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A Model for Estimating Viscosities of Aluminosilicate Melts Containing Alkali Oxides

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A model to estimate the viscosity of aluminosilicate melts, including alkali oxides, was constructed in the present study. The model is based on an earlier model, and considers the bonding state of oxygen in molten silicate and the flow mechanism of melts with a network structure. The straightforward method of Susa *et al.* to evaluate bonding states of oxygen in chemical compositions was applied to the present model since their method can easily be extended to any multi-component system. The calculation results of our model can express the dependence on viscosity in quaternary aluminosilicates containing alkali oxide and their subsystems.

KEY WORDS: viscosity; silicate melts; structure; aluminosilicate melts; alkali oxides.

1. Introduction

Demand of smelting furnaces for waste treatment has been increasing in the respect of detoxification as well as recycling of industrial waste such as asbestos,^{1,2)} shredder residue,^{1,3,4)} and glass dust containing lead.⁵⁾ The essential issue in smelting furnace operations is to elucidate adequate conditions with the aim of stabilizing processes due to the wide variety in the composition of industrial waste. In this regard, Miyabayashi *et al.*¹⁾ pointed out that the fluidity of slag is one of the crucial operating components. Although the fluidity of slag is typically evaluated by the viscosity measurement, the estimation of viscosity by models is considered to be much more helpful in evaluating viscosity in case of melting furnaces. This is because of the considerable difficulty in measuring viscosity of all kinds of slags in melting furnaces due to the diversity in composition of industrial waste. The system of the slag in melting furnaces for the waste including asbestos is the multi-component aluminosilicate containing CaO, FeO, Fe₂O₃, MgO, K₂O, Na₂O, *etc.*¹⁾

Many models to estimate the viscosity of slag melts have been developed in the past.^{6–8)} It has been accepted that the estimation of viscosity of molten slags is a difficult task since the abrupt and complicated structure changes of silicate melts are reflected by the viscosity. From this viewpoint, successful models based on the structure of molten slags have been proposed by Zhang and Jahanshahi,^{9–11)} and Kondratiev and Jak.^{12–15)} The three bonding states of oxygen in slag melts, which are (i) bridging oxygen, (ii) non-bridging oxygen ion, and (iii) free oxygen ion, are considered in their viscosity model. The authors^{16–21)} have also constructed a structurally-based viscosity model by consid-

ering the flow mechanism of silicate melts within the network structure as well as the bonding states of oxygen in molten silicate. In this model, the concentrations of non-bridging oxygen ions and free oxygen ions are calculated as bonding states of oxygen by the IRSID thermodynamic ‘cell model.’^{22,23)} This viscosity model can represent the composition dependence of viscosity in a wide composition range in the multi-component silicate system SiO₂–CaO–MgO–FeO–Al₂O₃ in blast furnace process. However, the IRSID “cell model” is not applicable to slag containing alkali oxides, which cannot be ignored in the slag of melting furnace, in spite of its wide validity system SiO₂–TiO₂–Ti₂O₃–Cr₂O₃–Al₂O₃–Fe₂O₃–CrO–FeO–MgO–MnO–CaO–CaF₂–S.

On the other hand, a predictive equation for the refractive indices of aluminosilicate melts was proposed by Susa *et al.*²⁴⁾ Assuming that the structure of aluminosilicate melts consists of only three kinds of chemical bonds, *i.e.* Si–BO (bridging oxygen in Si tetrahedral unit), Al–BO (bridging oxygen in Al tetrahedral unit with a charge-compensating cation), and Si–NBO (NBO: non-bridging oxygen connected with Si) with a charge-compensating cation, it is possible to calculate the bonding states of oxygen in molten aluminosilicate by the chemical composition of slag without any thermodynamic parameters. Owing to a simple method, the evaluation of the bonding states of oxygen can be conducted in various kinds of silicate systems including alkali oxides as well as alkaline earth oxides. Their equation succeeds in predicting the refractive index values with small error in six component silicate melts in spite of its simplicity.

In the present work, the earlier viscosity model developed by the authors was modified to the viscosity of alumi-

nosilicate melts containing alkali oxides in melting furnaces, SiO₂-CaO-MgO-FeO-K₂O-Na₂O-Al₂O₃ system, by applying the method of Susa *et al.* to evaluate the bonding states of oxygen in the molten silicate instead of thermodynamic models.

2. Model

2.1. Equation

The equation to describe the viscosity of molten silicate slag in the present model is based on the equation in the earlier model which was proposed considering the bonding state of oxygen in the network structure of silicate melts and its flow mechanism.¹⁶⁻²¹⁾ The concept of the model is as follows: Silicate slag has a network structure made of bonding SiO₄⁴⁻ units and Si tetrahedral ions, as shown in Fig. 1(a). Si tetrahedral ions are combined through bridging oxygen O⁰, the convex oxygen in the structure of Si tetrahedral ions. The non-bridging oxygen ion O⁻ and the free oxygen ion O²⁻ are generated by partially cutting off the network structure of Si tetrahedral in SiO₂ when adding some basic oxides such as CaO and Na₂O in silicate slag, as shown in Fig. 1(b). The non-bridging oxygen ion and the free oxygen ion have a larger mobility than the bridging oxygen in the network structure because there are “cutting-off” points. These are bonds of oxygen not connected to Si, just next to the non-bridging oxygen ion and the free oxygen ion due to the breaking of the network structure. Assuming that the movements of “cutting-off” points cause a viscous flow, therefore, an increase in the number of non-bridging oxygen ions and free oxygen ions yields a lowering of the activation energy of viscosity. In addition, it is assumed that these “cutting-off” points move in a random direction along the network structure of silicate melts. The equation of viscosity η in binary silicate system derived from the above concept in earlier studies¹⁶⁻²¹⁾ is given by the following equations:

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

$$E_V = \frac{E}{1 + \sqrt{\alpha \cdot (N_{O^-} + N_{O^{2-}})}} \dots\dots\dots(2)$$

where $A (=4.80 \times 10^{-8})$ is a constant, E_V is the activation energy for viscosity, R is the gas constant, and T is the temperature. $E (=5.21 \times 10^5 \text{ (J)})$ is the activation energy for viscosity of pure SiO₂, and α is the parameter relating to the weakness of the bonding between the cation and oxygen ion at the “cutting-off” point, which depends on the oxide component. N_{O^-} and $N_{O^{2-}}$ are fractions of the non-bridging oxygen ion and free oxygen ion, respectively. The N_{O^-} and $N_{O^{2-}}$ are evaluated by the IRSID ‘cell model’.^{22,23)}

In the evaluation of chemical bonds of oxygen, Susa *et al.*²⁴⁾ assumed that the structure of the aluminosilicate melts is composed of only three kinds of chemical bonds. Their assumption results in the calculation of chemical bonds of oxygen solely by the concentration of slag components. In addition, by considering the Al-BO bond in their equation, the oxygen states can be estimated in case that aluminum oxide works as network former.

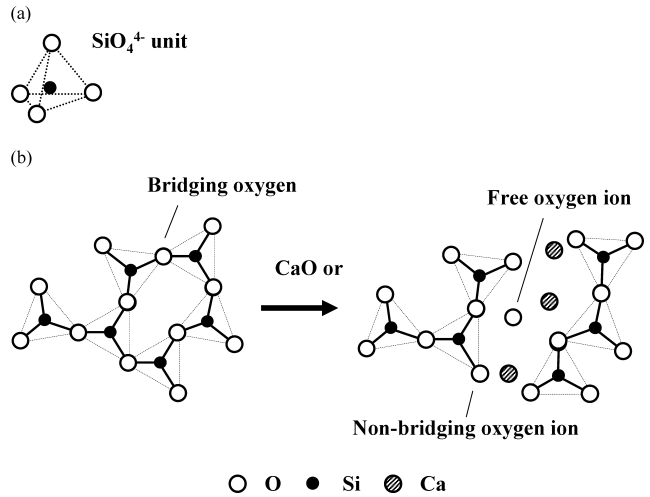


Fig. 1. Structure of silicate slag.

The equation to calculate the viscosity of silicate melts is modified to the following equations in order to apply the method of Susa *et al.* instead of the IRSID ‘cell model’ to the evaluation of the bonding states of oxygen:

$$\eta = A \cdot \exp\left(\frac{E_V}{RT}\right) \dots\dots\dots(3)$$

$$E_V = \frac{E}{1 + \sqrt{\sum_i \alpha_i \cdot N_{(NBO+FO)_i} + \sum_j \alpha_{j \text{ in Al}} \cdot N_{(Al-BO)_j}}} \dots\dots\dots(4)$$

where the activation energy E_V is a function of the sum of the fractions of non-bridging oxygen ion (NBO) and free oxygen ion (FO) $N_{(NBO+FO)_i}$, and the fraction of the bridging oxygen (BO) in the Al tetrahedral unit $N_{(Al-BO)_j}$; $N_{(NBO+FO)_i}$ is the same as the $(N_{O^-} + N_{O^{2-}})$ in Eq. (2). α_i and $\alpha_{j \text{ in Al}}$ are parameters. i is the component of melt except SiO₂, *i.e.* CaO, MgO, FeO, K₂O, Na₂O, Al₂O₃, and j is the charge-compensating ion from component i except Al₂O₃, *i.e.* Ca²⁺, Mg²⁺, Fe²⁺, K⁺ and Na⁺. A and E have the same values in the original equation, *i.e.* 4.80×10^{-8} and $5.21 \times 10^5 \text{ (J)}$ respectively. It is assumed that there are no differences between non-bridging oxygen ions and free oxygen ions in the respect of the influence of those ions on viscosity. The effect of the bridging oxygen in the Al tetrahedral unit on the activation energy is treated in the same manner as the effect of the non-bridging oxygen by assuming that the bridging oxygen in the Al tetrahedral unit has a somewhat different mobility from that of the bridging oxygen in the Si tetrahedral unit.

The fractions of two kinds of oxygen $N_{(NBO+FO)_i}$ and $N_{(Al-BO)_j}$ were calculated with reference of the method of Susa *et al.*²⁴⁾ as follows:

- (i) Binary system
- (i-1) $a\text{SiO}_2 - b_i(\text{M}_x\text{O}_y)_i \{a + b_i = 1 \text{ (mol)}\}$
 $(\text{M}_x\text{O}_y)_i = \text{CaO, MgO, FeO, K}_2\text{O or Na}_2\text{O}$ system

The addition of basic oxide to silicate provides non-bridging oxygen ions and free oxygen ions by breaking the Si-O bonds in the network structure of silicate; *i.e.* the number of oxygen bonds not connected to Si increases. When b_i mol of $(\text{M}_x\text{O}_y)_i$ is added to silicate, the number of the bonds of oxygen not connected to Si on basic oxide

$(M_xO_y)_i$ $n_{(O-M)_i}$ is $2b_i$ mol because 1 mol of $(M_xO_y)_i$ produces 2 mol of oxygen bonds not connected to Si. The total number of the bonds of oxygen in the system $aSiO_2-b_i(M_xO_y)_i$ $n_{Total-O}$ is $4a+2b_i$ mol. In our model, the ratio of the number of oxygen bonds not connected to Si $n_{(O-M)_i}$ to the total number of the oxygen bonds in the system $n_{Total-O}$ is treated as the sum of the fractions of non-bridging oxygen ions and free oxygen ions $N_{(NBO+FO)_i}$. In case of a binary system, the content of bridging oxygen in the Al tetrahedral $N_{(Al-BO)_i}$ is zero. Subsequently,

$$N_{(NBO+FO)_i} = n_{(O-M)_i} / n_{Total-O} = b_i / (2a + b_i) \dots\dots\dots(5)$$

$$N_{(Al-BO)_i} = 0 \dots\dots\dots(6)$$

(i-2) $aSiO_2-cAl_2O_3$ system $\{a+c=1 \text{ (mol)}\}$

In binary $SiO_2-Al_2O_3$ system, there is no charge-compensating cation from alkaline oxides and alkaline earth oxides, which requires the formation of Al tetrahedral; as a result, Al_2O_3 works as network modifier such as basic oxides. In the same manner as (i-1), the number of oxygen bonds not connected to Si $n_{(O-M)_i}$ is $6c$ mol with the addition of c mol Al_2O_3 . The total number of oxygen bonds in the $aSiO_2-cAl_2O_3$ system $n_{Total-O}$ is $4a+6c$ mol. Subsequently,

$$N_{(NBO+FO)_i} = n_{(O-M)_i} / n_{Total-O} = 3c / (2a + 3c) \dots\dots\dots(7)$$

$$N_{(Al-BO)_i} = 0 \dots\dots\dots(8)$$

(ii) Ternary $aSiO_2-b_i(M_xO_y)_i-cAl_2O_3$ system $\{a+b_i+c=1 \text{ (mol)}\}$

$((M_xO_y)_i = CaO, MgO, FeO, K_2O \text{ or } Na_2O)$

(ii-1) $b_i > c$

When the amount of basic oxide $(M_xO_y)_i$ b_i is higher than the amount of aluminum oxide c , it is assumed that aluminum oxide only works as network former since there is a sufficient charge-compensating cation j to produce Al tetrahedral in the melts. The number of oxygen bonds in the Al tetrahedral on cation j $n_{(O-Al \text{ in Al})_j}$ is $8c$ mol. The number of residual oxygen bonds not connected to Si $n_{(O-M)_i}$ is $2(b_i - c)$ mol because c mol of oxygen as well as c mol of charge-compensating cation is used for the Al tetrahedral in c mol of Al_2O_3 . The total number of oxygen bonds in the $aSiO_2-b_i(M_xO_y)_i-cAl_2O_3$ system $n_{Total-O}$ is $4a+2b_i+6c$ mol. In the present model, the ratio of the number of oxygen bonds in the Al tetrahedral $n_{(O-Al \text{ in Al})_j}$ to the total number of oxygen bonds in the system $n_{Total-O}$ is considered to be the content of the bridging oxygen in Al tetrahedral $N_{(Al-BO)_i}$. Subsequently,

$$N_{(Al-BO)_i} = n_{(O-Al \text{ in Al})_j} / n_{Total-O} = 4c / (2a + b_i + 3c) \dots\dots\dots(9)$$

$$N_{(NBO+FO)_i} = n_{(O-M)_i} / n_{Total-O} = (b_i - c) / (2a + b_i + 3c) \dots\dots\dots(10)$$

(ii-2) $b_i < c$

When the amount of basic oxide $(M_xO_y)_i$ b_i is lower than the amount of aluminum oxide c , it is assumed that basic oxide is used only as charge-compensating ion for the Al tetrahedral. Therefore, the number of oxygen bonds in the Al tetrahedral $n_{(O-Al \text{ in Al})_j}$ is $8b_i$ mol because 1 mol of basic oxide selected in this study results in 2 mol of Al tetrahedral, *i.e.* 8 mol of oxygen bonds in the Al tetrahedral. The number of residual oxygen bonds not connected to Si $n_{(O-M)_i}$ is $6(c - b_i)$ mol. This is the number of oxygen bonds pro-

duced from aluminum oxide except for the oxygen bonds in the Al tetrahedral. Therefore,

$$N_{(Al-BO)_i} = n_{(O-Al \text{ in Al})_j} / n_{Total-O} = 4b_i / (2a + b_i + 3c) \dots\dots\dots(11)$$

$$N_{(NBO+FO)_i} = n_{(O-M)_i} / n_{Total-O} = 3(c - b_i) / (2a + b_i + 3c) \dots\dots\dots(12)$$

(iii) Multi-component $aSiO_2-\sum_i b_i(M_xO_y)_i-cAl_2O_3$ system $\{a + \sum_i b_i + c = 1 \text{ (mol)}\}$

$((M_xO_y)_i = CaO, MgO, FeO, K_2O \text{ or } Na_2O)$

(iii-1) $\sum_i b_i > c$

When the sum of the amount of basic oxide $(M_xO_y)_i$ $\sum_i b_i$ is higher than the amount of aluminum oxide c , aluminum oxide works only as network former since there is a sufficient charge-compensating cation to produce the Al tetrahedral in the melt as mentioned above. Here, it is assumed that the supply of charge-compensating ions in each basic oxide is proportional to the content of basic oxide, meaning that the number of oxygen bonds in the Al tetrahedral $n_{(O-Al \text{ in Al})_j}$ with the charge-compensating cation j is $8c(b_i / \sum_i b_i)$ mol and that the number of the bonds of oxygen not connected to Si is $2b_i - 2c(b_i / \sum_i b_i)$ mol. Subsequently,

$$N_{(Al-BO)_j} = n_{(O-Al \text{ in Al})_j} / n_{Total-O} = 4c \left(b_i / \sum_i b_i \right) / \left(2a + \sum_i b_i + 3c \right) \dots\dots\dots(13)$$

$$N_{(NBO+FO)_i} = n_{(O-M)_i} / n_{Total-O} = \left\{ b_i - c \left(b_i / \sum_i b_i \right) \right\} / \left(2a + \sum_i b_i + 3c \right) \dots\dots\dots(14)$$

(iii-2) $\sum_i b_i < c$

When the sum of the amount of basic oxide $(M_xO_y)_i$ b_i is lower than the amount of aluminum oxide c , the equation is derived in the same manner as the equation in the ternary system. Subsequently,

$$N_{(Al-BO)_j} = n_{(O-Al \text{ in Al})_j} / n_{Total-O} = 4b_j / \left(2a + \sum_i b_i + 3c \right) \dots\dots\dots(15)$$

$$N_{(NBO+FO)_i} = n_{(O-M)_i} / n_{Total-O} = 3 \left(c - \sum_i b_i \right) / \left(2a + \sum_i b_i + 3c \right) \dots\dots\dots(16)$$

3. Results and Discussion

3.1. Determination of Parameters

There are two kinds of parameters, α_i and $\alpha_{j \text{ in Al}}$, in the present equation (4) for expressing the viscosity of molten aluminosilicates. The former parameter relates to the non-bridging oxygen ion and the free oxygen ion, and the latter is the parameter relating to the bridging oxygen in the Al tetrahedral. The α_i and $\alpha_{j \text{ in Al}}$ relate to the weaknesses in the bonds of non-bridging oxygen ion, and the weakness of bridging oxygen in the Al tetrahedral, respectively. In the present equation, therefore, the larger parameter values lead to a lower viscosity. These weaknesses of α_i and $\alpha_{j \text{ in Al}}$ depend on the cation next to the non-bridging oxygen ion and

the free oxygen ion, which is the cation produced by the addition of basic oxide $(M_xO_y)_i$ to silicate, and the charge-compensating cation near Al tetrahedral, which is also the cation produced by adding basic oxide $(M_xO_y)_i$ to silicate, respectively.

In this study, the parameters α_i and $\alpha_{j \text{ in Al}}$ were determined from experimental data in binary silicate systems²⁵⁻³⁴ and ternary aluminosilicate systems.^{26,34-36,39-41} The way to determine the parameters is as follows: (i) First, the value of α_i in each oxide i was obtained from the application of the above equation to fit the experimental values of the viscosity in each binary $\text{SiO}_2-(M_xO_y)_i$ system, where $(M_xO_y)_i$ is CaO, MgO, FeO, K₂O, Na₂O or Al₂O₃. (ii) Subsequently, the assessment of the value $\alpha_{j \text{ in Al}}$ in each charge-compensating cation j was conducted by fitting the calculated viscosity with parameter α_i determined in the binary system to the experimental data in each ternary $\text{SiO}_2-(M_xO_y)_i-\text{Al}_2\text{O}_3$ system, where $(M_xO_y)_i$ is CaO, MgO, FeO, K₂O or Na₂O. The experimental data²⁵⁻⁴¹ used for the determination of these parameters are shown in Table 1, and the assessed parameters are listed in Table 2.

3.2. Calculation Results

At first, the ability of the present model to represent viscosity using the evaluation manner for oxygen state with reference to Susa *et al.*'s model²⁴) was examined by comparing the calculated values with the literature data, which were used for the parameter determinations.

Table 1. Experimental data used for determining model parameters.

System		Temperature (K)	References
Binary	SiO ₂ -CaO	1723 - 2373	25-27
	SiO ₂ -MgO	1823 - 2273	27,28
	SiO ₂ -FeO	1473 - 1723	29-32
	SiO ₂ -K ₂ O	1373 - 1973	28,33
	SiO ₂ -Na ₂ O	1373 - 1973	28,33
	SiO ₂ -Al ₂ O ₃	1973 - 2373	26,34
Ternary	SiO ₂ -CaO-Al ₂ O ₃	1423 - 2273	26,35
	SiO ₂ -MgO-Al ₂ O ₃	1673 - 2073	36-39
	SiO ₂ -FeO-Al ₂ O ₃	1523 - 1573	40
	SiO ₂ -K ₂ O-Al ₂ O ₃	1523 - 1673	39
	SiO ₂ -Na ₂ O-Al ₂ O ₃	1523 - 1773	41

Table 2. Model parameters.

$(M_xO_y)_i$	α_i	j	$a_{j \text{ in Al}}$
CaO	4.00	Ca ²⁺	1.46
MgO	3.43	Mg ²⁺	1.56
FeO	6.05	Fe ²⁺	3.15
K ₂ O	6.25	K ⁺	-0.69
Na ₂ O	7.35	Na ⁺	0.27
Al ₂ O ₃	1.14		

The calculation results with the experimental data in binary systems, SiO₂-CaO, SiO₂-Na₂O and SiO₂-Al₂O₃, are shown in Figs. 2-4. The present model represents the com-

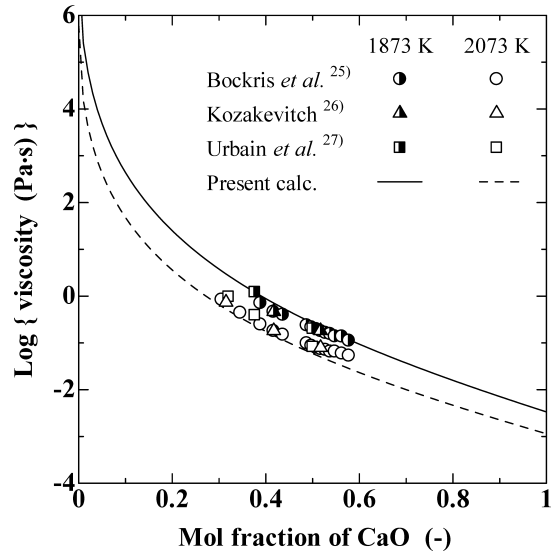


Fig. 2. Viscosity of SiO₂-CaO system.

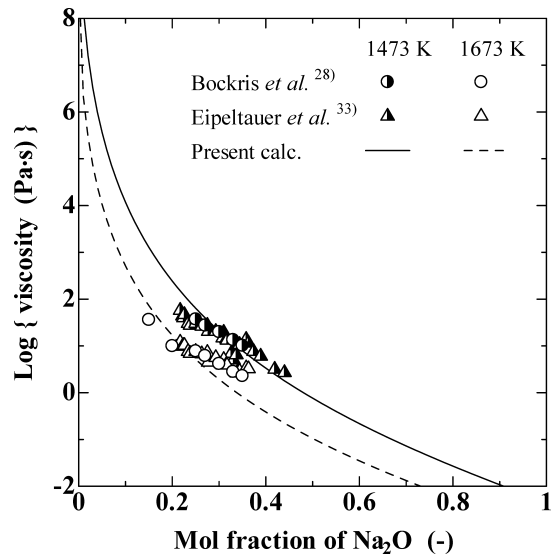


Fig. 3. Viscosity of SiO₂-Na₂O system.

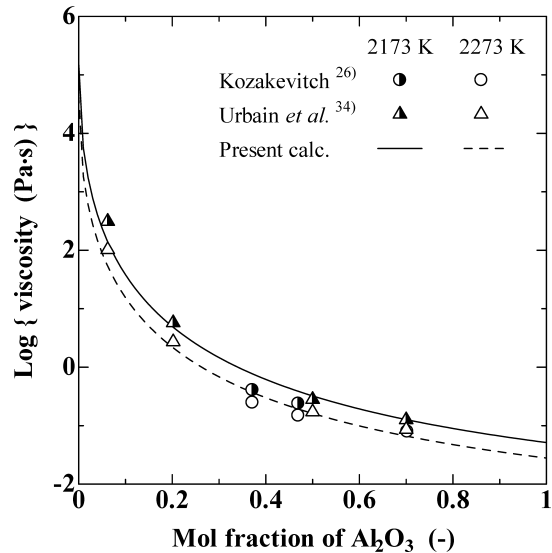


Fig. 4. Viscosity of SiO₂-Al₂O₃ system.

position dependences of viscosity in these binary systems. The calculated values tend to deviate slightly downward from the experimental values with higher CaO and Na₂O contents in SiO₂-CaO and SiO₂-Na₂O systems. This deviation could be due to the assumption that there are no differences between the influence of non-bridging oxygen ions and free oxygen ions on viscosity. In the previous studies,¹⁶⁻²¹⁾ the content of non-bridging oxygen ion and the content of free oxygen ion were individually calculated by the IRSID ‘cell model’, and the sum of these oxygen contents described the composition dependence of viscosity over a wide composition range. The thermodynamically calculated ($N_{O^-} + N_{O^{2-}}$) in a binary system, for example, increases until a certain composition, and then does not change so much. This behavior corresponds to the composition dependence of viscosity in binary systems, which shows a sharp decrease in viscosity in the range from pure SiO₂ to a certain composition, after which the viscosity decreases only slightly. In the present model, on the other hand, the sum of the fractions of non-bridging oxygen ions and free oxygen ions $N_{(NBO+FO)}$ was estimated only from the number of all oxygen bonds not connected to Si except for the bonds in Al tetrahedral, leading to a continuous increase of $N_{(NBO+FO)}$ with increasing the basic oxide in the whole composition range, *i.e.* the viscosity continues to decrease to some extent even at higher basic oxide content.

Figures 5 and 6 show the viscosities in ternary aluminosilicate systems, SiO₂-CaO-Al₂O₃ at 1973 K and SiO₂-K₂O-Al₂O₃ at 1673 K, respectively. In these figures, the lines are the iso-viscosities calculated by the present model and the dots represent experimental data. The iso-viscosity line breaks at a certain point in Fig. 5. This is the point in which the content of CaO is equal to the content of Al₂O₃ in mol. When the amount of CaO is higher than the amount of aluminum oxide, aluminum oxide works only as network former due to a sufficient amount of charge-compensating ion Ca²⁺ for producing the Al tetrahedral in the melts as mentioned above. On the other hand, at the Al₂O₃ side of the above point, aluminum oxide works as network modifier as well as network former because of the lack of charge-compensating ion Ca²⁺. The iso-viscosity lines calculated relating to this point by the present model describe the composition dependency of experimental viscosity over a wide composition region in the SiO₂-CaO-Al₂O₃ system at 1973 K, although the calculated results show a slightly lower viscosity than the experimental data at low SiO₂ contents, as well as in binary systems. In Fig. 6, the calculation results in SiO₂-K₂O-Al₂O₃ at 1673 K are in agreement with the experimental data although the composition region targeted in the present calculation is narrow.

The viscosity in quaternary aluminosilicate slags containing MgO or FeO was shown in **Figs. 7 and 8**. Figure 7 presents the viscosity of SiO₂-CaO-MgO-10mass%Al₂O₃ slag at 1723 K. The calculated iso-viscosity lines well express the composition dependency in viscosity measured by Machin *et al.*,^{42,43)} showing the lowering of viscosity with decreasing SiO₂. The viscosity in quasi-ternary SiO₂-CaO-FeO system at 20mass%Al₂O₃ by Gimmelfarb⁴⁴⁾ indicates an unusual trend in Fig. 8, where the viscosity decreases by increasing CaO or FeO at relatively high SiO₂ content, and more CaO or FeO yields the increase in viscosity. As can be

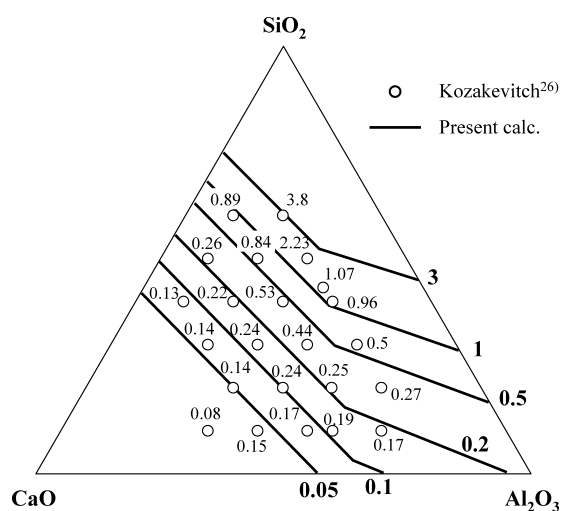


Fig. 5. Viscosity (Pa·s) of SiO₂-CaO-Al₂O₃ system (mass%) at 1973 K.

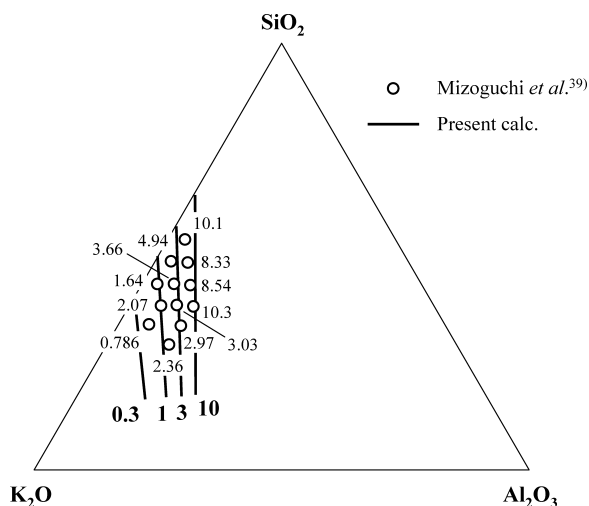


Fig. 6. Viscosity (Pa·s) of SiO₂-K₂O-Al₂O₃ system (mass%) at 1673 K.

appreciated from the liquidus line drawn with ‘FactSage’ in this figure, the data at low SiO₂ concentration exist in the zone of coexistence of solid and liquid, leading to a viscosity rise. Comparing the calculated viscosity with the literature data in a liquid region, it was found that the present model reproduces the viscosities in SiO₂-CaO-MgO-10mass%Al₂O₃ system.

Finally, the prediction of viscosity in the quaternary aluminosilicate system SiO₂-CaO-Al₂O₃-K₂O or Na₂O was attempted by using the present model. The viscosity measurements of the molten aluminosilicates containing alkali oxide have been conducted by the group of Nakashima *et al.*⁴⁵⁾ **Figure 9** shows the viscosity of quaternary aluminosilicate melts SiO₂-CaO-Al₂O₃-K₂O or Na₂O at 1873 K. Figure 9(a) shows the measured viscosity, whose values were taken from data points from Ref. 45), and Fig. 9(b) shows the calculated values by the present model. In Figs. 9(c) and 9(d), in addition, the calculations were conducted by the two generally-known models, (i) Riboud model⁴⁶⁾ and (ii) modified Iida model,⁴⁷⁾ which can be applied to the aluminosilicate systems containing alkaline oxides and have been recognized as models suited for estimating the

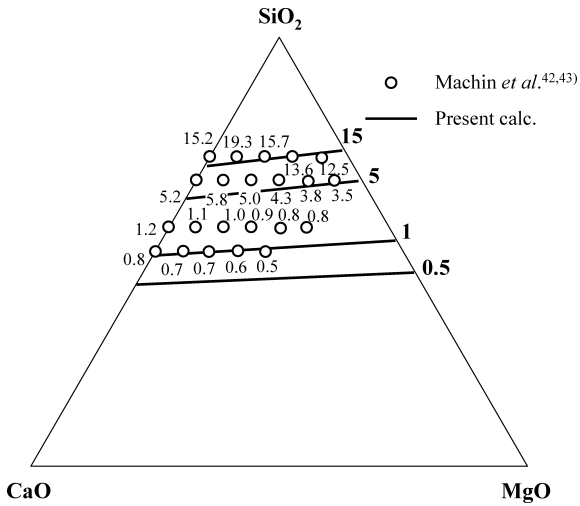


Fig. 7. Viscosity (Pa·s) of SiO₂-CaO-MgO-10Al₂O₃ system (mass%) at 1723 K.

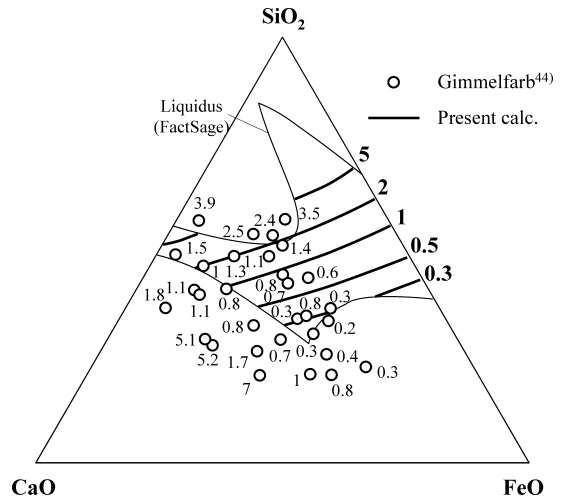


Fig. 8. Viscosity (Pa·s) of SiO₂-CaO-FeO-20Al₂O₃ system (mass%) at 1623 K.

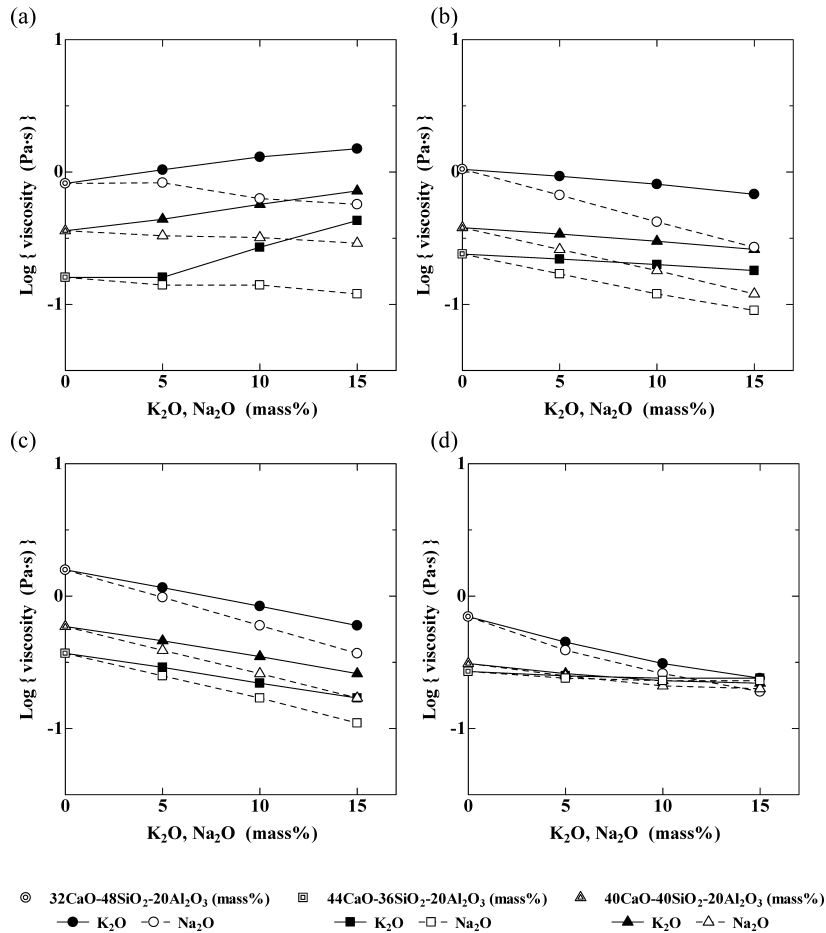


Fig. 9. Viscosity of SiO₂-CaO-Al₂O₃-K₂O or Na₂O system at 1873 K. (a) Experimental data,⁴⁵⁾ (b) present calculation, (c) Riboud model⁴⁶⁾ and (d) modified Iida model.⁴⁷⁾

viscosity of industrial slags.⁴⁸⁾ In Fig. 9(a), the viscosity of SiO₂-CaO-Al₂O₃-K₂O melts increases with increasing the content of K₂O, while the viscosity of SiO₂-CaO-Al₂O₃-Na₂O melts decreases with increasing content of Na₂O. On the other hand, the addition of Na₂O to molten SiO₂-CaO-Al₂O₃-Na₂O system lowers the viscosity, and the viscosity in SiO₂-CaO-Al₂O₃-K₂O indicates a slight decrease with the addition of K₂O in the calculation of the results in Fig. 9(b). As shown in Fig. 9(c), Riboud model has a simi-

lar trend as the present model, but with stronger decreasing influence on viscosity by increasing K₂O or Na₂O than the present model. In the calculation results of modified Iida model in Fig. 9(d), the additions of K₂O and Na₂O yield a similar composition dependence of viscosity. From this result, it was found that the present model clearly expresses the difference between the effect of K₂O addition and the effect of Na₂O addition to SiO₂-CaO-Al₂O₃ melts on viscosity in comparison with the other models, although the

calculation values don't describe the increment of viscosity of adding K_2O . In the present model, the following two parameters determine the behavior of viscosity with varying composition in aluminosilicate system: (i) the parameter $\alpha_{j\text{inAl}}$, which was introduced as the weakness of bridging oxygen in the Al tetrahedral with charge-compensating cation j , and (ii) the amount of each charge-compensating ion supplied to form Al tetrahedral. In the former case, the $\alpha_{j\text{inAl}}$ of K_2O is smaller than the $\alpha_{j\text{inAl}}$ of Na_2O , which means the bond of bridging oxygen in the Al tetrahedral with K^+ is stronger than Na^+ . The calculated results in two quaternary systems $SiO_2\text{-CaO-Al}_2O_3\text{-K}_2O$ and $SiO_2\text{-CaO-Al}_2O_3\text{-Na}_2O$ reflect the parameter $\alpha_{j\text{inAl}}$. In the latter case, it is reasonable to suppose that some of cations preferentially or with higher possibility work as charge-compensating ion since each cation has specific properties like interactions with other ions. Due to a lack of this information, however, in this study it was assumed that the supply of charge-compensating ion from each basic oxide was proportional to the content of basic oxide, which causes a poor reproducibility of composition dependence of experimental values in $SiO_2\text{-CaO-Al}_2O_3\text{-K}_2O$ system. For example, if K^+ works as charge-compensating ion strongly in comparison with Ca^{2+} , *i.e.* the amount of K^+ as charge-compensating ion is larger than that estimated with the present assumption and the amount of Ca^{2+} is smaller, the viscosity is higher than the viscosity calculated in the present work since $\alpha_{j\text{inAl}}$ of K^+ is smaller than $\alpha_{j\text{inAl}}$ of Ca^{2+} . As a result, this gives a better description of viscosity in $SiO_2\text{-CaO-Al}_2O_3\text{-K}_2O$ system.

4. Conclusions

The earlier viscosity model derived by considering the bonding states of oxygen in molten silicate slag and its flow mechanism was modified in order to estimate the viscosity of aluminosilicate melts including alkali oxides. In this modification, the concentration of non-bridging oxygen ions and free oxygen ions used in the calculation of bonding states of oxygen were evaluated with reference to the method of Susa *et al.* instead of a thermodynamic model. The present model can present the composition dependence of viscosity in ternary aluminosilicate systems as well as quaternary aluminosilicate systems containing MgO or FeO, and the distinction of the effects of K_2O and Na_2O on viscosity in quaternary aluminosilicate systems containing each alkali oxide without thermodynamic parameters.

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