VISCOSITY AND STRUCTURE OF QUATERNARY ALUMINOSILICATE MELTS

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ABSTRACT

In the present work, the effects of R₂O (R=Li, Na and K) or RO(R=Ba, Mg) additives on the viscosities of CaO-SiO₂-Al₂O₃ (CaO/SiO₂=0.67, 1.00 or 1.22, Al₂O₃=20mass%) melts have been measured by using rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ²⁷Al MAS-NMR. The viscosities of CaO-SiO₂-Al₂O₃-R₂O quaternary melts decreased with the addition of Li₂O or Na₂O. However, the viscosity of the melts increased with the addition of K₂O. In the case of CaO-SiO₂-Al₂O₃-RO quaternary melts, the viscosities of the melts with CaO/SiO₂=0.67 decreased with the addition of BaO or MgO, however, the viscosities of the melts with CaO/SiO₂=1.00 and 1.22 increased with the addition of BaO. In the case of CaO-SiO₂-Al₂O₃-R₂O, ²⁷Al MAS-NMR spectra indicated that the amount of Al³⁺ in tetrahedral coordination (Al³⁺(4)), which behaved as a network-former, was increased with addition of R₂O. However, no significant difference in quantity of Al³⁺(4) was observed among the glasses containing different kind of additives (Li₂O, Na₂O or K₂O). In the case of CaO-SiO₂-Al₂O₃-RO, the analysis of ²⁷Al MAS-NMR spectra indicated that the amount of Al³⁺(4) was not changed from CaO-SiO₂-Al₂O₃ ternary glass. These results suggest that the increase in viscosity of CaO-SiO₂-Al₂O₃-K₂O or CaO-SiO₂-Al₂O₃-BaO is not dependent on the increase of Al³⁺(4). It is estimated from the results that the polymerization degree of aluminosilicate anion have been affected by the kind of charge compensating cations.
INTRODUCTION

Several factors not only in a blast furnace but also melting furnace of waste or refuse incineration residue process, such as the rate of various reactions and the fluid flows, are affected by the properties of molten slag. It is also well known that the viscosity is an important physical property for understanding the network structure of slag melts and for simulating the rate of various phenomena in high temperature processes. The slags employed not only in iron-making process but also in melting treatments of the incineration residuals are mainly composed of CaO, SiO₂, Al₂O₃, R₂O (alkali oxide) and RO (alkaline earth oxide) [1]. In addition, amphoteric behavior of Al₂O₃ in molten slag is chemically complex. Hence it is important to determine the relationship between systematically varying composition and viscosity of aluminosilicate melts.

In the present work, the effect of R₂O (R=Li, Na and K) or RO (R=Ba and Mg) additives on the viscosity of CaO-SiO₂-Al₂O₃ (CaO/SiO₂=0.67, 1.00 or 1.22, Al₂O₃=20 mass%) slag has been measured by using rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ²⁷Al MAS-NMR spectra and then the amphoteric behaviors of Al₂O₃ have been discussed.

METHODOLOGY

Viscosity Measurements

The outer cylinder rotating viscometer [2] was employed for viscosity measurements. The samples for viscosity measurements were CaO-SiO₂-Al₂O₃ (CaO/SiO₂=0.67, 1.00 or 1.22, Al₂O₃=20mass%)-R₂O (R=Li, Na or K; R₂O=5, 10, 15mass%) quaternary slags and CaO-SiO₂-Al₂O₃ (CaO/SiO₂=0.67, 1.00 or 1.22, Al₂O₃=20mass%)-RO(R=Mg or Ba; RO=5, 10, 15mass%) quaternary slags. The Samples were prepared from reagent grade SiO₂, CaCO₃, Al₂O₃, Li₂O, Na₂O, K₂O, MgO or BaCO₃ powders. These reagents were precisely weighed to form given compositions, and mixed in an alumina mortar thoroughly. The sample was pre-melted in a resistance furnace using Pt crucible under air and then quenched on a copper plate. The sample was crushed into powder and then these powders were used for viscosity measurements.

²⁷Al MAS-NMR Spectroscopy

The samples for the measurements of ²⁷Al MAS-NMR spectroscopy were CaO-SiO₂-Al₂O₃(CaO /SiO₂=0.67, Al₂O₃=20mass%)-R₂O (R=Li, Na or K) and CaO-SiO₂-Al₂O₃ (CaO/SiO₂=1.22, Al₂O₃=20mass%)-RO(R=Ba and Mg) quaternary glasses. To make clear the effect of the kinds of R₂O or RO additives on the structure of glasses, the content of R₂O or RO additives on these glasses was kept the constant value of 10.8mol% or 7.0mol%, respectively. The glass samples were prepared from reagent grade SiO₂, CaCO₃, Al₂O₃, Li₂O, Na₂O, K₂O, MgO or BaCO₃ powders. These reagents were precisely weighed to form given compositions, and mixed in an alumina mortar thoroughly. The sample was pre-melted in a resistance furnace using Pt crucible for 90 min under air at 1873 K and then quenched on a copper plate. The sample was crushed into powder and then these powders were examined optically and by X-ray diffraction. No Crystalline material was detected. Measurements of ²⁷Al MAS-NMR were made with JEOL CMX300 spectrometer operated at 78.1 KHz (7.0 T). Powdered glass samples were packed in zirconia rotors, and ²⁷Al spectra were obtained using MAS rates of 12 KHz. The chemical shift referenced using aqueous Al₂(SO₄)₃ solution as standards.
RESULTS AND DISCUSSIONS

Viscosity Measurements

In the present work, the viscosities measurements were done at the temperature range from 1673 to 1873 K. Figures 1 shows the temperature dependence of the viscosity in CaO-SiO2-Al2O3-Li2O (CaO/SiO2=0.67, Al2O3=20mass%) quaternary melts, as examples. The relationships between reciprocal temperature and the logarithm of viscosity in CaO-SiO2-Al2O3-Li2O melts are linear in the present study. Therefore, the viscosity data can be described by an Arrhenius type Equation 1 over the entire temperature region in this study:

\[ \eta = A \exp \left( \frac{E_\eta}{RT} \right) \]  

where A, E\( \eta \), R and T are constant, apparent activation energy of viscous flow, gas constant and absolute temperature. The temperature dependences of the viscosities in other compositions also show the same tendency.

Figure 1: Temperature dependence of the viscosity fo (32CaO-48SiO2-20Al2O3)-Li2O(mass%) melts

Figure 2 illustrates the effect of alkali oxide (Li2O, Na2O and K2O) additives on the viscosity of CaO-SiO2-Al2O3 (CaO/SiO2=0.67, 1.00 or 1.22, Al2O3=20mass%) ternary melts at 1873 K. The horizontal axis shows the molar concentration of additive oxides by using the analyzed compositions. The viscosity of CaO-SiO2-Al2O3 ternary melts was found to decrease in order of increasing the basicity (CaO/SiO2). It was clearly found from Figure 2 that the viscosities of these quaternary melts decreased with increasing the additive content of Li2O or Na2O, however, the viscosities of the melts increased with increasing the additive content of K2O.
Figure 2: Effect of alkali oxide additives on the viscosity of CaO-SiO$_2$-Al$_2$O$_3$ (mass%) melts at 1873 K

Figure 3 shows the effect of alkaline earth oxide (BaO and MgO) additives on the viscosity of CaO-SiO$_2$-Al$_2$O$_3$ (CaO/SiO$_2$=0.67, 1.00 or 1.22, Al$_2$O$_3$=20 mass%) ternary melts at 1873 K. The horizontal axis also shows the molar concentration of additive oxides by using the analyzed compositions. It was clearly found from Figure 3 that the viscosities of the quaternary melts with CaO/SiO$_2$ = 0.67 decreased with increasing the additive content of BaO or MgO, however, the viscosities of the melts with CaO/SiO$_2$=1.00 and 1.22 increased by the increasing the additive content of BaO.

In the case of the Al$_2$O$_3$-free CaO-SiO$_2$ binary system, the viscosity of the melt decreased linearly with the addition of K$_2$O or BaO [3]. These results suggest that the behavior of Al$_2$O$_3$ will affect the viscosity of CaO-SiO$_2$-Al$_2$O$_3$-(R$_2$O or RO) quaternary melts. It is well known that Al$_2$O$_3$ is amphoteric oxide [4, 5] and its behavior depends on the basicity of...
melts to which it is added. In the present work, the amphoteric behavior of Al$_2$O$_3$ in the quaternary aluminosilicate melts has been clarified by using $^{27}$Al MAS-NMR spectroscopy.

$^{27}$Al MAS-NMR Spectroscopy

Figures 4 and 5 show the $^{27}$Al MAS-NMR spectra of CaO-SiO$_2$-Al$_2$O$_3$-R$_2$O (CaO/SiO$_2$= 0.67, Al$_2$O$_3$= 20 mass%) glasses, and that of CaO- SiO$_2$-Al$_2$O$_3$-RO (CaO/SiO$_2$=1.22, Al$_2$O$_3$=20 mass%) glasses. It is reported that $^{27}$Al MAS-NMR spectra of aluminosilicate glasses shows three different signals at -10~+20 ppm, at 37 ppm and at +50~+80 ppm, and that the signals at -10~+20 ppm, and at +50~+80 ppm are attributed to octahedrally (Al$^{3+}$(6)) and tetrahedrally (Al$^{3+}$(4)) coordinated Al$^{3+}$, and the signal at 37 ppm is attributed to distorted tricluster-forming Al-O$_4$ tetrahedra [6]. In this study, $^{27}$Al MAS-NMR spectra were reproduced two peaks for Al$^{3+}$(6) and Al$^{3+}$(4) as drawn with solid lines in Figures 4 and 5.

From Figure 4, the resonance position of spectra is shifted from ≈ 50 ppm of the mother glasses to a downfield with the addition of R$_2$O. It is also found that the peak for Al$^{3+}$(6) (network-modifier) of the mother glasses decrease, and the peak for Al$^{3+}$(4)(network-former) of the glasses increase with the addition of R$_2$O. No significant difference of the relative areas of Al$^{3+}$(6) (34.6±0.7%) or Al$^{3+}$(4) (65.4±0.7%) for the glasses with addition of the different kinds of R$_2$O is observed. These results suggest that the increase in viscosity of CaO-SiO$_2$-Al$_2$O$_3$-K$_2$O melts shown in Figure 2 is not dependent on the increase of Al$^{3+}$(4), which behaved as a network-former, in the glasses with the addition of K$_2$O.
Figure 5: $^{27}$Al MAS-NMR spectra of (CaO-SiO$_2$-Al$_2$O$_3$) - 7.0mol%RO (R=Mg and Ba, CaO/SiO$_2$=1.22) glasses

From Figure 5, the resonance position of spectra of the glasses with the addition of RO additives is found at $\approx 60$ ppm, and is not change from that of the mother glasses. Compared with the mother glasses, the deconvolution analysis indicated that no significant difference of the relative areas of Al$^{3+}$(6) (40.1±2.0%) or Al$^{3+}$(4) (59.9±2.0%) for the glasses with the addition of MgO or BaO is observed. These results suggest that the increase of Al$^{3+}$(4) in the glasses is not a major factor in the increase in viscosity of CaO-SiO$_2$-Al$_2$O$_3$-BaO melts shown in Figure 3.

Figure 6: Schematic representation of network of tetrahedra formed by Si$^{4+}$, Al$^{3+}$(4) and O$^{2-}$.
Effect of Charge Compensating Cations on the Behaviors of Al$^{3+}$(4) in Aluminosilicate Melts

$^{27}$Al NMR spectra of the quaternary aluminosilicate glasses suggest that the increase in viscosity of CaO-SiO$_2$-Al$_2$O$_3$-K$_2$O or CaO-SiO$_2$-Al$_2$O$_3$-BaO melts are not dependent on the increase of Al$^{3+}$(4).

When Al$^{3+}$(4) are incorporated into the silicate network, it is important that electrical charge-balance be maintained. Namely, AlO$_4$ tetrahedra require a charge compensating alkali or alkaline earth cations as shown in Figure 6. In addition, Varshal [7] pointed out that the strength of Al-O bonds depend on the field strength of a cation compensating for an AlO$_4$ . Therefore, there is a possibility that additive effect of Al$_2$O$_3$ on the viscosity of silicate melts depends on the kind of charge compensating cations.

Figures 7 and 8 show the additive effect of 5mol%Al$_2$O$_3$, which replaced with SiO$_2$, on the viscosity of binary alkali or alkaline earth silicate melts [8, 9]. From the figures, the viscosity of binary silicate melts increased with addition of 5mol%Al$_2$O$_3$. These data suggest that almost all Al$_2$O$_3$ behave as a network-former in those aluminosilicate melts. To evaluate the additive effect of Al$_2$O$_3$ on the viscosity of binary silicate melts quantitatively, the SiO$_2$-equivalence of Al$_2$O$_3$, which represents the additive effect of Al$_2$O$_3$ on the viscosity with reference to same amount of SiO$_2$, have been calculated by the Equation 2:

$$[\text{SiO}_2(\text{mol}%) = a \times \text{Al}_2\text{O}_3(\text{mol}%) + \text{SiO}_2(\text{mol}%)$$

(2)

where Al$_2$O$_3$(mol%) and SiO$_2$(mol%) are the content of Al$_2$O$_3$ and SiO$_2$ in aluminosilicate melts, respectively; [SiO$_2$(mol%)] is the SiO$_2$ content in pseudobinary system that Al$_2$O$_3$ content is converted into SiO$_2$ content. In the case of the composition denoted by the asterisk in Figure 7 (b), the value of [SiO$_2$(mol%)] is indicated by the circle. Figure 9 shows the relationship between Cationic Field Strength (CFS) of charge compensating cations (Equation 3) and the calculated the value a of the SiO$_2$-equivalence of Al$_2$O$_3$: 
Figure 8: Additive effect of Al$_2$O$_3$ on the viscosity of SiO$_2$-RO melts at 1823 K \[8, 9\].

Al$_2$O$_3$ additive was replaced with SiO$_2$ where $Z$ is the valence number of the cation, $r$ is the cationic radius. From the Figure 9 the SiO$_2$-equivalence of Al$_2$O$_3$ decreased with increasing cationic field strength of charge compensating cations. A number of workers have discussed the structure of aluminosilicate melts or glasses. Recently, Lee et al. [10] pointed out that the reaction (Equation 4) displaced to the right with increasing the CFS of charge compensating cation.

$$2(Si \cdot O \cdot Al) = (Al \cdot O \cdot Al) + (Si \cdot O \cdot Si)$$

In other word, the polymerization degree of aluminosilicate anion decreased with increasing the cationic field strength of charge compensating cation. Therefore the SiO$_2$-equivalence of Al$_2$O$_3$ decreased with increasing cationic field strength of charge compensating cations.

It is well known that viscosity of aluminosilicate melts depend on the polymerization degree of aluminosilicate anion, which composed of SiO$_4^{4-}$ and AlO$_4^{5-}$. Hence, the parameter $n$, which represents the amount of network-formers (SiO$_4^{4-}$ and AlO$_4^{5-}$) with the reference to SiO$_2$ in aluminosilicate melts, have been calculated for CaO-SiO$_2$-
Al₂O₃-R₂O (CaO/SiO₂=0.67, Al₂O₃=20mass%, R₂O= 10.8mol%) and CaO-SiO₂-Al₂O₃-RO (CaO/SiO₂=1.22, Al₂O₃=20mass%, R₂O= 7.0mol%) system by using the Equation 5:

\[ \text{Parameter } n = a \cdot \text{Al}_2\text{O}_3(\text{mol%}) + \text{SiO}_2(\text{mol%}) \]  

(5)

where \(a\) is the SiO₂-equivalence of Al₂O₃, Al₂O₃(mol%) is molar fraction of Al₂O₃ which behave as a network-former (analyzed by \(^{27}\text{Al}\) MAS-NMR spectra), SiO₂(mol%) is molar fraction of SiO₂. There are two kinds of cations (e.g. Ca²⁺-R⁺ or Ca²⁺-R²⁺) that compensate AlO₄⁻ in the quaternary aluminosilicate melts. In the present work, the AlO₄⁻ assumes to be compensated by cations with lower CFS [11]. Figure 10 shows the relationship between the parameter \(n\) and the viscosity of CaO-SiO₂-Al₂O₃-R₂O (CaO/ SiO₂=0.67, Al₂O₃=20mass%, R₂O=10.8mol%) and CaO-SiO₂- Al₂O₃-RO(CaO/SiO₂=1.22, Al₂O₃=20mass%, RO=7.0mol%) melts (interpolation value). From the figure, the viscosity of quaternary aluminosilicate melts found to be strongly associated with parameter \(n\). These results suggest that the increase in the viscosity of CaO-SiO₂-Al₂O₃-K₂O and CaO-SiO₂-Al₂O₃-BaO system caused by the increase of polymerization degree of aluminosilicate anion. Some ideas of industrial application will be presented on the day of the conference.

![Figure 10: Relationship between the viscosities of CaO-SiO₂-Al₂O₃-R₂O (CaO/SiO₂=0.67, Al₂O₃=20mass%, R₂O=10.8mol%) and CaO-SiO₂-Al₂O₃-BaO (CaO/SiO₂=1.22, Al₂O₃=20mass%, RO=7.0mol%) melts and parameter \(n\)](image)

CONCLUSIONS

The effect of R₂O (R=Li, Na and K) or RO(R=Ba, Mg) additives on the viscosities of CaO-SiO₂-Al₂O₃ (CaO/SiO₂=0.67, 1.00 or 1.22, Al₂O₃=20mass%) melts has been measured by using rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by \(^{27}\text{Al}\) MAS-NMR spectra.

- The viscosities of CaO-SiO₂-Al₂O₃-R₂O quaternary melts decreased with increasing the additive content of Li₂O or Na₂O. However, the viscosities of the melts increased with increasing the additive content of K₂O.

- \(^{27}\text{Al}\) MAS-NMR spectra indicated that the population of (Al³⁺(4)) in the glasses increased with the addition of R₂O, however, that of Al³⁺(4) was independent of the kinds of R₂O additives.
The viscosities of CaO-SiO$_2$-Al$_2$O$_3$-RO quaternary melts with CaO/SiO$_2$=0.67 decreased with increasing the additive content of BaO or MgO, however, the viscosities of the melts with CaO/SiO$_2$=1.00 and 1.22 increased with increasing the additive content of BaO.

$^{27}$Al MAS-NMR spectra indicated that no significant difference of the population of Al$^{3+}$(6) or Al$^{3+}$(4) for the glasses with the addition of MgO or BaO was observed.

The viscosity of CaO-SiO$_2$-Al$_2$O$_3$-R$_2$O (CaO/SiO$_2$=0.67, Al$_2$O$_3$=20mass%, R$_2$O=10.8mol%) and CaO-SiO$_2$-Al$_2$O$_3$-RO (CaO/SiO$_2$=1.22, Al$_2$O$_3$=20mass%, R$_2$O=7.0mol%) melts found to be strongly associated with parameter $n$.

Parameter $n = a\cdot$Al$_2$O$_3$(mol%) + SiO$_2$(mol%)