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Solubility of MgO in Chloride Melts Containing NdCl₃ or LaCl₃

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ABSTRACT

Due to extremely low solubility in conventional magnesium electrolyte, MgO tends to attach to cathode and causes cathodic passivation, which will dramatically lower current efficiency of magnesium electrolysis. In this paper, NdCl₃ or LaCl₃ was added to conventional magnesium electrolyte to increase MgO solubility. We investigated the effects of NdCl₃ or LaCl₃ content, the form of MgO, and temperature on the dissolution rate of MgO and on MgO solubility. MgO solubility increased with increasing MgCl₂ content or CaF₂ content in MgCl₂ -KCl-NaCl-CaCl₂-CaF₂ melt, the maximum being only 0.145% by weight in the above melt with 30% MgCl₂ by weight. Both MgO solubility and dissolution rate increased with increasing NdCl₃ concentration in MgCl₂-NaCl-KCl-NdCl₃ melts. The MgO solubility in MgCl₂-NaCl-KCl-NdCl₃ (15% by weight) melts can reach about 3.0 wt % at 780°C. Raising temperature from 700 to 800°C can slightly increase the MgO solubility and dissolution rate. Addition of LaCl₃ to the MgCl₂-NaCl-KCl-CaCl₂-LaCl₃ melt also improved MgO solubility, but it took more time (about 60 minutes) to achieve equilibrium between MgO and LaCl₃ in the melt. Formation of the stable NdOCl compound examined by XRD analysis indicated that MgO can react with NdCl₃ in chloride melts.

INTRODUCTION

The electrolytic process will most likely be the method for future large scale magnesium production projects. The electrolyte system for magnesium production is usually composed of multiple metal chlorides including anhydrous MgCl₂. The salt lakes in western China contain large amounts of bischofite (MgCl₂.6H₂O), which is a suitable raw material for electrolysis of magnesium following complete dehydration. Anhydrous MgCl₂ readily adsorbs water, both in air and as a component of a molten electrolyte in an electrolytic cell, and reacts with water to form oxygen-bearing compounds such as MgO and MgOHCl. The presence of oxygen-bearing compounds in the electrolyte is deleterious to the operation of the

magnesium electrolysis cell (Strelets 1977; Kipouros & Sadoway 1987; Mediaas et al. 1996). MgO may sink to the bottom of the electrolysis cell and deposit as a sludge, or dissolve in the electrolyte and be involved in an anodic electrochemical reaction to form carbon oxide or carbon monoxide. $MgOH^+$ and $Mg_2(OH)_2^{2+}$ ions existing in MgOHCl, as suggested in the literature (Boghosian et al. 1991), will migrate towards the cathode and can be reduced to $H_2(g)$ and $MgO(s)$, and due to extremely low solubility, the $MgO(s)$ will cover the cathodic surface to cause cathodic passivation and disperse the magnesium droplets produced at cathode which dramatically reduces current efficiency. Magnesium oxide also may increase the electrical resistance of the electrolyte which increases the power requirements for electrolytic separation of magnesium and chlorine. Therefore, MgO is regarded as one of the most harmful impurities in magnesium electrolysis.

How to solve the adverse effects of MgO on magnesium electrolysis has been a problem of the utmost concern for a long time. The ideal way is to transform the MgO into a soluble material, among which the oxygen ions or complex oxygen will not be involved in the electrochemical reaction and therefore the anode will not be consumed. However, thus far it is difficult to meet both the above requirements. In fact, MgO has limited solubility both in chloride melts such as the conventional magnesium electrolyte MgCl₂, NaCl, KCl and CaCl₂, and in fluoride melts (Bauxitbanya 1949). A mechanism for the dissolution of MgO in pure MgCl₂ was suggested according equation (1) (Combes et al. 1980; Boghosian et al. 1991). The solubility of MgO reaches up to 0.15% by weight (0.36 mol %) at 730°C.

$$MgO + MgCl_2 \rightarrow Mg_2OCl_2 \qquad (1)$$

Sharma (1994) found that a rare-earth chloride of NdCl₃ can greatly increase MgO solubility in NdCl₃-MgCl₂ melts by the suggested reaction:

$$MgO + NdCl_3 \rightarrow NdOCl + MgCl_2 \qquad (2)$$

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During the electrolysis from $MgO-NdCl_3-MgCl_2$ melts, it was observed that only chlorine with no CO or CO_2 was evolved at the anode at a higher current density at 700°C (Cathro et al. 1997), indicating that oxychloride species were not involved in the anodic electrochemical reaction at a temperature of 700°C. Therefore it was assumed that a small amount of $NdCl_3$ or $LaCl_3$ can be used in the $MgCl_2$-$NaCl-KCl-CaCl_2$ melt to dissolve impurities of MgO, and oxychloride species will not be oxidized at the anode at a higher current density at about 700°C. The purpose for the present work is to examine the solubility of MgO in a $MgCl_2-NaCl-KCl-CaCl_2$ melt with $NdCl_3$ or $LaCl_3$.

EXPERIMENTAL METHODS

Anhydrous magnesium chloride (0.0098 wt % MgO impurity) was used as the active component of magnesium electrolysis. Sodium chloride (> 99.5 wt %), potassium chloride (> 99.5 wt %), and anhydrous calcium chloride (> 96.0 wt %) served as supporting electrolyte for magnesium electrolysis, and MgO (> 98 wt %) was added to the above melt as an impurity during the experiments. Lanthanum chloride was prepared from $LaCl_3 \cdot 7H_2O$ as follows: (1) an aqueous solution was prepared by mixing NH_4Cl and $LaCl_3 \cdot 7H_2O$ (8:1 molar ratio); (2) the solution was heated to 120°C and maintained for 3 hours to remove water; (3) after water removal the solution was slowly heated to 200°C; and (4) the solution was held for 3 hours in an electric furnace heated to 340°C, and kept for 3 hours under vacuum. Anhydrous $NdCl_3$ was prepared similar to the above process for anhydrous $LaCl_3$. All chemicals were dried under vacuum for 4-5 hours at 200°C before use.

For the purposes of the experiment, an excess of MgO flake that had been compacted under 10^4 MPa pressure was placed at the bottom of an alumina crucible covered with chloride melts. Unless otherwise stated, MgO flake was used in the experiment. After melting and mixing uniformly at high temperature, about 2 g of molten salt was taken out from the crucible and dissolved in 10 ml hydrochloric acid solution (0.05 N) to measure MgO solubility in the melt. An acid consumption method was used to measure the MgO concentration in the melt. The dissolved MgO will react with part of the acid, and the remaining acid was then titrated with sodium hydroxide. The solubility of MgO can be calculated according to the amount of sodium hydroxide consumed. The experiment was carried out in an atmosphere of argon gas to avoid absorption of water from the air by the chloride melt.

All experiments were performed in an alumina crucible inside an electric furnace under an argon gas atmosphere. For each experiment, between 100 and 120 g of electrolyte was added to the crucible. Samples were quickly withdrawn from the melt using an iron rod to avoid water absorption from the air. The samples were immediately quenched and then placed into a hydrochloric acid solution (0.05 N) to determine MgO solubility.

EDTA volumetric analysis method was used to analyze the $NdCl_3$ and $LaCl_3$ concentration in the melt, among which xylenol orange was used as an indicator in order to avoid Mg^{2+} interference (China technical supervision bureau, GB/T 14635.2—1993).

Table 1–The dependence of amounts of dissolved MgO (g/100 g melt) with time.

Time (min)	0	0.5	1	1.5	2	3	5	10	15	30
Dissolved MgO (%)	0.0518	0.57	1.03	1.41	1.6	1.702	1.72	1.75	1.746	1.77
$NdCl_3$ concentration in the melt	10%	8%	6.15%	4.40%	3.60%	3.25%	3.10%	2.65%	2.49%	2.50%

Table 2–Amounts of dissolved MgO (g/100 g melt) chang over time at different temperatures (initial $NdCl_3$ concentration 10 wt %).

Time (min)	0	0.5	1	1.5	2	3	5	10	15
700 °C	0.0518	0.57	1.03	1.41	1.60	1.702	1.720	1.75	1.746
780 °C	0.0518	0.67	1.40	1.74	1.76	1.770	1.765	1.78	1.780
850 °C	0.0518	0.75	1.56	1.75	1.77	1.770	1.790	1.78	1.790

RESULTS AND DISCUSSION

MgO Solubility in MgCl₂ – NaCl – KCl - CaCl₂ - CaF₂/NaF/MgF₂ Melts

Figure 1 shows the effects of $MgCl_2$ on MgO solubility in NaCl-KCl-CaCl₂-CaF₂ melts (60:20:15:5% by weight) (total 100 g) at 810°C under an argon atmosphere. This treatment gave a rapid build up for MgO solubility in the melt with increasing $MgCl_2$ content. The dissolution mechanism for MgO in the above melt can be described by equations (3-5) (Mediaas 2000), indicating that an increasing $MgCl_2$ content favored the reaction in the right hand direction, thus increasing MgO solubility. Addition of fluorides such as NaF, MgF₂, or CaF₂ to the MgCl₂-NaCl-KCl-CaCl₂ melts increased MgO solubility as well, and addition of CaF₂ led to a higher MgO solubility than addition of NaF or MgF₂, as shown in Figure 2.
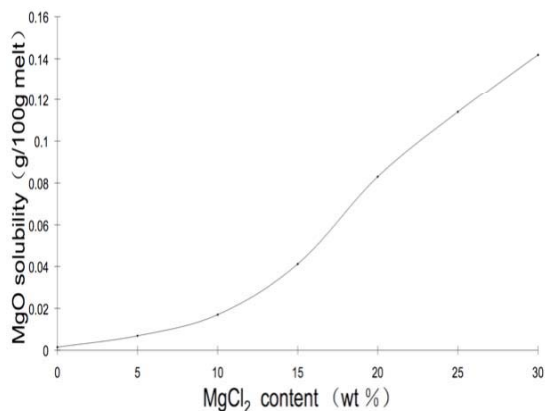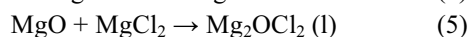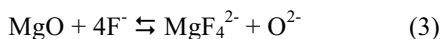
$$MgO + 4F^- \leftrightarrows MgF_4^{2-} + O^{2-} \qquad (3)$$
$$MgO + F^- \leftrightarrows MgOF^- \qquad (4)$$
$$MgO + MgCl_2 \rightarrow Mg_2OCl_2 \ (l) \qquad (5)$$

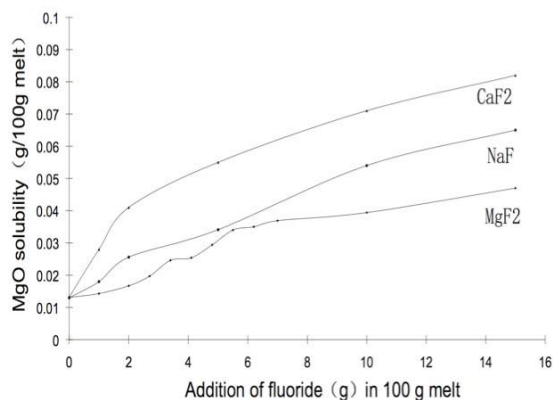**Figure 1**–The effect of MgCl₂ content on MgO solubility.

Figure 2–The effect of fluoride on MgO solubility.

MgO solubility in MgCl₂ - NaCl-KCl - NdCl₃ melts

However, the MgO solubility in the KCl-CaCl₂-CaF₂-NaCl-MgCl₂ melt is still quite low, the maximum value reaching only 0.145 g per 100 g (0.145 wt %) in the above melt with 30 wt % MgCl₂. Furthermore, during the routine magnesium electrolysis process, the melt usually contains 10-20% by weight of MgCl₂ with up to 2% by weight of CaF₂, which leads to a very low solubility of MgO (usually < 0.1 wt %).

Figure 3 shows the dissolved amount of MgO after different times in a NaCl-KCl-CaCl₂-MgCl₂ (15 wt %) melt containing between 5 and 15 weight percent of NdCl₃ at 780°C. The dissolved amount of MgO reached its maximum after approximately 5 minutes for all three concentrations of NdCl₃. MgO solubility increased for all three concentrations of NdCl₃ with increasing NdCl₃ content in the melt. After equilibrium with MgO in 30 minutes, 10 wt % NdCl₃ was not completely consumed, and 2.5 wt % NdCl₃ was still left in the melt. Probably this was NdCl₃ equilibrium concentration in the above melt due to the formation of a complicated complex with other chlorides.
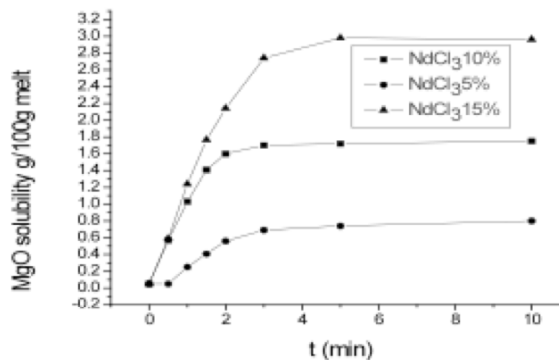

Figure 3–The relationship between the amount of dissolved MgO and time.

The dissolution rate of MgO also was dependent on the NdCl₃ concentration in the melt, as shown in Figure 4. The MgO dissolution rate gradually increased with increasing NdCl₃ concentration in the melt, and reached the maximum value at the initial stage with initial addition of 15 wt % NdCl₃ to the melt, but reduced the minimum value at the final stage with initial addition of 5 wt % NdCl₃ to the melt. A possible interpretation of this observation is that NdCl₃ first formed a kind of complicated complex with other chlorides, more NdCl₃ speeded up the reaction, and then the remaining NdCl₃ reacted with magnesium oxide. Powdered

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MgO initially dissolved more rapidly than flakes because of the relatively larger surface area, but the initial form of MgO had no effect on the final MgO solubility.

The effects of temperature on MgO dissolution rate and MgO solubility in NaCl-KCl-CaCl$_2$-MgCl$_2$ (20 wt %) melt with 10 wt % NdCl$_3$ was investigated (Table 2). The MgO solubility (g/100 g melt) slightly increased with temperature in the range from 700-850°C in NaCl-KCl-CaCl$_2$-MgCl$_2$ (20 wt %) melt with 10 wt % NdCl$_3$, and the MgO dissolution rate also increased with increasing temperature.

The X-ray diffraction patterns for the melt before and after MgO dissolution (Figure 5, 6) showed that NdOCl was formed after dissolution of MgO in the melt containing NdCl$_3$, indicating that MgO reacted with NdCl$_3$ to form NdOCl according to equation (2) as previously documented by Sharma (1994). This reaction occurs spontaneously according to negative free energy ΔGo (-20.2 kJ/mol at 700°C).
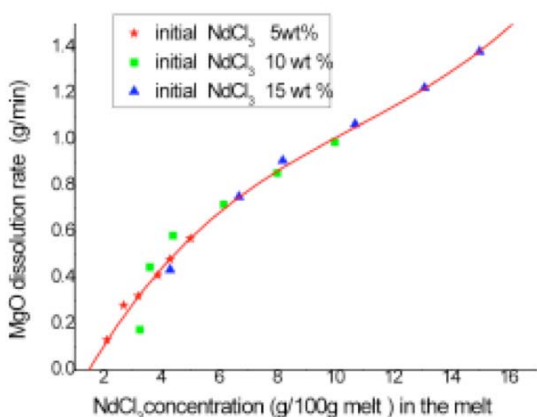

Figure 4–The relationship between the dissolution rate of MgO and NdCl$_3$ concentration.
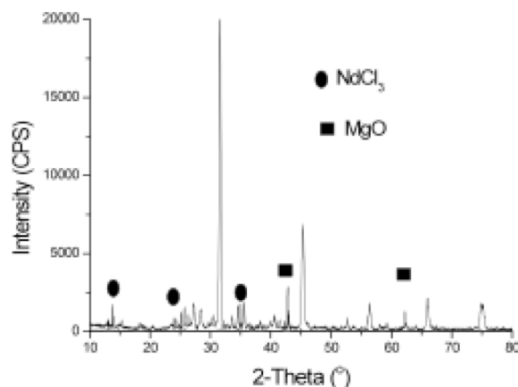

Figure 5–XRD patterns for a NaCl-KCl-MgCl$_2$-NdCl$_3$ (5:2:2:1 weight ratio) melt with MgO melts before dissolution.

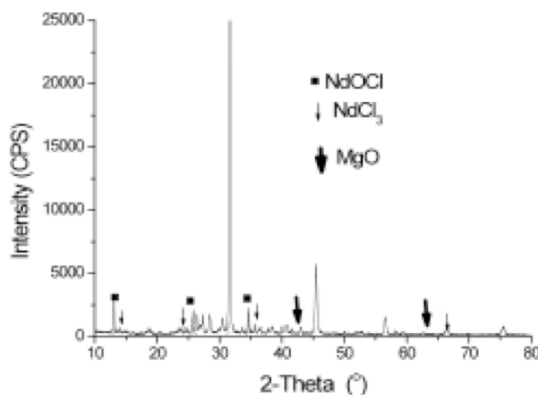**Figure 6**–XRD patterns for NaCl:KCl:MgCl$_2$:NdCl$_3$ (5:2:2:1 weight ratio) melts after dissolution of MgO.

The MgO dissolution process is thought to proceed in two steps. In the first step, crystalline MgO is eroded by the melt ion and MgO solute is formed (the MgO dissolution and activation process). In the second step MgO solute reacts with NdCl$_3$ to form NdOCl and MgCl$_2$.

MgO Solubility in NaCl-KCl - LaCl$_3$ Melt

LaCl$_3$ has the similar properties as NdCl$_3$, so it was assumed that LaCl$_3$ would react with MgO according to the following equation:

$$LaCl_3 + MgO \leftrightarrow LaOCl + MgCl_2 \qquad (6)$$

In this experiment, one hundred grams of KCl-NaCl (1:1 weight ratio) was melted in a corundum crucible and maintained at 720°C for 1 h. Then LaCl$_3$ was added to the melt and stirred, and the La^{3+} concentration was monitored until the melt was uniform. A MgO flake pressurized at 10^4 MPa was added to the melt, and the La^{3+} concentration was analyzed again when the melt was homogenous. MgO consumption can be estimated by the La^{3+} concentration difference, and the dependence of MgO consumption on time was shown in Figure 7. MgO consumption increased with time during the first 30 minutes and reached a stable value at 40 minutes. A time of 60 minutes was chosen for reaction equilibrium. Then MgO solubility in a KCl:NaCl (1:1 weight ratio, 100 g) melt with various LaCl$_3$ content was investigated at 720, 750, and 800°C. The La^{3+} concentration in the melt was analyzed at 60 minutes after LaCl$_3$ had been added to the melt.

Figure 8 shows that the MgO solubility has a linear relationship with LaCl$_3$ content in the melt, and increases with temperature from 720 to 800°C, as represented by the following equations:

$$Y_{MgO} = 7.82W_{LaCl3} - 0.0428 \quad 720^oC \qquad (7)$$
$$Y_{MgO} = 9.04W_{LaCl3} - 0.0573 \quad 750^oC \qquad (8)$$
$$Y_{MgO} = 10.59W_{LaCl3} - 0.0448 \quad 800^oC \qquad (9)$$

Figure 7–The dependence of the amount of dissolved MgO with time.
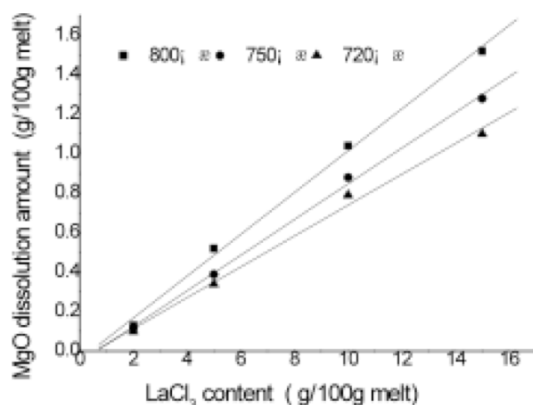
Figure 8–The effect of LaCl$_3$ content on the solubility of MgO (g/100 g melt).

CONCLUSIONS

The solubility of MgO increased with increasing MgCl$_2$ content in KCl-NaCl-CaCl$_2$-CaF$_2$, but it is still quite low, the maximum value reached being only 0.145 wt % in the above melt with 30 wt % MgCl$_2$. Addition of CaF$_2$ led to a higher MgO solubility than addition of NaF or MgF$_2$ in a MgCl$_2$-KCl-NaCl-CaCl$_2$ melt.

MgO solubility is clearly dependent on the NdCl$_3$ content in the melt. Both MgO solubility and dissolution rate increased with increasing NdCl$_3$ concentration in MgCl$_2$-NaCl-KCl-NdCl$_3$ melts. Raising the temperature from 700 to 850°C can slightly increase MgO solubility in MgCl$_2$-NaCl-KCl-NdCl$_3$ melts. The MgO solubility in MgCl$_2$-NaCl-KCl-NdCl$_3$ (15 wt %) melts can reach about 3.0 wt %

at 780°C. XRD pattern analysis clearly indicated that NdCl$_3$ reacted with MgO to form NdOCl in a melt containing NdCl$_3$.

Addition of LaCl$_3$ to a NaCl-KCl meltt can also improve MgO solubility, but dissolution of MgO took more time (about 60 minutes) to reach equilibrium with a melt containing LaCl$_3$. The solubility of MgO increased linearly with increasing melt temperatures between 720 and 800°C.
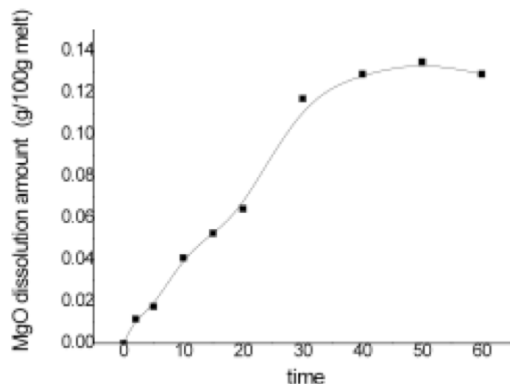
ACKNOWLEDGEMENTS

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