Effect of Potassium Oxide Addition on Viscosity of Calcium Aluminosilicate Melts at 1 673–1 873 K

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We investigated the changes induced in the viscosities of CaO–SiO2–Al2O3–K2O melts (CaO/SiO2 molar ratio = 0.68 ± 0.04, Al2O3 content = 13.4 ± 0.6 mol%) with the addition of K2O in amounts of 0–17.4 mol% for temperatures of 1 673–1 873 K using the rotating crucible method. The viscosity increased with an increase in the K2O content when K2O/Al2O3 molar ratio < 0.7. On the other hand, the viscosity decreased with the addition of K2O for K2O/Al2O3 molar ratio > 0.9. The maximum values of the viscosities were noticed in the range of 0.7 < K2O/Al2O3 molar ratio < 0.9. This behavior could not be explained on the basis of the polymerization degree of the aluminosilicate network structure. The 17O magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum of the 31.6CaO-44.2SiO2-13.4Al2O3-10.8K2O (mol%) glass suggested that K+ ions preferentially compensate the negative charge of AlO4 tetrahedra, while the Ca2+ ions primarily create non-bridging oxygens (NBOs). The viscosity data and the 17O MAS NMR spectrum also suggested that the increase in viscosity for K2O/Al2O3 molar ratio < 0.7 was because of the increase in the average bond strength of the aluminosilicate framework, which was attributable to the substitution of Ca2+ ions by K+ ions at the charge compensator sites. The activation energies for viscous flow indicated that the NBOs bonded with K+ ions, forming NBO-K species, for K2O contents greater than those corresponding to the viscosity maxima. Thus, the viscosities of aluminosilicate melts are indicative of the average bond strengths of the melts.

KEY WORDS: viscosity; K–Ca aluminosilicate melts and glasses; 17O MAS NMR spectroscopy.

1. Introduction

Calcium aluminosilicate melts, which are highly viscous liquids, are found in the blast furnace slags and mold fluxes produced during iron and steelmaking processes. The chemical compositions of these melts lie mostly in the percalcic region (CaO/Al2O3 molar ratio > 1)1−2) of the CaO–SiO2–Al2O3 ternary system. Similar melts can also be extracted from the melting furnaces used for the incineration of municipal waste.3) Since the viscosity (i.e., fluidity) of these melts is strongly linked to the efficiency of their formation and removal processes, controlling the viscosity of the melts, which is a basic physicochemical property, at high temperatures is an important goal. The viscosity of the melts is also indicative of their microstructures.

The conventional view holds that the structure of calcium aluminosilicate consists of a three-dimensional (3D) aluminosilicate network formed by connections between the framework species, such as SiO44− and AlO45− tetrahedra.4) In melts with percalcic compositions, there are enough Ca ions to compensate for the negative charges of the AlO4 tetrahedra (i.e., there are enough charge compensators).5) In addition, more Ca ions than are required for charge compensation are present, and these excessive ions break the connections between the framework species (i.e., they act as network modifiers), resulting in the creation of non-bridging oxygens (NBOs) in the melts.6) The viscosity of silicate-based systems has traditionally been explained in terms of the degree of polymerization of the above-mentioned 3D network structure. A common approach to decreasing the viscosity of the calcium aluminosilicate melts is to add alkali oxides such as Na2O, which can break the connections between the framework species. In fact, alkali oxide additives (Li2O, Na2O, and K2O) can effectively decrease the viscosity of calcium silicate melts that do not contain Al2O3.6,7) In contrast, it has been found8) that the viscosity of certain CaO–SiO2–Al2O3 melts (CaO/SiO2 molar ratio = 0.7–1.3, Al2O3 content = 10–14 mol%) increases after the addition of K2O, even though the degree of polymerization of the aluminosilicate network should decrease after the
addition. Similar phenomena have been observed by other researchers as well.\cite{1, 9–11} Recently, Zhang and Chou\cite{11} examined the effects of K\textsubscript{2}O addition on the viscosity of CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} melt for Al\textsubscript{2}O\textsubscript{3} content of 2–10 mol\%. They found viscosity of the 38.2CaO–59.8SiO\textsubscript{2}–2.0Al\textsubscript{2}O\textsubscript{3} (mol\%) melt increased with the K\textsubscript{2}O addition when K\textsubscript{2}O content was less than 3 mol\%, but decreased with K\textsubscript{2}O content when K\textsubscript{2}O content > 3 mol\%. (i.e., viscosity had the maximum point along the K\textsubscript{2}O content.) These findings indicate that the K–AlO\textsubscript{4} interaction has an impact on the viscosity of CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} melts. However, the underlying mechanism of this interaction remains to be elucidated. For instance, it is not known at which composition is the viscosity maximum when K\textsubscript{2}O is added to CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} melts containing Al\textsubscript{2}O\textsubscript{3} in large amounts (> 10 mol\%); such melts form a large fraction of the slags extracted from the melting furnaces used for the incineration of municipal waste.

In this study, we investigated the changes induced in the viscosity of a selected calcium aluminosilicate melt when K\textsubscript{2}O was added to it in different amounts. The experiments were performed using the rotating crucible method over temperatures of 1 673–1 873 K. \textsuperscript{17}O magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy was used to identify the bonding species present in the investigated quaternary aluminosilicate system. The viscosity data were compared with the recently reported structural models of alkaline and alkaline earth aluminosilicate melts and glasses.

2. Experimental

2.1. Viscosity Measurements

2.1.1. Apparatus

The viscosities of the sample melts were measured using the rotating crucible method.\cite{6, 8, 12} The measurement process has been described in detail previously.\cite{12} The crucible (inner diameter: 30 mm; thickness: 1 mm; height: 27 mm) and the bob (10 mm \times 4 mm) employed in the experiments were both made of Pt-20mass\%Rh. The relative torque exerted on the inner cylinder (bob), which was suspended by a steel wire (diameter: 0.30 mm) on top of the apparatus, was determined using a difference transformer, which transformed it into the equivalent electrical voltage. The apparent viscosity of the test sample was calculated on the basis of the relationship between the viscosity and the electrical voltage value, which was determined beforehand using several different silicone oils (viscosity range: 0.10–1.0 Pa s). The measured apparent viscosity was corrected to allow for the thermal expansion of the crucible and the bob using the following equation:

\[ \eta = \frac{\eta'}{(1 + \alpha T)} \]

where \(\eta, \eta', \alpha,\) and \(T\) are the viscosity, apparent viscosity, thermal expansion coefficient of the material used to make the bob and the crucible, and absolute temperature, respectively.

The viscometer was calibrated at a high temperature (1 523–1 673 K) using standard reference materials for high-temperature viscosity measurements (SRM2 type slags).\cite{12}

2.1.2. Measurement Procedure

The test sample, which was in the form of a powder (see Section 2.2.) was placed in the Pt-20mass\%Rh crucible and heated to 1 873 K in air. Then, the inner cylinder (i.e., the Pt-20mass\%Rh bob) was immersed (immersion depth: 10 mm) into the sample melt. Subsequently, the crucible was rotated at 60 rpm in order to measure the electrical voltage signal attributable to the torque on the bob. The viscosity measurements were performed during the cooling of the melt for temperatures that varied in steps of 25 or 50 K; the lower limit of the measurement temperature was 1 673 K. In case the melting points of the samples were higher than 1 673 K, the measurements were not performed below the melting point. The sample was melted at each examined temperature until the detected voltage (which was proportional to the viscosity of the sample) became constant. The viscosity was measured thrice at each investigated temperature. The repetitive errors in the viscosity measurements were around ±3%. Next, the sample was re-heated to 1 873 K and melted for 30 min. After the completion of the melting process, the crucible was removed from the top of the furnace, and the sample melt was poured on a copper plate and quenched to obtain a sample in the glassy state by pressing the melt with another copper plate. The quenched sample was then analyzed chemically.

2.2. Preparation of Samples for Viscosity Measurements

The test samples were prepared from reagent grade SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, CaCO\textsubscript{3}, and K\textsubscript{2}CO\textsubscript{3} powders (Sigma Aldrich, Inc.). The powders were weighed with precision in the correct amounts to form the melts with the target compositions and were thoroughly mixed in a mullite mortar. The powder mixture was placed in a Pt crucible and melted at 1 823 K in a resistance furnace for 20 min in air. Finally, the melt were quenched on a copper plate. The quenched sample was crushed into a powder, and this powder was employed for the viscosity measurements.

Table 1 shows the chemical compositions of the various samples after the viscosity measurements, as determined through wet chemical analyses. The Al\textsubscript{2}O\textsubscript{3} content and CaO/ SiO\textsubscript{2} molar ratio of the samples were 13.4 ± 0.6 mol\% and 0.68 ± 0.04, respectively. The amount of K\textsubscript{2}O present, which was mostly replaced by CaO and SiO\textsubscript{2}, was 0–17.4 mol\% (i.e., the K\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} molar ratio was 0–1.3). In addition,
some of the K$_2$O evaporated from the charged mixture during sample synthesis and the viscosity measurements. The fraction of the K$_2$O that evaporated from the charged mixture (i.e., the amount of K$_2$O that evaporated/amount of K$_2$O added ratio) was 7–13%. The samples were labeled according to the chemical compositions as CASK$_x$, with $x = K_2$O content (mol%). In the present paper, the relationship between the analyzed compositions of the samples after viscosity measurements and the viscosity data were discussed.

2.3. $^{17}$O MAS NMR Spectroscopy of 31.6CaO-44.2SiO$_2$-13.4Al$_2$O$_3$-10.8K$_2$O (mol%) Glass

Since $^{17}$O atoms are present naturally in amounts too low (0.037%) to allow for $^{17}$O NMR spectroscopy, their concentration in the test sample should be increased. However, the $^{17}$O enrichment of glass is a complicated process. Therefore, $^{17}$O MAS NMR spectroscopy was performed on a glass with a nominal composition of 31.6CaO-44.2SiO$_2$-13.4Al$_2$O$_3$-10.8K$_2$O (mol%) ($\text{CaO}/\text{SiO}_2 = 0.7$; Al$_2$O$_3$ content = 13.4 mol%). This $^{17}$O-enriched 31.6CaO-44.2SiO$_2$-13.4Al$_2$O$_3$-10.8K$_2$O (mol%) glass was fabricated by melting a mixture of CaCO$_3$, Al$_2$O$_3$, and K$_2$CO$_3$ powders (Sigma Aldrich, Inc.) and $^{17}$O-enriched SiO$_2$ at 1873 K for 90 min in an Ar atmosphere; the mixture was wrapped in a Pt foil. The $^{17}$O-enriched SiO$_2$ was prepared from 40% enriched H$_2$ $^{17}$O (ISOTEC) and SiCl$_4$ (Sigma Aldrich, Inc.), according to literature protocol. After the completion of the melting process, the melt was quenched on a copper plate. The quenched vitreous sample was then crushed into a powder and used for the NMR measurement.

An $^{17}$O MAS NMR spectrum was collected using a Varian Inova 500 (11.7 T) spectrometer at Larmor frequency of 67.76 MHz. A Varian/Chemagnetics 3.2 mm T3 HX MAS probe was used with a spinning rate of 20 kHz. A small (solids 18°) tip angle was applied for a single pulse experiment; a pulse recycle delay was long enough to allow full relaxation. The $^{17}$O chemical shift was referenced to pure water.

3. Results

3.1. Temperature Dependence of the Viscosities

Figure 1 and Table 2 show the temperature dependence of the viscosities of the CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts. The measured viscosity of the CAS melt was close to that reported for a melt with a similar composition by Machin and Yee. For the investigated range of temperatures, the temperature dependence of the viscosity can be expressed by the Arrhenius-type equation shown below.

$$\log \eta = A + B / T$$

where $\eta$ is the viscosity (Pa·s), $T$ is the absolute temperature, and $A$ and $B$ are the fit parameters, which were obtained using a linear regression model; the values of $A$ and $B$ are listed in Table 3. This type of an equation is normally used for the viscosity measurements of the various CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts. The temperatures in the parentheses are the melting points ($T_m$) of the samples determined by differential thermal analysis (DTA); the heating rate was 15 K/min and the analyses were performed in air.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>Viscosity, $\eta$/Pa·s</th>
</tr>
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<tbody>
<tr>
<td>1873</td>
<td>1.31</td>
</tr>
<tr>
<td>1848</td>
<td>–</td>
</tr>
<tr>
<td>1823</td>
<td>1.95</td>
</tr>
<tr>
<td>1798</td>
<td>–</td>
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<td>–</td>
</tr>
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<td>1723</td>
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</tr>
<tr>
<td>1698</td>
<td>–</td>
</tr>
<tr>
<td>1673</td>
<td>8.33</td>
</tr>
</tbody>
</table>

Fig. 1. Temperature dependence of the viscosities of the CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts. (a) Data for CAS, CASK8, and CASK10; the viscosity data for a 34CaO-53SiO$_2$-13Al$_2$O$_3$ (mol%) melt, measured by Machin and Yee, is also plotted. (b) Data for CASK12, CASK14, and CASK17.
to express the viscosity-temperature relationship for viscosities of 1–10$^4$ Pa·s.\textsuperscript{15,16} The activation energy of the viscous flow, $E$ (J·mol$^{-1}$), can be calculated using the following equation and the fit parameter $B$.

$$E = 2.303 \times R \times B \quad \text{(3)}$$

where $R$ is the gas constant (= 8.314 J·mol$^{-1}$·K$^{-1}$). The relationship between $E$ and the K$_2$O content is plotted in Fig. 2. The $E$ value increased with an increase in the amount of K$_2$O added for K$_2$O/Al$_2$O$_3$ molar ratio < 0.7. It is also worth noting the $E$ value decreased markedly in the range of 0.7 < K$_2$O/Al$_2$O$_3$ molar ratio < 0.9.

### 3.2. Change in Viscosity with K$_2$O Content

The change in the viscosity with the K$_2$O content is shown in Fig. 3 for three temperatures, namely, 1773 K, 1823 K, and 1873 K. The viscosity increased with an increase in the K$_2$O content when K$_2$O/Al$_2$O$_3$ molar ratio < 0.7, but decreased when the K$_2$O content was K$_2$O/Al$_2$O$_3$ molar ratio > 0.9. Otherwise, the maxima of the viscosity were noticed in the range of 0.7 < K$_2$O/Al$_2$O$_3$ molar ratio < 0.9 (i.e., in the 10.1–12.0 mol% K$_2$O region). This trend was observed for all the investigated temperatures.

### 3.3. $^{17}$O MAS NMR Spectrum of 31.6CaO-44.2SiO$_2$-13.4Al$_2$O$_3$-10.8K$_2$O (mol%) Glass

$^{17}$O NMR spectroscopy is a powerful technique for elucidating the structure of aluminosilicate systems from an oxygen-centered view.\textsuperscript{17,18} Because the cationic species in aluminosilicate glasses are linked by oxygen ions, the $^{17}$O NMR signal can be used to determine the type of bonding species present in the test sample.

The $^{17}$O MAS NMR spectrum of the 31.6CaO-44.2SiO$_2$-13.4Al$_2$O$_3$-10.8K$_2$O (mol%) glass is shown in Fig. 4. The spectrum had two main peaks, at 43 ppm and 110 ppm, respectively. The peak at 43 ppm could be assigned to the signal from bridging oxygens (BOs) in the glass.\textsuperscript{18,19} Further, the position of the peak at 110 ppm was similar to that of the NBO peaks reported in the case of CaO–SiO$_2$–Al$_2$O$_3$ glasses.\textsuperscript{18,19} Thus, the higher frequency side of the signal can be attributed to the NBOs connected to calcium ions (i.e., to NBO-Ca species). The area fraction corresponding to the NBO signal (i.e., the NBO concentration) was estimated to be 32.4 ± 0.3% using Gaussian fitting. It has been reported that NBO peak in potassium silicate glass (i.e., NBO-K peak) was found around 70 ppm.\textsuperscript{20,21} However, signal was not detected around 70 ppm in the present test sample. This indicates that most of the K$^+$ ions added to the glass did not act as network modifiers but behaved as charge
compensators with respect to AlO₄. This tendency indicates that larger cations with smaller charges (i.e., K⁺ ions) are more likely to behave as charge compensators for AlO₄. A similar type of atomic arrangement has been observed in Ca–Na aluminosilicate glasses as well. 📌

4. Discussion

4.1. Effect of Degree of Polymerization of the Network Structure on Viscosity

Toplis and Dingwell have suggested that, in the case of melts with viscosities of 1–10⁶ Pa·s, the viscosity is a reflection of the average bond strength in the melts. 📋 The strong bonds that exist between/among the framework species (i.e., the Si–O–Si and Si–O–Al bonds) become weak owing to the breakage of the connections; this occurs when NBOs (e.g., NBO-Ca and NBO-K species) are formed. In such a case, the extent of the connections in the melts (i.e., the degree of polymerization of the network structure) can be a rough measure of the average bond strength in the melts. In the present study, the degree of polymerization of the silicate and aluminosilicate network was expressed on the basis of the concentration of NBOs. 📊 The concentration of the NBOs, that is, the NBO fraction (%), can be calculated using the chemical compositions of the samples, shown in Table 1, as follows.

\[
\text{NBO fraction (\%)} = 100 \times \frac{2 \times \text{O(at\%)} - 4 \times \text{Si(at\%)} - 4 \times \text{Al(at\%)}}{\text{O(at\%)} - \ldots \ldots (4)}
\]

where O(at%), Si(at%), and Al(at%) are the atomic fractions of O, Si, and Al, respectively, in the melts. Figure 5 shows the changes in the NBO fraction and viscosities with the K₂O content. Equation (4) has been used previously as well to estimate the NBO fraction in percalcic aluminosilicate systems. In fact, the calculated NBO fraction was close to the value determined using ¹⁷O MAS NMR spectroscopy (32.4 ± 0.3%) (see Fig. 5). The NBO fraction increased monotonically with an increase in the K₂O content. That is to say, the aluminosilicate network structure depolymerized after the addition of K₂O. On the other hand, the viscosity increased for K₂O/Al₂O₃ molar ratio < 0.7 (see Fig. 3). This finding suggests that the average bond strength in aluminosilicate melts cannot be described on the basis of the degree of polymerization alone.

4.2. Variation in Average Bond Strength of Aluminosilicate Framework with the Type of Charge Compensator Cations

Roy and Navrotsky have reported that the average strength of bonds in the aluminosilicate network structure increases with a decrease in the cationic potential, Z/r, of the charge compensator cations in the fully polymerized alkali and alkaline-earth aluminosilicate glasses; here, Z is the valence number and r is the cationic radius. It was noticed that the viscosity of the fully polymerized aluminosilicate melts did increase with a decrease in the cationic potential, in keeping with the results of previous studies. 📊 The cationic potential of the K⁺ ions (0.72) was significantly smaller than that of the Ca²⁺ ions (2.0). The ¹⁷O MAS NMR spectrum showed clearly that, when the K⁺ ions were present in a large concentration, they compensated for the negative charge on AlO₄ when the nominal K₂O content was 10.8 mol%; the Ca²⁺ ions preferentially created NBOs. In this scenario, the increase in the viscosity after the addition of K₂O in the lower K₂O content region (K₂O/Al₂O₃ molar ratio < 0.7) is attributable to the increase in the average bond strength of the aluminosilicate framework, owing to the substitution of the charge compensator Ca²⁺ ions with K⁺ ions. In addition, the viscosity data imply that the increase in the average bond strength owing to the formation of AlO₄ that was compensated by K⁺ was larger than the decrease in the average bond strength owing to the formation of NBOs connected with Ca²⁺ ions (i.e., NBO-Ca).

The decrease in the viscosity for higher K₂O contents (K₂O/Al₂O₃ molar ratio > 0.9) may be indicative of the increase in the number of NBOs connected with K⁺ ions (i.e., in the number of NBO-K species). If that is the case, the activation energy for the viscous flow (E) also reflects the change in the structure of the melts. 📋 The E values for the binary alkali or alkaline earth silicate melts decreased gradually with an increase in the amount of alkali or alkaline earth oxides added when the concentration of the alkali or alkaline earth oxides > 20 mol%. On the other hand, the E values drastically changed with an increase in the valence number of the metallic cations; binary alkaline earth silicate melts have larger E values than those of binary alkali silicate melts. 📊 The difference in the activation energies of CASK10 and CASK12, which was 40 ± 2 kJ·mol⁻¹ (see Fig. 2), was close to the difference in the activation energies (~40–50 kJ·mol⁻¹) of binary alkaline earth silicate and alkalai silicate systems. This result indicated that NBO-K species were present in the case of K₂O contents higher than that corresponding to the viscosity maxima. However, ¹⁷O
MAS NMR measurements must be made in the higher K₂O content region (i.e., for K₂O/Al₂O₃ molar ratio > 0.9) in order to unambiguously prove the presence of NBO-K species.

5. Conclusion

The additive effect of K₂O on the viscosity of percalcic CaO–SiO₂–Al₂O₃ melts was investigated using the rotating crucible method. The increase in the viscosity with an increase in the amount of K₂O added implied that the average bond strength of the aluminosilicate framework increased significant with the addition of K₂O. This was owing to the substitution of Ca⁺ ions by K⁺ ions at the charge compensator sites in the lower K₂O content region (K₂O/Al₂O₃ molar ratio < 0.7). In contrast, the viscosity decreased with an increase in the amount of K₂O added when K₂O/Al₂O₃ molar ratio > 0.9; this phenomenon can be explained by the increase in the number of NBO-K species in the melts. The change in the activation energy for viscous flow was indicative of the presence of NBO-K species in the melts with K₂O contents higher than that corresponding to the viscosity maxima.

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