The Solubility of MgO in Molten MgCl_2 - CaCl_2 Salt

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The solubility of MgO in molten MgCl_2 and CaCl_2 has been studied. In pure MgCl_2 , the MgO solubility was determined to be 0.63–2.90 mol% at 1073–1373 K, while 0.24–0.63 mol% in pure CaCl_2 at 1223–1523 K. The effects of MgCl_2 and CaO addition to CaCl_2 were investigated, and the solubility product of MgO was found to increase with the amount of MgCl_2 addition, while CaO addition did not affect significantly. They were explained in terms of the activity coefficient of oxide ion (O^{2-}) as well as the enthalpy of mixing for the MgO- CaCl_2 system. From the experimental results, the corrosion possibility of MgO refractory by Cl-containing gas was considered.

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1. Introduction

Recently, waste plastics have been recycled in iron and steel making processes. One of the processes is to inject the plastics into the blast furnace with pulverized coal.¹⁾ The plastics containing chlorine, *e.g.* PVC, is separated, or used after removing chlorine in the process²⁾ due to the problem of dioxin and HCl generation. It is necessary to grasp the reactions between refractories and chlorine bearing gas in order to evaluate the effect of chlorine contamination in such high temperature processes.

Hirosumi *et al.*³⁾ and Miwa *et al.*⁴⁾ studied the dissolution mechanism of chlorine in the oxide melt. They clarified chlorine dissolved into molten oxides as Cl^- ion, and discussed the distribution of chlorine between molten oxides and gas phase. Accordingly, it is impatient to predict the possibility of corrosion of refractories by Cl-containing gas generated in the furnace. However, there is no research about the reaction between Cl-containing gas and refractory.

Chlorine is likely to exist as HCl, CaCl_2 , MgCl_2 etc. in the high temperature furnace. When MgO is a major refractory component, we can consider some types of corruptions such as the reaction between MgO and HCl gas and the dissolution of MgO in a molten chloride condensed at low temperature area.

Hence, the solubility of MgO in MgCl_2 - CaCl_2 melt becomes important because MgO can be corroded by HCl even when the activity of MgCl_2 is smaller than unity with a considerable solubility of MgO in MgCl_2 . When the solubility of MgO in CaCl_2 melt is large, the MgO based refractory will be corroded with smaller activity of CaCl_2 in the melt than that for the deposition of its condensed phases.

For the reasons, the solubility of MgO in the molten MgCl_2 - CaCl_2 system play an important role in the evaluation of the reactions. Although there are a few available data of the system,^{5–7)} there is no data at the desired temperature. In the present research, we measured the solubility of MgO in molten MgCl_2 or molten CaCl_2 , and discussed the thermodynamics of the MgO- CaCl_2 system. Based on the measurement, we investigated the possibility of corrosion of MgO based refractory on some assumptions.

2. Experimental

Fused MgO and reagent grade MgCl_2 and/or CaCl_2 powder, which were dried at 473 K for 3 h, were charged into the graphite crucible, and the crucible and graphite lid were sealed with alumina paste. Reagent grade MgO and CaO calcined from reagent grade CaCO_3 at 1173 K were added to the crucible when the initial oxygen content was adjusted. The crucible was kept in a hot zone of the furnace.

A SiC resistance furnace with a fused mullite tube was employed and experimental temperature (1073–1523 K) was controlled by a proportional integral differential (PID) controller and kept within ± 1 K with a Pt-6%Rh/Pt-30%Rh thermocouple. Schematic sketch inside the furnace is drawn in Fig. 1.

During experiment, purified Ar gas was flown onto the crucible at a rate of about $100 \text{ Ncm}^3/\text{min}$ in order to prevent its oxidation. In the gas purification system, P_2O_5 , soda lime and Mg flake at 823 K were used to remove H_2O , CO_2 and O_2 , respectively.

Fig. 1 Schematic cross section of the experimental apparatus.

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Table 1 Solubility of MgO in molten MgCl₂.

No.	Temp. (K)	Time (h)	Initial concentration	Equilibrium concentration		$\ln X_{\text{Mg}^{2+}} X_{\text{O}^{2-}}$
			$X_{\text{O}^{2-}}^0 \times 10^2$	$X_{\text{O}^{2-}} \times 10^2$	$X_{\text{Mg}^{2+}} \times 10^2$	
1-1	1073	3	0.17	0.32	100	-5.76
1-2	1173	3	0.18	0.72	100	-4.93
1-3	1173	3	0.18	0.70	100	-4.97
1-4	1273	3	0.34	1.08	100	-4.53
1-5	1373	3	0	1.47	100	-4.22

The experimental time was determined to be 3 h for the MgO-MgCl₂ system and 15 h or 24 h for the MgO-CaCl₂ system, which were confirmed to be enough for the equilibrium attainment by the preliminary experiment. After the experiment, the sample was withdrawn and quenched in the flushing Ar gas and subjected to chemical analyses.

The Ca and Mg contents of the samples were determined by inductively coupled plasma (ICP) emission spectrometry at the wavelengths of 318 and 279 nm, respectively. The oxygen content of the samples was determined by the following method. The grounded samples were dissolved in a certain amount of dilute hydrochloric acid (1/10 or 1/100 mol/l), then the excess acid was back-titrated with 1/10 or 1/100 mol/l NaOH aqueous solution using a phenolphthalein indicator, where HCl was consumed by the reaction (1).

Here in eq. (1), A represents the element, Ca or Mg.

3. Results

3.1 The MgO-MgCl₂ system

In order to determine experimental time, the time dependence of MgO solubility in molten MgCl₂ was measured at 1373 K as shown in Fig. 2, where O²⁻ content in molten MgCl₂ was regarded as the amount of MgO dissolved. The equilibration time was found to be less than 3 h from the result, hence the experimental time determined to be 3 h.

The solubility of MgO in MgCl₂ melt was measured at 1073–1373 K. Experimental conditions and results are summarized in Table 1 and Fig. 3. The solubility of MgO was from 0.63 mol% to 2.90 mol% at 1073–1373 K.

Fig. 2 Time dependence of the MgO solubility in molten MgCl₂ at 1373 K. Fig. 3 Temperature dependence of the MgO solubility in molten MgCl₂ or molten CaCl₂.

In the present work, the degree of freedom for the MgO-MgCl₂ system at a certain temperature is equal to zero, whereas that for the MgO-CaCl₂ system becomes to one. Accordingly, the MgO solubility was evaluated by the solubility product shown in eq. (2) for the MgO-CaCl₂ system together with that of the MgO-MgCl₂ system for comparison.

$$K_{\text{sp}}(\text{MgO}) = X_{\text{Mg}^{2+}} X_{\text{O}^{2-}} \quad (2)$$

Here $X_{\text{Mg}^{2+}}$ and $X_{\text{O}^{2-}}$ are the cation fraction of Mg²⁺ and the anion fraction of O²⁻, respectively, which are defined as eq. (3),

$$X_{\text{Mg}^{2+}} = \frac{n_{\text{Mg}^{2+}}}{n_{\text{Mg}^{2+}} + n_{\text{Ca}^{2+}}}, \quad X_{\text{O}^{2-}} = \frac{n_{\text{O}^{2-}}}{n_{\text{O}^{2-}} + n_{\text{Cl}^{-}}} \quad (3)$$

where n_i is the number of moles of i ion in the melt.

The solubility product of MgO in molten MgCl₂ is shown in Fig. 4 together with calculated from the data of Mediaas *et al.*⁷⁾ Its temperature dependence was obtained as eq. (4).

$$\ln K_{\text{sp}}(\text{MgO}) = -\frac{7400}{T} + 1.26 \quad (4)$$

3.2 The MgO-CaCl₂ system

In order to determine the experimental time for equilibration, MgO solubilities in molten CaCl₂ at various experimental time was measured at 1223 K and 1323 K as shown in Fig. 5, where Mg²⁺ content in molten CaCl₂ was regarded as the amount of MgO dissolved. The experimental time was determined to be 15 h at 1223–1323 K and 24 h at the temperature higher than 1323 K from the results.

Fig. 4 Temperature dependence of the solubility product of MgO in molten MgCl₂ or molten CaCl₂.

The solubility of MgO in CaCl₂ melt was measured at 1223–1523 K. Experimental conditions and results are summarized in Table 2 and Fig. 3. The solubility of MgO increased from 0.24 mol% to 0.63 mol% with increasing temperature from 1223 K to 1523 K.

As mentioned above, the solubility of MgO in molten CaCl₂ should be evaluated in terms of the solubility product in the present work. The temperature dependence of the solubility product of MgO is shown in Fig. 4, and it can be approximated by eq. (5).

$$\ln K_{sp}(\text{MgO}) = -\frac{10400}{T} - 2.44 \quad (5)$$

3.3 The MgO-CaCl₂(-CaO) and MgO-CaCl₂(-MgCl₂) systems

The solubility product of MgO in the CaCl₂ melt showed the considerably smaller value between the previous two

Fig. 5 Time dependence of the MgO solubility in molten CaCl₂ at 1223 K and 1323 K.

systems. This suggests that the solubility product may depend on the composition of molten salt such as $X_{\text{Mg}^{2+}}$ or $X_{\text{O}^{2-}}$.

Therefore, the effect of CaO and MgCl₂ addition on the solubility product of MgO in the CaCl₂ melt was investigated at 1373 K. The experimental conditions and results are summarized in Tables 3 and 4, and the dependence of the solubility product on $X_{\text{Mg}^{2+}}$ and $X_{\text{O}^{2-}}$ are shown in Fig. 6. As seen in the figure, the solubility product is dependent on $X_{\text{Mg}^{2+}}$ remarkably, whereas independent of the $X_{\text{O}^{2-}}$ in the range of $X_{\text{O}^{2-}} < 0.05$.

4. Discussions

4.1 The composition dependence of the solubility product of MgO

The dissolution reaction of MgO in molten salt is represented by eq. (6) and the equilibrium constant of the reaction is expressed as eq. (7).

Table 2 Solubility of MgO in molten CaCl₂.

No.	Temp. (K)	Time (h)	Initial concentration	Equilibrium concentration		$\ln X_{\text{Mg}^{2+}} X_{\text{O}^{2-}}$
			$X_{\text{O}^{2-}}^0 \times 10^2$	$X_{\text{O}^{2-}} \times 10^2$	$X_{\text{Mg}^{2+}} \times 10^2$	
2-1	1223	24	0	0.71	0.24	-11.0
2-2	1248	24	0	0.75	0.25	-10.9
2-3	1323	15	0	0.81	0.44	-10.2
2-4	1373	15	0	0.85	0.42	-10.2
2-5	1423	15	0	1.24	0.63	-9.46
2-6	1473	15	0	1.55	0.54	-9.39
2-7	1523	15	0	1.43	0.50	-9.55

Table 3 Solubility of MgO in the molten CaCl₂-CaO system.

No.	Temp. (K)	Time (h)	Initial concentration	Equilibrium concentration		$\ln X_{\text{Mg}^{2+}} X_{\text{O}^{2-}}$
			$X_{\text{O}^{2-}}^0 \times 10^2$	$X_{\text{O}^{2-}} \times 10^2$	$X_{\text{Mg}^{2+}} \times 10^2$	
3-1	1373	15	0.50	0.82	0.16	-11.2
3-2	1373	15	1.22	1.50	0.092	-11.2
3-3	1373	15	2.68	3.02	0.081	-10.6
3-4	1373	15	5.13	5.42	0.084	-10.0

Table 4 Solubility of MgO in the molten CaCl₂-MgCl₂ system.

No.	Temp. (K)	Time (h)	Initial concentration		Equilibrium concentration		$\ln X_{\text{Mg}^{2+}} X_{\text{O}^{2-}}$
			$X_{\text{O}^{2-}}^0 \times 10^2$	$X_{\text{Mg}^{2+}}^0 \times 10^2$	$X_{\text{O}^{2-}} \times 10^2$	$X_{\text{Mg}^{2+}} \times 10^2$	
4-1	1373	15	0	5.26	0.53	2.17	-9.08
4-2	1373	15	0	10.2	1.40	7.13	-6.91
4-3	1373	15	0	19.9	2.64	11.9	-5.76
4-4	1373	15	0	30.0	1.07	21.2	-6.09

Fig. 6 Composition dependence of the solubility product of MgO in molten CaCl₂ at 1323 K. Fig. 7 Activity of MgCl₂ or CaCl₂ at 1373 K calculated from the phase diagram of the MgCl₂-CaCl₂ system.

$$K_6 = \frac{a_{\text{Mg}^{2+}} a_{\text{O}^{2-}}}{a_{\text{MgO(s)}}} = a_{\text{Mg}^{2+}} a_{\text{O}^{2-}} = \gamma_{\text{Mg}^{2+}} \gamma_{\text{O}^{2-}} X_{\text{Mg}^{2+}} X_{\text{O}^{2-}} \quad (7)$$

where $a_{\text{Mg}^{2+}}$ and $a_{\text{O}^{2-}}$ are the activities of Mg^{2+} and O^{2-} ions, $\gamma_{\text{Mg}^{2+}}$ and $\gamma_{\text{O}^{2-}}$ are the activity coefficients of Mg^{2+} and O^{2-} ions, and K_6 is the equilibrium constant of reaction (6). Although we have to treat the activities of ions carefully, the standard states of Mg^{2+} and O^{2-} ions are assumed to be those of hypothetical pure liquid MgO in order to argue the relative change in the activity coefficient with composition.

The activities of MgCl₂ and CaCl₂ almost conform to ideal solution as shown in Fig. 7, which are calculated from the liquidus of the MgCl₂-CaCl₂ binary system⁸⁾ and the Gibbs energy of fusion for both components¹¹⁾ using Gibbs-Duhem integration and regular solution model. The activity of Mg^{2+} ion is proportional to the activity of MgCl₂ if the activity coefficient of Cl^- ion is independent of the cation fraction $X_{\text{Mg}^{2+}}$. Therefore, the activity coefficient of Mg^{2+} ion is considered to be constant in the system.

Using the experimental data, the composition dependence of $\gamma_{\text{O}^{2-}}$ can be estimated quantitatively. The Taylor series expansion of $\ln \gamma_{\text{O}^{2-}}$ at infinite dilution can be written as eq. (8), where we treated the first order terms neglecting the higher order terms due to the small MgO solubility in CaCl₂ melt.

$$\ln \gamma_{\text{O}^{2-}} = \ln \gamma_{\text{O}^{2-}}^0 + \varepsilon X_{\text{Mg}^{2+}} = \ln \gamma_{\text{O}^{2-}}^0 - 66.8 X_{\text{Mg}^{2+}} \quad (8)$$

Here $\gamma_{\text{O}^{2-}}^0$ is the activity coefficient of O^{2-} ion at infinite dilution, and ε is the constant, namely interaction parameter

Fig. 8 Dependence of the activity coefficient of O^{2-} ion on the molten salt composition at 1373 K.

between Mg^{2+} and O^{2-} , which corresponds to the slope of the line in Fig. 8.

This results can be explained qualitatively by the fact that the Coulomb interaction of Mg and O is stronger than that of Ca and O in molten salt. It can be predicted from the comparison of lattice energy of solid state MgO and CaO, 41.0 eV and 36.5 eV, respectively, which were calculated by Born and Madelung.⁹⁾

Therefore, O^{2-} ion interacted more strongly with Mg^{2+} ion in molten MgCl₂ than Ca^{2+} ion in molten CaCl₂, and $\gamma_{\text{O}^{2-}}$ decreases with increasing Mg^{2+} ion content in molten salt.

The result of eq. (8) can be interpreted by the theory of salt mixtures with two cations and two anions based on the assumption of regular solution developed by Flood.¹⁰⁾ Gibbs energy of the molten salt mixture with two cations (Mg^{2+} , Ca^{2+}) and two anion (O^{2-} , Cl^-), G , is represented by eq. (9).

$$G = G^0 + \Delta G^M \quad (9)$$

$$G^0 = n_{\text{MgO}} G_{\text{MgO(l)}}^0 + n_{\text{CaO}} G_{\text{CaO(l)}}^0 + n_{\text{MgCl}_2} G_{\text{MgCl}_2(\text{l})}^0 + n_{\text{CaCl}_2} G_{\text{CaCl}_2(\text{l})}^0 \quad (10)$$

where G^0 is the Gibbs energy of molten salt defined as eq. (10), ΔG^M is the Gibbs energy of mixing, G_i^0 is the standard molar Gibbs energy of compound i , and n_i is the numbers of moles for the compound i .

Numbers of moles for Mg^{2+} , Ca^{2+} , O^{2-} and Cl^- ion in the system are represented by $n_{\text{Mg}^{2+}}$, $n_{\text{Ca}^{2+}}$, $n_{\text{O}^{2-}}$ and n_{Cl^-} , respectively, and the cation fraction $X_{\text{Ca}^{2+}}$ and the anion fraction X_{Cl^-} are defined as eq. (11).

$$X_{\text{Ca}^{2+}} = \frac{n_{\text{Ca}^{2+}}}{n_{\text{Mg}^{2+}} + n_{\text{Ca}^{2+}}}, \quad X_{\text{Cl}^-} = \frac{n_{\text{Cl}^-}}{n_{\text{O}^{2-}} + n_{\text{Cl}^-}} \quad (11)$$

The condition of electroneutrality demands the following restriction.

$$n_{\text{Mg}^{2+}} + n_{\text{Ca}^{2+}} = n_{\text{O}^{2-}} + \frac{1}{2} n_{\text{Cl}^-} \quad (12)$$

If the cations are randomly arranged on cation sites and the anions on anion sites, G^0 and ΔG^M can be represented by eqs. (13)–(16).

$$G^0 = n_{\text{O}^{2-}} X_{\text{Mg}^{2+}} G_{\text{MgO(l)}}^0 + n_{\text{O}^{2-}} X_{\text{Ca}^{2+}} G_{\text{CaO(l)}}^0 + \frac{1}{2} n_{\text{Cl}^-} X_{\text{Mg}^{2+}} G_{\text{MgCl}_2(\text{l})}^0 + \frac{1}{2} n_{\text{Cl}^-} X_{\text{Ca}^{2+}} G_{\text{CaCl}_2(\text{l})}^0 \quad (13)$$

$$\Delta G^M = \Delta H^M - T \Delta S^M \quad (14)$$

$$\Delta H^M = \Omega X_{\text{MgO}} X_{\text{CaCl}_2} = \Omega X_{\text{Mg}^{2+}} X_{\text{Ca}^{2+}} \quad (15)$$

$$\Delta S^M = -R(n_{\text{Mg}^{2+}} \ln X_{\text{Mg}^{2+}} + n_{\text{Ca}^{2+}} \ln X_{\text{Ca}^{2+}} + n_{\text{O}^{2-}} \ln X_{\text{O}^{2-}} + n_{\text{Cl}^-} \ln X_{\text{Cl}^-}) \quad (16)$$

In eq. (15), Ω is the constant value independent of the salt composition.

Therefore, the partial molar Gibbs energy is calculated by eq. (17).

$$\begin{aligned} \bar{G}_{\text{MgO(l)}} &= \left(\frac{\partial G}{\partial n_{\text{MgO}}} \right)_{n_{\text{CaCl}_2}} = \left(\frac{\partial G}{\partial n_{\text{Mg}^{2+}}} \right)_{n_{\text{Ca}^{2+}}, n_{\text{Cl}^-}} \\ &= G_{\text{MgO(l)}}^0 + \frac{n_{\text{Cl}^-}}{n_{\text{Cl}^-} + 2n_{\text{O}^{2-}}} X_{\text{Ca}^{2+}} \Delta G_{18}^0 \\ &\quad + RT \ln X_{\text{Mg}^{2+}} X_{\text{O}^{2-}} + \Omega X_{\text{Ca}^{2+}}^2 \end{aligned} \quad (17)$$

$$\text{MgO(l)} + \text{CaCl}_2(\text{l}) = \text{CaO(l)} + \text{MgCl}_2(\text{l}) \quad (18)$$

Here ΔG_{18}^0 is the standard Gibbs energy change of the chemical reaction (18) and this value is 87320 J/mol at 1373 K.^{11,12)}

If we consider only the infinite dilute range of MgO, we may assume $n_{\text{O}^{2-}}$ and $X_{\text{Mg}^{2+}}^2$ in eq. (17) are considerably small. Hence, the following approximations can be developed.

$$\frac{n_{\text{Cl}^-}}{n_{\text{Cl}^-} + 2n_{\text{O}^{2-}}} = \frac{1}{1 + 2n_{\text{O}^{2-}}/n_{\text{Cl}^-}} \cong 1 \quad (19)$$

$$X_{\text{Ca}^{2+}}^2 = (1 - X_{\text{Mg}^{2+}})^2 \cong 1 - 2X_{\text{Mg}^{2+}} \quad (20)$$

Therefore, the relative partial molar Gibbs energy of MgO can be calculated by eq. (21).

$$\begin{aligned} \Delta \bar{G}_{\text{MgO(l)}} &= \bar{G}_{\text{MgO(l)}} - G_{\text{MgO(l)}}^0 = RT \ln a_{\text{MgO(l)}} \\ &= -(\Delta G_{18}^0 + 2\Omega) X_{\text{Mg}^{2+}} + RT \ln X_{\text{Mg}^{2+}} X_{\text{O}^{2-}} \\ &\quad + (\Delta G_{18}^0 + \Omega) \end{aligned} \quad (21)$$

The activity of MgO is written as eq. (22).

$$a_{\text{MgO(l)}} = K a_{\text{Mg}^{2+}} a_{\text{O}^{2-}} = K \gamma_{\text{Mg}^{2+}}^0 \gamma_{\text{O}^{2-}} X_{\text{Mg}^{2+}} X_{\text{O}^{2-}} \quad (22)$$

where K is a constant value independent of the composition of molten salt, and $\gamma_{\text{Mg}^{2+}}^0$ is the activity coefficient of Mg^{2+} ion, which is constant as mentioned above. From eqs. (21) and (22), eq. (23) can be obtained.

$$\begin{aligned} \ln \gamma_{\text{O}^{2-}} &= -\frac{\Delta G_{18}^0 + 2\Omega}{RT} X_{\text{Mg}^{2+}} \\ &\quad + \frac{\Delta G_{18}^0 + \Omega}{RT} - \ln K \gamma_{\text{Mg}^{2+}}^0 \end{aligned} \quad (23)$$

Therefore, the constant value ε defined in eq. (8) becomes

$$\varepsilon = -\frac{\Delta G_{18}^0 + 2\Omega}{RT} \quad (24)$$

The parameter Ω can be evaluated from the present work.

$$\Omega = 338000 [\text{J/mol}] \quad (25)$$

Hence, the reason of the small solubility of MgO in molten CaCl_2 is because the enthalpy of mixing for the MgO-CaCl_2 system is very large.

4.2 Possibility of the corrosion of the refractories

Using the present results, the possibility of corrosion of MgO refractory will be evaluated with some assumption. When the refractory of the furnace, where chlorine containing wastes are treated, consists of pure MgO and molten $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag is in equilibrium with gas phase, two types of corrosion by HCl and CaCl_2 in the gas phase can be considered. To start with the case of HCl corrosion, the value of $P_{\text{HCl}}^2/P_{\text{H}_2\text{O}}$ of the gas phase in equilibrium with molten slag at 1748 K can be derived by eq. (26), where P_{HCl} and $P_{\text{H}_2\text{O}}$ are the partial pressures of HCl and H_2O in the furnace, respectively.

$$\frac{P_{\text{HCl}}^2}{P_{\text{H}_2\text{O}}} = \frac{[\text{mass}\% \text{Cl}^-]^2}{C_{\text{Cl}^-}^2} \exp\left(-\frac{2\Delta G_{27}^0}{1748R}\right) \quad (26)$$

$$\frac{1}{2} \text{H}_2\text{O(g)} + \frac{1}{2} \text{Cl}_2(\text{g}) = \text{HCl(g)} + \frac{1}{4} \text{O}_2(\text{g}) \quad (27)$$

$$\Delta G_{27}^0 = 29620 - 34.307 [\text{J/mol}]^{11)} \quad (28)$$

Here R is the gas constant and its value is 8.314 J/mol·K, $[\text{mass}\% \text{Cl}^-]$ is the solubility of chlorine in the slag, C_{Cl^-} is chloride capacity defined by Hirosumi *et al.*³⁾ and ΔG_{27}^0 is the standard Gibbs energy change of the reaction (27).

The reaction between solid MgO and HCl gas is written as eq. (29).

Fig. 9 Temperature dependence of a_{MgCl_2} in gas phase at the surface of refractories. (The gas phase is in equilibrium with the slag of composition A or B at 1748 K.)

$$\Delta G_{29}^0 = 21110 + 22.32T[\text{J/mol}]^{(11)} \quad (30)$$

where ΔG_{29}^0 is the standard Gibbs energy change of the reaction (29). In equilibrium state, the activity of MgCl₂ is represented by eq. (31).

$$a_{\text{MgCl}_2} = \frac{P_{\text{HCl}}^2}{P_{\text{H}_2\text{O}}} \exp\left(-\frac{\Delta G_{29}^0}{RT}\right) \quad (31)$$

When the $P_{\text{HCl}}^2/P_{\text{H}_2\text{O}}$ is uniform in the furnace, the activity of MgCl₂ at the refractory surface can be calculated by eqs. (26) and (31).

On the other hand, the activity of MgCl₂ in MgCl₂ salt in equilibrium with solid MgO is close to molar fraction of MgCl₂ because the solubility of MgO in the melt is very small.

Temperature dependence of the activity of MgCl₂ calculated by eq. (31), $a_{\text{MgCl}_2}(\text{I})$, and that of the salt in equilibrium with solid MgO, $a_{\text{MgCl}_2}(\text{II})$, are shown in Fig. 9. Two typical slag compositions, CaO:SiO₂:Al₂O₃ = 52.2:0:47.8 (composition A) and CaO:SiO₂:Al₂O₃ = 32.0:48.9:19.1 (composition B) were selected, containing 0.1 mass% Cl⁻ at 1748 K. Chloride capacities for both slags are known as 58.4, and 20.1.³⁾ From the present calculation, MgO corrosion which produces the liquid MgCl₂ on its surface will not occur at any temperature for the activity of MgCl₂ in the furnace is smaller than that of the salt in equilibrium with solid MgO.

Secondly, the possibility of corrosion by CaCl₂ gas is considered. P_{CaCl_2} of the gas phase in equilibrium with molten slag at 1748 K can be derived by eq. (32).

$$P_{\text{CaCl}_2} = \frac{[\text{mass}\% \text{Cl}^-]^2 a_{\text{CaO}}}{C_{\text{Cl}^-}^2} \exp\left(-\frac{2\Delta G_{33}^0}{RT}\right) \quad (32)$$

$$\Delta G_{33}^0 = -1379 - 22.15T[\text{J/mol}]^{(11)} \quad (34)$$

Here a_{CaO} is the activity of CaO in the slag, ΔG_{33}^0 is the standard Gibbs energy change of the reaction (33).

When P_{CaCl_2} is assumed to be uniform in the furnace, the activity of CaCl₂ relative to the pure liquid CaCl₂ at the

Fig. 10 Temperature dependence of a_{CaCl_2} in gas phase at the surface of refractories. (The gas phase is in equilibrium with the slag of composition A or B at 1748 K.)

refractory surface can be obtained as follows.

$$\Delta G_{35}^0 = 234900 - 106.37T[\text{J/mol}]^{(11)} \quad (36)$$

The activity of CaCl₂ relative to pure liquid CaCl₂ in equilibrium with solid MgO is represented by eq. (37) when Temkin's model is assumed to be valid.

$$a_{\text{CaCl}_2} = X_{\text{Ca}^{2+}} X_{\text{Cl}^-}^2 \quad (37)$$

Temperature dependence of the activity of CaCl₂ relative to pure liquid CaCl₂ in gas phase, $a_{\text{CaCl}_2}(\text{I})$, and that of the salt in equilibrium with solid MgO, $a_{\text{CaCl}_2}(\text{II})$, is shown in Fig. 10. In this calculation, the condition was selected as [mass%Cl⁻] = 0.1, C_{Cl^-} = 58.4 and 20.1, a_{CaO} = 0.50 and 3.5×10^{-3} which corresponds to the activity data at 1823 K for the slags of composition A and B.¹³⁾

If $a_{\text{CaCl}_2}(\text{I})$ is larger than $a_{\text{CaCl}_2}(\text{II})$, solid MgO can be corroded by dissolution of MgO in molten CaCl₂. As shown in Fig. 10, this type of corrosion occurs at less than 1350 K for composition A and at less than 1200 K for composition B.

Hereafter, the corrosion temperature T_{corr} is defined as the temperature below which $a_{\text{CaCl}_2}(\text{I})$ is larger than $a_{\text{CaCl}_2}(\text{II})$ and the dependence of T_{corr} on the Cl content in the slag is shown in Fig. 11. Even a small amount of chlorine in the slag is

Fig. 11 Relationship between T_{corr} and [mass% Cl⁻].

shown to cause the corrosion of MgO refractory by the dissolution in molten CaCl_2 thermodynamically.

5. Conclusions

The solubility of MgO in the MgCl_2 - CaCl_2 system was measured and the following findings were obtained.

(1) The MgO solubility product in MgCl_2 melt was larger than that in CaCl_2 melt, and the temperature dependences of them were represented by the following equations, respectively.

$$\begin{aligned}\ln K_{\text{sp}}(\text{MgO}) &= \ln X_{\text{Mg}^{2+}}X_{\text{O}^{2-}} \\ &= -\frac{7400}{T} + 1.26 \quad (\text{in molten } \text{MgCl}_2)\end{aligned}$$

$$\begin{aligned}\ln K_{\text{sp}}(\text{MgO}) &= \ln X_{\text{Mg}^{2+}}X_{\text{O}^{2-}} \\ &= -\frac{10400}{T} - 2.44 \quad (\text{in molten } \text{CaCl}_2)\end{aligned}$$

(2) The solubility product of MgO in molten CaCl_2 increased with the content of Mg^{2+} ion in the salt. This dependence was considered to be due to the difference in the interaction between Mg-O and Ca-O.

(3) Some types of corrosion of MgO were discussed, and it

was predicted that MgO corrosion by the dissolution of MgO in molten CaCl_2 could happen at low temperature area.

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