Influence of Basicity and FeO Content on Viscosity of Blast Furnace Type Slags Containing FeO

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(Received on October 2, 2003; accepted in final form on April 22, 2004)

The viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$ slags were measured under conditions of $C/S=1.15\text{--}1.6$, $10\text{--}13\text{ mass\% Al}_2\text{O}_3$, $5\text{--}10\text{ mass\% MgO}$ and $0\text{--}20\text{ mass\% FeO}$. Slag viscosity decreased with increasing FeO content at a fixed basicity (CaO/SiO_2) of slag. Slag viscosity at low FeO ($<7.5\text{ mass\% FeO}$) exhibited a minimum value by increasing MgO content in slag. Viscosity decreased with increasing slag basicity up to 1.3 while it increased as slag basicity increased from 1.3 to 1.5. It was proposed that the driving force for the decrease of slag viscosity would be an increase in depolymerization of silicate network at $C/S \leq 1.3$, while the viscous behavior at $C/S > 1.3$ would be increased with increasing the chemical potential of primary solid phase *e.g.* dicalcium silicate. A thermodynamic approach for the activity of primary solid phase in molten slags resulted in a reasonable relationship between viscosity and slag components. Therefore, it was confirmed that slag viscosity in basic slags ($C/S > 1.3$) could be estimated by the chemical potential of dicalcium silicate.

KEY WORDS: viscosity; basicity; bosh slag; blast furnace; slag structure.

1. Introduction

Viscous behavior of blast furnace (BF) slags plays an important role to affect the operation efficiency since the flow pattern of molten slags has a significant influence on gas permeability, heat transfer, and the reduction of SiO_2 and FeO. Since the reduction of iron ores and the formation of slags with coke/coal ash proceed in the BF, basicity (CaO/SiO_2) and FeO content in slags continuously change from the composition of initial sintered ore. Because the slags do not fully assimilate with ash in the bosh region of the blast furnace, they exhibit relatively high CaO/SiO_2 (C/S) ratios of about $C/S=1.4\text{--}1.6$ and $5\text{--}20\text{ mass\% FeO}$,^{1,2)} which is compared with $C/S \approx 1.2$ and $\text{FeO} \leq 0.2\text{ mass\%}$ in tapped blast furnace slags.³⁾ A relatively high basicity of slag in bosh region is one of the main causes of slag formation problems.⁴⁾

Although the viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{(-MgO)}$ slags have been measured by several researchers,⁵⁻⁷⁾ the range of basicity in these studies was limited to approximately $C/S \approx 0.6\text{--}1.3$ in view of tapped slag composition. Recently, the viscosities of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$ slags with $C/S=1.2\text{--}1.5$ were measured by Sugiyama.²⁾ However, the viscosities of slags containing FeO were measured only at $\text{CaO/SiO}_2=1.2$, and these results were applied to other basicity regions by extrapolation.

Therefore, in the present study, the viscosities of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$ slags were measured to clarify the

viscous behavior of slag in BF under conditions of $C/S=1.15\text{--}1.6$, $10\text{--}13\text{ mass\% Al}_2\text{O}_3$, $5\text{--}10\text{ mass\% MgO}$ and $0\text{--}20\text{ mass\% FeO}$ in terms of considering the reduction of iron ore. In addition, the thermodynamic approach based on experimental results was carried out in order to obtain the relationship between viscosity and slag components.

2. Experimental

2.1. Preparation of Materials

All slag samples were prepared using reagent-grade chemicals. In order to prepare the pre-melted slag, 100 g of mixed powder comprising $\text{CaO-SiO}_2\text{-}10\text{ mass\% Al}_2\text{O}_3\text{-}5\text{ mass\% MgO}$ ($\text{CaO/SiO}_2=1.2$), was pre-melted in a graphite crucible in an Ar (0.2 L/min) atmosphere at 1773 K. Moisture and oxygen in Ar gas were removed by passing the gas through a CaSO_4 , silica gel and a column of magnesium turnings heated at 753 K. The temperature was controlled within $\pm 2\text{ K}$ using a Pt-10 mass%Rh/Pt-13 mass%Rh thermocouple and a proportional integral differential controller. After homogenization, the slag melt was quenched and was then crushed for later experiments.

2.2. Apparatus and Procedure

The rotating cylindrical method was employed for viscosity measurement. The experimental apparatus is shown in Fig. 1. A Brookfield digital viscometer (model LVDV-II+, Middleboro, MA), with a full-scale torque of $6.737 \times 10^{-5}\text{ N}\cdot\text{m}$, was used in the present study. The viscometer

Fig. 1. Experimental apparatus for the measurement of slag viscosity.

head was connected to the working spindle by a molybdenum wire (350 mm length, 1.5 mm diameter). The crucible used in the experiments was made of Pt–10mass%Rh, and the spindle was made of pure iron in order to maintain an Fe/FeO equilibrium state. The viscometer was calibrated at room temperature against Brookfield standard oils of 0.485, 0.96, 4.85, and 9.75 dPa·s.

A metallic sealing flange was employed to fill the gap between the molybdenum wire and the mullite reaction tube, and Ar gas (0.35 L/min) was flown into the reaction chamber to prevent the oxidation of the iron spindle and the suspending molybdenum wire.

115 to 120 g of slag samples for each measurement were prepared by adding proper amount of CaO, SiO₂, Al₂O₃, MgO, and FeO powders to the pre-melted slag in order to adjust the slag composition listed in **Table 1**.

The crucible containing slag sample was then placed into the reaction chamber in an Ar (0.35 L/min) atmosphere at 1 723 K. The slag sample was molten for more than 3 h and

Table 1. Measured results for the viscosity of the CaO–SiO₂–Al₂O₃–MgO(–FeO) slags.

Sample Number	C/S	Al ₂ O ₃	MgO	FeO	Viscosity(dPa.s)		
					1723K	1698K	1673K
1	1.6	10	5	20	2.2	2.9	5.1
2	1.6	10	7	20	2.6	3.1	3.7
3	1.6	10	10	20	2.6	3.0	
4	1.6	10	5	10	8.4	14.1	20.3
5	1.6	10	7	10	7.9	8.0	9.5
6	1.6	10	10	10	3.6	4.3	
7	1.5	10	5	5	14.4	18.8	
8	1.5	10	5	7.5	5.7	10.6	
9	1.5	10	5	10	3.2	6.5	10.6
10	1.5	10	7	5	10.4	12.9	
11	1.5	10	7	7.5	4.1	6.2	
12	1.5	10	7	10	2.4	3.8	8.6
13	1.5	10	7	20	0.9	1.0	1.8
14	1.5	10	10	5	20.3		
15	1.5	10	10	7.5	5.4	12.9	
16	1.5	10	10	10	3.4	14.4	
17	1.45	10	3.5	5	6.8	12.2	
18	1.45	10	5	5	4.8	9.0	15.8
19	1.45	10	7	5	9.2	13.7	
20	1.45	10	10	5	6.1		
21	1.4	10	7	5	3.7	5.4	11.0
22	1.3	10	5	5	3.3	3.3	4.2
23	1.3	10	7	5	3.0	3.0	3.7
24	1.3	10	10	5	2.8	4.7	
25	1.3	10	5	0	5.7	6.5	10.4
26	1.2	13	5	0	3.2		
27	1.2	13	7	0	3.0		
28	1.2	13	10	0	2.6		
29	1.15	13	5	0	5.7	6.8	8.5
30	1.15	13	7	0	5.4	6.1	7.6
31	1.15	13	10	0	4.5	5.1	7.6

Fig. 2. Dependence of the viscosity of the CaO-SiO₂-Al₂O₃ slag on temperature.

the rotating spindle was immersed into the slag and located in the middle of the melt. Three different rotating speeds (20, 30, and 60 rpm) were employed in 1723 K to ensure that the viscosity values were independent of the rotating speed and that the melt was homogeneous and behaving in a Newtonian manner at 1723 K. The repeatability of the viscosity values obtained at 1723 K was higher than 99%.

In order to confirm the reproducibility of slag viscosity values, some experiments for the same composition were carried out three times. The results showed that the standard deviation of the measured values at the same temperature increased from 0.5 to 4% with decreasing temperature from 1723 K. Thus, in the present study, the only values measured at 1723 K were evaluated considering the discrepancy.

After viscosity measurements were completed, slag samples were reheated up to 1773 K and then quenched in flushing Ar stream in order to measure slag composition (by using X-ray Fluorescence: Bruker, SRS3400), slag structure (by using FT-IR spectroscopy: JASCO, FT/IR-300 E) and liquidus temperature (by using DTA: SETARAM, CS92-1618). According to the composition analysis of post-measurement slag as well as pre-measurement slag, there was no significant change in the slag compositions (less than 1%).

The viscosity of the CaO-SiO₂-10mass%Al₂O₃ (C/S=0.8) system was preliminarily measured and compared with the values reported in literature.⁸⁾ Figure 2 confirms that the viscosity values measured in the present study are reasonable.

3. Results and Discussion

3.1. Measurement of Slag Viscosity

Experimental results are summarized in Table 1. Viscosity of molten slag linearly increases with decreasing temperature and abruptly increases at a specific temperature, which has been known as crystallization temperature or solidification temperature, *etc.*⁹⁾ This temperature ther-

Fig. 3. Viscosities of CaO-SiO₂-Al₂O₃-MgO-FeO system at C/S=1.6 with varying the content of MgO as a function of temperature.

Fig. 4. Viscosities of CaO-SiO₂-Al₂O₃-MgO-FeO system at C/S=1.5 with varying the content of FeO as a function of temperature.

modynamically coincides with the liquidus temperature at which the activity of primary solid phase approaches unity (It means that a primary solid phase precipitates). The effects of MgO and FeO content on slag viscosities are shown as a function of temperature in Figs. 3 and 4, respectively. In Fig. 3, MgO content does not significantly affect viscosity in the fully liquid region, but has a remarkable influence on crystallization temperature. The crystallization temperature is shifted to higher temperatures with increasing MgO content in slags. These phenomena can be caused by changing the chemical potential of primary solid phase, such as melilite (2CaO·MgO·2SiO₂-2CaO·Al₂O₃·SiO₂) or merwinite (3CaO·MgO·2SiO₂), which can be an initial primary solid phase in the slag compositions investigated. On the

Fig. 5. Viscosities of CaO-SiO₂-Al₂O₃-MgO-FeO system as a function of the content of FeO at 1723 K.

other hand, in Fig. 4, an increase of FeO content results in decreasing the crystallization temperature and slag viscosity at 1723 K. It can be expected from the fact that FeO having lower melting temperature than other oxides causes to increase the coexisting region of solid and liquid.¹⁰⁾

Dependence of slag viscosity on FeO content and slag basicity at 1723 K is shown in Fig. 5. The slag viscosities measured at a basicity of C/S=1.5 and 7 mass% MgO increase from about 2.5 to 10 dPa·s as FeO content decreases from 10 to 5 mass%. The slag viscosity increases with increasing basicity from 1.4 to 1.6 at a fixed MgO and FeO content. As shown in Fig. 5, the typical bosh slags containing FeO content less than 7.5 mass% exhibit relatively high viscosity, because the effect of basicity and MgO on the slag viscosity is believed to be dominant. Therefore, the slag fluidity in BF bosh level could be affected by the reduction rate of iron ore. Toop and Samis reported that in CaO-FeO-SiO₂ melts, FeO does not associate with the silicate groups in the low basicity region (C/S≤1.86) but supplies free Fe²⁺ and O²⁻ ions to the silicate melts and causes the mixing entropy of silicate melt to increase.¹¹⁾ It was also reported that FeO lowers the melting temperature of slags.¹²⁾ Thus, it can be suggested that the effect of FeO on the Gibbs free energy of mixing of molten slag would be more significant than those of other components, resulting in the decrease of melting temperatures and slag viscosities with increasing the FeO content.

In Fig. 6, the viscosities of CaO-SiO₂-Al₂O₃-MgO(-FeO) slags are shown as a function of basicity. Viscosity exhibits a minimum value at about C/S=1.3. In general, an increase in basicity decreases the viscosity of slags, because silicate structure changes from the three dimensional network to discrete anionic groups containing simple chains and/or rings as basic oxides are increased.^{13,14)} This analysis is based on the polymerization degree of silicate network and can be employed to explain the trend of slag viscosity in the composition of C/S≤1.3. On the other hand, the slag viscosities increase with in-

Fig. 6. Viscosities of CaO-SiO₂-Al₂O₃-MgO(-FeO) system as a function of the basicity at 1723 K.

creasing basicity at C/S>1.3, which cannot be explained by the depolymerization of the silicate network. This may be explained by the effect of the chemical potential of primary solid phase, *i.e.* 2CaO·SiO₂, on viscosity because the viscosity isotherms with composition are similar to phase diagrams of alloy and slag system.^{15,16)}

The viscous flow of relatively high basic slags can be understood by the effect of cation-anion interaction on viscosity.¹⁰⁾ This type of interaction is the most prominent at the compositions where stable compounds are formed at lower temperatures.^{10,16,17)} The effect of clustering at specific compositions on the variation of viscosity with composition has been found in the systems such as FeO-SiO₂,¹⁸⁾ PbO-SiO₂,¹⁹⁾ and Na₂O-SiO₂.²⁰⁾ In these systems, a peak in the viscosity is shown at the compound formation compositions at the temperatures higher than the liquidus. In the FeO-SiO₂ system, a local maximum has been observed at the fayalite composition from 1573 to 1673 K. This effect is more outstanding at lower temperatures. Thus, in the present study, the behavior of slag viscosity in the composition of C/S>1.3 at 1723 K can be affected by the cation-anion interaction corresponding to slag composition of solid compound such as dicalcium silicate, melilite, merwinite, *etc.* and can be explained qualitatively by the chemical potential for the formation of solid compound. It will be discussed in Sec. 3.2, later.

Figure 7 shows the effect of MgO and FeO on the slag viscosities measured at 1723 K. The addition of MgO does not affect the slag viscosities obtained at FeO content greater than 7.5 mass%, while a minimum value is observed at about 7 mass% MgO with 5 mass% FeO. Mudersbach *et al.* reported that the viscosity of CaO-SiO₂-Al₂O₃-MgO slags exhibited a minimum value by increasing MgO content at a fixed basicity (C/S=1.1) and Al₂O₃ content.²¹⁾ It is believed that MgO would behave as a network modifier in the composition less than 7 mass%, while MgO contributes to an increase of the slag melting point, resulting in the increase of slag viscosity at higher than 7 mass% of MgO.

Fig. 7. Viscosities of CaO-SiO₂-Al₂O₃-MgO-FeO system as a function of MgO content at 1723 K.

3.2. Relationship between Slag Components and Viscous Behavior of Bosh Slag

The viscosity models in literature have been reviewed and employed for the viscosity calculation of slags being dealt with in the present work.^{2,22-25} Most of the models in literature have been developed based on the fundamental concept related to the network modifier, network former, and amphoteric components. The current model was also formulated on the basis of the depolymerization mechanism of the silicate network, where the slag viscosity continuously decreases with increasing the content of the network modifier (basic oxide).

Figure 8 shows the dependence of slag viscosity on the slag basicity at 1723 and 1773 K. The slag viscosity at 1773 K continuously decreases with increasing basicity up to about 1.2 and a decreasing rate of viscosity decreases at the higher basicity than C/S=1.2. On the other hand, the viscosity at 1723 K exhibits a minimum value at about C/S=1.3. This means that the slag viscosity in a wide range of basicity could not be described by only the depolymerization mechanism.

In order to study this viscous behavior in detail, the investigation using infrared spectra and the measurement of liquidus temperature (T_{LQ}) using DTA were carried out for these samples. Figure 9 exhibits the infrared spectra of the CaO-SiO₂-12mass%Al₂O₃-7mass%MgO(-5mass%FeO) slags as a function of wave number (cm⁻¹) at different C/S ratio. As the C/S ratio increases from 0.9 to 1.45, the IR bands for [SiO₄]-tetrahedra with non-bridging oxygen per silicon (NBO/Si)=1, 2, 3 and 4 (1030, 980, 940 and 850 cm⁻¹ bands, respectively) become prominent.²⁶ And, the relative intensity of the IR bands for [SiO₄]-tetrahedra with NBO/Si=3+4 increases with increasing the C/S ratio, while that of the IR bands for [SiO₄]-tetrahedra with NBO/Si=1+2 decreases with increasing the slag basicity. Also, the center of gravity of the [SiO₄]-tetrahedral bands at about 1170-750 cm⁻¹ shifts from about 980 to 940 cm⁻¹ and an increase in a C/S ratio results in shifting of lower limit IR bands for the [SiO₄]-tetrahedra from 760-730

Fig. 8. Viscosities of CaO-SiO₂-Al₂O₃-MgO(-FeO) system as a function of the basicity at 1773 and 1723 K.

Fig. 9. The infrared spectra of the CaO-SiO₂-12%Al₂O₃-7%MgO(-5%FeO) slags as a function of wave number (cm⁻¹) at different C/S ratio.

cm⁻¹. These results indicate that the degree of polymerization of silicate units continuously decreases with increasing the C/S ratio from 0.9 to 1.45.²⁶ Thus, the slag viscosity should be decreased as the C/S ratio increases. However, the viscosity at 1723 K increases at the higher C/S than about 1.3 in Fig. 8. Of course, because the liquidus temperature of slag is increased by increasing the C/S ratio, the slag phase at 1723 K may become the coexisting phase of solid and liquid, resulting in increasing the viscosity at 1723 K. However, it cannot be concluded that the viscous behavior of slag at C/S>1.3 is resulted from it without considering the melting temperature of slag.

Figure 10 shows the liquidus temperatures of the CaO-SiO₂-12mass%Al₂O₃-7mass%MgO(-5mass%FeO) slags as a function of the slag basicity. In Fig. 10, it can be known that the liquidus temperature is lower than 1723 K and any solid compound does not precipitate at those slag

Fig. 10. The liquidus temperatures of the $\text{CaO-SiO}_2\text{-12\%Al}_2\text{O}_3\text{-7\%MgO(-5\%FeO)}$ slags as a function of the slag basicity.

composition. Also, it is observed in Fig. 10 that the difference between the T_{LQ} and the experimental temperature (1723 K) decreases from about 175 to 35 K with increasing the C/S ratio from 0.9 to 1.5 and is especially below 50 K at above C/S=1.35. Therefore, it indicates that the slag viscosity can be affected by not only the depolymerization mechanism of silicate network but also the other mechanism although a slag behaves as a homogeneous liquid at a fixed temperature.

In general, silicate structure changes from the three dimensional network to discrete anionic groups containing simple chains and/or rings according to an increase in CaO content. If the content of CaO greater than a specific composition increases, the silicate network will be sufficiently dissociated and the melting temperature of slag will be increased. However, it can cause the liquid slag to contract, resulting in increasing the frictional force between the silicate units because the nearest-neighbor distances and coordination numbers in the liquid state at or near the melting temperature are closely similar to those in the solid state^{17,27)}; the increased Ca^{2+} ions can bind the dissociated silicate anions because of the electrical interaction between cation and anion as if the bond between two Ca^{2+} or more and $[\text{SiO}_4]^{4-}$ comprising solid phase is loosened. In Fig. 9, it can be known that the relative intensity of the IR bands for $[\text{SiO}_4]$ -tetrahedra with NBO/Si=3+4 becomes prominent at C/S=1.45 and excess Ca^{2+} ion exists at C/S=1.45 from the peak of Ca-O bonding at about 420 cm^{-1} .²⁶⁾ Therefore, from Figs. 8 to 10, the behavior of viscosity with C/S>1.3 can be affected by the liquid structure similar to the structure of solid formed at lower temperatures although the silicate structure become simpler and smaller. In the present study, it was assumed that the viscosity would be decreased by the depolymerization of silicate network with increasing the C/S ratio at C/S≤1.3, while that of slag at C/S>1.3 would be increased by the liquid structure related to the structure of primary solid phase e.g. dicalcium silicate as the slag basicity increases.

Fig. 11. Dependence of slag viscosity on the activity of $2\text{CaO}\cdot\text{SiO}_2$ in liquid slags at 1723 K.

Fredericci *et al.* concluded that the initial precipitating solid phases were merwinite ($3\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2$), melilite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2\text{-2CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) and dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) in the blast furnace slags of C/S=1.2.²⁸⁾ It was also reported that because the composition of bosh slags in the blast furnace ranges $1.3\leq\text{C/S}\leq 1.5$, it can shift toward the primary field of dicalcium silicate.¹⁾ In addition, a thermodynamic calculation by FACTSageTM 5.2 (thermochemical software) for the present slag system indicates that dicalcium silicate could be a primary solid phase. Therefore, in the present study, it was assumed that the liquid structure in C/S>1.3 could be affected by dicalcium silicate. And, the thermodynamic activity of $2\text{CaO}\cdot\text{SiO}_2$ in molten slags was investigated to estimate the viscosity of relatively basic slags (C/S>1.3) because a thermodynamic activity contains the structural and chemical meanings.

The standard free energy change for the formation of $2\text{CaO}\cdot\text{SiO}_2$ is represented by Eq. (1):

$$\Delta G_1^\circ = -126\,400 - 5.02T \text{ (J/mol)}^{29)} \quad \text{.....(2)}$$

$$K_1 = \frac{a_{2\text{CaO}\cdot\text{SiO}_2}}{a_{\text{CaO}}^2 \cdot a_{\text{SiO}_2}} \quad \text{.....(3)}$$

Equations (1) and (3) indicate that the activity of $2\text{CaO}\cdot\text{SiO}_2$ in molten slags can be enhanced by increasing a_{CaO} in the slags at a fixed temperature. Furthermore, they indicate that the activity of $2\text{CaO}\cdot\text{SiO}_2$ increases with increasing slag basicity (C/S) and can be evaluated based on the activities of CaO and SiO_2 in the slags. The activity of each component was calculated by applying the regular solution model to the present slag system.³⁰⁾ In Fig. 11, the relationship between the slag viscosity and activity of $2\text{CaO}\cdot\text{SiO}_2$ at 1723 K is shown. Most of the calculated activities of $2\text{CaO}\cdot\text{SiO}_2$ based on the activity values of CaO and SiO_2 are less than unity at 1723 K. It means that $2\text{CaO}\cdot\text{SiO}_2$ was not precipitated in present experiments in view of thermodynamic calculation. Although the data are

somewhat scattered in Fig. 11, the slag viscosity increases with increasing the activity of dicalcium silicate in slags. It indicates that the viscosity of relatively basic slags is affected by the chemical potential of primary solid phase, even in homogeneous liquid phase (even though solid compounds are not precipitated). Thus, in the present study, it was assumed that the slag viscosity could be expressed by the ratio of $2\text{CaO} \cdot \text{SiO}_2$ activity to the stability factor affecting the formation of $2\text{CaO} \cdot \text{SiO}_2$ in liquid slags by the following equation:

$$\text{Slag viscosity} \propto \frac{\text{Activity of } 2\text{CaO} \cdot \text{SiO}_2}{\text{Stability factor of } 2\text{CaO} \cdot \text{SiO}_2 \text{ in slag}} \quad (4)$$

In Eq. (4), the stability factor is the factor controlling the formation of $2\text{CaO} \cdot \text{SiO}_2$. If other ions substitute for Ca^{2+} and silicate anion and occupy their sites, the interaction of Ca^{2+} and $[\text{SiO}_4]^{4-}$ will be weakened and its number will be smaller. That is, the competition of Ca^{2+} and $[\text{SiO}_4]^{4-}$ with other ions for the same sites can cause to be unstable formation of the $2\text{CaO} \cdot \text{SiO}_2$. In the present study, this effect was defined as the stability factor of $2\text{CaO} \cdot \text{SiO}_2$.

It is well known that MgO and Al_2O_3 decrease the region of $2\text{CaO} \cdot \text{SiO}_2$ in slag.^{31,32} It indicates that Mg^{2+} and aluminate anions can substitute for Ca^{2+} and silicate anions, respectively. Consequently, MgO and Al_2O_3 deteriorate the stability of $2\text{CaO} \cdot \text{SiO}_2$. Because the bonding energy is higher as the formation enthalpy change negatively increases, it can be confirmed from the formation enthalpy changes per mole of SiO_2 for solid compounds at 1723 K, as follows³³:

$$\Delta H_f(2\text{CaO} \cdot \text{SiO}_2) = -99.7 \text{ (kJ/mol SiO}_2\text{)}$$

$$\Delta H_f(3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2) = -127.0 \text{ (kJ/mol SiO}_2\text{)}$$

$$\Delta H_f(2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2) = -127.7 \text{ (kJ/mol SiO}_2\text{)}$$

$$\Delta H_f(2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2) = -100.1 \text{ (kJ/mol SiO}_2\text{)}$$

Also, it can be assumed that FeO can disturb the encounter of Ca^{2+} with silicate anions because it increases the mixing entropy of slag system. Thus, it can be assumed that the stability factor controlling the formation of $2\text{CaO} \cdot \text{SiO}_2$ in liquid slags comprises the activities of MgO , Al_2O_3 and FeO in slag. That is, Eq. (4) can be expressed by the following equation:

$$\eta \propto \frac{a_{2\text{CaO} \cdot \text{SiO}_2}}{a_{\text{MgO}} \times a_{\text{Al}_2\text{O}_3} \times a_{\text{FeO}}} \quad (5)$$

A variable, F , could be semi-empirically defined as Eq. (6) by using Eq. (5) and fitting with measured viscosity. That is, authors tried to find out the variable showing the best fit with measured viscosities. As the result, the F among the other variables had a best linear correlation with the viscosities measured as shown in Fig. 12. However, Eq. (6) contains the mentioned relationship in Eq. (5) although the second term on the right-hand side of Eq. (6) was deduced during fitting.

$$F = \log \frac{a_{2\text{CaO} \cdot \text{SiO}_2}}{a_{\text{Al}_2\text{O}_3} \times a_{\text{MgO}} \times a_{\text{FeO}}} - \left(\frac{1.6}{C/S} \right)^4 \quad (6)$$

Fig. 12. Viscosities of slags as a function of F at 1698 and 1723 K.

Fig. 13. Viscosities calculated from the present and NSC models as a function of measured data.

where the second term on the right-hand side of Eq. (6) may be understood as the background factor related to the variation of silicate structure with basicity. Thus, the semi-empirical equation for predicting the viscosity of relatively basic slags ($C/S > 1.3$) could be given as Eq. (7) by fitting the relationship between the measured viscosity and F as shown in Fig. 12.

$$\log \eta (\text{dPa} \cdot \text{s}) = -2.7 + 0.55 F \quad (r^2 = 0.8, 1.3 < C/S < 1.6) \quad (7)$$

where Eq. (7) contains the temperature dependence of viscosity because the activity coefficients of each components in Eq. (6) was derived by the regular solution model³⁰ and those contains the temperature dependence.

The estimated viscosities of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$ slags by the present equation and the NSC model² are compared in Fig. 13. The viscosities predicted by the NSC model are in good agreement with the mea-

sured data at $C/S \leq 1.3$ in this study. However, in the relatively basic slags ($C/S > 1.3$), there is significant difference between the calculated and measured values. On the other hand, it is observed that the viscosity at $C/S = 1.7$ in the literature³⁴⁾ can be predicted by the present equation with little variation. Consequently, it was confirmed that the viscosity of relatively basic BF slags ($C/S > 1.3$) could be predicted by employing the thermodynamic concept based on the chemical potential of dicalcium silicates. However, it should need the more studies because the thermodynamic data and the liquidus temperature of the present slag system have been ambiguous, so far.

4. Conclusions

The viscosities of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$ slags were measured under conditions of $C/S = 1.15\text{--}1.6$, 10–13 mass% Al_2O_3 , 5–10 mass% MgO and 5–20 mass% FeO . The viscosity of the BF type slag decreased by increasing the FeO content at a fixed basicity (CaO/SiO_2) of slags. Slag viscosity at low FeO (< 7.5 mass% FeO) exhibited a minimum value by increasing MgO content in slag. The addition of MgO does not affect the viscosity at $\text{FeO} \geq 7.5$ mass%, while a minimum value is observed at about 7 mass% MgO with 5 mass% FeO .

Viscosity decreased with increasing slag basicity up to 1.3 while it increased as slag basicity increased from 1.3 to 1.5. Therefore, it was proposed that, with increasing the slag basicity, the driving force for the decreases of slag viscosity would be an increase in depolymerization of silicate network at $C/S \leq 1.3$, while the driving force for the increase of slag viscosity at $C/S > 1.3$ is an increase in the chemical potential of solid compound such as dicalcium silicate.

The slag viscosities predicted by using the current model are in good agreement with the measured data for the low basicity ($C/S \leq 1.3$), but in highly basic slags ($C/S > 1.3$), the calculated viscosities are significantly different from the measured values. However, in basic slags ($C/S > 1.3$), viscosities were affected by the chemical potential of dicalcium silicate calculated by applying a regular solution model. A thermodynamic approach for the activity of a primary solid phase ($2\text{CaO} \cdot \text{SiO}_2$) in molten slags on viscosity resulted in a reasonable relationship between viscous behavior of basic BF (*i.e.*, bosh) slags and slag components.

Acknowledgment

This work received financial support from POSCO. And one of the authors (LYS) was supported by the Brain Korea 21 Project.

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