Sulfide Capacity of $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd.}}$ Slag

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The sulfide capacities of $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd.}}$ slag were measured at 1 823 K over a wide range of compositions using the thermochemical equilibrating technique. The experimental results indicated that MgO had a marginal effect on desulfurization because of its low thermodynamic driving force for sulfur ion stabilization in slag, whereas Al_2O_3 decreases the sulfide capacity because of its acidic behavior in the present slag system. The effect of FeO on desulfurization can be changed by the slag basicity because the Fe^{2+} cation competes with the Ca and Mg cations, which is reflected in changes in the sulfide stability of FeS in the slag. The depletion of Ca^{2+} cations in an acidic slag electrically bound Ca^{2+} ions with near non-bridging oxygen to create electric neutrality because of its higher ionicity. Thus, the competitive affinity of Fe, Ca, and Mg with sulfur in the slag plays an important role in the effect of the basicity of the slag on the stability of sulfide in a moderate slag composition range. Nonetheless, S^{2-} ions form CaS instead of FeS in a basic slag because there are excess free Ca^{2+} ions.

KEY WORDS: sulfide capacity; sulfide stability; MgO saturated slag; FeO (iron oxide); sulfide ion stabilization.

1. Introduction

In recent decades, advances have been made in electric arc furnace (EAF) process technology to increase awareness about the harmful effects of scrap and the importance of energy efficiency.^{1–3)} Because of the strict global regulation of greenhouse gases, these recent technological improvements have gained attention due to their environmental benefits.

Recently, the most important energy technology innovation has played an exceptionally significant role in increasing EAF productivity and reducing electrical energy consumption because the bath absorbs a large quantity of chemical heat released from the oxidation of iron and carbon by oxygen. Various applications of chemical heating energy by oxidation into the EAF has provided significant results in implementing the reliable slag foam to increase the energy efficiency to the maximum possible level as well as several other advantages.^{2,4)}

With the innovative energy technology involved in the EAF process, slag design technology has also focused on optimizing slag-foaming and slag-refining abilities, which depend on the EAF's basicity and FeO content. In particular, the optimization of the FeO content of the slag is one of the major efforts to increase both productivity and energy efficiency and add values to the slag. The partial reduction of FeO in molten slag by reducing agents was also proposed to modify the slag composition in order to add value.^{5,6)} For example, the change in chemical composition with FeO content in the slag-aided reduction with aluminum resources reflects the physicochemical properties of the viscosity,

interfacial energy, and refining ability of impurities, such as P and S. Knowledge of the sulfide capacity of EAF slag reduction with Al resources during tapping is essential to improve the cleanliness of steel when the EAF operating conditions have low basicity and FeO content.

The pioneering studies on the concept of sulfide capacity of slag by Fincham and Richardson provided the fundamentals for a number of studies on desulfurization.^{7–13)} Despite earlier extensive investigations on the desulfurization of slag, to the best of our knowledge, the majority of research has focused on the desulfurization of relatively high-basicity slag with low FeO content, because the basicity and low oxygen potential positively affect the sulfide capacity of the slag.

St. Pierre and Chipman¹⁴⁾ reported a comparable or lower effect of FeO than CaO on the sulfide capacity of basic slag melts, whereas the effect of FeO on the sulfide capacities of high-FeO-content slags with lower basicity was unclear. Investigations on the sulfide capacity of binary slags have indicated that CaO-SiO_2 slags have lower sulfide capacities than the corresponding FeO-SiO_2 slags in the acidic region.⁷⁾ The effects of basic oxides on the sulfide capacity were compared by several authors. Shim and Banya¹⁵⁾ reported that the effect of MgO on the sulfur distribution between liquid iron and the ternary slags of FeO-MgO-SiO_2 , which was saturated with MgO, was considerably lower than that of FeO and CaO. Bronson and Pierre also reported a similar result for the function of FeO, where the $(a_{\text{O}^{2-}} / f_{\text{S}^{2-}})$ ratio increased because of the substitution of FeO for CaO, whereas the $(a_{\text{O}^{2-}} / f_{\text{S}^{2-}})$ ratio significantly decreased if CaO was replaced with MgO in the $\text{CaO-SiO}_2\text{-FeO}$ and $\text{CaO-SiO}_2\text{-MgO}$ ternary systems.⁸⁾ Kang and Park¹⁶⁾ re-examined these results of the effect of FeO on desulfurization with more precise thermodynamic

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assessments and compared the desulfurization abilities of CaO, FeO, and MnO. Recently, Park *et al.*^{17,18)} proposed that the effect of metallic cations on the sulfide capacity could vary under different basic conditions. The effect of FeO on desulfurization under low-basicity and high-FeO conditions has not yet been established.

Therefore, the effect of FeO over a wide range of compositions must be clarified. In the present study, the sulfide capacity of CaO-SiO₂-FeO-Al₂O₃-MgO_{satd.}-bearing slag for the EAF process at 1 823 K was measured for a broad range of chemical compositions using the thermochemical equilibrating technique. The effects of FeO on desulfurization at different basic conditions are discussed in detail from a thermodynamic viewpoint.

2. Thermodynamic Considerations

The sulfur-oxygen exchange equilibrium reaction and sulfur potential are expressed by Eqs. (1) and (2), respectively.¹⁹⁾

$$\frac{1}{2}S_2(g) = [S]_{in Fe}, \Delta G^{\circ} = -125\,100 + 18.5T \text{ (J/mol)} \dots (2)$$

The sulfide capacity, which was originally defined by Fincham and Richardson, is determined from Eq. (3).¹³⁾

$$C_{S^{2-}} = \frac{K_{(1)} \cdot a_{O^{2-}}}{f_{S^{2-}}} = (wt\%S) \cdot \left(\frac{P_{O_2}}{P_{S_2}} \right)^{0.5} \dots\dots\dots (3)$$

where $C_{S^{2-}}$ is the sulfide capacity of the slag; (wt%S) is the sulfur content in weight percent in the slag; P_{O_2} and P_{S_2} are the partial pressures of oxygen and sulfur, respectively; and $K_{(1)}$, $a_{O^{2-}}$, and $f_{S^{2-}}$ denote the equilibrium constant of Eq. (1), activity of free oxygen ion in the slag, and activity coefficient of sulfide ion in the molten slag, respectively.

The activity coefficient of sulfide is calculated using Eqs. (4) and (5).

$$\log \gamma_{MS} = -\frac{\Delta G_4^{\circ}}{2.303RT} + \log a_{MO} - \frac{1}{2} \log \left(\frac{P_{O_2}}{P_{S_2}} \right) - \log X_{MS} \dots (5)$$

where M is the metallic cation and γ_{MS} and X_{MS} are the activity coefficient and mole fraction of MS, respectively. The thermodynamic stability of the sulfide can be deduced from the activity coefficient (γ_{MS}).

3. Experimental Procedure and Methods

3.1. Experimental Procedure

The slag-metal equilibrium method was introduced in the present study. All experiments were performed in a super-kanthal vertical resistance furnace. **Figure 1** shows the experimental apparatus in this study. The temperature was controlled within ± 2 K using a B-type (Pt-30%Rh/Pt-6%Rh) thermocouple and proportional integral differential

Fig. 1. Experimental apparatus for the measurement of sulfide capacity.

controller. Reagent-grade CaCO₃ was pre-calcined for 12 h at 1 273 K to prepare CaO. The slag was prepared from mixtures of analytical-grade Al₂O₃, CaO, SiO₂, FeO and MgO. Then, 4 g of slag and 4 g of pre-melted electrolytic iron were equilibrated in MgO crucible for 8 h, which was confirmed to be a sufficient amount of time to reach the thermo-chemical equilibrium based on preliminary experiments. The atmosphere was controlled under a constant flow rate of 500 cm³/min high-purity Ar (99.9999%) gas using a mass flow controller. The oxygen partial pressure at the slag-metal interface was controlled using the equilibrium of Fe and FeO according to Reaction (6).²⁰⁾

$$\Delta G_{(6)}^{\circ} = -256\,000 + 53.68T \text{ (J/mol)}$$

$$K_{(6)} = \frac{a_{FeO}}{a_{Fe} \cdot P_{O_2}^{1/2}} = \exp \left(-\frac{\Delta G_{(6)}^{\circ}}{RT} \right) \dots\dots\dots (7)$$

3.2. Chemical Analysis and Thermodynamic Assessment

The samples were quickly drawn from the furnace and quenched in an Ar stream after equilibration. The quenched slag was crushed to less than 100 μ m for the chemical analysis. The chemical compositions and sulfur content of the slag and metal were determined using an X-ray fluorescence spectroscope (Bruker, S4 Explorer, Billerica, Massachusetts, USA) and a combustion analyzer (LECO,

CS-200, St. Joseph, Michigan, USA), respectively. The activity of each component in the slag phase was calculated using the commercial thermochemical computing software FactSage6.1TM with the “FToxid” database. According to past publications, this database appears applicable for estimating the thermodynamic properties of oxide systems through a wide temperature and composition range.^{21–27)}

4. Results and Discussion

4.1. Effect of the MgO, Al₂O₃ and FeO Content on the Sulfide Capacity of CaO-SiO₂-FeO-Al₂O₃-MgO_{satd.} Slag

The equilibrium slag composition and sulfur content are provided in **Table 1**. Present experimental results are plotted with the results of various slag systems in **Fig. 2**. The sulfide capacity appears to increase with the extended basicity while there is a discrepancy in slopes among the slag systems. In particular, the experimental results at the basicity under unity show a wide range of sulfide capacity based on the chemical composition. The quantitative correlation between the extended basicity and sulfide capacity is difficult to assess from Fig. 2. Thus, the individual effect of each basic oxide component on the sulfide capacity must

Table 1. Equilibrium compositions (mass%) and sulfide capacity of the slags.

CaO	SiO ₂	FeO	Al ₂ O ₃	MgO	(%S)	[%S]	log C _S
35.64	32.19	9.79	0.00	22.38	0.10	0.54	-2.51
30.74	27.52	19.04	0.00	22.70	0.16	0.50	-2.35
28.58	25.63	26.78	0.00	19.02	0.23	0.53	-2.92
24.26	21.72	34.47	0.00	19.56	0.27	0.49	-2.68
29.79	29.55	13.41	7.44	19.81	0.16	0.58	-2.52
25.88	25.63	23.82	7.22	17.46	0.17	0.51	-2.32
22.96	22.75	30.73	7.34	16.22	0.18	0.43	-3.10
19.11	20.01	38.69	7.23	14.95	0.21	0.35	-2.92
26.83	26.74	11.28	14.55	20.60	0.14	0.65	-2.67
24.37	23.52	18.31	15.00	18.80	0.13	0.53	-2.50
20.80	20.07	27.14	15.05	16.93	0.16	0.46	-2.77
17.27	16.46	35.27	15.35	15.65	0.21	0.46	-2.87
19.36	18.25	25.59	17.74	19.06	0.16	0.55	-2.70
18.97	17.61	23.58	20.34	19.50	0.12	0.47	-2.47
14.90	13.77	31.06	22.40	17.88	0.15	0.46	-2.70
11.60	10.39	39.71	22.08	16.23	0.31	0.63	-2.47
36.89	19.02	11.37	18.82	13.91	0.29	0.44	-2.74
31.54	15.54	19.48	18.30	15.13	0.34	0.49	-2.53
25.89	12.17	29.37	18.97	13.59	0.37	0.51	-2.39
18.80	9.41	37.54	19.22	15.02	0.38	0.54	-2.33
48.46	15.97	12.40	15.65	7.53	0.56	0.38	-2.56
44.94	14.53	18.59	14.22	7.72	0.54	0.31	-2.31
41.20	13.35	24.15	13.66	7.64	0.51	0.28	-2.17
38.89	12.60	28.71	12.08	7.72	0.50	0.28	-2.11

be examined.

The change in sulfide capacity and MgO solubility are shown as a function of the CaO/SiO₂ ratio in **Fig. 3**. The sulfide capacity is increased with CaO/SiO₂ ratio while the MgO solubility is decreased. The tendency of the MgO solubility change is well explained by the result that has reported by Kim and Min.²⁹⁾ Typically, MgO is known as basic oxide and hence could facilitate the desulfurization reaction in particular slag compositions. But in Fig. 3, the result which has higher CaO/SiO₂ ratio shows the higher sulfide capacity despite of the lower MgO solubility, *i.e.* the MgO concentration in saturated condition. This result could

Fig. 2. Relationship between the (%CaO+%FeO+%MnO+%MgO)/(%SiO₂+%Al₂O₃) ratio and the sulfide capacity of slags.

Fig. 3. Relationship between the basicity and sulfide capacity, MgO solubility of the CaO-SiO₂-FeO-(Al₂O₃)-MgO_{satd.} slags.

be explained in view of the thermodynamic stability of the sulfide ion as following. A relative insignificant effect of MgO on sulfide capacity in several slag systems in similar case have been reported.^{16,28,30)} Those results were based on the fact that the free energy change for the MgS formation is less favorable than that for other basic oxides. Therefore, the sulfide capacity is mainly determined by the content of other basic oxides when MgO coexists with abundant amounts of CaO or FeO in a slag.

Figure 4 shows the effect of Al_2O_3 on the sulfide capacity of $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd.}}$ slag when the CaO/SiO_2 ratio is 1.0. The sulfide capacity decreases at constant FeO concentration. According to the ionic potential (Z/r^2) and structural behavior of Al_2O_3 , Al_2O_3 behaves as an amphoteric oxide in the ternary $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ melts, as identified by Banya.³¹⁾ However, considering the CaO/SiO_2 ratio in weight percent and the Al_2O_3 concentration, the composition of the present slag in Fig. 4 places the slag chemistry in the peralkaline alumino-silicate region, where Al^{3+} is typically in a tetrahedral configuration with oxygen. In this case, the slag basicity decreases because of the free-oxygen-ion consumption by the added Al_2O_3 . Thus, the sulfide capacity of the Al_2O_3 -containing slag decreases with increasing Al_2O_3 concentration, as shown in Fig. 4.

To determine the effect of FeO on the sulfide capacity, the FeO concentration and sulfide capacity of the slag are shown in **Fig. 5**. The sulfide capacity of the MnO-containing system is also plotted. As shown in Fig. 5, the sulfide capacity increases linearly with the FeO and MnO content. This result indicates that FeO is the basic oxide in this slag system. The slopes for the ternary system and MgO saturated system are nearly identical. This result can be explained by the aforementioned difference in thermodynamic affinity between each oxide and sulfide ion in the slag. In terms of Gibbs free energy, Mg^{2+} ion has a low affinity with S^{2-} ion in the slag, whereas Fe^{2+} and Mn^{2+}

ions have higher affinities.^{16,32)} Therefore, Mg^{2+} does not contribute to the desulfurization reaction when the amounts of Fe^{2+} or Mn^{2+} in the slag are sufficient. The previously reported iso-sulfide capacity lines in $\text{CaO-SiO}_2\text{-MgO}$ and FeO-MgO-SiO_2 systems by Nzotta *et al.*^{10,32)} also indicate this trend. Those results represent that a significant change of the sulfide capacity is occurred when the concentration of CaO or FeO is varied, whereas the change of MgO concentration has little effect.

4.2. Effect of FeO Activity on the Sulfide Capacity of $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd.}}$ Slag

Considering the thermodynamic constraints in the quinary slag system, the activity of FeO is examined, which includes the effect of both the fraction of FeO in the melt and the activity coefficients. The sulfide capacity of $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd.}}$ slag is plotted in **Fig. 6** against the activity of FeO in a logarithmic scale at several fixed basicities. Based on the definition of the sulfide capacity in Eq. (3), the slope of the logarithmic plot of the O^{2-} activity and sulfide capacity is expected to be unity.

$$\log C_{\text{S}^{2-}} = \log a_{\text{O}^{2-}} - \log f_{\text{S}^{2-}} + \log K_{(1)} \quad \text{..... (8)}$$

where $K_{(1)}$ is the equilibrium constant of Eq. (1), $a_{\text{O}^{2-}}$ is the activity of O^{2-} ions, and $f_{\text{S}^{2-}}$ is the Henrian activity coefficient of S^{2-} ions in the slag.

The activity of FeO in the slag is assumed to be proportional to the basicity of the slag because CaO/SiO_2 is fixed and MgO is saturated.^{17,18)}

$$(\text{FeO}) = (\text{Fe}^{2+}) + (\text{O}^{2-}) \quad \text{..... (9)}$$

$$\log a_{\text{FeO}} = \log a_{\text{O}^{2-}} + \log a_{\text{Fe}^{2+}} - \log K_{(9)} \quad \text{..... (10)}$$

By combining Eqs. (8) and (10) and substituting for $\log a_{\text{O}^{2-}}$, the following relationship is obtained:

Fig. 4. Relationship between ($\%\text{Al}_2\text{O}_3$) and sulfide capacity $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd.}}$ slag.

Fig. 5. Effect of FeO and MnO content on the sulfide capacity of slags.

Fig. 6. Relationship between the activity of FeO and the sulfide capacity of slags.

$$\log C_{S^{2-}} = \log a_{FeO} - \log a_{Fe^{2+}} - \log f_{S^{2-}} + C \quad \text{..... (11)}$$

Equation (11) illustrates that the sulfide capacity is affected by the activity of FeO, activity of Fe^{2+} ions, and activity coefficient of S^{2-} ions in the slag. Because C is mainly a function of temperature in Eq. (11) and is less sensitive to the slag composition, the activity of FeO represents the basicity of the slag, whereas the terms with the activity of Fe^{2+} ions and activity coefficient of S^{2-} ions represent the stability of iron sulfide in the slag. Hence, considering the non-linear behavior in the slopes of Fig. 6, there is a combined effect of the basicity and sulfide stability. In other words, the slope in Fig. 6 deviates from unity, likely because of the sulfide stability difference. The increasing rate of the sulfide capacity with the activity of FeO appears to gradually decrease with the increase in slag basicity. Intuitively, the olivine and silica saturated system has a lower basicity than the lime-based slag. The slope of the FeO activity and sulfide capacity plot for the slag with $CaO/SiO_2=3.0$ is higher than that of the slag with $CaO/SiO_2=1.0$ in the present work. The slopes that Kim *et al.*,³³⁾ Nzotta *et al.*¹⁰⁾ and Shim *et al.*¹⁵⁾ obtained for olivine and silica saturated systems also increased with the basicity of the slag system.

4.3. Thermodynamic Stability of Sulfides in CaO-SiO₂-FeO-Al₂O₃-MgO_{satd.} Slags

The components of a molten slag are well known to exist in their ionic state. The sulfide ion is considerably affected by the metal cations in the slag.³⁴⁾ Therefore, the thermodynamic stability of the sulfide ion or corresponding sulfide compound is strongly affected by the cation species, which is the nearest neighbor with the S^{2-} ions in the slag.¹⁶⁾ In the case of FeS, the activity of Fe^{2+} and S^{2-} ions is expressed by the FeS activity according to Eq. (12).

Fig. 7. Relationship between the activity of FeO and activity coefficient of FeS at various basicity in CaO-SiO₂-FeO-Al₂O₃-MgO_{satd.} slag.

$$FeS = (Fe^{2+}) + (S^{2-}) \quad \text{..... (12)}$$

The activity coefficient of FeS can be determined from the equilibrium of Eqs. (13), (14), and (15).

$$K_{(13)} = \frac{a_{FeS} \cdot P_{O_2}^{1/2}}{a_{FeO} \cdot P_{S_2}^{1/2}} \quad \text{..... (14)}$$

$$\gamma_{FeS} = \frac{K_{(13)} \cdot a_{FeO} \cdot P_{S_2}^{1/2}}{X_{FeS} \cdot P_{O_2}^{1/2}} \quad \text{..... (15)}$$

where γ_{FeS} and X_{FeS} are the activity coefficient and mole fraction of FeS in the molten slag, respectively, and P_i is the partial pressure of gaseous species i . **Figure 7** shows the calculated activity coefficient of FeS in various slag systems. The sulfur is assumed to be completely stabilized by Fe^{2+} ions. Based on Eq. (13), the FeS formation tends to increase with increasing FeO activity. Although the absolute value of γ_{FeS} is lower in a high-basicity slag, the decreasing rate of γ_{FeS} gradually changes with the basicity of each slag. This result indicates that a large portion of the added Fe^{2+} contributes to sulfur binding in a low-basicity slag, which occurs because the following ionic properties of metallic cations.

The results arise from the characteristic thermodynamic affinity of cations with anions, such as O^{2-} and S^{2-} , in slags. Based on Pauling's equation, the ionic bond character of oxides is calculated using Eq. (16).

Table 2. Ionic properties for Ca^{2+} , Mn^{2+} , and Fe^{2+} .

Ion	r_c (nm)	r_c/r_o	Coordinate Number	I	Electronegativity of element	Ionicity of bonding
Fe^{2+}	0.075	0.54	6	0.87	1.8	51
Mn^{2+}	0.080	0.57	6	0.83	1.5	63
Ca^{2+}	0.099	0.71	7,8,9	0.7	1	79

Fig. 8. Schematic diagram of sulfur ion stabilization in low basicity and high basicity slag.

$$i(\text{amount of ionic bond character}) = 1 - e^{-\frac{1}{4}(x_A - x_B)^2} \dots (16)$$

where x_A and x_B are the electronegativities of the A and B atoms, respectively. Because CaO has greater ionic bonding characteristics than FeO , CaO dominantly contributes to the depolymerization of the silicate network structures, where Ca^{2+} ions are preferentially electrically balanced with two non-bridging oxygen ions (O^-) in the melt. In such a case, the Fe^{2+} ion is relatively free from the role of network modifier and participates in the desulfurization reaction in a low-basicity slag. However, there are excess free Ca^{2+} ions in a relatively high-basicity slag. Ca^{2+} ions compete with Fe^{2+} ions, where CaS dominantly forms because S^{2-} has a higher affinity with Ca^{2+} ion than with Fe^{2+} ion. This metallic cation effect on sulfide ion stabilization is schematically represented in **Fig. 8**. The same tendency of the cationic effect in the $\text{CaO-SiO}_2\text{-MnO}$ and $\text{CaO-SiO}_2\text{-MnO-Al}_2\text{O}_3\text{-MgO}$ systems is reported by Park *et al.*^{17,18)} earlier. According to Park, Ca^{2+} and Mn^{2+} ions compete for sulfide ion stabilization in an identical manner. This result is not a coincidence, because the related ionic properties of Mn^{2+} and Fe^{2+} ions are notably similar. The ionic properties of Ca^{2+} , Fe^{2+} , Mn^{2+} and Mg^{2+} ions are shown in **Table 2**. Hence, the portion

Fig. 9. Iso-sulfide capacity line in $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd}}$ slag at 1 823 K.

of sulfide ions that are stabilized with Fe^{2+} increases more rapidly in a low-basicity slag than in high-basicity slag. This phenomenon is represented by the decreasing rate of γ_{FeS} in **Fig. 7**. The acidic slag has a steeper slope because of the considerable Fe-S stabilization, whereas γ_{FeS} of the basic slag is early constant because the Ca-S stabilization by excess Ca^{2+} ions is dominant.

Figure 9 shows a schematic of the iso-sulfide capacity line in the $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd}}$ slag at 1 823 K. The predicted liquid solution region based on $\text{CaO-SiO}_2\text{-FeO}$ system is presented as colored area. The sulfide capacity contour appears to rotate clockwise with respect to the chemical composition. This result is analogous to those of Nzotta for the $\text{CaO-SiO}_2\text{-FeO}$ system and Park for the $\text{CaO-SiO}_2\text{-MnO}$ and $\text{CaO-SiO}_2\text{-MnO-Al}_2\text{O}_3\text{-MgO}$ systems.^{10,17,18)} As the slag basicity decreases, the effect of FeO on the stability of the sulfide ion, *i.e.*, $f_{\text{S}^{2-}}$, gradually increases, as previously discussed. Because Ca^{2+} is a major reactant to interact with S^{2-} ions in highly basic slag systems, the sulfide capacity decreases with increasing FeO/CaO ratio. However, the sulfide capacity increases for highly acidic slag systems with increasing FeO/CaO ratio because of the higher contribution of Fe^{2+} ions.

5. Conclusions

The sulfide capacity of $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}_{\text{satd}}$ slag was measured at 1 823 K over a wide composition range using the slag-metal chemical equilibrium method. The effect of FeO on the sulfide capacity was investigated

considering the slag basicity and the role of metallic cation for the stabilization of the S^{2-} ions. The specific findings of the present study are as follows.

(1) The sulfide capacity of the $CaO-SiO_2-FeO-Al_2O_3-MgO_{satd.}$ slag increased with increasing FeO content at a fixed CaO/SiO_2 ratio. The effect of the modified Vee ratio of the present slag system on the sulfide capacity is positively related to the other lime base, FeO-containing slag systems.

(2) The sulfide capacity increased with the FeO activity. However, the slope of the sulfide capacity vs. FeO activity, which was plotted in logarithmic scale, was larger than 1.0 because of the effect of the activity coefficient of the S^{2-} ion, and this tendency was stronger in a lower-basicity slag.

(3) Assuming that the activity coefficient of the S^{2-} ion is proportional to the activity coefficient of sulfide in a molten slag, γ_{FeS} was investigated. The thermodynamic preference for FeS formation increased with FeO activity when the CaO/SiO_2 ratio was 1.0, but this preference was nearly constant when the CaO/SiO_2 ratio is 3.0 because of the competitiveness of Ca^{2+} and Fe^{2+} for the S^{2-} ion stabilization. The S^{2-} ion is stabilized mainly because of Ca^{2+} ions when there are excess free Ca^{2+} ions. Consequently, the Fe^{2+} ion has a relatively larger effect on the sulfide capacity in a lower-basicity slag.

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