EVALUATION OF VISCOSITY OF MOLTEN SLAGS IN BLAST FURNACE OPERATION

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Synopsis: In order to accumulate the information on the viscosity of molten slags, which have low liquidus temperature, the authors have measured the viscosity of molten SiO₂-CaO-MgO-Al₂O₃ slags and derived a model to evaluate the viscosity of molten slag. The experimental results show that the slag of a high CaO composition with 35 mass% Al₂O₃ has the liquidus temperature below 1673 K and indicates the viscosity lower than 0.6 Pa·s at 1673 K which is one of the candidates to satisfy the fluidity in the blast furnace operation at low temperature.

Key words: viscosity, molten silicate slag, blast furnace, network structure

1. Introduction

Information on various physico-chemical properties of molten slags at wide temperature range is indispensable in a new blast furnace operation, of which reactions are expected to proceed at lower temperature than now in use in order to save the energy consumption. Among various physico-chemical properties of molten slags, the viscosity of molten silicate varies largely with temperature as well as the concentration of SiO₂. In particular, when we try to operate blast furnaces at lower temperature, the viscosity of molten slag increases, which causes various troubles in the operation. Therefore, we should search for adequate slag which has low liquidus temperature and good fluidity, in other words, low viscosity even at low temperature. Iwase proposed that the liquid phase, of which liquidus temperature is under 1673K, exists in CaO-SiO₂-MgO-Al₂O₃ system shown in Fig.1. The information on the viscosity of the slags at the compositions of ACMS1, ACMS2 & ACMS3 in Fig.1 gives us an important guide to find an adequate molten slag for the development of the above new operation of blast furnaces at lower temperature.

The purpose of the present work is to measure the viscosity of molten slags at the compositions of ACMS1, ACMS2 & ACMS3 in Fig.1 and to derive a viscosity model of molten SiO₂-CaO-FeO-MgO-Al₂O₃ slag.


The authors constructed the apparatus by using the rotating cylinder method shown in Fig.2 to measure the viscosity of molten slags. The specimens were prepared from Al₂O₃, CaCO₃, MgO and SiO₂ powders where CaCO₃ powder is burned for 5 hours at 1273 K to make CaO. The mixed powder, which corresponds to a given composition of molten slag, is melted in Fe crucible for 1 hour under Ar gas atmosphere to make molten slag. The procedure to measure the viscosity of molten slag is as follows:

1) The crucible made of Fe, in which the specimen produced above is placed, is set in a given position in the furnace where temperature distribution is uniform. 2) The viscometer (Broockfield Rheometer: model...
L/min (s. t. p.) to a given temperature. 4) After the specimen is held at the temperature for 1 hour, the spindle is immersed in molten slag. 5) The torque values are measured for 4 kinds of rotating velocity of the spindle to determine the viscosity of molten slag.

The composition of molten slags and their experimental results of the viscosity are shown in Table 1 and Fig.3.

As can be seen in Fig.3, since the molten slag at the composition of ACMS2 indicates the viscosity below 0.6 Pa·s at 1673 K, which is almost the same as the viscosity of molten slag now in use in blast furnace at 1773 K, the molten slag of the composition at ACMS2 is one of the candidates to satisfy the fluidity in the blast furnace operation at 1673 K.

3. Viscosity model of molten slag

In the present work, the authors have assumed that the viscosity of molten silicate slag is determined from the frequency of the formation of “cutting-off” or “non-bridging” of network structure in silicates. Those “non-bridging” produce a small “space” adjacent to them. When sheer stress is applied to the liquid, a “fluid unit”, e.g. ion, adjacent to the non-bridging point is dropped into the small “space”. Those movements of the fluid unit into the “space” cause a viscous flow. If there exist small numbers of the space adjacent non-bridging points, or it is hard for the fluid unit to drop into the space, it is recognized that the liquid has high viscosity. A silicate slag has the network structure, which is made from bonding of $\text{SiO}_2^4$ units, and those $\text{SiO}_2^4$ ions are combined each other through bridging oxygen ions $O^\circ$. When some basic oxides such as $\text{CaO}, \text{Na}_2\text{O}$ are added in the silicate slags, the network structure are cut off partially by the cations from those basic oxides to produce some numbers of the free oxygen ion $O^2$ and the non-bridging oxygen ion $O^\circ$. Zhang & Jahanshahi$^3$ have paid attention to the numbers of the free oxygen ion $O^2$ and $N_0$, and the non-bridging oxygen ions $O^\circ$ and $N_0$, which are produced from the addition of the basic oxides. Then, they have derived an excellent viscosity model which consists of a regression equation of $N_0$ and $N_0^\circ$.

On the basis of the above ideas, we have derived the following viscosity model of molten slags. In our model, it is assumed that the silicate slag has lower viscosity as the slag has larger size of the “space” adjacent non-bridging and more numbers of those spaces. We supposed that the space is created from the non-bridging of silicate network which is caused by the addition of the basic oxides. The size of the space $\alpha^\circ$ is dependent upon the cations of the basic oxides added into the silicate solvent. In addition, the
numbers of the space are determined from the number of the free oxygen ion \(O^2-\), \(N_o^2\) and the non-bridging oxygen ion \(O^-, N_o^-\). Consequently, the total volume of the space are \(\alpha (N_o^2 + N_o^-)\). Pure SiO\(_2\) has its own fluidity, which means that there are some non-bridging space in the pure SiO\(_2\) and the volume of those space are assumed to be \(\beta\). The following Arrhenius type equation is applied to express the temperature dependence of viscosity \(\eta\):

\[
\eta = A \exp\left(\frac{E_v}{RT}\right) \quad (1)
\]

We have assumed that the activation energy \(E_v\) decreases as the volume of the spaces increases as follows:

\[
E_v = E' = \frac{E'}{R_\beta + R_{3\text{SiO}}} = \frac{E'}{(\beta')^{1/2}} = \frac{E'}{1 + \{(N_o^- + N_o^2) \cdot \alpha'\}^{1/2}}
\]

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\]

Here, \(A\) and \(E\) can be determined from the viscosity of pure molten SiO\(_2\)\(^{4,9}\), and the following values are obtained:

\[
A = 4.80 \times 10^6, \quad E = 5.21 \times 10^5 \quad (J) \quad (3)
\]

\(N_o^2\) and \(N_o^-\) are evaluated from Gaye's model\(^{10}\) stored in thermodynamic database. The value of \(\alpha\) for various basic oxides are determined from the application of the above equation to various SiO\(_2\)-MO\(_2\) binary systems as follows:

\[
\begin{align*}
\alpha & = 2.0: \text{CaO} \quad \alpha = 3.8: \text{FeO} \\
\alpha & = 1.8: \text{MgO} \quad \alpha = 0.95: \text{AlO}_3
\end{align*}
\]

The above Eq.(2) has been derived on the basis of the following idea:

The activation energy becomes smaller as the distance \(R\) of a space adjacent non-bridging point moving at a given time becomes longer as shown in the first term of the right-hand-side of Eq.(2). Here, the unit step distance of a space moving at unit time interval and the frequency of the step movement are defined as \(r\) and \(n\), respectively. Then, the average moving distance of a space after \(n\) times step movements is \(R = n \cdot r\) on the basis of the random walk theory. In addition, the frequency of the step movement of a space in pure SiO\(_2\) is defined as \(n_p\), and when MO is added in SiO\(_2\), the frequency \(n_{MO}\) is assumed to be expressed as the numbers of free oxygen ion and non-bridging oxygen ion multiplied by a space volume \(\alpha\). Thus, the final term in Eq (2) is derived as shown in Eq.(2). In Eq.(2), \(R_p\) and \(R_{3\text{SiO}}\) are average moving distances of a space in SiO\(_2\) and SiO\(_2\)-MO mixture, respectively. \(n_p\) and \(n_{MO}\) are the frequencies of the step movements in SiO\(_2\) and SiO\(_2\)-MO mixture, respectively.

When the above model is extended to multi-component systems, the activation energy \(E_v\) is assumed to be as follows:

\[
E_v = \frac{E}{1 + (\Sigma \alpha_i \cdot X_{\alpha_i})^{1/2}} \quad (5)
\]

where \(X_{\alpha_i}\) indicates the ratio of the number of cations except Si\(^{4+}\) to those of cations neighboring free oxygen and non-bridging oxygen ions.

The calculated results of the viscosity of molten SiO\(_2\)-CaO-FeO at 1673 K.

![Fig. 4 Viscosity of molten SiO\(_2\)-CaO-FeO at 1673 K.](image)

![Fig. 5 Viscosity of molten SiO\(_2\)-CaO-AlO\(_3\) at 1737 K.](image)
SiO$_2$-CaO-FeO\(^{11}\) and SiO$_2$-CaO-Al$_2$O$_3$\(^{12}\) ternary systems are shown in Figs. 4 and 5. As shown in Fig. 5, in SiO$_2$-CaO-Al$_2$O$_3$ ternary system, the viscosity decreases as increasing Al$_2$O$_3$ content at high concentration of SiO$_2$. On the other hand, the viscosity increases as Al$_2$O$_3$ content increases at high CaO composition region. Thus, the present model shows amphoteric behaviour of Al$_2$O$_3$ in wide composition range.

Figure 6 shows the comparison of the calculated results of the viscosity at the composition ACMS\(_1\), ACMS\(_2\) and ACMS\(_3\) with the present experimental results.

![Fig.6 Temperature dependence of the viscosity of molten SiO$_2$-CaO-MgO-Al$_2$O$_3$ slags at ACMS\(_1\), ACMS\(_2\) and ACMS\(_3\) composition. (Iida model : ref.(13))](image)

### 4. Concluding Remarks
We have measured the viscosity of molten SiO$_2$-CaO-MgO-Al$_2$O$_3$ slags and derived an evaluation model for the viscosity of molten slag to accumulate the information on the viscosity of molten slags, which have low liquidus temperature. The present results shows that the slag, of which composition at a high CaO with 35 mass\% Al$_2$O$_3$ has the liquidus temperature below 1673 K and indicates the viscosity below 0.6 Pa·s at 1673 K.

### 5. References