The Solubility of MgO in Molten MgCl2-CaCl2 Salt

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The solubility of MgO in molten MgCl2 and CaCl2 has been studied. In pure MgCl2, the MgO solubility was determined to be 0.63–2.90 mol% at 1073–1373 K, while 0.24–0.63 mol% in pure CaCl2 at 1223–1523 K. The effects of MgCl2 and CaO addition to CaCl2 were investigated, and the solubility product of MgO was found to increase with the amount of MgCl2 addition, while CaO addition did not affect significantly. They were explained in terms of the activity coefficient of oxide ion (O2−) as well as the enthalpy of mixing for the MgO-CaCl2 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, CaCl2, MgCl2 etc. in the high temperature furnace. When MgO is a major refractory component, we can consider some types of corrosions 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 MgCl2-CaCl2 melt becomes important because MgO can be corroded by HCl even when the activity of MgCl2 is smaller than unity with a considerable solubility of MgO in MgCl2. When the solubility of MgO in CaCl2 melt is large, the MgO based refractory will be corroded with smaller activity of CaCl2 in the melt than that for the deposition of its condensed phases.

For the reasons, the solubility of MgO in the molten MgCl2-CaCl2 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 MgCl2 or molten CaCl2, and discussed the thermodynamics of the MgO-CaCl2 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 MgCl2 and/or CaCl2 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 CaCO3 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 Ncm3/min in order to prevent its oxidation. In the gas purification system, P2O5, soda lime and Mg flake at 823 K were used to remove H2O, CO2 and O2, respectively.

Fig. 1 Schematic cross section of the experimental apparatus.
The experimental time was determined to be 3 h for the MgO-MgCl$_2$ system and 15 h or 24 h for the MgO-CaCl$_2$ 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).

$$AO + 2HCl = ACl_2 + H_2O$$  \(1\)

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

### 3. Results

#### 3.1 The MgO-MgCl$_2$ system

In order to determine experimental time, the time dependence of MgO solubility in molten MgCl$_2$ was measured at 1373 K as shown in Fig. 2, where O$^{2-}$ content in molten MgCl$_2$ was regarded as the amount of MgO dissolved. The equilibrium 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 MgCl$_2$ 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.

#### 3.2 The MgO-CaCl$_2$ system

In order to determine the experimental time for equilibrium, MgO solubilities in molten CaCl$_2$ at various experimental time was measured at 1223 K and 1323 K as shown in Fig. 5, where Mg$^{2+}$ content in molten CaCl$_2$ 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.
The solubility of MgO in CaCl$_2$ 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 CaCl$_2$ 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).

\[ \ln K_{sp}(\text{MgO}) = \frac{-10400}{T} - 2.44 \]  

(5)

### 3.3 The MgO-CaCl$_2$(-CaO) and MgO-CaCl$_2$(-MgCl$_2$) Systems

The solubility product of MgO in the CaCl$_2$ melt showed the considerably smaller value between the previous two 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 MgCl$_2$ addition on the solubility product of MgO in the CaCl$_2$ 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).

\[
\text{MgO} + \text{CaCl}_2 = \text{MgCl}_2 + \text{CaO}
\]

\[ K_{eq} = \frac{[\text{MgCl}_2][\text{CaO}]}{[\text{MgO}][\text{CaCl}_2]} \]
The Solubility of MgO in Molten MgCl$_2$-CaCl$_2$ Salt

Table 4 Solubility of MgO in the molten CaCl$_2$-MgCl$_2$ system.

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (K)</th>
<th>Time (h)</th>
<th>Initial concentration</th>
<th>Equilibrium concentration</th>
<th>ln$X_{Mg^{2+}}X_{O^{2-}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$X_{O^{2-}} \times 10^2$</td>
<td>$X_{Mg^{2+}} \times 10^2$</td>
<td></td>
</tr>
<tr>
<td>4–1</td>
<td>1373</td>
<td>15</td>
<td>0</td>
<td>5.26</td>
<td>0.53</td>
</tr>
<tr>
<td>4–2</td>
<td>1373</td>
<td>15</td>
<td>0</td>
<td>10.2</td>
<td>1.40</td>
</tr>
<tr>
<td>4–3</td>
<td>1373</td>
<td>15</td>
<td>0</td>
<td>19.9</td>
<td>2.64</td>
</tr>
<tr>
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<td>1373</td>
<td>15</td>
<td>0</td>
<td>30.0</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Fig. 6 Composition dependence of the solubility product of MgO in molten CaCl$_2$ at 1323 K.

Fig. 7 Activity of MgCl$_2$ or CaCl$_2$ at 1373 K calculated from the phase diagram of the MgCl$_2$-CaCl$_2$ system.

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

MgO(s) = Mg$^{2+}$ + O$^{2-}$

$K_b = \frac{a_{Mg^{2+}}a_{O^{2-}}}{a_{MgO(s)}} = a_{Mg^{2+}}a_{O^{2-}} = \gamma_{Mg^{2+}}\gamma_{O^{2-}}X_{Mg^{2+}}X_{O^{2-}}$

where $a_{Mg^{2+}}$ and $a_{O^{2-}}$ are the activities of Mg$^{2+}$ and O$^{2-}$ ions, $\gamma_{Mg^{2+}}$ and $\gamma_{O^{2-}}$ are the activity coefficients of Mg$^{2+}$ and O$^{2-}$ ions, and $K_b$ 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 MgCl$_2$ and CaCl$_2$ almost conform to ideal solution as shown in Fig. 7, which are calculated from the liquidus of the MgCl$_2$-CaCl$_2$ binary system$^8$ and the Gibbs energy of fusion for both components$^9$ using Gibbs-Duhem integration and regular solution model. The activity of Mg$^{2+}$ ion is proportional to the activity of MgCl$_2$ if the activity coefficient of Cl$^{-}$ ion is independent of the cation fraction $X_{Mg^{2+}}$. Therefore, the activity coefficient of Mg$^{2+}$ ion is considered to be constant in the system.

Using the experimental data, the composition dependence of $\gamma_{O^{2-}}$ can be estimated quantitatively. The Taylor series expansion of $\ln \gamma_{O^{2-}}$ 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 CaCl$_2$ melt.

$\ln \gamma_{O^{2-}} = \ln \gamma_{O^{2-}}^{0} + \varepsilon X_{Mg^{2+}} = \ln \gamma_{O^{2-}}^{0} - 66.8X_{Mg^{2+}}$

Here $\gamma_{O^{2-}}^{0}$ is the activity coefficient of O$^{2-}$ ion at infinite dilution, and $\varepsilon$ is the constant, namely interaction parameter 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.$^3$

Therefore, O$^{2-}$ ion interacted more strongly with Mg$^{2+}$ ion in molten MgCl$_2$ than Ca$^{2+}$ ion in molten CaCl$_2$, and $\gamma_{O^{2-}}$ 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).

\[
G = G^0 + \Delta G^M
\]

\[
G^0 = n_{\text{MgO}} G_{\text{MgO}}^0 + n_{\text{CaO}} G_{\text{CaO}}^0 + \frac{n_{\text{Cl}^-}}{n_{\text{O}^2-}} G_{\text{Cl}^-}^0 + \frac{n_{\text{O}^2-}}{n_{\text{Cl}^-}} G_{\text{O}^2-}^0
\]

\[
\Delta G^M = RT \ln \frac{n_{\text{Cl}^-} + 2n_{\text{O}^2-}}{n_{\text{Cl}^-} + 2n_{\text{O}^2-}} - \Delta G_{\text{Cl}^-}^0
\]

Where \(G^0\) is the Gibbs energy of molten salt defined as eq. (10), \(\Delta G^M\) is the Gibbs energy of mixing, \(G^0\) is the standard molal 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\(^{-}\) in the system are represented by \(n_{\text{Mg}^{2+}}, n_{\text{Ca}^{2+}}, n_{\text{O}^{2-}}\) and \(n_{\text{Cl}^{-}}\), respectively, and the cation fraction \(X_{\text{Ca}^{2+}}\) and the anion fraction \(X_{\text{Cl}^{-}}\) are defined as eq. (11).

\[
X_{\text{Ca}^{2+}} = \frac{n_{\text{Ca}^{2+}}}{n_{\text{Mg}^{2+}} + n_{\text{Ca}^{2+}}} \quad X_{\text{Cl}^{-}} = \frac{n_{\text{Cl}^{-}}}{n_{\text{O}^{2-}} + n_{\text{Cl}^{-}}}
\]

The condition of electroneutrality demands the following restriction.

\[
n_{\text{Mg}^{2+}} + n_{\text{Ca}^{2+}} = n_{\text{O}^{2-}} + n_{\text{Cl}^{-}}
\]

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

\[
G^0 = n_{\text{O}^{2-}} X_{\text{Mg}^{2+}} G_{\text{MgO}}^0 + n_{\text{O}^{2-}} X_{\text{Ca}^{2+}} G_{\text{CaO}}^0 + \frac{1}{2} n_{\text{Cl}^{-}} X_{\text{Mg}^{2+}} G_{\text{Cl}^-}^0 + \frac{1}{2} n_{\text{Cl}^{-}} X_{\text{Ca}^{2+}} G_{\text{O}^{2-}}^0
\]

\[
\Delta G^M = \Delta H^M - T \Delta S^M
\]

\[
\Delta H^M = \Omega X_{\text{MgO}} X_{\text{Cl}^-} = \Omega X_{\text{MgO}} X_{\text{CaO}}\]

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

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

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

\[
\hat{G}_{\text{MgO}} = \left(\frac{\partial G}{\partial n_{\text{MgO}}}\right)_{n_{\text{CaO}}, n_{\text{Cl}^{-}}, X_{\text{Mg}^{2+}}, X_{\text{O}^{2-}}} = \left(\frac{\partial G}{\partial n_{\text{Cl}^{-}}}\right)_{n_{\text{CaO}}, n_{\text{O}^{2-}}, X_{\text{O}^{2-}}} = G_{\text{MgO}}^0 + \frac{n_{\text{Cl}^{-}}}{n_{\text{O}^{2-}} + 2n_{\text{O}^{2-}}} X_{\text{Mg}^{2+}} G_{\text{Mg}^{2+}}^0 + RT \ln X_{\text{Mg}^{2+}} X_{\text{Cl}^-} \Delta G_{\text{Cl}^-}^0 + \Omega X_{\text{Mg}^{2+}}^2
\]

\[
\text{MgO(l) + CaCl}_2(l) = \text{CaO(l) + MgCl}_2(l)
\]

Here \(\Delta G_{\text{Cl}^-}^0\) 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 \(X_{\text{Mg}^{2+}}\) in eq. (17) are considerably small. Hence, the following approximations can be developed.
The activity of $\text{CaCl}_2$ can be derived by eq. (32).

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

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

On the other hand, the activity of $\text{MgCl}_2$ in molten $\text{CaCl}_2$ at the refractory surface can be obtained as follows.

$$\text{CaCl}_2(\text{I}) = \text{CaCl}_2(g) \quad (35)$$

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

The activity of $\text{CaCl}_2$ relative to pure liquid $\text{CaCl}_2$ in equilibrium with solid MgO is represented by eq. (37) when Temkin’s model is assumed to be valid.

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

Temperature dependence of the activity of $\text{CaCl}_2$ relative to pure liquid $\text{CaCl}_2$ 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 $[\text{mass\% Cl}^-] = 0.1$, $C_{\text{Cl}} = 58.4$ and 20.1, $a_{\text{CaO}} = 0.50$ and $3.5 \times 10^{-3}$ 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 CaCl$_2$. 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 $T_{\text{corr}}$ 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 $T_{\text{corr}}$ on the Cl content in the slag is shown in Fig. 11. Even a small amount of chlorine in the slag is...
shown to cause the corrosion of MgO refractory by the dissolution in molten CaCl\textsubscript{2} thermodynamically.

5. Conclusions

The solubility of MgO in the MgCl\textsubscript{2}-CaCl\textsubscript{2} system was measured and the following findings were obtained.

1. The MgO solubility product in MgCl\textsubscript{2} melt was larger than that in CaCl\textsubscript{2} melt, and the temperature dependences of them were represented by the following equations, respectively.

\[
\ln K_{sp}(\text{MgO}) = \ln \frac{X_{\text{Mg}^{2+}}X_{\text{O}^{2-}}}{C_0} = \frac{7400}{T} + 1.26 \quad \text{(in molten MgCl}_2) \\
\ln K_{sp}(\text{MgO}) = \ln \frac{X_{\text{Mg}^{2+}}X_{\text{O}^{2-}}}{C_0} = \frac{-10400}{T} - 2.44 \quad \text{(in molten CaCl}_2)
\]

2. The solubility product of MgO in molten CaCl\textsubscript{2} increased with the content of Mg\textsuperscript{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\textsubscript{2} could happen at low temperature area.

REFERENCES