Viscosity and Solidification Temperature of SiO$_2$–CaO–Na$_2$O Melts for Fluorine Free Mould Flux

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Fluorine-free mould flux has been required to reduce corrosion of continuous casters. In this paper, Na$_2$Ca$_2$Si$_3$O$_9$ has been applied to an alternative crystalline phase of Ca$_4$Si$_2$O$_7$F$_2$ (cuspidine) that crystallized in commercial flux films. Effects of basicity described as T.CaO/SiO$_2$ and additions of Li$_2$O, Na$_2$O, MgO and/or MnO into Na$_2$Ca$_2$Si$_3$O$_9$ composition mould flux on viscosity and solidification temperature were studied and the solidified specimens were examined by X-ray diffraction to identified crystalline phases.

The viscosity of the mould flux is reduced with increasing of the basicity or the basic components contents. The solidification temperature decreased slightly as the basicity increased from 0.47 to 0.60, whereas it increased steeply with increasing of the basicity from 0.60 to 0.70. The solidification temperature also steeply increased when large amounts of these basic components were added. With increasing of the basic components amounts, the first peak intensity of the target phase, Na$_2$Ca$_2$Si$_3$O$_9$, decreased while that of Na$_2$Ca$_2$Si$_2$O$_7$, which had higher melting point than the target phase, increased. It is indicated that the solidification temperature is related to Na$_2$Ca$_2$Si$_2$O$_7$ crystallization.

Carbon steel was cast with one of the developed fluorin-free mould fluxes and slab without any surface cracking was obtained.

KEY WORDS: continuous casting; mould flux; fluorine; viscosity; Na$_2$Ca$_2$Si$_3$O$_9$.

1. Introduction

Fluorine is an important component to adjust physical properties of mould flux appropriately as well as to crystalize Ca$_4$Si$_2$O$_7$F$_2$ (cuspidine) in flux films to control a heat transfer for mild cooling. Therefore, the crystallization of cuspidine has been studied about phase relation, primary field and precipitation. Gibbs energy of formation of cuspidine has been also determined.

On the other hand, a reaction between the mould flux and secondary cooling water causes fluorine dissolution into the water and generates hydrogen fluorine that corrodes plant equipment. Thus, fluorine-free mould flux has been required. Recently, Fox et al. and Nakada et al. have submitted B$_2$O$_3$ and TiO$_2$ which are alternative substitutes for CaF$_2$ in the mould fluxes, respectively. These reports indicate possibility of fluorine-free mould fluxes.

In this study, SiO$_2$–CaO–Na$_2$O system is focused as a base system of the fluorine-free mould flux. Na$_2$Ca$_2$Si$_3$O$_9$, which has a melting point of 1 280–1 290 degree Celsius, is thought to be an applicable crystalline phase which substitutes for cuspidine. Effects of additions of Li$_2$O, Na$_2$O, MgO and/or MnO to Na$_2$Ca$_2$Si$_3$O$_9$ composition of the mould flux mixed with law materials on solidification temperatures, viscosities and crystalline phase have been studied.

2. Experimental

2.1. Specimen Preparation

The equilibrium phase diagram of SiO$_2$–CaO–Na$_2$O system is shown in Fig. 1. The primary field of Na$_2$Ca$_2$Si$_3$O$_9$ consulted with the reference is also illustrated in Fig. 1. Specimen components of SiO$_2$, CaO and Na$_2$O correspond to the shaded region in Fig. 1, and Li$_2$O, MgO and/or MnO were added into them. These specimens were prepared by mixing industrial raw materials. The compositions of these

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specimens are shown in Table 1. Rs in Table 1 named “soda ratio” in this paper is defined as a ratio of Na2O mass divided by total mass of SiO2, CaO and Na2O.

2.2. Measurements Procedure and Analysis

The viscosities and the solidification temperature of the mould fluxes were evaluated with the oscillating-plate viscometer.12) 1 kg of the sample was melted at 1 673 K in a carbon crucible under argon atmosphere. Then its temperature was decreased at a rate of 2 K/min, and the viscosity was measured continuously. When the sample began to solidify, the viscosity rose rapidly. A breakpoint found in relationship between the temperature and the viscosity was defined as the solidification temperature.

After the physical properties were measured, a solidified specimen in the crucible was crushed into powder and analysed by X-ray diffraction. From peak patterns of the X-ray diffraction, crystalline phase was identified. An intensity of the X-ray diffraction at the first peak of each crystalline phase was used as an index of the crystallization.

3. Results and Discussion

3.1. Solidification Temperature and Crystalline Phase

The relationship between the basicity and the solidification temperature is illustrated in Fig. 2. The solidification temperature decreased slightly as the basicity increased from 0.47 to 0.60, whereas it increased steeply with increasing of the basicity from 0.60 to 0.70. The effect of an amount of Li2O, Na2O or MgO into Na2Ca2Si3O9 composition fluxes on the solidification temperature is shown in Fig. 3. The solidification temperature decreased as the amount of Li2O or MgO increased. When the content of Na2O was less than 6 mass%, it had little influence on the solidification temperature. On the other hand, the solidification temperature increased a little at around 10 mass% Na2O.

The peak patterns of the X-ray diffraction showed that Na2Ca2Si3O9 crystallized in all specimens and Na2Ca2Si2O7 crystallized in several specimens. The relationship between the basicity and intensities of the first peaks of these two kinds of crystalline phases is illustrated in Fig. 4. The first peak intensity of Na2Ca2Si3O9 decreased as the basicity increased from 0.60 to 0.70, whereas the first peak intensity of Na2Ca2Si2O7 increased with increasing of the basicity from 0.60 to 0.70. Effects of Na2O content on the first peak intensities of Na2Ca2Si3O9 and Na2Ca2Si2O7 were shown in Fig. 5. With increasing of Na2O content, the first peak intensity of Na2Ca2Si3O9 decreased and the intensity of Na2Ca2Si2O7 increased. While the addition of Li2O or MgO caused the first peak intensity of Na2Ca2Si3O9 to decrease, Na2Ca2Si2O7 was little observed.

From Figs. 2–5, it is indicated that the solidification tempera-
Temperature increased with increasing the first peak intensity of Na$_2$Ca$_2$Si$_2$O$_7$. A “compositional length”, $L$, which is defined in Eq. (1), is applied to investigate the effect of the composition at the basicity of around 0.60 on the first peak intensities of these two kinds of crystalline phases and the solidification temperatures.

$$L = \sum_{i} (X_i - Y_i)^2$$  \hspace{1cm} (1)

Here, $X_i$ and $Y_i$ are the mole fractions of specimens and Na$_2$Ca$_2$Si$_3$O$_9$, respectively. This length represents a compositional distance between specimens and the target phase. Relationships between the compositional length and the first peak intensities of Na$_2$Ca$_2$Si$_3$O$_9$ and Na$_2$Ca$_2$Si$_2$O$_7$ and the solidification temperatures are shown in Fig. 6. The first peak intensity of Na$_2$Ca$_2$Si$_3$O$_9$ steeply decreased and that of Na$_2$Ca$_2$Si$_2$O$_7$ gradually increased with the compositional length increase. The solidification temperature increased steeply as the compositional length increased from 0.10 to 0.17, where the first peak intensity of Na$_2$Ca$_2$Si$_2$O$_7$ was relatively high. This result indicates that the solidification temperature is increased with crystallization of Na$_2$Ca$_2$Si$_2$O$_7$, which has about 170 degree Celsius higher melting point than Na$_2$Ca$_2$Si$_3$O$_9$. At the constant basicity, increasing of amounts of Li$_2$O, Na$_2$O, MgO and/or MnO, which are obviously basic components, cause both activities of SiO$_2$ to decrease and of CaO to increase. Accordingly, it is considered that Na$_2$Ca$_2$Si$_2$O$_7$, which has higher basicity than Na$_2$Ca$_2$Si$_3$O$_9$, crystallizes with increasing of the compositional length.

### 3.2. Viscosity

The relationship between the basicity and the viscosity at 1 300 degree Celsius is illustrated in Fig. 7. The viscosity decreased with increasing of the basicity. The effect of the additive amount of Li$_2$O, Na$_2$O or MgO on the viscosity at 1 300 degree Celsius is shown in Fig. 8. Figure 8 expresses that these basic components, especially Li$_2$O, affect on decreasing of the viscosity. The viscosity behaviors including Li$_2$O or MgO with different soda ratio are shown in Figs. 9 and 10. From these two figures, it is demonstrated that the Li$_2$O or MgO addition conducts the viscosity reducing and it is more effective with lower contents of Na$_2$O. The relationship between the compositional length and the viscosity at 1 300 degree Celsius at the basicity of around 0.60 is shown in Fig. 11. The viscosity was indicated to decrease as the compositional length increased because the basic components, except for Al$_2$O$_3$, were added.

Viscosity is considered to depend on the network of silicate, and activity of SiO$_2$ is applied as an index of the viscosity. The activity of SiO$_2$ in molten flux decreases with increasing of the basic components, as same as the viscosity decrease. The relationship between the viscosity at 1 300 degree Celsius and the SiO$_2$ activity at same temperature.
calculated by using FactSage thermodynamic software and FToxide Database\textsuperscript{13} is shown in Fig. 12. Because FToxide does not support a solution database including Li$_2$O, the results seen in Fig. 12 are comprised without Li$_2$O. Figure 12 demonstrates that the viscosity at 1 300 degree Celsius decreases linearly as the SiO$_2$ activity decreases in the range of composition applied in this study.

### 3.3. Prospective Composition

As described above, the addition of basic components into Na$_2$Ca$_2$Si$_3$O$_9$ composition flux mixed with industrial materials causes Na$_2$Ca$_2$Si$_3$O$_9$ crystallization to decrease while it is required to reduce the viscosity. From Figs. 6 and 11, however, there are available specimens as the mould fluxes in the range of compositional length from 0.05 to 0.10. In this range, the first peak intensity of Na$_2$Ca$_2$Si$_3$O$_9$ is much higher than that of Na$_2$Ca$_2$Si$_2$O$_7$, and it is indicated that Na$_2$Ca$_2$Si$_3$O$_9$ mainly crystallizes in flux films and the compositions in this range prevent steep increases of the solidification temperature caused by Na$_2$Ca$_2$Si$_2$O$_7$ crystallization. Tsutsumi et al.\textsuperscript{14} have observed that the critical cooling rate for glass formation of Li$_2$O–SiO$_2$, Na$_2$O–SiO$_2$ and Na$_2$O–CaO–SiO$_2$ systems by hot-thermocouple methods with DTA. From the report, it is estimated that the critical cooling rate of mould flux whose basicity is 0.62 achieves around 20 mass% Na$_2$O and shows little change with more Na$_2$O added, and that Li$_2$O has more effect on the critical cooling rate than Na$_2$O. These are important information on the crystallization of the present mould flux.

In the components range used in the present study, the lowest viscosities at 1 300 degree Celsius are around 3 poise, which are thought to be an available viscosity for casting since the viscosities of commercial mold fluxes\textsuperscript{15,16} are approximately from 1 to 4 poise at that temperature.

### 4. Casting Test

#### 4.1. Casting Condition

One of the developed fluorine-free mould fluxes shown in Table 2 and 3, whose composition was given in the above discussion, was applied to steel casting with our test continuous caster for slab casting. The casting test with the conventional mould flux seen in Tables 2 and 3 was also carried out. 0.47%C steel, whose composition was shown in Table 4, was casted under the condition of velocity of 0.70 m/min, oscillation stroke of 7 mm, and negative strip ratio of 40%.

#### 4.2. Casting Results

There were no cracks found on the surface of each slab. Several thermocouples were installed longitudinally-arranged in the centre position in width of the casting mould. The temperatures measured by the thermocouples during casting are shown in Fig. 13. The temperatures decreased as the distances from meniscus increased. While the each temperature shown in Fig. 13(b) is a little higher than ones in Fig. 13(a), it is an acceptable difference. If a poor flow of mould flux between the mould and the initial solidified shell or unstable heat transfer in the flux film occurred, the temperatures measured by the thermocouples would show a large change though the casting. Figure 13,
however, expresses that the temperature changes seen in the casting with the developed mould flux are as small as with the conventional one. It is demonstrated that stable casting is achieved by using the fluorine-free mould flux.

5. Conclusions

In the present study, the fluorine-free mould flux has been developed. Na₂Ca₂Si₃O₉ turned to be available for main crystalline phase in the flux film in the mould, instead of cuspidine for the conventional. The reasonable viscosity for lubrication is obtained by adjusting the contents of the basic components without fluorine. In the actual casting, the developed flux brings stable lubrication, heat transfer and surface quality of without any cracking.

REFERENCES

13) FactSage, www.factsage.com