Sulfide Capacity of CaO–SiO₂–MnO–Al₂O₃–MgO Slags at 1 873 K

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The sulfide capacities of the CaO–SiO₂–MnO–Al₂O₃–5 mass% MgO slags were measured at 1 873 K over a wide composition range using a gas–slag equilibration method. The effects of basicity and the activity coefficient of sulfide on the sulfide capacity of molten slag were also investigated based on the structural view of silicate melts. In the multicomponent silicate melts containing high MnO (up to about 50 mass%), the sulfide capacity mainly increased with increasing MnO content. The capacity and modified Vee ratio, *i.e.* (CaO+MnO+MgO)/(SiO₂+Al₂O₃), showed a good linear relationship. Assuming that the basicity and the stability of sulfide ions in the slag are proportional to the activity of basic oxides and the activity coefficient of sulfides, the composition dependency of the sulfide capacity is well described by changes in the a_{MO} to γ_{MS} (M=Ca, Mn) ratio. The substitution of silica by alumina did not affect the sulfide capacity of the slags not only because of an increase in the activity of basic oxides but also because of a decrease in the stability of sulfides as Al₂O₃/SiO₂ ratio increased. In the high silica melts of which silica content greater than about 30 mass%, the sulfide capacity increased with increasing MnO/CaO ratio, whereas it decreased by increasing the MnO/CaO ratio in the low silica melts (< about 30 mass%). This tendency of sulfide capacity resulted in the clock-wisely rotating iso-capacity contours in the CaO–SiO₂–MnO–Al₂O₃–MgO system at 1 873 K. The dissolution mechanism of sulfur in the MnO-containing calcium silicate melts can be explained not only by the difference in the structural role of Ca²⁺ and Mn²⁺ ions but also by the changes in the content of O²⁻ ions according to the silica content.

KEY WORDS: sulfide capacity; CaO–SiO₂–MnO–Al₂O₃–MgO slag; basicity; sulfide stability; silicate structure; free oxygen.

1. Introduction

Desulfurization has been emphasized over several decades in iron- and steelmaking processes.^{1–7)} Sulfur is harmful to the mechanical properties of steel products (*e.g.*, strength, ductility and toughness). Therefore, it is necessary to remove sulfur from molten steel to under several ppm in order to improve mechanical properties. Additionally, the demand for ferrous and non-ferrous manganese alloys has increased continuously due to the introduction of advanced high strength steels such as transformation induced plasticity (TRIP) and twinning induced plasticity (TWIP) aided steels that were recently developed to contain manganese up to about 30 mass%.^{8–12)} Thus, the desulfurization of manganese (ferro-)alloys and high manganese steels is an important issue.

Even though many researchers have investigated the sulfide capacities of molten slags, there are few experimental data regarding high MnO-containing multicomponent slags. We recently investigated experimental and modeling approaches for the CaO–SiO₂–MnO ternary system.^{6,7)} In the present paper, we focus on sulfur dissolution behavior into multicomponent calcium manganosilicate melts containing Al₂O₃ and MgO.

Nzotta *et al.*¹³⁾ measured the sulfide capacities of the CaO–SiO₂–MnO–Al₂O₃ quaternary system at temperatures

from 1 773 to 1 923 K by a gas–slag equilibration method and proposed iso-sulfide capacity contours calculated from their KTH model for the system of $X_{\text{CaO}} = 0.13$. In their modeling results, the sulfide capacity of the slags dominantly increased by increasing the MnO content, independent of the Al₂O₃/SiO₂ ratio. The effect of MnO on the sulfide capacity of low-silica (6 to 8 mass%) CaO–Al₂O₃–MnO–SiO₂ slags was the same.²⁾ Nzotta¹⁴⁾ and Nilsson *et al.*¹⁵⁾ also measured the sulfide capacities of the CaO–SiO₂–MnO–MgO slags at temperatures from 1 773 to 1 923 K to develop model parameters based on experimental data. They proposed iso-sulfide capacity contours that were calculated from the KTH model of $X_{\text{MnO}} = 0.05$ system. In their modeling results, the sulfide capacity of the slags were strongly decreased by increasing the silica content and moderately decreased with increasing MgO/CaO ratio at given silica and alumina contents.

The sulfide capacities of the CaO–SiO₂–MnO–Al₂O₃–MgO quinary system were measured by Seetharaman *et al.*^{13,15)} In these studies, the sulfide capacities of the six composition systems were measured at temperatures from 1 773 to 1 923 K. The calculated sulfide capacity of the 5 component slags with $X_{\text{CaO}} = 0.07$ and $X_{\text{MgO}} = 0.36$ generally increased with increasing MnO content, with a minimum at about $X_{\text{Al}_2\text{O}_3} = 0.1$ at a fixed MnO/SiO₂ ratio. In more recent work by Taniguchi *et al.*,²⁾ the sulfide capacities of low-

silica (3 to 11 mass%) CaO–Al₂O₃–MnO–SiO₂–4 mass% MgO slags were measured at 1 673 to 1 723 K. Manganese oxide increased the sulfide capacities of slags, with its addition being more effective at lower temperatures. The addition of MgO (4 mass%) increased the sulfide capacities of slags in the 0 to 10 mass% MnO range, but there was no substantial effect above 10 mass% MnO.

Therefore, in the present study we measured the sulfide capacities of the CaO–SiO₂–MnO–Al₂O₃–5 mass% MgO slags at 1 873 K through a wide composition range, and also discussed the thermodynamic effects of basicity and the stability of sulfide on the dissolution behavior of sulfur into the CaO–SiO₂–MnO–Al₂O₃–MgO slags.

2. Experimental Procedure

A kanthal super vertical electric resistance furnace was used for equilibration between the CaO–SiO₂–MnO–Al₂O₃–MgO slag and gas phase at 1 873 K. The temperature was controlled within ± 2 K using an installed B-type thermocouple and a proportional integral differential controller. The slag samples were prepared using reagent-grade SiO₂, MnO, Al₂O₃, MgO and CaO calcined from CaCO₃ at 1 273 K. A slag sample of 1.2 g was maintained in a platinum crucible, which was held in a porous alumina holder under the CO–CO₂–SO₂–Ar gas mixture for 8 hours. The flow rate of each gas and the calculated oxygen and sulfur potentials are listed in **Table 1**.⁶⁾ The schematic diagram of the experimental apparatus and detailed experimental conditions are available in our earlier work.⁶⁾

After equilibration, each 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 steel and agate mortars for chemical analysis. The contents of sulfur and each component in the slag were determined by a combustion analyzer and X-ray fluorescence spectroscopy, respectively. The activity of each component in the slag phase was calculated by a commercial thermochemical computing program, FactSageTM 6.2.^{16,17)} This database has been successfully used for the estimation of the thermodynamic properties of multicomponent oxide systems over wide temperature and composition ranges.^{1,6,7,18–31)}

3. Results and Discussion

3.1. Effect of MnO Content on Sulfide Capacity of CaO–SiO₂–MnO–Al₂O₃–MgO Slags

The experimental compositions and results are listed in **Table 2**. These were designed to elucidate the effect of MnO at a given Vee ratio (= CaO/SiO₂ = 1.1 and 0.5) and to study the replacement effect of CaO by MnO at a fixed silica content (40 mass%) and the substitution effect of alumina for

silica at a fixed CaO and MnO contents. **Figure 1** shows the effect of MnO content on the sulfide capacity of the CaO–SiO₂–MnO–20 mass% Al₂O₃–5 mass% MgO slags at 1 873 K under each condition. The sulfide capacity increases with increasing MnO content, indicating that MnO behaves as a basic oxide in the present slag system. Also, the higher the Vee ratio, the greater the capacity is obtained at a given MnO content, which is in good agreement with theoretical expectations. It seems that sulfide capacity slightly increases by increasing the MnO/CaO ratio at 40 mass% SiO₂ from MnO-free to CaO-free systems. The experimental data for the CaO–SiO₂–MnO ternary slag system at 1 873 K is also shown in Fig. 1.⁶⁾ It is interesting that the sulfide capacity of the ternary and quinary slags are not so much different at the similar C/S condition, although it seems that the capacity of the quinary slag at C/S=1.0 is slightly higher than that of

Table 2. Equilibrium compositions (mass%) and sulfide capacities of the slags.

CaO	SiO ₂	MnO	Al ₂ O ₃	MgO	Sulfur	log C _S
20.3	37.7	18.1	19.5	4.4	0.0598	–3.34
17.1	31.0	27.5	20.0	4.5	0.0898	–3.16
13.5	24.4	37.2	20.3	4.6	0.2027	–2.81
9.7	17.8	47.2	20.7	4.6	0.4940	–2.42
37.1	38.9	0.0	19.4	4.3	0.0223	–3.76
27.1	40.2	9.0	19.3	4.4	0.0391	–3.52
16.9	40.5	18.8	19.5	4.3	0.0271	–3.68
5.7	40.5	30.2	19.3	4.2	0.0378	–3.54
18.8	35.9	31.0	9.8	4.5	0.1405	–2.97
18.8	31.3	30.2	15.3	4.4	0.1336	–2.99
19.1	26.6	29.8	20.0	4.6	0.1356	–2.98
19.4	20.8	29.5	25.7	4.6	0.1761	–2.87
39.9	36.3	0.0	19.3	4.4	0.0355	–3.56
35.6	33.1	7.1	19.9	4.4	0.1561	–2.92
31.1	28.4	15.4	20.4	4.7	0.1763	–2.87
26.3	23.5	24.7	20.8	4.7	0.2896	–2.65
26.8	49.3	0.0	19.3	4.4	0.0154	–3.94
23.8	43.4	8.4	20.0	4.4	0.0223	–3.78

Fig. 1. Effect of MnO content on the sulfide capacity of the slags at (%CaO)/(%SiO₂) = 0.5 and 1.1, and at 40 mass% SiO₂.

Table 1. Mass flow of each gas and calculated oxygen and sulfur partial pressures.

Mass flow of gas phases (ml/min)					Gas potential (atm)	
CO	CO ₂	SO ₂	Ar	Total	P_{O_2}	P_{S_2}
125	160	15	100	400	2.80×10^{-7}	4.71×10^{-3}

ternary system at low MnO content.

Figure 2 shows the relationship between the sulfide capacity of the CaO–SiO₂–MnO–Al₂O₃–MgO slags at 1873 K and the mass ratio of (MnO+CaO+MgO)/(SiO₂+Al₂O₃), including the reference data from Taniguchi *et al.*²⁾ at 1673 and 1773 K. The sulfide capacity of the CaO–SiO₂–MnO ternary slag at 1873 K is also compared.⁶⁾ Even though the simple Vee ratio has been widely used to evaluate the basicity of slags, the modified Vee ratio shows a good composition dependency of the sulfide capacity in the CaO–SiO₂–MnO ternary and the CaO–SiO₂–MnO–Al₂O₃–MgO quinary slags. Comparing both experimental data, the sulfide capacity of the low-silica (3 to 11 mass%) slag systems is similar to that of the relatively high-silica (18 to 49 mass%) slag systems, even though the experimental temperature of the former is about 100 to 200 K lower than that of the latter. This is in good correspondence to the sulfide capacity difference in between calcium silicates and calcium aluminates.^{6,32–34)}

3.2. Effect of MnO Activity on Sulfide Capacity of CaO–SiO₂–MnO–Al₂O₃–5%MgO Slags

The sulfide capacity of the CaO–SiO₂–MnO–Al₂O₃–5 mass% MgO slags at 1873 K is plotted in **Fig. 3** against the activity of MnO on a logarithmic scale. Based on a def-

Fig. 2. Relationship between the $(\% \text{MnO} + \% \text{CaO} + \% \text{MgO}) / (\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3)$ ratio and the sulfide capacity of slags at 1873 K.

Fig. 3. Relationship between the activity of MnO and the sulfide capacity of slags at 1873 K.

inition of sulfide capacity, Eq. (2),³²⁾ it is expected to be proportional to the activity of O²⁻ ion in a logarithmic scale as indicated in Eq. (3) assuming that the activity coefficient of S²⁻ ion is not significantly affected by slag composition.

$$\frac{1}{2} \text{S}_2(\text{g}) + (\text{O}^{2-}) = (\text{S}^{2-}) + \frac{1}{2} \text{O}_2(\text{g}) \quad \text{..... (1)}$$

$$C_{\text{S}^{2-}} \equiv \frac{K_{(1)} \cdot a_{\text{O}^{2-}}}{f_{\text{S}^{2-}}} = (\text{mass}\% \text{S}) \cdot \left(\frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right)^{0.5} \quad \text{..... (2)}$$

$$\log C_{\text{S}^{2-}} = \log a_{\text{O}^{2-}} - \log f_{\text{S}^{2-}} + \log K_{(1)} \quad \text{..... (3)}$$

where $K_{(1)}$ is the equilibrium constant of Eq. (1), $a_{\text{O}^{2-}}$ is the activity of O²⁻ ion, and $f_{\text{S}^{2-}}$ is the Henrian activity coefficient of S²⁻ ion in the slag. However, due to thermodynamic restriction, the activity of basic oxide is assumed to be proportional to that of O²⁻ ion based on Eqs. (4) and (5).

$$(\text{MnO}) = (\text{Mn}^{2+}) + (\text{O}^{2-}) \quad \text{..... (4)}$$

$$\log a_{\text{MnO}} = \log a_{\text{O}^{2-}} + \log a_{\text{Mn}^{2+}} - \log K_{(4)} \quad \text{..... (5)}$$

By combining Eqs. (3) and (5), the following relationship can be deduced.

$$\log C_{\text{S}^{2-}} = \log a_{\text{MnO}} - \log a_{\text{Mn}^{2+}} - \log f_{\text{S}^{2-}} + C \quad \text{..... (6)}$$

where C may be assumed less sensitive to slag composition. As shown in Fig. 3, there is a linear correlation between $\log C_{\text{S}^{2-}}$ and $\log a_{\text{MnO}}$ with the slope of about 0.84 (obtained from a linear regression analysis), which is relatively close to the theoretical value of unity within experimental scatters. This means that an increasing rate of $a_{\text{Mn}^{2+}}$ would be balanced with a decreasing rate of $f_{\text{S}^{2-}}$ as the activity of MnO increases.

3.3. Effect of Al₂O₃/SiO₂ Substitution on Sulfide Capacity of 20%CaO–30%MnO–5%MgO–SiO₂–Al₂O₃ Slags

Sulfide capacity does not change by the substitution of alumina for silica at a given Al₂O₃+SiO₂ (=45 mass%) condition as shown in **Fig. 4**. Here, the contents of MnO and CaO were fixed at 30 and 20 mass%, respectively. This is in good agreement with the result of Nzotta *et al.*¹³⁾ for the CaO–MnO–SiO₂–Al₂O₃ ($X_{\text{CaO}} = 0.13$) system. Because the

Fig. 4. Effect of the $(\% \text{Al}_2\text{O}_3) / (\% \text{Al}_2\text{O}_3 + \% \text{SiO}_2)$ ratio on the sulfide capacity of the slags at 1873 K.

effect of sulfide stability on capacity must be independently investigated, we incorporated the activity coefficient of MS ($M=Ca, Mn$) calculated from Eq. (8) into the thermodynamic assessment as follows.^{3,7)}

$$MO(l) + \frac{1}{2} S_2(g) = MS(l) + \frac{1}{2} O_2(g),$$

$$\Delta G_{(7)}^{\circ} = 66\,300\text{ J/mol (for Ca)}, \quad 83\,800\text{ J/mol (for Mn)}$$

$$\dots\dots\dots (7)$$

$$\log \gamma_{MS} = -\frac{\Delta G_{(7)}^{\circ}}{2.303RT} + \log a_{MO} - \frac{1}{2} \log \left(\frac{p_{O_2}}{p_{S_2}} \right) - \log X_{MS}$$

$$\dots\dots\dots (8)$$

where γ_{MS} and X_{MS} are the activity coefficient and the mole fraction of MS in molten slag, a_{MO} is the activity of MO, and p_i is the partial pressure of gaseous component i .

Figure 5 shows the activity of basic oxides such as CaO and MnO, and the activity coefficient of CaS and MnS as a function of $Al_2O_3/(Al_2O_3+SiO_2)=A/(A+S)$ ratio, assuming that the sulfur is stabilized by totally Ca^{2+} or totally Mn^{2+} ions as an extreme condition at this composition range. However, the more detailed discussion will be given in the following section. The activity of basic oxides ($\log a_{CaO}$, $\log a_{MnO}$) and the activity coefficient of sulfides ($\log \gamma_{CaS}$, $\log \gamma_{MnS}$) both increase with increasing $A/(A+S)$ ratio. It is unambiguous that the activity of basic oxides increases by decreasing the amount of SiO_2 . Furthermore, the recent investigation of Lee *et al.*^{35,36)} in regard of phase equilibria

Fig. 5. The activity of basic oxides and the activity coefficient of sulfides against the $(\%Al_2O_3)/(\%Al_2O_3+\%SiO_2)$ ratio (a_{MO} ; calculated using the FactSageTM6.2 program).

of the $MnO-MnS-SiO_2-Al_2O_3$ and the $CaO-CaS-SiO_2-Al_2O_3$ systems, wherein the solubility of MnS or CaS decreased by alumina addition at a given MnO/SiO_2 or CaO/SiO_2 ratio, indicates that the activity coefficient of MnS or CaS increased with increasing alumina content. This is in good agreement to the present thermodynamic assessment. Consequently, assuming that the basicity and the stability of sulfide ions in slags are proportional to the activity of basic oxides and the activity coefficient of sulfides, respectively, a constant sulfide capacity during $Al_2O_3 \leftrightarrow SiO_2$ substitution (Fig. 4) originates from the increase in both $a_{O^{2-}}$ and $f_{S^{2-}}$ in a similar degree by increasing the $A/(A+S)$ ratio at a fixed temperature.

3.4. Iso-Sulfide Capacity of $CaO-SiO_2-MnO-20\%Al_2O_3-5\%MgO$ Slags

The iso-sulfide capacity of the $CaO-SiO_2-MnO-20\text{ mass}\%Al_2O_3-5\text{ mass}\%MgO$ slags at 1873 K is shown in **Fig. 6**. The phase diagram of the system is predicted using the FactSageTM6.2 program.^{16,17)} The capacity contours seem to rotate clock-wisely from the MnO-free quaternary side to the MnO-rich corner, which is very similar tendency to that of the $CaO-SiO_2-MnO$ ternary slag system.^{6,7)} Thus, the sulfide capacity increases by increasing the MnO/CaO ratio at a fixed silica content which is greater than about 35 mass%, whereas it decreases by increasing the MnO/CaO ratio at silica content lower than about 35 mass%. According to the authors' previous work,⁶⁾ the CaO which has more ionic bond character, *i.e.* 79% based on the Pauling's equation (Eq. (9)), dominantly contributes to the depolymerization of silicates than the MnO of which ionic bond character is 63% does.^{37,38)}

$$i \text{ (amount of ionic bond character)} = 1 - e^{-\frac{1}{4}(x_A - x_B)^2} \dots\dots (9)$$

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, 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. 1 and 6. In thermodynamic analysis using the modified quasichemical

Fig. 6. Iso-sulfide capacity contours in the $CaO-SiO_2-MnO-20\%Al_2O_3-5\%MgO$ slag at 1873 K.

Fig. 7. Oxygen proportions in the (a) CaO–MnO–50%SiO₂–5%MgO–20%Al₂O₃ slag and (b) CaO–MnO–20%SiO₂–5%MgO–20%Al₂O₃ slag at 1873 K (calculated using the FactSage™6.2 program).

model (MQM),⁷⁾ the relative fraction of non-bridging oxygen in the silica-rich calcium silicates was greater than that in the silica-rich manganese silicate melts, resulting in the higher concentration of free oxygen in manganese silicate melts than that in calcium silicate melts, which is also shown in Fig. 7(a).

However, in the relatively low silica region, *viz.* less than about 35 mass% SiO₂, the amount of Ca²⁺ cations balancing with non-bridging oxygen is reduced and thus Ca²⁺ and Mn²⁺ cations competitively react with the S²⁻ ions, resulting in the dominant contribution of Ca²⁺ ↔ S²⁻ attraction which is greater than Mn²⁺ ↔ S²⁻ attraction in terms of the stability of each sulfide which was determined from the Gibbs free energy of the formation of CaS ($\Delta G_{f, \text{CaS}}^\circ = 66.3$ kJ/mol) and MnS ($\Delta G_{f, \text{MnS}}^\circ = 83.8$ kJ/mol) at 1873 K.⁷⁾ This indicates that the contribution of Ca²⁺ to the stabilization of S²⁻ ions would be larger than that of Mn²⁺ in the relatively low silica region. Furthermore, in thermodynamic analysis which is similar to that mentioned above, the relative fraction of free oxygen slightly decreases with increasing MnO/CaO ratio at low silica region, while that of bridging oxygen increases with MnO content as shown in Fig. 7(b).

By combining the present results and that of previous studies,^{6,7)} in the high silica melts (> 30(±5) mass% SiO₂), the sulfide capacity increases with increasing MnO/CaO ratio, which originates from the fact that the content of O²⁻ ions (~ basicity) increases with increasing MnO/CaO ratio

Fig. 8. Schematics of the effect of slag composition on the dissolution mechanism of sulfur in the CaO–MnO–SiO₂–(Al₂O₃–MgO) slags.

and that the stability of S²⁻ ions increases because large amounts of Ca²⁺ ions should be balanced with O⁻ ions, resulting in the stabilization of S²⁻ ions by interacting with Mn²⁺ ions. However, in the low silica melts (< 30(±5) mass% SiO₂), the sulfide capacity decreases with increasing MnO/CaO ratio, which originates from the fact that the content of O²⁻ ions does not change with increasing MnO/CaO ratio and that the stability of S²⁻ ions decreases because the amounts of Ca²⁺ ions balancing with O⁻ ions are very small, almost of S²⁻ ions are stabilized by interacting with free Ca²⁺ ions, of which amount decreases with increasing MnO/CaO ratio. Consequently, the sulfide capacity results in the clockwise rotating iso-capacity contours in the CaO–SiO₂–MnO–(Al₂O₃–MgO) system at 1873 K. This mechanism is schematically described in Fig. 8.

5. Conclusions

The sulfide capacities of the CaO–SiO₂–MnO–Al₂O₃–5 mass% MgO slags were measured at 1873 K over a wide composition range using a gas–slag equilibration method. The effects of basicity and the activity coefficient of sulfide on the sulfide capacity of molten slag were also investigated based on the structural view of silicate melts. The specific findings of the present study are summarized below;

(1) In the multicomponent silicate melts containing high MnO (up to about 50 mass%), the sulfide capacity mainly increased with increasing MnO content. The capacity and modified Vee ratio, *i.e.* (CaO+MnO+MgO)/(SiO₂+Al₂O₃), showed a good linear relationship in the CaO–SiO₂–MnO–Al₂O₃–MgO slags.

(2) Assuming that the basicity and the stability of sulfide ions in the slag are proportional to the activity of basic oxides and the activity coefficient of sulfides, the composition dependency of the sulfide capacity is well described by changes in the a_{MO} to γ_{MS} (M=Ca, Mn) ratio.

(3) The silica ↔ alumina substitution did not affect the sulfide capacity of the slags not only because of an increase in the activity of basic oxides but also because of a decrease in the stability of sulfides as Al₂O₃/SiO₂ ratio increases.

(4) In the high silica melts (> 30(±5) mass% SiO₂), the sulfide capacity increased with increasing MnO/CaO ratio, whereas it decreased by increasing the MnO/CaO ratio in the low silica melts (< 30(±5) mass% SiO₂). This tendency

of sulfide capacity resulted in the clock-wisely rotating iso-sulfide capacity in the CaO–SiO₂–MnO(–Al₂O₃–MgO) system at 1873 K. The dissolution mechanism of sulfur in the MnO-containing calcium silicate melts can be explained not only by the difference in the structural role of Ca²⁺ and Mn²⁺ ions but also by the changes in the content of O²⁻ ions according to the silica content.

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REFERENCES

- 1) J. H. Park and D. J. Min: *Mater. Trans.*, **47** (2006), 2038.
- 2) Y. Taniguchi, N. Sano and S. Seetharaman: *ISIJ Int.*, **49** (2009), 156.
- 3) Y. B. Kang and A. D. Pelton: *Metall. Mater. Trans. B*, **40B** (2009), 979.
- 4) M. K. Cho, J. Cheng, J. H. Park and D. J. Min: *ISIJ Int.*, **50** (2010), 215.
- 5) T. Tanaka, Y. Ogiso, M. Ueda and J. Lee: *ISIJ Int.*, **50** (2010), 1071.
- 6) G. H. Park, Y. B. Kang and J. H. Park: *ISIJ Int.*, **51** (2011), 1375.
- 7) Y. B. Kang and J. H. Park: *Metall. Mater. Trans. B*, **42B** (2011), 1211.
- 8) Y. Sutou, N. Kamiya, R. Umino, I. Ohnuma and K. Ishida: *ISIJ Int.*, **50** (2010), 893.
- 9) K. H. So, J. S. Kim, Y. S. Chun, K. T. Park, Y. K. Lee and C. S. Lee: *ISIJ Int.*, **49** (2009), 1952.
- 10) K. T. Park, K. G. Jin, S. H. Han, S. W. Whang, K. Choi and C. S. Lee: *Mater. Sci. Eng. A*, **527** (2010), 3651.
- 11) J. E. Jin and Y. K. Lee: *Mater. Sci. Eng. A*, **527** (2009), 157.
- 12) J. K. Kim, L. Chen, H. S. Kim, S. K. Kim, G. S. Kim, Y. Estrin and B. C. De Cooman: *Steel Res. Int.*, **80** (2009), 493.
- 13) M. M. Nzotta, D. Sichen and S. Seetharaman: *ISIJ Int.*, **38** (1998), 1170.
- 14) M. M. Nzotta: *High Temp. Mater. Process.*, **16** (1997), 261.
- 15) R. Nilsson, M. M. Nzotta, Du Sichen and S. Seetharaman: Proc. of 5th Int. Conf. on Molten Slags, Fluxes and Salts, ISS, Warrendale, PA, (1996), 177.
- 16) www.factsage.com (accessed September 2011).
- 17) C. W. Bale, E. Belisle, P. Chartrand, S. A. Decterov, G. Eriksson, K. Hack, I. H. Jung, Y. B. Kang, J. Melancon, A. D. Pelton, C. Robelin and S. Petersen: *Calphad*, **33** (2009), 295.
- 18) J. H. Park: *J. Am. Ceram. Soc.*, **89** (2006), 608.
- 19) J. H. Park and Y. B. Kang: *Metall. Mater. Trans. B*, **37B** (2006), 791.
- 20) J. H. Park: *Calphad*, **31** (2007), 149.
- 21) J. H. Park: *Calphad*, **31** (2007), 428.
- 22) J. H. Park, S. B. Lee and H. R. Gaye: *Metall. Mater. Trans. B*, **39B** (2008), 853.
- 23) M. O. Suk and J. H. Park: *J. Am. Ceram. Soc.*, **92** (2009), 717.
- 24) J. H. Park, I. H. Jung and S. B. Lee: *Met. Mater. Int.*, **15** (2009), 677.
- 25) J. H. Park: *Met. Mater. Int.*, **16** (2010), 987.
- 26) J. H. Park, G. H. Park and Y. E. Lee: *ISIJ Int.*, **50** (2010), 1078.
- 27) J. H. Park and H. Todoroki: *ISIJ Int.*, **50** (2010), 1333.
- 28) J. H. Park, J. G. Park, D. J. Min, Y. E. Lee and Y. B. Kang: *J. Eur. Ceram. Soc.*, **30** (2010), 3181.
- 29) J. H. Park, M. O. Suk, I. H. Jung, M. Guo and B. Blanpain: *Steel Res. Int.*, **81** (2010), 860.
- 30) K. Y. Ko and J. H. Park: *Metall. Mater. Trans. B*, **42B** (2011), 1224.
- 31) J. H. Park: *Calphad*, **35** (2011), 455.
- 32) C. J. B. Fincham and F. D. Richardson: *J. Iron Steel Inst.*, **178** (1954), 4.
- 33) K. P. Abraham, M. W. Davies and F. D. Richardson: *J. Iron Steel Inst.*, **196** (1960), 309.
- 34) R. A. Sharma and F. D. Richardson: *Trans. Metall. Soc. AIME*, **223** (1965), 1586.
- 35) D. H. Woo and H. G. Lee: *J. Am. Ceram. Soc.*, **93** (2010), 2098.
- 36) Y. B. Kang and H. G. Lee: unpublished work, private communication, (2011).
- 37) L. Pauling: *The Nature of Chemical Bond and the Structure of Molecules and Crystals*, 3rd Ed., Cornell University Press, NY, (1960), 97.
- 38) Y. Waseda and J. M. Toguri: *The Structure and Properties of Oxide Melts*, World Scientific, Singapore, (1998), 1.