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Effect of Structure on the Viscosity of Silicate Melts

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The composition dependence of the viscosity of binary silicate melts is calculated from a new theoretical model based on the silicate structure described by the bonding state of oxygen ion. Gaye's model¹⁾ is used to evaluate the bonding state of oxygen ion using thermodynamic database.

1. Introduction

The viscosity of silicate melts is a crucial parameter in the control of many high temperature processes, such as ironmaking and steelmaking processes. In the classical hole theory, the temperature dependence of the viscosity on silicate melts is usually given in the form of Arrhenius relationship expressed as Eq.(1).

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

where A , E_f , R and T are Arrhenius parameter, the activation energy, the gas constant and the absolute temperature. Here, each parameter has been extracted from measurements.²⁾⁻⁶⁾ Analysis of such measurements for silicate melts reveals that the activation energy is given as a function of composition, and may be related to the structure of the silicate melts.

A silicate melt has a network structure, which is made from bonding of SiO_4^{4-} units, and those of SiO_4^{4-} ions are combined each other through bridging oxygen ions O^0 . When some basic oxides such as CaO , Na_2O are added in the silicate melts, the network structure is 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^- . Zhang and Jahanshahi⁶⁾ firstly proposed a structurally related model, but this model consists of a regression equation of the numbers of the free oxygen and bridging oxygen using reported measurements.

In the present study, we discuss the effect of structure of binary silicate melts on the viscosity with a new model derived by our research team. The new model reflects the network structure of silicate melts with the bonding state of oxygen ion: the total volume of holes created by adding basic oxides decreases the viscosity. In this model, the bonding states of oxygen ion are estimated by Gaye's model¹⁾ using thermodynamic database.

2. Model**2.1 Viscosity of Silicate Melts**

Pure SiO_2 melt has its own fluidity, which means that there are some inherent holes in the pure SiO_2 melt. **Figure 1** shows temperature dependence of the viscosity of silicate melts in the temperature range between 1973 and 2673K. The best fit result of Arrhenius relationship with the reported measurements⁷⁾⁻¹²⁾ yields the following values.

$$A = 4.80 \times 10^{-8}, \quad E_f = 5.21 \times 10^5 \text{ (J)} \quad (2)$$

Here, the activation energy can be simply assumed to be inversely proportional to the total net movement ($\frac{1}{R}$) of holes in unit time and unit volume. Thus, when E_f decreases, the fluidity of silicate increases.

$$E_f \propto \frac{1}{\left| \frac{1}{R} \right|} \quad (3)$$

Since the hole may move randomly in the silicate, the net movement of the holes is given as Eq.(4) based on the random walk theory.

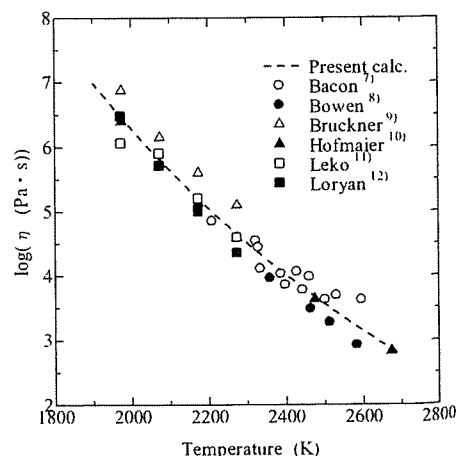


Fig.1 Viscosity of pure SiO_2 melts.

$$R = \sqrt{\beta \cdot N_\beta} \cdot r \quad \left(|\vec{R}| = \sqrt{\beta \cdot N_\beta} \cdot |\vec{r}| \right) \quad (4)$$

where N_β is the total hole number in unit volume, β is the size factor of each hole and $\vec{r}$ is unit vector for each jump, i.e., the hole may move the distance of $\sqrt{\beta} \cdot r$ at each jump. Then, the activation energy is given as Eq.(5).

$$E_V = \frac{E'}{\sqrt{\beta N_\beta} \cdot r} = \frac{E'}{\beta'^{1/2} r} \quad (5)$$

where E' and β' are constants.

2.2 Viscosity of Binary Melts

The holes in binary silicate melts are inherently different from those in SiO_2 melts, so that the inherent holes and the holes created by addition of basic oxides may move independently. Thus, the total movement of holes is the sum of each movement.

$$R = \sqrt{\beta'} \cdot r + \sqrt{\alpha' (N_{O^{2-}} + N_{O^-})} \cdot r \quad (6)$$

where α' is the size factor of the hole created by addition of basic oxides. Similarly as we derive for SiO_2 , we can obtain the activation energy for binary silicate melts as Eq.(7).

$$E_V = \frac{E'/r}{\beta'^{1/2} + \{(N_{O^{2-}} + N_{O^-}) \cdot \alpha'\}^{1/2}} \quad (7)$$

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

Here, E is the activation energy for pure SiO_2 and α is a relative size factor ($\alpha = \alpha'/\beta'$). This equation shows that the activation energy for viscous flow of silicate melts decreases with the total volume of the free and non-bridging oxygen ions.

Figures 2-4 show the calculated results of the present study with reported measurements of the viscosity in binary silicate melts; SiO_2 -CaO, SiO_2 -MgO and SiO_2 - Al_2O_3 , respectively. $N_{O^{2-}}$ and N_{O^-} are evaluated from Gaye's model stored in thermodynamic database. The size factor of each basic oxide was determined from the application of the above equations to each binary system⁽¹³⁾⁻⁽¹⁸⁾ as follows:

$$\alpha = 2.0 : \text{CaO}, \quad \alpha = 1.8 : \text{MgO} \quad \alpha = 0.95 : \text{Al}_2\text{O}_3 \quad (8)$$

In Fig.5, the change in $N_{O^{2-}}$, N_{O^-} and N_{O^0} with SiO_2 content in the SiO_2 -CaO, SiO_2 -MgO and SiO_2 - Al_2O_3 binary systems are shown. It is noteworthy that N_{O^0} is negligible in the range of $X_{\text{SiO}_2} = 0 - 0.3$ (or 0.4) for SiO_2 -CaO (or MgO) system. Accordingly, the viscosity in this region shows almost constant value. (Figures 2 and 3)

3. Discussion

The size factor α is determined with reported measurements in the present study, and this value may be related to activity of the oxygen ion in the silicate structure or the ionic radius of cations. In Fig.6, the comparison between the size factor and the relative theoretical optical basicity (Λ_{rel}) or the relative ionic radius of cations (Ra_{rel}).

$$\Lambda_{rel} = \Lambda_B / \Lambda_{\text{SiO}_2} \quad (9)$$

$$Ra_{rel} = Ra_{M^{m+}} / Ra_{\text{Si}^{4+}} \quad (10)$$

where Λ_B and Λ_{SiO_2} denote the theoretical optical basicity of basic oxide and SiO_2 respectively. Duffy *et al.*⁽¹⁹⁾⁻⁽²²⁾ proposed the optical basicity using electronegativity, whereas Nakamura *et al.*⁽²³⁾⁻⁽²⁴⁾ suggested the optical

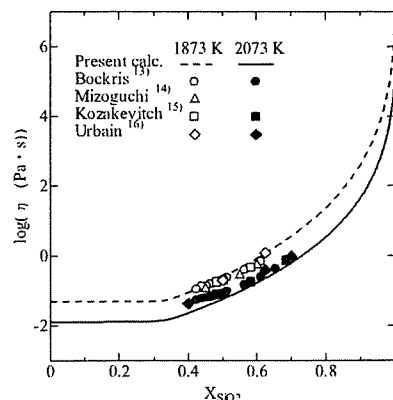


Fig.2 Viscosity of SiO_2 -CaO melts.

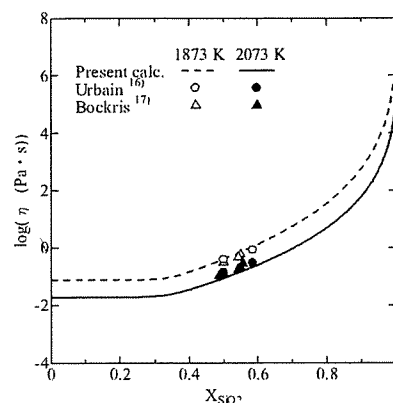


Fig.3 Viscosity of SiO_2 -MgO melts.

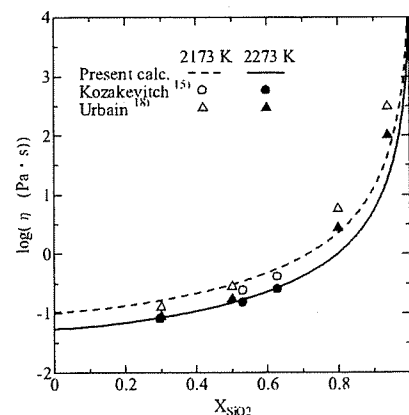


Fig.4 Viscosity of SiO_2 - Al_2O_3 melts.

basicity using the average electron density. In this calculation, the latter case was used. (The theoretical optical basicity calculated by the electronegativity shows almost the same value as that by the electron density.) As shown in Fig.6, the size factor shows reasonable accordance with the relative theoretical optical basicity. The size factor also has a linear relationship with relative ionic radius of cations, which supports that the hole size would increase with the cation size nearby. The physical meaning of the size factor is unclear at the present, but is considered to have some relation with the electronic state of the free or non-bridging oxygen ions that may be affected by the cations nearby.

It is known that Arrhenius plots used in the present work for silicate shows a slight curvature, so that the parameter A in Eq.(1) should be expressed as a function of temperature dependence over a wide range of temperature. Weymann relation²⁵⁾ expressed by Eq.(10) may reasonably display experimental data in much wide temperature range, but theoretical approach has not been proved enough.

$$\eta = A_w T \exp\left(\frac{E_w}{RT}\right) \quad (10)$$

4. Conclusions

In the present study, a new model was suggested which describes the viscosity of binary silicate melts. This model reflects the structure of silicate melts with theoretical variables using Gaye's model: as the total volume of holes (or total number of free or non-bridging oxygen ions) created by adding basic oxides increases, the viscosity of binary silicate melts decreases.

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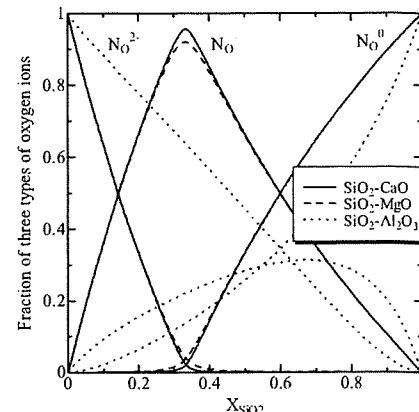


Fig.5 Composition dependence of the fractions of three types of oxygen ions.

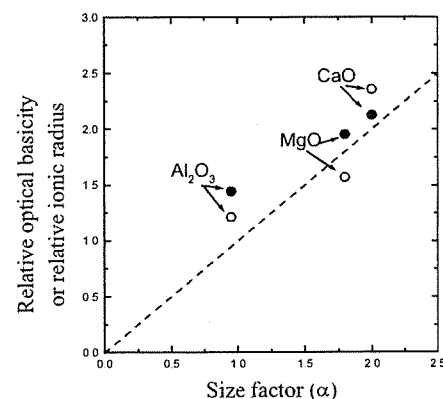


Fig.6 Comparison between the size factor and the relative optical basicity (solid circles) or the relative ionic radius of cations (open circles)