Equilibria of Manganese and Sulfur between Liquid Iron and CaO–SiO₂–Fe₃O₄–MgO–MnO Slags Saturated with 2CaO · SiO₂ and MgO

Sung-Mo JUNG

Graduate School of Iron and Steel Technology, Pohang University of Science and Technology, Pohang 790-784 Korea.

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The equilibria of manganese and sulfur between liquid iron and CaO–SiO₂–Fe₃O₄–MgO slags saturated with dicalcium silicate and MgO were studied in the temperature range of 1 823 to 1 923 K. The solubility of MgO decreases with increasing Fe₃O₄ content. The values of (%MnO)/[%Mn] increase with increasing Fe₃O₄ content and its relation was formulated by an empirical equation. The activity of Fe₃O₄ for the present slag system almost stays unchanged with increasing Fe₃O₄ content investigated. The oxygen content of metal in equilibrium with (39.9–49.9 mass%)CaO–(11.9–15.2 mass%)SiO₂–(25.2–35.7 mass%)Fe₃O₄–(6.1–7.0 mass%)MgO slags saturated with 2CaO · SiO₂ and MgO is expressed by the following equation.

\[
\log[\text{mass\%O}] = \frac{5690}{T} + 0.011
\]

The logarithm of the sulfide capacity for the present slags increases with increasing the theoretical optical basicity and its correlation was formulated. Using the relations obtained in this work and mass balance, the charging amount of Mn ore (MnO) for a final manganese content when adding MnO to BOF was predicted and the desulfurized content affected by the addition of Mn ore was also estimated.

KEY WORDS: manganese; BOF process; dicalcium silicate; equilibrium manganese and sulfur distribution; sulfide capacity; optical basicity.

1. Introduction

Manganese is essential for the production of virtually all grades of steels, and steelmaking constitutes its principal use. It is primarily used to remove the detrimental effects of sulfur and prevent hot shortness or brittleness, which otherwise would develop in steels that contain sulfur. In addition, manganese is added to steels in the form of ferroalloys to control the oxygen concentration, and to improve strength, toughness, hardness, and hardenability of steels. In order to reduce the consumption of ferromanganese alloy usually added in ladle process, the smelting reduction of less expensive Mn ores in the BOF process is being conducted in order to control Mn content of steel in practical operations.

Numerous studies were made on the manganese equilibrium between metals and slags containing manganese oxide. Görl et al. measured the distribution of manganese and sulfur between the CaO–SiO₂–FeO–MnO slag and iron. Suito and Inoue measured the manganese distribution between liquid iron and MgO-saturated CaO–SiO₂–FeO–MnO slags (MnO<5.3 mass%) containing P₂O₅ or S in the temperature range of 1 823 to 1 923 K. According to their results, the manganese distribution ratio was found to increase with an increase in SiO₂ content and decrease in temperature. Recently Morales and Fruehan investigated the thermodynamics of manganese oxide and iron oxide of CaO–SiO₂–FeO–MgO–MnO–P₂O₅ slags with high MnO contents (MnO<25 mass%) relevant to the smelting of MnO ores in steelmaking. However, most of the previous work for the manganese equilibrium have been done for the slags saturated with MgO only.

The objective of this research was to understand the fundamental features of manganese oxide for CaO–SiO₂–FeO–MgO slags saturated with dicalcium silicate (2CaO · SiO₂) and MgO, which compositions are obtained at the final stage of the BOF process and to determine the parameters that describe the manganese equilibrium for slag compositions intended for the smelting reduction of Mn ores in steelmaking. Therefore, the distribution of manganese and sulfur between liquid iron and CaO–SiO₂–FeO–MnO slags saturated with 2CaO · SiO₂ and MgO have been measured based on the tetrahedron-type phase diagram completed by Trömel et al. in the temperature range of 1 823 to 1 923 K.

In addition, the thermodynamic properties of these slags such as the activity of Fe₃O₄, the Fe³⁺/Fe²⁺ ratios and sulfide capacities have been discussed.

2. Experimental

A chemical equilibration technique was employed in this

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3. Thermodynamic Considerations

3.1. Measurement of the MnO Activity

A slag containing manganese oxide was brought into equilibrium with liquid iron in a MgO crucible. The activity of MnO in slags can be determined by measuring the equilibrium constant of reaction (11). The desulfurization reaction between liquid iron and slag can be represented by Eq. (8).

\[
\frac{1}{2}S_2(g) + (O^{2-})_{\text{slag}} = \frac{1}{2}O_2(g) + (S^{2-})_{\text{slag}} \quad \text{(10)}
\]

where:
- \(K_\text{eq} = \frac{(\text{mass}\%S)}{[\text{mass}\%S]} \) where \(\text{mass}\%S\) and \([\text{mass}\%S]\) denote mass percent of sulfur in the slag and liquid iron, respectively.
- \(C_s = \frac{(\text{mass}\%S^2)}{[\text{mass}\%S]} \) where \(\text{mass}\%S^2\) = Mass percent of \(S^{2-}\) dissolved in the slag
- \(p_{S_2} = \) Sulfur partial pressure in equilibrium with sulfur in liquid iron
- \(p_{O_2} = \) Oxygen partial pressure in equilibrium with oxygen in liquid iron
- \(K_{eq} = \) Equilibrium constant of reaction (10)
- \(a_{O^{2-}} = \) Activity of oxygen ion
- \(f_{S^{2-}} = \) Activity coefficient of sulfide ion in the slag

The partial pressure of sulfur can be calculated from the sulfur content in metal and the available thermodynamic data for reaction (12).

\[
\frac{1}{2}S_2(g) = S_{(\text{mass}\% \text{ Fe})} \quad \text{(12)}
\]

\[\Delta G_{12}^\circ = -125 100 + 18.5T \quad \text{J/mol}\]
where \([\text{mass}\% S]\) and \(f_s\) are mass percent of sulfur and activity coefficient of sulfur in 1 mass\% standard state, respectively.

The partial pressure of oxygen, \(P_{O_2}\), can be evaluated from the standard free energy formation of \(\text{FeO}\) and the activity of \(\text{FeO}\) in the slag:

\[
\Delta G_{15}^\circ = -234.620 + 46.90T \quad \text{J/mol} ^7 \quad \text{(15)}
\]

\[
K_{15} = \frac{a_{\text{FeO}}}{P_{\text{FeO}}^{1/2}} \quad \text{ (17)}
\]

### 3.4. Optical Basicity

Duffy and Ingram\(^9\) realized that the shifts in frequency of the absorption band involved with the \(6s \rightarrow 6p\) transition observed in the UV region of the spectrum can be related to the basicity of a glass or slag. By making numerous measurements, mainly using \(\text{Pb}^{2+}\) as the probe ion, they found out that the “optical basicity” of an oxide \(A_{\text{AO}}\) has some relationship with the Pauling electronegativity, \(\chi\), of the cation by the following equation:

\[
A_{\text{AO}} = \frac{0.74}{\chi - 0.26} \quad \text{ (18)}
\]

Thereafter the concept of the optical basicity was introduced and applied to metallurgy by Duffy et al.\(^10\).

The optical basicity for any oxide in a slag can be calculated by using Eq. (18) and the values are listed in Table 1. Görl et al.\(^12\) previously per-

In Eq. (19), \(X\) is the equivalent cation fraction that can be obtained by Eq. (20).

\[
X = \frac{\text{mole fraction of component} \times \text{No. of oxygen atoms in oxide molecule}}{\sum \text{(mole fraction of component} \times \text{No. of oxygen atoms in oxide molecule)})} \quad \text{ (20)}
\]

### 4. Results and Discussion

#### 4.1. CaO–SiO\(_2\)–FeO–MgO Quaternary Phase Diagram

Figure 1 shows the quaternary phase diagram of the CaO–SiO\(_2\)–FeO–MgO system completed by Trömel et al.\(^5\) where the curve connected between point \(\square\) and \(\square\) represents the compositions of the slags saturated with \(2\text{CaO} \cdot \text{SiO}_2\) and \(\text{MgO}\). The compositions obtained in the present experiment are located around the curve, although the initial slags contain approximately 0.5 mass\% FeS and 3 mass\% MnO. The analytical results obtained in this work are summarized in Table 2. Görl et al.\(^12\) previously per-

![Fig. 1. Representation of liquidus surfaces of CaO(9–10–13–12–9), (Fe,Mg)O(12–13–14–15–5–6–11–12), 2(Fe,Mg)SiO\(_2\) (5–15–4–5), 3CaO SiO\(_2\)(9–12–11–8–9) and 2CaO SiO\(_2\) (11–8–7–6–11) based solution phases in the system CaO–FeO–MgO–SiO\(_2\) in contact with metallic iron at 1873 K after Trömel et al.\(^5\) with permission.](image)

| Heat No. | Mn (mass\%) | O (mass\%) | S (mass\%) |
|----------|-------------|------------|------------|
| 2CSFM01  | 0.027       | 0.064      | 0.014      |
| 2CSFM02  | 0.031       | 0.065      | 0.015      |
| 2CSFM03  | 0.029       | 0.092      | 0.022      |
| 2CSFM04  | 0.047       | 0.100      | 0.040      |
| 2CSFM05  | 0.043       | 0.084      | 0.047      |
| 2CSFM06  | 0.045       | 0.064      | 0.041      |
| 2CSFM07  | 0.086       | 0.044      | 0.029      |
| 2CSFM08  | 0.032       | 0.058      | 0.016      |
| 2CSFM09  | 0.040       | 0.061      | 0.016      |
| 2CSFM10  | 0.041       | 0.068      | 0.014      |
| 2CSFM11  | 0.044       | 0.074      | 0.014      |

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[1]-1823K, [2]-1848K, [3]-1898K, [4]-1923K
formed a study on the slags saturated with lime (CaO), tricalcium silicate (3CaO·SiO₂), or dicalcium silicate (2CaO·SiO₂) employing CaO crucibles. According to their results, the slags were finally saturated with CaO, 3CaO·SiO₂, and 2CaO·SiO₂ depending on the slag compositions investigated. Matsushima et al.¹³ also reported that 2CaO·SiO₂ was formed between a rotating CaO cylinder and CaO–SiO₂–Fe₂O₃ slags. Therefore, one piece of a CaO crucible was placed on the slags in a MgO crucible so that the slags investigated in this study could be saturated with 2CaO·SiO₂ and MgO simultaneously.

### 4.2. Compositions of CaO–SiO₂–Fe₂O₃–MgO–MnO Slags Saturated with 2CaO·SiO₂

The compositions of the present slag system are shown in Fig. 2 together with the liquidus after Muan and Osborn.¹⁴ In Fig. 2, the slag compositions for CaO–SiO₂–Fe₂O₃–MgO–MnO slags being studied were plotted by the parallel projection of the present slag systems onto the CaO–SiO₂–Fe₂O₃ ternary phase diagram, in which the sum of mass percent of CaO, SiO₂, and Fe₂O₃ is 100%. The compositions of the slags investigated are in approximate agreement with the estimated curve (dotted line) drawn by the parallel projection of the curve between point 6 and point Ⅳ in Fig. 1.

**Figure 3** indicates that the solubility of MgO decreases with increasing Fe₂O₃ content, as expected from the phase diagram shown in Fig. 1. As seen in Fig. 3, the solubility of MgO is slightly lower than that by Trömel et al.,⁵ where point Ⅳ denotes the composition(44.0mass%CaO–38.5 mass%SiO₂–17.5mass%MgO) and point Ⅲ represents the composition (46.0mass%CaO–13.0mass%SiO₂–36.0mass%Fe₂O₃–5.0mass%MgO).⁵¹ The tendency in Fig. 3 is considered to be due to the effect of the addition of 3mass%MnO to the slags at the same Fe₂O₃ content since both MnO and MgO are basic oxides.

### 4.3. Effect of Fe₂O₃ on the Equilibrium Mn distribution between Liquid Iron and CaO–SiO₂–Fe₂O₃–MgO Slags Saturated with 2CaO·SiO₂ and MgO

**Figure 4** shows that the Mn distribution ratio between the present slag system and liquid iron linearly increases with increasing Fe₂O₃ content, which means that the manganese content in the liquid iron decreases as the Fe₂O₃ concentration in the slags increases. The results obtained in this work have been compared to the previous results obtained by Jung et al.⁶ for Mn distribution between liquid iron and CaO–SiO₂–Fe₂O₃–MgO slags, Morales and Fruehan⁴ for experiments on Mn equilibrium between liquid iron and CaO–SiO₂–MnO–Fe₂O₃–P₂O₅–MgO slags and that of Pata et al.⁷ for measurements on Mn distribution between liquid iron and CaO–SiO₂–Fe₂O₃ slags at 1 873 K. Most of the results in Fig. 4 show a similar tendency one another although some data are scattered at low Fe₂O₃ content. The values of (%MnO)/[%Mn] for the slags plotted in Fig. 4 can be formulated by an empirical equation, Eq. (21), as a function of Fe₂O₃ content in slags.

\[
\frac{(%\text{MnO})}{[%\text{Mn}]} = 36.98(\pm6.30) + 1.67(\pm0.17)(\text{mass}\% \text{ Fe}_2\text{O}_3)
\]

Consequently, the Mn distribution ratio between slag and liquid iron is dominantly determined by the Fe₂O₃ content in slags, that is, oxygen partial pressure between slag and metal, which can be estimated by oxygen content in liquid iron.

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**Fig. 2.** Experimental slag composition shown by parallel projection onto the CaO–SiO₂–Fe₂O₃ ternary phase diagram at 1 873 K.

**Fig. 3.** Effect of Fe₂O₃ content on the solubility of MgO in CaO–SiO₂–Fe₂O₃–MgO slags saturated with 2CaO·SiO₂ at 1 873 K.

**Fig. 4.** Distribution of manganese as a function of Fe₂O₃ content of the CaO–SiO₂–Fe₂O₃–MgO slags saturated with 2CaO·SiO₂ at 1 873 K.
The linear tendency of (\%MnO)/[\%Mn] values observed in Fig. 4 can be understood by Eq. (23). The value of $g_{\text{Mn}}$ in Eq. (23) is the same as that of $g_{\text{Mn}}^0$ since the Mn content in liquid iron is in the Henrian range. The linear relationship between MnO/Mn and FeO in Fig. 4 indicates a constant value of the $\gamma_{\text{FeO}}/\gamma_{\text{MnO}}$ ratio in Eq. (23) over the measured FeO concentration range.

\[ \frac{\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe}(l)}{X_{\text{Mn}}} = K_{22} \cdot \gamma_{\text{Mn}} \cdot \frac{\gamma_{\text{FeO}}(0)}{\gamma_{\text{MnO}(0)}} \cdot X_{\text{FeO}} \]  

(23)

The constant value of $\gamma_{\text{FeO}(0)}/\gamma_{\text{MnO}(0)}$ ratio in Eq. (23) can be confirmed by Fig. 5 and Fig. 6. Figure 5 shows the variation of the calculated activity coefficient of MnO as a function of FeO content. The activity coefficients of MnO, $\gamma_{\text{MnO}(0)}$, with respect to a pure solid state have been obtained by Eqs. (1) to (3). The values of $\gamma_{\text{MnO}(0)}$ decrease with increasing FeO content in the slags, as shown in Fig. 5. In addition, as can be seen in Fig. 6, the activity values of FeO remain unchanged with increasing FeO content in slags over the measured concentration range. This means that $\gamma_{\text{FeO}(0)}$ decreases with increasing FeO content. Therefore, the $\gamma_{\text{FeO}(0)}/\gamma_{\text{MnO}(0)}$ ratio becomes constant in Eq. (23).

4.4. Activities of FeO and Fe$^{3+}$/Fe$^{2+}$ Equilibrium in CaO–SiO$_2$–FeO–MgO$_{\text{sat}}$ Slags Saturated with 2CaO·SiO$_2$

As previously mentioned, Fig. 6 plots the relationship between the activity of FeO and $X_{\text{FeO}}$ for CaO–SiO$_2$–FeO–MgO slags saturated with 2CaO·SiO$_2$ and MgO. The activity of FeO for the present slag system almost stays unchanged with increasing FeO content, which can also be observed in the result of Jung et al.\cite{16} for CaO$_{\text{sat}}$–SiO$_2$–FeO–MgO$_{\text{sat}}$ slags. This appears to arise from the decrease of the activity coefficient of FeO as the FeO content increases. According to the quaternary phase diagram shown in Fig. 1, the increase of FeO accompanies the decrease of MgO solubility along the curve connecting point $\Box$ and point $\Box$. On the other hand, the values of $a_{\text{FeO}}$ for CaO$_{\text{sat}}$–SiO$_2$–FeO–MgO$_{\text{sat}}$ slags are slightly higher than those obtained by Pata et al.\cite{17} for CaO$_{\text{sat}}$–SiO$_2$–FeO$_2$ slags. It is believed that replacing CaO with MgO in CaO$_{\text{sat}}$–SiO$_2$–FeO$_2$ slags increases the activity of FeO, which has been previously reported by Shim and Banya.\cite{18}

The oxygen content in the liquid iron is plotted as a function of mass\% FeO at 1873 K in Fig. 7 for CaO–SiO$_2$–FeO–MgO$_{\text{sat}}$ slags saturated with 2CaO·SiO$_2$. The oxygen concentration increases with increasing FeO content and starts to decrease around 20 mass\% FeO. The oxygen content ranges from 0.040 to 0.10 mass\% with increasing the FeO content. The maximum oxygen content observed in
the result of Görl et al.\textsuperscript{19} is believed to correspond to the point \(\Box\) in Fig. 1. As can be seen in Fig. 7, the oxygen content in liquid iron ranges from 0.050 to 0.100 mass% for CaO-saturated slags.\textsuperscript{16,20,21} However, the reason for this tendency is not clearly known.

One important factor in determining the properties of a slag is the concentrations of Fe\(^{2+}\) and Fe\(^{3+}\). As shown in Fig. 8, the Fe\(^{3+}/\text{Fe}^{2+}\) ratio is plotted as a function of SiO\(_2\) content. The values of the Fe\(^{3+}/\text{Fe}^{2+}\) ratio decrease with increasing SiO\(_2\) content. Accordingly, the Fe\(^{3+}/\text{Fe}^{2+}\) equilibrium may be expressed by Eq. (24), in which a ferric ion(Fe\(^{3+}\)) combines with oxygen ions to form complex ions.\textsuperscript{20}

\[
\frac{3}{2} \text{Fe}^{2+} + n\text{O}^{2-} = \frac{1}{2} \text{Fe}(l) + \text{FeO}_{n-1}^{2-} \quad \ldots \ldots \ldots \ldots \ldots (24)
\]

The results in the present work indicate that the addition of saturated MgO to CaO-saturated slags or 2CaO-SiO\(_2\)-saturated slags causes SiO\(_2\) to behave as an acidic oxide, which is not obvious in the result of Nakamura et al.\textsuperscript{20} for CaO\(_{sat}\)-SiO\(_2\)-Fe\(_2\)O systems. To compare the effect of CaO with that of MgO, Shim and Banya\textsuperscript{18} showed that the values of Fe\(^{3+}/\text{Fe}^{2+}\) decreased by replacing CaO with MgO in the CaO-SiO\(_2\)-Fe\(_2\)O-MgO slag systems. Therefore, the results in Fig. 8 indicate that MgO is less basic than CaO in this system, as generally accepted. These also demonstrate that FeO\(_{2n-1}\) is formed according to reaction (24) and the CaO-saturated slags are more basic than MgO-saturated slags.

4.5. Temperature Dependence of Oxygen Content in Liquid Iron

In Fig. 9, the oxygen content of liquid iron in equilibrium with (39.9—49.9) mass%CaO—(11.9—15.2) mass%SiO\(_2\)—(25.2—35.7) mass%Fe\(_2\)O—(6.1—7.0) mass%MgO slags saturated with 2CaO-SiO\(_2\) and MgO has been measured in the temperature range of 1823 to 1923K and is expressed by Eq. (25).

\[
\log[\text{mass}\%\text{O}] = -\frac{5690}{T} + 0.011 \quad \ldots \ldots \ldots \ldots \ldots (25)
\]

As shown in Fig. 9, the temperature dependence of oxygen content in liquid iron for the present slag is similar to that for CaO\(_{sat}\)-SiO\(_2\)-Fe\(_2\)O-MgO\(_{sat}\).\textsuperscript{16} This is because the activity of Fe\(_2\)O is not significantly changed by CaO saturation or 2CaO-SiO\(_2\) saturation for the slags saturated with MgO, as indicated in Eq. (25). Figure 9 also shows the results for pure Fe\(_2\)O from Taylor and Chipman,\textsuperscript{6} for Fe\(_2\)O-MgO\(_{sat}\) slags from Shim and Banya,\textsuperscript{18} for Fe\(_2\)O-CaO\(_{sat}\) slags from Bishop et al.,\textsuperscript{22} and those for Fe\(_2\)O-SiO\(_2\)-MgO\(_{sat}\) slags from Fischer and Ende.\textsuperscript{23} In comparison with other slag systems, the present work shows lower oxygen content, which is considered to be due to the decrease in the activity of iron oxide in the multicomponent slag systems. Bishop et al.\textsuperscript{22} previously reported that the effect of MgO on iron oxide activity was not equivalent to that of CaO, and that the substitution of MgO with CaO decreased the activity coefficient of iron oxide, which is obviously shown in Fig. 9, comparing the results obtained in this work and those for Fe\(_2\)O-CaO\(_{sat}\) slags.

4.6. Equilibrium of Sulfur between Liquid Iron and CaO–SiO\(_2\)–Fe\(_2\)O–MgO Slags Saturated with 2CaO–SiO\(_2\) and MgO

There has been a growing emphasis on developing new steelmaking processes (e.g. hot metal pretreatment-slag minimum process) for the production of ultra clean steels. In particular, it was reported that the reduction of MnO from slag to metal can be accompanied by desulfurization.\textsuperscript{20} Therefore, it is significant to measure sulfur distribution ratio and sulfide capacity for the present slags which compositions are obtained at the final stage of the BOF processes.

In Fig. 10, the sulfur distribution ratios \(L_s = (\text{mass}\%S)/(\text{mass}\%S)\) are plotted as a function of SiO\(_2\) content. The values of \(L_s\) decrease with increasing SiO\(_2\) content along the composition curve in the direction from point \(\Box\) toward point \(\Box\) in Fig. 1. The results obtained in this work are in

\[\text{Fig. 8.}\ \text{Fe}^{3+}/\text{Fe}^{2+}\ \text{ratio for the CaO–SiO}_2–\text{Fe}_2\text{O}–\text{MgO}_\text{sat} \text{slags saturated with 2CaO–SiO}_2 \text{as a function of SiO}_2 \text{content at 1873K.}\]

\[\text{Fig. 9.}\ \text{Solubility of oxygen in liquid iron in equilibrium with (39.9–49.9)\text{mass%CaO}–(11.9–15.2)\text{mass%SiO}_2–(25.2–35.7)\text{mass%Fe}_2\text{O}–(6.1–7.0)\text{mass%MgO} \text{slags saturated with 2CaO–SiO}_2 \text{and MgO.}\]

\[\text{Fig. 10.}\ \text{Sulfur distribution ratios } L_s = (\text{mass}\%S)/(\text{mass}\%S) \text{plotted as a function of SiO}_2 \text{content. The values of } L_s \text{decrease with increasing SiO}_2 \text{content along the composition curve in the direction from point } \Box \text{toward point } \Box \text{in Fig. 1. The results obtained in this work are in}\]
approximate agreement with those by Trömel et al.5) And the values of \( L \) range from 10 to 12 up to 10 mass% SiO\(_2\) for CaO–saturated slags,17) CaO and MgO-saturated slags16) and 2CaO·SiO\(_2\) and MgO-saturated slags. From the results in Fig. 10, it can be concluded that the desulfurization reaction is strongly dominated by the activity of CaO in slags, as generally understood by Eq. (8).

The desulfurization power of the slags can be expressed as the sulfide capacity defined by Eq. (11). The relation between the logarithm of sulfide capacity (\( \log C_S \)) and SiO\(_2\) content is also shown in Fig. 10. The sulfide capacity (\( C_S \)) for the present slags gradually decreases with increasing SiO\(_2\) content. It is obvious that the \( C_S \) values for the present slags are almost the same as those for CaO-saturated CaO–SiO\(_2\)–Fe\(_2\)O\(_3\)–MnO slags obtained by Pata et al.17) and those of CaO and MgO-saturated CaO–SiO\(_2\)–Fe\(_2\)O\(_3\)–MnO slags measured by Jung et al.16) in the concentration range of SiO\(_2\) less than 10 mass%. As indicated in Fig. 10, average value of \( \log C_S \) for CaO-saturated slags and CaO and MgO-saturated slags is \(-1.25\) in less than 10 mass% SiO\(_2\).

Recently, several attempts25–27) have been made to correlate the sulfide capacity of the slags with the theoretical optical basicity, which can be calculated from the Pauling electronegativity and the equivalent cation fraction of components, as previously explained. In order to compare the present result with those of previous investigators, the theoretical optical basicity was applied and the values for the optical basicities were taken from the literature based on Pauling electronegativity. In comparison to the present work, the correlation (27) by Sosinsky and Sommerville25) was mainly based on the slag systems involving CaO, SiO\(_2\), Al\(_2\)O\(_3\), and MgO, and then the optical basicity values of transition metal oxides (e.g. TiO\(_2\), Fe\(_2\)O\(_3\), FeO, and MnO) were calculated from the sulfide capacity data.28)

\[
\log C_S = \left( \frac{22.690 - 54.460L}{T} \right) + 43.6L - 25.2
\]  \ ...(27)

In Fig. 11, the correlation is shown as a dotted line, which was obtained by using Eq. (27) at 1 873 K. The present results show higher values of sulfide capacity than those estimated by Eq. (27) at the same optical basicities. The reason is that the present slags being dealt with are saturated with 2CaO·SiO\(_2\) and MgO containing much content of transition metal oxides (e.g. FeO, Fe\(_2\)O\(_3\)) and that the optical basicity is based on the Pauling electronegativity. In comparison to the present work, the correlation (27) by Sosinsky and Sommerville25) was mainly based on the slag systems involving CaO, SiO\(_2\), Al\(_2\)O\(_3\), and MgO, and then the optical basicity values of transition metal oxides (e.g. TiO\(_2\), Fe\(_2\)O\(_3\), FeO, and MnO) were calculated from the sulfide capacity data.28)

4.7. Industrial Application

In Table 3, one composition of steelmaking slags expected in the final stage of BOF process is exemplified. Based on the composition in Table 3, Mn distribution ratio less than 64 is expected applying the relation (21). Using the mass balance given in Eq. (28), it is possible to predict the charging amount (\( W_{\text{MnO}} \)) of Mn ores (MnO) for a given final manganese content, [%Mn], when adding some Mn ores (MnO) to BOF.

\[
\log C_S = \left( \frac{22.690 - 54.460L}{T} \right) + 43.6L - 25.2
\]  \ ...(27)
where:

\[ W_{\text{MnO}} = \text{Charging amount of MnO in unit of kg/ton-Fe} \]

\[ [\%\text{Mn}]_i = \text{Initial manganese content in liquid iron} \]

\[ [\%\text{Mn}]_f = \text{Final manganese content in liquid iron} \]

\[ MW_{\text{MnO}} = \text{Molecular mass of manganese oxide, MnO} \]

\[ MW_{\text{Mn}} = \text{Molecular mass of manganese} \]

\[ W_{\text{slag}} = \text{Mass of slag in unit of kg} \]

\[ L_{\text{Mn}} = \text{Mn distribution ratio} \]

For example, in order to obtain 0.5 mass% of Mn in liquid iron, about 45 kg of MnO should be added per 1 ton of liquid iron under the condition of the smelting reduction process employing 100 kg of the slag system listed in Table 3 and initial Mn content of 0.1 mass%.

On the other hand, the final sulfur content affected by the addition of Mn ores can be estimated based on the result in Fig. 10 and mass balance given in Eq. (29). In Fig. 10, sulfur distribution ratio greater than 7 for the slag given in Table 3 is possible. Accordingly, the final sulfur content obtained in the final stage of BOF process will be about 0.017% for [\%\text{S}]_i=0.03 and [\%\text{S}]_{\text{slag}}=0.05.

\[ [\%\text{S}] = \frac{1000\times [\%\text{S}]_i + W_{\text{slag}}\times [\%\text{S}]_{\text{slag}}}{1000 + (W_{\text{slag}} + W_{\text{MnO}})\times L_S} \quad \quad \quad (29) \]

where:

\[ [\%\text{S}]_f = \text{Final sulfur content in liquid iron} \]

\[ [\%\text{S}]_i = \text{Initial sulfur content in liquid iron} \]

\[ [\%\text{S}]_{\text{slag}} = \text{Sulfur content in slag} \]

\[ L_S = \text{Sulfur distribution ratio} \]

5. Conclusions

Thermodynamic studies of manganese and sulfur in liquid iron in equilibrium with CaO–SiO_2–FeO–MnO slags saturated with 2CaO·SiO_2 and MgO were performed in the temperature range of 1823 to 1923 K. From the findings, the following conclusions were obtained.

(1) The solubility of MgO decreases with increasing FeO content and it is slightly lower than that by previous investigator.

(2) The values of [\%\text{MnO}]/[\%\text{Mn}] increase with increasing FeO content and its relation was formulated by an empirical equation (21) as a function of FeO content in slags.

\[ [\%\text{MnO}]/[\%\text{Mn}] = 36.98(\pm 6.30) + 1.67(\pm 0.17)(\text{mass}\%\text{FeO}) \quad \quad \quad (21) \]

(3) The oxygen content ranges from 0.04 to 0.10 mass% with increasing the FeO content in the CaO–SiO_2–FeO–MgO slags saturated with 2CaO·SiO_2 up to 36 mass% FeO.

(4) The activity of FeO for the present slag system almost stays unchanged with increasing FeO content investigated.

(5) The oxygen content of liquid iron in equilibrium with (39.9–49.9 mass%)CaO–(11.9–15.2 mass%)SiO_2–(25.2–35.7 mass%)FeO–(6.1–7.0 mass%)MgO slags saturated with 2CaO·SiO_2 and MgO has been measured in the temperature range of 1823 to 1923 K and is expressed by Eq. (25).

\[ \log[\text{mass}\%\text{O}] = - \frac{5690}{T} + 0.011 \quad \quad \quad (25) \]

(6) The logarithm of the sulfide capacity increases with increasing the theoretical optical basicity and its correlation was formulated by Eq. (26).

\[ \log C_s = 24.0(\pm 6.12)A - 18.7(\pm 4.4) \quad \quad \quad (26) \]

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