Structure-Viscosity Relationship of Low-silica Calcium Aluminosilicate Melts

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The structure-viscosity relationship of the low-silica ($\text{SiO}_2 \leq 10$ wt%) calcium aluminosilicate melts, which represent the secondary refining ladle slag systems, was investigated by employing the rotating-cylinder viscosity measurement in conjunction with the Raman spectroscopy measurement for linking the macroscopic thermophysical property and molecular (ionic) structural information. Furthermore, the influence of CaF_2 on the structure-property relationship was explored. The viscosity of low-silica calcium aluminosilicate melts decreased with increasing both $\text{CaO}/\text{Al}_2\text{O}_3$ and CaO/SiO_2 ratios. However, the effect of the former on the viscosity of low-silica calcium aluminosilicate melts was larger than that of the latter. By employing the Neuville's structure model, in which the silicate structural units with various NBO, *i.e.* Q^n_{Si} are located at the boundary of the AlO_4 aluminate, and the Raman scattering data of the glass samples, it was demonstrated that the aluminate and silicate units are more effectively modified by increasing the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio at fixed silica content. The addition of small amounts of CaF_2 (~5 wt%) to the low-silica calcium aluminosilicate melts decreased the viscosity of the melts. From the analysis of Raman scattering data, the liberation of SiO_4^{4-} (Q^0_{Si}) units from the AlO_4 aluminate structure by addition of CaF_2 was understood. However, the effect of CaF_2 addition on the viscosity became less discernible at higher CaF_2 content (≥ 10 wt%) region, where the F ions simply substitute for the non-bridging oxygen ions in AlO_4 tetrahedra.

KEY WORDS: structure; viscosity; low-silica calcium aluminosilicate; ladle slag; Raman spectroscopy; thermophysical property; non-bridging oxygen (NBO); calcium fluoride (CaF_2).

1. Introduction

It is necessary to remove the inclusions from molten steel to enhance the cleanliness of steel products in secondary refining processes. There are following consecutive processes for the removal of inclusions, *viz.* (i) flotation of inclusions to the steel melt-slag interface, (ii) separation into the slag phase and (iii) dissolution into the slag phase, among which the final step was reported to be a rate controlling process for the removal of inclusions.¹⁾ When the dissolution process is controlled by diffusion, the total dissolution time (τ) will be:

$$\tau = \frac{\rho \cdot R_o^2 \cdot 3\pi a \eta}{2kT\Delta C} \dots\dots\dots (1)$$

where R_o is the inclusion radius, ρ is the inclusion density, k is the Boltzmann constant, T is the temperature, a is the ionic diameter, ΔC is the driving force for the dissolution and η is the viscosity of the slag. Therefore, the viscosity of the slag is an important factor affecting the dissolution time of the inclusions into the slag phase.

The slag system generally used in the secondary refining processes is low-silica calcium aluminosilicate melts with

(or without) CaF_2 so that it is highly important to understand the viscous flow behavior of the alumina-rich systems based on the systematic knowledge of structure in the viewpoint of molecular dimension.

In the literature, it has been widely investigated that alumina is an amphoteric oxide in view of thermophysical properties including viscosity of calcium aluminosilicate melts of which silica content is as higher as about 30 wt%.²⁻⁴⁾ The structural unit of aluminate anion is very complicated and thus Al coordination number varies from 4 to 6, *viz.* AlO_4 , AlO_5 and AlO_6 units.^{5,6)} The AlO_4 species is known to be observed with an increase in the viscosity of silica-rich slags with charge compensation by cations such as 0.5 M^{2+} and/or M^+ , whereas the AlO_5 and AlO_6 units are generally known to originate a decrease in the viscosity of silicate melts. Consequently, the AlO_4 species is appointed as a network former, whereas the AlO_5 and AlO_6 units are called as a network modifier in the silica-rich aluminosilicate melts.²⁻⁴⁾

However, the distribution of aluminate structural units varies as a function of alumina concentration in the silica-free $\text{CaO}-\text{Al}_2\text{O}_3$ binary system. The average Al coordination number and a distribution of aluminate species in the $\text{CaO}-\text{Al}_2\text{O}_3$ melts was investigated using ion dynamics in conjunction with ^{27}Al magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectroscopy by McMillan *et al.*^{7,8)} The relative fraction of AlO_4 species increases with CaO

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addition, whereas that of AlO_5 and AlO_6 units decreases as shown in **Fig. 1**.⁷⁾

Because Ca^{2+} ion, which plays a role of charge compensator for the stabilization of AlO_4 species, becomes sufficient with increasing CaO content, the AlO_5 and AlO_6 units are transformed to the AlO_4 unit. Therefore, the most dominant unit of aluminate is tetrahedral form in high CaO content region, *i.e.* > 50 wt% in the $\text{CaO-Al}_2\text{O}_3$ binary melts. The Ca^{2+} ions are localized near the negatively charged AlO_4 tetrahedron for charge balance.⁹⁾ The fully polymerized aluminates (Q^4_{Al} ; non-bridging oxygen per aluminum, *i.e.* $\text{NBO}/\text{Al}=0$) are depolymerized into Q^2_{Al} ($\text{NBO}/\text{Al}=2$) and Q^3_{Al} ($\text{NBO}/\text{Al}=1$) units by addition of Ca^{2+} ions at molar ratio of CaO to Al_2O_3 is greater than unity in the $\text{CaO-Al}_2\text{O}_3$ binary system.^{7,10)} Hence, the viscosity of the $\text{CaO-Al}_2\text{O}_3$ melts decreases with increasing content of CaO because the Ca^{2+} ions not only compensate the negative charge of the AlO_4 unit but also modifies the polymerized AlO_4 unit into Q^2_{Al} and Q^3_{Al} units.¹⁰⁾

Structural change of calcium aluminosilicate melts was investigated by addition of Al_2O_3 or SiO_2 .⁹⁻¹¹⁾ The aluminate unit in Q^4_{Al} increases with the introduction of Al_2O_3 or SiO_2 in the low-silica calcium aluminosilicate melts, *i.e.* the Al in Q^2_{Al} and Q^3_{Al} is polymerized to form Q^4_{Al} unit. Nevertheless, the Si in Q^n_{Si} units is not affected by the addition of Al_2O_3 or SiO_2 in low-silica calcium aluminosilicate melts. The Al atoms become localized preferentially in Q^4_{Al} , whereas the Si atoms have no site preference and thus are distributed in various Q^n_{Si} units.^{11,12)} Therefore, the Q^n_{Si} units are localized at the boundary of Q^4_{Al} units in the low-silica calcium aluminosilicate melts.^{9,10)}

Even though a few reports on the structural changes in the low-silica calcium aluminosilicate melts have been published by glass scientists and chemical geologists, the relationship between the viscosity and the structure of the melts, which potentially correspond to the secondary refining ladle slags, is not fully developed yet. Therefore, in the present study, the structure-viscosity relationship of the low-silica ($\text{SiO}_2 \leq 10$ wt%) calcium aluminosilicate melts was investi-

Fig. 1. The distribution of aluminum coordination species, AlO_n ($n=4, 5, 6$), for liquids along the $\text{CaO-Al}_2\text{O}_3$ join determined by ion dynamics simulation at 3000 K (modified from Ref. 7). (Online version in color.)

gated by employing the rotating-cylinder viscosity measurement in conjunction with the Raman spectroscopy measurement for linking the macroscopic thermophysical property and molecular (ionic) structural information. Furthermore, the influence of CaF_2 on the structure-property relationship was discussed.

2. Experimental

2.1. Procedure of Viscosity Measurements

The reagent grade SiO_2 , Al_2O_3 , and CaF_2 were used in the present experiments. The CaO and MgO were obtained from the reagent grades CaCO_3 and MgCO_3 which were calcined at 1273 K for 10 hours. The powders were weighed for required composition and mixed for 1 hour to obtain homogeneous mixtures. The mixtures were melted in a Pt-10 wt% Rh alloy crucible (diameter 40 mm, depth 60 mm) under a purified Ar atmosphere in a super kanthal electric furnace. After 2 hours, the rotating cylinder method was used to measure viscosity of slags. A schematic diagram of the experimental apparatus is shown in **Fig. 2**.

A rotating viscometer (Brookfield, model LV-DV II+ Pro) was set on the super kanthal electric furnace and the composition of slag which was analyzed using X-ray fluorescence spectroscopy is listed in **Table 1**. Because the composition changes during viscosity measurements were confirmed to be less than 10% point of initial composition, the initial value is shown in Table 1 for the sake of convenience. The temperature in the furnace was measured by an R-type (Pt/Pt-13 wt% Rh) thermocouple within ± 2 K. For an exact temperature control, a temperature difference in between the outer surface of the reaction tube and the crucible position in the reaction tube was preliminarily calibrated before viscosity measurement. The more detailed descriptions for the viscosity measurement and a dimension of spindle and connecting wires are available in our previous articles.¹³⁻¹⁵⁾

Fig. 2. Experimental apparatus for the measurement of slag viscosity. (Online version in color.)

Table 1. Composition of slag samples (wt%) and the relative fraction of each structural unit obtained from Gaussian deconvolution and the relative intensity of Al–O–Al bond.

Sample number	CaO	Al ₂ O ₃	SiO ₂	MgO	CaF ₂	Q ² _{Al}	Q ³ _{Al}	Q ⁴ _{Al}	Q ⁰ _{Si}	Q ¹ _{Si}	Q ² _{Si}	Al–O–Al
A-1	42	35	8	5	10	6.06	21.31	48.90	8.67	7.69	7.36	0.36
A-2	46	31	8	5	10	10.61	21.62	43.04	10.97	7.396	5.81	0.32
A-3	50	28	8	5	10	16.39	21.21	38.90	12.64	8.20	2.65	0.20
A-4	53	24	8	5	10	21.44	11.79	36.27	17.66	10.46	2.37	0.15
S-1	43	25	18	5	10	0.99	3.72	43.99	23.72	16.48	11.11	0.26
S-2	46	28	12	5	10	5.73	13.71	40.58	22.43	11.91	5.65	0.24
S-3	49	28	8	5	10	16.98	21.43	38.46	12.06	6.72	4.35	0.21
S-4	52	28	5	5	10	30.72	23.61	37.18	4.89	2.77	0.83	0.20
F-1	57	31	7	5	0	21.87	22.49	38.66	6.87	6.50	3.61	0.24
F-2	53	30	7	5	5	21.43	22.79	38.17	10.16	5.28	2.15	0.21
F-3	50	28	7	5	10	18.59	22.39	57.54	13.48	5.17	2.84	0.24
F-4	46	26	8	5	15	17.28	21.46	37.62	15.09	5.91	2.64	0.24

Table 2. Identification of Qⁿ_{Al} and Qⁿ_{Si} structural units at specific Raman scattering wavenumbers. (Online version in color.)

	NBO/Al			NBO/Si		
	2(Q ²)	1(Q ³)	0(Q ⁴)	4(Q ⁰)	3(Q ¹)	2(Q ²)
Structural unit
wave-numbers (cm ⁻¹)	730	780	850	850–880	900–920	950–1 000

2.2. Procedure of Raman Spectra Measurements

The glass samples for Raman spectroscopy measurements were prepared by quenching some part of slag taken from the crucible just before starting the viscosity measurements. All the samples were confirmed to be glassy using an X-ray diffraction analysis. The Raman spectra of the quenched glass samples were collected at room temperature in the range 100–1 900 cm⁻¹ using an Ar excitation laser source having wavelength 514.5 nm coupled with Jobin-Yvon Horiba (LabRam HR, France) micro-Raman spectrometer.^{16–19)}

Raman shifts were measured with a precision of 0.3 cm⁻¹ and the spectra resolution was of the order 1 cm⁻¹. The quantitative peak deconvolution was carried out through the range of Raman shifts from about 650 to 1 050 cm⁻¹. The spectrum data were fitted by Gaussian function with an aid of the 'PeakFit' program within ±0.5% error limit and thus the relative abundance of the Qⁿ_i (*i*=Si and Al) units was calculated from the area fraction of the best-fitted Gaussian curves at the frequency for the symmetric stretching vibration of each Qⁿ_i unit, which is given in Table 1.^{16–19)}

Figure 3 shows a typical deconvolution result for the CaO–Al₂O₃–8 wt% SiO₂–5 wt% MgO–10 wt% CaF₂ (CaO/Al₂O₃=1.2) system. Peak identification at a specific wave-

Fig. 3. Typical deconvolution result for the CaO–Al₂O₃–8%SiO₂–5%MgO–10%CaF₂ (CaO/Al₂O₃=1.2) system. (Online version in color.)

number is listed in **Table 2**. Quantitative analysis of Raman spectra allowed determination of the configuration of each aluminate (Qⁿ_{Al}, n=2 to 4) and silicate (Qⁿ_{Si}, n=0 to 2) unit

according to bulk composition. The compositions and the relative area fractions of the fitted Gaussian bands are listed in Table 1. Mysen *et al.*^{20–23)} confirmed that the anionic structural units in the aluminosilicate melts are the same before and after quenching, and thus the structural features of quenched glasses are applicable to molten state. Because all the glass samples for Raman spectra analysis was quenched from 1873 K, the structural similarity in between molten state and quenched state can be assumed in the present study.

3. Results

3.1. Effect of CaO/Al₂O₃ Ratio on the Viscosity and Structure of CaO-Al₂O₃-8%SiO₂-5%MgO-10%CaF₂ Slags

The viscosity of the CaO-Al₂O₃-8 wt% SiO₂-5 wt% MgO-10 wt% CaF₂ slags at temperatures from 1773 to 1873 K is shown as a function of CaO/Al₂O₃ (C/A) ratio in Fig. 4. The viscosity of the slags continuously decreases by increasing the C/A ratio and it decreases about 60% in average with increasing C/A ratio from 1.2 to 2.2 at SiO₂=8 wt%.

The effect of C/A ratio on the Raman bands of the CaO-Al₂O₃-8 wt% SiO₂-5 wt% MgO-10 wt% CaF₂ slags is shown as a function of wavenumbers in Fig. 5. The intensity of Raman band at around 550 cm⁻¹ drastically decreases with increasing C/A ratio. This Raman band is related to the transverse motion of bridging oxygen within the Al–O–Al linkage (Table 2).²⁴⁾ Therefore, a decrease in the relative intensity of Raman band at 550 cm⁻¹ indicates that the number of bridging oxygen decreases by increasing the C/A ratio, viz. the aluminate structure is partly broken (or modified) by the increase in the C/A ratio.

The Raman band at around 850 cm⁻¹ shifts to lower wavenumbers and a shoulder at around 730 cm⁻¹ gradually grows with the increase of C/A ratio, whereas a shoulder at around 780 cm⁻¹ become lessened. The Raman bands at 730 cm⁻¹, 780 cm⁻¹ and 850 cm⁻¹ is the Al–O stretching vibration in AlO₄ tetrahedral units with the NBO/Al=2 (Q²_{Al}), NBO/Al=1 (Q³_{Al}) and NBO/Al=0 (Q⁴_{Al}), respectively.²⁴⁾

3.2. Effect of CaO/SiO₂ Ratio on the Viscosity and Structure of CaO-27%Al₂O₃-SiO₂-5%MgO-10%CaF₂ Slags

The viscosity of the CaO-27 wt% Al₂O₃-SiO₂-5 wt% MgO-10 wt% CaF₂ slags at temperatures from 1773 to 1873 K is shown as a function of CaO/SiO₂ (C/S) ratio in Fig. 6. The viscosity of the slags slightly decreases by increasing the C/S ratio. It decreases about 40% in average with increasing C/S ratio from 2.0 to 10 at Al₂O₃=27(±1) wt%. It is clearly noticeable that a tendency of decrease in the viscosity of the melts with increasing C/S ratio is in good agreement with the previous results for the viscosity of similar (but CaF₂-free) slag systems measured by Song *et al.*²⁵⁾ Moreover, it is confirmed that the effect of CaF₂ on the viscosity of slags is more significant at lower temperatures.^{15,26)}

Comparing Figs. 4 and 6, it was found that the effect of C/A ratio on the viscosity at fixed silica content is higher than that of C/S ratio at fixed alumina content even though the composition range varied in the former is less than that

Fig. 4. Viscosities of the CaO-Al₂O₃-8%SiO₂-5%MgO-10%CaF₂ melts as a function of CaO/Al₂O₃ ratio. (Online version in color.)

Fig. 5. Effect of CaO/Al₂O₃ ratio on Raman scattering of the CaO-Al₂O₃-8%SiO₂-5%MgO-10%CaF₂ system. (Online version in color.)

Fig. 6. Viscosities of the CaO-27%Al₂O₃-SiO₂-5%MgO-10%CaF₂ melts as a function of CaO/SiO₂ ratio. (Online version in color.)

Fig. 7. Effect of CaO/SiO₂ ratio on Raman scattering of the CaO-27%Al₂O₃-SiO₂-5%MgO-10%CaF₂ system. (Online version in color.)

of the latter. The composition-property (viscosity) relationship of the slag can be understood based on the following structural information of molten slags.

The effect of C/S ratio on the Raman bands of the CaO-27 wt% Al₂O₃-SiO₂-5 wt% MgO-10 wt% CaF₂ slags is shown as a function of wavenumbers in Fig. 7. The intensity of Raman band at around 550 cm⁻¹ slightly decreases with increasing C/S ratio. Because this Raman band is related to the bridging oxygen within the Al–O–Al linkage as discussed in Section 3.1, a decrease in the relative intensity of Raman band at 550 cm⁻¹ indicates that the number of bridging oxygen decreases by increasing the C/S ratio. However, comparing Figs. 5 and 7, the effect of C/S ratio on a decrease in the relative fraction of bridging oxygen in the Al–O–Al linked networks is weaker than that of the C/A ratio. The more detailed discussion in regard of this finding will be given in Section 4.

The Raman band at around 850 cm⁻¹ (NBO/Al=0 (Q⁴_{Al})) shifts to lower wavenumbers and a relative intensity decreases with the increase of C/S ratio, whereas a broad band ranges from about 660 cm⁻¹ to 800 cm⁻¹, containing 730 cm⁻¹ (NBO/Al=2 (Q²_{Al})) and 780 cm⁻¹ (NBO/Al=1 (Q³_{Al})) peaks, becomes strong with increasing C/S ratio. Therefore, the network-forming aluminate structure is continuously modified by increasing the C/S ratio at fixed alumina content.

3.3. Effect of CaF₂ Addition on the Viscosity and Structure of CaO-Al₂O₃-SiO₂-5%MgO-CaF₂ (C/A=1.8, C/S=6.0) Slags

The viscosities of the CaO-Al₂O₃-SiO₂-5 wt% MgO-CaF₂ slags (C/A=1.8, C/S=6.0) are shown in Fig. 8 as a function of CaF₂ content from 0 to 15 wt%. It decreases by addition of CaF₂ and this tendency is more dominant at lower CaF₂ content (~5 wt%) region as well as at lower temperatures. The influence of CaF₂ on the viscosity of the slags is less significant at CaF₂ content greater than about 10 wt% even at lower temperatures, indicating that the depolymerization mechanism of alumina-rich slag melt is changed as a function of CaF₂ content.

The Raman bands of the slags are shown in Fig. 9 as a

Fig. 8. Viscosities of the CaO-Al₂O₃-SiO₂-5%MgO-CaF₂ melts as a function of CaF₂ content. (Online version in color.)

Fig. 9. Effect of CaF₂ content on Raman scattering of the CaO-Al₂O₃-SiO₂-5%MgO-CaF₂ (C/A=1.8, C/S=6.0) system. (Online version in color.)

function of CaF₂ content. The relative intensity of the band at around 550 cm⁻¹ is not significantly changed by addition of CaF₂, indicating that the CaF₂ does not affect the fraction of bridging oxygen in the Al–O–Al linkage. The relative intensity of broad band ranges from about 660 cm⁻¹ to 800 cm⁻¹, containing Q²_{Al} (730 cm⁻¹) and Q³_{Al} (780 cm⁻¹) units, very slightly decreases with increasing CaF₂ content. The intensity of 850 cm⁻¹ (=Q⁴_{Al}, NBO/Al=0) band was not severely changed by CaF₂ addition. Therefore, it is supposed that the addition of CaF₂ doesn't significantly modify the polymerized aluminate network structure. This means that a decrease in viscosity by addition of CaF₂ (Fig. 8) possibly originates from a depolymerization reaction of silicate units, which will be discussed in detail in Section 4.3.

4. Discussion

4.1. Variation of Structural Units as a Function of CaO/Al₂O₃ Ratio of CaO-Al₂O₃-8%SiO₂-5%MgO-10%CaF₂ Slags

McMillan *et al.*²⁷⁾ measured a Raman spectroscopy of

glasses in the $\text{SiO}_2\text{--CaO--Al}_2\text{O}_3$ system and suggested that four peaks at 1140, 1000, 925 and 890 cm^{-1} in the $\text{SiO}_2\text{--CaAl}_2\text{O}_4$ join are due to symmetric stretching vibrations of silicate tetrahedron in conjunction with 1, 2, 3 and 4 fully polymerized aluminate, respectively. These Si–O–Al stretching regions in the Raman scattering are overlapped with the symmetric stretching vibrations of Si–O bonds with different number of NBO/Si.^{21,28)}

Based on experimental and theoretical studies,^{11,12,29)} it was investigated that Al atoms have preference to be positioned in AlO_4 unit in the $\text{CaO--Al}_2\text{O}_3$ binary system (molar $\text{CaO}/\text{Al}_2\text{O}_3 \geq 1$) as discussed in Fig. 1, while the Si atoms do not have site preference with introduction of SiO_2 . The AlO_4 unit is partly polymerized, viz. $\text{NBO} \neq 0$, and the Si atoms are localized at the boundary of AlO_4 unit with various numbers of NBO in the alumina-rich calcium aluminosilicate melts.⁹⁾ Therefore, the stretching vibrations of Q^0_{Si} ($\text{NBO}/\text{Si}=4$), Q^1_{Si} ($\text{NBO}/\text{Si}=3$) and Q^2_{Si} ($\text{NBO}/\text{Si}=2$) should be considered in the present calcium aluminosilicate melts, of which silica content is lower than 10 wt%, in order to understand the structural changes as a function of melt composition.

The Gaussian deconvolution of the Raman bands in the low-silica calcium aluminosilicate slags has been carried out and the results are shown in Fig. 10 as a function of $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. The relative height of Al–O–Al network-forming bond (550 cm^{-1}) is also included in Fig. 10(a). The fraction of the polymerized aluminate unit (Q^4_{Al} , $\text{NBO}=0$) dramatically decreases by increasing the C/A ratio and the

relative height of Al–O–Al bond also decreases with similar tendency. Some of Al atoms are distributed in the depolymerized aluminate units, i.e. Q^2_{Al} ($\text{NBO}/\text{Al}=2$) and Q^3_{Al} ($\text{NBO}/\text{Al}=1$) in the low-silica calcium aluminosilicate melts,^{29,30)} indicating that the fully polymerized Q^4_{Al} units are modified to the simple Q^2_{Al} and Q^3_{Al} units with increasing C/A ratio. Specifically, the relative fraction of Q^2_{Al} unit linearly increases with increasing C/A ratio, whereas that of Q^3_{Al} unit does not vary significantly.

Silicate units are located at the boundary of polymerized aluminate units, viz. the Q^4_{Al} units are surrounded by silicate tetrahedra, Q^n_{Si} ($n=0, 1, 2$) units.^{11,12)} In Fig. 10(b), the fractions of Q^0_{Si} ($\text{NBO}/\text{Si}=4$) and Q^1_{Si} ($\text{NBO}/\text{Si}=3$) units increase with increasing C/A ratio, whereas that of Q^2_{Si} ($\text{NBO}/\text{Si}=2$) unit slightly decreases. An increase in the C/A ratio provided the breaking event of Q^2_{Si} unit into Q^0_{Si} and Q^1_{Si} units, resulting in a decrease of the degree of polymerization of aluminosilicate networks. Therefore, it is suggested that the SiO_4 units with $\text{NBO}=2$ (Q^2_{Si}) localized at the boundary of polymerized AlO_4 unit (Q^4_{Al}) had come off.

4.2. Variation of Structural Units as a Function of CaO/SiO_2 Ratio of $\text{CaO-27\%Al}_2\text{O}_3\text{-SiO}_2\text{-5\%MgO-10\%CaF}_2$ Slags

The results of the Gaussian deconvolution of the Raman bands in Fig. 7 is shown as a function of CaO/SiO_2 ratio in Fig. 11. The fraction of Q^4_{Al} unit and the relative height of the Al–O–Al network bond slightly decrease, whereas the

Fig. 10. Relative fraction of Q^n_i ($n=0$ to 4, $i=\text{Al}$ (a) or Si (b)) structural units in the $\text{CaO--Al}_2\text{O}_3\text{--}8\%\text{SiO}_2\text{--}5\%\text{MgO--}10\%\text{CaF}_2$ system as a function of $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. (Online version in color.)

Fig. 11. Relative fraction of Q^n_i ($n=0$ to 4, $i=\text{Al}$ (a) or Si (b)) structural units in the $\text{CaO--}27\%\text{Al}_2\text{O}_3\text{--SiO}_2\text{--}5\%\text{MgO--}10\%\text{CaF}_2$ system as a function of CaO/SiO_2 ratio. (Online version in color.)

fractions of Q^2_{Al} and Q^3_{Al} units commonly increase with increasing CaO/SiO₂ ratio. Therefore, it is certain that the effect of C/S ratio on the modification of aluminate network structure (Fig. 11(a)) is different from that of C/A ratio on it (Fig. 10(a)). That is, the fraction of Q^3_{Al} unit, which is the more polymerized one compared to Q^2_{Al} unit, also increases by increasing the C/S ratio (Fig. 11(a)), while it was not significantly affected by the C/A ratio from 1.2 to 1.8, after which the fraction of Q^3_{Al} decreased by increasing the C/A ratio (Fig. 10(a)).

As the C/S ratio increases at fixed alumina content, the Q^2_{Al} and Q^3_{Al} units are created at the expense of Q^4_{Al} unit, during which the partly broken silicate units, *i.e.* Q^0_{Si} (NBO/Si=4), Q^1_{Si} (NBO/Si=3) and Q^2_{Si} (NBO/Si=2), disappear in the low-silica aluminosilicate melts. Allwardt *et al.*¹¹⁾ investigated the environment of oxygen in the calcium aluminosilicates with an increase of silica using ¹⁷O MAS-NMR spectroscopy. The proportion of Si-NBO increased with the increase of silica concentration, whereas that of Al-NBO decreased and the latter was almost eliminated at molar ratio of Si/(Al+Si)=0.5. Consequently, the relationship between the silicate and aluminate structural units was expressed by the following equation:

As discussed above in Fig. 11(a), the influence of the C/S ratio on the depolymerization of aluminate networks was weaker than that of C/A ratio. As shown in Fig. 11(b), the fractions of all Q^n_{Si} units, localized at the boundary of polymerized AlO_4 tetrahedra, decrease with increasing C/S ratio.

4.3. Variation of Structural Units as a Function of CaF₂ Content in CaO-Al₂O₃-SiO₂-5%MgO-CaF₂ (C/A=1.8, C/S=6.0) Slags

The addition of CaF₂ to the aluminosilicate melts rarely modifies the bridging oxygen connected with aluminum (Al-O-Al linkage bond), whereas it slightly affects the Al-NBO (Q^2_{Al} and Q^3_{Al}) units, which was found in Raman scattering analysis (Fig. 9). In the aspect of viscosity, the addition of CaF₂ has a little effect on a decrease in the viscosity even though the relative intensity of the Al-NBO bands slightly decreases by addition of CaF₂. This means that the CaF₂ does not effectively break the Al-O bonds in the polymerized aluminate networks.

The relative fractions of Q^n ($n=0, 1, 2, 3, 4$) structural units for aluminate and silicate as a function of CaF₂ content is presented in Fig. 12. The relative fraction of Q^4_{Al} unit and the relative height of the Al-O-Al linkage bond are nearly constant irrespective of CaF₂ content (Fig. 12(a)), indicating that CaF₂ does not effectively modify the polymerized aluminate networks. The fraction of Q^0_{Si} unit, however, increases with increasing content of CaF₂ as shown in Fig. 12(b) without any change in the fraction of Q^4_{Al} unit and bridging oxygen connected with aluminum (Fig. 12(a)). It is believed that the F⁻ ion substitutes the meta-stable bridging oxygen in silicate which is localized at the boundary of polymerized aluminate networks, resulting in the liberation of Q^0_{Si} unit from aluminate networks as CaF₂ is added. Therefore, the relative fraction of Q^0_{Si} unit increases by

Fig. 12. Relative fraction of Q^n ($n=0$ to 4, $i=Al$ (a) or Si (b)) structural units in the CaO-Al₂O₃-SiO₂-5%MgO-CaF₂ (C/A=1.8, C/S=6.0) system as a function of CaF₂ content. (Online version in color.)

addition of CaF₂ in Fig. 12(b).

At higher CaF₂ content region, the F⁻ ion not only causes the liberation of Q^0_{Si} unit from aluminate networks but also slightly decreases the Al-NBO units (Q^2_{Al} and Q^3_{Al}) in aluminosilicate melts. Despite the fraction of Q^4_{Al} unit and the intensity of bridging oxygen combined with aluminum are nearly constant, the non-bridging oxygen in aluminate is affected by F⁻ ion. Therefore, the non-bridging oxygen is substituted by F⁻ ion to form AlO_xF_{4-x} complexes,³¹⁾ which cause a decrease in the fraction of the Al-NBO in the Raman band (Fig. 12(b)). Because CaF₂ has an effect on the fraction of Al-NBO in low-silica aluminosilicate melts instead of liberation of SiO_4^{4-} (Q^0_{Si}) units, the effect of CaF₂ addition on the viscosity becomes less effective at higher CaF₂ region.

5. Conclusions

The structure-viscosity relationship of the low-silica (SiO₂ ≤ 10 wt%) calcium aluminosilicate melts was investigated by employing the rotating-cylinder viscosity measurement in conjunction with the Raman spectroscopy measurement for linking the macroscopic thermophysical property and molecular (ionic) structural information. Furthermore, the influence of CaF₂ on the structure-property relationship was explored.

The viscosity of low-silica calcium aluminosilicate melts at fixed MgO (=5 wt%) and CaF₂ (=10 wt%) decreased with

increasing both CaO/Al₂O₃ and CaO/SiO₂ ratios. However, the effect of the former on the viscosity of low-silica calcium aluminosilicate melts was larger than that of the latter. By employing the Neuville's structure model, in which the silicate structural units with various NBO, *i.e.* Qⁿ_{Si} are located at the boundary of the AlO₄ aluminate, and the Raman scattering data of glass samples, it was demonstrated that the aluminate and silicate units are more effectively modified by increasing the CaO/Al₂O₃ ratio at fixed silica content.

The addition of small amounts of CaF₂ (~5 wt%) to the low-silica calcium aluminosilicate melts decreased the viscosity of the melts. From the analysis of Raman scattering data, the liberation of SiO₄⁴⁻ (Q⁰_{Si}) units from the AlO₄ aluminate structure by addition of CaF₂ was understood. However, the effect of CaF₂ addition on the viscosity became less discernible at higher CaF₂ content (10 wt%) region, where the F ions simply substitute for the non-bridging oxygen ions in AlO₄ tetrahedra.

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