffusion coefficient D and supersaturation ratio k determine the dissolution rate. In this study, the diffusion coefficient is a function of temperature and is independent of salt composition (eq 10). According to the definition of k (eq 2), it is a parameter correlated to the solubility of Nd₂O₃, molar volume, and composition of the melt. The Nd₂O₃ solubility and molar density are functions of temperature and salt composition. Thus, the influence of these factors, i.e., temperature and salt composition, will be discussed based on the experimental observations in the following sections.

The product of D and k in LiF-23NdF₃ at different temperatures have been derived by means of eq 8 from the observed completion time τ in combination with the initial radius r₀. The results are shown in Figure 7. The KD values increase with temperature, suggesting that the dissolution rate is enhanced at elevated temperatures.

The effects of temperature on the diffusion coefficient are given in eq 10. It is evident that the diffusion coefficient increases with temperature. According to the experimental conditions, Nd₂O₃ was not present in the original melts, i.e., aCM = 0. The influence on the k values merely reflects the change of the solubility and molar volume.

The previous research²² shows that the relationship between solubility and temperature can be expressed as

\[ s_{\text{NdO}_3} = x \exp \left( - \frac{A}{RT} \right) \]  

where \( x \) is a function related to the melt composition, and \( A \) is a positive constant in J/mol. For LiF-NdF₃ melt,²² the Nd₂O₃ solubility can be calculated via

\[ s_{\text{NdO}_3} (\text{mol} \%) = (1.1x_{\text{NdF}_3} - 0.12x_{\text{LiF}}) \exp \left( - \frac{40 \text{kJ/mol}}{RT} \right) \]  

where \( x_i \) is the mole fraction of compound \( i \) in the original melt without dissolved Nd₂O₃. It is easy to figure out that the Nd₂O₃ solubility in LiF-NdF₃ increases with temperature.

The melt density has a linear relationship with temperature, expressed as²³

\[ \rho = a - bT \]  

where \( \rho \) is the melt density in g/cm³ at temperature \( T \), and \( a \) and \( b \) are two positive constants. The relationship shown in eq 13 is retained for both pure compounds and mixtures. The values of \( a \) and \( b \) depend on melt composition. The molar volume is correlated to the density via

\[ V_m = \frac{M}{1000\rho} \]  

where \( M \) is the molecular weight in g/mol. According to eqs 13 and 14, the melt density decreases with temperature, while the molar volume increases with temperature.

The solubility of Nd₂O₃ in fluorides is somewhat limited, usually far less than 1 mol %.²² Its influence on the molar volume of the salts can be ignored. In this paper, the solution with dissolved Nd₂O₃ will be treated as a quasi-binary salt system for density calculations. Due to the lack of the density data of LiF-NdF₃ melt, its molar volume will be calculated from the density of pure LiF and NdF₃. The molar volume of an ideal binary mixture can be calculated from

\[ V_m = x_1V_{m1} + x_2V_{m2} \]  

where \( V_{m1} \) and \( V_{m2} \) are the molar volumes of the respective components. For AF-REF binary systems containing LiF, the real values agree quite well with the estimated values from ideal mixtures.²³ In this paper, all binary salts will be treated as ideal mixtures when calculating their molar volumes.

The values of the parameters in eq 13 are obtained for LiF and NdF₃ from ref 9, see Table 4. These parameters are used for calculating the molar volume of LiF and NdF₃ at different temperatures.

Combining eqs 12–15 and parameters in Table 4, the k values in LiF-NdF₃ with different NdF₃ concentrations and at different temperatures are calculated and shown in Figure 8. It is clear that the k values increase with temperature in the temperature and composition range concerned.

As shown in Figure 5 and Figure 8, both k and D in LiF-NdF₃ melt increase with temperature in the temperature range.
of this study. Increasing temperature can accelerate the dissolution of NdO_3 in LiF-NdF_3 melt. With the increase in NdF_3 content, the dependence of \( k \) on temperature becomes more significant (Figure 8). This influence extends to the dissolution rate, and the temperature has more impacts on the dissolution rate in the melt with higher NdF_3 content.

3.4.2. NdF_3 Concentration. The dissolution of NdO_3 in LiF-NdF_3 melts with different NdF_3 concentrations was observed, and the results show that increasing NdF_3 concentration can accelerate the dissolution (see Table 3). It can be found that the \( kD \) values increase with varying NdF_3 concentration as shown in Figure 9.

As discussed previously, the diffusion coefficient is independent of the salt composition. Therefore, the influence of NdF_3 concentration mainly acts on the \( k \) values, more precisely, on the NdO_3 solubility and molar volume of the melt.

According to eqs 11 and 12, the NdO_3 solubility is proportional to the NdF_3 concentration in LiF-NdF_3 melt.\(^{21}\) Even though eq 12 is not suitable to estimate the solubility in LiF-NdF_3 with a NdF_3 concentration lower than 10 mol %, the proportional relationship between the solubility and NdF_3 concentration is retained.\(^{21}\) Thus, the solubility can be expressed as

\[
s_{NdO_3} = m + nx_{NdF_3}
\]  

where \( m \) and \( n \) are constants. Per eq 15, the molar volume of LiF-NdF_3 can be calculated via

\[
V_{m(LiF-NdF_3)} = x_{LiF}V_{m(LiF)} + x_{NdF_3}V_{m(NdF_3)} = V_{m(LiF)} + (V_{m(NdF_3)} - V_{m(LiF)})x_{NdF_3}
\]  

where the molar volume of LiF and NdF_3, i.e., \( V_{m(LiF)} \) and \( V_{m(NdF_3)} \), can be obtained based on the data in Table 4. Therefore, the composition dependence of \( k \) can be expressed as

\[
\frac{\partial k}{\partial x_{NdF_3}} = \frac{2}{C_p} \frac{\partial C_i}{\partial x_{NdF_3}} = \frac{2}{C_p} nV_{m(LiF)} - m(V_{m(NdF_3)} - V_{m(LiF)}) \left[ V_{m(LiF)} + (V_{m(NdF_3)} - V_{m(LiF)})x_{NdF_3} \right]^2 = \epsilon
\]  

Thus,

\[
\frac{\partial (kD)}{\partial x_{NdF_3}} = D \frac{\partial k}{\partial x_{NdF_3}} = \epsilon D
\]  

The experimental results (Table 3 and Figure 9) show that the value of \( kD \) increases with NdF_3 concentration, which indicates that \( \epsilon \) is positive. In addition, \( \epsilon \) is a parameter decreasing with increasing NdF_3 concentration, indicating that the gradient of the curve decreases with increasing concentration. The shape of the trend line in Figure 9 is consistent with this conclusion.

3.4.3. Alkali Metal Fluorides. Figure 10 shows the influence of the type of alkali metal fluoride on NdO_3 dissolution in AF-23NdF_3.

\[
\text{Figure 8. Calculated } k \text{ values in LiF-NdF}_3 \text{ with different NdF}_3 \text{ concentrations and at different temperatures.}
\]

\[
\text{Figure 9. Experimental values of } kD \text{ as a function of NdF}_3 \text{ concentration in LiF-NdF}_3 \text{ at 1241 K (the solid line is a guide to the eye).}
\]

\[
\text{Figure 10. Influence of type of alkali metal fluoride on NdO}_3 \text{ dissolution in AF-23NdF}_3 \text{ at 1141 K.}
\]
\[ V_{m(LiF)} < V_{m(NaF)} < V_{m(KF)} \]  
According to eq 15, it can be derived that
\[ V_{m(LiF-23NdF)} < V_{m(NaF-23NdF)} < V_{m(KF-23NdF)} \]
(20)

The solubility of rare earth oxides is found to be associated with the charge density of the cations in the melt.\textsuperscript{23} With higher charge density, it is more likely to form stable M–O–F (M = metal) complex anions, which are the products of the interaction between Nd\textsubscript{2}O\textsubscript{3} and the fluoride melt.\textsuperscript{22} Higher concentration of the M–O–F complex in the Nd\textsubscript{2}O\textsubscript{3}–fluoride system means that the melt dissolves more Nd\textsubscript{2}O\textsubscript{3}. The concentration of NdF\textsubscript{3} is the same in these three melts. Given the same Nd\textsuperscript{3+} concentration, it only needs to compare the charge density of the other cation in the melt. As indicated in ref 22, the charge density decreases in the order of Li\textsuperscript{+}, Na\textsuperscript{+}, and K\textsuperscript{+}. It can be inferred that the Nd\textsubscript{2}O\textsubscript{3} solubility should decrease in the order of LiF-23NdF\textsubscript{3}, NaF-23NdF\textsubscript{3}, and KF-23NdF\textsubscript{3}, i.e.,
\[ s_{LiF-23NdF} > s_{NaF-23NdF} > s_{KF-23NdF} \]
(21)

According to eq 4, this implies
\[ C_i(LiF-23NdF) > C_i(NaF-23NdF) > C_i(KF-23NdF) \]
(22)
As per its definition (eq 6), the parameter \(k\) of the systems follows the order
\[ k_{LiF-23NdF} > k_{NaF-23NdF} > k_{KF-23NdF} \]
(23)

Since absolute \(k\) values are not available, it is not possible to obtain the diffusion coefficient in NaF/KF-23NdF\textsubscript{3}. Nevertheless, the dissolution experiments in this study confirm that LiF-NdF\textsubscript{3} is a suitable solvent for Nd\textsubscript{2}O\textsubscript{3} regarding kinetic aspects. Also, the solubility in LiF-NdF\textsubscript{3} is higher than that in NaF/KF-23NdF\textsubscript{3}, which means that the former is a better solvent considering the thermodynamic factor. As an electrolyte, the addition of LiF can improve the electrical conductivity of the melt due to the low resistance of movement and high mobility of Li\textsuperscript{+} cation.\textsuperscript{9} Considering all these advantages, LiF-NdF\textsubscript{3} is justifiably chosen as the primary electrolyte for electrowinning neodymium in industrial production.

4. CONCLUSIONS

In this research, the dissolution behavior of Nd\textsubscript{2}O\textsubscript{3} particles in molten fluorides was investigated via in situ observation with CSLM, providing a better understanding of the dissolution mechanisms and its influencing factors, i.e., temperature, salt type, and composition, and offering a method to estimate the dissolution time in LiF-NdF\textsubscript{3} melt. The main conclusions can be formulated as follows:

1) The dissolution of Nd\textsubscript{2}O\textsubscript{3} in molten fluoride is a diffusion-controlled process. The diffusion coefficient increases from 2.6 \times 10^{-9} to 5.9 \times 10^{-8} m\textsuperscript{2}/s when the temperature rises from 1141 to 1291 K, and the activation energy is determined to be 68 kJ/mol.

2) Increasing temperature and NdF\textsubscript{3} concentration in LiF-NdF\textsubscript{3} melt can accelerate the dissolution, while LiF-23NdF\textsubscript{3} is shown to be a better solvent for Nd\textsubscript{2}O\textsubscript{3} than NaF-23NdF\textsubscript{3} and KF-23NdF\textsubscript{3} regarding the dissolution rate.

3) The activation energy for diffusion and the pre-exponential factor \(D_0\) obtained are two critical parameters in this kinetic study. Together with solubility and density data, it is possible to estimate the total dissolution time of Nd\textsubscript{2}O\textsubscript{3} in LiF-NdF\textsubscript{3} melt with 5–23 mol % NdF\textsubscript{3} in the temperature range of 1141–1291 K.

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