1. Introduction

Viscosity of molten slag changes in wide range depending on temperature and composition. 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 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. Numerous viscosity measurements have been carried out for binary or ternary slag in last decades. Although practical slags related to the processes mentioned above are multi-component systems, there are few data available on their viscosities. Furthermore, errors in the values of viscosity depending on published data range within 25–50%. Thus, the accuracy of measurements in viscosity for multi-component slag is strongly required for understanding of the reaction behavior in high temperature processes.

The slag obtained not only in iron- and steel-making process but also in melting treatments of the incineration residuals are mainly composed of CaO, SiO2 and Al2O3. Here, the effect of adding R2O (R=Li, Na and K) or RO (R=Ba, Mg) on the viscosity of CaO–SiO2–Al2O3 (CaO/SiO2=0.67, 1.00 or 1.22, Al2O3=20 mass%) melts has been measured by rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by 27Al and 29Si MAS-NMR spectra.

The viscosities of CaO–SiO2–Al2O3–R2O quaternary melts decreased with increasing the additive content of Li2O or Na2O. However, the viscosity of the melts increased with increasing the additive content of K2O. In the case of CaO–SiO2–Al2O3–RO quaternary melts, the viscosities of the melts with CaO/SiO2=0.67 decreased with increasing the additive content of BaO or MgO, however, the viscosities of the melts with CaO/SiO2=1.00 and 1.22 increased with increasing the additive content of BaO.

In the case of CaO–SiO2–Al2O3–R2O, the analysis of 27Al MAS-NMR spectra and 29Si MAS-NMR spectra indicated that the degree of polymerization of silicate anions in the glasses decreased with the addition of Li2O or Na2O, and that the degree of polymerization of aluminosilicate anions in the glasses increased with the addition of K2O. It was estimated from the results that the increase in viscosities of CaO–SiO2–Al2O3–K2O melts was dependent on increase of aluminosilicate anions in the melts with the addition of K2O.

In the case of CaO–SiO2–Al2O3–RO, the analysis of 27Al MAS-NMR spectra and 29Si MAS-NMR spectra indicated that the degree of polymerization of silicate and aluminosilicate anions in the glasses decreased with the addition of MgO. The degree of polymerization of aluminosilicate anions in the glasses increased with the addition BaO. It was estimated from the results that the increase in viscosities of CaO–SiO2–Al2O3–BaO melts was dependent on increase of aluminosilicate anions in the melts with the addition of BaO.

KEY WORDS: CaO–SiO2–Al2O3–(R2O or RO); viscosity; 27Al MAS-NMR; 29Si MAS-NMR.
made by using reference slag (SRM2 type slag). The experimental conditions used in this study are summarized in Table 1.

### 2.2. Sample preparation

Samples for viscosity measurement were prepared from reagent grade SiO$_2$, Al$_2$O$_3$, CaCO$_3$, Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, BaCO$_3$ and MgO powders (Sigma-Aldrich Japan). These reagents were precisely weighed to form given compositions (cf. Table 2), and mixed in an alumina mortar thoroughly. The sample was pre-melted in a resistance furnace using Pt crucible for an hour under air. The sample was crushed into powder and then used for measurements.

### 2.3. Viscosity Measurements

The crucible filled with slag powder was placed in a crucible supporter in the furnace and heated up to 1873 K. After then, the molten slag was kept at that temperature until the detected voltage value (Viscosity) became constant.

The measurements were carried out three times at every 50 K interval on cooling. Thereafter, the measurements were repeated at the same temperature on heating. The thermal equilibration time at each temperature setting point was chosen to be 30 min. The average value of these six measurements was used for the measured potential difference. An apparent viscosity was calculated based on the reference relationship between the viscosity and the potential difference, which was obtained by using various silicone oils beforehand. The values were corrected for the thermal expansions of the crucible and the bob using the following equation.

$$\eta = \eta'/(1 + \alpha T)^3 \quad \text{(1)}$$

Where $\eta$, $\eta'$, $\alpha$ and $T$ are viscosity, apparent viscosity, thermal expansion coefficient and absolute temperature, respectively. The scatter of the measured values between on cooling and on heating, and the repetitive error of measurements were both within ±3%. After the viscosity measurements, the quenched slags were used for chemical analysis.

### 2.4. $^{27}$Al and $^{29}$Si MAS-NMR Spectroscopy

The aluminum or silicon environment was investigated by solid-state magic angle spinning-nuclear magnetic resonance (MAS-NMR) of $^{27}$Al or $^{29}$Si on a high-resolution apparatus (CMX300, JEOL, Japan). This corresponds to $^{27}$Al and $^{29}$Si frequencies of 78.1 and 59.5 KHz, respectively. Powdered glass samples were packed in zirconia rotors, and $^{27}$Al and $^{29}$Si spectra were obtained using MAS rates of 12 and 3 KHz. The chemical shifts of $^{27}$Al and $^{29}$Si spectra were referenced using aqueous $\text{Al}_2(\text{SO}_4)_3$ solution and polydimethylsilane (PDMS) as standards.
3. Results and Discussion

3.1. Viscosity of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O Quaternary Melts

Figures 2–4 show the temperature dependence of the viscosity in CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O (R=Li, Na and K, CaO/SiO$_2$=1.00, Al$_2$O$_3$=20 mass%) quaternary melts, as examples. The present result for 40CaO–40SiO$_2$–20Al$_2$O$_3$ (mass%) melts shown in Fig. 2 was in good agreement with the results reported by Machin et al.\textsuperscript{13} and Kozakevitch.\textsuperscript{14} The viscosity of this ternary melts decreased with increasing the additive content of Li$_2$O or Na$_2$O. However, the viscosity of this ternary melts increased with increasing the additive content of K$_2$O.

Figure 5 illustrates the effect of adding oxide (Li$_2$O, Na$_2$O and K$_2$O) 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 shows the molar concentration of additive oxides by using the analyzed compositions. The viscosity of CaO–SiO$_2$–Al$_2$O$_3$ ternary melts was found to decrease in order of increasing the basicity (CaO/SiO$_2$). It was clearly found from Fig. 5 that the viscosities of these quaternary melts decreased with increasing the additive content of Li$_2$O or Na$_2$O, however, the viscosities of the melts increased with increasing the additive content of K$_2$O.

3.2. Viscosity of CaO–SiO$_2$–Al$_2$O$_3$–RO Quaternary Melts

Figures 6 and 7 show the temperature dependence of the viscosity in CaO–SiO$_2$–Al$_2$O$_3$–RO (R=Ba and Mg, CaO/SiO$_2$=1.00, Al$_2$O$_3$=20 mass%) quaternary melts, as
examples. The viscosity of this ternary melts decreased with increasing the additive content of MgO. However, in the case of BaO, the viscosity of the melts increased with increasing the addition content.

Figure 8 illustrates the effect of adding oxide (BaO and MgO) 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 1 873 K. The horizontal axis also shows the molar concentration of additive oxides by using the analyzed compositions. It was clearly found from Fig. 8 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.

It is well known that Al$_2$O$_3$ is amphoteric oxide$^{15,16}$ and its behavior depends on the basicity of melts to which it is added. In the case of the mole ratio Al$_2$O$_3$/RO $<$ 1 (RO: basic oxide), Al$_2$O$_3$ would behave as acid oxide (network former), as described in references.$^{15-17}$ Moreover, the viscosity of 50CaO–50SiO$_2$ (mass%) slag increased linearly with increasing Al$_2$O$_3$ content.$^{10}$ 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.

3.3. Structural Characterizations by $^{27}$Al and $^{29}$Si MAS-NMR

In this study, $^{27}$Al and $^{29}$Si MAS-NMR spectra have been measured for CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$ = 0.67, Al$_2$O$_3$ = 20 mass%)–R$_2$O (R=Li, Na and K) and CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$ = 1.22, Al$_2$O$_3$ = 20 mass%)–RO (R= Ba and Mg) quaternary glasses. To make clear the effect of the kinds of adding R$_2$O or RO on the structure of glasses, the content of adding R$_2$O or RO in these glasses was kept the constant value of 10.8 mol% or 7.0 mol%. The occurrence and relative amount of different units was obtained by deconvolution of $^{27}$Al and $^{29}$Si MAS-NMR spectra.$^{18,19}$
3.3.1. $^{27}$Al MAS-NMR Spectra

*Figures 9 and 10 show* $^{27}$Al 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(6)) and tetrahedrally (Al(4)) coordinated Al, and the signal at $37$ ppm is attributed to distorted tricluster-forming Al–O$_4$ tetrahedra.

In this study, $^{27}$Al NMR spectra were reproduced two peaks for Al(6) and Al(4) as drawn with solid lines in Figs. 9 and 10.

From Fig. 9, the resonance position of spectra is shifted from $\approx 50$ ppm of the mother glasses to a downfield with the addition of R$_2$O. It is also found that the peak for Al(6) of the mother glasses decrease, and the peak for Al(4) of the glasses increase with the addition of R$_2$O. No significant difference of the relative areas of Al(6) (34.6$\pm$0.7%) or Al(4) (65.4$\pm$0.7%) for the glasses with adding the different kinds of R$_2$O is observed. These results suggest that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts shown in Fig. 5 is not dependent on the increase of Al(4) in the glasses with adding of K$_2$O.

From Fig. 10, the resonance position of spectra of the glasses with adding of RO 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(6) (40.1$\pm$2.0%) or Al(4) (59.9$\pm$2.0%) for the glasses with the addition of MgO or BaO is observed. These results suggest that the increase of Al(4) in the glasses is not a major factor in the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–BaO melts shown in Fig. 8.

3.3.2. $^{29}$Si MAS-NMR Spectra

In aluminosilicates, $^{29}$Si MAS-NMR can provide quantitative information on the fractions of silicon present in different tetrahedral environments. According to widespread use, SiO$_4^{4-}$ units are identified according to their mutual connectivity as Q$^n$(mAl), where n is the number of bridging oxygen (BO) atoms, and m is the number of neighbor aluminate groups.$^{21,22}$ In general, silicon chemical shift becomes less negative with the number of bridging oxygen (BO) decreasing from four to zero.$^{23}$ Adjacent aluminum tetrahedra (Al(4)) also affect the silicon chemical shift. Namely, silicon nuclei are deshielded and d value (ppm) becomes less negative as the number of neighboring aluminum atoms increases from zero to four. Table 3 lists the experimentally determined chemical shift ranges associated with species.$^{23-25}$

*Figure 11 shows* $^{29}$Si 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. It is found from Fig. 11 that the resonance position of spectra is shifted from $\approx -85$ ppm of the mother glasses to a downfield with the addition of R$_2$O. It is also found that the peak of spectra of the glasses with Li$_2$O or Na$_2$O become sharp, and that with K$_2$O become broad. The $^{29}$Si NMR spectra of these glasses resolved four peaks, and relative areas of the peaks were calculated by spectra deconvolution. In the deconvolution analysis, the peak of Q$^4$(1Al) and the peak of Q$^1$ overlapped each other so that the peak at $-75$–$-80$ ppm showed as Q$^4$(1Al)+Q$^1$. The summary of the deconvolution results is listed in Table 4. It is found that the $^{29}$Si NMR spectra of the mother glasses and that of the glasses with the addition of R$_2$O consist of Q$^2$, Q$^3$, Q$^1$(1Al)+Q$^1$ and Q$^4$(1Al). It is estimated that the peaks at $\approx -75$–$-80$ ppm in Table 4 mainly consist of Q$^4$(1Al).$^{16,26}$ From the deconvolution analysis (Table 4), the degree of polymerization of silicate anions decrease with the addition of Li$_2$O or Na$_2$O, namely the relative area of Q$^4$ decrease in Li$_2$O- and Na$_2$O-containing glasses compared with the mother glasses as shown in Table 4. On the other hand, the degree of polymerization of aluminosilicate anions increase, namely the relative area of Q$^4$(1Al) increase in K$_2$O-containing glasses compared with the mother glasses as shown in Table 4. It is estimated from the results that the increase in viscosity of

| Table 3. Isotropic $^{29}$Si chemical shift ranges for Q$^n$–Q$^m$ units in crystalline silicates and aluminosilicates. |
|---|---|---|---|---|
| R$_2$O | Q$^n$ units (ppm) | Q$^m$ units (ppm) | Q$^n$ units (ppm) | Q$^m$ units (ppm) |
| n=0 | -68–-97 | -75–-102 | -88–-99 | -102–-114 |
| n=1 | -63–-92 | -70–-97 | -85–-99 | -96–-107 |
| n=2 | -84–-86 | -93–-102 | -88–-97 | -96–-107 |
| n=3 | -76 | -88 | -89 | -89 |

| Table 4. Deconvolution results of $^{29}$Si MAS-NMR spectra of (32CaO–48SiO$_2$–20Al$_2$O$_3$)–R$_2$O glasses. |
|---|---|---|---|---|
| R$_2$O | Chemical shift (ppm) | Relative area (%) |
| Li$_2$O | -93.5 | -89.9 | -84.8 | -80.0 | 17.8 | 14.6 | 32.0 | 35.6 |
| Na$_2$O | -90.0 | -86.5 | -81.9 | -77.1 | 11.0 | 13.6 | 34.2 | 41.2 |
| K$_2$O | -91.0 | -86.6 | -81.0 | -75.7 | 23.0 | 23.6 | 38.9 | 26.4 |

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CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts shown in Fig. 5 is dependent on increase of aluminosilicate anions (Q$^7$(1Al)) in the melts with the addition of K$_2$O.

Figure 12 shows $^{29}$Si NMR spectra of CaO–SiO$_2$–Al$_2$O$_3$–RO glasses. It is found that the resonance position of spectra is found at $\approx$ -80 ppm, and it is not change from that of the mother glasses. The $^{29}$Si NMR spectra of these glasses resolved three peaks, and the relative areas of the peaks were calculated by spectra deconvolution. In the deconvolution analysis, the peaks of Q$^4$(1Al) and Q$^7$ or that of Q$^7$(1Al) and Q$^4$ overlapped each other so that the peak at $\approx$ -75 ppm or at $\approx$ -80 ppm showed as Q$^4$(1Al)+Q$^7$ or Q$^7$(1Al)+Q$^4$. The summary of the deconvolution results is listed in Table 5. It is estimated that the peaks at $\approx$ -75 ppm or at $\approx$ -80 ppm in Table 5 mainly consist of Q$^4$(1Al) or Q$^7$(1Al). From these considerations, the degree of polymerization of silicate and aluminosilicate anions decrease in the glasses with MgO, namely the relative area of Q$^2$ and of Q$^7$(1Al) decrease, and the relative area of Q$^4$(1Al) increase in this glasses compared with the mother glasses as shown in Table 5. On the other hand, the degree of polymerization of aluminosilicate anions increase in the glasses with BaO, namely the relative area of Q$^7$(1Al) increase in this glasses compared with the mother glasses as shown in Table 5. It is estimated from the results that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–BaO melts shown in Fig. 8 is dependent on increase of aluminosilicate anions (Q$^7$(1Al)) in the melts with the addition of BaO.

4. Conclusions

The effect of adding R$_2$O (R=Li, Na and K) or RO (R=Ba, Mg) on the viscosities of CaO–SiO$_2$–Al$_2$O$_3$ (CaO/SiO$_2$=0.67, 1.00 or 1.22, Al$_2$O$_3$=20 mass%) melts has been measured by rotating crucible viscometer. In addition, structural characterizations of these quenched vitreous samples have been investigated by $^{27}$Al and $^{29}$Si MAS-NMR spectra.

(1) The viscosities of CaO–SiO$_2$–Al$_2$O$_3$–R$_2$O quaternary melts decreased with increasing the additive content of Li$_2$O or Na$_2$O. However, the viscosities of the melts increased with increasing the addition content of K$_2$O.

(2) $^{27}$Al MAS-NMR spectra indicated that the population of (Al(4)) in the glasses increased with adding of R$_2$O, however, that of Al(4) was independent of the kinds of adding R$_2$O.

(3) $^{29}$Si MAS-NMR spectra indicated that the degree of polymerization of silicate anions in the glasses decreased with the addition of Li$_2$O or Na$_2$O, and that the degree of polymerization of aluminosilicate anions in the glasses increased with the addition of K$_2$O. It was estimated from the results that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–K$_2$O melts was dependent on increase of aluminosilicate anions in the melts with the addition of K$_2$O.

(4) 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.

(5) $^{27}$Al MAS-NMR spectra indicated that no significant difference of the population of Al(6) or Al(4) for the glasses with the addition of MgO or BaO was observed.

(6) $^{29}$Si MAS-NMR spectra indicated that the degree of polymerization of silicate and aluminosilicate anions in the glasses decreased with the addition of MgO. The degree of polymerization of aluminosilicate anions increased in the glasses with BaO. It was estimated from the results that the increase in viscosity of CaO–SiO$_2$–Al$_2$O$_3$–BaO melts was dependent on increase of aluminosilicate anions in the melts with the addition of BaO.

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