A Model for Estimating the Viscosity of Molten Aluminosilicate Containing Calcium Fluoride

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A model to estimate the viscosity of aluminosilicate melts including alkali oxides, as derived in our previous study, was extended to molten slag systems containing CaF₂. The bonding state of oxygen in molten silicate and the flow mechanism of melts with a network microstructure were considered for this model. To evaluate the bonding states of oxygen for given chemical compositions, a model proposed by Susa et al. was applied. Their model is easily extended to any multi-component molten slag system without the need to consider thermodynamic parameters. In this work, the above-mentioned viscosity model was applied to evaluate the effect of CaF₂ on the viscosity of molten SiO₂–CaO–CaF₂, SiO₂–CaO–Al₂O₃–CaF₂ and SiO₂–Al₂O₃–CaO–CaF₂–Na₂O–MgO systems.

KEY WORDS: viscosity; silicate melts; structure; aluminosilicate melts; calcium fluoride.

1. Introduction

Demand has been increasing for the treatment of waste from smelting furnaces, in terms of detoxification, as well as the recycling of industrial waste such as asbestos, shredder residue and glass dust containing lead. The essential issue in smelting furnace operations is the determination of adequate conditions for stabilization of the process operation against the wide variety of chemical compositions in industrial wastes. For example, slag containing asbestos is a multi-component aluminosilicate composed of SiO₂, Al₂O₃, CaO, FeO, Fe₂O₃, MgO, K₂O and Na₂O etc. In addition, fluorides like CaF₂ are also occasionally present. To control the process operation we decided to use a specific property and monitored the change in its physical value during the operation. Miyabayashi et al.1) pointed out that the fluidity of molten slag can be a crucial operating factor. The fluidity of molten slag is generally evaluated by measuring its viscosity, but the estimation of viscosity by physical models is also considered useful because of the difficulty in measuring the viscosity of molten slags containing a wide variety of chemical compositions. The authors thus derived a physical model to evaluate the viscosity of molten slags in multi-component systems.2) For this model, the authors focused on the network structure of silicate slags and examined the number of non-bridging oxygens and free oxygen ions to evaluate the viscosity of silicate melts. Viscosity is expected to decrease when the amount of those oxygen ions increase, and this increase severs the network structure.

In a previous paper,3) this viscosity model was modified for application to aluminosilicate melts containing alkali oxides in melting furnaces, i.e., SiO₂–CaO–MgO–FeO–K₂O–Na₂O–Al₂O₃ systems. The bonding state of oxygen in molten silicate and the flow mechanism of melts composed of a network structure were considered for this model. In addition, the method used to evaluate bonding states of oxygen in the molten silicate as proposed by Susa et al. was incorporated into the above-mentioned viscosity model. Their model can be easily extended to any multi-component molten slag system without any consideration of thermodynamic parameters. The number of non-bridging oxygens and free oxygen ions for given chemical compositions may thus be evaluated.

In this work, the above-mentioned viscosity model was extended to evaluate the effect of CaF₂ on the viscosity of molten SiO₂–CaO–CaF₂, SiO₂–CaO–Al₂O₃–CaF₂ and SiO₂–Al₂O₃–CaO–CaF₂–Na₂O–MgO systems.

2. Aluminosilicate Melts Containing Calcium Fluoride

The authors have previously proposed a model for estimating the viscosity of silicate melts by considering the bonding state of oxygen and the flow mechanism of melts with a network structure in molten silicates.2) The model is summarized as follows: silicate slag has a network structure that consists of bonded SiO₄⁻⁴ units (Si tetrahedral ions) as shown in Fig. 1(a). Si tetrahedral ions are connected through bridging oxygens O¹⁰, which are convex oxygens within the structure of Si tetrahedral ions. The non-bridging oxygen ion O⁻ (NBO) and the free oxygen ion O²⁻ (FO) are generated by partially severing the network structure of the tetrahedral Si in SiO₂ upon addition of basic oxides such as CaO in the silicate slag as shown in Fig. 1(b). The NBO and the FO are more mobile than bridging oxygens within the network structure because there are “severance” points near NBO and FO ions. Assuming that movement of
“severance” points causes viscous flow, an increase in the number of non-bridging oxygen ions and free oxygen ions lowers the activation energy \( \eta \) of viscosity. The equation for viscosity \( \eta \) is given by:

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

\[
E_v = \frac{E}{1 + \sum_i \alpha_i \cdot N_{\text{NBO+FO}} + \sum_j \alpha_{i,\text{in}Al} \cdot N_{\text{Al-BO}}} \tag{2}
\]

where Arrhenius’s equation is applied to describe the viscosity in the same way in our previous work \(^{3)} \). \( A \) \((=4.80 \times 10^{-8})\) is a constant, \( E_v \) is the activation energy for viscosity, \( R \) is the gas constant and \( T \) is the temperature. \( E \) \((=5.21 \times 10^4 \text{ (J)})\) is the activation energy for the viscosity of pure \( \text{SiO}_2 \). The activation energy \( E_v \) is a function of the sum of the fractions of NBO and FO \( N_{\text{NBO+FO}} \) as well as the bridging oxygen (BO) fraction in the \( \text{Al} \) tetrahedral unit \( N_{\text{Al-BO}} \). \( \alpha_i \) and \( \alpha_{i,\text{in}Al} \) are parameters that relate to the weakness of the bonding between the cation and the oxygen ion at the “severance” point. \( i \) is a component of the melt excluding \( \text{SiO}_2 \), i.e., \( \text{CaO}, \text{MgO}, \text{FeO}, \text{K}_2\text{O}, \text{Na}_2\text{O} \) and \( \text{Al}_2\text{O}_3 \). \( j \) is the charge-compensating ion of component \( i \) excluding \( \text{Al}_2\text{O}_3 \), i.e., \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Fe}^{2+}, \text{K}^+, \text{Na}^+ \).

To evaluate bonding states of oxygen in the molten silicate the model proposed by Susa et al. \(^{4)} \) was incorporated into the above-mentioned model. Their model is easily extended to any multi-component molten slag system without the need to consider thermodynamic parameters and thus the number of NBO and FO for a given chemical composition may be evaluated. In the model proposed by Susa et al., the ratio of the number of oxygen bonds except for bridging oxygen to Si to the total number of the oxygen bonds in silicate melts is treated as the sum of the fractions of non-bridging oxygen ions and free oxygen ions \( N_{\text{NBO+FO}} \), where non-bridging oxygen ions and free oxygen ions are not distinguished each other. In addition, the ratio of the number of oxygen bonds in the \( \text{Al} \) tetrahedral to the total number of oxygen bonds in the melts is considered to be the content of the bridging oxygen in \( \text{Al} \) tetrahedral \( N_{\text{Al-BO}} \). \(^{5)} \) In the method of Susa et al., \(^{4)} \) F ions do not sever the network structure in aluminosilicate melts. In other words, F ions do not form Si–F and/or Al–F bonds but form O–Ca–F bonds when the network is severed by adding \( \text{CaO} \). In addition, Susa et al. \(^{4)} \) reported that their model supports the structural model proposed by Bills model, \(^{5)} \) where O–Ca–F bonds formed by the addition of \( \text{CaF}_2 \) promoted a “severance” as shown in Fig. 2. As a result, it is likely that formation of O–Ca–F bonds lowers the viscosity.

The effect of the O–Ca–F bond on viscosity from Bills model can be applied to the present viscosity model by introducing a parameter \( \alpha_{\text{CaF}_2} \) and a variable \( N_{\text{CaO}} \) corresponding to the O–Ca–F bond, to the term \( \sum_i \alpha_i \cdot N_{\text{NBO+FO}} \) in Eq. (2). Here, the ratio of the number of O–Ca–F bond to the total number of the oxygen bonds in the system is as \( N_{\text{NCaO}} \). The number of charge-compensating \( \text{Ca}^{2+} \) ions and the number of NBOs and FOs produced by adding \( \text{CaO} \) decreased by an increment determined by the number of O–Ca–F bonds. The composition range where this model is applicable is limited to where the content of \( \text{CaO} \) is larger than the content of \( \text{CaF}_2 \). Therefore, \( N_{\text{CaO}} \) and \( N_{\text{Al-BO}} \) in the multi-component \( a\text{SiO}_2–\sum bi(M_iO_{j+2})–c\text{Al}_2\text{O}_3–d\text{CaO}–e\text{CaF}_2 \) systems \( \{a+\sum bi+c+d+e=1 \text{ (mol)}, d\leq e\} \) \((M_iO_{j+2})=\text{MgO}, \text{FeO}, \text{K}_2\text{O}, \text{Na}_2\text{O}\) are given as follows:

\[
N_{\text{NBO+FO}} = e(2a + \sum bi) + 3c + d) \tag{3}
\]

\[
N_{\text{Al-BO}} = 4c(b/(\sum bi) + d)/(2a + \sum bi + 3c + d) \tag{4}
\]

\[
N_{\text{Al-BO}} = 4c(d–e)/(\sum bi + d)/(2a + \sum bi + 3c + d) \tag{5}
\]

\[
N_{\text{CaO}} = e(b–c(\sum bi))/(2a + \sum bi + 3c + d) \tag{6}
\]

\[
N_{\text{CaF}_2} = (d–e)–c(d–e)/(\sum bi))/((2a + \sum bi + 3c + d) \tag{7}
\]

3. Determination of Parameters

There are two types of parameters, \( \alpha_i \) and \( \alpha_{i,\text{in}Al} \), in Eq. (2). The former parameter relates to the NBO and the FO while the latter is a parameter that relates to the bridging oxygen in tetrahedral \( \text{Al} \).

In this study, \( \alpha_i \) and \( \alpha_{i,\text{in}Al} \) were determined from experimental data of the viscosity in binary silicate systems, \(^{6–15)} \) ternary aluminosilicate systems, \(^{12–17, 18–20)} \) and ternary \( \text{SiO}_2–\text{CaO}–\text{CaF}_2 \) systems. \(^{21–23)} \) The parameters were deter-
mined as follows:

(i) The value of \( a_i \) for each oxide \( i \) was determined by applying the above equation to fit the experimental values of the viscosity for each binary \( \text{SiO}_2-(\text{M}_x\text{O}_y)_i \) system where \( (\text{M}_x\text{O}_y)_i \) is \( \text{CaO}, \text{MgO}, \text{FeO}, \text{K}_2\text{O}, \text{Na}_2\text{O} \) or \( \text{Al}_2\text{O}_3 \).

(ii) Subsequently the \( a_j\text{Al} \) value was assessed for each charge-compensating cation \( j \) by fitting the calculated viscosity with \( a_j \) for the binary system as determined in (i) to the experimental data for each ternary \( \text{SiO}_2-(\text{M}_x\text{O}_y)_i-\text{Al}_2\text{O}_3 \) system where \( (\text{M}_x\text{O}_y)_i \) is \( \text{CaO}, \text{MgO}, \text{FeO}, \text{K}_2\text{O} \) or \( \text{Na}_2\text{O} \).

(iii) Finally, assessment of the \( a_{\text{CaF}_2} \) value was done by fitting the calculated viscosity with parameter \( a_i \) as determined in (i) and (ii) above to the experimental data in ternary \( \text{SiO}_2-\text{CaO}-\text{CaF}_2 \). The assessed parameters are listed in Table 1.

4. Calculated Results of Molten Silicate Viscosity

To investigate the reliability of the viscosity obtained from the above procedures the calculated results were compared with literature values as quoted above to determine the parameters. Figure 3 shows the viscosity of molten \( \text{SiO}_2-\text{CaO}-\text{CaF}_2 \) at 1873 K. In this figure, the iso-viscosity curves obtained from the present model are shown in the area where the mole fraction of \( \text{CaO} \) is more than that of \( \text{CaF}_2 \). Plots of solid lines in this figure are experimental results reported in Refs. 21 and 22). The ratio of \( a_{\text{CaF}_2}/a_{\text{CaO}} \) was 2.7, which showed that the influence of \( \text{CaF}_2 \) on the viscosity of molten \( \text{SiO}_2-\text{CaO}-\text{CaF}_2 \) was 2 or 3 times larger than that of \( \text{CaO} \). This value is similar to that reported by Shiraishi et al.\(^{22} \) for the addition of \( \text{CaF}_2 \) to molten \( \text{SiO}_2-\text{CaO}-\text{CaF}_2 \), which decreased the viscosity 2.2 times more than \( \text{CaO} \) did. The viscosity of the molten quaternary \( \text{SiO}_2-\text{CaO-}\text{Al}_2\text{O}_3-\text{CaF}_2 \) system is shown in Figs. 4 and 5. In these figures, solid lines are iso-viscosities calculated by the present model and plots indicate experimental data\(^{24,25} \) which show that the viscosity decreased as the concentration of \( \text{CaF}_2 \) decreased. The influence of \( \text{CaF}_2 \) on the viscosity is reproduced well although there is a small difference between the experimental values and the calculated values.

The viscosity of the molten quaternary \( \text{SiO}_2-\text{CaO-}\text{Na}_2\text{O-}\text{CaF}_2 \) system is shown in Fig. 6. In this figure, the solid lines are iso-viscosities calculated by the present model and the plots represent experimental data\(^{25} \) which

![Fig. 3. Viscosity (Pa·s) of SiO2–CaO–CaF2 (mass%) at 1873 K.\(^{21,22}\)](image)

![Fig. 4. Viscosity of SiO2–CaO–Al2O3–CaF2.\(^{24}\)](image)

![Fig. 5. Viscosity of molten SiO2–CaO–Al2O3–CaF2.\(^{25}\)](image)

Table 1. Model parameters.

<table>
<thead>
<tr>
<th>((\text{M}_x\text{O}_y)_i)</th>
<th>( a_i )</th>
<th>( j )</th>
<th>( a_j\text{Al} )</th>
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</thead>
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<tr>
<td>( \text{CaO} )</td>
<td>4.00</td>
<td>( \text{Ca}^{2+} )</td>
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<td>( \text{MgO} )</td>
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<td>( \text{Mg}^{2+} )</td>
<td>1.56</td>
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<tr>
<td>( \text{FeO} )</td>
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<td>( \text{Fe}^{3+} )</td>
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<tr>
<td>( \text{K}_2\text{O} )</td>
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<td>( \text{K}^- )</td>
<td>-0.69</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>7.35</td>
<td>( \text{Na}^- )</td>
<td>0.27</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>1.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CaF}_2 )</td>
<td>10.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Shiraishi et al.\(^{22} \) for the addition of \( \text{CaF}_2 \) to molten \( \text{SiO}_2-\text{CaO-}\text{CaF}_2 \), which decreased the viscosity 2.2 times more than \( \text{CaO} \) did. The viscosity of the molten quaternary \( \text{SiO}_2-\text{CaO-}\text{Al}_2\text{O}_3-\text{CaF}_2 \) system is shown in Figs. 4 and 5. In these figures, solid lines are iso-viscosities calculated by the present model and plots indicate experimental data\(^{24,25}\) which show that the viscosity decreased as the concentration of \( \text{CaF}_2 \) decreased. The influence of \( \text{CaF}_2 \) on the viscosity is reproduced well although there is a small difference between the experimental values and the calculated values.

The viscosity of the molten quaternary \( \text{SiO}_2-\text{CaO-}\text{Na}_2\text{O-}\text{CaF}_2 \) system is shown in Fig. 6. In this figure, the solid lines are iso-viscosities calculated by the present model and the plots represent experimental data\(^{25}\) which...
shows that the viscosity decreased as the concentration of CaF$_2$ decreased.

The viscosity of the molten SiO$_2$–Al$_2$O$_3$–CaO–CaF$_2$–Na$_2$O–MgO system is shown in Fig. 7. For our calculation the effect of Li$_2$O was not considered although Li$_2$O was included in the system quoted in Ref. 26. Although the calculated viscosity is less than the experimental data in order of D2, D3, D4 and D12, the calculated results show a similar composition dependence of the viscosity.

5. Iso-viscosity Curves in a Molten SiO$_2$–CaO–CaF$_2$ Ternary System

The composition dependence of iso-viscosity curves in a molten SiO$_2$–CaO–CaF$_2$ ternary system has recently been discussed in detail by Sasaki et al. and Park. They focused on the influence of CaF$_2$ on the structure of the silicate melt.

As CaF$_2$ was assumed to act as a diluent for a given composition ratio of SiO$_2$/CaO in a molten SiO$_2$–CaO–CaF$_2$ ternary system Sasaki et al. presumed that the fraction of complex ion units such as SiO$_4^{4-}$, Si$_2$O$_5^{6-}$, Si$_3$O$_6^{4-}$, Si$_4$O$_7^{2-}$ and SiO$_2$ does not change although their absolute amounts decreased due to the addition of CaF$_2$. The viscosity was thus assumed constant along the straight composition line that connects the fixed composition in the SiO$_2$–CaO binary system and pure CaF$_2$. This is true if the viscosity is simply determined by polymerization of the silicate network structure in the molten SiO$_2$–CaO–CaF$_2$ ternary system. In actuality, the viscosity decreases gradually, although the ab-

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Fig. 6. Viscosity (Pa·s) of the SiO$_2$–CaO–Na$_2$O–CaF$_2$ system (mass%) at 1773 K. The calculations were conducted at (a) 8mass%CaF$_2$ and (b) 17mass%CaF$_2$.

Fig. 7. Viscosity of SiO$_2$–Al$_2$O$_3$–CaO–CaF$_2$–Na$_2$O–MgO.26)
solute amounts of the above complex ions decrease due to the addition of CaF₂. Park et al. also considered the influence of basicity on the amount and the size of the above-mentioned complex ion units and discussed composition dependence of the viscosity for the molten SiO₂–CaO–CaF₂ ternary system in detail. Nakamoto and Tanaka also investigated composition dependence of the viscosity for the molten SiO₂–CaO–CaF₂ ternary system by producing an iso-viscosity map based on literature values. They concluded that the substitution of CaO by CaF₂ results in a decrease of the viscosity in an acid composition area where the SiO₂ concentration is high but shows little increase or is constant in the basic composition area with high CaO content. Mills et al. proposed that iso-viscosity curves are convex from the SiO₂–CaO binary area to the pure CaF₂ area and they are symmetric from the CaO · SiO₂ area composition to the pure CaF₂ area. The composition dependence of the viscosity for the molten SiO₂–CaO–CaF₂ system is currently unclear.

Recently, Hanao and Tanaka et al. reported that the mold flux viscosity of multi-component systems can be evaluated with high accuracy by neural network computations. The composition dependency on the viscosity of the molten SiO₂–CaO–CaF₂ system was evaluated by a neural network computation for this work. The data used for the regression calculation was the same data used for the determination of the CaF₂ parameter in the viscosity model derived in this work. The total number of data points was 175. The temperature range was 1 607–1 925 K and the composition regions were SiO₂ 17–65 mol%, CaO 20–61 mol% and CaF₂ 0–34 mol%. The neural network computation software NEUROSIM/L produced by FUJITSU Ltd. was used to calculate the viscosity in this research. The input paragraph was temperature and concentrations of SiO₂, CaO and CaF₂. The output paragraph was viscosity. The number of interlayers selected was 4. The number of iterations for the procedure was 300 000. Figure 8 shows a comparison between the neural network’s calculated viscosities and experiment values. As shown by this figure they are in good agreement with each other. The error as evaluated by \( \frac{\sum (\eta_{calc} - \eta_{exp})}{\eta_{calc}} \times 100 \) (%) was 22.0%. Iso-viscosity curves of the molten SiO₂–CaO–CaF₂ system as determined by the neural network computation are shown in Fig. 9. The gray area in this figure indicates composition areas where viscosity data were quoted in the above computation. Iso-viscosity curves showed that the viscosity increased with SiO₂ content in the acid composition area where the SiO₂ concentration was high. Substitution of CaO by CaF₂ decreased the viscosity and this tendency weakened in the basic composition area where the CaO concentration was high. This composition dependence was similar to results obtained by Nakamoto and Tanaka. Although the calculated result obtained by the present viscosity model shows the same composition dependence of the viscosity as the results of the neural network computation in the acid composition area, the difference between them increases in the basic composition area. The iso-viscosity curves obtained by Sasaki et al. and Park agreed well with the calculated results from the neural network computation in the basic composition area but the tendency in the acid composition area, with low CaF₂ concentration, was different.

The effect of CaF₂ on the silicate structure as proposed by Bills, to which we referred in this work, is different to the model given by Sasaki et al. In Bills’ model, O–Ca–F is formed by the addition of CaF₂ when the network has been severed by CaO. On the other hand, in the model of Sasaki et al. CaF₂ is assumed to act as a diluent and is not integrated into the silicate network structure to produce a Ca–2F bond. Figure 10 shows both these structural changes for molten SiO₂–CaO–CaF₂ systems obtained by...
replacing CaO with CaF₂. In this figure, one Si–O–Si bond is added to substitute a CaO by a CaF₂. This structural change agreed with some experimental results as the substitution of CaO by CaF₂ increased the degree of polymerization in the SiO₂–CaO–CaF₂ system. This data was obtained from experiments by Luth et al. on the effect of CaO substitution by CaF₂ on the polymerization by using Raman scattering spectroscopy and by Hayashi et al. using X-ray photoelectron spectroscopy.

Consequently, as described above, we assume that the composition dependence of the viscosity for the molten SiO₂–CaO–CaF₂ system may be explained by considering that the silicate network structure changes with the composition of the silicate melt. Essentially the structural change proposed by Bills et al. occurs in the acidic composition region with high SiO₂ content and a different structural change, based on the model by Sasaki et al., occurs in the basic composition region with high CaO content. This composition dependence of the change in the silicate structure enables us to produce the iso-viscosity curve, as obtained by the neural network computation. Experimental evidence which would clearly explain the composition dependence and the influence of CaF₂ on the structure of the SiO₂–CaO–CaF₂ system has, however, not been reported.

From a thermodynamic viewpoint, however, research on activities that support the composition dependency of the influence of CaF₂ on the structure of the SiO₂–CaO–CaF₂ system, as discussed in this work, have been reported by Nagata and Hayashi et al. They studied the activities of CaF₂ at several regions, where two solid compounds and a liquid phase coexist, and found that the activity of CaF₂ was low in the composition area with low CaF₂ and high SiO₂ content, while at lower SiO₂ content the activity of CaF₂ was high. The activity of CaF₂ was based on the models of Bills and Sasaki et al. and it describes structural changes corresponding to iso-viscosity curves. A Neural Network Computation at high SiO₂ and at low SiO₂ was applied to evaluate the bond-}


ting state of oxygen in molten silicate and the flow mechanism of melts with a network microstructure. A model proposed by Susa et al. was applied to evaluate the bonding states of oxygen for given chemical compositions. The composition dependence of the viscosity for molten SiO₂–CaO–CaF₂, SiO₂–CaO–Al₂O₃–CaF₂ and SiO₂–Al₂O₃–CaO–CaF₂–Na₂O–MgO systems was determined from the above model as well as a neural network computation to show the effect of CaF₂ on the viscosity of molten silicates.

**REFERENCES**