Crystallization of CaO–SiO₂–TiO₂ Slag as a Candidate for Fluorine Free Mold Flux

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(Received on July 19, 2005; accepted on October 28, 2005)

The time-temperature-transformation diagram (TTT diagram) of CaO–SiO₂–TiO₂ slag has been determined by using differential thermal analysis (DTA) in order to investigate the crystallization of the slag as a candidate for fluorine free mold flux. The incubation time of CaOΣSiO₂TiO₂ in CaO–SiO₂–TiO₂ slag is as small as that of cuspidine (3CaO₂SiO₂CaF₂) in commercial mold fluxes. This finding indicates that the CaOΣSiO₂TiO₂ crystallizes rapidly in the slag film between the mold and the steel in the continuous casting machine, similar to cuspidine in commercial mold fluxes. CaOΣSiO₂TiO₂ in CaO–SiO₂–TiO₂ slag is substituted for cuspidine in commercial mold fluxes. The thickness of the crystalline layer of CaOΣSiO₂TiO₂ is smaller than that of cuspidine. In order to improve the heat transfer control of CaO–SiO₂–TiO₂ slag, it is necessary to decrease the incubation time of CaOΣSiO₂TiO₂ at high temperature.

KEY WORDS: heat transfer control; TTT diagram; CaO–SiO₂–TiO₂ slag; fluorine free mold flux.

1. Introduction

In the continuous casting of steel, mold flux which mainly consists of CaO–SiO₂–CaF₂ system has many functions. The important functions are (1) lubrication between the steel and the mold and (2) heat transfer control for decreasing of the heat flux from the steel to the mold in order to prevent longitudinal cracks on the steel surface.¹,²) The crystallization of cuspidine (3CaO₂SiO₂CaF₂) from mold flux is thought to be the most effective way for the heat transfer control. Although the mechanism of the heat transfer control by the crystallization of cuspidine has not been determined yet, two ideas for the mechanism have been proposed. One is that radiation heat flux is decreased by scattering at the boundary between the crystalline and the liquid layers³–⁸) and the other is that total heat flux is decreased by the large thermal resistance of the air gap formed as a result of the solidification shrinkage.⁵,⁹–¹⁵) Anyway, the crystallization of cuspidine from mold flux has the great effect on the heat transfer control.

However, fluorine which is a main component of cuspidine (3CaO₂SiO₂CaF₂) exerts the harmful influence on environment. Therefore, fluorine free mold flux has been strongly required. Any fluorine free mold flux has not been proposed yet. The roles of CaF₂ addition to commercial mold fluxes are to decrease the liquidus temperature and the viscosity in CaO–SiO₂–CaF₂ system⁶,¹⁷) for the lubrication and to compose cuspidine for the heat transfer control, respectively. Resembling to the role of CaF₂, TiO₂ decreases the liquidus temperature and the viscosity in CaO–SiO₂–TiO₂ slag.¹⁸,¹⁹) This tendency expects that CaO–SiO₂–TiO₂ slag has the same role of the lubrication as commercial mold fluxes. In order to propose CaO–SiO₂–TiO₂ slag as a candidate for fluorine free mold flux, it is required that CaO–SiO₂–TiO₂ slag has the heat transfer control function. It is necessary that the crystals of CaO–SiO₂–TiO₂ system precipitate like cuspidine in commercial mold fluxes. Therefore, it is essential to study the crystallization behavior of CaO–SiO₂–TiO₂ slag.

Figure 1 shows the microstructure of the crystalline layer of the commercial mold flux used in KOBE steel.²⁰) The crystalline layer of cuspidine takes dendrite and cubic structures. Table 1 summarizes the microstructure of commercial mold fluxes.¹¹,²⁰,²¹) Any commercial mold flux provides the crystalline layer of cuspidine as reported by Grievson et al.²²) The crystalline layer in the commercial mold fluxes also presents cubic structure.

Fig. 1. Microstructure of the commercial mold flux on the mold side.²⁰)
on the mold side with lower temperature and dendrite structure from middle to the shell side with higher temperature. It is considered that cuspidine with the dendrite structure crystallizes rapidly from liquid on the shell side and cuspidine with the cubic structure precipitates from once quenched glass on the mold side. As shown Table 1, although the amount of the dendrite and the cubic structures varies with each commercial mold flux, most of the crystalline layer takes the dendrite structure. This finding that cuspidine is able to crystallize from liquid rapidly as primary crystal. Actually, Hanao et al. reported that the rapid crystallization of cuspidine brings the great effect on the heat transfer control i.e. the crystallization of cuspidine from liquid as primary crystal brings the great effect on the heat transfer control. Thus, it is necessary that the crystallization rate of the crystals in CaO–SiO2–TiO2 slag is compared with that of cuspidine in commercial mold fluxes. The crystallization rate of the crystals is defined as the incubation time in the time-temperature-transformation diagram (TTT diagram) of CaO–SiO2–TiO2 slag.

The aim of this study is to investigate TTT diagram of CaO–SiO2–TiO2 slag and to examine whether CaO–SiO2–TiO2 slag is proposed as a candidate for fluorine free mold flux.

2. Experimental

2.1. Sample Preparation

Figure 2 shows the equilibrium phase diagram of CaO–SiO2–TiO2 system. In this study, two series of glassy sample were prepared. The samples of glass CST series with the basicity of 0.83 were prepared in the initial field of CaO-SiO2-TiO2 and the samples of glass CS series with the basicity of 0.84 were prepared in the initial field of CaO-SiO2. Table 2 shows the chemical compositions of the samples. The compositions of the samples were selected from the reason that the liquidus temperature and the viscosity of the samples are similar to those of commercial mold fluxes in CaO–SiO2–CaF2 system. The samples of glass CST series have the same composition but have the different cooling rate of DTA varying from 0.183 to 2.36 K/s. In a similar way, the samples of glass CS series have the same composition but have the different cooling rate varying from 0.173 to 6.83 K/s. The composition of the samples was determined with accuracy using the quantitative analysis of electron probe micro analysis (EPMA). CaO-SiO2-TiO2 crystal was used as the standard material for the quantitative analysis. The samples were prepared from regent grade SiO2, TiO2 and CaCO3 powders. CaCO3 was decomposed into CaO at 1273 K for 24 h. The mixtures of SiO2, TiO2 and CaO were melted in a platinum crucible at
1 723 K for 1 h in air and then quenched by sandwiching the melt with two copper blocks. In order to produce the glassy sample, the samples were identified to be amorphous by X-ray diffraction.

2.2. Measurement

The continuous-cooling-transformation diagram (CCT diagram) was experimentally determined by using differential thermal analysis (DTA) and was transformed into TTT diagram by using the additivity rule of Schiel.\textsuperscript{23,24)}

DTA measurement were carried out in order to decide the crystallization temperature and the crystallization time at each continuous cooling rate, as shown in Table 2. About 50 mg of ground glassy samples were enclosed into a Pt container fixed onto the thermocouple directly. Ground glassy samples were melted completely above the melting point for 5 min and the molten samples were cooled at the constant cooling rate in Ar gas flow of 50 mL/min. Exothermic peaks on the continuous cooling process indicates the crystallization from the molten samples. The temperature and the time at each exothermic peak were measured as the crystallization temperature and the crystallization time of the samples, respectively. Pure $\alpha$-Al$_2$O$_3$ powder was selected as the reference material of DTA measurement. In order to correct the influence of the cooling rate and the Pt container, the measured crystallization temperature was calibrated by using the known melting points of CaF$_2$ and MgF$_2$.

X-ray diffraction studies were carried out by using Cu-K$_\alpha$ radiation and the crystals of the samples after DTA measurement were identified. The microstructure of the samples was observed by EPMA in order to identify the crystals of the samples and determine the sequence of the crystallization during the continuous cooling. The accelerator voltage of electron beam was 15 kV. Sample current image (SC image) and back scattered electron image (BSE image) of the samples were obtained. The characteristic X-ray images of Ca, Si, Ti and O were measured in order to identify the crystal of the samples and compared with the results of X-ray diffraction.

3. Results

3.1. CCT Diagram of Glass CST

3.1.1. Identification of Phases by DTA Measurement, X-ray Diffraction and EPMA for Glass CST

Figure 3(a) shows the DTA curve of glass CST-A sample whose cooling rate is 0.183 K/s. In glass CST-A sample, there are two exothermic peaks. The peak with higher temperature and the peak with lower temperature are named to be Peak 1 and Peak 2, respectively. In Table 2, the crystallization temperature and the crystallization time of the sam-
samples are summarized. The melting points of the samples are determined by the heating process of DTA measurement. Three kinds of the exothermic peak, Peak 1–Peak 3, are detected. Peak 1 is detected only in glass CST-A sample and Peak 3 is detected in glass CST-C sample and glass CST-D sample.

Figure 4 shows the characteristic X-ray image of Ti for glass CST-B sample. Glassy phases and the phase which consists of the small grains of CaOSiO₂TiO₂ and CaOSiO₂ were observed. In Table 3, the crystals observed by EPMA are summarized. Glass CST-C sample with Peak 2 and Peak 3 in DTA data is composed of two phases of CaOSiO₂TiO₂ and glass. Glass CST-D sample with only Peak 3 has only glassy phase.

Figures 5(a) and 5(b) show the X-ray diffractions of glass CST-A sample and glass CST-C sample, respectively. In glass CST-A sample, CaOSiO₂TiO₂ and CaOSiO₂ are identified, while in glass CST-C sample only CaOSiO₂TiO₂ is.

Table 3. Results of X-ray diffraction studies and microstructure observation by EPMA.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>cooling rate of DTA measurement /Ks⁻¹</th>
<th>crystal identified by XRD</th>
<th>crystal observed by EPMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass CST-A</td>
<td>0.173</td>
<td>CaOSiO₂TiO₂ + CaOSiO₂</td>
<td>-</td>
</tr>
<tr>
<td>glass CST-B</td>
<td>0.373</td>
<td>CaOSiO₂TiO₂ + CaOSiO₂</td>
<td>CaOSiO₂TiO₂ + CaOSiO₂ + glassy</td>
</tr>
<tr>
<td>glass CST-C</td>
<td>1.94</td>
<td>CaOSiO₂TiO₂</td>
<td>CaOSiO₂TiO₂ + glassy</td>
</tr>
<tr>
<td>glass CST-D</td>
<td>2.36</td>
<td>undetected</td>
<td>glassy</td>
</tr>
<tr>
<td>glass CS-A</td>
<td>0.173</td>
<td>CaOSiO₂TiO₂ + CaOSiO₂</td>
<td>cancelate (CaOSiO₂TiO₂ + CaOSiO₂) + columnar (CaOSiO₂TiO₂ + CaOSiO₂) + SiO₂ (small grain)</td>
</tr>
<tr>
<td>glass CS-B</td>
<td>0.600</td>
<td>CaOSiO₂TiO₂ + CaOSiO₂</td>
<td>-</td>
</tr>
<tr>
<td>glass CS-C</td>
<td>0.633</td>
<td>CaOSiO₂TiO₂ + CaOSiO₂</td>
<td>cancelate (CaOSiO₂TiO₂ + CaOSiO₂) + columnar (CaOSiO₂TiO₂ + CaOSiO₂) + SiO₂ (small grain) + glassy</td>
</tr>
<tr>
<td>glass CS-D</td>
<td>0.800</td>
<td>CaOSiO₂TiO₂ + CaOSiO₂</td>
<td>-</td>
</tr>
<tr>
<td>glass CS-E</td>
<td>0.917</td>
<td>undetected</td>
<td>columnar (CaOSiO₂TiO₂ + CaOSiO₂) + SiO₂ (small grain) + glassy</td>
</tr>
<tr>
<td>glass CS-G</td>
<td>1.22</td>
<td>undetected</td>
<td>-</td>
</tr>
<tr>
<td>glass CS-J</td>
<td>3.35</td>
<td>-</td>
<td>columnar (CaOSiO₂TiO₂ + CaOSiO₂) + SiO₂ (small grain) + glassy</td>
</tr>
</tbody>
</table>
is identified. In Table 3, the crystals identified by X-ray diffraction are summarized. The phases observed by EPMA can be identified by X-ray diffraction. However, no crystal phase is identified in glass CST-D sample.

3.1.2. Determination of the CCT Diagram of Glass CST

As shown in Table 3, in glass CST-D sample only glassy phase is observed by EPMA and no crystal is identified by X-ray diffraction. These results indicate that the temperature of Peak 3 in DTA data corresponds to the glass transition temperature. This is consistent with the tendency that Peak 3 is detected in samples whose cooling rate is large e.g. glass CST-C sample and glass CST-D sample. As shown in Fig. 4, the microstructure of glass CST-B sample includes the glassy phase, although Peak 3 is not detected in DTA data because of the small amount of the glassy phase.

Table 2 shows that glass CST-C sample has Peak 2 and Peak 3. As shown in Table 3, CaOSiO$_2$TiO$_2$ and glassy phases are observed by EPMA and only CaOSiO$_2$TiO$_2$ is identified by X-ray diffraction as shown in Fig. 5(b). Since Peak 3 corresponds to the glass transition point, it is concluded that Peak 2 is equivalent to the crystallization of CaOSiO$_2$TiO$_2$. The critical cooling rate for the crystallization of CaOSiO$_2$TiO$_2$ is defined, in this study, as 1.94 K/s due to no detection of Peak 2 in glass CST-D sample.

Figure 5(a) shows that glass CST-A sample includes both CaOSiO$_2$TiO$_2$ and CaOSiO$_2$. As shown in Table 2, Peak 1 and Peak 2 are detected in glass CST-A sample. Since Peak 2 is equivalent to the crystallization of CaOSiO$_2$TiO$_2$, it can be decided that Peak 1 represents the crystallization of CaOSiO$_2$. Although the result of DTA measurement shows that glass CST-B sample does not include Peak 1, CaOSiO$_2$ is identified by X-ray diffraction and EPMA. Due to the overlaps of Peak 1 with Peak 2, the crystallization of both CaOSiO$_2$TiO$_2$ and CaOSiO$_2$ occurs at the same temperature. Since in glass CST-C sample CaOSiO$_2$ is not identified by X-ray diffraction and EPMA, the critical cooling rate for the crystallization of CaOSiO$_2$ is defined as 0.373 K/s.

**Figure 6(a)** illustrates the CCT diagram of glass CST. Closed circles, opened triangles and opened squares represent Peak 1, Peak 2 and Peak 3, respectively. The line connected the closed circles expresses the crystallization of CaOSiO$_2$ and the line connected the opened triangles expresses the crystallization of CaOSiO$_2$TiO$_2$.

3.2. CCT Diagram of Glass CS

3.2.1. Identification of Phases by DTA Measurement, X-Ray Diffraction and EPMA in Glass CS

Figure 3(b) shows the DTA curve of glass CS-C sample whose cooling rate is 0.633 K/s. In glass CS-C sample, there are three exothermic peaks and these peaks are named to be Peak 1, Peak 2 and Peak 3, as shown in Fig. 3(b).

In Table 2, the crystallization temperature and the crystallization time determined by the exothermic peak positions of DTA data are summarized. The melting points of the samples are determined by the heating process of DTA measurement. Three kinds of peaks are observed. Peak 1 is identified in the samples whose cooling rate is relatively small. Peak 2 is identified in the samples except glass CS-L sample. Peak 3 is identified in the samples except glass CS-A sample.

**Figure 7(a)** shows the characteristic X-ray image of Ti for glass CS-C sample. The middle area of Fig. 7(a) con-
sists of the cancellate structure of CaOSiO₂TiO₂ and CaO-SiO₂. The right upper area consists of the two columnar structures of CaOSiO₂TiO₂ and CaO-SiO₂ including the small grain of SiO₂. In addition, the glassy phase is observed in the left lower area. Figure 7(b) shows the characteristic X-ray image of Ca for glass CS-J sample. In the down area of Fig. 7(b) glassy phase exists. In the upper area of Fig. 7(b) the microstructure consisting of the two columnar structures of CaOSiO₂TiO₂ and CaO-SiO₂ including the small grain of SiO₂ exists. The microstructure is the same structure as the right upper area of Fig. 7(a). In Table 3, the crystals observed by EPMA observation are summarized. The microstructure consisting of the two columnar structures is observed in all samples. The cancellate structure of CaO-SiO₂TiO₂ and CaO-SiO₂ are observed in glass CS-A sample and glass CS-C sample. No cancellate structure is observed in glass CS-E sample and glass CS-J sample. Glassy phase is observed in glass CS-C sample, glass CS-E sample and glass CS-J sample where Peak 3 is detected.

Figures 8(a) and 8(b) show X-ray results of glass CS-A sample and glass CS-C sample, respectively. CaO-SiO₂TiO₂, CaO-SiO₂ and SiO₂ are identified in glass CS-A sample and only SiO₂ is not identified in glass CS-C sample due to the small intensity of the peak. In Table 3, the results of X-ray diffraction are summarized. The crystals observed by EPMA were identified by X-ray diffraction for each sample.

3.2.2. Determination of the CCT Diagram of Glass CS

Tables 2 and 3 show that the samples except glass CS-A sample include Peak 3 in DTA data and glassy phase in EPMA data. These results indicate that Peak 3 is equivalent to the glass transition point.

As shown in Fig. 7(b), the two columnar structures of CaO-SiO₂TiO₂ and CaO-SiO₂ including the small grain of SiO₂ and glassy phase were observed in glass CS-J sample. Peak 2 and Peak 3 were detected in DTA data of glass CS-J sample. Since the glassy phase shown in Fig. 7(b) is formed at Peak 3, it can be concluded that CaO-SiO₂TiO₂, CaO-SiO₂ and SiO₂ crystallize at Peak 2 simultaneously. The critical cooling rate of CaO-SiO₂TiO₂, CaO-SiO₂ and SiO₂ is decided as 5.70 K/s, because Peak 2 is not detected in glass CS-L sample.

Figure 7(a) shows that the microstructure of glass CS-C sample consists of the cancellate structure of CaO-SiO₂TiO₂ and CaO-SiO₂, the two columnar structures of CaO-SiO₂TiO₂ and CaO-SiO₂ including the small grain of SiO₂ and glassy phase. Glassy phase and the two columnar structures of CaO-SiO₂TiO₂ and CaO-SiO₂ include the small grain of SiO₂ form at Peak 3 and at Peak 2, respectively. Thus, it can be concluded that Peak 1 represents the crystallization of the cancellate structure of CaO-SiO₂TiO₂ and CaO-SiO₂. The critical cooling rate of the crystallization of CaO-SiO₂TiO₂ and CaO-SiO₂ is decided as 1.22 K/s, because Peak 1 is not detected in glass CS-H sample. Although it is expected that glass CS-F sample should include Peak 1 in DTA data, Peak 1 is not detected in glass CS-F sample by the result of DTA measurement. The intensity of Peak 1 is very small in glass CS-F sample whose cooling rate is close to the critical cooling rate. On the other hand, Peak 1 is detected in glass CS-G sample regardless of the very small intensity of Peak 1.

Villegas et al. 25) reported that phase separation is a very common phenomenon in CaO–SiO₂–TiO₂ glass because TiO₂ induces liquid–liquid immiscibility. They observed the microstructure of the strong phase separation as a droplet with the size between 0.3 μm and 2 μm. As shown in Figs. 7(a) and 7(b), the small grain included in the two columnar structures, in this study, has the size of 5 μm. In addition, SiO₂ is identified by X-ray diffraction of glass CS-A sample. Thus, these results conclude that the observed small grain included in the two columnar structures is identified as not the glassy droplet of the phase separation as reported but SiO₂ crystal.

Figure 6(b) illustrates the CCT diagram of glass CS. The closed circles and the opened triangles represent the crystallization of CaO-SiO₂TiO₂ and CaO-SiO₂ and the crystallization of CaO-SiO₂TiO₂, CaO-SiO₂ and SiO₂, respectively. The opened squares express the glass transition point.

4. Discussions

4.1. Transformation of CCT Diagram into TTT Diagram

The CCT diagrams of glass CST and glass CS shown in Fig. 6 were transformed into the TTT diagrams based on the additivity rule of Scheil. 23,24) In this rule, it is assumed that the continuous cooling curve of CCT diagram consists of a lot of isothermal steps. The application of Scheil’s rule provides the following Eq. (1).

\[ \sum_{i=1}^{n} \frac{\Delta t_i}{t_i} = 1 \] ..............................(1)

In Eq. (1), \( \Delta t_i \) and \( t_i \) represent the time period for \( i \)-th isothermal step and the ideal incubation time of TTT diagram at the same temperature as that of \( i \)-th isothermal step. Figures 9(a) and 9(b) show the TTT diagrams of glass CST and glass CS sample, respectively. The TTT diagram of glass CST indicates that the nose incubation time of
CaO\textsubscript{2}TiO\textsubscript{2} crystallizing at low temperature is far smaller than that of CaO\textsubscript{2} crystallizing at high temperature. The TTT diagram of glass CS indicates that CaO\textsubscript{2}TiO\textsubscript{2} and CaO\textsubscript{2} crystallize in the temperature far below the melting point. It can be stated by both TTT diagrams that CaO\textsubscript{2}TiO\textsubscript{2} has the large crystallization rate in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag with the basicity of around 0.8 and TiO\textsubscript{2} addition less than 17 mol%.

4.2. Proposal of CaO–SiO\textsubscript{2}–TiO\textsubscript{2} Slag for Fluorine Free Mold Flux

4.2.1. Heat Transfer Control Function in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} Slag

The important roles of commercial mold fluxes are the lubrication and the heat transfer control. It has been already described in the introduction that CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag is expected to have the lubrication function because the liquidus temperature and the viscosity are almost the same as those of CaO–SiO\textsubscript{2}–CaF\textsubscript{2} system. Thus, in this section, the problem whether CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag has the heat transfer control function will be discussed.

Heat transfer control is largely affected by the rapid crystallization of cuspidine in commercial mold fluxes. Thus, it is necessary that the incubation time of the crystal in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag is as small as that of cuspidine in commercial mold fluxes. Figure 10 illustrates the TTT diagrams of CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag and the commercial mold flux including CaF\textsubscript{2} reported by Kashiwaya et al.\textsuperscript{26} in order to compare the incubation time. The TTT diagrams indicate that the incubation time of CaO2TiO3 is as small as that of crystals in the commercial mold flux, cuspidine and 2CaO\textsubscript{2}SiO\textsubscript{2}TiO\textsubscript{2}. This finding means that CaO\textsubscript{2}TiO\textsubscript{2} crystallizes rapidly in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag like cuspidine in the commercial mold flux. Therefore, it is considered that CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag has the heat transfer control function.

4.2.2. The Substitute Crystal for Cuspidine

The basicity (CaO/SiO\textsubscript{2}) of commercial mold fluxes is approximately 0.8 to 1.4. As shown in Fig. 2, in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag, the crystals which crystallize in the composition area with basicity of 0.8 to 1.4 are CaO\textsubscript{2}TiO\textsubscript{2}, CaO\textsubscript{2}SiO\textsubscript{2} and CaOTiO\textsubscript{2}. CaOTiO\textsubscript{2} crystallizes from liquid as the following reaction (2).

\[
\text{Ca}^{2+} + \text{TiO}_3^{2-} = \text{CaOTiO}_2 \quad \text{(2)}
\]

After CaO which is a basic oxide in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag decomposes to Ca\textsuperscript{2+} and O\textsuperscript{2-}, Ca\textsuperscript{2+} modifies the silicate network. If Ca\textsuperscript{2+} is consumed by the reaction (2) as a result of the crystallization of CaOTiO\textsubscript{2} from liquid, the remained slag will change more acidic. Consequently, the crystallization of CaOTiO\textsubscript{2} increases the viscosity of the remained slag largely and the lubrication in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag is lost. Therefore, CaOTiO\textsubscript{2} is not appropriate for the substitution of cuspidine. On the other hand, since the crystallization of CaO\textsubscript{2}TiO\textsubscript{2} and CaO\textsubscript{2}SiO\textsubscript{2} consume both CaO which is a basic oxide and SiO\textsubscript{2} which is an acidic oxide, the viscosity of the remained slag does not increase largely. As shown in Fig. 10, the incubation time of CaO\textsubscript{2}TiO\textsubscript{2} is as small as that of cuspidine, while the incubation time of CaO\textsubscript{2}SiO\textsubscript{2} is far larger than that of cuspidine. These results indicate that CaO\textsubscript{2}TiO\textsubscript{2} crystal in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag is substituted for cuspidine in commercial mold fluxes.

4.3. Effect of the Thickness of the Crystalline Layer on Heat Transfer Control

As shown in Fig. 10, especially at high temperature, the incubation time of CaO\textsubscript{2}TiO\textsubscript{2} is far large while that of cuspidine is small. The crystalline and the liquid layers exist between the shell and the mold in commercial mold fluxes with temperature gradient from 1 800 to 500 K.\textsuperscript{10} The difference of the incubation time at high temperature causes the problem that the thickness of the crystalline layer in CaO–SiO\textsubscript{2}–TiO\textsubscript{2} slag is smaller than that of commercial mold fluxes. The heat transfer control is largely affected by the crystalline layer of cuspidine in commercial mold fluxes. Therefore, it is essential to discuss the effect of the thickness of the crystalline layer on the heat transfer control.

Previously, the present authors reported the effect of thermal and optical properties of mold fluxes on the heat trans-
fer control using the heat transfer modeling. In this study, the effect of the thickness of the crystalline layer on the heat transfer control is also investigated using the same modeling as follow.

The large effect of the heat transfer control means that the total thermal resistance of mold flux between the shell and the mold is large. Therefore, it is necessary to clear the relation between the thickness of the crystalline layer and the total thermal resistance of mold flux. In already reported modeling, the total thermal resistance of mold flux between the shell and the mold is considered as shown in Fig. 11. Heat transfer through mold flux consists of both conduction and radiation transfer of the liquid and the crystalline layers. Convection transfer through mold flux can be neglected. The air gap formed by the solidification shrinkage of the crystalline layer is also taken into consideration. As shown in Fig. 11, the temperature of the boundary between the liquid and the crystalline layers corresponding to \( T_1 \), and the temperature of the boundary between the crystalline layer and the air gap corresponding to \( T_2 \) are calculated. The total thermal resistance of mold flux is calculated in the already reported way. Watanabe et al. 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. This indicates that the heat transfer control function starts to work after 20 s from the casting. Figure 10 shows that the crystallization temperature after 20 s in glass CS and the commercial mold flux are below 1 300 K and 1 450 K, respectively. Since the crystallization temperature is equivalent to the temperature \( T_1 \) shown in Fig. 11, the temperature \( T_1 \) varies from 1 300 to 1 450 K. By the heat transfer modeling, the variation of the temperature \( T_1 \) corresponds to the variation of the thickness of the crystalline layer from 700 to 800 \( \mu \text{m} \) based on the assumption that the total thickness between the shell and the mold is 1 mm. Figure 12 shows the relation between the thickness of the crystalline layer and the total thermal resistance of mold flux. The total thermal resistance of mold flux increases with increasing the thickness of the crystalline layer. Thus, in order to propose CaO–SiO\(_2\)–TiO\(_2\) slag as a candidate for fluorine free mold flux, it is necessary to decrease the incubation time of CaO–SiO\(_2\)–TiO\(_2\) at high temperature.

In commercial mold fluxes including CaF\(_2\), the additional compound like Na\(_2\)O is needed for adjusting the viscosity and the liquidus temperature. It is reported that Na\(_2\)O addition to CaO–SiO\(_2\)–CaF\(_2\) synthetic slag decreases the incubation time of cuspidine. Therefore, there is a possibility that the additional compound like Na\(_2\)O also decreases the incubation time of CaO–SiO\(_2\)–TiO\(_2\). In future, it is worth investigating the effect of Na\(_2\)O addition to CaO–SiO\(_2\)–TiO\(_2\).

5. Conclusions

Our conclusions are as follows.

(1) The TTT diagram was prepared in CaO–SiO\(_2\)–TiO\(_2\) slag at the composition with the basicity of about 0.8 and TiO\(_2\) addition less than 17 mol%. CaO–SiO\(_2\)–TiO\(_2\) and CaO–SiO\(_2\)–TiO\(_2\) crystallize in this slag and the incubation time of CaO–SiO\(_2\)–TiO\(_2\) is as small as that of cuspidine in the commercial mold flux.

(2) The crystallization of CaO–SiO\(_2\)–TiO\(_2\) does not increase the viscosity of the remained slag and maintain the lubrication. Thus, CaO–SiO\(_2\)–TiO\(_2\) is substituted for cuspidine in commercial mold fluxes.

(3) The total thermal resistance increases with increasing the thickness of the crystalline layer. Thus, in order to propose CaO–SiO\(_2\)–TiO\(_2\) slag as a candidate for fluorine free mold flux, it is necessary to increase the thickness of the crystalline layer. It is necessary to decrease the incubation time of CaO–SiO\(_2\)–TiO\(_2\) at high temperature.

REFERENCES

13) A. Yamachii, K. Sorimachi and T. Yamachii: Ironmaking Steel-
making, 29 (2002), No. 3, 203.