Crystallization Characteristics of B\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}-bearing Glassy Fluoride-Free Mold Fluxes

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Abstract
To explore the effects of TiO\textsubscript{2} and/or B\textsubscript{2}O\textsubscript{3} on crystallization of the glassy fluoride-free slag film near the copper mould, the crystallization characteristics of glassy fluoride-free mold fluxes with fluoride being substituted by TiO\textsubscript{2} and/or B\textsubscript{2}O\textsubscript{3} were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM) and differential thermal analysis (DTA) techniques. The glass forming ability index (K\textsubscript{gl}) of the glassy fluoride-free mold fluxes was studied using Hruby’s method. The XRD and SEM analysis show that Ca\textsubscript{2}Al\textsubscript{2}SiO\textsubscript{7}, CaTiO\textsubscript{3} and CaSiO\textsubscript{3} are the dominant crystals of this fluoride-free mold fluxes system. With the content of TiO\textsubscript{2} increasing from 0 to 7%, the crystallization of Ca\textsubscript{2}Al\textsubscript{2}SiO\textsubscript{7} and CaSiO\textsubscript{3} are inhibited and the formation of CaTiO\textsubscript{3} is also weak, so crystallization tendency of the glassy fluoride-free mold fluxes weakens. But as TiO\textsubscript{2} content reaches 10%, the crystallization tendency strengthens because of the strong crystallization of CaTiO\textsubscript{3}. An increase of B\textsubscript{2}O\textsubscript{3} inhibits the crystallization of calcium silicate, so it weakens the crystallization tendency of the glassy fluoride-free mold fluxes. The crystallization processes of the studied fluoride-free mold fluxes correspond to the surface crystallization mechanism. This research provides important reference for further investigation on the heat transfer behavior of the TiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}-bearing slag between copper mould and slab to evaluate the feasibility of B\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}-bearing fluoride-free mold fluxes.

Keywords: fluoride-Free mold fluxes; crystallization; slag; glass forming ability index; surface crystallization; TiO\textsubscript{2}
1. Introduction

Mold flux is an indispensable material in the continuous casting process. It helps to lubricate steel shell to prevent sticking against the mold surface and control the heat transfer to achieve uniform shell [1-7]. The stability of the continuous casting process and the surface quality of products are restricted to good performance of the above functions, which are closely related to the physiochemical properties of the mold flux, such as viscosity, melting temperature, crystallization behavior [4-11]. And the implementation of the above mentioned functions is bound up with the existence of fluorides in traditional mold fluxes, which plays significant roles in adjusting physio-chemical properties of the mold fluxes. However, the fluorides can lead to erosion to continuous caster, pollution of environment, acidification of the cooling water, human health hazard, and a series of other harmful influences [6, 12-16]. Thus, there is a pressing need for fluoride-free mold fluxes, and the investigation on it has become a research area of interest.

Previous studies show that adding B₂O₃ and/or TiO₂ to mold fluxes without fluoride can adjust the properties of the slag to make it have similar characteristics with the traditional fluoride containing mold fluxes [5, 6, 10, 13-16]. On one hand, the addition of TiO₂ to mold fluxes without fluoride can ensure the crystallization of mold fluxes to make sure that the fluoride-free mold fluxes show similar heat transfer performance with the traditional fluoride containing mold fluxes [2, 5, 6, 10, 13, 17]. Also, as amphoteric oxide, TiO₂ can influence the viscosity of fluoride-free mold fluxes obviously [13], so that help to control the lubrication performance. Besides, B₂O₃, as an effective fluxing agent to lower the melting point of mold fluxes, has been taken into consideration for being added to mold fluxes to adjust the viscosity or melting properties of slag [5, 13-19]. Or a new crystalline phase of Ca₁₁Si₄B₂O₂₂ in fluorine-free mold fluxes formed by the addition of B₂O₃ shows a great potential to replace the cuspidine phase in traditional mold fluxes [17, 19]. Therefore, B₂O₃ and TiO₂ are potential to replace the fluoride in traditional mold fluxes, and fluoride-free mold fluxes bearing B₂O₃ and/or TiO₂ is the promising substitutes. So it is absolutely essential to investigate the properties of mold fluxes simultaneously containing B₂O₃ and TiO₂ to develop the optimal fluoride-free mold fluxes.

According to survey performed by the present author, investigations on the properties of mold fluxes containing both B₂O₃ and TiO₂ are limited [16, 20-25]. The present authors investigated the crystallization of molten mold fluxes containing both B₂O₃ and TiO₂ and explored the effects of B₂O₃ and TiO₂ on incubation time for crystallization of molten fluxes [24]. However, besides molten layer, there is glass layer in the gap between steel shell and mold wall [3]. And the crystallization of glassy mold fluxes, i.e. devitrification of glassy mold fluxes, is also important to heat transfer between steel shell and mold. According to Watanabe et al [26, 27], mold fluxes can inevitably absorb some heat released from the solidification of liquid steel, which produces reheating to the mold fluxes. This reheating process could lead to the crystallization of glassy slag film near the copper mold, which changes crystalline layer thickness and surface roughness of solidified mold fluxes, and thereby has great effect on horizontal heat transfer and lubrication. So it would be essential to carry out the research on crystallization characteristics of glassy mold fluxes simultaneously containing B₂O₃ and TiO₂ to examine the feasibility of B₂O₃ and TiO₂-bearing fluoride-free mold fluxes.

In this work, the crystallization characteristic of B₂O₃ and TiO₂-bearing fluoride-free mold fluxes in glassy state has been investigated. Crystals precipitating from the studied glassy mold fluxes with variable TiO₂ and B₂O₃ content were identified by X-ray diffraction (XRD) and scanning electron
microscope (SEM) analysis, and the crystallization mechanisms were revealed. The influences of TiO$_2$ and B$_2$O$_3$ on crystallization tendency of B$_2$O$_3$ and TiO$_2$-bearing fluoride-free mold fluxes were examined by analyzing characteristic temperatures for crystallization of the glassy fluoride-free mold fluxes determined by differential thermal analysis (DTA).

2. Experimental

2.1 Sample Preparation

Analytical grade CaO, SiO$_2$, Al$_2$O$_3$, MgO, TiO$_2$, Na$_2$CO$_3$ and H$_3$BO$_3$ (from Sinopharm Chemical Reagent Co., Ltd) were taken as raw materials, with Na$_2$CO$_3$ and H$_3$BO$_3$ being substitutes for Na$_2$O and B$_2$O$_3$, respectively. Table 1 presents the chemical compositions (wt. %) of the investigated samples.

| Sample Name | R=w(CaO)/w(SiO$_2$) | Al$_2$O$_3$ | MgO | Na$_2$O | TiO$_2$ | B$_2$O$_3$ |
|-------------|----------------------|-------------|------|--------|---------|------------|
| No.1-0%TiO$_2$ | 1.0                | 7           | 2    | 10     | 0       | 5          |
| No.2-3%TiO$_2$ | 1.0                | 7           | 2    | 10     | 3       | 5          |
| No.3-5%TiO$_2$-5%B$_2$O$_3$ | 1.0    | 7           | 2    | 10     | 5       | 5          |
| No.4-7%TiO$_2$ | 1.0                | 7           | 2    | 10     | 7       | 5          |
| No.5-10%TiO$_2$ | 1.0                | 7           | 2    | 10     | 10      | 5          |
| No.6-0%B$_2$O$_3$ | 1.0                | 7           | 2    | 10     | 5       | 0          |
| No.7-3%B$_2$O$_3$ | 1.0                | 7           | 2    | 10     | 5       | 3          |
| No.8-7%B$_2$O$_3$ | 1.0                | 7           | 2    | 10     | 5       | 7          |
| No.9-10%B$_2$O$_3$ | 1.0                | 7           | 2    | 10     | 5       | 10         |

Glass samples with different TiO$_2$ and B$_2$O$_3$ content were prepared by the conventional melting and quenching method. After well mixed, Raw materials was taken into a platinum crucible and then melted in high temperature furnace at approximately 1573K in air atmosphere. The samples were held at 1573K for nearly 3h to make sure complete melting and homogenization. After melting, the melts were quenched by water and then bulk glass samples are formed. These glass samples are proved to be amorphous by XRD, and Figure 1 gives the XRD patterns for the quenched samples. The liquidus temperature of this system has been studied in another work of our team [28], and it is showed that the liquidus temperatures of all the samples are far blow 1573K. So when the samples were heated to 1573K and held for 3 h, it is completely melted and there is definitely no crystal formed. The XRD results in Figure 1 are in accordance with the results of liquidus temperature study.
Figure 1. The XRD patterns for the quenched glass samples

2.2 Differential Thermal Analysis

The glass samples were pulverized into powder (less than 0.74μm) for DTA measurement. For each sample, about 30mg glass powder was taken into a platinum crucible to be subjected to the differential thermal analysis using Netzsch STA 449C TG-DTA calorimeter at a heating rate of 10K/min. During the whole measurement process, Argon was used as a shielding gas. α-Al₂O₃ was used as a reference material.

2.3 X-ray Diffraction Analysis

The glass samples were heated in a Pt-crucible, held for approximately 4 hours at each exothermic peak temperature obtained by DTA curves and then quenched in air. Then each of the heat treated samples was subjected to XRD analysis to identify the products of crystallization. The XRD measurement was performed using a MAC M21XRHF22 (21KW) X-ray diffractometer with Cu Ka radiation.

2.4 Scanning Electron Microscope Measurement

The bulk glass samples were heated in a Pt-crucible, held for approximately 4 hours at each exothermic peak temperature obtained by DTA curves and then quenched in air. Then each of these heat treated samples was embedded with resin, rubbed with fine sandpaper and polished with polishing paste. The surface of each sample was experienced carbon spray coating. After that, the samples were subjected to scanning electron microscope (SEM) measurement using ZEISS EVO MA18 to obtain the microstructure of the crystallization products and the phases were identified by energy dispersive spectroscopy (EDS) attached to SEM analyzer.
3. Results and Discussion

![Graph showing DTA results with different TiO₂ or B₂O₃ content]

**Figure 2.** DTA results of glassy fluoride-free mold fluxes with different TiO₂ or B₂O₃ content

Figure 2 and Figure 3 respectively presents the DTA and TG curves of glassy fluoride-free mold fluxes samples with different TiO₂ or B₂O₃ content. It can been seen from Figure 3 that weight loss of each sample is little, so volatilization during the DTA measurement mainly caused by Na₂O and B₂O₃ can be ignored and it is supposed that the chemical composition of each sample is invariable. From Figure 2, the glass transition temperatures (T_g), onset crystallization temperature (T_x), crystallization peak temperatures (T_c) and liquidus temperature (T_l) can be obtained. According to Boettinger et al’s definition [29], acquisition method of these characteristic temperatures for crystallization process have been marked in Figure 2 a). And the corresponding characteristic temperatures for each sample can be obtained using the same method, which are summarized in Table 2.
3.1 Crystal Phase Identification

To identify the phase precipitated at each crystallization peak temperature, each heat treated samples was investigated by XRD and SEM-EDS. Figure 4, Figure 5 and Figure 6 respectively gives the XRD and SEM results for crystallized fluoride-free mold fluxes samples of CaO-SiO$_2$-Al$_2$O$_3$-MgO-Na$_2$O-TiO$_2$-B$_2$O$_3$ system.

It can be seen from Figure 4 (a) and Figure 5 that for the sample free of TiO$_2$, gehlenite (Ca$_2$Al$_2$SiO$_7$) and wollastonite (CaSiO$_3$) can precipitate from the slag, and with the addition of TiO$_2$, besides gehlenite and wollastonite, another crystal, perovskite (CaTiO$_3$), forms during the crystallization of the glassy fluoride-free mold fluxes. And the small white crystal particles in Figure 5 b), c) and e) are too small to be marked by “3”, indicating the CaTiO$_3$ phase. Meanwhile, with the increase of TiO$_2$
content, the peaks for CaTiO$_3$ in XRD patterns (Figure 4 (a)) strengthen, and there are more crystal particles for CaTiO$_3$ in SEM-BSE pictures (Figure 5 b), c), d) and e)). That is, the increase of TiO$_2$ can promote the crystallization of perovskite.

**Figure 4.** XRD patterns for the crystallized fluoride-free mold fluxes with different TiO$_2$ or B$_2$O$_3$ content
Figure 5. SEM-BSE images for the crystallized fluoride-free mold fluxes with different TiO$_2$ content, a)-0% TiO$_2$, b)-3% TiO$_2$, c)-5% TiO$_2$, d)-7% TiO$_2$, e)-10% TiO$_2$ and 1: Ca$_2$Al$_2$SiO$_7$, 2: CaSiO$_3$, 3: CaTiO$_3$

Figure 6. SEM-BSE images for the crystallized fluoride-free mold fluxes with different B$_2$O$_3$ content, a)-0% B$_2$O$_3$, b)-3% B$_2$O$_3$, c)-5% B$_2$O$_3$, d)-7% B$_2$O$_3$, e)-10% B$_2$O$_3$ and 1: Ca$_2$Al$_2$SiO$_7$, 2: CaSiO$_3$, 3: CaTiO$_3$, 4: Ca$_2$SiO$_4$

From the XRD results for samples with different B$_2$O$_3$ content in Figure 4 a), it can be seen that as the content of is low (0-3%), there form gehlenite, dicalcium silicate (Ca$_2$SiO$_4$) and perovskite during
the crystallization of the glass slag samples. But in SEM-BSE pictures (Figure 6 a, b)), it is hard to observe the gehlenite phase, because it is weak in crystallization. This may be due to that as the content of B2O3 is low, most of SiO2 exists in the slag in form of $\text{SiO}_2^4-$ (Q0) [21], which is favorable to the precipitation of Ca$_2$SiO$_4$, so the crystallization of gehlenite is suppressed. However, with the increase of B2O3, on one hand, Ca$^{2+}$ associates with boron preferentially in borosilicate slag system [30-34] so that some of CaO participates the formation of Ca-O-B bonds preferentially and there is no enough CaO to form Ca$_2$SiO$_4$; on the other hand, proportion of bridging oxygen increases, so the ratio of Q$^0$ decreases. These lead to the disappearance of Ca$_2$SiO$_4$, while wollastonite and more gehlenite, the formation of which could occupy more bridging oxygen, appear. Above all, with the increase of B2O3, Ca$_2$SiO$_4$ disappears gradually, gehlenite and wollastonite form, so the primary crystal phases in the slag turn into gehlenite, wollastonite and perovskite.

Based on all the above results, the crystal phases formed in the crystallized fluoride-free mold fluxes samples of CaO-SiO$_2$-Al$_2$O$_3$-MgO-Na$_2$O-TiO$_2$-B$_2$O$_3$ system have been summarized in Table 3. In short, Ca$_2$Al$_2$SiO$_7$, CaTiO$_3$ and CaSiO$_3$ are the dominant crystals of the investigated TiO$_2$ and B$_2$O$_3$-bearing fluoride-free mold fluxes. Since crystals’ critical effect on horizontal heat transfer from mould to strand, the investigation on thermal resistance of slag films containing Ca$_2$Al$_2$SiO$_7$, CaTiO$_3$ and CaSiO$_3$ would be carried out in a future study.

**Table 3** Crystals precipitating from the studied fluoride-free mold fluxes with different TiO$_2$ or B$_2$O$_3$ content

| Sample Name | crystals         |
|------------|-----------------|
| No.1-0%TiO$_2$ | Ca$_2$Al$_2$SiO$_7$ CaSiO$_3$ |
| No.2-3%TiO$_2$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ CaSiO$_3$ |
| No.3-5%TiO$_2$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ CaSiO$_3$ |
| No.4-7%TiO$_2$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ CaSiO$_3$ |
| No.5-10%TiO$_2$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ CaSiO$_3$ |
| No.6-0%B$_2$O$_3$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ Ca$_2$SiO$_4$ |
| No.7-3%B$_2$O$_3$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ Ca$_2$SiO$_4$ |
| No.8-7%B$_2$O$_3$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ CaSiO$_3$ |
| No.9-10%B$_2$O$_3$ | Ca$_2$Al$_2$SiO$_7$ CaTiO$_3$ CaSiO$_3$ |

### 3.2 Crystallization Mechanism

There are limited reports on the mechanism of mold fluxes crystallization from glass (devitrification of the glassy mold fluxes) [35-37]. Generally, surface crystallization mechanism has been proposed by some researchers in the study of crystallization of glassy mold fluxes [36, 37]. Mizuno et al. [37] studied the crystallization of glassy mold fluxes using light optical microscopy and laser confocal microscopy and found that crystal grains precipitated on the surface and grew toward the center of the specimen. In this study, similar phenomenon is observed. It is observed that, after being heat-treated, the surface of the sample is opaque, but the center of the sample is nearly transparent. By SEM measurement (Figure 7), it is found that there are plenty of crystal grains near
the surface of the sample and the crystal phase is dense, while there is less columnar crystal grains in the center of the sample and the columnar crystal grains is nearly perpendicular to the surface. This is consistent with McMillan’s description about crystallization process of glass, that is, crystals grow inwards from the glass surface and quite often they are oriented at 90° to the glass surface [38]. So it is inferred that crystallization processes of the studied fluoride-free mold fluxes correspond to the surface crystallization mechanism, which is consistent with the previous investigations on crystallization of glassy mold fluxes or glass [35-38].

Figure 7. Observation of surface crystallization for the studied fluoride-free mold fluxes by SEM-BSE (the arrow indicates the crystal growth direction)

3.3 Effects of TiO₂ and B₂O₃ on Crystallization of Glassy Fluoride-free Mold Fluxes

It is known that, for a silicates slag system, the more easily of glass forming, the more stable the glass and the weaker the crystallization tendency [39]. So the crystallization tendency of the studied fluoride-free mold fluxes with changes of TiO₂ and B₂O₃ content can be examined by investigating stability of the glass from TiO₂ and B₂O₃-bearing fluoride-free mold fluxes.

Many indexes have been proposed to estimate the stability of glass, and Hruby’s method has been widely accepted [39-40]. According to Hruby et al [40], the glass forming ability index (K_{gl}) is expressed as the following equation:

\[ K_{gl} = \frac{T_x - T_g}{T_l - T_x} \] (1)

Based on the explanation of Hruby et al [40], a short interval T_x−T_g signifies that the glass contains some structural units with higher crystallization tendency, i.e., the original melt is unfavorable to the formation of glass, while a short temperature interval T_l−T_x indicates that the crystalline phase, which is formed at T_x, has relatively lower melting point, that is, the original melt has relatively low solidification temperature, i.e., it is favorable to formation of glass. Hruby suggests that T_x−T_g is directly proportional to the glass-forming tendency and T_l−T_x is indirectly proportional to the glass-forming tendency. It is reported that the bigger difference T_x−T_g and the smaller temperature interval T_l−T_x result in a greater K_{gl}, which indicates the lower tendency of crystallization and more stable for
glasses [25, 41]. According to the characteristic temperatures ($T_p$, $T_x$, and $T_l$) in Table 2, the value of $K_{gl}$ for each sample has been calculated and presented in Table 4.

Table 4 The $K_{gl}$ value for each fluoride-free mold fluxes sample with different TiO$_2$ or B$_2$O$_3$ content

| Sample Name | $K_{gl}$ |
|-------------|---------|
| No.1-0%TiO$_2$ | 0.33 |
| No.2-3%TiO$_2$ | 0.37 |
| No.3-5%TiO$_2$-5%B$_2$O$_3$ | 0.39 |
| No.4-7%TiO$_2$ | 0.42 |
| No.5-10%TiO$_2$ | 0.25 |
| No.6-0%B$_2$O$_3$ | 0.19 |
| No.7-3%B$_2$O$_3$ | 0.27 |
| No.8-7%B$_2$O$_3$ | 0.42 |
| No.9-10%B$_2$O$_3$ | 0.59 |

The relationship between $K_{gl}$ and TiO$_2$ content in Table 4 has been plotted in Figure 8. It can be found that the $K_{gl}$ values of the glassy fluoride-free mold fluxes samples increase as the content of TiO$_2$ increases from 0 to 7%, but as the content of TiO$_2$ increases to 10%, $K_{gl}$ shows an obvious decrease. That is, adding no more than 7% TiO$_2$ can weaken crystallization of the glassy fluoride-free mold fluxes, and as the addition of TiO$_2$ reaches 10%, crystallization tendency of the glassy fluoride-free mold fluxes strengthens. From the crystals formed in the slag, it can be seen that some of CaO reacts with TiO$_2$ to form CaTiO$_3$ with the addition of TiO$_2$, so the activity of CaO which participates in the formation of gehlenite and wollastonite decreases. Consequently, the crystallization of gehlenite and wollastonite weakens. In addition, wollastonite shares a pyroxene stoichiometry, and $\text{SiO}_3^{2-}$ ($Q^2$) chain is the main structure unit, which is favourable to formation of wollastonite [42]. A previous study on the same slag system by the present author has revealed that in the TiO$_2$-free sample, $Q^2$ is the dominant structure group, but increase of TiO$_2$ leads to the obvious decrease of $Q^2$ structural unit in the slag [21]. So the crystallization of wollastonite weakens. However, the crystallization of gehlenite and wollastonite are still predominant and crystallization of CaTiO$_3$ is insufficient due to the low content of TiO$_2$, so the crystallization ability of the mold fluxes is still controlled by the precipitation of gehlenite and wollastonite. Therefore, the crystallization tendency of the glassy fluoride-free mold fluxes weakens with TiO$_2$ content changing from 0 to 7%. But with the content of TiO$_2$ reaches 10%, the crystallization of CaTiO$_3$ is significantly enhanced, so the crystallization tendency of the glassy fluoride-free mold fluxes strengthens.
The relationship between $K_{gl}$ and $\text{TiO}_2$ content in Table 4 has been plotted in Figure 8. It can be found that the $K_{gl}$ values increase with the increase of $\text{B}_2\text{O}_3$ content. That is, $\text{B}_2\text{O}_3$ weakens the crystallization tendency of the glassy fluoride-free mold fluxes. On one hand, as a glass former, $\text{B}_2\text{O}_3$ can increases the glass-forming tendency of the investigated slag. On the other hand, as was mentioned previously, $\text{Ca}^{2+}$ associates with boron preferentially, and with the increase of $\text{B}_2\text{O}_3$, some of $\text{CaO}$ participates the formation of $\text{CaO}-\text{B}$ bonds preferentially. So the crystallization of gehlenite, perovskite and wollastonite are inhibited, and thereby weakening the crystallization tendency of the glassy fluoride-free mold fluxes.

In a word, with the content of $\text{TiO}_2$ increasing from 0 to 7%, the glass-forming tendency of the fluoride-free mold fluxes is enhanced, while as $\text{TiO}_2$ content reaches 10%, the crystallization tendency of the fluoride-free mold fluxes shows an increase. $\text{B}_2\text{O}_3$ weakens the crystallization tendency of the glassy fluoride-free mold fluxes.

Figure 8. Relationship between the glass forming ability index ($K_{gl}$) and TiO$_2$ content

Figure 9. Relationship between the glass forming ability index ($K_{gl}$) and $\text{B}_2\text{O}_3$ content
4. Conclusions

The crystallization characteristics of TiO$_2$ and B$_2$O$_3$-bearing fluoride-free mold fluxes have been investigated. XRD and SEM analyses showed that Ca$_2$Al$_2$SiO$_7$, CaTiO$_3$ and CaSiO$_3$ are the dominant crystals of the investigated fluoride-free mold fluxes system. Increase of TiO$_2$ can enhance the crystallization of CaTiO$_3$, and particularly, decrease of B$_2$O$_3$ can promote the formation of Ca$_2$SiO$_4$ as well as inhibit the crystallization of CaSiO$_3$. Due to inhibition effect of TiO$_2$ on crystallization of Ca$_2$Al$_2$SiO$_7$ and CaSiO$_3$, the crystallization tendency of the glassy fluoride-free mold fluxes is weakened with the content of TiO$_2$ increasing from 0 to 7%, and then strengthened as TiO$_2$ content reaches 10% because of the enhancement of CaTiO$_3$ formation. B$_2$O$_3$ weakens the crystallization tendency of the glassy fluoride-free mold fluxes. Crystallization processes of the studied fluoride-free mold fluxes correspond to the surface crystallization mechanism. This research provides important reference for further investigation on heat transfer behavior of the TiO$_2$ and B$_2$O$_3$-bearing slag between copper mould and slab to explore fluoride-free mold fluxes.

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