Viscous behaviour of CaO-SiO₂-Al₂O₃-MgO-FeO slag

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The viscosities of CaO-SiO₂-Al₂O₃-MgO-FeO slags were measured under conditions of CaO/SiO₂=1.15–1.6, 10–13 percent Al₂O₃, 5–10 percent MgO and 5–20 percent FeO. Slag viscosity decreased with increasing FeO content at a fixed basicity (CaO/SiO₂) of slag. Slag viscosity at low FeO (<7.5 percent 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. Thus, it was proposed that the driving force for the decreases of slag viscosity would be an increase in depolymerization of silicate network at C/S≤1.3, while the viscous behaviour 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 system (C/S>1.3) could be determined by the chemical potential of dicalcium silicate.

Keywords: viscosity, basicity, bosh slag, blast furnace, slag structure, FT-IR

Introduction

Viscous behaviour of blast furnace (BF) slags plays an important role that affects operation efficiency since the flow pattern of molten slags has a significant influence on gas permeability, heat transfer, and the reduction of SiO₂ and FeO. Since the reduction of iron ores and the formation of slags with coke/coal ash proceed in the BF, basicity (CaO/SiO₂) 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/SiO₂ (C/S) ratios of about C/S=1.4–1.6 and 5–20 percent FeO, which is compared with C/S~1.2 and FeO ≤ 0.2 mass% in tapped blast furnace slags. A relatively high basicity of slag in the bosh region is one of the main causes of slag formation problems.

Although the viscosities of CaO-SiO₂-Al₂O₃-MgO slags have been measured by several researchers⁵-⁷, the range of basicity in these studies was limited to approximately C/S~0.6–1.3 in view of tapped slag composition. Recently, the viscosities of the CaO-SiO₂-Al₂O₃-MgO-FeO slags with C/S=1.2–1.5 were measured by Sugiyama.² However, the viscosities of slags containing FeO were measured only at CaO/SiO₂=1.2, and these results were applied to other basicity regions by extrapolation. Therefore, in the present study, the viscosities of CaO-SiO₂-Al₂O₃-MgO-FeO slags were measured to understand the viscous behaviour of slag in BF under conditions of C/S=1.15–1.6, 10–13 percent Al₂O₃, 5–10 percent MgO and 5–20 percent FeO. In addition, the thermodynamic approach based on experimental results was carried out in order to obtain the relationship between viscosity and slag components.

Experimental

The rotating cylindrical method was employed for viscosity measurement. The experimental apparatus is shown in Figure 1. A Brookfield digital viscometer (model LVDV-II+, Middleboro, MA) was used in the present study. The
The crucible used in the experiments was made of Pt-10 percent 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 oxidation of the iron spindle and the suspended molybdenum wire.

All of the slag samples were prepared using reagent-grade chemicals. In order to measure viscosity of slag, 120 g of mixed powder comprising each component was held in Pt-10 percent Rh crucible.

The crucible containing slag sample was placed inside the reaction chamber maintained in an Ar (0.35 L/min) atmosphere at 1723 K. The slag sample was molten for above 3 h. Then, the rotating spindle was immersed into the slag and was located at a middle position in the melt. Three different speeds (20, 30, and 60 rpm) of rotation were employed in 1723 K to ensure that the viscosity values were independent of the rotation speeds and that the melt was homogeneous and behaving in a Newtonian manner at 1723 K. The scatter in the values at 1723 K was less than 1%. In order to confirm the reproducibility of slag viscosity, some experiments for the same composition were carried out three times. The results showed that the deviation between measured values at same the temperature increased from 0.5% to 4% with decreasing temperature from 1723 K. Thus, in the present study, only the values at 1723 K were employed for evaluation considering the discrepancy.

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

**Results and discussion**

**Measurement of slag viscosity**

Dependence of slag viscosity on FeO content and slag basicity at 1723 K is shown in Figure 2. The viscosity of slags at a basicity of C/S=1.5 increases from about 2.5 to 10 dPa•s as FeO content decreases from 10 to 5 percent. The viscosity of slags increases with increasing basicity from 1.4 to 1.6 at a fixed MgO and FeO content. As shown in Figure 2, the typical bosh slags containing FeO content less than 7.5 percent exhibit relatively high viscosity, because the effect of basicity and MgO on the slag viscosity could be dominant. Therefore, the slag fluidity in the 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.8 It was also reported that FeO lowers the melting temperature of slags.9 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 the melting point and slag viscosities with increasing the FeO content.

In Figure 3, the viscosities of CaO-SiO2-Al2O3-MgO(-FeO) slags are shown as a function of the basicity at 1723 K.
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 the alloy and slag system.12

The viscous flow of relatively high basic slags can be understood by the effect of cation-anion interaction on viscosity.13 This type of interaction is the most prominent at the compositions where stable compounds are formed at lower temperatures.13,14 The effect of clustering at specific compositions on the variation of viscosity with composition has been found in the systems such as FeO-SiO₂,15 and Na₂O-SiO₂.16 In these systems, a peak in the viscosity is shown at the compound formation compositions at the temperatures higher than the liquidus. This effect is more pronounced at lower temperatures. Thus, in the present study, the behaviour of slag viscosity in the composition of C/S>1.3 at 1723 K can be affected by solid compounds such as dicalcium silicate, melilite, merwinite, etc. and can be explained qualitatively by the chemical potential for the formation of solid compounds.

Figure 4 shows the effect of MgO and FeO on the viscosity of slags at 1723 K. The addition of MgO does not affect the viscosity of the slags at FeO content greater than 7.5 percent, while a minimum value is observed at about 7 percent MgO with 5 percent 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.17 It could be believed that MgO would behave as a network modifier in the composition less than 7 percent, while MgO contributes to an increase of the slag melting point, resulting in the increase of slag viscosity at higher than 7 percent of MgO.

The relationship between slag components and viscous behaviour

The viscosity models in literature have been reviewed and employed for the viscosity calculation of slags being dealt with in the present work. 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 models were 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 5 shows the dependence of slag viscosity on the slag basicity at 1723 and 1773 K. The viscosity of slag 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 would mean that the slag viscosity in a wide range of basicity couldn’t be described by only the depolymerization mechanisms.

In order to investigate this viscous behaviour in detail, the investigation using infrared spectra and the measurement of liquidus temperature (T_LQ) using DTA were carried out for these samples.

Figure 6 exhibits the infrared spectra of the CaO-SiO₂-Al₂O₃-MgO(-FeO) slags as a function of wave number (cm⁻¹) at different C/S ratios. 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 (1090, 990, 930 and 850 cm⁻¹ bands, respectively) become prominent. 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 centre of gravity of the [SiO₄]-tetrahedral bands at about 1170–750 cm⁻¹ shifts from about 990 to 930 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 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. Thus, the viscosity of slag should be decreased as the C/S ratio increases. However, the viscosity at 1723 K increases at the C/S higher than about 1.3 in...
of course, because the liquidus temperature of slag is increased by the increase in 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 behaviour of slag at C/S>1.3 results from it without an investigation into the melting point of slag.

Figure 7 shows the liquidus temperatures of the CaO-SiO$_2$-12 percent Al$_2$O$_3$-7 percent MgO(-5 percent FeO) slags as a function of the slag basicity. In Figure 7, it can be seen that the liquidus temperature is below 1723 K. Also, it is observed that the difference between the TLQ and the experimental temperature (1723 K) decreases from about 173 to 33 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. This trend at above C/S>1.35 corresponds with the viscous behaviour at C/S>1.3 in Figure 5.

Therefore, although a slag behaves as a homogeneous liquid at a fixed temperature, it can be proposed that the viscosity of slag is affected by not only the depolymerization mechanisms of silicate network but also the melting point of slag from Figures 5, 6 and 7. That is, the effect of depolymerization of silicate melt on viscosity can be stronger than that of the melting point of slag at the temperature higher than the melting point of slag, and vice versa in the case of the small difference between the T and TLQ.

Therefore, in the present study, it was assumed 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 with increasing the C/S ratio, while the viscous behaviour at C/S>1.3 would be increased with increasing the chemical potential of primary solid phase e.g. dicalcium silicate as the slag basicity increases (Figures 3 and 5).

Fredericci et al. concluded that the initial precipitating solid phases were merwinite (3CaO-MgO-SiO$_2$), mellilitile (2CaO-MgO-2SiO$_2$-2CaO+Al$_2$O$_3$+SiO$_2$) and dicalcium silicate (2CaO-SiO$_2$) in the BF slags of C/S=1.2. It was also reported that because the composition of bosh slags is in the BF ranges 1.3 \leq C/S \leq 1.5, it can shift toward the primary field of dicalcium silicate. In addition, a thermodynamic calculation by FACTSage™ 5.1 (thermochemical software) for the present slag system indicates that dicalcium silicate could be a primary solid phase. Therefore, in the present study, the activity of 2CaO•SiO$_2$ in molten slags has been investigated to estimate the viscosity of relatively basic slags (C/S>1.3).

The standard free energy change for the formation of 2CaO•SiO$_2$ is represented by Equation [1]:

$$
\Delta G_i = -30,200 - 1.2T \text{(cal/mol)}^{22}.
$$

Equations [1] and [3] indicate that the activity of 2CaO•SiO$_2$ in molten slags can be enhanced by increasing $a_{\text{CaO}}$ in the slags at a fixed temperature. Also, they indicate that the activity of 2CaO•SiO$_2$ increases with increasing basicity (C/S) of slag and can be deduced by the activities of CaO and SiO$_2$ in the slag. The activity of each component was calculated by applying the regular solution model to the present slag system. In Figure 8, the relationship between the slag viscosity and activity of 2CaO•SiO$_2$ at 1723 K is shown. Most of the calculated activities of 2CaO•SiO$_2$ based on the activity values of CaO and SiO$_2$ are less than unity at 1723 K. Although the data are somewhat scattered, 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 2CaO•SiO$_2$ activity to the factor affecting the solubility of 2CaO•SiO$_2$ in liquid slags by the following equation:
It is well known that MgO and Al₂O₃ substitute for CaO and SiO₂ in 2CaO·SiO₂, respectively, and increase the solubility limit of 2CaO·SiO₂ into slag. Also, as previously mentioned, FeO increases the effect of the Gibbs free energy of mixing molten slag and lowers the melting point of slags. Thus, it can be assumed that the factor affecting the solubility of 2CaO·SiO₂ in liquid slags comprises the activities of MgO, Al₂O₃ and FeO in slag. Equation [4] can be expressed as:

\[ \eta \propto \frac{a_{2\text{CaO} \cdot \text{SiO}_2}}{a_{\text{MgO}} \times a_{\text{Al}_2\text{O}_3} \times a_{\text{FeO}}} \]  

A variable, \( F \), can be defined by Equation [6] and the viscosities measured in the present work show a linear correlation with \( F \) in Figure 9.

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

where the second term on the right-hand side of Equation [6] was deduced during fitting and may be understood as the background factor related to the variation of viscosity with basicity. Thus, the equation for predicting the solubility of relatively basic slags (C/S>1.3) can be given by Equation [7] from the relationship between the measured viscosity and \( F \) as shown in Figure 9.

\[ \log \eta (\text{dPa} \cdot \text{s}) = -2.7 + 0.55F \]  

\( r^2 = 0.8, 1.3 < C/S < 1.6 \)  

The estimated viscosities of the CaO-SiO₂-Al₂O₃-MgO-FeO slags by the present equation and the NSC model are compared in Figure 10. The viscosities predicted by the NSC model are in good agreement with the measured data at C/S<1.3 in this study. However, in the relatively basic slags (C/S>1.3), the calculated viscosities exhibit significant variation from the measured values. On the other hand, it is observed that the viscosity at C/S=1.7 in the literature 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) can be predicted by employing the thermodynamic concept based on the chemical potential of dicalcium silicates.

Conclusions

The viscosities of the CaO-SiO₂-Al₂O₃-MgO-FeO slags were measured under conditions of C/S=1.15–1.6, 10–13 percent Al₂O₃, 5–10 percent MgO and 5–20 percent FeO. The viscosity of the BF type slag decreased by increasing the FeO content at a fixed basicity (CaO/SiO₂) of slags. Slag viscosity at low FeO (<7.5 percent FeO) exhibited a minimum value by increasing MgO content in slag. The addition of MgO does not affect the viscosity at FeO>7.5 percent, while a minimum value is observed at about 7 percent MgO with 5 percent 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<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 compounds such as dicalcium silicate.

The slag viscosities predicted by using the current models are in good agreement with the measured data for the low basicity (C/S<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 (2CaO·SiO₂) in molten slags on viscosity resulted in a reasonable relationship between viscous behaviour of basic BF (i.e., bosh) slags and slag components.
References


