Influence of Na_2O on Phase Relation between Mold Flux Composition and Cuspidine

Masahito HANAO, Masayuki KAWAMOTO and Tadao WATANABE

Corporate Research and Development Laboratories, Sumitomo Metal Industries, Ltd., 16-1 Sunayama, Hasaki, Kashima, Ibaraki 314-0255 Japan.

(Received on November 12, 2003, accepted in final form on January 29, 2004)

Phase relation between mold flux composition and cuspidine was researched fundamentally. Solidification temperatures of the mold flux were measured at various compositions, and crystal compositions in their solidified structure were identified by X-ray diffraction analysis. Based on these results, the phase relation between the mold flux composition and cuspidine was considered. In the relation between basicity ($T.\text{CaO}/\text{SiO}_2$) and the solidification temperature, there was a peak of the solidification temperature and the basicity at the peak varied according to the contents of Na_2O and F. Taking the affinity of F to Na rather than Ca into consideration, NaF was considered to exist as a component of the molten flux. Treating the mold flux composition as $\text{CaO}-\text{SiO}_2-\text{CaF}_2-\text{NaF}$ system, it became possible to estimate the phase relation between the mold flux composition and crystal composition such as cuspidine, CaF_2 and $\text{NaCa}_2\text{FSiO}_4$ accurately.

According to this study, conventional compositions of the mold flux were estimated to be out of the primary crystallization field of cuspidine. On the other hand, the composition of the mold flux, that enabled the high speed casting of hypoperitectic steel slabs at 5.0m/min without longitudinal surface cracking, was estimated to be in the field and close to be cuspidine.

KEY WORDS: continuous casting; mold flux; crystallization; cuspidine; phase relation; $\text{CaO}-\text{SiO}_2-\text{CaF}_2-\text{NaF}$ system.

1. Introduction

In recent years, control of heat transfer from solidified shell in mold has become to be considered as one of the main functions of mold flux for continuous casting.¹⁾ Especially, the mold flux is useful and effective for mild cooling of the solidified shell in order to prevent unevenness which causes longitudinal cracking on the surface of slabs.

The mild cooling with the mold flux can be realized by promotion of crystallization in a film of the mold flux that lies in the gap of the mold and the solidified shell. The crystallization in the flux film can be promoted with increase of basicity (mass fraction ratio of $T.\text{CaO}/\text{SiO}_2$), so the basicity of the mold flux for medium carbon steel is usually raised to 1.2/1.4.²⁾ And it is known that decrease of Al_2O_3 or MgO , and addition of ZrO_2 in the mold flux is effective to promote the crystallization.³⁻⁵⁾

Here, the mold flux has been designed as lubricant and its physical properties at liquid state such as viscosity or solidification temperature has been controlled. As a result, compositions of the mold flux have been converged to a certain area empirically. Thus the methods mentioned above to promote the crystallization have been conducted in this finite area of the mold flux composition.

Cuspidine ($3\text{CaO} \cdot \text{SiO}_2 \cdot \text{CaF}_2$) is known as a typical crys-

tal composition in the flux film. Though thermo-dynamic data or phase diagram for cuspidine has begun to be reported recently,⁶⁾ it was not necessarily recognized as an important phase on metallurgy, and it does not exist on the phase diagram of $\text{CaO}-\text{SiO}_2-\text{CaF}_2$ system.⁷⁾

Furthermore, the mold flux composition is difficult to be expressed accurately in the phase diagram because of its complication with many components, CaO , SiO_2 , Al_2O_3 , MgO , Na_2O , F, for examples.

Because of these reasons, phase relation between the mold flux composition and cuspidine has never been considered or researched, and the methods to promote the crystallization have been no more than one-dimensional control with the basicity or the content of Al_2O_3 , MgO or ZrO_2 .

Authors found that it is possible to estimate the phase relation between mold flux composition and cuspidine accurately, taking the familiarity of F^- ion with $\text{Na}^{+8)}$ into consideration.⁹⁾ According to this consideration, the mold flux whose composition becomes quite close to cuspidine in its molten state was developed, and this was applied to high-speed continuous casting of hypoperitectic steel slabs in medium thickness. As a result, longitudinal cracking on the surface of slabs was prevented even at the casting speed of 5.0 m/min.¹⁰⁾

In this study, the result of the fundamental research which formed the foundation of the development of the

mold flux¹⁰⁾ is reported.

2. Experimental Conditions

2.1. Mold Flux Composition

The mold flux for this study was prepared by mixing such general materials as cement, silica sand, soda ash and fluorspar. Main components of the mold flux were CaO, SiO₂, Na₂CO₃ (Na₂O, substantially) and CaF₂. The compositions of the mold flux are shown in **Table 1**. Basicity (T.CaO/SiO₂) was varied within the range from 0.8 to 2.1 under constant contents of Na₂O and F, and its influence on solidification temperature was researched. The total content of Na₂O and F was constant at 20 mass% and the combination of their contents was changed to 4 conditions so that its influence on the relation between the basicity and the solidification temperature could be researched. The combinations of (Na₂O, F) were as follows: (a): (12 mass%, 8 mass%), (b): (10 mass%, 10 mass%), (c): (8 mass%, 12 mass%) and (d): (6 mass%, 14 mass%). Al₂O₃ and MgO were included in the mold flux as inevitable impurities, and their total content was less than 5 mass%.

2.2. Measurement and Analysis

Solidification temperature of the mold flux was evaluated from the measurement of viscosity with oscillating-plate viscometer.¹¹⁾ 1 kg of the mold flux was melted at 1723 K in carbon crucible under argon atmosphere. Then its temperature was decreased at 2 K/min and the viscosity of the molten flux was measured continuously. When the mold flux in carbon crucible began to solidify, viscosity began to rise rapidly, and a break point became to exist in the relation between the temperature and the viscosity. This break point was defined as solidification temperature.

After the measurements, solidified specimens in the carbon crucible were crushed into powder and supplied to the analysis of X-ray diffraction. Based on the peak patterns of the X-ray diffraction, crystal compositions in the solidified structures were identified. Intensity of X-ray diffraction at the first peak of each crystal composition was used as an index of the crystallization.

The solidification structure of some specimens was observed with scanning electron microscope (SEM).

3. Results

3.1. Viscosity and Solidification Temperature

The typical behavior of the mold flux viscosity in the process of cooling is shown in **Fig. 1** for an example. This is the case of the mold flux whose basicity was 1.3 and whose Na₂O content and F content were both 10 mass% (condition (b)). The viscosity in logarithm increased at a linear gradient with decreasing of the temperature. The gradient became very steep after the beginning of the solidification and the break point was observed in Fig. 1. This behavior of the viscosity was common to all the mold flux in this study and the break point was clearly identified as the solidification temperature. The solidification temperature changed within the range from 1300 to 1530 K approximately, according to the compositions of the mold flux.

Table 1. Compositions of mold flux.

Basicity (T.CaO/SiO ₂)	0.8~2.1
Content of Na ₂ O and F	(a) Na ₂ O:12mass%, F: 8mass% (b) Na ₂ O:10mass%, F:10mass% (c) Na ₂ O: 8mass%, F:12mass% (d) Na ₂ O: 6mass%, F:14mass%
Content of Al ₂ O ₃ and MgO	Less than 5mass% as amount

Fig. 1. Relation between temperature and $\log \mu$.

Fig. 2. Relation between basicity and solidification temperature.

3.2. Relation between Basicity and Solidification Temperature

Relation between the basicity and the solidification temperature is shown in **Fig. 2**. When the contents of Na₂O and F were constant, there was a peak in the relation between the basicity and the solidification temperature. This behavior was common to all of the condition of Na₂O and F contents, but the basicity at the peak varied according to the condition of Na₂O and F contents.

3.3. Solidified Structure of Mold Flux after Measuring of Viscosity

A SEM image and the results of mapping analysis of the solidified structure of the mold flux is shown in **Fig. 3**, for the same mold flux of Fig. 1. There were crystal grains on the SEM image, and the matrix consisted of two phases. Ca, Si, O and F distributed in the region of the crystal grains. Si, Al, Mg, Na, O and F distributed in the matrix region, on the other hand. Especially, Al, Mg and Na seemed to be exhausted from the crystal region. Furthermore, in the matrix region, O and F were distributed exclusively and their dis-

Fig. 3. Mapping analysis of solidified structure (T.CaO/SiO₂: 1.3, Na₂O: 10 mass%, F: 10 mass%).

tribution agreed with the two phases on the SEM image. Si, Al, Mg and Na distributed on the O distribution, and only Na on the F distribution.

3.4. Crystal Compositions in Solidified Structure

Results of X-ray diffraction are shown in Fig. 4 for examples. These are the results of mold flux whose Na₂O content and F content are both 10 mass%, and Fig. 4(a) is for the basicity of 1.3, 4(b) for 0.8 and 4(c) for 1.9. In the relation between the diffraction angle (2θ) and the intensity of X-ray diffraction of Fig. 4(a), the typical pattern of cuspidine was observed. In Figs. 4(b) and 4(c), the peak pattern of CaF₂ or NaCa₂FSiO₄ was observed in addition to cuspidine.

The crystal compositions in the solidified structure of each composition are listed in Table 2 (a), (b), (c) and (d). Intensity of X-ray diffraction at the first peak of each crystal composition is classified quantitatively in 5 grades; more than 10 kcps, between 5 and 10 kcps, between 2 and 5 kcps, between 1 and 2 kcps and less than 1 kcps. In all of the cases of mold flux composition, the strongest intensity of X-ray diffraction indicated cuspidine. Other crystals were identified and the states of peaks were different according to the compositions of mold flux. The tendency was as follows:

(a) Na₂O: 12 mass% and F: 8 mass%

In the range of basicity higher than the peak of the solidification temperature (>1.3), NaCa₂FSiO₄ was identified. Its intensity got stronger while the basicity increased after the peak of solidification temperature. Therefore, NaCa₂FSiO₄ reached almost the same intensity as that of cuspidine at the basicity of 1.5. Additionally, crystals containing Na such as NaCaSi₃O₈, NaAlSiO₄ (nepheline) and Na₆Al₄Si₄O₁₇ were identified slightly. CaF₂ was not identified.

(b) Na₂O: 10 mass% and F: 10 mass%

As well as the case of (a), in the range of the basicity higher than the peak of the solidification temperature (>1.6), NaCa₂FSiO₄ was identified. Its intensity got stronger while basicity became away from the peak. CaF₂

was identified in the basicity range less than 1.0 or higher than 2.0. In contrast to this CaF₂ range, NaF was identified in the range from 1.2 to 1.9. Additionally, Ca₂SiO₄ was identified slightly at the basicity of 2.1.

(c) Na₂O: 8 mass% and F: 12 mass%

As well as the case of (2), in the range of the basicity higher than the peak of the solidification temperature, NaCa₂FSiO₄ was identified. CaF₂ was identified in the regions that the basicity was less than 1.5 or higher than 2.1. NaF was identified in the range from 1.7 to 1.9.

(d) Na₂O: 6 mass% and F: 14 mass%

CaF₂ was identified in whole range of the basicity and the intensity of its peak was almost constant.

4. Discussions

4.1. Solidification Process of Molten Flux

According to the results of crystal compositions analyzed by X-ray diffraction, the crystal grain shown in Fig. 3, where Ca, Si, O and F were distributed, can be considered as cuspidine. And the two phases that made up the matrix region can be considered as oxide of MgO–Al₂O₃–SiO₂–Na₂O system and NaF. Furthermore, CaF₂, NaCa₂FSiO₄, NaCaSi₃O₈, nepheline or Na₆Al₄Si₄O₁₇ is seems to exist in the matrix region according to the composition of mold flux.

Morphology of the crystals in the solidified structure, shown in Fig. 3, indicates that solidification of molten flux occurs with crystallization of cuspidine. The grains of cuspidine crystallize primarily from the molten flux. As this crystallization progresses, components such as Al₂O₃, MgO and Na₂O, which are not concerned with cuspidine, are exhausted from the grains and they come to exist in the matrix region among the crystal grains. This matrix region solidifies as eutectic.

4.2. Solidification Temperature as an Index of Crystallization of Cuspidine

When the temperature is higher than the solidification

Fig. 4. Results of X-ray diffraction (target: Co.)

temperature, the change of viscosity shown in Fig. 1 is considered to behave as a physical property of molten flux. On the other hand, when the temperature becomes lower than the solidification temperature, the viscosity change is considered to indicate the generation of solid phase with crystallization of cuspidine. The solidification temperature in this study is near the liquidus evaluated by DTA analysis and is lowered by tens of degrees. Details are described later.

The behavior of the viscosity change shown in Fig. 1 was common to all of the mold flux, and main crystal composition was cuspidine for all of them. Because of these results, solidification temperature can be taken as an index that means the crystallization extent of cuspidine, as far as the mold flux composition is in the range of this study.

It seems that the crystallization of cuspidine is mostly promoted at the peak of the solidification temperature, and the corresponding basicity is the most suitable value for the promotion. Furthermore, the result that the basicity at the peak varied according to contents of Na₂O and F suggests that the most suitable composition of the mold flux for the promotion of the crystallization is affected by Na₂O and F.

4.3. Influence of Na₂O to the Phase Relation between Mold Flux Composition and Cuspidine

It is a remarkable phenomenon that Na₂O affects the crystallization of cuspidine. Na₂O is considered to have certain influence on the phase relation between the mold flux composition and cuspidine.

The mold flux, which is a mixture of cement of CaO–

Table 2. Crystal compositions in solidified structure of mold flux.

(a) Na₂O:12mass%, F: 8mass%

Basicity	Classification of X-ray diffraction intensity						
	Cuspidine	CaF ₂	NaF	NaCa ₂ FSiO ₄	Na ₂ CaSi ₃ O ₈	Na ₆ Al ₄ Si ₄ O ₁₇	CaSiO ₄
1.0	a	-	-	-	-	-	-
1.1	a	-	-	-	c	-	-
1.2	a	-	-	-	c	c	-
1.3**	a	-	-	-	d	c	-
1.4	a	-	-	c	-	c	-
1.5	b	-	-	b	-	c	-

*) a:10kcps< b:5/10kcps c:2/5kcps d:1/2kcps -:<1kcps

**) Maximum point of solidification temperature

(b) Na₂O:10mass%, F:10mass%

Basicity	Classification of X-ray diffraction intensity						
	Cuspidine	CaF ₂	NaF	NaCa ₂ FSiO ₄	Na ₂ CaSi ₃ O ₈	Na ₆ Al ₄ Si ₄ O ₁₇	CaSiO ₄
0.8	b	c	-	-	-	-	-
1.0	a	c	-	-	-	-	-
1.2	a	-	d	-	-	-	-
1.3	a	-	c	-	-	-	-
1.4	a	-	c	-	-	-	-
1.5**	a	-	c	-	-	-	-
1.6	a	-	c	c	-	-	-
1.7	a	-	D	c	-	-	-
1.9	b	-	d	b	-	-	-
2.1	b	d	-	b	-	-	d

*) a:10kcps< b:5/10kcps c:2/5kcps d:1/2kcps -:<1kcps

**) Maximum point of solidification temperature

(c) Na₂O:8mass%, F:12mass%

Basicity	Classification of X-ray diffraction intensity						
	Cuspidine	CaF ₂	NaF	NaCa ₂ FSiO ₄	Na ₂ CaSi ₃ O ₈	Na ₆ Al ₄ Si ₄ O ₁₇	CaSiO ₄
1.3	a	c	-	-	-	-	-
1.5	a	d	-	-	-	-	-
1.6	a	-	-	-	-	-	-
1.7**	a	-	c	-	-	-	-
1.8	a	-	c	-	-	-	-
1.9	b	-	c	d	-	-	-
2.1	b	c	-	b	-	-	-

*) a:10kcps< b:5/10kcps c:2/5kcps d:1/2kcps -:<1kcps

**) Maximum point of solidification temperature

(d) Na₂O:6mass%, F:14mass%

Basicity	Classification of X-ray diffraction intensity						
	Cuspidine	CaF ₂	NaF	NaCa ₂ FSiO ₄	Na ₂ CaSi ₃ O ₈	Na ₆ Al ₄ Si ₄ O ₁₇	CaSiO ₄
1.7	a	c	-	-	-	-	-
1.8	a	c	-	-	-	-	-
1.9**	a	c	-	-	-	-	-
2.0	a	c	-	-	-	-	-
2.1	b	c	-	-	-	-	-

*) a:10kcps< b:5/10kcps c:2/5kcps d:1/2kcps -:<1kcps

**) Maximum point of solidification temperature

SiO₂, silica sand of SiO₂, fluorspar of CaF₂ and soda ash of Na₂O before it melts, becomes molten slag of multi-component oxide including F at high temperature. The molten slag is considered to be a mixture of ions.¹²⁾

F⁻ has a stronger affinity to Na⁺ than to Ca²⁺. In terms of molecular formula, this affinity for Na⁺ of F⁻ can be expressed as follows.⁸⁾

Because of Eq. (1) above, the mold flux composition should be considered to be CaO–SiO₂–CaF₂–NaF system under the condition that F⁻ exists adequately in molten

flux. A phase diagram of this quaternary system is originally displayed by a regular tetrahedron, as shown in Fig. 5. CaO, SiO₂, CaF₂ and NaF are the vertices. Cuspidine exists on the bottom face of CaO–SiO₂–CaF₂ and mold flux compositions exist within the solid.

When the mold flux composition is projected from NaF vertex, the projected point exists on the bottom face of CaO–SiO₂–CaF₂. The distance between the projected point and cuspidine on the CaO–SiO₂–CaF₂ face shows the phase relation between them, because the mass fraction of NaF in CaO–SiO₂–CaF₂–NaF system is less than 0.18 for all of the mold flux in this study.

Fig. 5. Mold flux composition in the phase diagram of CaO-SiO₂-CaF₂-NaF system. (Mold flux composition is projected to CaO-SiO₂-CaF₂ face from NaF vertex.)

Fig. 6. Results of X-ray diffraction (intensity of cuspidine).

Fig. 8. Results of X-ray diffraction (intensity of CaF₂).

Fig. 7. Relation between mass fraction ratio of CaO/SiO₂ in CaO-SiO₂-CaF₂-NaF system and solidification temperature.

The mold flux compositions projected on the CaO-SiO₂-CaF₂ face are shown in Fig. 6. The shape of the symbols represents the condition of Na₂O and F content and the design of the symbols means the X-ray diffraction intensity of cuspidine. Under the condition that contents Na₂O and F are both constant, the mold flux compositions exist in parallel with CaO-SiO₂ line. So the plots of the mold flux compositions make 4 lines according to the conditions of Na₂O and F content. The X-ray diffraction intensity of cuspidine becomes strongest at the closest composition to cuspidine, and this is common to all conditions of Na₂O and F content.

Figure 7 shows the relation-SiO₂-CaF₂-NaF system and the solidification temperature shown in Fig. 2. All the mass fraction ratios at the peak agree in the range from 1.3 to 1.4, corresponding to the value of cuspidine (1.4), though

they indicated the various basicity (T.CaO/SiO₂) according to the condition of Na₂O and F content as shown in Fig. 2. This result suggests that the phase relation is kept to be most stable and the crystallization of cuspidine is mostly promoted at the closest composition to cuspidine.

Thus, Na₂O in the mold flux affects the phase relation between the mold flux composition and cuspidine, through the formation of NaF. Taking this affection into consideration, the estimation of the phase relation comes to be accurate.

4.4. Phase Relation between Mold Flux Compositions and the Other Crystal Compositions

By the method mentioned above, the phase relation can be estimated accurately between the mold flux composition and other crystal composition such as CaF₂, NaF, or NaCa₂FSiO₄, as well as cuspidine.

X-ray diffraction intensity of CaF₂ is shown on the CaO-SiO₂-CaF₂ phase in Fig. 8. In this case, the analytical result of X-ray diffraction also agrees with the phase equilibrium in the CaO-SiO₂-CaF₂ phase. The peak of CaF₂ is absent at the compositions in the triangle enclosed with cuspidine-CaO·SiO₂-2CaO·SiO₂, and it is identified at the compositions out of the triangle. The composition in the triangle cannot keep equilibrium to CaF₂. So the analytical results of X-ray diffraction are found to agree with the phase equilibrium in the CaO-SiO₂-CaF₂ system.

X-ray diffraction intensity of NaF is shown on the CaO-SiO₂-CaF₂ phase in Fig. 9. In the triangle of cuspidine-CaO·SiO₂-2CaO·SiO₂, where the peak of CaF₂ is not identified, the peak of NaF is identified contrastively. In the triangle, cuspidine can not keep equilibrium to CaF₂ but to NaF.

Fig. 9. Results of X-ray diffraction (intensity of NaF).

Fig. 10. Results of X-ray diffraction (intensity of $\text{NaCa}_2\text{FSiO}_4$).

But in the condition (a) of Na_2O and F contents, the peak of NaF is not identified though the compositions are in the triangle. This seems to have concern with the experimental result that Na did not compose NaF but oxide crystals such as $\text{NaCaSi}_3\text{O}_8$, $\text{Na}_6\text{Al}_4\text{Si}_4\text{O}_{17}$ and nepheline in the solidified structure.

X-ray diffraction intensity of $\text{NaCa}_2\text{FSiO}_4$ is shown on the $\text{CaO-SiO}_2\text{-NaF}$ phase in Fig. 10. In this case, mold flux compositions were projected on $\text{CaO-SiO}_2\text{-NaF}$ face from the vertex of CaF_2 in the tetrahedron. It is obvious that the intensity of $\text{NaCa}_2\text{FSiO}_4$ becomes stronger as the mold flux composition comes to be close to $\text{NaCa}_2\text{FSiO}_4$.

It seems that the precipitation of $\text{NaCa}_2\text{FSiO}_4$ prevented the crystallization of cuspidine. So it is important to consider the precipitation of $\text{NaCa}_2\text{FSiO}_4$ for the control of the crystallization of cuspidine. In order to get the more mild cooling effect with the crystallization of cuspidine in mold, $\text{NaCa}_2\text{FSiO}_4$ should be prevented from precipitation.

These results suggest that NaF is necessary to be considered as a component of the mold flux. In the conventional designing of the mold flux, F was treated as a single substance as well as C or S, but it should be essentially treated as fluorides, and not only CaF_2 but also NaF should be considered to exist in the molten flux composition.

4.5. Influence of NaF Content to Solidification Temperature

As NaF is considered to be one of the components in the mold flux, its effect on the crystallization of cuspidine should be discussed. Then, further research was conducted about the influence of Al_2O_3 , MgO or NaF content to solidification temperature. Some additional mold flux was prepared for this research based on the mold flux whose composition was near cuspidine in the mass fraction ratio

Fig. 11. Relation between total mole fraction of Al_2O_3 , MgO and NaF and solidification temperature.

among CaO , SiO_2 and CaF_2 . The additional mold flux was varied in their content of Al_2O_3 , MgO or NaF.

The solidification temperature is shown in Fig. 11 as a function of the total mole fraction of Al_2O_3 , MgO and NaF, treating the mold flux composition as $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaF}_2\text{-NaF}$ system. Solidification temperature decreased with increase of total mole fraction, and in spite of the varied components, all of data existed on the same line.

On the X-axis, the composition is pure cuspidine and its melting point is reported to be 1680 K. At the composition of cuspidine-8mass%NaF, liquidus is reported to be 1619 K and solidus to be 1068 K (by differential thermal analysis).¹³ In this study, the solidification temperature at this composition was evaluated to be 1579 K by the oscillating-plate viscometer. This result suggests that the solidification temperature by the oscillating-plate viscometer is close to the liquidus and lower than it for several tens of degrees. Melting point of cuspidine, and solidification temperature at the composition of cuspidine-8mass%NaF also existed on that same line.

This result suggests that NaF acts as solvent in the molten flux, as well as Al_2O_3 or MgO.

But it is not obvious why the solidification temperature depends on the content of NaF as well as Al_2O_3 , MgO. It is hard to be considered that the chemical action of NaF to cuspidine or its components (CaO , SiO_2 and CaF_2) is same as that of Al_2O_3 or MgO. Further study in detail is necessary about this problem.

4.6. Compositions of Conventional Mold Flux and Primary Crystallization Field of Cuspidine

Phase relation between the compositions of conventional mold flux and cuspidine is discussed, here.

The compositions of conventional mold flux are shown in Fig. 12. The curve surrounding cuspidine indicates the primary crystallization field of cuspidine.⁶ It seems that compositions of conventional mold flux converge to a certain area by $\text{CaO} \cdot \text{SiO}_2$. This area lies out of the primary crystallization field of cuspidine. It is considered that cuspidine, in this case, can precipitate but cannot crystallize primarily. The methods to promote crystallization in the flux film such as the increase of basicity and the decrease of Al_2O_3 or MgO were conducted in this converged area of the conventional mold flux compositions.

Compositions of the mold flux reported in the former paper¹⁰⁾ are shown in Fig. 12. The compositions of the mold flux A and B exist in the same area as conventional mold flux. On the other hand, the mold flux C, which enabled prevention of longitudinal surface cracking on the surface of pypoperitectic steel slabs even at 5.0 m/min, exists in the primary crystallization field of cuspidine and quite near it.

In order to promote crystallization of cuspidine and make the mild cooling effective, it is necessary to design the mold flux composition in the primary crystallization field of cuspidine.

4.7. Effect of Primary Crystallization of Cuspidine on the Crystallization of Flux Film

Cross section of the flux film near the meniscus in mold is shown in Fig. 13 about mold flux B and C.¹⁰⁾ In mold flux B, fine crystal layer of 200/300 μm thick lied along the mold, and glassy phase lied inside. On the other hand, in mold flux C, the fine crystal layer that is the same as in mold flux B lied along mold and long columnar crystals lied across the film.

This difference is considered to depend on the phase relation between the mold flux composition and cuspidine. Thus, in the case that the mold flux composition exists out of the primary crystallization field, the mold flux solidifies as glass initially and cuspidine precipitates in the glass. On the other hand, in the case that the mold flux composition exists in the primary crystallization field, cuspidine crystal-

lize primarily from the molten flux.

The effect of designing the mold flux composition to be in the primary crystallization field of cuspidine appears as the crystallization rate in flux film. Rapid crystallization in flux film brings stable mild cooling effect in mold.

4.8. An Optimization Method of Mold Flux Composition for the Promotion of Crystallization

From the study in this work, an optimization method of the mold flux composition can be proposed as follows, in terms of the promotion of crystallization:

- (1) Control the stoichiometric ratio among CaO , SiO_2 and CaF_2 in the mold flux to be close to cuspidine.
- (2) Choose the solvent such as Al_2O_3 , MgO , NaF and so on according to casting conditions such as casting speed and steel grade.
- (3) Control the solidification temperature or physical properties of the molten flux with the contents of the solvents.

5. Conclusions

Phase relation between mold flux composition and cuspidine were researched fundamentally. As a result, some information was attained. It is as follows:

- (1) When the contents of Na_2O and F were constant, the solidification temperature of the mold flux had a peak in the relation to the basicity, and its basicity varied according to the condition of Na_2O and F contents.
- (2) Taking the affinity of F to Na into consideration and treating the mold flux composition as $\text{CaO-SiO}_2\text{-CaF}_2\text{-NaF}$ system, it became possible to estimate accurately the phase relation between the mold flux composition and such a crystal composition as cuspidine, CaF_2 , $\text{NaCa}_2\text{FSiO}_4$ and so on. Thus, the influence of Na_2O to this phase relation appears through the formation of NaF in molten flux.
- (3) The compositions of the conventional mold flux converge in the certain area out of the primary crystallization field of cuspidine. By means of control the mold flux composition into the primary crystallization field, crystallization of the flux film can be promoted effectively.
- (4) The effect of designing the mold flux composition

Fig. 12. Conventional compositions of mold flux in $\text{CaO-SiO}_2\text{-CaF}_2$ system.

Fig. 13. Micrographs of flux film on longitudinal section (about 8 mm below meniscus level).¹⁰⁾

to be in the primary crystallization field of cuspidine appears as the crystallization rate in the flux film. Rapid crystallization in the flux film brings stable and mild cooling effect in the mold.

REFERENCES

- 1) History of Steel Continuous Casting Technology in Japan, ISIJ, Tokyo, (1996), 529.
- 2) K. Ichikawa, A. Morita and Y. Kawabe: *Shinagawa Techno-report*, **36** (1993), 99.
- 3) J. Fukuda, T. Kondou and K. Tsutsumi: *CAMP-ISIJ*, **5** (1992), 281.
- 4) K. Watanabe, M. Suzuki, K. Murakami, H. Kondou, A. Miyamoto and T. Shiomi: *Tetsu-to-Hagané*, **83** (1997), 115.
- 5) S. Hiraki, T. Kanawaza, K. Nakajima, T. Murakami, K. Nakai and Y. Shirai: *CAMP-ISIJ*, **4** (1991), 1284.
- 6) T. Watanabe, H. Fukuyama and K. Nagata: *ISIJ Int.*, **42** (2002), 489.
- 7) Schlackenatlas, Verein Deutscher Eisenhüttenleute, Committee for Fundamental Metallurgy, Düsseldorf, (1981), 64.
- 8) K. C. Mills: *Ironmaking Steelmaking*, **15** (1988), 175.
- 9) M. Hanao, M. Kawamoto, M. Hara, T. Murakami and T. Watanabe: *CAMP-ISIJ*, **14** (2001), 886.
- 10) M. Hanao, M. Kawamoto, M. Hara T. Murakami, K. Hanazaki and H. Kikuchi: *Tetsu-to-Hagané*, **88** (2002), 23.
- 11) T. Iida, M. Kawamoto, S. Fujimoto and Z. Morita: *Tetsu-to-Hagané*, **71** (1985), 1490.
- 12) Physico-chemistry of Metal, 4th, The Japan Institute of Metals, Sendai, (1982), 143.
- 13) H. Takahashi, H. Fukuyama and K. Nagata: *CAMP-ISIJ*, **14** (2001), 885.