A Model for Estimation of Viscosity of Molten Silicate Slag

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A model to evaluate the viscosity of silicate melts is proposed on the basis of the bonding states of oxygen, *i.e.* non-bridging oxygen and free oxygen ions, in the silicate structure, considering the flow mechanism of the melts with the network structure. Gaye's model is applied to evaluate the bonding state of oxygen ions using thermodynamic databases. The present model can reproduce the composition dependence of the viscosities for silicate melts in binary systems with a single model parameter, as well as the composition dependence of the viscosities for ternary systems in a wide composition range.

KEY WORDS: viscosity; silicate melts; network-structure; flow mechanism.

1. Introduction

Many measurements of viscosity for molten slag systems have been conducted since the viscosity of molten slag plays an important role in high temperature industrial processes. Silicate melts indicate an abrupt and complicated viscosity change with composition, so that it is difficult to comprehend the composition dependence of viscosity over wide composition ranges with just the available experimental data. Thus, there are pressing demands for a model to estimate the viscosity of molten silicate over a broad composition range.

Riboud *et al.*[1] and Iida *et al.*[2] proposed equations for predicting the viscosities of mold fluxes and slag by considering the effects on the structure of slag melts of the acidity and basicity of the components. In their equations, they expressed these effects as a linear function of the concentrations of slag constituents. On the other hand, the structures of silicate melts do not always change linearly with the concentrations of the components. Their models cannot be applied over a wide composition range with constant model parameters; sometimes those parameters have to be changed to fit the viscosity in each composition range within a given region. Seetharaman *et al.*[3–5] estimated the viscosities of ionic melts using a model based on the absolute reaction-rate theory for the description of flow processes, utilizing the Gibbs energies of mixing of the silicate melts. Although the use of thermodynamic data allows for the calculation of viscosities applicable to a wide composition range, the features of the silicate melts are not directly considered in their model.

In light of the above, there is a need to develop a model that is based on the features of silicate melts and can evaluate viscosity over a wide composition range. Zhang and Jahanshahi[6,7] derived a viscosity model as a function of bridging oxygen and free oxygen ions to describe the network structure of molten slag. However, the physical significance of each parameter, which is multiplied according to the fractions of bridging oxygen and free oxygen ions in their model, is obscure since the equation was derived empirically from a regression analysis of the activation energy as a function of the fraction of the oxygen ions. Consequently, we have attempted to derive an equation for predicting the viscosity of molten silicate by considering not only the structure of silicate melts but also the flow mechanism, which provides model parameters with definite physical significance.

2. Model

Silicate slag has a network structure, made of the bonding of SiO_4^{4-} units, in which SiO_4^{4-} ions are combined with each other through bridging oxygen O^0, the vertex oxygen in tetrahedron structure of SiO_4^{4-} units. When some basic oxides such as CaO, Na_2O are added in the silicate slag, the network structures are partially cut off by oxygen ions decomposed from basic oxides to produce some numbers of non-bridging oxygen O^- and free oxygen ion O^{2-}. It has been suggested that as the degree of polymerization of the melt diminishes owing to the cutting-off of the network structure, there is a corresponding decrease in the viscosity of the slag.[2,8,9] In these concepts, polymerized anions in the silicate melts have been recognized as flow units. However, it is difficult to consider such a large polymerized anion as a fluid unit because some spaces have to be provided for the polymerized anion to drop into if their movements are assumed. Therefore, we need to discuss the details of a new flow mechanism for silicate melts. In the present work, we have paid attention to "cutting-off" points, which exist adjacent to non-bridging oxygen and the free oxygen ions, in silicate network structures. Oxygen ions adjacent to the "cutting-off" points have large mobility, since bonding in
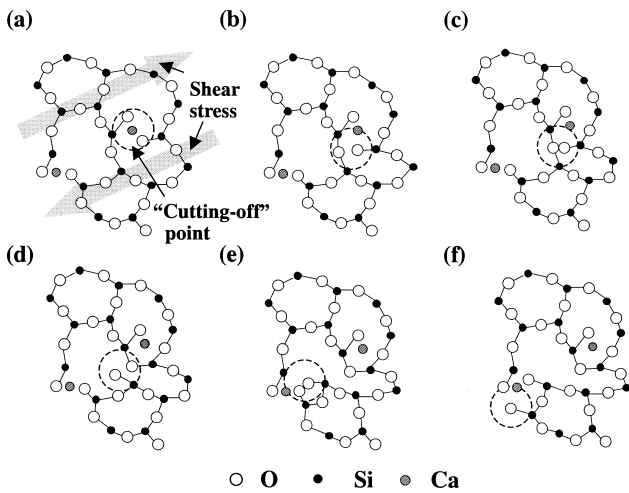
Fig. 1. Flow mechanism for silicate melts.

the network structure at these points are weakened.

When shear stress is applied to the liquid, oxygen ions adjacent to "cutting-off" points move and break the networks around the "cutting-off" points (**Figs. 1**(a)–1(d)) to produce new "cutting-off" points (Figs. 1(d)–1(e)). The "cutting-off" points are transmitted in the network structures by repeating those processes, as shown in Figs. 1(a)–1(f). We assumed that these "cutting-off" point movements cause a viscous flow; therefore, it was considered that the viscosity of molten silicate slag is dependent on the frequency of the occurrence of "cutting-off" of a network structure in silicate slag. This frequency is determined by the number of non-bridging oxygen and the free oxygen ions.

On the basis of the above ideas, we have derived a viscosity model for silicate slag. The following Arrhenius type equation is applied to express the temperature dependence of viscosity η:

$$\eta = A \cdot \exp\left(\frac{E_V}{RT}\right) \quad\quad\quad\quad\quad (1)$$

where A is constant, and E_V is the activation energy for viscosity.

It is assumed that the activation energy is inversely proportional to the distance S, in which the "cutting-off" point moves when shear stress is applied to the liquid.

$$E_V \equiv \frac{E'}{S} \quad\quad\quad\quad\quad (2)$$

As explained above, when shear stress is applied to a silicate melt, some parts of the network structure are assumed to be broken by the transmission of a "cutting-off" point. The number of broken points originated from one "cutting-off" point is defined as n_B, which is related to the weakness of the bonding between cations and oxygen ions at the "cutting-off" point. It also depends upon cations which are decomposed from the basic oxide added into the silicate melt and exist near the "cutting-off" point. The distance, in which a "cutting-off" point moves from one "cutting-off" point position to the next-neighbor "cutting-off" point position, is expressed as s. Thus, the distance that the "cutting-off" point moves from its initial position due to the application of the shear stress is $n_B \cdot s$. When there are a total n

"cutting-off" points in the network structure of a silicate slag, the total moving distance of n "cutting-off" points in the melts due to the shear stress is $n_B \cdot n \cdot s$. However, it is considered that a "cutting-off" point does not transmit in a straight direction, because the molten silicate has a random network structure. We then assumed that each point moves in a random direction along the network structure in the melts. The total moving distance of n "cutting-off" points is $S = (n_B \cdot n)^{1/2} \cdot s$ on the basis of the random walk theory.[10] Further, the number of the networks broken by a "cutting-off" point due to the application of shear stress to the melts n_B is proportional to the mobility of oxygen ions adjacent to the "cutting-off" points, *i.e.* the weakness of the bonding between cations and oxygen ions at the point, which is assumed to be expressed as α', *i.e.* $n_B = k \cdot \alpha'$, where k is a proportional constant. The total moving distance of n "cutting-off" points is expressed in Eq. (3).

$$S = (k \cdot \alpha' \cdot n)^{1/2} \cdot s \quad\quad\quad\quad\quad (3)$$

The "cutting-off" point number n is determined from the number of non-bridging oxygen n_{O^-} and the free oxygen ion $n_{O^{2-}}$. Pure SiO_2 has its own fluidity, which means that the above flow mechanism concept can be applied to pure SiO_2. In other words, the fluid flow of pure SiO_2 is caused by the "cutting-off" points, which do not originate from non-bridging oxygen and the free oxygen ions. The α' and n above are assumed to be expressed as β' and $n_{\beta'}$ in pure SiO_2 melt, respectively. The total moving distances of the "cutting-off" points in the $SiO_2-(M_i)_{ui}O_{vi}$ (M_i is cation, ui and vi are the stoichiometric coefficients of $(M_i)_{ui}O_{vi}$) system is the sum of the moving distance of the "cutting-off" points generated from the non-bridging oxygen and the free oxygen ions $S_\alpha = \{k \cdot \alpha' \cdot (n_{O^-} + n_{O^{2-}})\}^{1/2} \cdot s$ and the moving distance of the "cutting-off" points, which are independent of these oxygens, $S_\beta = (k \cdot \beta' \cdot n_{\beta'})^{1/2} \cdot s$. Here, it is assumed that s is constant in any composition. Then, the activation energy can be written as follows:

$$E_V \equiv \frac{E'}{S_\beta + S_\alpha} = \frac{E'}{(k \cdot \beta' \cdot n_{\beta'})^{1/2} \cdot s + \{k \cdot \alpha' \cdot (n_{O^-} + n_{O^{2-}})\}^{1/2} \cdot s}$$

$$= \frac{E'}{(k \cdot \beta' \cdot n_{\beta'})^{1/2} \cdot s + \left\{\dfrac{k \cdot \alpha' \cdot (n_{O^0} + n_{O^-} + n_{O^{2-}}) \cdot (n_{O^-} + n_{O^{2-}})}{n_{O^0} + n_{O^-} + n_{O^{2-}}}\right\}^{1/2} \cdot s}$$

$$= \frac{E' / \{(k \cdot \beta' \cdot n_{\beta'})^{1/2} \cdot s\}}{1 + \left\{\dfrac{k \cdot \alpha' \cdot (n_{O^0} + n_{O^-} + n_{O^{2-}}) \cdot (N_{O^-} + N_{O^{2-}})}{(k \cdot \beta' \cdot n_{\beta'})}\right\}^{1/2}}$$

$$= \frac{E}{1 + \alpha \cdot (N_{O^-} + N_{O^{2-}})^{1/2}} \quad\quad\quad\quad\quad (4)$$

where n_{O^0} is the number of bridging oxygen, E is the activation energy of pure SiO_2, N_{O^-} and $N_{O^{2-}}$ are the fractions of non-bridging oxygen and free oxygen ions, respectively. Here, α is considered to be a parameter relating to the weakness of the bonding between cation and oxygen ion at the "cutting-off" point.

With respect to pure molten SiO_2, E_V becomes E since $(N_{O^-} + N_{O^{2-}})$ is zero in pure SiO_2, and Eq. (1) can be ex-

pressed as the following equation:

$$\eta = A \cdot \exp\left(\frac{E}{RT}\right) \quad ....(5)$$

We first investigated the composition dependence of the term A by considering it as a function of $(N_{O^-} + N_{O^{2-}})$ and α. We found that the effect of the composition on A is negligibly small when the viscosity is expressed in the form of Eq. (5). Thus, it is assumed that here A is constant in the present model. A and E can be determined from the temperature dependence of the viscosity for pure molten SiO_2 as shown in **Fig. 2**. Reported values[11–16] are reproduced by the calculated viscosity curve obtained from Eq. (5). The following values are obtained:

$$A = 4.80 \times 10^{-8}, \quad E = 5.21 \times 10^5 \, (J) \quad ....(6)$$

N_{O^-} and $N_{O^{2-}}$ are evaluated from Gaye's model,[17] which is the only structural model that can evaluate the bonding state of oxygens, such as bridging and non-bridging oxygen, and free oxygen ions, among several thermodynamic models for slag systems stored in thermodynamic database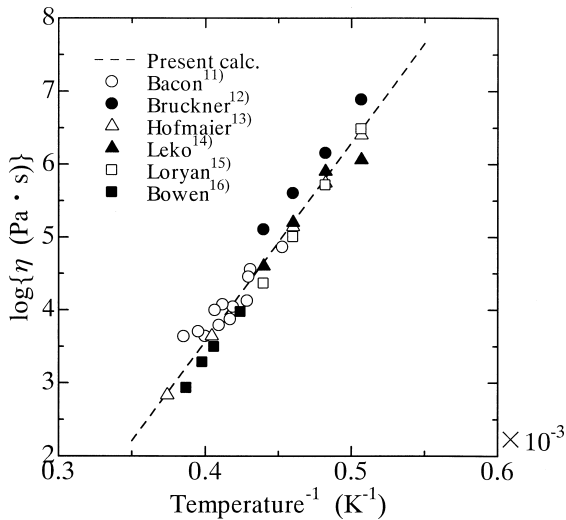s, by c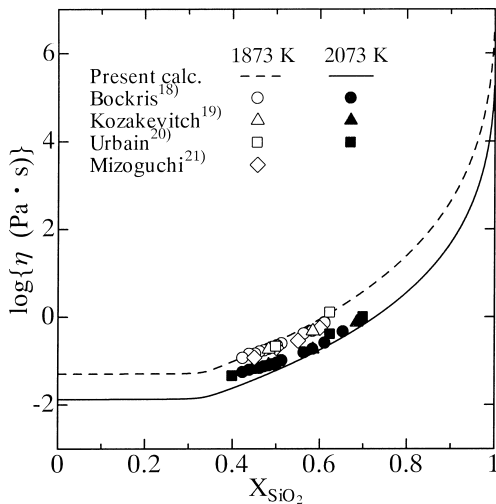onsidering thermodynamic interactions among the components in a multi-component slag system. The values of α for various basic oxides are determined from the application of the above equations to fit with the experimental data of the viscosity in various SiO_2–$(M_i)_{ui}O_{vi}$ $((M_i)_{ui}O_{vi}$= CaO, FeO, Al_2O_3) binary systems (**Figs. 3** through **5**)[18–27] as follows:

$$\alpha_{CaO} = 2.0, \quad \alpha_{FeO} = 3.8, \quad \alpha_{Al_2O_3} = 0.95 \quad ....(7)$$

In the case of multi-component systems, the activation energy E_V is defined in Eq. (8).

Fig. 2. Viscosity for pure molten SiO_2.

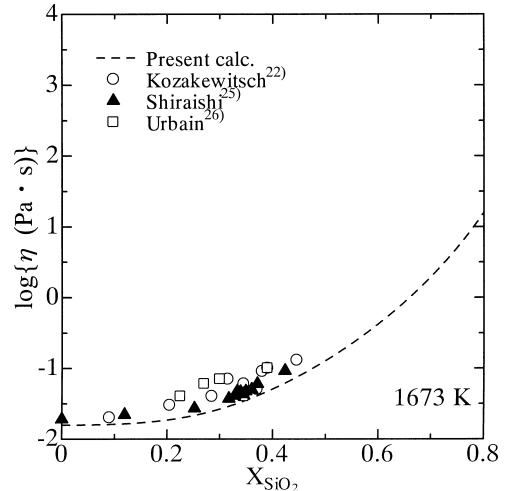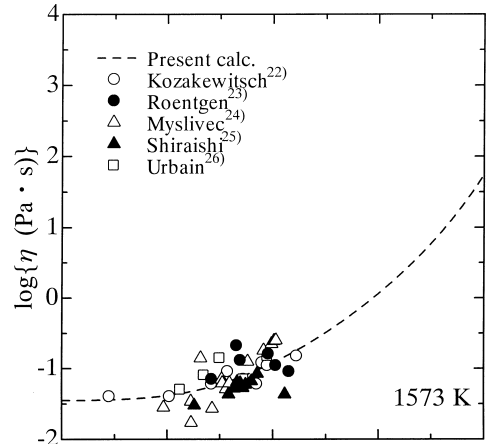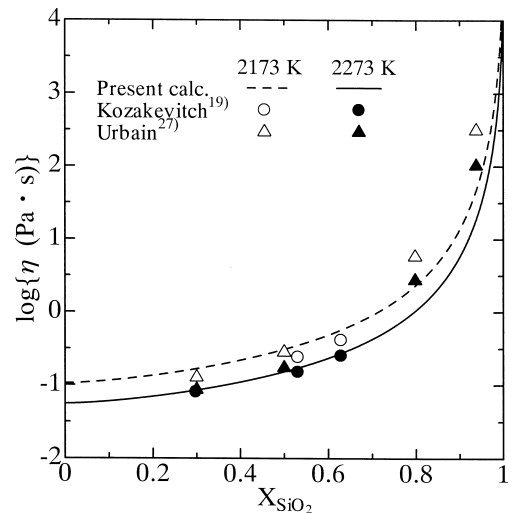**Fig. 4.** Viscosity for the molten SiO_2–FeO system.

Fig. 3. Viscosity for the molten SiO_2–CaO system.

Fig. 5. Viscosity for the molten SiO_2–Al_2O_3 system.

$$E_V \equiv \frac{E}{1+(\alpha_m)^{1/2}} \quad \dots\dots\dots\dots\dots(8)$$

α_m is evaluated by the following equation.

$$\alpha_m = \sum_{i=1}^{m} \alpha_{(M_i)_{ui}O_{vi}} \cdot (N_{Si-O-M_i} + N_{M_i-O-M_i})$$

$$+ \sum_{i=1}^{m-1} \sum_{j=1+1}^{m} \frac{(\alpha_{(M_i)_{ui}O_{vi}} + \alpha_{(M_j)_{uj}O_{vj}})}{2} \cdot N_{M_i-O-M_j} \quad \dots\dots\dots(9)$$

where m is the number of oxides except for SiO_2, N_{Si-O-M_i} and $N_{M_i-O-M_i}$ are the fractions of the non-bridging oxygen and the free oxygen ions, respectively. The second term was introduced to evaluate the contribution from free oxygen ions that exist between two different cations because free oxygen ions produced from each of the cations can not be distinguished from each other.

3. Results and Discussion

Figure 6 shows the fractions of the bridging oxygen N_{O^0}, the non-bridging oxygen N_{O^-}, the free oxygen ion $N_{O^{2-}}$ and $(N_{O^-}+N_{O^{2-}})$ for the SiO_2–CaO system at 1 873 K, as calculated from Gaye's model.[17] The fraction of bridging oxygen decreases while the fraction of non-bridging oxygen increases with decreasing concentration of SiO_2, since network structures are gradually cut off by the oxygen ions decomposed from CaO. The fraction of non-bridging oxygen has a maximum at $X_{SiO_2}=0.33$, suggesting that a network structure fully fragments in the equilibrium state of the following reaction.

$$2CaO + SiO_2 = SiO_4^{4-} + 2Ca^{2+} \quad\dots\dots\dots\dots(10)$$
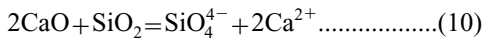
SiO_4^{4-} tetrahedral and Ca^{2+} mainly exist in this state. The fraction of free oxygen ion begins to increase when the content of SiO_2 decreases further than $X_{SiO_2}=0.33$. $(N_{O^-}+N_{O^{2-}})$ increases sharply with decreasing concentration of SiO_2. Then, $(N_{O^-}+N_{O^{2-}})$ reached about 1 at $X_{SiO_2}=0.33$. Whereas, the viscosity of silicate slag for the SiO_2–CaO system is decreased abruptly by the addition of CaO until $X_{SiO_2}=0.33$, as shown in Fig. 3. The composition dependence of $(N_{O^-}+N_{O^{2-}})$ corresponds to the composition dependence of the viscosity for the molten SiO_2–CaO system.

A comparison of the viscosity calculated from the present model with available experimental data is shown in Figs. 3 through 5, which show the composition dependences of viscosity in SiO_2–CaO, SiO_2–FeO and SiO_2–Al_2O_3 systems at two temperatures, respectively. In those systems, the experimental data are fitted well by the present model. It should be noted that our model reproduces the composition dependence of the viscosity in binary silicate slag as a function of $(N_{O^-}+N_{O^{2-}})$ with α.

Figures 7 and **8** illustrate iso-$(N_{O^-}+N_{O^{2-}})$ curves for a SiO_2–CaO–FeO system at 1 673 K and a SiO_2–CaO–Al_2O_3 system at 1 973 K, both calculated from Gaye's model.[17] In Fig. 7, $(N_{O^-}+N_{O^{2-}})$ decreases with increasing concentration of SiO_2. On the other hand, the iso-$(N_{O^-}+N_{O^{2-}})$ curves indicate a positive gradient at high concentrations of SiO_2 in the SiO_2–CaO–Al_2O_3 system (Fig. 8). The gradient decreas-
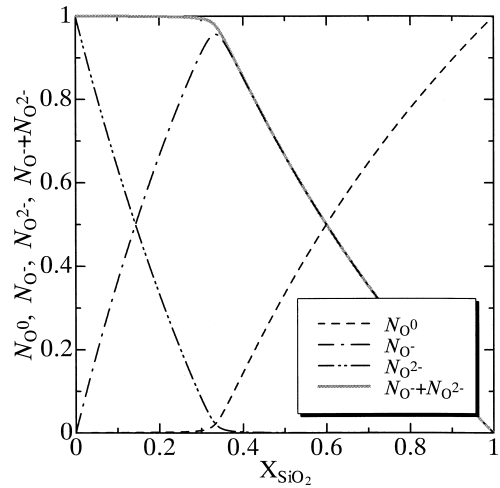

Fig. 6. Change in the fractions of the bridging oxygen ion N_{O^0}, the nonbridging oxygen ion N_{O^-}, the free oxygen ion $N_{O^{2-}}$, and $(N_{O^-}+N_{O^{2-}})$ for the SiO_2–CaO system at 1 873 K.
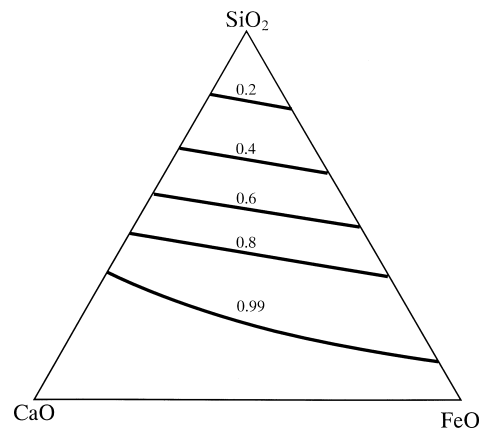

Fig. 7. Iso-$(N_{O^-}+N_{O^{2-}})$ curves of the SiO_2–CaO–FeO system at 1 673 K.
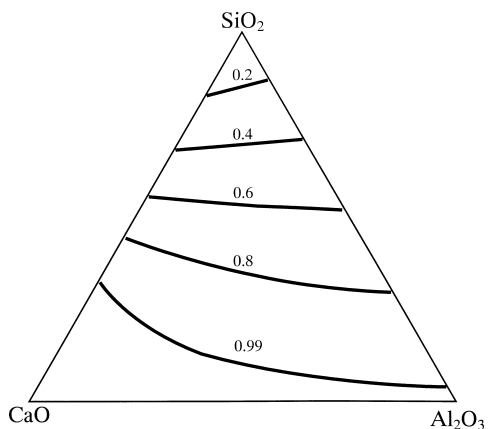

Fig. 8. Iso-$(N_{O^-}+N_{O^{2-}})$ curves of the SiO_2–CaO–Al_2O_3 system at 1 973 K.

es gradually with a decrease in SiO_2 concentration. Then, its gradient becomes negative, and the iso-$(N_{O^-}+N_{O^{2-}})$ curves indicate a negative convex at a low SiO_2 composition region.

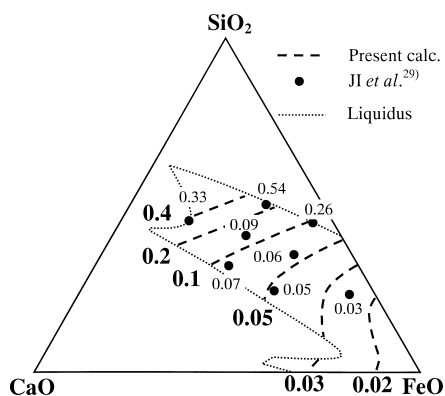**Figure 9** shows the viscosity for the molten SiO_2–CaO–FeO system[29] at 1 673 K. The composition dependence of

Fig. 9. Viscosity (Pa·s) for the molten SiO₂–CaO–FeO system at 1673 K.

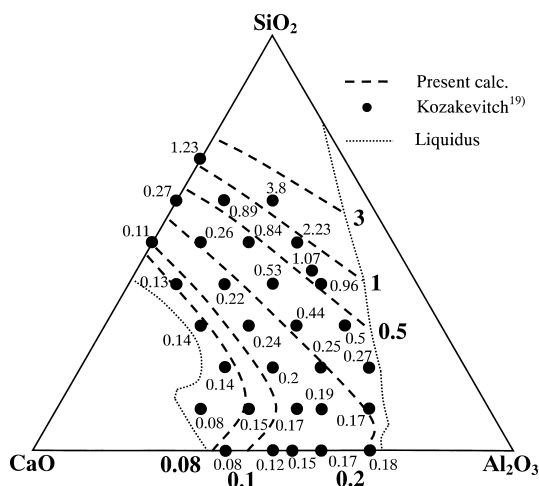**Fig. 10.** Viscosity (Pa·s) for the molten SiO₂–CaO–Al₂O₃ system at 1973 K.

the viscosity is reproduced by the present model. The calculated results of the viscosity of the molten SiO_2–CaO–Al_2O_3 system[19] at 1973 K are shown in **Fig. 10**, where it is seen that the viscosity decreases with increasing Al_2O_3 content at a high SiO_2 concentration, while the viscosity increases as Al_2O_3 content increases at a high CaO composition region. Thus, the present model shows the effect of Al_2O_3 as an amphoteric oxide on viscosity in a wide composition range.

From Figs. 9 and 10 it is found that the calculated results of the viscosity agree well with reported values over a wide composition range in ternary systems, even though here only N_{O^-}, $N_{O^{2-}}$ and α were used as parameters in the model. From Figs. 7 to 10, it can be seen that the viscosity of SiO_2 based slag is strongly dependent upon the SiO_2 concentration, and that this composition dependence corresponds to the distribution of $(N_{O^-}+N_{O^{2-}})$ in ternary systems as well as in binary systems, as shown in Fig. 6. In general, it is difficult to describe the abrupt and complicated changes in viscosity with SiO_2 content over a wide composition range by applying polynomial functions of the concentrations of the components that are usually used in conventional viscosity models. However, the introduction of the term $(N_{O^-}+N_{O^{2-}})$ as a parameter in the present viscosity model enables us to obtain a good description of the composition dependence of the viscosity. The idea of introducing the bonding states of oxygen has been already been pointed out by Zhang *et*

al.[6,7] However, since they used a polynomial function of N_{O^0} and $N_{O^{2-}}$, where N_{O^0} is the fraction of bridging oxygen, the physical meaning of the coefficients is obscure. In the present model, we further introduced the parameter α to express the effect of each component on the silicate network structure; the physical role of which has been explained in detail. In the present work, it has been established that the composition dependence of silicate slag can be evaluated in ternary systems by applying $(N_{O^-}+N_{O^{2-}})$ and α over a wide composition range.

4. Conclusion

A model to evaluate the viscosity of silicate melts was developed by considering the flow mechanism of melts with a network structure and the bonding state of oxygen in molten silicate. The present model considers that movements of "cutting-off" points in the network structure of silicate melts cause a viscous flow when shear stress is applied to the liquid. We expressed these "cutting-off" points as non-bridging oxygen and free oxygen ions, which are produced by the addition of some basic oxides. The sum of the fractions of the oxygens $(N_{O^-}+N_{O^{2-}})$ was introduced into our model as a feature of the molten silicate structure. The present model can reproduce not only the composition dependence of the viscosities for silicate melts in binary systems with a single model parameter α, which is related to the weakness of the bonding in "cutting-off" points, but also the composition dependence of viscosities in ternary systems over a wide composition range.

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