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Relationship between the dissolution behaviours and current efficiencies of La, Ce, Pr and Nd in their chloride molten salts

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Abstract

The dissolution behaviours of La and Nd in their chloride molten salts were studied by means of the see-through cell, electrochemical weak polarization and quantum chemistry (extended Hückel molecular orbital). The reasons for the low current efficiencies of rare earth metals and the difference between La and Nd in their own chloride electrolytes on the basis of the solubility, rate of dissolution, and existing state of the metals dissolved as well as the structure of the melts, are discussed.

Keywords: Dissolution behaviour; Current efficiency; Rare earth; Molten salt; Quantum chemistry

1. Introduction

It was found in our previous work that current efficiencies of rare earth metals were rather low and there existed a big difference among Ln (rare earth) metals in the electrolysis of molten chlorides. The current efficiency of light rare earth metals decreases significantly from La to Sm, and even no metal Sm can be obtained. The Sm and Nd are harmful elements for the current efficiency of mischmetal [1]. Studies of the electrode process were carried out in order to explain some electrochemical phenomena [2,3]. The dissolution of the deposited metal as well as the second oxidation are responsible for the low current efficiency in the electrolysis of molten salts. The interactions between rare earth metals and their own molten salts were mainly studied from the thermodynamic properties [4,5]. In this work, the dissolution behaviours of La (Nd) in LaCl_3 (NdCl_3) + KCl, taken as a typical example, were investigated using the see-through cell, electrochemical weak polarization and quantum chemistry (extended Hückel molecular orbital (EHMO)). The reasons for the low current efficiency for La and Nd in the electrolysis of their molten chlorides are discussed from the viewpoint of the dissolution behaviours of La and Nd in the melts.

2. Experimental details

In order to observe visually the dissolution behaviours of metallic La and Nd in their chloride melts, a see-through quartz cell with size of 40 mm \times 40 \times 75 mm was designed, so that the motion of "metal fog" during the dissolution processes of metals could be investigated by visual observation or photography. The electrochemical corrosion of the metals was studied by measuring the weak electrochemical polarization with an HA-501 potentiostat. The molten electrolytes consist of $x\text{LaCl}_3(x\text{NdCl}_3) + y\text{KCl}$ (KCl, NaCl). The purity of both La and Nd metal was above 99.5%. All experiments were performed under the protection of inert Ar with a purity of 99.999%.

The method of quantum chemical EHMO calculation was taken from Ref. [6]. The parameters required in the EHMO calculation were taken from Refs. [7,8].

3. Results and discussion

3.1. Relationship between the current efficiency and solubility

Both the current efficiency and the solubility [9] are listed in Table 1 for the metals La, Ce, Pr and Nd in their chloride molten salts. It can be seen from Table 1

Table 1
Relationship between the current efficiency and solubility

Ln metal	Molten salts	Solubility (metal at. (mol salt) ⁻¹)	Current efficiency (%)
La	LaCl ₃	12	80
Ce	CeCl ₃	9	77
Pr	PrCl ₃	22	60
Nd	NdCl ₃	31	30

that the current efficiency decreases significantly with the increase in solubility of the rare earth metals in their own chlorides. Therefore, it was certain that some of the metals electrolysed would be dissolved into molten salts: the greater the solubility of the metal, or the larger the loss of it, the lower the current efficiency. It is also found that there are large differences in the current efficiency among rare earth metals, especially between La and Nd.

3.2. Visual observation of dissolution of La and Nd in their molten chlorides

3.2.1. Dissolution of La (Nd) in LaCl₃ (NdCl₃)–KCl melts

It is usually very difficult to observe visually the formation processes of the rare metal fog in halide melts because of the corrosion and easier oxidation as well as sensitivity to water at high temperature. We have first observed and photographed the La and Nd metal fogs in a specialized see-through quartz electrolysis bath.

A weighed sample of electrolyte with composition 40 wt.% NdCl₃ + 60 wt.% KCl was melted in a quartz cell under the protection of gas at 850 °C. When clean Nd metal was placed into the transparent NdCl₃–KCl melt, which was light pink in colour, a substance like black smog, the metal fog shown in Fig. 1(a), rose rapidly and then spread out in all directions from the surface of the metallic Nd. After dissolution for about

60 s, the melt was full of the black metal fog and was not be transparent. The behaviour of the dissolution of La in LaCl₃–KCl melt was similar to that of Nd. In the former experiment, the white transparent molten salt LaCl₃ + KCl was completely filled with the black La metal fog and no longer transparent within a dissolution time of 90 s. Although black metal fog is formed for both La and Nd in their molten salts, the dissolution rate of Nd is much higher than that of La.

3.2.2. Dissolution of La (Nd) in LaCl₃ (NdCl₃)–KCl molten salt under electrolysis

The dissolution behaviours of La and Nd in their own molten salts have been described above. If we found that the metal fog of La or Nd occurs during the electrolysis, the course of the lower current efficiency could be explained directly. In this experiment, after the graphite anode and metal Nd cathode were inserted into NdCl₃–KCl electrolyte, the electrolysis was carried out with a bath voltage of 7.0 V and a current density of 7.0 A cm⁻². It could be seen that the black metal fog evolved slowly from the surface of metal Nd cathode, as shown in Fig. 1(b). The dissolution rate of the metal was not as high as that without electrolysis. When the metal fog approached the bottom surface of the anode, some of it rose continuously along the path between the anode and the bath wall, and the rest facing vertically the graphite anode rose slowly as a result of the obstruction of flowing electrolyte. After electrolysis for 90 s or so, the whole melt was full of the metal fog and no longer transparent. The behaviour of La metal fog was analogous to that of Nd metal fog under electrolysis, but it took about 120 s to spread out gradually throughout the entire molten salt electrolyte and to be no longer transparent during electrolysis.

According to the above studies, it can be concluded that the dissolution and diffusion of La and Nd in the melts still occur under the protection of cathodic polarization. The dissolution rate of Nd is faster than that of La in their own melts. The dissolved La and Nd may exist in the form of particles with different valences.

3.3. Electrochemical corrosion of La (Nd) in the LaCl₃ (NdCl₃)–KCl, NaCl system

Although it is noticed that there is a serious corrosion phenomenon in molten salts at high temperature, few results on the electrochemical corrosion of La (Nd) in LaCl₃ (NdCl₃)–KCl, NaCl have been reported. In this section, the dynamic parameters of the electrochemical corrosion of La (Nd) in the composition 32 wt.% LaCl₃ (NdCl₃) + 68 wt.% KCl, NaCl were studied by measuring the weak electrochemical polarization.

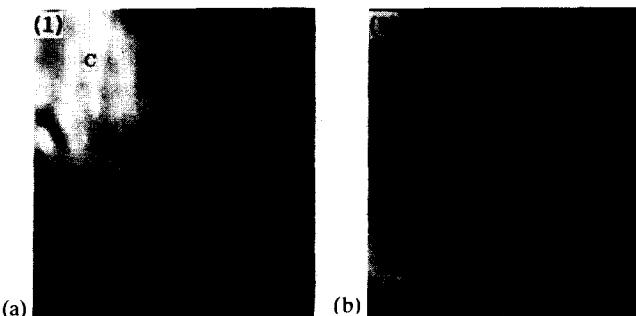


Fig. 1. (a) Dissolution of the metal Nd into molten salt NdCl₃ + KCl (A, metal fog; B, metal Nd; C, pink molten salt electrolyte NdCl₃ + KCl) and (b) under electrolysis (D, metal fog; E, metal Nd cathode; F, graphite anode; G, electrolyte NdCl₃ + KCl).

After the electrolyte was melted at 800 °C, the metal La (or Nd) working electrode, Ag/AgCl ($x = 0.1$) reference electrode and Pt counterelectrode were inserted into the molten salt. It was found that the corrosion potentials of La and Nd remained stable at -1795 mV and -1733 mV at 800 °C and -1729 mV and -1679 mV at 860 °C, respectively. The dynamic parameters of electrochemical corrosion were calculated according to the dynamic electrochemical corrosion equation

$$i_A = i_{\text{corr}}[\exp(-E/b_a) - \exp(-E/b_c)]$$

and are listed in Table 2. The corrosion current density i_{corr} of metallic La or Nd in the molten salt is greater at high temperature than that at low temperature. This means that the rate of electrochemical dissolution increases with increasing temperature. The rate of corrosion dissolution of Nd is much higher than that of La, which is consistent with the conclusion based on the behaviours of their metallic fogs as mentioned above. On the contrary, there is no obvious variation in the electrochemical corrosion processes between La and Nd because the ratio b_a/b_c changes little.

3.4. Quantum chemical extended Hückel molecular orbital calculation

As we found above, the dissolution process of La (or Nd) in its own chloride still occurs even though the metal La or Nd electrode is polarized cathodically. It is implied that the La (or Nd) atoms react chemically with La^{3+} (or Nd^{3+}) in the melt. The mechanism of interaction between La (or Nd) and La^{3+} (or Nd^{3+}) was further studied by EHMO quantum chemical calculation. The 2La^{3+} –La and 2Nd^{3+} –Nd atomic clusters were taken into account for the EHMO calculation. It is found by the calculation that the net charge of each particle in La_3^{6+} and Nd_3^{6+} is about +2.0. Therefore, the dissolved La, Nd really reacts chemically with La^{3+} , Nd^{3+} ions respectively in their own chloride. In fact, the present authors [10] confirmed by X-ray diffraction analysis that different particles, such as $\text{NdCl}_{2.27}$, $\text{NdCl}_{2.37}$, NdCl_2 and La^{2+} , exist in the melt containing the metal fog.

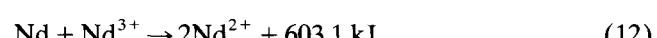
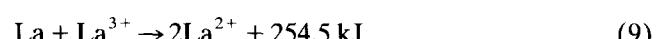
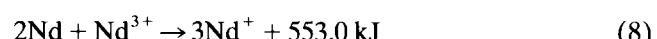
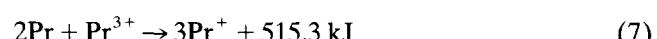
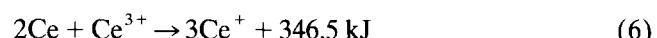
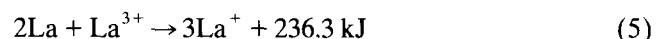
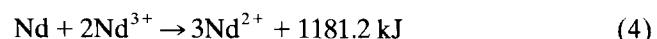
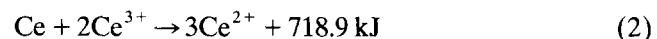
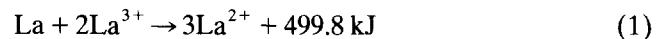
Table 2
Dynamic parameters of electrochemical corrosion of metallic La and Nd

System	Temperature (°C)	i_{corr} (mA cm $^{-2}$)	b_a (mV)	b_c (mV)
La + LaCl_3 –KCl, NaCl	800	17.4	57.8	51.9
Nd + NdCl_3 –KCl, NaCl	800	29.9	74.9	85.5
La + LaCl_3 –KCl, NaCl	860	26.0	62.1	67.7
Nd + NdCl_3 –KCl, NaCl	860	46.9	74.8	86.1

It is known that La^{3+} (or Nd^{3+}) has one more vacant valence electron orbital than La^{2+} (or Nd^{2+}). When the La^{3+} (or Nd^{3+}) and La^{2+} (or Nd^{2+}) approach each other, the covalent bond between La^{3+} (or Nd^{3+}) and La^{2+} (or Nd^{2+}) may be made due to the delocalization of valence electrons. The electron populations obtained from EHMO calculations are listed in Table 3. It can be seen that a tendency for covalent bonds to form between La^{3+} (or Nd^{3+}) and La^{2+} (or Nd^{2+}) exists to a certain extent. A quantum chemical self-consistent field DVX calculation also proved the possibility of interaction between Nd^{3+} and Nd^{2+} ions [11]. The atomic cluster ions Ln_m^{n+} may be formed among Ln^{2+} and Ln^{3+} ions in the melt. Xu et al. [12] showed by the method of Monte Carlo computer simulation that the atomic cluster ion Ln_m^{n+} is probably formed in the La– LaCl_3 –KCl system. The formation of atomic cluster ions Ln_m^{n+} will be beneficial to the dissolution of metallic Ln in the molten salt.

3.5. The thermochemical calculation

Thermal effects of reactions between the Ln atom and its cation were also calculated according to their ionization potentials [13] as follows:



The above exothermic reactions also indicate that the Ln^{2+} ion is more stable than other ions, which is

Table 3
Results of quantum chemical extended Hückel molecular orbital calculation

System	Internuclear distance (Å)	Electron population
La^{2+} + La^{3+}	2.19	0.407
Nd^{2+} + Nd^{3+}	2.18	0.180

consistent with the result obtained from EHMO quantum chemical calculation as well as X-ray diffraction analysis. The amount of exothermicity increases with the following order of elements: La, Ce, Pr and Nd.

4. Conclusion

With the increase in the solubility of La, Ce, Pr and Nd in their own chloride molten salts, the current efficiency decreases rapidly. The formation of the metal fog is due to the dissolution of metal into the chloride molten salt.

It is concluded that the dissolution and electrochemical corrosion of Nd are much faster than those of metallic La in their own chloride molten salts. The dissolution of rare earth metallic La or Nd in the melt, in fact, is due to chemical reaction and electrochemical processes between the Ln atom and the Ln^{3+} ion. According to the quantum chemical EHMO calculation and thermochemistry, the formation of Ln^{2+} ions is reasonable in chloride molten salt and the stability of La^{2+} , Ce^{2+} , Pr^{2+} as well as Nd^{2+} ions increases successively. In addition, there is also considerable tendency for atomic clusters Ln_m^{n+} to form owing to the interaction among Ln^{2+} and Ln^{3+} ions. The formation of the atomic cluster Ln_m^{n+} is further beneficial to the dissolution of the metals. Therefore, the

current efficiency of rare earth metals is usually lower in chloride molten salt.

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