Coordination Environment of Fluorine in the CaO–SiO₂–CaF₂ Glasses Bearing Na₂O: A Solid-state ¹⁹F MAS NMR Study

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The coordination environment of fluorine in the CaO–SiO₂–CaF₂–Na₂O glasses has been measured by ¹⁹F MAS NMR over a wide composition range including the similar compositions to those of mould fluxes so as to determine the composition dependence of the coordination environment of F⁻. Most of F⁻ are fourfold-coordinated by Ca²⁺ for the samples having the value of \( n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}}) \lesssim 0.3 \), where \( n \) represents the mole fraction of each cation. On the other hand, the samples having the value of \( n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}}) \gtrsim 0.4 \) contain F⁻ coordinated with both Na⁺ and Ca²⁺ and F⁻ sixfold-coordinated by Na⁺.

KEY WORDS: mould flux; coordination; fluorine; ¹⁹F MAS NMR spectroscopy.

1. Introduction

Increasing casting speed of continuous casting process is required to improve the productivity for steel-making industries. However, high-speed casting tends to cause the variability of heat flux between the steel shell and the mould, which can lead to longitudinal cracking. To minimize longitudinal cracking, it is necessary to reduce the heat flux between the steel shell and the mould by creating a crystallized mould flux film. The interfacial thermal heat flux between the steel shell and the mould by creating a crystallized mould flux film is largely reduced due to the air gap between the mould and the solidified slag film. However, to the best knowledge of the authors, there is no previous report demonstrating that the equilibrium of the reaction (1) is largely shifted to the right hand side in molten silicates.

\[
\text{Na}_2\text{O} + \text{CaF}_2 \rightarrow \text{CaO} + 2\text{NaF} \quad \text{(1)}
\]

In order to examine this, it is useful to elucidate the magnitude of affinity between Na⁺ and F⁻ in molten mould fluxes by observing the coordination environment of fluorine in glassy samples by spectroscopic measurements. Present authors have investigated the chemical state of fluorine in the CaO–SiO₂–CaF₂ glasses using the X-ray photoelectron spectroscopy (XPS), and found that the fluorine is dominantly coordinated with calcium rather than silicon from the inspection of F1s XPS spectra. However, in terms of the CaO–SiO₂–CaF₂–Na₂O glasses, it might be difficult to determine the chemical state of fluorine by XPS measurements. The binding energy of CaF₂ (684.63, 684.8, 684.9 eV) is very close to that of NaF (683.7, 684.27, 684.5 eV) compared to the uncertainty of the measured binding energy (±0.7 eV) at the peak position. On the other hand, it has been presented that ¹⁹F magic-angle-spinning nuclear magnetic resonance (¹⁹F MAS NMR) can produce highly informative spectra having distinct chemical shifts even in multi-component systems. Stebbins and Zeng have successfully determined the coordination environment of F⁻ for two CaO–SiO₂–CaF₂–Na₂O glasses by ¹⁹F MAS NMR, and have detected two distinct F⁻ coordinated only with Na⁺, and both Ca²⁺ and Na⁺, respectively. However, their samples have much lower CaO and CaF₂ and much higher Na₂O concentrations than commercial mould fluxes. Since the coordination environment of F⁻ could be significantly dependent on the chemical composition of glasses, it is necessary to study F⁻ sites for the samples having the similar compositions to those of mould fluxes. Consequently, the aim of this study is to measure F⁻ sites in the CaO–SiO₂–CaF₂–Na₂O glasses by ¹⁹F MAS NMR over a wide composition range so as to determine the composition dependence of the coordination environment of F⁻. The commercial mould fluxes have also been measured. Moreover, we have compared the coordination envi-
environment of F⁻ for a glassy sample with crystallized sample by annealing, to observe structure changes during solidification and crystallization.

2. Experimental

2.1. Sample Preparation

The nominal compositions of the synthesized samples are given in Table 1. Since commercial mould fluxes generally contain 5 to 10 mass% Na₂O, the Na₂O content was set at 10.5 mol% for the samples A and B and 8.0 mol% for the samples C–G. The samples are classified into four groups:

1. The samples A and B having the same compositions were prepared from different raw materials, i.e., CaO, SiO₂, CaF₂ and Na₂O, and CaO, SiO₂, CaF₂ and NaF, respectively, to confirm that the difference in raw materials does not yield the difference in the coordination environment of F⁻.

2. In the group of samples C–E, the (mol% CaO)/(mol% SiO₂) ratio is varied between 0.68 and 1.28. The CaF₂ and Na₂O contents are kept constant at 13.8 and 8.0 mol%, respectively, to confirm that the difference in raw materials does not yield the difference in the coordination environment of F⁻.

3. In the group of samples D, F and G, the CaF₂ content is varied between 9.2 and 18.4 mol%. The (mol% CaO)/(mol% SiO₂) ratio is kept constant at 1.00.

4. In the group of samples D and H–L, the value of \( n_{Na}/(n_{Na} + n_{Ca}) \), where \( n \) represents the mole fraction for each cation, is varied between 0.23 and 0.70. The SiO₂ and CaF₂ contents are kept constant at 39.1 and 13.8 mol%, respectively.

Table 2 shows the compositions of the commercial mould fluxes. In order to compare glassy and crystallized samples, the samples D, J and L were annealed in air at 873 K for 1 h. The crystal structures of the annealed samples were determined by X-ray diffraction with CuKα radiation. For all samples, 0.2 mass% CoO was added to speed up spin-lattice relaxation for NMR measurements.

Samples were prepared from reagent grade SiO₂, CaF₂, Na₂CO₃ and CaCO₃ powders, the last being decomposed to CaO by heating at 1 573 K for 12 h. Powders of SiO₂, CaF₂ and Na₂CO₃ were dried at elevated temperatures before use. Weighed mixtures of SiO₂ and Na₂CO₃ were placed in platinum crucibles and melted in air for 0.5 h at about 100 to 200 K above the liquidus temperatures. After degassed, the NaO–SiO₂ glasses were prepared by pouring the melt onto a water-cooled copper plate and crushed. Subsequently, the glasses were mixed with powders of CaO, SiO₂, CaF₂ and CoO to obtain the desired compositions. About 20 g of these mixtures were melted in platinum crucibles under a pure argon flow for 0.5 h at temperatures between 1 623 and 1 723 K. Glassy samples were quenched by pouring the melts onto a water-cooled copper plate and immediately after that pressing another copper plate on top of the melts. X-ray diffraction revealed that the quenched glass samples were amorphous.

2.2. ¹⁹F MAS NMR Spectroscopy Measurements

¹⁹F MAS NMR measurements were carried out using a Bruker ASX200WB spectrometer at Larmor frequency of 188.28 MHz. A Bruker MAS probehead was used with a 4 mm rotor at sample spinning rates of 8, 10 and 12 kHz. One-pulse excitation was used with delay times between pulses chosen to ensure complete relaxation for quantitative experiments. Small background signals from F in the rotor cap materials were subtracted after carefully matched measurements using the same rotor without samples. Spectra
were referenced to hexafluorobenzene (C$_6$F$_6$) taken as 0 ppm.

3. Results

Figures 1 through 5 show the $^{19}$F MAS NMR spectra for all as-quenched samples. The dots in the figures represent the spinning sidebands. The position of the spinning sideband has been determined by comparing the spectra measured by different sample spinning rates. Table 1 shows the chemical shifts at the peak position for all samples. The coordination environment of fluorine can be determined by comparing the chemical shifts with model compounds. The reported chemical shifts of CaF$_2$ crystal (58.6 ppm)$^{12}$, NaF crystal (−58.3 ppm)$^{12}$ and Si(O−)$_n$F$_n$(3 to 31 ppm)$^{13,14}$ are indicated in Figs. 1–4. Duncan et al.$^{15}$ have carried out the $^{19}$F NMR measurement for fluorine-doped silica glass prepared by the chemical vapour deposition process, and detected a peak having the chemical shift of 24 ppm, which is assigned to Si(O−)$_n$F$_n$. The chemical shift of Na$_2$SiF$_6$ crystal was reported as 14.6 ppm$^{12}$ although not shown in the figures.

Figure 1 shows the $^{19}$F MAS NMR spectra for the samples A and B. Both spectra in Fig. 1 show one peak with the chemical shift close to that of CaF$_2$ crystal. This result leads to the following conclusions;

(i) F$^−$ for both samples are in environments similar to those in CaF$_2$ crystal, i.e., F$^−$ is fourfold-coordinated by Ca$^{2+}$,

(ii) both samples have the same coordination environment of F$^−$ in spite of the different methods of fluoride addition to the samples, which means the coordination structure in the melts has attained the equilibrium state.$^{16}$

Figures 2 and 3 show the $^{19}$F MAS NMR spectra for the samples in the groups (2) and (3), respectively. All the spectra exhibit a peak with the chemical shift close to that of CaF$_2$ crystal although the spectra of the samples E and G show two sharp peaks superimposed onto a broad peak. The two sharp peaks are due to cuspidine (3CaO·2SiO$_2$·CaF$_2$)$^{17}$ precipitated in the samples E and G. It can be found from Figs. 2 and 3 that most of F$^−$ is fourfold-coordinated by Ca$^{2+}$ for the samples C–G despite...
of the different values of (mol%CaO)/(mol%SiO₂) and CaF₂ concentrations.

Figure 4 shows the ¹⁹F MAS NMR spectra for the samples in the group (4). For samples of \( \frac{n_{Na}}{(n_{Na}+n_{Ca})}/H_1=0.3 \), the spectra show only one peak (peak I) with the chemical shift close to CaF₂ crystal, which demonstrates F⁻ is coordinated by four Ca²⁺. On the other hand, in addition to this peak, two new peaks (peaks II and III) appear at about 10 and 60 ppm for samples with \( \frac{n_{Na}}{(n_{Na}+n_{Ca})}/H_1=0.4 \). The intensity of peak I decreases and the intensities of the other two peaks increase with increasing \( \frac{n_{Na}}{(n_{Na}+n_{Ca})} \). The peak positions have been determined by deconvoluting the spectra into three curves described by the following equation.

\[
F(\delta) = A \exp \left[ -\frac{(\delta-\delta_0)^2}{2\sigma^2} \right] + B_I \exp \left[ -\frac{(\delta-\delta_0+\delta_{SSB,I})^2}{2\sigma^2} \right] + B_{II} \exp \left[ -\frac{(\delta-\delta_0-\delta_{SSB,II})^2}{2\sigma^2} \right]
\]

where \( \delta_0, \delta_0\pm\delta_{SSB,I} \) and \( \delta_0\pm\delta_{SSB,II} \) are the peak positions of the main peak (an isotropic peak) and of the first and the second spinning sidebands, respectively. \( \sigma \) is the full width at half maximum (FWHM) of the peak, and \( A, B_I \) and \( B_{II} \) are the intensity of the isotropic peak and of the first and the second spinning sidebands, respectively. The values of \( \delta_{SSB,I} \) and \( \delta_{SSB,II} \) are assumed to be 58.4 ppm (10.995 kHz), 109 ppm (20.523 kHz), 0.15 \( A \) and 0.08 \( A \), respectively, for all samples by best fit to the experimental curves. Theoretically, the peak positions of the spinning sidebands are multiple numbers of the sample spinning rate, namely, in this case, the values of \( \delta_{SSB,I} \) and \( \delta_{SSB,II} \) should be 53.1 ppm (10 kHz) and 106 ppm (20 kHz), respectively. The difference between the adopted values of \( \delta_{SSB,I} \) and \( \delta_{SSB,II} \) and the theoretical ones is due to the error in the phase correction of the signal. The chemical shifts of the isotropic peaks are summarized in Table 1. It is found that the chemical shift of peak I decreases with an increase of \( \frac{n_{Na}}{(n_{Na}+n_{Ca})} \) although the chemical shifts of the other two peaks remain constant. The peaks for the samples with the value of \( \frac{n_{Na}}{(n_{Na}+n_{Ca})} \geq 0.4 \) will be identified in Discussion.

Figure 5 shows the ¹⁹F MAS NMR spectra for two commercial mould fluxes. Both spectra show one broad peak with the chemical shift close to CaF₂ crystal superimposed by two sharp peaks due to cuspidine. This indicates that most of F⁻ for the commercial mould fluxes are in environments similar to CaF₂ crystal, i.e., F⁻ is fourfold-coordinated by Ca²⁺.
The samples D, J and L were annealed in air at 873 K for 1 h. The X-ray diffraction profiles for the annealed samples D, J and L are shown in Fig. 6. Three crystals, Na$_2$CaSiO$_4$, cuspidine (3CaO·2SiO$_2$·CaF$_2$) and Na$_2$Ca$_2$(SiO$_3$)$_3$, have been detected for the sample D. Four crystals, Na$_2$CaSiO$_4$, NaF, cuspidine and Na$_2$Ca$_2$(SiO$_3$)$_3$, have been identified for the samples J and L. Figure 7 shows $^{19}$F MAS NMR spectra of the annealed samples D, J and L together with those of the as-quenched ones. Peaks at about 60 and −60 ppm in the annealed samples are attributed to cuspidine and NaF, respectively. As for the samples J and L, the intensity of the peak at about −10 ppm is much lower for the annealed samples than for the as-quenched samples even when the spinning sidebands from both cuspidine and NaF overlapping the peak at −10 ppm are considered. Disappearance of the peak at −10 ppm for the annealed samples reflects the precipitation of cuspidine and NaF from the glassy samples.

4. Discussion

From Fig. 4, samples having the value of $n_{Na}/(n_{Na}+n_{Ca}) \geq 0.3$ show single peak with the chemical shift close to CaF$_2$ crystal. On the other hand, in addition to this peak, two new peaks appear at about −10 and −60 ppm for samples with $n_{Na}/(n_{Na}+n_{Ca}) \geq 0.4$. Peak I gradually shifts from 60 to 26.4 ppm with increasing $n_{Na}/(n_{Na}+n_{Ca})$ from 0.23 to 0.70, while positions of the other peaks are constant irrespective of the value of $n_{Na}/(n_{Na}+n_{Ca})$. Considering the chemical shift of Si(O−)$_4$−F$_n$ (3 to 31 ppm) and Na$_2$SiF$_6$ (14.6 ppm), peaks are neither due to F$^−$ coordinated only with Si$^{4+}$ nor both Si$^{4+}$ and Na$^+$. In Na$_2$SiF$_6$ crystal, F$^−$ is coordinated with one Si$^{4+}$ and about two Na$^+$, i.e., two SiF$^6_2$− are bonded to each other through Na$^+$. To the best knowledge of the authors, there is no data for the chemical shift of F$^−$ coordinated with both Si$^{4+}$ and Ca$^{2+}$. However, it can be predicted that even if Na$^+$ is replaced by Ca$^{2+}$ in Na$_2$SiF$_6$ crystal, the chemical shift may not vary significantly from 14.6 ppm because of the weak chemical bond between F$^−$ and Na$^+$. Therefore, it is considered that no peaks are also attributed to F$^−$ coordinated with both Si$^{4+}$ and Ca$^{2+}$.
Ca²⁺. Stebbins and Zeng[10] have observed peaks at 20 and −10 ppm for the CaO–SiO₂–CaF₂–Na₂O system. They have reported that these two peaks are due to F⁻ coordinated with both Ca²⁺ and Na⁺, however, they have not presented the detailed coordination environment for the peaks. In order to propose the appropriate coordination structural model corresponding to the peaks, the followings are considered.

1) By analogy with the peak positions of AlO₄, AlO₅ and AlO₆ in ²⁷Al NMR spectra, peaks I, II and III are attributed to fourfold-, fivefold- and sixfold-coordinated F⁻ ions, respectively.

2) Considering the chemical shift of NaF crystal (−58.3 ppm),[12] peak III is assigned to F⁻ having the environments similar to NaF crystal, i.e., that F⁻ is sixfold-coordinated by Na⁺ (see Fig. 8(c)).

3) The shift of the peak from 60 to 26.4 ppm with an increase of \( \frac{n_{Na}}{n_{Na}+n_{Ca}} \) may imply the increase of the number of Na⁺ ions occupying the ligands with an increase of \( \frac{n_{Na}}{n_{Na}+n_{Ca}} \).

Based on the aforementioned points, we propose the coordination structure model as shown in Fig. 8; peak I may be due to F⁻ fourfold-coordinated by Ca²⁺ and Na⁺ (see Fig. 8(a)). The shift of the peak implies that Ca²⁺, by which F⁻ is fourfold-coordinated, is gradually replaced by Na⁺ with increasing \( \frac{n_{Na}}{n_{Na}+n_{Ca}} \). Peak II may be due to F⁻ coordinated with four Na⁺ and one Ca²⁺ as illustrated in Fig. 8(b). Peak III is due to F⁻ sixfold-coordinated by Na⁺.

Figures 2 to 4 show that most of F⁻ are fourfold-coordinated by Ca²⁺ for the samples of \( \frac{n_{Na}}{n_{Na}+n_{Ca}} \) ≤ 0.3. This is in accordance with the result reported by Stebbins and Zeng,[10] i.e., that there is a preference of the coordination of F⁻ to Ca²⁺ rather than Na⁺ relative to a random distribution of ions. They have suggested that cation field strength differences lead to significant non-randomness in the coordination shells of F⁻ ions, which seem to have some energetic preference for smaller and more highly charged cations.

The structure of slags is relevant to the thermochemical and thermophysical properties of slags.[18] Here, the preference of the coordination of F⁻ to Ca²⁺ rather than Na⁺ is examined from the thermodynamic point of view. The following equilibrium relation exists among Na₂O, CaF₂, CaO and NaF.

\[
\text{Na}_2\text{O} + \text{CaF}_2 = \text{CaO} + 2\text{NaF} \quad \text{(3)}
\]

The free energy change of this reaction is written as follows:

\[
\Delta G = \Delta G_0 + RT \ln \frac{a_{\text{CaO}} a_{\text{NaF}}^2}{a_{\text{Na}_2\text{O}} a_{\text{CaF}_2}} \quad \text{(4)}
\]

The standard free energy change \( \Delta G_0 \) of the reaction (3) is −135 and −131 kJ at 1400 and 1700 K, respectively.[19] Since no activity data of the CaO–SiO₂–CaF₂–Na₂O system has been reported, \( a_{\text{CaO}} \) of the CaO–SiO₂ system[20] (see Fig. 9(a)) and \( a_{\text{Na}_2\text{O}} \) of the CaO–SiO₂–Na₂O system[21] (see Fig. 9(b)) are considered to discuss Eqs. (3) and (4). As shown in Fig. 9, \( a_{\text{Na}_2\text{O}} \) is much smaller than \( a_{\text{CaO}} \), which indicates that the equilibrium of Eq. (3) is largely shifted to the left hand side in molten fluxes. Consequently, the number of F⁻ coordinated with Na⁺ may become too small to be detected by NMR. As increasing Na₂O content, i.e., increasing \( a_{\text{Na}_2\text{O}} \), the equilibrium of Eq. (3) is gradually shifted to the right hand side, resulting in the increased number of F⁻ coordi-
nated with Na$^+$. As for commercial mould fluxes, the values of CaO/SiO$_2$ and $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$ are generally 0.8–1.2 and 0.1–0.2, respectively. Since these values are similar to those of samples A, B, D, E, F and D, it is expected that F$^-$ ions exist as CaF$_2$ for commercial mould fluxes.

5. Conclusions

The coordination environment of fluorine in the CaO–SiO$_2$–CaF$_2$–Na$_2$O glasses has been measured by $^{19}$F MAS NMR over a wide composition range including the similar compositions to those of mould fluxes. The coordination environment of F$^-$ for a glassy sample has been compared with crystallized sample to observe structure change during solidification and crystallization. The obtained results are summarized as follows.

(1) F$^-$ are fourfold-coordinated by Ca$^{2+}$ for samples of $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$≤0.3, where n represents the mole fraction of each cation.

(2) As $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$ increases from 0.23 to 0.70, the peak at 60 ppm due to F$^-$ fourfold-coordinated by Ca$^{2+}$ is gradually shifted to 26.4 ppm. Samples of $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$≥0.4, additional peaks are observed at −10 and −60 ppm. The peak at −60 ppm is due to F$^-$ sixfold-coordinated by Na$^+$. We propose the following coordination structure model; the shift of the peak position having the highest chemical shift implies that Ca$^{2+}$, by which F$^-$ is fourfold-coordinated, is gradually replaced by Na$^+$ with increasing $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$. The peak at −10 ppm may be due to F$^-$ fivefold-coordinated with four Na$^+$ and one Ca$^{2+}$.

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