Sulfide Capacity of the CaO–SiO₂–MnO Slag at 1 873 K

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The sulfide capacity of the CaO–SiO₂–MnO slag through the entire composition range was measured at 1 873 K using a gas–slag equilibration method and the effect of basicity and the activity coefficient of sulfide on the sulfide capacity of molten slag was investigated. Furthermore, the relationship between the sulfide capacity and the optical basicity of MnO-containing slags was evaluated in view of industrial applications. Sulfide capacity of the slag linearly increased by increasing the content of MnO not only at a given silica content but also at a fixed Vee ratio (=CaO/SiO₂). The capacity and the modified Vee ratio (=[CaO+MnO]/SiO₂) showed a good linear relationship. Assuming that the basicity and the stability of sulfide ion in the slag are proportional to the activity of MnO (aMnO) and the activity coefficient of MnS (γMnS), respectively, the composition dependency of sulfide capacity was well described by the changes in the ratio of aMnO to γMnS. The iso–sulfide capacity of the CaO–SiO₂–MnO slag at 1 873 K was constructed in the present study. The capacity contours seemed to rotate clock–wisely from the CaO–SiO₂ binary side to the MnO–corner. The sulfide capacity increased with increasing ratio of MnO to CaO at relatively acidic region in which silica content greater than about 40 mass%, while the substitution of CaO by MnO does not significantly affect the capacity in the low silica region. The sulfide capacity generally increased with increasing content of MnO regardless of changes in the content of other constituents in multicomponent MnO-containing slags. It is necessary to take different values for the theoretical optical basicity of MnO in order to estimate the sulfide capacity of MnO–containing slags depending on the content of silica.

KEY WORDS: sulfide capacity; CaO–SiO₂–MnO slag; basicity; activity; activity coefficient; optical basicity.

1. Introduction

In the steelmaking process, the importance of desulfurization has been emphasized during several decades.¹⁻⁵ It is well known that the sulfur is harmful to the mechanical properties of steel products such as strength, ductility and toughness, etc. Therefore, it is necessary to remove the sulfur from molten steel under several ppm in order to improve the mechanical properties of steel products. Also, the demand of ferrous and non-ferrous manganese alloys is continuously increasing because the advanced high strength steels such as TRIP (TRansformation Induced Plasticity) and TWIP (TWin Induced Plasticity) aided steels which continuously increasing because the advanced high strength steels such as TRIP (TRansformation Induced Plasticity) and TWIP (TWin Induced Plasticity) aided steels are recently developed contain manganese up to about 30 mass%. Therefore, the desulfurization of manganese (ferro–) alloys as well as high manganese steels has recently been issued. Even though many researchers have investigated the sulfide capacity of molten slags, there are a few experimental data for the CaO–SiO₂–MnO ternary system at 1 873 K. Abraham et al.⁶ measured the sulfide capacity for the pseudo–binary system along the CaSiO₃–MnSiO₃ join at 1 773 through 1 923 K. The sulfide capacity increased with increasing ratio of MnO to CaO at a given silica content, which was explained by the similar tendency of the activity of MnO. But, the effect of the stability of sulfide on the sulfide capacity was not fully discussed in their study. Hino and Fuwa measured the sulfide capacity of the same slag at 1 823 K.⁷ Although the tendency of the iso–sulfide capacity constructed in these studies is very similar to each other, the value measured by Abraham et al.⁶ at 1 848 K is about 3 times greater than that by Hino and Fuwa at 1 823 K. It seems that this is quite large discrepancy even 25 K difference in temperature. Nilsson and Seetharaman investigated the sulfide capacity of the CaO–SiO₂–MnO slag in the temperature range from 1 798 to 1 873 K.³⁻⁶ However, the slag composition was so limited and the results were used in the modeling of sulfide capacity. Therefore, it is needed not only to measure the sulfide capacity of the CaO–SiO₂–MnO slag at 1 873 K through the entire composition range but also to discuss the thermodynamic effect of basicity and the stability of sulfide on the dissolution behavior of sulfur into the CaO–SiO₂–MnO slag.

On the other hand, Sosinsky and Sommerville proposed the correlation between the sulfide capacity of various slags and the optical basicity by incorporating the temperature effect.⁹ This relationship has been widely used not only in academia but also in industries during last decades. They determined the effective (or empirical) optical basicity for several transition metal oxides including MnO, however the effective optical basicity for manganese oxide (ΛMnO = 1.2) was greater than the theoretical value (ΛMnO = 1.0) originally.
calculated from Pauling’s electronegativity of cation by Duffy et al.\textsuperscript{10–12} Hence, some researchers have been confused to employ the optical basicity concept to predict the sulfide capacity of the MnO–containing slags.

Therefore, in the present study, the sulfide capacity of the CaO–SiO\textsubscript{2}–MnO slag through the entire composition range was measured at 1873 K using a gas–slag equilibration method and the effect of basicity and the activity coefficient of sulfide on the sulfide capacity of molten slag was investigated. Furthermore, the relationship between the sulfide capacity of MnO–containing slags and the optical basicity was evaluated in view of industrial applications.

2. Thermodynamic Consideration

The sulfide capacity \( C_{\text{S\textsuperscript{2}–}} \) has been used as the main index for desulfurizing ability of a slag from a thermodynamic point of view since Fincham and Richardson originally defined it as given in Eq. (2) deduced from the desulfurization reaction (Eq. (1)) based on a gas–slag equilibrium.\textsuperscript{13,14}

\[
\frac{1}{2} \text{S}_2(g) + (\text{O}^{2–}) = (\text{S}^{2–}) + \frac{1}{2} \text{O}_2(g) \quad \text{.................. (1)}
\]

\[
C_{\text{S\textsuperscript{2}–}} = \frac{K_{(1)} \cdot a_{\text{O}^{2–}}}{f_{\text{S}^{2–}}} = (\text{mass}\% \text{S}^{2–}) \left( \frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right)^{\frac{1}{2}} \quad \text{.................. (2)}
\]

where \( K_{(1)} \): equilibrium constant of Eq. (1)

\( a_{\text{O}^{2–}} \): activity of \( \text{O}^{2–} \) ion in slag (= basicity of slag)

\( f_{\text{S}^{2–}} \): activity coefficient of sulfide ion \( (\text{S}^{2–}) \) in slag

\( p_i \): partial pressure of gaseous component \( i \), atm

From Eq. (2), the sulfide capacity is known to be a function of basicity, the stability of sulfide ion in slag, and temperature. Thus, it is a unique function of slag composition at a given temperature and can be determined from the sulfur partial pressure determined from Eq. (9).\textsuperscript{15}

\[
\log a_{\text{MnS}} = -\frac{\Delta G^\circ_{\text{MnS}}}{2.303RT} + \log a_{\text{MnO}} - \frac{1}{2} \log \left( \frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right) - \log X_{\text{MnS}}
\]

\[
\text{.................. (7)}
\]

where \( a_{\text{MnS}} \) and \( X_{\text{MnS}} \) is the activity coefficient and the mole fraction of MnS, respectively. Hence, the stability of reaction products could be evaluated by taking the activity coefficient of MnS calculated from Eq. (7).

3. Experimental Procedure

A super–kanthal vertical electric resistance furnace was used for the equilibration between the CaO–SiO\textsubscript{2}–MnO slag and gas phase at 1873 K. The temperature was controlled within \( \pm 2 \) K using an installed B–type (Pt–30%Rh/Pt–6%Rh) thermocouple and a proportional integral differential controller. The furnace temperature was also calibrated using an external B–type thermocouple before experiment. The slag samples were prepared using reagent–grade SiO\textsubscript{2}, MnO and CaO calcined form CaCO\textsubscript{3} at 1273 K. The slag sample of 1.2 g was maintained in a platinum crucible which was held in the porous alumina holder under the CO–CO\textsubscript{2}–SO\textsubscript{2}–Ar gas mixture for 8 hours. A constant flow rate of 400 ml/min was maintained during the equilibration of the slag with gas mixture at the experimental temperature. The schematic diagram of the experimental apparatus is shown in Fig. 1.

Each gas was passed through the purification system to introduce the impurities. The oxygen partial pressure was calculated by Eq. (9), and the partial pressure of gaseous sulfur was obtained from Eq. (11) by incorporating the oxygen partial pressure determined from Eq. (9).\textsuperscript{15}

\[
\text{CO}_2(g) = \text{CO}(g) + \frac{1}{2} \text{O}_2(g), \quad \Delta G^\circ_{(8)} = 281100 – 85.3 \ T \ (J/mol) \quad \text{.................. (8)}
\]

\[
K_{(8)} = \frac{p_{\text{CO}} \cdot p_{\text{O}_2}^{1/2}}{p_{\text{CO}_2}} = \exp \left\{ \frac{\Delta G^\circ_{(8)}}{RT} \right\} \quad \text{.................. (9)}
\]

\[
\text{SO}_2(g) = \frac{1}{2} \text{S}_2(g) + \text{O}_2(g), \quad \Delta G^\circ_{(10)} = 361800 – 72.7 \ T \ (J/mol) \quad \text{.................. (10)}
\]

![Fig. 1. A schematic diagram of the experimental apparatus.](image-url)
The flow rate of each gas and the calculated oxygen and sulfur potentials are listed in Table 1.

After equilibration, the sample was quickly drawn from the furnace and then quenched by dipping it into brine. The quenched samples were crushed to less than 100 μm using stainless and agate mortars for chemical analysis. The content of sulfur and each component in the slag were determined by combustion analyzer (LECO, CS-200) and X-ray fluorescence spectroscopy (Bruker, S4 Explorer), respectively. The activity of each component in slag phase was calculated by commercial thermochemical computing program, FactSage6.1TM with ‘FToxid’ database. This database was successfully used for the estimation of the thermodynamic properties of oxide systems through a wide temperature and composition range.

4. Results and Discussion

4.1. Sulfide Capacity of the CaO–SiO₂–MnO Slag

The experimental compositions and results are listed in Table 2. These were designed to elucidate the effect of MnO at a given lime to silica ratio (= Vee ratio = C/S = 1.0 and 0.5) and to study the replacement effect of CaO by MnO at a fixed silica content (50 mass%). Figure 2 shows the effect of MnO content on the sulfide capacity of the CaO–SiO₂–MnO slag at 1873 K in each condition. The sulfide capacity increases with increasing MnO content, indicating that the MnO behaves as a basic oxide in the present slag system. Also, the higher the Vee ratio is, the greater the capacity is obtained at a given MnO content, which is in good agreement with the theoretical expectation. Comparing C/S = 1.0 and 0.5 conditions, it is interesting that the effect of basicity on the sulfide capacity increases by increasing the content of MnO. This will be discussed in detail later.

Figure 3 shows the relationship between the sulfide capacity of the CaO–SiO₂–MnO ternary slag and the mass ratio of (MnO+CaO)/(SiO₂) including the reference data measured by Abraham et al. at 1848 K, and Nilsson and Seetharaman at 1873 K. Even though the simple Vee ratio (=C/S) has been widely used to evaluate the basicity of slags, the modified Vee ratio (=(C+M)/S) shows a good composition dependency of the sulfide capacity in the CaO–SiO₂–MnO slag system. Comparing these experimental data, the temperature difference about 25 K would not be such a significant factor affecting the experimental scatters. This qualitatively indicates that small amounts of temperature fluctuation in the industrial operations would be taken into account within acceptable error range. Alternatively, the effect of composition on the sulfide capacity is more significant factor, viz the capacity linearly increases about 100 times as the (C+M)/S ratio changes from 0.5 to 2.5 in the...
Especially, the sulfide capacity increases when the CaO is replaced by MnO at 50 mass% SiO$_2$ as shown in Fig. 4, where the content of MnO is expressed by mole% to compare the present result to that of Abraham et al. In their work, it was concluded that the sulfide capacity was dominantly affected by the activity of MnO because of significantly smaller activity of CaO than MnO. Thus, it was provided from this tendency that there were no unexpectedly great difference between the activity coefficients of CaS and MnS in this pseudo–binary system. However, because it is certain that the effect of sulfide stability on the capacity should be independently investigated, we incorporated the activity coefficient of MnS calculated from Eq. (7) into thermodynamic assessment as follows.

**Figure 5** shows the activity of MnO and the activity coefficient of MnS as a function of MnO content. The activity of MnO ($\alpha_{\text{MnO}}$) initially increases while the activity coefficient of MnS ($\gamma_{\text{MnS}}$) remains nearly constant until $X_{\text{MnO}} = 0.15$, followed by level off in the $\alpha_{\text{MnO}}$ and continuous decrease in the $\gamma_{\text{MnS}}$. Assuming that the basicity and the stability of sulfide ion in slag are proportional to the activity of MnO and the activity coefficient of MnS, respectively, a slight increase in sulfide capacity at $X_{\text{MnO}} < 0.15$ (Fig. 4) originates from the increase in basicity, whereas from a significant decrease in the activity coefficient of MnS at $X_{\text{MnO}} > 0.15$.

By combining Eqs. (2) and (4), the following relationship can be deduced.

$$\log C_{S^2^-} = \log \alpha_{\text{MnO}} - \log \alpha_{\text{Mn}^{2+}} - \log f_{S^2^-} + C \quad \ldots \quad (12)$$

where $C$ may be assumed less sensitive to slag composition and it is assumed that the $\alpha_{\text{Mn}^{2+}}$ in Eq. (4) is determined by $(\text{MnO}) = (\text{Mn}^{2+}) + (\text{O}^{2-})$ reaction. The sulfide capacity of the CaO–SiO$_2$–MnO slag at 1873 K is plotted in **Fig. 6** against the activity of MnO in a logarithmic scale. There is a good linear correlation between them with the slope of 1.3 ($r^2 = 0.95$) which was obtained from a linear regression analysis. This means that the last three terms in Eq. (12), either each of them or in total, are not strictly constant, and in particular, a decreasing rate of the $f_{S^2^-}$ would be greater than an increasing rate of $\alpha_{\text{Mn}^{2+}}$ as the activity of MnO increases probably due to a strong interaction not only between Mn$^{2+}$ and S$^{2-}$ but also between Ca$^{2+}$ and S$^{2-}$ ions in the low silica region. This suggests that $C_{S^2^-}$ in the present slag system should be interpreted by not only the presence of MnS but also the presence of CaS. Therefore, additional contribution from CaS to the $C_{S^2^-}$ should also be considered, in particular for the low silica region as well as low MnO region.

The iso–sulfide capacity of the CaO–SiO$_2$–MnO slag at 1873 K is drawn in **Fig. 7**. The capacity contours seem to rotate clock–wisely from the CaO–SiO$_2$ binary side to the MnO–corner. Thus, the sulfide capacity increases by addi-
tion of MnO at a fixed CaO/SiO₂ ratio and this tendency is more dominant in the composition range near the Ca₃SiO₅ saturating liquidus line. Furthermore, the sulfide capacity increases with increasing ratio of MnO to CaO at relatively acidic region of which silica content greater than about 40 mass%, while the substitution of CaO by MnO does not significantly affect the capacity in the low silica region. This is very important and interesting result indicating the competitiveness of CaO and MnO not only in silicate depolymerization but also in desulfurization reactions. In the relatively high silica region, the CaO which has more ionic bond character, i.e. 79% based on the Pauling’s equation (Eq. (13)), dominantly contributes to the depolymerization of silicates than the MnO of which ionic bond character is 63% does.²⁵,²⁶

\[ i = 1 - e^{-\frac{x_A - x_B}{x_A + x_B}} \]  
...(13)

where \( x_A \) and \( x_B \) are, respectively, the electronegativity of A and B atoms. Hence, the large amount of Ca\(^{2+}\) cations are electrically balanced with two non-bringing oxygen ions (O\(^-\)), indicating that the Mn\(^{2+}\) cations are relatively free from the role of network modifier and mainly participate into the desulfurization reaction in high silica region. This is in good correspondence to the results shown in Figs. 5 and 6.

However, in the relatively low silica region, viz. less than 40 mass% SiO₂, the amount of Ca\(^{2+}\) cations balancing with O\(^-\) ions is reduced and thus Ca\(^{2+}\) and Mn\(^{2+}\) cations competitively react with the S\(^2-\) ions, resulting in the less effectiveness in the CaO ↔ MnO substitution. This indicates that the contribution of CaO and MnO to the stabilization of S\(^2-\) ions would be comparable to each other in the relatively low silica region. The more detailed discussion in regard of the role of CaO and MnO in the depolymerization of silicate network as well as desulfurization reaction will be treated in a separate publication of the present authors.²⁷

Figure 8 shows the sulfide capacity of various MnO-containing slags at temperature range from 1573 to 1923 K as a function of molar MnO content. The literature data thoroughly collected are as follows: For binary systems, the MnO–SiO₂ at 1773 to 1923 K from Richardson et al.,²⁸ at 1823 K from Hino and Fuwa,⁷ and at 1523 K from Kobayashi;²⁹ the MnO–Al₂O₃ at 1923 K from Sharma and Richardson,²⁸ and at 1773 to 1923 K from Nzotta et al.,³⁰ the MnO–TiO₂ at 1773 K from Karsrud,³¹ and at 1723 K from Kim et al.³² For ternary systems, the MnO–CaO–SiO₂ at 1773 to 1923 K from Abraham et al.,³³ at 1798 to 1873 K from Nilsson and Seetharaman,³⁰ at 1823 K from Hino and Fuwa,⁷ and at 1873 K from the present study; the MnO–MgO–SiO₂ at 1823 to 1923 K from Nzotta,³³ at 1923 K from Sharma and Richardson,²⁸ and at 1823 K from Hino and Fuwa;³⁷ the MnO–SiO₂–Al₂O₃ at 1923 K from Sharma and Richardson,²⁸ and at 1873 K from Nzotta,³⁰ the MnO–Al₂O₃–TiO₂ at 1673 to 1873 K from Ohta and Morita;³⁵ the MnO–SiO₂–TiO₂ at 1673 K from Ito et al.;³⁶ the MnO–FeO–SiO₂ at 1823 K from Hino and Fuwa. For quaternary systems, the CaO–MnO–SiO₂–Al₂O₃ at 1773 to 1923 K from Nzotta et al.,³⁰ and at 1673 K from Taniguchi et al.³¹ for quinary systems, the CaO–MnO–Al₂O₃–SiO₂–MgO at 1673 K from Taniguchi et al.¹

The sulfide capacity generally increases with increasing content of MnO regardless of changes in the content of other components. The present result is in good consistence with that of previous works.³–⁸ The sulfide capacities of the MnO–SiO₂ system are in good correspondence among several authors,⁶,⁷,²⁸,²⁹ whereas those of the MnO–Al₂O₃ system show a large discrepancy, i.e. about 10 times between two experimental data.²⁸,³⁰ Even though the reason for this scatter is not known, Nzotta et al.³⁰ commented the gas mixture they used, viz. CO–CO₂–SO₂–Ar, which is different from that used by Sharma and Richardson, CO–H₂–SO₂–N₂ mixture. However, it is believed to be questionable in Nzotta et al.’s work that the sulfide capacity was measured at 1773 K, at which temperature the liquid phase would not be formed based on the phase diagram of the MnO–Al₂O₃ system, viz. the eutectic temperature is about 1808 K.³⁷ Therefore, it is suggested that the sulfide capacity of the MnO–Al₂O₃ binary liquid phase should be confirmed in the future.

4.2. Sulfur Distribution Ratio between CaO–SiO₂–MnO Slag and Ferrous and Non-ferrous Metallic Melts

The sulfur distribution ratio \( L_S \) between slag and metal is defined as follows using Eq. (2).

\[ [S] + [O^2-] = [S^2-] + \frac{1}{2} O_2(g) \]  
...(14)

\[ \log L_S = \frac{\log (\text{mass}\% S)}{\text{mass}\% S} = \log C_S^\bullet - \log f_S - \frac{1}{2} \log p_O \]  
...(15)

where \( f_S \) represents the Henrian activity coefficient of sulfur in metal phase. Thus, the sulfur distribution ratio between slag and metal can be estimated from the composition of metal and oxygen potential of the system if the sulfide
capacity of the slag is available. Also, from the simple mass balance of sulfur between slag and metal phases, the equilibrium sulfur content in molten metal can be deduced from the weight of slag and metal as shown in Eq. (16).

\[ W_{\text{M}} \cdot [\text{mass}\% \text{S}] = W_{\text{S}} + W_{\text{S}} \cdot L_{\text{S}} \]  

(16)

where \( W_{\text{M}} \), \( W_{\text{S}} \), and \([\text{mass}\% \text{S}]\) are, respectively, the weight of metal and slag, and initial content of sulfur in molten metal. In this study, it is assumed that \( W_{\text{M}} = 100 \text{ metric tone} \), \( W_{\text{S}} = 5 \text{ metric tone} \), and \([\text{mass}\% \text{S}]\) = 0.03% for the conditions of ladle refining of low carbon steel, TWIP steel, austenitic stainless steel (STS304), and ferronickel (FeNi) melts. The representative compositions of the steels and FeNi are listed in Table 3. The content of oxygen in Table 3 was calculated from the following thermodynamic information.38,39

\[ \frac{1}{2} \text{O}_2(g) = [\text{O}] \]  

(17)

\[ \log K_{(17)} = \frac{6120}{T} + 0.18 \]  

(18)

The oxygen potential at slag/metal interface was assumed to be controlled by the \([\text{Si}]/(\text{SiO}_2)\) equilibrium, in which condition the \( P_{\text{O}_2} = 10^{-14} \to 10^{-12} \text{ atm} \) at high temperatures according to the composition of slag, i.e., the activity of \( \text{SiO}_2 \).38,39 The more detailed is given in the previous literature by the authors.40 Thus, in the present calculation, it is assumed that \( P_{\text{O}_2} = 10^{-13} \text{ atm} \). The activity coefficient of sulfur in each system was calculated from the following equation using interaction parameters between S and Cr, Ni, C, Mn, Si, and P listed in Table 4.38,39

\[ \log f_S = \rho \text{S} \cdot [\text{mass}\% \text{C}] + \rho \text{S} \cdot [\text{mass}\% \text{Ni}] + \rho \text{S} \cdot [\text{mass}\% \text{Cr}] + \rho \text{S} \cdot [\text{mass}\% \text{Si}] + \rho \text{S} \cdot [\text{mass}\% \text{Mn}] + \rho \text{S} \cdot [\text{mass}\% \text{P}] + \rho \text{S} \cdot [\text{mass}\% \text{S}] \]  

(19)

The equilibrium sulfur content in each metallic system which is in equilibrium with the \( \text{CaO–SiO}_2–\text{MnO} \) slags at 1873 K is shown in Fig. 9. The linear correlation between the sulfide capacity and the \((\text{C+M})/\text{S}\) ratio within experimental scatters in Fig. 3 was taken into account. Even though this is qualitative estimation, the final sulfur content is lower than 30 mass ppm and decreases by increasing the \((\%\text{MnO}+\%\text{CaO})/(\%\text{SiO}_2)\) ratio of the slag. The sulfur content in TWIP steel is greater than that in other metallic systems which is due to the attraction between manganese and sulfur as shown in Table 4. The critical values of the \((\text{C+M})/\text{S}\) ratio for obtaining ultra low sulfur (<3 ppm) in FeNi, low carbon steel, STS304 and TWIP steel are about 1.0, 1.2, 1.4, and 1.7, respectively.

### 4.3. Relationship between Sulfide Capacity and Optical Basicity

The effect of slag composition on the sulfide capacity can be expressed by employing an optical basicity concept as an indirect basicity index which was proposed by Sosinsky and Sommerville.39 The optical basicity of slag melts can be calculated from Eq. (20) and the sulfide capacity of the slags can be estimated from Eq. (21) as functions of optical basicity and temperature.9,12

\[ \Lambda_{\text{metal}} = \sum \frac{x_i n_i \Lambda_i}{\sum x_i n_i} \]  

(20)

where \( x_i \) is mole fraction of oxide component \( i \) \( n_i \) : number of oxygen in each oxide component \( i \) \( \Lambda \) : theoretical optical basicity of pure oxide component \( i \), i.e., \( \Lambda_{\text{CaO}} = 1.0, \Lambda_{\text{MnO}} = 1.2 \) or 1.0, \( \Lambda_{\text{SiO}_2} = 0.48 \).

\[ \log C_{\text{S}} = \frac{22690 - 54650 \Lambda}{T} + 43.6 \Lambda - 25.2 \]  

(21)

Duffy et al.10–12 originally proposed the theoretical optical basicity of MnO to be 1.0 \( (\Lambda_{\text{MnO}} = 1.0) \) from the Pauling’s electronegativity,25 whereas Sosinsky and Sommerville suggested the effective (or empirical) value to be 1.2 \( (\Lambda_{\text{MnO}} = 1.2) \) for the estimation of the sulfide capacity of the metallurgical slags containing MnO.9 Therefore, we have taken these two values in the present study and compared the calculated and the measured results for each case, i.e., \( \Lambda_{\text{MnO}} = 1.0 \) and \( \Lambda_{\text{MnO}} = 1.2 \).

As shown in Fig. 10, the sulfide capacity of the slags calculated using \( \Lambda_{\text{MnO}} = 1.0 \) is generally underestimated than the measured one, whereas the capacity is overestimated when \( \Lambda_{\text{MnO}} = 1.2 \) is taken. These discrepancies between

### Table 3. Compositions of carbon steel, TWIP steel, stainless steel (STS304), and ferronickel for the estimation of equilibrium sulfur content.

| Process          | Content of elements [mass%] | Cr | Ni | C | Si | Mn | P | O* | S* |
|------------------|-----------------------------|----|----|---|----|----|---|----|----|
| Carbon steel     |                             | 0  | 0.01| 0.5| 0.5| 0.02| 0.02| 0.010| 0.03|
| TWIP steel       |                             | 0  | 0.60| 0.5| 0.5| 0.02| 0.02| 0.0064| 0.03|
| STS304           |                             | 18 | 8  | 0.05| 0.5| 1.0| 0.02| 0.0037| 0.03|
| Ferronickel      |                             | 25 | 1.50| 1.0| 1.0| 0.5| 0.02| 0.0033| 0.03|

*calculated from Eq. (18) and the interaction parameters, \( e_{ij} \) in Table 4.

### Table 4. Interaction parameters used in the present calculation.

| System | Cr | Ni | C | Si | Mn | P | S |
|--------|----|----|---|----|----|---|---|
| S      | -0.01| 0  | 0.111| 0.075| -0.026| 0.035| -0.046|
| O      | -0.032 | 0.006| -0.421| -0.066| -0.037| 0.07| -0.133|
calculated and measured results originated from the fact that Sosinsky and Sommerville employed the experimental data for the MnO–containing slags measured by Richardson et al. in their estimation. The experimental composition investigated by Richardson et al. was limited to the relatively high silica content of which was greater than about 40 mass%, where the CaO mainly contributes to the depolymerization of silicate network, thus the MnO behaves as the more strong sulfide stabilizer than the CaO does in this region as discussed in Sec. 4.1. Thus, the $\Lambda_{\text{MnO}} = 1.2$ is believed to be fitted well to the experimental results in Sosinsky and Sommerville’s work. However, in the composition ranges of silica content of which is lower than 40 mass%, CaO and MnO are competitively react with sulfur as discussed in Sec. 4.1, indicating that the original value $\Lambda_{\text{MnO}} = 1.0$ would be reasonable.

Consequently, it is necessary to take different values for the theoretical optical basicity of MnO in order to estimate the sulfide capacity of MnO-containing slags using Eq. (21) depending on the content of silica as shown in Fig. 11, where a good linear relationship between measured and calculated results is obtained. However, it should be very careful for one to apply this empirical analysis for the estimation of sulfide capacity of slags. More detailed discussions on this issue will be presented in a separated paper of the present authors.27)

5. Conclusions

The sulfide capacity of the CaO–SiO$_2$–MnO slag through the entire composition range was measured at 1873 K using a gas–slag equilibration method and the effect of basicity and the activity coefficient of sulfide on the sulfide capacity of molten slag was investigated. Furthermore, the relationship between the sulfide capacity of MnO–containing slags and the optical basicity was evaluated in view of industrial applications. The specific findings of the present study are summarized below:

(1) Sulfide capacity of the slag linearly increased by increasing the content of MnO not only at a given silica content but also at a fixed Vee ratio. The capacity and the modified Vee ratio, i.e. $(\text{CaO+MnO})/\text{SiO}_2$ show a good linear relationship in the CaO–SiO$_2$–MnO slag.

(2) Assuming that the basicity and the stability of sulfide ion in the slag are proportional to the activity of MnO ($a_{\text{MnO}}$) and the activity coefficient of MnS ($\gamma_{\text{MnS}}$), respectively, the composition dependency of sulfide capacity is well described by the changes in the ratio of $a_{\text{MnO}}$ to $\gamma_{\text{MnS}}$.

(3) The iso–sulfide capacity of the CaO–SiO$_2$–MnO slag at 1873 K is constructed in the present study. The capacity contours seem to rotate clockwise from the CaO–SiO$_2$ binary side to the MnO–corner. The sulfide capacity increases with increasing ratio of MnO to CaO at relatively acidic region of which silica content greater than about 40 mass%, while the substitution of CaO by MnO does not significantly affect the capacity in the low silica region.

(4) The sulfide capacity generally increases with increasing content of MnO regardless of changes in the content of other constituents in multicomponent MnO–containing slags. The sulfide capacities of the MnO–SiO$_2$ system are in good correspondence among several authors, whereas those of the MnO–Al$_2$O$_3$ system show a large discrepancy. Therefore, it is suggested that the sulfide capacity of the MnO–Al$_2$O$_3$ binary system should be confirmed in the future.

(5) The sulfide capacity of the slags calculated using $\Lambda_{\text{MnO}} = 1.0$ is generally underestimated than the measured one, whereas the capacity is overestimated when $\Lambda_{\text{MnO}} = 1.2$ is taken. It is useful to take different values for the theoretical optical basicity of MnO in order to estimate the sulfide capacity of MnO–containing slags depending on the content of silica.

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