Crystallization Behaviors of Mold Fluxes Containing Li$_2$O Using Single Hot Thermocouple Technique

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Minor addition of Li$_2$O (<2 mass%) can significantly alter the melting temperature and viscosity of a mold flux. However, the crystallization tendency of mold fluxes containing Li$_2$O more than 2 mass% hasn’t been understood. In this paper, single hot thermocouple technique, X-ray diffraction, and Back Scattered Electron (BSE) were employed to investigate the crystallization behavior concerned with CCT and TTT diagrams of mold fluxes containing high content of Li$_2$O.

The critical cooling rate and crystallization rate of samples were increased with the addition of Li$_2$O, whether there is Na$_2$O or not. But the incubation time was reduced obviously with Li$_2$O more than 6 mass% in mold fluxes. The critical cooling rate and incubation time of NL$_{1.5}$ sample (Na$_2$O=8 mass%, Li$_2$O=1.5 mass%) were close to those of L$_3$ sample (Na$_2$O=0 mass%, Li$_2$O=7 mass%). Moreover, there is no difference in the crystal phase of the two samples, and the crystal phases precipitated at high temperature and low temperature were respectively Ca$_2$(SiO$_4$) and Ca$_4$Si$_2$O$_7$F$_2$. Li-cuspidine was promoted to precipitate when the basicity of the sample was increased. The small, dense grains of cuspidine were observed in NL$_{1.5}$ sample, and the thickness of slag film was 0.4 mm more than that of L$_3$ sample. The heat flux of NL$_{1.5}$ sample measured was 10% less than that of L$_3$ sample, as expected. Therefore, high content of Li$_2$O can be substituted by the combination of Na$_2$O and minor of Li$_2$O, as is the composition in the commercial mold fluxes.

KEY WORDS: mold fluxes; single hot thermocouple technique; critical cooling rate; incubation time.

1. Introduction

Mold fluxes which are based on the CaO–SiO$_2$–Al$_2$O$_3$ system with additions of CaF$_2$ and Na$_2$O have many functions. The several essential functions include: (i) protecting the meniscus of the steel from oxidation; (ii) providing thermal insulation to prevent the steel from freezing; (iii) providing liquid lubrication for the strand; (iv) controlling the horizontal heat transfer between the strand and mold according to the steel grade being cast; and (v) absorbing inclusions from the steel.1–5) When inclusions were picked up, such as Al$_2$O$_3$ and TiO$_2$, it would result in significant changes in the physical properties of mold fluxes, such as viscosity, break temperature, or degree of solid slag film crystallinity.$^5$–$^10$) So the additives of Li$_2$O, MgO and B$_2$O$_3$ were often added to keep the stable physical properties of mold fluxes.3,11) And the powders were tried to make lower viscosity, melting point and higher melting rate for high speed casting by adding Na$_2$O, CaF$_2$ and Li$_2$O. The results show that the effects were obvious with minor addition of Li$_2$O.$^{12–15}$) Therefore, Li$_2$O was often added in the mold fluxes for high speed casting.

The physical properties of mold fluxes, such as viscosity and solidification temperature are critical elements in the design of optimized mold fluxes for high speed casting. Minor addition of Li$_2$O (<2 mass%) can significantly alter the physical properties of a mold flux, provide adequate lubrication to prevent sticking and produce strands with defect free. So the productivity and quality of steels are improved. The crystallization rate of mold fluxes can be obviously increased by the addition of Na$_2$O to form the high-density crystalline layer,16) so Li$_2$O and Na$_2$O are often found in the commercial mold fluxes. But it was reported that Na$_2$O and MgO were substituted by high content of Li$_2$O to form Li-cuspidine and increase the crystallization rate.17) The lubrication can be improved by increasing the content of Li$_2$O, but the influence of high content of Li$_2$O on the heat transfer hasn’t been reported. And the heat transfer through the slag film in the mold primarily depends on two parameters of the mold fluxes, namely the thickness of the slag film layer and crystallization tendency.$^{18–20}$) However, the influence of Li$_2$O on the crystallization tendency of mold fluxes hasn’t been understood. Therefore, there is a need to investigate the influence of Li$_2$O on the crystallization behavior of mold fluxes containing high content of Li$_2$O.

It is usually thought that the onset of crystallization in mold fluxes must be a function of cooling rate. The average cooling rate of the mold fluxes in mold may be about 50–100°C/s,$^{21}$ especially near the meniscus. So the critical cooling rate required for the glass formation is one of the important characteristics for the utilization of mold fluxes.
Moreover, the crystal morphology, chemistry, growth rate and the time evolution fraction of solid are important parameters in the effect on heat transfer of mold fluxes. Therefore, either continuous cooling transformation diagrams (CCT curves) or isothermal time temperature transformation diagrams (TTT curves) must be constructed to comprehensively understand the crystallization tendency of mold fluxes.21–24) And hot thermocouple techniques which combine video observation and image analysis were developed to meet the requirements of cooling rates. In this paper, single hot thermocouple technique (SHTT) was chosen to investigate the crystallization behavior concerned with CCT and TTT diagrams of mold fluxes containing Li$_2$O.

### 2. Experimental

#### 2.1. Sample Preparation

Experimental samples have two systems: NL samples (Na$_2$O=8 mass%, Li$_2$O=0–3 mass%) and L samples (Na$_2$O=0, Li$_2$O=2–8 mass%). The basicity ((CaO+56/78CaF$_2$)/SiO$_2$), Al$_2$O$_3$ and F of all the samples are 1.25, 4 mass% and 6 mass%, respectively. Synthesized samples were prepared by mixtures of high purity CaCO$_3$, SiO$_2$, Al$_2$O$_3$, CaF$_2$, Li$_2$CO$_3$ and Na$_2$CO$_3$ powders (99.5 mass%). These powders were weighed at various initial compositions and melted in graphite crucibles in air atmosphere using MoSi$_2$ furnace. The liquid mixture was held at 1400°C for 10 min. Each sample was quenched in water, and then dried, crushed, grounded and sieved by 200 mesh screen. It was confirmed that the samples were amorphous by X-ray diffraction (Rigaku Co. D/MAK-3C). The melting temperature and viscosity were measured by hemisphere point and rotating viscometer. The chemical compositions (mass%) calculated and physical properties of experimental samples are shown in Table 1.

| Table 1. Chemical composition (mass%) and physical properties of experimental mold fluxes. |
|---|---|---|---|---|---|---|---|
| samples | \((\text{CaO})_{56/78}\) | CaO | SiO$_2$ | Al$_2$O$_3$ | CaF$_2$ | Na$_2$O | Li$_2$O | \(X_{\text{Li}_{2}O}/X_{\text{Na}_{2}O}\) | Melting | Viscosity, \(\eta_{1500}\) |
| NL$_0$ | 1.25 | 38.12 | 37.57 | 4.00 | 12.32 | 8.00 | 0 | 0.20 | 1123 | 0.360 |
| NL$_{0.5}$ | 1.25 | 37.84 | 37.35 | 4.00 | 12.32 | 8.00 | 0.50 | 0.24 | 1118 | 0.350 |
| NL$_1$ | 1.25 | 37.56 | 37.12 | 4.00 | 12.32 | 8.00 | 1.00 | 0.27 | 1094 | 0.340 |
| NL$_{1.5}$ | 1.25 | 37.29 | 36.90 | 4.00 | 12.32 | 8.00 | 1.50 | 0.30 | 1063 | 0.276 |
| NL$_2$ | 1.25 | 37.01 | 36.68 | 4.00 | 12.32 | 8.00 | 2.00 | 0.33 | 1025 | 0.244 |
| NL$_{2.5}$ | 1.25 | 36.73 | 36.46 | 4.00 | 12.32 | 8.00 | 2.50 | 0.36 | 1011 | 0.199 |
| NL$_3$ | 1.25 | 36.45 | 36.23 | 4.00 | 12.32 | 8.00 | 3.00 | 0.39 | 990 | 0.175 |
| L$_2$ | 1.25 | 41.45 | 40.23 | 4.00 | 12.32 | 0 | 2.00 | 0.10 | 1268 | 0.430 |
| L$_3$ | 1.25 | 40.90 | 39.79 | 4.00 | 12.32 | 0 | 3.00 | 0.16 | 1137 | 0.303 |
| L$_4$ | 1.25 | 40.34 | 39.35 | 4.00 | 12.32 | 0 | 4.00 | 0.21 | 1095 | 0.267 |
| L$_5$ | 1.25 | 39.79 | 38.90 | 4.00 | 12.32 | 0 | 5.00 | 0.26 | 1062 | 0.207 |
| L$_6$ | 1.25 | 39.23 | 38.46 | 4.00 | 12.32 | 0 | 6.00 | 0.32 | 1016 | 0.167 |
| L$_7$ | 1.25 | 38.67 | 38.01 | 4.00 | 12.32 | 0 | 7.00 | 0.38 | 962 | 0.143 |
| L$_8$ | 1.25 | 38.12 | 37.57 | 4.00 | 12.32 | 0 | 8.00 | 0.44 | 930 | 0.112 |

2.2. Experimental Process

The heating and cooling of the SHTT can be controlled by means of a computer program, so continuous cooling experiments and isothermal experiments can be performed. Pure K$_2$SO$_4$ was used to calibrate the temperature measurement occurring from a contact potential difference between the electrode and relay circuit. Figure 1(a) shows the thermal cycle employed in the continuous cooling experiment. First of all, a small sample was heated on the tip of the thermocouple at the rate of 15°C/s. The sample was held at 1500°C for 60 s to eliminate bubbles, and homogenize its composition and temperature. Then the sample was cooled down to 900°C at different cooling rates. The cooling rate at which there is no crystals precipitated is defined as the critical cooling rate. CCT diagrams were constructed by recording the crystallization temperature and the beginning time of crystallization at different cooling rates.

The thermal cycle employed in the isothermal experiment is shown in Fig. 1(b). The sample was held at 1500°C for 10 min. Each sample was quenched in water, and then dried, crushed, grounded and sieved by 200 mesh screen. X-ray diffraction was also performed to confirm the amorphous nature of the samples. The experimental samples were then kept in a desiccator to avoid moisture affecting the results. The isothermal experiments were conducted at 1500°C for 10 min, and then cooled at different cooling rates. The cooling rate at which no crystals precipitated is defined as the critical cooling rate. TTT diagrams were constructed by recording the crystallization temperature and the beginning time of crystallization at different cooling rates.
for 60 s, and then it was rapidly cooled down at the cooling rate of 80°C/s to different isothermal temperatures. That is the starting of the isothermal experiment. TTT diagrams were constructed by recording the onset time of crystallization at various isothermal temperatures.

Figure 2 shows the crystallization process of a sample. The mold fluxes start to crystallize when the crystals can be observed, and the volume fraction of crystallization is defined as 0.5% by image analysis. SEM (Tescan Vega II LMU) was used on quenched samples which were melted on the SHTT at 1500°C and quickly cooled to a desired temperature to measure the microstructure of these samples. As the amount of sample quenched from SHTT was very small (<5 mg), it is very difficult to use XRD with a small sample. Therefore, another quenched experiment was tried. Samples (100 g) were melted in graphite crucibles in air atmosphere at 1400°C for 5 min, and cooled at 10°C/min to various isothermal temperatures, and held for 30 min. The samples were taken out from the furnace and quenched in water. The phases of the quenched samples were analyzed by XRD.

3. Experimental Results

3.1. The Results of Continuous Cooling Experiment

3.1.1. Mold Fluxes Containing Li2O and Na2O

The CCT diagram of NL1.5 (Na2O = 8 mass%, Li2O = 1.5 mass%) sample was shown in Fig. 3(a). The crystallization temperature of mold fluxes lowers as the cooling rate increases, as expected. As is shown in Fig. 3(b), the critical cooling rate of NL samples first appreciably reduces, then increases with the increase of $\frac{X_{\text{Li}_2\text{O}}}{X_{\text{Li}_2\text{O}} + X_{\text{Na}_2\text{O}}}$, which is consistent with the results of Ota et al.25) NL1.5 sample has the minimum critical cooling rate 3°C/s obtained from CCT diagram, and the critical cooling rate of NL samples was increased 6°C/s per 1 mass% Li2O to obviously strengthen the crystallization tendency.

3.1.2. Mold Fluxes Containing High Content of Li2O

Figure 4 is the continuous cooling results of L samples without Na2O, and the mold fluxes were easily glass formation when the content of Li2O was less than 6 mass%. When Li2O is over 6 mass%, the critical cooling rate of L samples increased 4°C/s per 1 mass% Li2O. Also, the results previously reported by Tsutsumi et al.26) were shown for comparison. It’s indicated that the influence of Li2O on the crystallization tendency of mold fluxes found by Tsutsumi et al. was more obvious owing to the addition of high content of Li2O in CaO–SiO2–Li2O slag system.

3.2. TTT Diagrams

3.2.1. Mold Fluxes Containing Li2O and Na2O

Figure 5(a) shows that the incubation time of NL samples became shorter with the addition of Li2O, and the incu-
bation time was reduced by 25 s when the content of Li$_2$O was increased from 0.5 to 1.5 mass%. But there is no obvious influence on the crystallization rate to further increase the content of Li$_2$O.

3.2.2. Mold Fluxes Containing High Content of Li$_2$O

From Fig. 5(b), we can see that the incubation time of L samples was shortened by 50 s when the content of Li$_2$O was increased from 6 to 7 mass%. Considering the result of Omoto et al.\textsuperscript{17} indicates that Li$_2$O has a positive effect on the crystallization rate of mold fluxes. The incubation time of L$_8$ sample is close to zero to increase the frequency of sticking type breakout. And there’s no crystals precipitated at temperature over 1050°C for L$_6$ sample, so it goes against to control the heat transfer in the region of meniscus. It was reported that after 20 s from the casting the crystallization of cuspidine starts and the thermal resistance of mold flux increases in commercial mold fluxes.\textsuperscript{24} It is interesting to note that the incubation time of the L$_7$ sample was 20 s to form appropriate thickness of the crystalline layer.

4. Discussion

4.1. The Critical Cooling Rate

As is shown in Fig. 3 and Fig. 4, the crystallization tendency of mold fluxes was strengthened with the addition of Li$_2$O, whether there is Na$_2$O or not. Besides, the influences of Li$_2$O on the critical cooling rate in both NL and L samples were close to each other. The electrostatic potential of Li$^+$ (1.47 Å) is very close to that of SiO$_4$$^{4-}$ (1.44 Å)\textsuperscript{27} and the cationic size order and the order of cationic strength is Na$^+$>Li$^+$ and Li$^+$>Na$^+$.\textsuperscript{28} So other cations would be hindered to combine with SiO$_4$$^{4-}$ by the addition of Li$_2$O in mold fluxes. But the polarization of Li$^+$ to SiO$_4$$^{4-}$ was too small to divide the Si$_x$O$_y$ polymeric. Therefore, the minor additive of Li$_2$O would improve the glass formation of mold fluxes. With the increase of M$_2$O/SiO$_2$ ratio the chain breakdown of silica network continued, and the crystallization property of mold fluxes would be strengthened.

It’s interesting to note that the critical cooling rate of NL and L samples started to increase when the value of (X$_{Li_2O}$/X$_{Na_2O}$)/X$_{SiO_2}$ was over 0.30. It’s indicated that the oxygen ion of alkali oxide divides the silicate flow unit as a non-bridging oxygen with (X$_{Li_2O}$/X$_{Na_2O}$)/X$_{SiO_2}$ =0.30 in the composition range of experimental samples. But the relation needs to be verified in the future work.

4.2. Crystallization Rate

The crystallization rate of mold fluxes was improved by the addition of Li$_2$O (shown in Fig. 5), and the incubation time of mold fluxes containing Li$_2$O more than 6 mass% was decreased much more obviously. The cationic strength of alkali ions increases in the order of Li$^+$>Na$^+$, thus the presence of cations with lower strength results in the interaction of a higher ratio of bridge oxygen.\textsuperscript{29} Consequently, the viscosity of L samples was greatly reduced to promote
the precipitation of solids.

Cramb et al.\textsuperscript{16} pointed out that the incubation time of mold fluxes became shorter with the addition of Na\textsubscript{2}O, so there is often some Na\textsubscript{2}O found in the composition of commercial mold fluxes. Alkali oxides have similar influence on the melting temperature and viscosity of mold fluxes, and the influences of Li\textsubscript{2}O, Na\textsubscript{2}O on the critical cooling rate and incubation time were close to each other.\textsuperscript{30} Therefore, Li\textsubscript{2}O can be substituted by Na\textsubscript{2}O to reduce the cost. NL\textsubscript{1.5} (Na\textsubscript{2}O=8 mass%, Li\textsubscript{2}O=1.5 mass%) and L\textsubscript{7} (Na\textsubscript{2}O=0, Li\textsubscript{2}O=7 mass%) samples were chosen owing to similar critical cooling rate.

Figure 6 shows TTT diagrams of NL\textsubscript{1.5} and L\textsubscript{7} samples, and the incubation time of the two samples was close to each other in the temperature below 1 100°C. But the crystals precipitated could be observed over 1 150°C in NL\textsubscript{1.5} sample. NL\textsubscript{1.5} sample has 100°C higher melting point to provide more driving force of crystallization. The high density crystalline layer was formed by the fast crystallization at high temperature to increase the interfacial thermal resistance.

4.3. The Results of XRD and BSE

The mineralogical phase of the precipitated crystals provides additional information to understand the crystallization behavior of mold fluxes. If Li\textsubscript{2}O was substituted by Na\textsubscript{2}O, the following substitution reaction (1) should be taken into account according to Y asushi \textit{et al.}\textsuperscript{31–35} But it was found that most of F\textsuperscript{−} ions are fourfold coordinated by Ca\textsuperscript{2+} rather than Na\textsuperscript{+} for samples of \( n_{Na}/(n_{Na}+n_{Ca}) \approx 0.3 \), and the presence of Na\textsubscript{2}O may not prevent the precipitation of cuspidine from the mold fluxes.\textsuperscript{36–39} In the composition range of experimental samples, the value of \( n_{Na}/(n_{Na}+n_{Ca}) \) was less than 0.3, and it was confirmed by XRD that there was precipitation of cuspidine for all the samples. So Li\textsubscript{2}O substitution by Na\textsubscript{2}O has no effect on the crystal morphology in the crystalline film layer.

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

The TTT diagrams of NL\textsubscript{1.5} and L\textsubscript{7} were divided into two “C” regions, which suggested two separate nucleation events. Figures 7(a) and 7(b) show XRD results of the two samples, and there is no difference in the crystal phase precipitated. The crystal at higher temperature was dicalcium silicate (Ca\textsubscript{2}(SiO\textsubscript{4})), and cuspidine (Ca\textsubscript{4}Si\textsubscript{2}O\textsubscript{7}F\textsubscript{2}) was the dominant phase measured at low temperature. But there's no Li-cuspidine found in the high content of Li\textsubscript{2}O samples reported by Omoto.\textsuperscript{17}

When the basicity ((CaO+56/78CaF\textsubscript{2})/SiO\textsubscript{2}) and Li\textsubscript{2}O in mold fluxes are 2.2 and 4 mass%, a quantity of 350 g slag was melted in an apparatus to obtain the slag film layer. The details of the experimental apparatus have been reported in literature.\textsuperscript{40} The copper detector was lifted up and the attached solid slag was removed after an immersion time of 45 s. The solid slag film was grounded and sieved by 200 mesh screen to measure the precipitated phase by XRD. It was confirmed that Li-cuspidine was found in the solid slag film (shown in Fig. 7(c)).

It's assumed by the authors that reaction (2) took place, where 1 mol cuspidine reacted with 1 mol Li\textsubscript{2}O to form 2 mol Li-cuspidine. The viscosity of basicity 2.2 sample was 0.019 Pa·s to break the Si–O–Si bond of cuspidine, and Li\textsuperscript{+} was compensated to the Si–O unit owing to the smaller size and higher strength. The breakdown of the silicate network with the addition of Li\textsubscript{2}O to mold fluxes was...
shown in Fig. 8. The viscosity of L_8 was 0.112 Pa·s, too high to break the Si–O–Si bond of cuspidine. It is consistent with the results that no Li-cuspidine was found in the high content of Li_2O samples. But the assumption on the formation mechanism of Li-cuspidine needs to be verified in the future work.

Ca_4Si_2O_7F_2 + Li_2O = 2LiCa_2FSiO_4 ................(2)

The microstructure of quenched samples melted on the SHTT is shown in Fig. 9 and Fig. 10, and the crystalline ratio of NL_1.5 and L_7 increased with the decrease of the isothermal temperature. The crystals of NL_1.5 at 1 100°C took dendrite structure, and the crystals became small and dense when the temperature was reduced. It is considered that cuspidine with the dendrite structure crystallizes rapidly from liquid.

But the crystals of L_7 sample presented coarse and sparse structure. The viscosity of NL_1.5 is 0.276 Pa·s, two times of that of L_7, so it was more favorable for the nucleation.

4.4. Heat Flux through the Solid Slag Film

An apparatus for simulating copper mold was also used to measure the heat flux of the slag film, which was calculated based on the temperature difference of water between outlet and inlet against immersion time. As is shown in Table 2, NL_1.5 sample has 10% less heat flux, and the thickness of slag film was 0.4 mm more than that of L_7.

As the critical cooling rates of NL_1.5 and L_7 samples were too small to promote the crystals precipitated in the cooling rate range of the apparatus, no crystal was identified by XRD in the slag film. So the two samples were melted in MoSi_2 furnace, held at 1 000°C for 10 min, and then poured into water. Figure 11 shows the BSE results of quenched samples. The crystal phase which consists of small grains of dendrite Ca_4Si_2O_7F_2 was observed in NL_1.5 sample. But glassy phases and the large grains of Ca_4Si_2O_7F_2 were observed in L_7 sample.
served in the L7 sample, and the crystals presented bone structure. The results of quenched samples were consistent with those of SHTT.

The thickness of the slag film layer and crystallization tendency of NL1.5 both contributed to the decrease of the heat transfer through the slag film, which provided the bedstone to increase the speed casting for crack-sensitive steels. It's necessary to note that the mold fluxes containing high content of Li2O didn’t have obvious influence on the heat transfer through the slag film layer.

4.5. Kinetics Analysis of Crystallization

When the growth and nucleation of crystals were both considered, the Johnson–Mehl–Avrami equation was often used, as is shown in Eq. (3), where n represents the mechanism of crystal growth and K is a coefficient corresponding to the nucleation and growth mechanism. And the exponent n can be described by a growth constant (q) and a nucleation constant (p), according to Eq. (4). Equation (3) can be rewritten in the form of Eq. (5), which is suitable of the evaluation of K and n for each sample.

\[ X_R = 1 - \exp(-K \cdot t^n) \] ...........................................(3)

\[ n = p + q \] ...........................................(4)

\[ \ln(-\ln(1-X_R)) = n \cdot \ln t + \ln K \] ...........................................(5)

The comparison of volume fraction of NL1.5 and L7 samples between observation and calculation is shown in Fig. 12. And we can see that the exponent of NL1.5 sample is 3, indicating two dimensional growth and the interface reaction was the dominant condition. While the exponent n of L7 sample is close to 4, which means that the limit case of three dimensional growth with constant nucleation and growth rates. This result is similar to the crystallization mechanism of the mold fluxes reported by Kashiwaya et al.22) The following expressions (6)–(9) give acceptable calculation results that fit the measured incubation time as a function of temperature.

NL1.5:

\[ t_{0.005} = \frac{7.8 \times 10^{15}}{(1200 - T)^2 (T - 850)^{3.8}}, \quad 950^\circ C < T < 1080^\circ C \] ...........................................(7)

\[ L7: \]

\[ t_{0.005} = \frac{1.0 \times 10^{16}}{(1170 - T)^{0.3} (T - 1000)^{2}}, \quad 1065^\circ C < T < 1140^\circ C \] ...........................................(8)

\[ t_{0.005} = \frac{1.6 \times 10^{9}}{(1200 - T)^{1.1} (T - 700)^{2.2}}, \quad 900^\circ C < T < 1065^\circ C \] ...........................................(9)

5. Conclusions

In this paper, SHTT, XRD and BSE were employed to study the crystallization behavior of mold fluxes containing Li2O. And the conclusions are as follows:

(1) The critical cooling rate of NL and L samples increased 6°C/s and 4°C/s per 1 mass% Li2O, and the incubation time was reduced by 25 s and 50 s, respectively. The crystallization rate was promoted obviously in mold fluxes containing high content of Li2O.

(2) The critical cooling rate and incubation time of NL1.5 sample were close to those of L7 sample, and the precipitation of cuspidine wasn’t prevented by addition of Na2O.

(3) There is no difference in the crystal phase of NL1.5 and L7 samples, and it was confirmed by XRD that the crystal phases precipitated at high temperature and low temperature were Ca2(SiO4) and Ca4Si2O7F2, respectively. Li-cuspidine was promoted to precipitate when the basicity of the sample was increased.

(4) The small and dense grains of cuspidine were observed in NL1.5 sample, and the thickness of slag film was 0.4 mm more than that of L7 sample. The heat flux of NL1.5 sample was 10% less than that of L7 sample, as expected. Mold fluxes containing high content of Li2O didn’t have obvious influence on the heat transfer through the slag film layer. Therefore, high content of Li2O can be substituted by the combination of Na2O and minor of Li2O, as is the composition found in the commercial mold fluxes.

Fig. 12. The comparison of volume fraction between observation and calculation.
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