VISCOSITY AND STRUCTURE OF QUATERNARY ALUMINOSILICATE MELTS

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ABSTRACT

In the present work, the effects of R_2O (R=Li, Na and K) or RO(R=Ba, Mg) additives on the viscosities of CaO-SiO_2-Al_2O_3 (CaO/SiO_2=0.67, 1.00 or 1.22, Al_2O_3=20mass%) melts have been measured by using rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ^{27}Al MAS-NMR. The viscosities of CaO-SiO_2-Al_2O_3-R_2O quaternary melts decreased with the addition of Li_2O or Na_2O. However, the viscosity of the melts increased with the addition of K_2O. In the case of CaO-SiO_2-Al_2O_3-RO quaternary melts, the viscosities of the melts with CaO/SiO_2=0.67 decreased with the addition of BaO or MgO, however, the viscosities of the melts with CaO/SiO_2=1.00 and 1.22 increased with the addition of BaO. In the case of CaO-SiO_2-Al_2O_3-R_2O, ^{27}Al MAS-NMR spectra indicated that the amount of Al^{3+} in tetrahedral coordination ($Al^{3+}(4)$), which behaved as a network-former, was increased with addition of R_2O. However, no significant difference in quantity of $Al^{3+}(4)$ was observed among the glasses containing different kind of additives (Li_2O, Na_2O or K_2O). In the case of CaO-SiO_2-Al_2O_3-RO, the analysis of ^{27}Al MAS-NMR spectra indicated that the amount of $Al^{3+}(4)$ was not changed from CaO-SiO_2-Al_2O_3 ternary glass. These results suggest that the increase in viscosity of CaO-SiO_2-Al_2O_3-K_2O or CaO-SiO_2-Al_2O_3-BaO is not dependent on the increase of $Al^{3+}(4)$. 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 of 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, SiO_2, Al_2O_3, R_2O (alkali oxide) and RO (alkaline earth oxide) [1]. In addition, amphoteric behavior of Al_2O_3 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 R_2O (R=Li, Na and K) or RO (R=Ba and Mg) additives on the viscosity of CaO-SiO_2-Al_2O_3 (CaO/SiO_2=0.67, 1.00 or 1.22, Al_2O_3=20 mass%) slag has been measured by using rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by ^{27}Al MAS-NMR spectra and then the amphoteric behaviors of Al_2O_3 have been discussed.

METHODOLOGY

Viscosity Measurements

The outer cylinder rotating viscometer [2] was employed for viscosity measurements. The samples for viscosity measurements were CaO-SiO_2-Al_2O_3 (CaO/SiO_2=0.67, 1.00 or 1.22, Al_2O_3=20mass%)-R_2O (R=Li, Na or K; R_2O=5, 10, 15mass%) quaternary slags and CaO-SiO_2-Al_2O_3 (CaO/SiO_2=0.67, 1.00 or 1.22, Al_2O_3=20mass%)-RO(R=Mg or Ba; RO=5, 10, 15mass%) quaternary slags. The Samples were prepared from reagent grade SiO_2, $CaCO_3$, Al_2O_3, Li_2O, Na_2O, K_2O, MgO or $BaCO_3$ 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 cupper plate. The sample was crushed into powder and then these powders were used for viscosity measurements.

^{27}Al MAS-NMR Spectroscopy

The samples for the measurements of ^{27}Al MAS-NMR spectroscopy were CaO-SiO_2-Al_2O_3(CaO /SiO_2=0.67, Al_2O_3=20mass%)-R_2O (R=Li, Na or K) and CaO-SiO_2-Al_2O_3 (CaO/SiO_2=1.22, Al_2O_3=20mass%)-RO (R=Ba and Mg) quaternary glasses. To make clear the effect of the kinds of R_2O or RO additives on the structure of glasses, the content of R_2O 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 SiO_2, $CaCO_3$, Al_2O_3, Li_2O, Na_2O, K_2O, MgO or $BaCO_3$ powders. These reagents were precisely weighed to form given compositions, and mixed in an alumina mortar thoroughly. The sample was premelted in a resistance furnace using Pt crucible for 90 min under air at 1873 K and then quenched on a cupper 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 ^{27}Al 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 ^{27}Al spectra were obtained using MAS rates of 12 KHz. The chemical shift referenced using aqueous $Al_2(SO_4)_3$ 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 $CaO-SiO_2-Al_2O_3-Li_2O$ (CaO/SiO_2=0.67, Al_2O_3=20mass%) quaternary melts, as examples. The relationships between reciprocal temperature and the logarithm of viscosity in $CaO-SiO_2-Al_2O_3-Li_2O$ 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:

$$\eta = A\,exp\left(\frac{E_\eta}{RT}\right) \tag{1}$$

where A, E_η, 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.

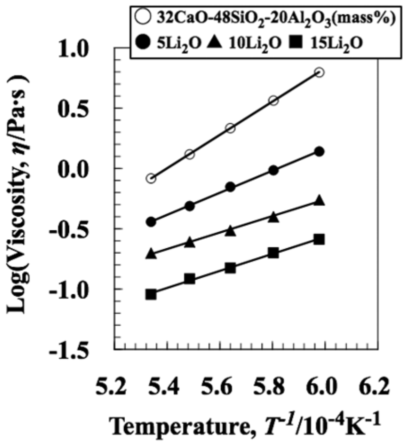

Figure 1: Temperature dependence of the viscosity fo ($32CaO-48SiO_2-20Al_2O_3$)-Li_2O(mass%) melts

Figure 2 illustrates the effect of alkali oxide (Li_2O, Na_2O and K_2O) additives on the viscosity of $CaO-SiO_2-Al_2O_3$ (CaO/SiO_2=0.67, 1.00 or 1.22, Al_2O_3=20mass%) ternary melts at 1873 K. The horizontal axis shows the molar concentration of additive oxides by using the analyzed compositions. The viscosity of $CaO-SiO_2-Al_2O_3$ ternary melts was found to decrease in order of increasing the basicity (CaO/SiO_2). It was clearly found from Figure 2 that the viscosities of these quaternary melts decreased with increasing the additive content of Li_2O or Na_2O, however, the viscosities of the melts increased with increasing the additive content of K_2O.

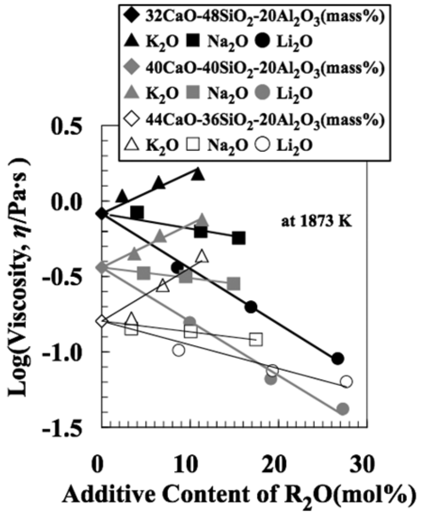

Figure 2: Effect of *alkadi* oxide additives on the viscosity of CaO-SiO_2-Al_2O_3(mass%) melts at 1873 K

Figure 3 shows the effect of alkaline earth oxide (BaO and MgO) additives on the viscosity of CaO-SiO_2-Al_2O_3 (CaO/SiO_2=0.67, 1.00 or 1.22, Al_2O_3=20mass%) 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.

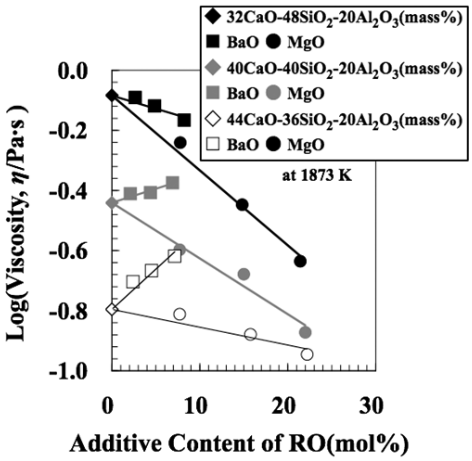

Figure 3: Effect of *alkadi*-earth oxide additives on the viscosity of CaO-SiO_2-Al_2O_3 melts at 1873 K

In the case of the Al_2O_3-free CaO-SiO_2 binary system, the viscosity of the melt decreased linearly with the addition of K_2O or BaO [3]. These results suggest that the behavior of Al_2O_3 will affect the viscosity of CaO-SiO_2-Al_2O_3-(R_2O or RO) quaternary melts. It is well known that Al_2O_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_2O_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_2O_3-R_2O (CaO/SiO_2= 0.67, Al_2O_3= 20 mass%) glasses, and that of CaO- SiO_2-Al_2O_3-RO (CaO/SiO_2=1.22, Al_2O_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 MNR spectra were reproduced two peaks for Al^{3+}(6) and Al^{3+}(4) as drawn with solid lines in Figures 4 and 5.

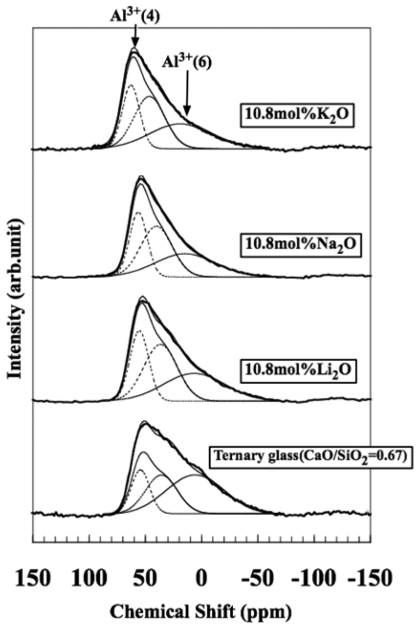

Figure 4: ^{27}Al MAS-NMR spectra of (CaO-SiO_2-Al_2O_3)-10.8 mol%R_2O (R=Li, Na and K, CaO/SiO_2=0.67) glasses

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_2O. 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_2O. 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_2O is observed. These results suggest that the increase in viscosity of CaO-SiO_2-Al_2O_3-K_2O 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_2O.

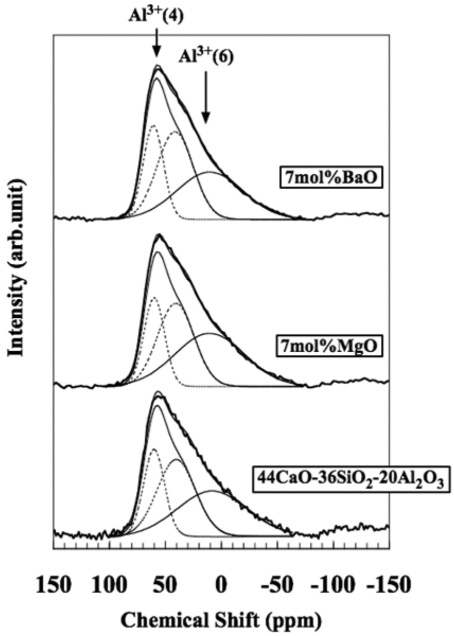

Figure 5: ^{27}Al MAS-NMR spectra of (CaO-SiO_2-Al_2O_3)- 7.0mol%RO (R=Mg and Ba, CaO/SiO_2=1.22) glasses

From Figure 5, the resonance position of spectra of the glasses with the addition of RO additives is found at ≈ 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_2O_3-BaO melts shown in Figure 3.

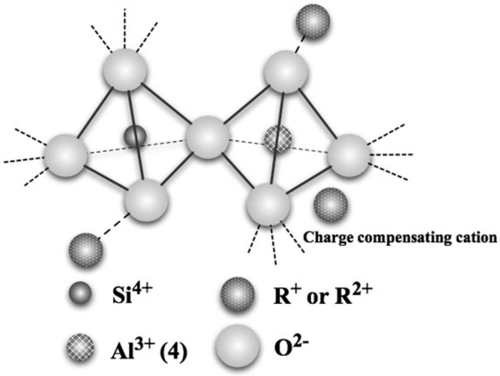

Figure 6: Schematic representation of network of tetrahedra formed bye Si^{4+}, Al^{3+}(4) and O^{2-}

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_2O_3-K_2O or CaO-SiO_2-Al_2O_3-BaO melts are not dependent on the increase of $Al^{3+}(4)$.

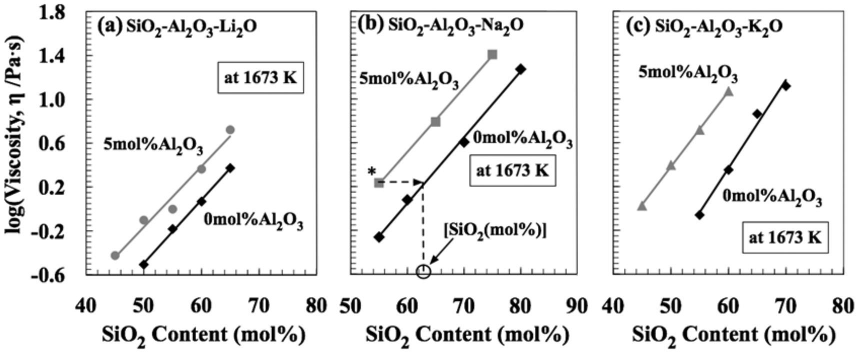

Figure 7: Additive effect of Al_2O_3 on the viscosity of SiO_2-R_2O melts at 1673 K [8, 9]. Al_2O_3 additive was replaced with SiO_2

When $Al^{3+}(4)$ are incorporated into the silicate network, it is important that electrical charge-balance be maintained. Namely, AlO_4^{5-} 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^{5-}. Therefore, there is a possibility that additive effect of Al_2O_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_2O_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_2O_3. These data suggest that almost all Al_2O_3 behave as a network-former in those aluminosilicate melts. To evaluate the additive effect of Al_2O_3 on the viscosity of binary silicate melts quantitatively, the SiO_2-equivalence of Al_2O_3, which represents the additive effect of Al_2O_3 on the viscosity with reference to same amount of SiO_2, have been calculated by the Equation 2:

$$[SiO_2(mol\%)] = \boldsymbol{a} \cdot Al_2O_3(mol\%) + SiO_2(mol\%) \tag{2}$$

where $Al_2O_3(mol\%)$ and $SiO_2(mol\%)$ are the content of Al_2O_3 and SiO_2 in aluminosilicate melts, respectively; $[SiO_2(mol\%)]$ is the SiO_2 content in pseudobinary system that Al_2O_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_2O_3:

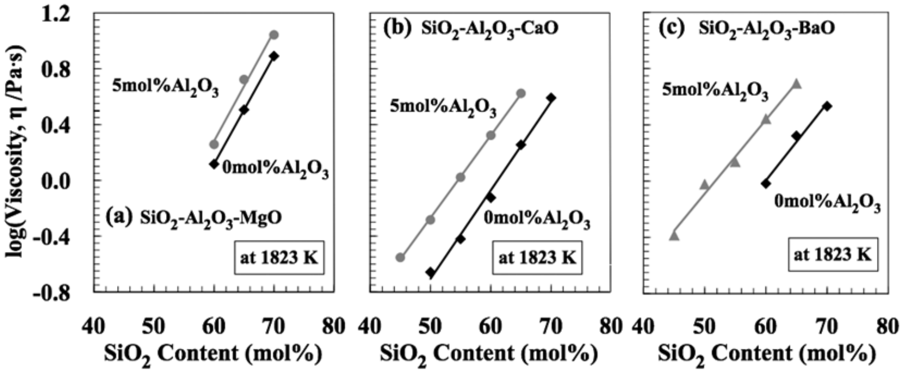

Figure 8: Additive effect of Al_2O_3 on the viscosity of SiO_2-RO melts at 1823 K [8, 9]. Al_2O_3 additive was replaced with SiO_2

$$CFS = \frac{Z}{r^2} \tag{3}$$

where Z is the valence number of the cation, r is the cationic radius. From the Figure 9 the SiO_2-equivalence of Al_2O_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.

$$2(Si\text{-}O\text{-}Al) = (Al\text{-}O\text{-}Al) + (Si\text{-}O\text{-}Si) \tag{4}$$

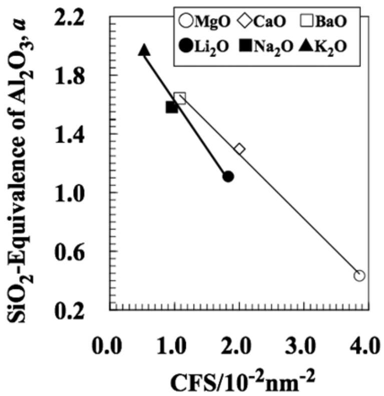

Figure 9: Relationship between the cationic field strength (CFS) and the SiO_2-equivalence of Al_2O_3

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_2O_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-

Al_2O_3-R_2O (CaO/SiO_2=0.67, Al_2O_3=20mass%, R_2O= 10.8mol%) and CaO-SiO_2-Al_2O_3-RO (CaO/SiO_2=1.22, Al_2O_3=20mass%, R_2O= 7.0mol%) system by using the Equation 5:

$$\text{Parameter } \boldsymbol{n} = \boldsymbol{a} \cdot Al_2O_3(mol\%) + SiO_2(mol\%) \quad (5)$$

where *a* is the SiO_2-equivalence of Al_2O_3, Al_2O_3(mol%) is molar fraction of Al_2O_3 which behave as a network-former (analyzed by ^{27}Al MAS-NMR spectra), SiO_2(mol%) is molar fraction of SiO_2. There are two kinds of cations (e.g. Ca^{2+}-R^{+} or Ca^{2+}-R^{2+}) that compensate AlO_4^{5-} in the quaternary aluminosilicate melts. In the present work, the AlO_4^{5-} assumes to be compensated by cations with lower CFS [11]. Figure 10 shows the relationship between the parameter *n* and the viscosity of CaO-SiO_2-Al_2O_3-R_2O (CaO/SiO_2=0.67, Al_2O_3=20mass%, R_2O=10.8mol%) and CaO-SiO_2- Al_2O_3-RO(CaO/SiO_2=1.22, Al_2O_3=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-SiO_2-Al_2O_3-K_2O and CaO-SiO_2-Al_2O_3-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.

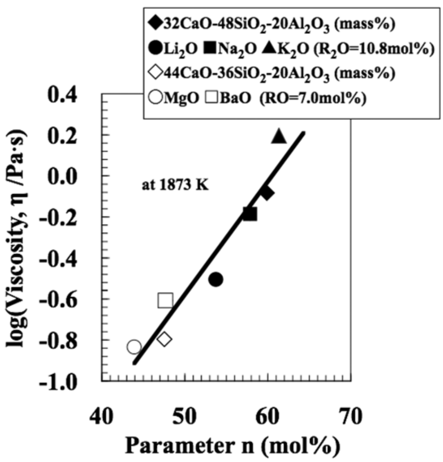

Figure 10: Relationship between the viscosities of CaO-SiO_2-Al_2O_3-R_2O (CaO/SiO_2=0.67, Al_2O_3=20mass%, R_2O=10.8mol%) and CaO-SiO_2-Al_2O_3-BaO (CaO/SiO_2=1.22, Al_2O_3=20mass%, RO=7.0mol%) melts and parameter *n*

CONCLUSIONS

The effect of R_2O (R=Li, Na and K) or RO(R=Ba, Mg) additives on the viscosities of CaO-SiO_2-Al_2O_3 (CaO/SiO_2=0.67, 1.00 or 1.22, Al_2O_3=20mass%) melts 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.

- The viscosities of CaO-SiO_2-Al_2O_3-R_2O quaternary melts decreased with increasing the additive content of Li_2O or Na_2O. However, the viscosities of the melts increased with increasing the additive content of K_2O.
- ^{27}Al MAS-NMR spectra indicated that the population of (Al^{3+}(4)) in the glasses increased with the addition of R_2O, however, that of Al^{3+}(4) was independent of the kinds of R_2O additives.

- The viscosities of CaO-SiO_2-Al_2O_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_2O_3-R_2O (CaO/SiO_2=0.67, Al_2O_3=20mass%, R_2O=10.8mol%) and CaO-SiO_2-Al_2O_3-RO (CaO/SiO_2=1.22, Al_2O_3=20mass%, R_2O=7.0mol%) melts found to be strongly associated with parameter n.

Parameter $n = a \cdot Al_2O_3(\text{mol\%}) + SiO_2(\text{mol\%})$

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