Calcium and Magnesium Deoxidation in Fe–Ni and Fe–Cr Alloys Equilibrated with CaO–Al₂O₃ and CaO–Al₂O₃–MgO Slags

Hiroki OHTA and Hideaki SUITO

Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagiken 980-8577 Japan.

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Calcium and magnesium deoxidation equilibria in Fe–20 to 60mass%Ni, Fe–10 to 40mass%Cr and Fe–18mass%Cr and 8mass% Ni alloys saturated with CaO–Al₂O₃ and CaO–Al₂O₃–MgO slags have been studied at 1873 K using CaO, Al₂O₃ and MgO crucibles. Based on these results, the interaction coefficients between Ca and O and between Mg and O are estimated for Fe–Ni, Fe–Cr and Fe–Ni–Cr alloys. The solubilities of CaO and MgO calculated by using these interaction coefficients are compared with the observed values. The phase stability regions in the Fe–40mass%Ni–Al–O–M system and the Fe–20mass%Cr–Al–O–M (M=Ca and Mg) systems are presented at 1873 K.

KEY WORDS: Ca deoxidation; Mg deoxidation; interaction coefficient; iron–nickel alloy; iron–chromium alloy.

1. Introduction

The compositional and morphological control of non-metallic inclusions is important for the improvement of product cleanliness in Fe–Ni and Fe–Cr alloys. The contents of Ca and Mg have significant effects on inclusion compositions. Therefore, for a clear understanding of inclusions formation, knowledge of thermodynamics on the deoxidation equilibria with Ca and Mg is of crucial importance. Although numerous studies were made to determine the solubilities of CaO and MgO in pure iron, systematic studies on the Ca and Mg deoxidation equilibria in Fe–Ni, Fe–Cr and Fe–Ni–Cr alloys have not been made so far.

In the previous study, the equilibrium experiments between CaO–Al₂O₃, CaO–Al₂O₃–SiO₂, CaO–Al₂O₃–MgO, and CaO–Al₂O₃–SiO₂–MgO slags and liquid pure Fe were carried out at 1873 K using CaO, Al₂O₃ and MgO crucibles. In this study, the relationships between Ca and O and between Mg and O have been determined in Fe–Ni, Fe–Cr and Fe–Ni–Cr alloys in pure iron, systematic studies on the Ca and Mg deoxidation equilibria in Fe–Ni, Fe–Cr and Fe–Ni–Cr alloys have not been made so far.

The results of AC and CA slags were used to determine the interaction coefficients between Ca and O and those of MCA slag were used to determine the interaction coefficients between Mg and O.

3. Results and Discussion

The chemical compositions of metal and slag phases in CaO–Al₂O₃ slags are already described in the preceding article. The chemical compositions of metal and slag phases in CaO–Al₂O₃–MgO slags are given in Table 1. The CaO–Al₂O₃ slags saturated with an Al₂O₃ and CaO crucible are denoted by AC and CA slags, respectively, and the CaO–Al₂O₃–MgO slag saturated with a MgO crucible denotes MCA slag, hereinafter. The results of AC and CA slags were used to determine the interaction coefficients between Ca and O and those of MCA slag were used to determine the interaction coefficients between Mg and O.

3.1. Ca Deoxidation

Calcium deoxidation equilibrium in an Fe–X alloy (X= Ni or Cr) is represented by

$$\text{CaO} + \text{Fe}_x \rightarrow \text{Ca}_x \text{Fe}_x \quad (1)$$

The equilibrium constant of Eq. (1) for pure iron, $K_{\text{CaO/Fe}}$, can be written, using the activities of Ca and O in liquid Fe–X alloy relative to an infinite dilute solution of 1mass%
standard state, which are defined based on pure iron.

\[
\log K_{\text{CaO(Fe)}} = \log \left( \frac{[\text{Ca}] \cdot [\text{O}]}{\text{a} \cdot \text{CaO}} \right) + \log f_{\text{CaO(Fe)}} + \log f_{\text{CaO(Fe)}}^0 + \sum_i \left( \frac{e_{\text{CaO(Fe)}i}}{M_i} \right) \cdot \text{X}_i 
\]

where \(i\) and \(j\) represent the component other than O and Ca, respectively. The \(f_{\text{CaO(Fe)}}^0\) and \(f_{\text{CaO(Fe)}}\) values represent the activity coefficient of calcium and oxygen in Henry’s state, referred to 1 mass%, based on pure iron, respectively. \(e_{\text{CaO(Fe)}i}\) and \(r_{\text{CaO(Fe)}i}\) are the first-order and second-order interaction coefficients based on pure iron, respectively.

In Fe-X (X= Ni or Cr) alloy, the \(f_{\text{CaO(Fe)}}^0\) values are defined as Eqs. (3) and (4), respectively.

\[
\log f_{\text{CaO(Fe)}i} = e_{\text{CaO(Fe)}i} \cdot \frac{[\text{Ca}] \cdot [\text{O}] \cdot [\text{X}]}{\text{a} \cdot \text{CaO}} 
\]

The following relations\(^8\) can be derived based on the reciprocal and conversion relationships of the interaction coefficients.

\[
e^i_j = M_i / M_j \cdot e^j_i \quad \text{(5)}
\]

\[
r^i_j = (M_i / M_j)^2 \cdot r^j_i \quad \text{(6)}
\]

\[
r^j_i = (M_i / M_j)^2 \cdot r^i_j \quad \text{(7)}
\]

\[
r^i_j = M_i / M_j \cdot r^i_j \quad \text{(8)}
\]

where \(e^i_j\) and \(r^i_j\) are the first-order and second-order interaction coefficients, respectively, and \(M_i\) and \(M_j\) are the atomic weights of the solutes of \(i\) and \(j\), respectively.

The following relation can be deduced from Eq. (2), coupled with Eqs. (3) through (8). Details of the derivation are given in the previous article.\(^9\)
where $A$ is given by $(\sum e_{CaO}^{f} \cdot \%Ca^{f} + \sum r_{CaO}^{f} \cdot \%Ca^{f}) + (\sum e_{OCa}^{f} \cdot \%O^{f} + \sum r_{OCa}^{f} \cdot \%O^{f})$, in which $i$ and $j$ represent the component other than O and Ca, respectively.

In Fig. 1, the terms on the right-hand side of Eq. (9) are plotted against the values of ($\%Ca^{f}$+2.51($\%O^{f}$))·($\%Cr^{f}$) for Fe–10, 20 and 40mass%Cr alloys equilibrated with CaO–Al$_2$O$_3$ (AC, CA) slag. In this calculation, the log $K_{CaO(Fe)}$ value calculated as 10.22 at 1873 K from the $D_{G}^{\circ}CaO(Fe)$ value ($D_{G}^{\circ}CaO(Fe)/R = 148.7$ J/mol$^1$), the respective interaction coefficients given in Table 2,8,12–17) and the $r_{CaO}^{f}$, $r_{OCa}^{f}$, and $r_{CaO}^{f}$ values estimated based on pure iron7) given in Table 3 were used together with the activities of CaO for AC(0.11)18) and CA(1)18) slags. The value of $r_{O,Cr}^{f}$ is estimated as 12.3 from the slope of the line shown in Fig. 1 and the value of $r_{O,Cr}^{f}$ is obtained as 30.7 by using the relation given in Eq. (8).

Similarly, the terms on the right hand-side of Eq. (9) are plotted against the values of ($\%Ca^{f}$+2.51($\%O^{f}$))·($\%Ni^{f}$) for Fe–20, 40 and 60mass%Ni alloys in Fig. 2. In this calculation, the respective interaction coefficients given in Tables 2 and 3 were used. The finding that the linear relationship is not observed suggests that the interaction coefficient between Ca and O based on pure iron cannot be used for an Fe–Ni alloy in the range of $\%Ni^{f} \approx 20$.

In an Fe–Ni alloy, therefore, the following method was used to determine the activity coefficients of Ca ($f_{Ca}^{f}$) and O ($f_{O}^{f}$).

**Table 2.** Interaction coefficients based on pure iron at 1873 K used in the present study.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$j$</th>
<th>$e_{i}^{f}$ ($r_{j}^{f}$)</th>
<th>Range</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Ni</td>
<td>0.003 (0.0003)</td>
<td>&lt; 40% Cr</td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>-0.0431 (0.0003)</td>
<td>&lt; 40% Cr</td>
<td>(14)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>-0.83</td>
<td>&lt; 1% Al</td>
<td>(8)</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>-0.021</td>
<td></td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.2</td>
<td></td>
<td>(12)</td>
</tr>
<tr>
<td>Al</td>
<td>Ni</td>
<td>-0.029</td>
<td>&lt; 40% Ni</td>
<td>(8)</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>0.0006</td>
<td>&lt; 40% Cr</td>
<td>(8)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>0.045 (0.0001)</td>
<td></td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>—</td>
<td></td>
<td>(8)</td>
</tr>
<tr>
<td>Ca</td>
<td>Ni</td>
<td>-0.043</td>
<td>&lt; 40% Ni</td>
<td>(15)</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>0.014</td>
<td>&lt; 30% Cr</td>
<td>(15)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>—</td>
<td></td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>—</td>
<td></td>
<td>—</td>
</tr>
<tr>
<td>Mg</td>
<td>Ni</td>
<td>-0.026</td>
<td>&lt; 43% Ni</td>
<td>(16)</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>0.010</td>
<td>&lt; 9.4% Cr</td>
<td>(17)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>—</td>
<td></td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>—</td>
<td></td>
<td>—</td>
</tr>
</tbody>
</table>

**Table 3.** Interaction coefficients between Ca and O in liquid iron alloys at 1873 K.

<table>
<thead>
<tr>
<th>Pure Fe (Ref.7)</th>
<th>$e_{Ca}^{f}$</th>
<th>$r_{Ca}^{f}$</th>
<th>$e_{O}^{f}$</th>
<th>$r_{O}^{f}$</th>
<th>$r_{O,Cr}^{f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$e_{Ca}^{f}$</td>
<td>$r_{Ca}^{f}$</td>
<td>$e_{O}^{f}$</td>
<td>$r_{O}^{f}$</td>
<td>$r_{O,Cr}^{f}$</td>
</tr>
<tr>
<td></td>
<td>$e_{Ca}^{f}$</td>
<td>$r_{Ca}^{f}$</td>
<td>$e_{O}^{f}$</td>
<td>$r_{O}^{f}$</td>
<td>$r_{O,Cr}^{f}$</td>
</tr>
<tr>
<td>Fe–Cr alloy</td>
<td>$e_{Ca}^{f}$</td>
<td>$r_{Ca}^{f}$</td>
<td>$e_{O}^{f}$</td>
<td>$r_{O}^{f}$</td>
<td>$r_{O,Cr}^{f}$</td>
</tr>
<tr>
<td>[Cr]</td>
<td>$e_{Ca}^{f}$</td>
<td>$r_{Ca}^{f}$</td>
<td>$e_{O}^{f}$</td>
<td>$r_{O}^{f}$</td>
<td>$r_{O,Cr}^{f}$</td>
</tr>
<tr>
<td>20% Ni</td>
<td>$e_{Ca}^{f}$</td>
<td>$r_{Ca}^{f}$</td>
<td>$e_{O}^{f}$</td>
<td>$r_{O}^{f}$</td>
<td>$r_{O,Cr}^{f}$</td>
</tr>
<tr>
<td>60% Ni</td>
<td>$e_{Ca}^{f}$</td>
<td>$r_{Ca}^{f}$</td>
<td>$e_{O}^{f}$</td>
<td>$r_{O}^{f}$</td>
<td>$r_{O,Cr}^{f}$</td>
</tr>
</tbody>
</table>

Fig. 1. A plot for the relation expressed by Eq. (9) in Fe–10, 20 and 40mass%Cr alloys.

Fig. 2. An plot for the relation expressed by Eq. (9) in Fe–20, 40 and 60mass%Ni alloys.
If the contents of Ca and O are considerably low compared with the content of Ni, the equilibrium constant of Eq. (1) based on pure Fe, $K_{CaO(Fe)}$ in Fe–Ni alloy can be expressed approximately as follows:

$$\log K_{CaO(Fe)} = \log[\alpha_{CaO(Fe)}]_0 + \log f_{Fe}^{Ni} + \log f_{O}^{Fe}$$ ....(10)

By using Eq. (10), the equilibrium constant of Eq. (1) based on Fe–Ni system, $K_{CaO(Fe–Ni)}$, can be defined as follows:

$$\log K_{CaO(Fe–Ni)} = \log K_{CaO(Fe)} + \log f_{Fe}^{Ni} + \log f_{O}^{Fe}$$

$$= \log K_{CaO(Fe)} - \frac{N_{Ca}(\%Ni)}{e_{Fe–Ni}(\%Ni)} - \frac{N_{O}(\%Ni)}{r_{Fe–Ni}(\%Ni)^2}$$ ............(11)

The log $K_{CaO(Fe–Ni)}$ values for Fe–20, 40 and 60mass%Ni alloys can be calculated from Eq. (11) by using the interaction coefficients ($e_{Fe–Ni}(\%Ni)$ and $r_{Fe–Ni}(\%Ni)$) given in Table 2.

The activities of Ca and O in Fe–Ni alloys can be defined based on either pure iron or Fe–Ni alloys. Thus, these activity coefficients based on the Fe–Ni system can be defined as follows:

$$\log f_{Ca}^{Fe–Ni} = e_{Ca}^{Fe–Ni}(\%O) + r_{Ca}^{Fe–Ni}(\%O)^2 + r_{Ca}^{Fe–Ni}(\%O)$$............(12)

$$\log f_{Ca}^{Fe–Ni} = e_{Ca}^{Fe–Ni}(\%Ca) + r_{Ca}^{Fe–Ni}(\%Ca) + r_{Ca}^{Fe–Ni}(\%Ca)$$............(13)

where $e_{Fe–X}$ and $r_{Fe–X}$ ($r_{Fe–X}$) are the first-order and second-order interaction coefficients based on Fe–Ni alloy, respectively.

Using a similar equation to Eq. (2) with respect to the Fe–Ni system together with Eqs. (5) to (7) and Eqs. (11) to (13), the following equation can be derived.

$$\log K_{CaO(Fe–Ni)} = -\log(\%Ca) - \log(\%O) + \log a_{CaO} - B$$

where $B$ is given by $(\sum e_{Fe–Ni}(\%Ca) + \sum r_{Fe–Ni}(\%Ca)^2) + (\sum r_{Fe–Ni}(\%O) + \sum r_{Fe–Ni}(\%O)^2)$, in which $i$ is the component other than O and Ni and $j$ is the component other than Ca and Ni.

In Fig. 3, the term on the left-hand side of Eq. (14) denoted by $Y$ is plotted against the second term without $r_{Fe–Ni}^{Ca}$ on the right-hand side of Eq. (14), which is denoted by $X$. In this calculation, the value for log $K_{CaO(Fe–Ni)}$ was calculated from Eq. (11) and it was assumed that the values for the interaction coefficients based on Fe–Ni system in B term correspond to those based on pure Fe. As predicted from Eq. (14), the intercept and slope for a given X correspond to the values for $e_{Ca}^{Fe–Ni}$ and $r_{Ca}^{Fe–Ni}$, respectively. The values for $e_{Ca}^{Fe–Ni}$ and $r_{Ca}^{Fe–Ni}$, with respect to Fe–20, 40 and 60mass%Ni alloys were estimated by using the following method.

The data points shown in Fig. 3 are expressed approximately by a continuous function of $X$ as follows:

$$Y = a + b \log X + c(\log X)^2$$ ............(15)

where $a = -6770 \pm 610$, $b = -6990 \pm 630$ and $c = -1890 \pm 170$ in Fe–20mass%Ni alloy and $a = -2040 \pm 80$, $b = -2510 \pm 100$ and $c = -823 \pm 33$ in Fe–40mass%Ni alloy and $a = -856 \pm 68$, $b = -1170 \pm 90$ and $c = -443 \pm 35$ in Fe–60mass%Ni alloy.

The values for $e_{Ca}^{Fe–Ni}$ and $r_{Ca}^{Fe–Ni}$ can be estimated from the intercept and slope for a given $X$, respectively, as predicted from Eq. (14). In the case of strong interaction such as between Ca and O, the first-order and second-order interaction coefficients cannot be simply determined in an usual method. In previous study, therefore, the interaction coefficients were expressed as a function of Ca and O contents. It is assumed that these interaction coefficients satisfy the relations given by Eqs. (5) to (8). These values which are given in Table 3 are determined from the following relations:

$$e_{Ca}^{Fe–Ni} = -X(dY/dX)$$

$$= (a - 0.434) + (b - 0.869c) \log X + c(\log X)^2$$ ....(16)

$$r_{Ca}^{Fe–Ni} = (dY/dX)$$

$$= 0.434(b + 2c \log X)/X$$ ............(17)

Details of these derivations are given in the previous paper.

A similar procedure is used for Fe–18mass%Cr–8mass%Ni alloy and the values for $a = -6300 \pm 380$, $b = -6770 \pm 410$ and $c = -1880 \pm 110$ were obtained.

The relations between Ca and O contents were calculated at $a_{CaO} = 1$ from Eq. (14) by using the interaction coefficients estimated from the present and previous studies4,11–17 which are summarized in Tables 2 and 3, and the Ca deoxidation equilibrium constant of Eq. (1) for pure Fe. The results for Fe–20, 40 and 60mass%Ni alloys are shown in Fig. 4 together with the results of pure Fe. The data points shown in Fig. 4 correspond to the experimental results for Fe–20, 40 and 60mass%Ni alloys equilibrated with CA slag ($a_{CaO} = 1$). It is seen that the data points correspond reasonably well to the respective calculated lines. The discrepancy is observed between the experimental and calcu-
lated results for the alloys in the range of [%Al]/H11022 0.1. This is attributed to the effect of aluminium on oxygen activity. The results for Fe–10, 20 and 40mass%Cr alloys are shown in Fig. 5, indicating that the experimental data points fall approximately on the corresponding lines. However, the data of [%Al]/H11022 0.1 show the disagreement. When the oxygen content is higher than 5 ppm, the Ca content at a given oxygen level increases with an increase in Cr content. The relationships between Ca and O contents in Fe–18mass%Cr–8mass%Ni alloy equilibrated with CaO at 1873 K are shown in Fig. 6. The experimental data points of [%Al]/H11022 0.1 fall approximately on the line of Fe–18mass%Cr–8mass%Ni alloy.

3.2. Mg Deoxidation

Mg deoxidation equilibrium is represented by

\[ \log K_{\text{MgO(Fe)}} = -\log([\%\text{Mg}] + 1.52[\%\text{O}]/[\%\text{Fe}]) - C \]

where \( C \) is given by \( (\sum \epsilon_{\text{Mg(Fe)}}[\%i] + \sum r_{\text{Mg(Fe)}}[\%j] + \sum r_{\text{Fe(Fe)}}[\%j]^2) \), in which \( i \) and \( j \) represent the component other than O and Mg, respectively.

In Fig. 7, the terms on the right-hand side of Eq. (19) are plotted against the values of ( [%Mg] + 1.52[ %O] ) - [ %Ni ] for Fe–20, 40 and 60mass%Ni alloys. Similarly, the terms on the right-hand side of Eq. (19) are plotted against the values of ( [%Mg] + 1.52[ %O] ) - [ %Cr ]
for Fe–10, 20 and 40 mass% Cr alloys. The values for \( r_{\text{MgO}} \) are estimated as 0.25 from the slope of the line in Fig. 8.

The relationships between Mg and O contents were calculated for Fe–Ni or Fe–Cr alloy by using the iterative method. \(^2\) The present estimated values for the interaction coefficients between Mg and O given in Table 4 were used in this calculation.

The results for Fe–20, 40 and 60 mass% Ni alloys are shown in Fig. 9, together with the results of pure Fe and pure Ni. The data points shown in Fig. 9 correspond to the experimental results for Fe–20, 40 and 60 mass% Ni alloys equilibrated with the MCA slag (\( a_{\text{MgO}} = 1 \)). The half-filled marks represent the data of [ppm Ca] < 2 ppm. It can be seen that the experimental data of [ppm Ca] < 2 ppm are in good accordance with the respective calculated lines. The discrepancy between the experimental and calculated results in the range of [ppm Ca] > 2 ppm is attributed to the effect of calcium on oxygen activity. The magnesium content at a given oxygen level increases with an increase in nickel content.

The relationships between Mg and O contents in Fe–10, 20 and 40 mass% Cr alloys are shown in Fig. 10. It is seen that the experimental data points of [ppm Ca] < 2 ppm fall approximately on the corresponding lines. The magnesium content at a given oxygen level increases with an increase in chromium content.

The relationships between Mg and O contents in Fe–18 mass% Cr–8 mass% Ni alloy equilibrated with MCA slag at 1873 K are shown in Fig. 11, where the lines were calculated by the iterative method using the equilibrium constant of Eq. (18) based on pure iron and the interaction parameters estimated in this study for Fe–Ni and Fe–Cr alloys given in Tables 2 and 3. The experimental data points of [ppm Ca] < 2 ppm fall approximately on the line of Fe–18 mass% Cr–8 mass% Ni alloy. These results indicate that the interaction parameters obtained in this study for Fe–Ni and Fe–Cr alloys can be used to the Mg deoxidation equilibrium in Fe–Cr–Ni alloys.

### 3.3. Phase Stability Diagram

The relations between Al and Ca contents in equilibrium with AlO\(_2\), calcium aluminate, liquid oxide and CaO phases were calculated at 1873 K by the iterative method using the respective interaction coefficients. In this calculation, the free energy change for the formation of calcium...

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**Table 4. Interaction coefficients between Mg and O in liquid iron alloys at 1873 K.**

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>( e_i^j )</th>
<th>( r_i^j )</th>
<th>( r_i^{\text{MgO}} )</th>
<th>( r_i^{\text{Ni}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Mg</td>
<td>-300</td>
<td>16,000</td>
<td>48,000</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>O</td>
<td>-460</td>
<td>37,000</td>
<td>48,000</td>
<td>0</td>
</tr>
<tr>
<td>Fe–Cr alloy (&lt; 40% Cr)</td>
<td>O</td>
<td>-300</td>
<td>16,000</td>
<td>48,000</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>O</td>
<td>-460</td>
<td>37,000</td>
<td>48,000</td>
<td>0</td>
</tr>
<tr>
<td>Fe–Ni alloy (&lt; 60% Ni)</td>
<td>O</td>
<td>-300</td>
<td>16,000</td>
<td>48,000</td>
<td>0.88</td>
</tr>
<tr>
<td>Mg</td>
<td>O</td>
<td>-460</td>
<td>37,000</td>
<td>48,000</td>
<td>1.34</td>
</tr>
</tbody>
</table>

*; assessed in the present study
aluminate \( \{\text{CaO} \cdot \text{Al}_2\text{O}_3(\text{CA})\}, \text{CaO} \cdot 2\text{Al}_2\text{O}_3(\text{CA}_2) \) and \( \text{CaO} \cdot 6\text{Al}_2\text{O}_3(\text{CA}_6) \)\) and the interaction coefficients between Ca and O contents given in Table 3 were used. The results for pure Fe, Fe–40mass%Ni and Fe–20mass%Cr alloys are shown in Figs. 12, 13 and 14, respectively. The experimental results obtained in AC and CA slags are shown by open circle and square marks, respectively, in Figs. 13 and 14. The results obtained by CA slags are in good accordance with the liquid oxide–CaO boundary line, and those obtained by AC slag fall roughly on the liquid oxide–CaO · Al2O3(CA) phase boundary line except for a few data points at ppm Al \( \approx 10 \).

The relations between Al and Mg contents in equilibrium with \( \text{Al}_2\text{O}_3, \text{MgO} \cdot \text{Al}_2\text{O}_3(\text{MA}) \) and MgO phases were calculated at 1873 K by the iterative method using the respective interaction coefficients. In this calculation, the free energy change for the formation of MgO · Al2O3(\text{MA})\) and the interaction coefficients between Mg and O given in Table 4 were used. The results for Fe–40mass%Ni and Fe–20mass%Cr are shown in Figs. 15 and 16, respectively, together with those for pure Fe, in which the experimental data (MCA) obtained at the slag compositions double-saturated with MgO · Al2O3(\text{MA}) and MgO phases are also shown. These results for ppm Ca \( > 1 \) are slightly above the MgO · Al2O3(\text{MA})–MgO phase boundary line. The stability
region in the Fe–Ni(Cr)–Al–Mg–O system is affected by the presence of Ca in such a manner that the Mg content for a given Al level in alloy in equilibrated with the slag saturated MgO and MgO·Al2O3(MA) or MgO·Al2O3(MA) and Al2O3 phases increases with an increase of Ca level.

4. Summary

The applicability of the Wagner’s interaction coefficients to the deoxidation equilibria of Ca and Mg has been studied for Fe–20, 40 and 60mass%Ni, Fe–10, 20 and 40mass%Cr and Fe–18mass%Cr–8mass%Ni alloys.

(1) It was found in Fe–Cr alloy that the Ca deoxidation equilibrium could be explained by the log
\[ \log f_{\text{Ca}}(\text{O}) \] and
\[ \log f_{\text{O}}(\text{Ca}) \] values which are defined as Eqs. (3) and (4), respectively. The values for \( r_{\text{O}(\text{Fe})}^\text{Ca,Cr} \) were estimated by using the value for \( e_{\text{O}} \) and \( r_{\text{Ca}}^\text{O} \) for pure iron obtained in previous studies. However, the Ca deoxidation equilibrium in Fe–20, 40 and 60mass%Ni and Fe–18mass%Cr–8mass%Ni alloys could not be explained by the aforementioned method for Fe–Cr alloy. Therefore, the relation given by Eq. (14) is used in order to determine the interaction coefficients between Ca and O.

(2) In Fe–Ni and Fe–Cr alloys, the values for \( r_{\text{Mg}}^\text{Ni} \) and \( r_{\text{Mg}}^\text{Cr} \) were estimated by using the value for \( e_{\text{O}} \) and \( r_{\text{Ca}}^\text{O} \) for pure iron obtained in previous studies. It was found that the interaction coefficients obtained in this study for Fe–Ni and Fe–Cr alloys could be used for the Mg deoxidation equilibrium in Fe–Cr–Ni alloys.

(3) Phase stability regions with respect to the relation between Al and Ca contents in the Fe–40mass%Ni–Al–Ca–O and Fe–20mass%Cr–Al–Ca–O systems were estimated by using the interaction coefficients between Ca and O obtained in this study. Phase stability regions with respect to the relation between Mg and Al contents in the Fe–40mass%Ni–Al–Mg–O and Fe–20mass%Cr–Al–Mg–O systems were estimated by using the interaction coefficients between Mg and O obtained in this study.

REFERENCES