Activities of FeO$_{1.33}$ in the FeO$_x$–CaO–SiO$_2$ and FeO$_x$–CaO–SiO$_2$–Al$_2$O$_3$ Slags at 1 573 K Under Oxygen Partial Pressures between 10$^{-6}$ and 10$^{-2}$ atm

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Qualities of sinters such as reducibility and strength are controlled by morphologies and mineral phases in iron ore sinters. Main mineral phases are hematite, magnetite and calcium ferrite. Slag phases are also included in sinters, which have been mainly liquid phases during the sintering process. Since iron ions in slags are hardly reduced to metallic iron in blast furnace, iron oxides such as hematite and magnetite and calcium ferrite should be precipitated from molten slags during the sintering process. Precipitation of iron oxides and calcium ferrites from molten slags depends on the activity of FeO in molten slags from the thermodynamic viewpoint. Therefore, the activities of FeO$_{1.33}$ have been measured over the wide ranges of chemical compositions in the single liquid phases of the FeO$_x$–CaO–SiO$_2$ and FeO$_x$–CaO–SiO$_2$–Al$_2$O$_3$ slags at 1 573 K under oxygen partial pressures between 10$^{-6}$ and 10$^{-2}$ atm. It has been found that the $\gamma_{\text{FeO}_{1.33}}$ values have maximum at the CaO/SiO$_2$(mass%) ratios of 0.9–1.0 and 1.3–1.4 for the samples with 35 mass%FeO$_x$ equilibrated at $P_{O_2} = 1.0 \times 10^{-2}$ atm and $1.0 \times 10^{-4}$ atm, respectively. For the samples at $P_{O_2} = 2.5 \times 10^{-6}$ atm, on the other hand, $\gamma_{\text{FeO}_{1.33}}$ monotonically increases with increasing the CaO/SiO$_2$ ratio within the compositional range of the single liquid region. As for the effect of the Al$_2$O$_3$ addition on the activities, the dependency of the activity on the CaO/SiO$_2$ ratio becomes moderate with increasing the Al$_2$O$_3$ addition on the sample at $P_{O_2} = 2.5 \times 10^{-6}$ atm.

KEY WORDS: FeO$_x$–SiO$_2$–CaO system; oxygen partial pressure; Al$_2$O$_3$; FeO$_x$ activity.

1. Introduction

Qualities of sinters such as reducibility and strength are controlled by morphologies and mineral phases in iron ore sinters.

Molten slags play an important role as a binder of powdery raw materials of sinters during the sintering process. However, if excessive amount of molten slags are produced during the sintering process, large amount of slags remaining in sinters seriously reduces the strength of sinters. Presence of slags in sinters also causes a problem when the considerable amount of iron ions exists in the slag phases. Iron ions in slags are hardly reduced to metallic iron in blast furnace because the rate of reducing agent supply into slags is substantially low. Therefore, iron oxide phases such as hematite and magnetite and calcium ferrite should be precipitated from molten slags during the sintering process so as to suppress the production of slag phases in sinters. Precipitation of iron oxides and calcium ferrites from molten slags depends on the activity of FeO in molten slags from the thermodynamic viewpoint. Therefore, it is of great importance to know the variation with compositions of the FeO activities for designing of iron ore sinters. However, to the best of authors’ knowledge, there are only few reports with respect to the FeO activities measured at the experimental conditions (temperatures and oxygen partial pressures in atmospheres) aiming for the development of iron ore sintering.

FeO activities in molten slags have been intensively measured at iron saturation on steelmaking slags. In such experimental conditions, most iron ions exist as Fe$^{2+}$ and the contents of Fe$^{3+}$ in the slags are negligibly small. On the other hand, since the oxygen partial pressures in sintering processes are higher than those at iron saturation, the slags in sinters must contain higher Fe$^{3+}$ contents than the slags at iron saturation, and the activities of iron oxides in the slags must be more strongly affected by the ratio of Fe$^{2+}$/Fe$^{3+}$. Henao et al. have measured the activities of FeO and the activity coefficients of FeO$_{1.33}$ in the FeO$_x$–CaO–SiO$_2$ system at 1 573 K under intermediate oxygen partial pressures between two extremes of iron saturation.

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and air atmosphere. However, they have only measured the activities in the limited compositional areas. The present authors have previously determined the compositional areas of the single liquid phases in the FeO$_x$–CaO–SiO$_2$ and the FeO$_x$–CaO–SiO$_2$–Al$_2$O$_3$ systems at 1 573 K at three different oxygen partial pressures of $10^{-6}$, $10^{-4}$ and $10^{-2}$ atm, and have found that the areas for which Henao and have found that the areas of the single liquid phases are much larger than the areas for which Henao et al. have measured the activities. Therefore, the aim of this study is to measure the activities of FeO$_{1.33}$ over the wider ranges of chemical compositions in the single liquid phases at 1 573 K under oxygen partial pressures between $10^{-6}$ and $10^{-2}$ atm so as to clarify the effect of the slag compositions on the activities.

2. Experimental

2.1. Equilibrium Experiments

Three series of samples were prepared:

Series 1: 35(mass%)Fe$_2$O$_3$–65CaO–65(1–a)SiO$_2$

Series 2: b(48.00–b)CaO–0.52(100–b)SiO$_2$

Series 3: 35(100–c)SiO$_2$–(65–c)CaO–65c(1–d)Al$_2$O$_3$

Samples were prepared from reagent grade Fe$_2$O$_3$, SiO$_2$, Al$_2$O$_3$, and CaCO$_3$ powders, the last being decomposed to CaO by heating at 1 373 K for 12 h in air. The reagents were weighted to the desired compositions and mixed in an alumina mortar. About 0.4 g of these mixtures were contained in a Pt crucible which was folded from Pt foil (12 mm × 35 mm and 0.02 mm in thickness), then suspended by a Pt wire within the uniform temperature region of a SiC resistance furnace. Experiments were carried out in air or in a flow of Ar–O$_2$ gases (50 ml/min.). Oxygen partial pressures in the Ar–O$_2$ gases were confirmed using an oxygen sensor to be $2.5 \times 10^{-6}$ atm, $1.0 \times 10^{-4}$ atm and $1.0 \times 10^{-2}$ atm. The temperature at a uniform temperature region was controlled within 1 573 ± 2 K. In accordance with the preliminary experiment described in the section 2.2, the heating durations of the samples were set to be 72 h, which is long enough for the samples to be thermodynamically equilibrated with the gas phase as well as the Pt foil. The samples held at 1 573 K were quenched into iced water. The phases of the samples were determined by X-ray diffraction (XRD) analyses. The chemical compositions of liquid phases were measured by an electron probe microanalyzer (EPMA) with an accelerating voltage of 15 kV and a probe current of 20 nA. A homogeneous glassy sample having the composition of 24.58 mass%Fe, 25.53 mass%Ca, 12.84 mass%Si, 1.06 mass%Al and 35.98 mass%O was used as a standard sample for quantitative analyses by EPMA. The composition of the standard sample was calculated using the mixture fractions of the Fe$_2$O$_3$, CaO, SiO$_2$, and Al$_2$O$_3$ powders and the Fe$^{2+}$/Fe$^{3+}$ ratio analyzed by Mössbauer spectroscopy.

2.2. Calculation Methodology of the Activity of FeO$_{1.33}$

The FeO$_{1.33}$ activities in the slag samples are estimated based on the following chemical reaction,

$$\text{Fe}(\text{in Pt}) + \frac{2}{3} \text{O}_2 (\text{in gas}) = \text{FeO}_{1.33} (\text{in slag}) \quad \ldots (1)$$

Here, a slag sample is assumed to be in equilibrium with the gas atmosphere of known oxygen partial pressure and the Pt crucible containing Fe. Namely, Fe content in the Pt crucible is assumed to be controlled by Eq. (1). The standard Gibbs energy of the formation of solid FeO$_{1.33}$, $\Delta G^o$, is written as

$$\Delta G^o / \text{Jmol}^{-1} = -367 414 + 102.47T = -RT \ln \frac{a_{\text{FeO}_{1.33}}}{a_{\text{Fe}} a_{\text{O}_2}} \quad \ldots (2)$$

where $T$, $a_{\text{FeO}_{1.33}}$, $a_{\text{Fe}}$ and $a_{\text{O}_2}$ represent the temperature, the activity of FeO$_{1.33}$, the activity of Fe and the oxygen partial pressure, respectively. The standard states of $a_{\text{FeO}_{1.33}}$ and $a_{\text{Fe}}$ are taken as solid FeO$_{1.33}$ and pure solid iron at the experimental temperature, respectively. The values of $a_{\text{FeO}_{1.33}}$ can be unambiguously determined when the slag is in the equilibrium state. From Eq. (2), the $a_{\text{FeO}_{1.33}}$ values in the samples can be calculated using the $a_{\text{Fe}}$ values in the Pt foil and the $a_{\text{O}_2}$ values in the gas phase. The $a_{\text{Fe}}$ values in the Pt foil were obtained by the method described in the section 2.4. The $a_{\text{O}_2}$ values in the gas phase were measured by an oxygen sensor as aforementioned.

2.3. Measurement of Fe Contents in Pt Foils in Equilibrium with Slags

Figure 1 shows a back-scattered electron (BSE) image of a sample heated for 24 h (a), the line profile of the Fe element for the same sample (b), and the line profile of the Fe element for the sample heated for 72 h (c). In the samples, the equilibrated phases consist of a liquid phase and magnetite. The area with “B.G.” corresponds to the resin used for the sample preparation for the EPMA observation. It can be seen from Fig. 1(b) that the Fe distribution across the thickness of the Pt foil is uniform, demonstrating that the equilibrium could be attained in 24 h. The Fe content in the Pt foil was calculated by comparing the X-ray intensity in the Pt foil and that in the slag (liquid phase) after the background intensity was subtracted from both. Here, the Fe content in the slag was preliminarily analyzed by spot analyses as aforementioned in the section 2.1. It has been found that the Fe contents in the Pt foils of the samples heated for 24 h and 72 h are identical within the analytical errors. This also supports that the equilibrium could be attained in 24 h. On the other hand, one of the present authors have reported that the time demanded for the coordination structures of iron ions to settle down at the equilibrium state is about three times as long as that for the valence states of iron ions in the same slags. Therefore, the authors have adopted 72 h as the heating duration in this study.

2.4. Determination of Fe Activities in Pt Foils in Equilibrium with Slags

$a_{\text{Fe}}$ was obtained by multiplying the Fe content (= $N_{\text{Fe}}$) in the Pt foil by the activity coefficient of Fe (= $\gamma_{\text{Fe}}$) in the Fe–Pt alloy. $N_{\text{Fe}}$ was measured in the same manner as described in the section 2.3. The $\gamma_{\text{Fe}}$ values of Fe–Pt alloys have been investigated by several authors. The experimental
data available in the literatures were carefully compared by Fredriksson and Seetharaman. The discrepancies can be recognized particularly in the lower Fe concentrations. Therefore, the $\gamma_{Fe}$ values were also measured in this study.

The $\gamma_{Fe}$ values can be experimentally obtained by measuring the $N_{Fe}$ values in the Pt foil equilibrated with the slags composed of magnetite and a liquid phase at known oxygen partial pressures because the CaO and SiO$_2$ solid solutions in magnetite are negligible: Magnetite is thermodynamically stable at oxygen partial pressures of $2.5 \times 10^{-6}$ atm, $1.0 \times 10^{-4}$ atm and $1.0 \times 10^{-2}$ atm. According to the Fe–O phase diagram, magnetite is a nonstoichiometric compound, deviating from the stoichiometric compound of Fe$_3$O$_4$ toward the O-rich compositional region. The atomic ratios of O/Fe in magnetite have been reported by Phillips and Muan as functions of temperature and oxygen partial pressure, where the O/Fe ratios ($x = \frac{O}{Fe}$) in magnetite, FeO$_x$, at 1 573 K are found to be 1.337, 1.339 and 1.346 at $P_{O_2} = 2.5 \times 10^{-6}$ atm, $1.0 \times 10^{-4}$ atm and $1.0 \times 10^{-2}$ atm, respectively. Spencer and Kubaschewski have reported the standard Gibbs energy of formation of nonstoichiometric magnetite, $\Delta G_f^0$, as a function of the Fe/O ratio. The $\Delta G_f^0$ values at 1 573 K can be estimated to be $-206.68$ kJ/mol, $-206.59$ kJ/mol and $-206.31$ kJ/mol at $x = 1.337, 1.339$ and 1.346, respectively. Therefore, the $\gamma_{Fe}$ values in Pt can be calculated using the following equation.

$$Fe + \frac{1}{2}O_2 = FeO_{x} \quad \Delta G_f^0 = -RT \ln \frac{a_{FeO_{x}}}{\gamma_{Fe}N_{Fe}P_{O_2}^{\frac{1}{2}}} \quad (3)$$

where the activity of FeO$_x$, $a_{FeO_{x}}$, is unity for the slags in equilibrium with FeO$_x$.

3. Results

Tables 1 through 3 show the compositions of either single liquid phase or a liquidus phase in equilibrium with solid magnetite, 2CaO·SiO$_2$ (hereinafter denoted as C2S) or CaO·SiO$_2$ (hereinafter denoted as CS). The FeO$_x$ contents

<table>
<thead>
<tr>
<th>Series</th>
<th>No.</th>
<th>$P_{O_2}$ (atm)</th>
<th>Phase</th>
<th>compositions of liquidus phase (mass%)</th>
<th>C/S</th>
<th>Heating duration (hours)</th>
<th>$N_{Fe}$ in Pt (mol%)</th>
<th>log $\gamma_{Fe}$</th>
<th>log $a_{FeOx}_{x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A01</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq.</td>
<td>FeO$_x$ 31.55 34.95 33.50 0.00</td>
<td>1.04</td>
<td>72</td>
<td>0.092</td>
<td>-3.644</td>
<td>-1.564</td>
<td></td>
</tr>
<tr>
<td>2 A06</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq.</td>
<td>FeO$_x$ 38.42 30.76 30.83 0.00</td>
<td>1.00</td>
<td>72</td>
<td>0.126</td>
<td>-3.085</td>
<td>-0.871</td>
<td></td>
</tr>
<tr>
<td>1 A08</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq.</td>
<td>FeO$_x$ 30.09 37.52 32.39 0.00</td>
<td>1.16</td>
<td>72</td>
<td>0.121</td>
<td>-3.155</td>
<td>-0.957</td>
<td></td>
</tr>
<tr>
<td>1 A10</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq.</td>
<td>FeO$_x$ 27.09 30.11 42.80 0.00</td>
<td>0.70</td>
<td>72</td>
<td>0.084</td>
<td>-3.795</td>
<td>-1.757</td>
<td></td>
</tr>
<tr>
<td>1 A19</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq.</td>
<td>FeO$_x$ 38.23 21.70 40.07 0.00</td>
<td>0.54</td>
<td>72</td>
<td>0.086</td>
<td>-3.766</td>
<td>-1.720</td>
<td></td>
</tr>
<tr>
<td>2 A02</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq. + Magnetite 41.04 30.67 28.29 0.00</td>
<td>1.08</td>
<td>72</td>
<td>0.178</td>
<td>-2.371</td>
<td>-0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 A09</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq. + CS 21.62 41.63 36.76 0.00</td>
<td>1.13</td>
<td>72</td>
<td>0.074</td>
<td>-3.973</td>
<td>-1.988</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 A07</td>
<td>2.5 $\times$ 10^{-6}</td>
<td>Liq. + C2S 40.15 35.98 23.87 0.00</td>
<td>1.51</td>
<td>72</td>
<td>0.112</td>
<td>-3.313</td>
<td>-1.151</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. A back-scattered electron (BSE) image of a sample heated for 24 h (a), the line profile of the Fe element for the same sample (b), and the line profile of the Fe element for the sample heated for 72 h (c).
Table 2. Equilibrated liquidus compositions and $a_{FeO_{1.33}}$ values at $P_{O_2} = 1.0 \times 10^{-4}$ atm and mass%$Al_2O_3 = 0$ (a) and at $P_{O_2} = 1.0 \times 10^{-4}$ atm and mass%$Al_2O_3 > 0$ (b).

(a) FeO values by Henao et al.11) have been calculated by considering FeO as FeO.

Figure 2 shows the relation between the $\gamma_Fe$ and $N_{Fe}$ (mol%) values at 1 573 K. The previous data11,19) are also included in Fig. 2, where the $\gamma_Fe$ values by Henao et al.11) have been re-calculated by the present authors using their tabulated raw data of Fe concentrations in Pt crucibles. The
values reported by Henao et al.\textsuperscript{11} are in good agreement with the present data. However, the values by Tayler et al.\textsuperscript{19} do not accord with the others at lower $N_{Fe}$ values. Tayler et al.\textsuperscript{19} observed the weight change of a pellet prepared by sintering Fe$_2$O$_3$ and platinum mixtures by thermogravimetry while reducing the oxygen pressure from the air atmosphere ($P_{O2} = 0.21$ atm) to the desired pressure, so that the Fe concentrations in Pt can be estimated assuming that the Fe/Pt atomic ratio is constant during the heating experiment. In their method, the accuracy of the measured $N_{Fe}$ values may be worse at lower Fe concentrations owing to the smaller weight change. Therefore, the relation between the $\gamma_{Fe}$ and $N_{Fe}$ (mol%) values have been determined using the present data at the $N_{Fe}$ values lower than 0.18 as follows:

$$\log \gamma_{Fe} = -34.589N_{Fe}^2 + 24.162N_{Fe} - 5.5796 \quad \cdots \quad (4)$$

This equation has been subjected to the derivation of the

Figures 3 through 5 show the activities of FeO$_{1.33}$, $\alpha$FeO$_{1.33}$, on the FeO$_x$-CaO-SiO$_2$ slags with and without Al$_2$O$_3$ at $P_{O2} = 2.5 \times 10^{-6}$ atm, $1.0 \times 10^{-4}$ atm and $1.0 \times 10^{-2}$ atm, respectively. The standard state of the activities is taken as the stoichiometric solid FeO$_{1.33}$. The data of slags equilibrated with a solid phase of either magnetite, CS or C2S are

![Graph 2](image2.png)

Fig. 2. Relation between the $\gamma_{Fe}$ and $N_{Fe}$ (mol%) values at 1573 K.

![Graph 3](image3.png)

Fig. 3. Activities of FeO$_{1.33}$ at $P_{O2} = 2.5 \times 10^{-6}$ atm and mass%Al$_2$O$_3 = 0$ (a) and at $P_{O2} = 2.5 \times 10^{-4}$ atm and mass%Al$_2$O$_3 > 0$ (b).

![Graph 4](image4.png)

Fig. 4. Activities of FeO$_{1.33}$ at $P_{O2} = 1.0 \times 10^{-4}$ atm and mass%Al$_2$O$_3 = 0$ (a) and at $P_{O2} = 2.5 \times 10^{-6}$ atm and mass%Al$_2$O$_3 > 0$ (b).

![Graph 5](image5.png)

Fig. 5. Activities of FeO$_{1.33}$ at $P_{O2} = 1.0 \times 10^{-2}$ atm and mass%Al$_2$O$_3 = 0$ (a) and at $P_{O2} = 2.5 \times 10^{-4}$ atm and mass%Al$_2$O$_3 > 0$ (b).
Therefore, the result was omitted from Fig. 7. The FeO\textsubscript{1.33} single liquid phase, but includes C\textsubscript{2}S with a liquid phase.

4. Discussion

4.1. Relation between $a_{\text{FeO}_{1.33}}$ Values and FeO\textsubscript{x} Concentrations

Figure 6 shows the relations between the $a_{\text{FeO}_{1.33}}$ Values and the FeO\textsubscript{x} concentrations for the samples having a single liquid phase with the CaO/SiO\textsubscript{2}(mass%) ratio of 0.93 (Series 2), which is equivalent to the CaO/SiO\textsubscript{2}(mol%) ratio of unity, at $P_{O_2} = 2.5 \times 10^{-6}$ atm, $1.0 \times 10^{-4}$ atm and $1.0 \times 10^{-2}$ atm. It has been found that the samples with 20 mass%Fe\textsubscript{2}O\textsubscript{3} in Series 2 equilibrated at all the experimental oxygen partial pressures contain CS as well as a liquid phase, and those with 60 and 80 mass% Fe\textsubscript{2}O\textsubscript{3} in Series 2 magnetite together with a liquid phase. Figure 6 also includes the line denoted as “ideal solution” obeying the linear variation of $a_{\text{FeO}_{1.33}}$ with respect to molar fraction of FeO\textsubscript{x} below the liquidus line in equilibrium with magnetite at $P_{O_2} = 1.0 \times 10^{-4}$ atm. The measured $a_{\text{FeO}_{1.33}}$ values exhibit negative deviation from the ideal solution line, which implies that the Fe ions are located in the stable states by taking a specific structure rather than the random structure.

4.2. Relation between $a_{\text{FeO}_{1.33}}$ Values and CaO/SiO\textsubscript{2} Ratios

Figure 7 shows the $a_{\text{FeO}_{1.33}}$ Values for the samples with 35 mass%FeO\textsubscript{x} (Series 1) as a function of the CaO/SiO\textsubscript{2}(mass%) ratio. The samples were equilibrated at either $P_{O_2} = 2.5 \times 10^{-6}$ atm, $1.0 \times 10^{-4}$ atm or $1.0 \times 10^{-2}$ atm. It has been found that the sample with the CaO/SiO\textsubscript{2}(mass%) ratio of 1.87 at $P_{O_2} = 2.5 \times 10^{-6}$ atm does not consist of a single liquid phase, but includes C\textsubscript{2}S with a liquid phase. Therefore, the result was omitted from Fig. 7. The $a_{\text{FeO}_{1.33}}$ values have peaks at the CaO/SiO\textsubscript{2}(mass%) ratios of 0.9–1.0 and 1.3–1.4 for the samples equilibrated at $P_{O_2} = 1.0 \times 10^{-2}$ atm and $1.0 \times 10^{-4}$ atm, respectively. For the samples at $P_{O_2} = 2.5 \times 10^{-6}$ atm, the $a_{\text{FeO}_{1.33}}$ value monotonically increases with increasing the CaO/SiO\textsubscript{2} ratio within the compositional range of the single liquid region. As for the effect of the slag basicity on the iron oxide activity, Sano\textsuperscript{9}) has measured the FeO activities in the FeO\textsubscript{x}–Na\textsubscript{2}O–SiO\textsubscript{2} slags at iron saturation, and has suggested that the iso-activity contour have the noses at the Na\textsubscript{2}O/SiO\textsubscript{2}(mol%) ratio of unity based on his data as well as the Richardson’s model.\textsuperscript{20}) He has also explained using the same model that the iso-activity contours for FeO in the FeO\textsubscript{x}–CaO–SiO\textsubscript{2} slags at iron saturation have the noses at the line joining the compositions FeO and C\textsubscript{2}S. In fact, C\textsubscript{2}S is known to be the most stable intermediate compound in the CaO–SiO\textsubscript{2} binary system. Therefore, it is considered that as the CaO/SiO\textsubscript{2}(mol%) ratio approaches to two, the affinity of FeO with matrix CaO–SiO\textsubscript{2} in the FeO\textsubscript{x}–CaO–SiO\textsubscript{2} system could become less, resulting in the higher activity of FeO. This consideration is consistent with the monotonical increase in the $a_{\text{FeO}_{1.33}}$ values with the CaO/SiO\textsubscript{2} ratio for the sample at $P_{O_2} = 2.5 \times 10^{-6}$ atm, as shown in Fig. 7. However, the variation of the $a_{\text{FeO}_{1.33}}$ values exhibit maximum in the CaO/SiO\textsubscript{2} ratio lower than two for the samples at $P_{O_2} = 1.0 \times 10^{-2}$ atm and $1.0 \times 10^{-4}$ atm. This may be relevant to the increase in the ratio of Fe\textsuperscript{3+} to the total iron ions in the slags. Fe\textsuperscript{3+} ions are incorporated in the matrix CaO–SiO\textsubscript{2}, polymerizing the silicate network structure.\textsuperscript{21}) As a consequence, Fe\textsuperscript{3+} ions may suppress the tendency that the activity of FeO\textsubscript{x} is dominated by the CaO/SiO\textsubscript{2} ratio.

Figures 8 and 9 show the effects of Al\textsubscript{2}O\textsubscript{3} addition on the relation between the $a_{\text{FeO}_{1.33}}$ values and the CaO/SiO\textsubscript{2}(mass%) ratios for the samples of Series 3 equilibrated at $P_{O_2} = 2.5 \times 10^{-6}$ and $1.0 \times 10^{-2}$ atm, respectively. It can

![Fig. 6. Activity of FeO\textsubscript{1.33} in the FeO\textsubscript{x}–CaO–SiO\textsubscript{2} system at the CaO/SiO\textsubscript{2}(mass%) ratio of 0.93, which is equivalent to the CaO/SiO\textsubscript{2}(mol%) ratio of unity, as a function of the FeO\textsubscript{x} concentrations. The line denoted as “ideal solution” is the linear variation of $a_{\text{FeO}_{1.33}}$ with respect to molar fraction of FeO\textsubscript{x} below the liquidus line in equilibrium with magnetite at $P_{O_2} = 1.0 \times 10^{-4}$ atm.]

![Fig. 7. Activity of FeO\textsubscript{1.33} in the 35(mass%)FeO\textsubscript{x}–CaO–SiO\textsubscript{2} slags (Series 1) as a function of the CaO/SiO\textsubscript{2}(mass%) ratio.]

![Fig. 8. Effect of Al\textsubscript{2}O\textsubscript{3} addition on the relation between the FeO\textsubscript{1.33} activities and the CaO/SiO\textsubscript{2}(mass%) ratio for the samples equilibrated at $P_{O_2} = 2.5 \times 10^{-6}$, 1.0 \times 10^{-2}$ atm and 1.0 \times 10^{-4}$ atm.]}
be seen that the dependency of the activity on the CaO/SiO$_2$ ratio becomes moderate with increasing the Al$_2$O$_3$ addition on the sample at $P_{O_2} = 2.5 \times 10^{-6}$ atm although the variation of the activity with the CaO/SiO$_2$ ratio is identical irrespective of the Al$_2$O$_3$ addition on the sample at $P_{O_2} = 1.0 \times 10^{-2}$ atm. Al$_2$O$_3$ addition may play the same role as Fe$^{3+}$ ions on the $a_{FeO1.33}$ values: Al$_2$O$_3$ addition polymerizes the silicate network structure. Therefore, the Al$_2$O$_3$ addition may weaken the C2S formation effect on the affinity of FeO$_x$ with the matrix silicates.

5. Conclusions

The activities of FeO$_{1.33}$ in the single liquid phases of the FeO$_x$–CaO–SiO$_2$ and the FeO$_x$–CaO–SiO$_2$–Al$_2$O$_3$ systems have been measured at 1 573 K under oxygen partial pressures between $10^{-6}$ and $10^{-2}$ atm so as to clarify the effect of the slag compositions on the activities. The obtained results are summarized as follows.

(1) The obtained relations between the $a_{FeO1.33}$ values and the FeO$_x$ concentrations for the samples having a single liquid phase with the CaO/SiO$_2$(mol%) ratios of unity indicate that the $a_{FeO1.33}$ values exhibit negative deviation from the ideal solution model. This implies that the Fe ions are located in the stable states by taking a specific structure rather than the random structure.

(2) It can be seen from the relation between the $a_{FeO1.33}$ values and the CaO/SiO$_2$ ratios for the samples with 35 mass%FeO$_x$ that the $a_{FeO1.33}$ values have peaks at $P_{O_2} = 0.9$–1.0 and 1.3–1.4 at $P_{O_2} = 1.0 \times 10^{-2}$ atm and $1.0 \times 10^{-4}$ atm, respectively. For the samples at $P_{O_2} = 2.5 \times 10^{-6}$ atm, on the other hand, the $a_{FeO1.33}$ value monotonically increases with increasing the CaO/SiO$_2$ ratio within the compositional range of the single liquid region. The CaO/SiO$_2$ ratio at the maximum of the $a_{FeO1.33}$ value may be dependent on the ratio of Fe$^{3+}$ to the total iron ions in the slags: Fe$^{3+}$ ions are incorporated in the matrix CaO–SiO$_2$, polymerizing the silicate network structure. As a consequence, Fe$^{3+}$ ions may suppress the tendency that the activity of FeO$_x$ is dominated by the CaO/SiO$_2$ ratio.

(3) The dependency of the FeO$_{1.33}$ activities on the CaO/SiO$_2$ ratio becomes moderate with increasing the Al$_2$O$_3$ addition on the sample at $P_{O_2} = 2.5 \times 10^{-6}$ atm. This could be because Al$_2$O$_3$ addition may play the same role as Fe$^{3+}$ ions on the silicate network structures.

REFERENCES

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