Effect of NaF Addition to Mold Flux on Cuspidine Primary Field

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The phase diagram of cuspidine (3CaO2SiO2CaF2)–CaF2–NaF pseudo ternary system has been established in order to research the effect of NaF addition to mold flux on cuspidine primary field. The phase diagram was established based on both phase diagrams of cuspidine–NaF pseudo binary system and 8mass%NaF–cuspidine–CaF2 pseudo binary system which were determined experimentally by DTA measurement and equilibrium experiment by quenching method. The phase diagram of cuspidine–CaF2–NaF pseudo ternary system was found to be ternary eutectic. The effects of NaF addition on cuspidine primary field are to leave cuspidine primary field large and to lower the liquidus temperature in cuspidine primary field down to 1 068 K. It is possible that the large NaF addition to mold flux completes both main functions of the heat transfer control and the lubrication.

KEY WORDS: mold flux; phase diagram; cuspidine primary field; liquidus temperature and cuspidine–CaF2–NaF pseudo ternary system.

1. Introduction

In the continuous casting of steel, the mold flux, which mainly consists of CaO–SiO2–CaF2 system, has two main functions: (1) lubrication between solidified shell and water cooled cooper mold and (2) heat transfer control between steel shell and copper mold. The heat transfer control is very important function for the surface quality of steel especially at the initial stage of the solidification in casting. Middle carbon steel with peritectic reaction (0.1mass%C–0.18mass%C) has the serious problem that the solidification shrinkage during δ–γ transformation brings about the longitudinal crackings on the steel surface.1,2) It has been revealed that the decrease of the heat flux through mold flux attains the uniform heat removal from steel and consequently prevents the surface longitudinal crackings.3,4) The most effective way for the decrease of the heat flux is the crystallization of cuspidine (3CaO2SiO2CaF2) from mold flux. The reasons for the crystallization of cuspidine to accomplish the heat transfer control can be classified into two views. One is that the radiation heat flux in the liquid layer is scattered at the front of the crystalline layer of cuspidine,5,6) the other is that the solidification shrinkage of mold flux forms the surface roughness on the mold interface and the large thermal resistance on the mold interface decreases the heat flux.7,11–17) In order to design the effective mold flux for both heat transfer control and lubrication, it is necessary to control the crystallization of cuspidine from mold flux. Thus, Watanabe et al.18) reported the cuspidine primary field in the phase diagram of CaO–SiO2–CaF2 ternary system.

However, it is too difficult to treat the initial composition of commercial mold fluxes as that in CaO–SiO2–CaF2 ternary system, because many other additional compounds such as Na2O, Al2O3 and MgO are included in most commercial mold fluxes.19) Especially, Na2O is about 10mass% mixture into the commercial mold fluxes in order to adjust the liquidus temperature and the viscosity for the lubrication.19) Mills et al.20) reported that the additional Na2O should be treated as NaF in mold flux according to the following reaction.

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

Thus, Hanao et al.21) simply treated the initial composition of the commercial mold fluxes as that in CaO–SiO2–CaF2–NaF system. They concluded that the mold flux with the initial composition in cuspidine primary field crystallizes cuspidine rapidly and is effective for the heat transfer control. However, they projected the initial composition in CaO–SiO2–CaF2–NaF system onto the face of CaO–SiO2–CaF2 ternary system reported by Watanabe et al.,18) because the cuspidine primary field in CaO–SiO2–CaF2–NaF system has never been researched yet. Therefore, in order to design the effective mold flux for both heat transfer control and lubrication, it is of great importance to reveal the effect of NaF addition on cuspidine primary field in CaO–SiO2–CaF2–NaF system. For this purpose, as a first step, cuspidine primary field in the phase diagram of cuspidine–CaF2–NaF pseudo ternary system is investigated in this study.

The aim of this study is to prepare experimentally the cuspidine primary field in cuspidine–CaF2–NaF pseudo ternary system in order to elucidate the effect of NaF addition on cuspidine primary field. The following three steps are provided in this study. Figure 1 shows the schematic phase diagram of cuspidine–CaF2–NaF pseudo ternary system to explain the three steps. The phase diagrams of cuspi-
dine–CaF$_2$ pseudo binary system$^{22}$) and CaF$_2$–NaF binary system$^{23}$ have been reported to be eutectic. Thus, at the step 1, the phase diagram of cuspidine–NaF pseudo binary system corresponding to the line 1 is established. At the step 2, the phase diagram of 8mass%NaF–cuspidine–CaF$_2$ pseudo binary system corresponding to the line 2 is established in order to determine the ternary phase relations of cuspidine–CaF$_2$–NaF system. For the aim of this study, at the step 3, the phase diagram of cuspidine–CaF$_2$–NaF pseudo ternary system corresponding to the area 3 is elucidated based on both phase diagrams of cuspidine–NaF system and 8mass%NaF–cuspidine–CaF$_2$ system.

2. Experimental

2.1. Sample Preparation

Tables 1–3 show the initial compositions of the samples for DTA measurement, equilibrium experiment by quenching method and isothermal annealing experiment, respectively. The samples were prepared from the regent grade of SiO$_2$, CaF$_2$, CaO, NaF, pure cuspidine and pure Na$_2$O$_2$SiO$_2$-2CaO. CaO was prepared by heating CaCO$_3$ at 1423 K for 12 h in air. Pure cuspidine and pure Na$_2$O$_2$SiO$_2$-2CaO were prepared by melting the mixture at the stoichiometric molar ratio in closed platinum tubes above the liquidus temperature for 30 min and cooling the melt to room temperature in electric resistance furnace. The samples for DTA measurement and equilibrium experiment by quenching method

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<th>Table 1. Initial compositions and experimental results of DTA measurement.</th>
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<td>step 2 (8mass%NaF–cuspidine–CaF$_2$ system)</td>
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<th>Table 2. Initial compositions and experimental results of equilibrium experiment by quenching method.</th>
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<td>sample E-1021-24</td>
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<td>sample E-1019-73</td>
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<td>sample E-1020-123</td>
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<td>step 2 (8mass%NaF–cuspidine–CaF$_2$ system)</td>
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<td>sample J-1412-54</td>
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<td>sample L-1203-99</td>
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<td>sample L-1014-24</td>
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were enclosed in platinum containers in order to prevent the change of the initial compositions by the following reactions (1) and (2).

\[
\text{CaF}_2 (s) + \text{H}_2\text{O (g)} = \text{CaO (s)} + 2\text{HF (g)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

\[
\text{cuspidine (3CaO}_2\text{SiO}_2\text{CaF}_2 (s) + \text{H}_2\text{O (g)} = 2(2\text{CaO}_2\text{SiO}_2) (s) + 2\text{HF (g)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

The samples for isothermal annealing experiment were enclosed in vacuum glass tubes in order to prevent the reactions (1) and (2).

### 2.2. Measurement

Differential thermal analysis (DTA) was carried out in order to determine the transformation temperature. Before DTA measurement, the samples were pre-melted above 1 723 K for 12 h and cooled to room temperature in electric resistance furnace. As a result of being pre-melted, the samples were considered to be the mixture of the equilibrium compounds. The endothermic peaks of DTA curve on the heating process represent the melting of the equilibrium compound. About 50 mg of the samples in the platinum container were fixed directly onto the top of the thermocouple of DTA. The samples were heated at the heating rate of 10 K/min and were cooled to room temperature at the cooling rate of 80 K/min under Ar gas flow of 50 ml/min. Pure \(\alpha\)-\text{Al}_2\text{O}_3 was selected as the reference material of DTA measurement. The calibration for the heating rate and the platinum closed container was carried out using the given melting points of MgF\(_2\) and CaF\(_2\). In another measurement, the samples were checked to melt completely in the course of DTA measurement by breaking the platinum closed container.

Equilibrium experiment by quenching method was carried out in order to determine the phase equilibrium relation at the predefined temperature. The samples enclosed in the platinum container were melted completely above 1 723 K for 20 min and cooled to room temperature at the slow rate of 0.5 K/min in electric resistance furnace. Isothermal holding at the predefined temperature was carried out for 24–123 h which is enough time for the samples to attain the equilibrium state. The samples at the predefined temperature were quenched into water. In order to determine the phase equilibrium relation at the predefined temperature, the present crystals of the samples were detected by X-ray diffraction study (XRD) with Cu-K\(\alpha\) radiation and electron probe micro analysis (EPMA). The predefined temperature and the isothermal holding time of the sample were summarized in Table 2.

Additionally, in order to determine the phase equilibrium relation at low temperature in cuspidine–NaF pseudo binary system, isothermal annealing experiment was carried out. The mixed powders were pressed into pellets and wrapped by platinum foil. The samples enclosed in vacuum glass tubes were annealed directly at the temperature shown in Table 3 without melting. The samples were quenched in air after being annealed and the crystal phases of the samples were identified by X-ray diffraction.

### 3. Results

#### 3.1. Cuspidine–NaF Pseudo binary System (Step 1)

Figure 2 shows the DTA profile of sample B. Three peaks were detected. Table 1 (step 1) summarizes the experimental results of DTA measurement in cuspidine–NaF pseudo binary system. Sample B, sample C, sample D and sample E have three peaks. The temperature of peak 1 varies largely with the composition of the samples, while the temperatures of peak 2 and peak 3 represent almost the same value despite the composition of the samples.

**Fig. 2.** DTA profile of sample B.

**Figures 3(a) and 3(b) show the characteristic X-ray images of sodium; fluorine, calcium and silicon of the samples:** (a) sample B-1093-47 of equilibrium experiment and (b) sample B-1003-75 of equilibrium experiment. Cuspidine and NaF were identified by X-ray diffraction in the samples.

**Figures 4(a) and 4(b) show the X-ray diffraction profiles of the samples:** (a) sample B-1093-47 of equilibrium experiment and (b) sample B-1003-75 of equilibrium experiment. Cuspidine and NaF were identified by X-ray diffraction in the samples.

Table 2 (step 1) summarizes the experimental results of equilibrium experiment in cuspidine–NaF pseudo binary system.
The eutectic structure of cuspidine and NaF was observed by EPMA in the samples except sample C-1295-60. Cuspidine and NaF crystals were also identified by X-ray diffraction in the samples. In sample C-1295-60, the microstructure consisting of Na, Ca, Si, O and F is identified to be liquid phase because of the existence of all elements of the sample and no corresponding crystal in the result of XRD. The two different phases consisting of Na, Ca, Si and O and consisting of Ca and F were observed by EPMA in sample B-1003-75, sample E-1021-24, sample E-1019-73 and sample E-1020-123. However, no crystals corresponding to the two different phases were identified by X-Ray diffraction.

### 3.2. 8mass%NaF–Cuspidine–CaF$_2$ Pseudo binary System (Step 2)

Table 1 (step 2) summarizes the experimental results of DTA measurement in 8mass%NaF–cuspidine–CaF$_2$ pseudo binary system. Peak 3 represents almost the same temperature for the samples, while the temperature of peak 1 and peak 2 varies largely with the composition of the samples.

Figure 5 show the characteristic X-ray image of sample L-1014-24 of equilibrium experiment. The large area is the binary eutectic structure of cuspidine and CaF$_2$ and the left upper area is the ternary eutectic structure of cuspidine, CaF$_2$ and NaF. The characteristic X-ray image of sodium was provided by electron probe being scanned doubly in order to distinguish between the ternary and the binary eutectic structures. The small amount of sodium in the binary structure as a result of double scanning was ignored.

Table 2 (step 2) summarizes the experimental results of
equilibrium experiment in 8mass%NaF–cuspidine–CaF₂ pseudo binary system. The phases observed by EPMA are also identified by X-ray diffraction. The samples have the phase relation between cuspidine, CaF₂ and NaF and no ternary compound can be observed in 8mass%NaF–cuspidine–CaF₂ pseudo binary system.

4. Discussions

4.1. The Phase Diagram of Cuspidine–NaF Pseudo binary System (Step 1)

In Table 1 (step 1), the temperature of peak 1 represents the liquidus temperature because of the large temperature change with the composition of the samples and the complete melting of the samples above peak 1. Table 1 indicates that the temperature of peak 2 represents almost the same value. Table 2 indicates that the samples whose predefined temperature is below peak 2 have the eutectic structure of cuspidine and NaF. Thus, it is concluded that peak 2 represents the binary eutectic reaction of liquid to form cuspidine and NaF. Thus, the phase relation in temperature between peak 2 and peak 3 is cuspidine+NaF.

4.1.1. Phase Relation at Low Temperature

The different two phases observed by EPMA were not identified by X-ray diffraction in sample B-1003-75, sample E-1021-24, sample E-1019-73 and sample E-1020-123 whose predefined temperature is below peak 3. The more discussion is needed about the identification of peak 3 and the different two phases in order to decide the phase relation in temperature below peak 3.

The identification of the different two phases consisting of Na, Ca, Si and O and consisting of Ca and F has two possibilities. One possibility is that the two different phases are glassy phases and peak 3 is glass transition temperature. In the case, the phase relation below peak 3 is also cuspidine+NaF. The other possibility is that the two different phases are Na₂O₂SiO₂₂CaO and CaF₂ and peak 3 represents the following reaction (3).

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

Na₂O₂SiO₂₂CaO and CaF₂ are only possible crystal phases made from cuspidine and NaF which are the equilibrium phases in temperature between peak 2 (eutectic temperature) and peak 3. Figure 6(a) shows the phase equilibrium relations in NaF–CaF₂–SiF₄–Na₂O–CaO–SiO₂ system. The upper surface and the lower surface of the triangle pole represent the ternary systems of fluorides and oxides, respectively, which are approached by J. Rutlin et al. ²⁴ Cuspidine, NaF, Na₂O₂SiO₂₂CaO and CaF₂ are on the same face shown in Fig. 6(a). Figure 6(b) shows the phase equilibrium relation in temperature between peak 2 (eutectic temperature) and peak 3. As shown earlier, the phase equilibrium relation in the temperature area is cuspidine+NaF. The border line of the phase equilibrium relation can be drawn on cuspidine–NaF system. Figure 6(c) shows the phase equilibrium relation below peak 3. Considering the occurrence of the reaction (3) at the temperature of peak 3, the phase equilibrium relation of cuspidine–NaF binary system is divided into two areas. One area where the molar ratio of cuspidine is large has the phase relation of Na₂O₂SiO₂₂CaO+CaF₂+ cuspidine, and the other area where the molar ratio of NaF is large has the phase relation of Na₂O₂SiO₂₂CaO+CaF₂+NaF.

The identification of the different two phases is cleared by isothermal annealing experiment. Table 3 shows the initial compositions of the experiment. In the experiment, although sample X and sample X’ of pair 1 and sample Y and sample Y’ of pair 2 consist of the different initial component, each sample is designed to present the same compositions after the reaction (3). If the earlier possibility that the two different phases should be glassy phases is correct, the initial compositions of sample X and sample Y should change into Na₂O₂SiO₂₂CaO+CaF₂+ cuspidine and into Na₂O₂SiO₂₂CaO+CaF₂+NaF after the occurrence of the reaction (3). On the other hand, if the later possibility that the two different phases are Na₂O₂SiO₂₂CaO and CaF₂ is correct, the initial compositions of sample X’ and sample Y’ should change into Na₂O₂SiO₂₂CaO+CaF₂+ cuspidine into Na₂O₂SiO₂₂CaO+CaF₂+NaF after the occurrence of the reaction (3), respectively. Figure 7 shows X-ray diffraction profiles of sample Y (a) before annealing and (b) after annealing. As shown in Fig. 7(b), the initial composition of sample Y, NaF+Na₂O₂SiO₂₂CaO+CaF₂ changes into cuspidine+NaF. Table 3 summarizes the results of the isothermal annealing experiment. Also the initial composition of sample X, cuspidine+Na₂O₂SiO₂₂CaO+CaF₂ change into cuspidine+NaF with a small amount of CaF₂. It is considered that the small amount of CaF₂ is the excess amount of the reaction (3). On the other hand, the initial compositions of sample X’ and sample Y’, cuspidine+NaF does not change in the course of annealing. Thus, it is decided that the two different phases are glassy phases and peak 3 repre-
sents glass transition temperature. Therefore, the phase equilibrium relation below the temperature of peak 3 is also cuspidine+NaF. It is considered that the two different glassy phases observed by EPMA could not be identified by X-ray diffraction.

4.1.2. The Phase Diagram of Cuspidine–NaF Pseudo Binary System

Figure 8 shows the phase diagram of cuspidine–NaF pseudo binary system. This phase diagram was made based on the results of DTA measurement, equilibrium experiment and isothermal annealing experiment. The melting points of cuspidine and NaF are given by literatures.21) Opened triangle dots and closed circle dots represent the liquidus temperature and the eutectic reaction of liquid to form cuspidine and NaF, respectively. Our conclusion is that the phase diagram of cuspidine–NaF binary system is eutectic. The eutectic composition is 96(mol)% NaF–4% cuspidine and the eutectic temperature is 1 142 K.

4.2. The Phase Diagram of 8mass%NaF–Cuspidine–CaF2 Pseudo binary System (Step 2)

It is determined that peak 1 shown in Table 1 (step 2) represents liquidus temperature because of the large temperature change with the composition of the samples and the complete melting of the samples above the temperature of peak 1. It can be seen from Table 1 (step 2) and Table 2 (step 2) that peak 3 represents the ternary eutectic reaction of liquid to form cuspidine, CaF2, and NaF, because sample L-1014-24 has the ternary eutectic structure of cuspidine+CaF2+NaF. Thus, it is concluded that peak 2 represents the binary eutectic reaction of liquid to form cuspidine and CaF2. In addition, no ternary compound exists in cuspidine–CaF2–NaF system.

Figure 9 shows the phase diagram of 8mass%NaF–cuspidine–CaF2 pseudo binary system. The liquidus temperature of the 8mass%NaF–CaF2 composition is given by literature.23) It was determined that the phase diagram is ternary eutectic and the ternary eutectic temperature is 1 068 K. It is revealed that cuspidine, CaF2, and NaF have the phase relation directly at low temperature. It can be suggested from these results that the phase diagram of cuspidine–CaF2–NaF pseudo ternary system should be also eutectic.

4.3. The Phase Diagram of Cuspidine–CaF2–NaF Pseudo ternary System (Step 3)

The three binary phase diagrams of cuspidine–NaF system, cuspidine–CaF2 system and CaF2–NaF system are eutectic. The phase diagram of 8mass%NaF–cuspidine–CaF2 pseudo binary system concludes that cuspidine, CaF2, and NaF have the phase relation directly at low temperature. It can be suggested from these results that the phase diagram of cuspidine–CaF2–NaF pseudo ternary system should be also eutectic.

Figure 10 shows the method to establish the phase diagram of cuspidine–CaF2–NaF pseudo ternary system based on the experimental phase diagram of 8mass%NaF–cuspidine–CaF2 pseudo binary system. The liquidus temperature of the opened circles and the open triangles in the phase diagram of 8mass%NaF–cuspidine–CaF2 system correspond to the liquidus temperature of the opened circles and the opened triangles in the phase diagram of cuspidine–CaF2–NaF system, respectively. The phase diagram of 8mass% NaF–cuspidine–CaF2 system shows that the compositions of the opened triangles have the binary eutectic point at 1300 K represented as the closed triangle. Thus, in the phase diagram of cuspidine–CaF2–NaF pseudo ternary sys-
tem, the intersecting point of both extending lines from cuspidine and CaF$_2$ represents the point of 1 300 K on primary field boundary. In the same way, the ternary eutectic point corresponds to the closed circle. Figure 11 shows the phase diagram of cuspidine–CaF$_2$–NaF pseudo ternary system established by the method.

4.4. The Effects of NaF Addition on Cuspidine Primary Field

The cuspidine primary is revealed in the phase diagram of cuspidine–CaF$_2$–NaF pseudo ternary system. The effect of NaF addition on cuspidine primary field are to leave cuspidiue primary field large and to lower the liquidus temperature in cuspidine primary field down to 1 068 K. It is possible that the large NaF addition to mold flux completes both main functions of the heat transfer control and the lubrication.

5. Conclusions

In order to reveal the effects of NaF addition on cuspidine primary field, the phase diagram of cuspidine–CaF$_2$–NaF pseudo ternary system was established. The following conclusions were obtained.

(1) The phase diagram of cuspidine–NaF pseudo binary system is determined experimentally to be binary eutectic. The eutectic composition is 96(mol%)cuspidine–4%NaF and the eutectic temperature is 1 142 K.

(2) The phase diagram of 8mass%NaF–cuspidine–CaF$_2$ pseudo binary system is determined experimentally. No ternary compound exists in cuspidine–CaF$_2$–NaF pseudo ternary system and cuspidine, CaF$_2$ and NaF have the phase relation directly at low temperature.

(3) The phase diagram of cuspidine–CaF$_2$–NaF pseudo ternary system is established based on both phase diagram of cuspidine–NaF pseudo binary system and 8mass%NaF–cuspidine–CaF$_2$ pseudo binary system. The phase diagram of cuspidine–CaF$_2$–NaF pseudo ternary system is ternary eutectic, and the eutectic composition and the eutectic temperature are 4.4(mol%)cuspidine–27.8%CaF$_2$–67.8%NaF and 1 068 K, respectively.

(4) The effects of NaF addition on cuspidine primary field are to leave cuspidine primary field large and to lower the liquidus temperature in cuspidine primary field down to 1 068 K. It is possible that the large NaF addition to mold flux completes both main functions of the heat transfer control and the lubrication.

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