Effect of Na₂O on Crystallization of Mould Fluxes for Continuous Casting of Steel

Miyuki HAYASHI, Takashi WATANABE, Hideko NAKADA and Kazuhiro NAGATA

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8552 Japan.

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The effect of Na₂O on the behavior and mechanism of the precipitation of cuspidine from the CaO–SiO₂–CaF₂–Na₂O quaternary slags has been investigated by solid-state ¹⁹F nuclear magnetic resonance spectroscopy, differential thermal analysis and X-ray diffraction analysis. It is found that F[−] predominantly bonds with Ca²⁺ rather than Na⁺ in the composition range of the commercial mould fluxes. This result indicates that the presence of Na₂O may not prevent the precipitation of cuspidine from the slags. The glass transformation temperature and the crystallization temperature of cuspidine decrease with increasing Na₂O content. The mass fraction of cuspidine in the samples heated at 973 K was obtained as a function of heat treatment time. It is found that the mass fraction of cuspidine significantly increases at the early stage of the heat treatment, but levels off later on. The mass fraction of cuspidine at the leveling-off is the largest for the sample with 4 mass% Na₂O, and is smaller as the Na₂O content is either smaller or larger than 4 mass%. It is also found that the incubation period is observed before the crystallization starts, and that the incubation period is shorter as the Na₂O content in the sample is larger.

KEY WORDS: cuspidine; ¹⁹F nuclear magnetic resonance spectroscopy; glass transformation temperature; crystallization temperature; isothermal heat treatment.

1. Introduction

The most important roles of the mould flux in continuous casting are to provide liquid flux to lubricate the strand, and to provide the optimum level of horizontal heat transfer for the steel grade being cast.¹⁾ It is obviously desirable that a liquid flux should lubricate the strand throughout the length of the mould since the partial solidification of the flux would give rise to the high frictional forces associated with solid/solid contact.²⁾ It has also been known that to minimize longitudinal cracking, it is necessary to reduce the horizontal heat flux by creating a crystallized mould flux film.³⁾

Mould fluxes are essentially mixtures of SiO₂, CaO, Na₂O and CaF₂ with minor additions of Al₂O₃ and MgO.⁴⁾ The main crystalline phase in the solidified mould flux film is generally cuspidine (3CaO·2SiO₂·CaF₂).⁵⁾ The authors have investigated the behavior and mechanism of the precipitation of cuspidine from the CaO–SiO₂–CaF₂ ternary slag, and have found that (i) cuspidine is precipitated even from the glassy samples having the compositions out of the primary crystallization field of cuspidine, as well as in the compatibility triangle of CaO·SiO₂–SiO₂–CaF₂, and (ii) the possible reason the metastable phase of cuspidine is formed is that the coordination environment of fluorine ions in glassy slag is similar to that in CaF₂ and/or cuspidine.⁶⁾

In commercial mould fluxes, Na₂O is also one of the main components. However, there are very few reports with respect to the effect of Na₂O on lubrication and heat transfer of mould fluxes. Mills²⁾ has evaluated the relationship

between Na₂O concentration and liquidus temperature and viscosity of mould fluxes. In the present study, the effect of Na₂O on the behavior and mechanism of the precipitation of cuspidine from the CaO–SiO₂–CaF₂–Na₂O quaternary slags has been investigated.

2. Coordination Environment of Fluorine in the CaO–SiO₂–CaF₂–Na₂O Quaternary Slags⁷⁾

The authors have investigated the coordination environment of fluorine in the CaO–SiO₂–CaF₂ ternary slags by X-ray photoelectron spectroscopy (XPS)⁸⁾ and solid-state ¹⁹F nuclear magnetic resonance spectroscopy (¹⁹F NMR),⁹⁾ and have found that F[−] is dominantly coordinated with Ca²⁺ and does not break the Si–O–Si bonds. On the other hand, with respect to the CaO–SiO₂–CaF₂–Na₂O quaternary slags, it has been proposed from the thermodynamic point of view that F[−] predominantly bonds with Na⁺ rather than Ca²⁺, and that Na₂O and CaF₂ react to form NaF by the following reaction^{2,10)}:

If this reaction takes place, the presence of Na₂O could prevent the precipitation of cuspidine from the slags because cuspidine is composed of the Ca–F bonds. The aim of the present study is to measure the coordination environment of fluorine in the CaO–SiO₂–CaF₂–Na₂O quaternary slags and the commercial mould fluxes by ¹⁹F magic-angle-spinning nuclear magnetic resonance spectroscopy (¹⁹F MAS NMR)

Table 1. Chemical compositions (mol%) and chemical shifts (ppm) of samples.

Sample	CaO	SiO ₂	CaF ₂	Na ₂ O	CaO/SiO ₂	$n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$	Chemical shift [#]
D	39.1	39.1	13.8	8.0	1.00	0.23	60.5
H	36.4	39.1	13.8	10.7	0.93	0.30	58.3
I	31.9	39.1	13.8	15.2	0.82	0.40	50.6, -8.21, -62.0
J	26.8	39.1	13.8	20.3	0.69	0.50	38.1, -9.9, -59.4
K	21.0	39.1	13.8	26.1	0.54	0.60	32.0, -10.9, -62.0
L	14.3	39.1	13.8	32.8	0.37	0.70	26.4, -10.4, -56.6

[#] In ppm, relative to hexafluorobenzene (C₆H₆)**Table 2.** Chemical compositions of commercial mould fluxes (mol%).

Sample	CaO	SiO ₂	CaF ₂	Na ₂ O	Li ₂ O	Al ₂ O ₃	CaO/SiO ₂	$n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$
M	34.8	33.0	17.9	5.0	7.1	2.2	1.05	0.16
N	33.5	41.1	15.4	3.7	2.4	3.8	0.82	0.13

Fig. 1. ¹⁹F MAS NMR spectra of the synthesized samples.

so as to elucidate the effect of Na₂O on the precipitation of cuspidine.

Table 1 shows the nominal compositions of the synthesized samples. The value of $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$, 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. The details of sample preparation and measurements have been reported elsewhere.⁷⁾

Figure 1 shows the ¹⁹F MAS NMR spectra of the synthesized samples. For samples of $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}}) \leq 0.3$, the spectra show only one peak (peak I) with the chemical shift close to that of CaF₂ crystal, which demonstrates that 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

Fig. 2. Coordination structure model for the synthesized samples.

-10 and -60 ppm for samples with $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}}) \geq 0.4$. The intensity of peak I decreases and the intensities of the other two peaks increase with increasing $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$. The chemical shifts of the peaks obtained by the deconvolution of the spectra using Gaussian functions are summarized in Table 1. It is found that the chemical shift of peak I gradually shifts from 60 to 26.4 ppm with increasing $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$ from 0.23 to 0.70 although the chemical shifts of the other two peaks remain constant.

The proposed coordination structure model is shown in **Fig. 2**. Peak I may be due to F⁻ fourfold-coordinated by Ca²⁺ and Na⁺ (see Fig. 2(a)). The shift of the peak implies that Ca²⁺ ions, which F⁻ is fourfold-coordinated by, are gradually replaced by Na⁺ ions with increasing $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$. Peak II may be due to F⁻ coordinated with four Na⁺ and one Ca²⁺ as illustrated in Fig. 2(b). Peak III is due to F⁻ sixfold-coordinated by Na⁺ owing to the fact that the chemical shift of NaF crystal is reported as -58.3 ppm.¹¹⁾ As a consequence, it is found that most of F⁻ ions are fourfold-coordinated by Ca²⁺ for the samples of $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}}) \leq 0.3$. This is consistent with the result reported by Stebbins and Zeng,¹²⁾ i.e., there is a preference of the coordination of F⁻ to Ca²⁺ rather than Na⁺ relative to the random distribution of F⁻ ions.

Fig. 3. ^{19}F MAS NMR spectra for two commercial mould fluxes.

Figure 3 shows the ^{19}F MAS NMR spectra for two commercial mould fluxes. Both spectra show one broad peak with the chemical shift close to that of CaF_2 crystal superimposed by two sharp peaks due to cuspidine. It can be concluded that F^- predominantly bonds with Ca^{2+} rather than Na^+ in the composition range of the commercial mould fluxes, which indicates that the presence of Na_2O may not prevent the precipitation of cuspidine from the slags.

3. Precipitation Behavior of Cuspidine in the $\text{CaO-SiO}_2\text{-CaF}_2\text{-Na}_2\text{O}$ Quaternary Slags¹³⁾

The precipitation behavior of cuspidine from the glassy samples has been observed for five samples. This study may demonstrate the crystallization behavior of the mould flux adjacent to the mould in the practical continuous casting. The chemical compositions of the samples are shown in Fig. 4. The $(\text{mass}\%\text{CaO})/(\text{mass}\%\text{SiO}_2)$ ratio and the CaF_2 content are kept constant at 1.07 and 13 mass%, respectively, and the Na_2O content is varied from 0 to 8 mass%. As for the molar % notation of the compositions, the SiO_2 and CaF_2 contents are 38.7–41.9 and 9.2–10.0 mol%, respectively, and the value of $n_{\text{Na}}/(n_{\text{Na}}+n_{\text{Ca}})$ is varied from 0 to 0.26. Consequently, according to the results of the ^{19}F MAS NMR spectroscopy, it can be considered that F^- ions are mostly coordinated with Ca^{2+} in these samples.

Samples were prepared from reagent grade SiO_2 , CaF_2 , NaF and CaCO_3 powders, the last being decomposed to CaO by heating at 1373 K for 12 h in air. The reagents were weighted to the desired compositions and mixed in a mul-lite mortar. These mixtures were melted in platinum crucibles for 0.5 h at temperatures between 1623 and 1673 K in a flow of pure argon dehydrated by silicagel and P_2O_5 . Glassy samples were quenched by pouring the melts onto a copper plate and immediately after that pressing another copper plate on top of the melts. X-ray diffraction revealed that the quenched samples were amorphous.

Differential thermal analysis (DTA) was carried out to

Fig. 4. Chemical compositions of the samples for the observation of precipitation behavior of cuspidine.

Fig. 5. Calibration curve of the internal standard X-ray diffraction method.

obtain the glass transformation temperature and the onset of the crystallization temperature. A heating rate of 25 K/min was used for the analysis. The crystalline phase corresponding to each exothermic peak was determined by X-ray diffraction analysis in the following manner. The sample heated at a heating rate of 25 K/min up to just above the crystallization temperature was cooled down at a cooling rate of 80 K/min and was measured by X-ray diffraction to determine the phase.

The mass fraction of precipitated cuspidine in the isothermally heat-treated glasses has been measured as a function of heat treatment time by the use of the internal standard X-ray diffraction method.¹⁴⁾ The samples were heated at 973 K in a flow of pure argon for 0.6–28.8 ks. The heat treatment temperature of 973 K has been chosen because it is found from the results of DTA that this temperature is above the glass transformation temperatures for all the samples so that the crystallization takes place. Five standards of 0, 25, 50, 75 and 100 mass% cuspidine bearing glasses were prepared by mixing desired amounts of cuspidine powders with the base glass powders. All the samples and the standards were mixed with the equal weight of $\alpha\text{-Al}_2\text{O}_3$ powders respectively and were subjected to quantitative X-ray diffraction analysis. The ratio of the intensity of (221) peak due to cuspidine to that of (012) peak due to $\alpha\text{-Al}_2\text{O}_3$ ($I_{\text{cuspidine}}/I_{\text{Al}_2\text{O}_3}$) was calculated in each case. The ratios are plotted against mass fraction of cuspidine for the standards as shown in Fig. 5. The mass fractions of precipitated cuspidine in the samples were evaluated using the calibra-

Fig. 6. DTA curves: ● denotes the glass transformation temperature, ○, ▲ and △ denotes the onset of the crystallization temperature for cuspidine, $\text{CaO} \cdot 3\text{SiO}_2 \cdot \text{Na}_2\text{O}$ and $\text{CaO} \cdot \text{SiO}_2$, respectively.

Fig. 7. Mass fraction of cuspidine in the samples heated at 973 K as a function of heat treatment time.

tion curve.

Figure 6 shows DTA curves for all the samples. It can be seen that the glass transformation temperature and the crystallization temperature of cuspidine decrease with increasing Na_2O content.

Figure 7 shows the mass fraction of cuspidine in the samples heated at 973 K as a function of heat treatment time. It is found that the mass fraction of cuspidine significantly increases during the initial part, but levels off in the later part. The mass fraction of cuspidine at the leveling-off is the largest for the sample with 4 mass% Na_2O , and is smaller as the Na_2O content is either smaller or larger than 4 mass%. This result is in accordance with the report by Mills *et al.*¹⁵⁾; they have reported that the crystalline tendency becomes lower when the Na_2O content is larger than 5 mass% for commercial mould powders.

Supposing that the samples are in the equilibrium states at 973 K, the precipitation amounts of cuspidine as well as

Table 3. Theoretical fractions (mass%) of the constituent phases in the samples assuming that the samples are in the equilibrium states at 973 K.

mass% Na_2O	-	$\text{CaO} \cdot \text{SiO}_2$	CaF_2	cuspidine
0	-	57.19	4.93	37.88
mass% Na_2O	NaF	$\text{CaO} \cdot \text{SiO}_2$	$3\text{CaO} \cdot 2\text{SiO}_2$	cuspidine
2	2.71	48.55	0.76	47.98
4	5.42	39.91	19.74	34.93
6	8.13	31.27	38.71	21.89
8	10.84	22.63	57.69	8.94

Fig. 8. Ratio of the mass fraction of cuspidine in the sample heated at 973 K for 28.8 ks to that calculated by assuming that the sample is in the thermodynamically equilibrium state at 973 K.

the other constituents can be calculated. Here, we performed the calculation based on the fact that the composition of the sample with 0 mass% Na_2O is in the compatibility triangle of $\text{CaO} \cdot \text{SiO}_2$ – CaF_2 –cuspidine¹⁶⁾ and that those of the samples with 2 to 8 mass% Na_2O are in the compatibility triangular pyramid of NaF – $\text{CaO} \cdot \text{SiO}_2$ – $3\text{CaO} \cdot 2\text{SiO}_2$ –cuspidine.¹⁷⁾ When the initial composition of the sample described by the molar % notation is $a(\text{mol}\%)\text{Na}_2\text{O}$ – $b\text{CaO}$ – $c\text{SiO}_2$ – $d\text{CaF}_2$ ($a=2$ – 8), the fractions (mol%) of the equilibrium phases, $x(\text{mol}\%)\text{NaF}$ – $y(\text{CaO} \cdot \text{SiO}_2)$ – $z(3\text{CaO} \cdot 2\text{SiO}_2)$ – $w(\text{cuspidine})$, can be calculated as follows by considering the mass balance of each element:

$$x = 2a \times 100 / (a - b + 2c) \dots\dots\dots (2)$$

$$y = (-2a - 2b + 3c) \times 100 / (a - b + 2c) \dots\dots\dots (3)$$

$$z = (2a + b - c - d) \times 100 / (a - b + 2c) \dots\dots\dots (4)$$

$$w = (-a + d) \times 100 / (a - b + 2c) \dots\dots\dots (5)$$

Table 3 tabulates the fractions of the equilibrium phases described by the mass% notation, which are converted from those described by the mol% notation.

Figure 8 shows the ratio of the mass fraction of cuspidine in the sample heated at 973 K for 28.8 ks to that calculated by assuming that the sample is in the thermodynamically equilibrium state at 973 K shown in Table 3. It can be seen that the ratios are larger than unity except for the sample with 0 mass% Na_2O . This result implies that the samples are not in the thermodynamically equilibrium states even after the samples are heated for an extended period of time, but the samples contain larger amount of cuspidine than estimated by assuming that the sample is in the equi-

librium state. It is considered that such crystallization behavior is relevant to the structure of the glassy samples before heating.

The authors have demonstrated by the use of ^{19}F NMR that in the $\text{CaO-SiO}_2\text{-CaF}_2$ glassy samples the fluorine ions are not distributed homogeneously but form Ca-F clusters, the structure of which is similar to that of CaF_2 and/or cuspidine.⁹⁾ The fluorine ions would also form Ca-F clusters in the $\text{CaO-SiO}_2\text{-CaF}_2\text{-Na}_2\text{O}$ glassy samples. Owing to the presence of Ca-F clusters in the glassy samples, the precipitation of cuspidine can easily take place by a slight rearrangement of the configuration of ions during heating. As a result, it is possible that the fraction of cuspidine in the heat-treated sample becomes even larger than that in the equilibrium state.

It is also found from Fig. 8 that the ratio of the mass fraction of cuspidine in the heated sample to that in the equilibrated sample is larger as the Na_2O content is larger. It can be considered that the ratio is relevant to the size and/or the number density of Ca-F clusters in the glassy samples, *i.e.*, the ratio becomes larger as the size and/or the number density of clusters is larger. With respect to the mechanism of the formation of Ca-F clusters, we haven't experimentally clarified yet whether Ca-F clusters are present in the melt or are only formed during quenching of the melt. Although some researchers have proposed that crystal embryos may exist in melts even above the liquidus temperature,^{18,19)} we presume so far that Ca-F clusters are formed during quenching. The clusters could be formed by the migration of ions due to the viscous flow during quenching. In this case, it is considered that the size and/or the number density of clusters are larger in the samples having lower glass transformation temperature, *i.e.*, higher Na_2O content. This might be the reason that the samples with higher Na_2O content have larger ratio as shown in Fig. 8.

It is found from Fig. 7 that the incubation period is observed before the crystallization starts, and that the incubation period is shorter as the Na_2O content is larger. Incubation period corresponds to the required time for the size and the number density of cuspidine to become large enough that cuspidine can be detected by X-ray diffraction. It has been reported that in general the nucleation and the crystal growth rates are inversely proportional to the viscosity.²⁰⁾ In fact, the samples having larger Na_2O content exhibit lower viscosity because Na_2O is a network-breaking component. Therefore, it can be considered that the samples having larger Na_2O content exhibit larger nucleation and crystal growth rates, resulting in shorter incubation period.

4. Conclusions

The effect of Na_2O on the precipitation of cuspidine from the $\text{CaO-SiO}_2\text{-CaF}_2\text{-Na}_2\text{O}$ quaternary glassy samples has been investigated from the structural point of view based on the solid-state ^{19}F MAS NMR studies. The behavior of the precipitation of cuspidine has been observed using the DTA and X-ray diffraction studies, and the mechanism of the precipitation has been discussed by considering the thermo-

dynamically equilibrium state. The obtained results are summarized as follows.

- F^- predominantly bonds with Ca^{2+} rather than Na^+ in the composition range of the commercial mould fluxes, which indicates that the presence of Na_2O may not prevent the precipitation of cuspidine from the slags.
- The results of DTA reveal that the glass transformation temperature and the crystallization temperature of cuspidine decrease with increasing Na_2O content.
- For the isothermal heat-treated samples, the mass fraction of cuspidine significantly increases at the early stage of the heat treatment, but levels off later on. The mass fraction of cuspidine at the leveling-off is the largest for the sample with 4 mass% Na_2O , and is smaller as the Na_2O content is either smaller or larger than 4 mass%.
- The incubation period is observed before the crystallization starts, and the incubation period is shorter as the Na_2O content is larger.
- The aforementioned influence of Na_2O on the behavior of the precipitation of cuspidine could be relevant to the decrease in the viscous flow of the glassy samples by the Na_2O addition.

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