Crystallization Kinetics of CaO-SiO$_2$(CaO/SiO$_2$=1)-TiO$_2$-10 mass%B$_2$O$_3$ Glassy Slag by Differential Thermal Analysis

Zhen WANG, Qifeng SHU*, and Kuochih CHOU

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Haidian district, Beijing, 100083 China. 2) State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Haidian district, Chinese Academy of Sciences, Beijing, 100190 China. 3) School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Haidian district, Beijing, 100083 China.

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Crystallization characteristics of the CaO-SiO$_2$-TiO$_2$-10%B$_2$O$_3$ glassy slag at w(CaO)/w(SiO$_2$)=1 have been studied by Differential Thermal Analysis (DTA) and Matusita-Sakka method. Crystallization products have been distinguished by employing X-ray diffraction (XRD) and Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy (SEM-EDS). As the TiO$_2$ content is within 10–18%, the crystal phase precipitated is mainly CaSiO$_3$, and the effective activation energies for crystal growth increase with the increase of TiO$_2$ content. Crystallization mechanism for CaSiO$_3$ shifted from surface crystallization to one-dimensional growth with increase of TiO$_2$. As the TiO$_2$ content in slag further increases to 22% and 26%, CaTiSiO$_5$ becomes the predominant crystal phase precipitated, and the effective activation energies for crystal growth decrease with the increase of TiO$_2$ content. Crystallization mechanism for CaTiSiO$_5$ is mainly surface crystallization. Therefore, with the increase of TiO$_2$ content, the crystallization ability of the CaO-SiO$_2$-TiO$_2$-10%B$_2$O$_3$ glass system decreases initially and then increases.

KEY WORDS: fluoride-free mould fluxes; crystallization; differential thermal analysis.

1. Introduction

Mould flux has two most important functions in continuous casting of steel. It helps to lubricate to prevent sticking against the mould surface, and control the heat transfer for the achievement of uniform shell. Lubrication and heat-transfer behavior which control performances of mould fluxes between copper mould and steel shell are very sensitive to the viscosity and crystallization characteristics. The crystallization of mould fluxes reduces the horizontal heat transfer by two effects: (1) radiation thermal conductivity could be decreased by crystallites which scatter the radiation; (2) interfacial resistance between mould and solidified slag can be increased with formation of more air gaps accompanying crystallization due to the fact that the density of the crystalline phase is greater than that of the glass. Accordingly, it is essential to carry out investigations on the crystallization behaviour of slags. In addition, the solid film of mold flux can inevitably absorb some heat released from the solidification of liquid steel, consequently, producing reheating to the mold flux, which could lead to the crystallization of glassy slag film, i.e., devitrification, near wall of the copper mould, and produce strong effects on horizontal heat transfer and lubrication by critically affecting thickness of crystalline layer and surface roughness of solidified mould flux. This suggests that study on the crystallization characteristics of glassy mold fluxes is of important significance for optimal steel casting.

Due to seriously harmful influence of the fluorides in traditional mold fluxes on the natural environment and continuous casting equipment, the investigation and development of fluorine free mould fluxes have received more and more interests in recent years. Some reports have shown that B$_2$O$_3$ and/or TiO$_2$ may become most promising substitute for fluorides in traditional mould fluxes. According to some previous studies, the existence of TiO$_2$ in mould fluxes can easily lead to the formation of some crystals (e.g. CaTiO$_3$ or CaTiSiO$_5$) with high melting point, which is potential to replace the cuspidine generated by fluorine in mould fluxes and ensure the crystallization ability of slag to achieve good heat transfer performance. Besides, B$_2$O$_3$, as an effective fluxing agent to lower the melting point of mould flux, has been taken into consideration for being added to mould fluxes to adjust the viscosity or melting properties of slag. Accordingly, it is important to investigate the properties of slag containing B$_2$O$_3$ and/or TiO$_2$ for the development of optimal fluorine free mould fluxes.

CaO–SiO$_2$ slag is the basic system in most of the metallurgical slags. Thus, in our work, the CaO–B$_2$O$_3$–SiO$_2$–TiO$_2$ system is selected as the basic system for the further development of fluorine free mould fluxes. To the best of our knowledge, there are only limited investigations on the physio-chemical properties of the CaO–B$_2$O$_3$–SiO$_2$–TiO$_2$ system. Thus, in the present work, the method of differential thermal analyses (DTA) has been...
employed to carry out the study of crystallization kinetics of the CaO–B2O3–SiO2–TiO2 system. The DTA measurements with various heating rates are carried out to investigate non-isothermal crystallization kinetics of the CaO–B2O3–SiO2–TiO2 system in glass state. The non-isothermal kinetics data was dealt with a wide employed methods named Matusita-Sakka model, which would be described in detail in the subsequent part of this paper. Through analyzing the characters of the crystallization kinetic parameters, the crystallization behaviour of CaO–B2O3–SiO2–TiO2 system can be understood, which can provide reliable reference for the research of physical-chemical properties of B2O3 and TiO2-bearing fluorine free mould fluxes.

2. Experimental

2.1. Sample Preparation

Analytical grade CaCO3, SiO2, TiO2 and H3BO3 were taken as raw materials, with H3BO3 being substitutes for B2O3. CaO was obtained by calcination of CaCO3 in the air at approximately 1 273 K for 12 hours, and then it was detected by X-Ray diffraction (XRD) analysis to identify the 100% completion of decomposition reaction. Table 1 presents the chemical compositions (wt.% of the glass samples investigated.

Glass samples with different compositions were prepared by the conventional melting and quenching method. Raw materials were mixed, taken into a platinum crucible and then melted in high temperature furnace at approximately 1 623 K in air atmosphere. The samples were held at 1 623 K for nearly 2 h 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 as shown in Fig. 1. B2O3 contents in glassy slags were measured by dissolving glass in hydrochloric and hydrofluoric acid mixture and determining concentration of boron ions using ICP-AES (OPTIMA 7000DV, Perkin Elmer). Analyzed B2O3 contents in slags were shown in Table 1. It could be seen from the table that there are only slight differences between nominal B2O3 contents and analyzed B2O3 contents, indicating that the evaporation during melting is negligible.

2.2. Differential Thermal Analysis

The glass samples were pulverized into powder (150–200 mesh) for DTA measurement. Differential thermal analysis was performed on each of the glass powder samples in a platinum crucible using Netzsch STA 449C TG-DTA calorimeter at different heating rates, 5 K/min, 10 K/min, 20 K/min and 30 K/min respectively. During the whole measurement process, Argon was used as a protecting gas. Al2O3 was used as a reference material. Temperature calibration and enthalpy calibration were performed before DTA measurements using high purity metals of In, Bi, Zn, Al and Au with known melting points and enthalpies. Enthalpy calibration for DTA was performed in sensitivity calibration of instruments by employing the melting enthalpy of In, Bi, Zn, Al and Au. The measured area underneath melting peak was compared with enthalpy value of melting, and then sensitivity values could be obtained.

2.3. X-ray Diffraction Analysis

The powdered glass samples were heated in a Pt-crucible, held for approximately 8 hours at each exothermic peak temperature and then quenched by air. In order to identify the products of crystallization, each of the heat treated samples was subjected to XRD analysis which was performed using a MAC M21XRHF22 (21KW) X-ray diffractometer with Cu Ka radiation.

2.4. Microstructural of Crystal Phases

The bulk glass samples were heated in a Pt-crucible, held for approximately 8 hours at each exothermic peak temperature and then quenched by air. Then these heat treated samples were embedded with resin, ground with fine sandpaper and polished with polishing paste respectively. The surfaces of each sample were experienced carbon spray coating. After that, the samples were subjected to scanning electron microscope (SEM) examinations using ZEISS EVO MA18 to investigate the microstructure of the crystallization products. The working voltage was 20 kV.

3. Results and Discussion

Figure 2 shows the results of DTA measurements at different heating rates for glass samples with different TiO2 content. As could be seen in Fig. 2, a strong exothermic peak could be found between 800°C and 1 000°C in each DTA curve, and the peak temperature increases with increase of heating rate. The strong exothermic peaks between 800°C and 1 000°C were attributed to crystallization of glassy slag. Figure 3 exhibits the XRD analysis

Table 1. Chemical composition (wt.%) of the glass samples studied in present work.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Chemical compositions</th>
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<tr>
<td></td>
<td>CaO</td>
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<tr>
<td>1</td>
<td>40</td>
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<tr>
<td>2</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>36</td>
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<td>4</td>
<td>34</td>
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<td>5</td>
<td>32</td>
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</table>

Fig. 1. XRD pattern of the quenched samples with different contents of TiO2 in CaO-SiO2-TiO2-10%B2O3 system.
Fig. 2. Continued.
results for the CaO-SiO$_2$-TiO$_2$-10%B$_2$O$_3$ glass samples of different TiO$_2$ contents heat treated at peak temperature determined by DTA curves (10 K/min). The SEM micrographs for the CaO-SiO$_2$-TiO$_2$-10%B$_2$O$_3$ glass samples of different TiO$_2$ contents with R=1.0 are shown in Fig. 4.

### 3.1. Identification of the Crystal Phases

It can be seen in Fig. 3 that, for the samples with R=1.0, as the content of TiO$_2$ being in the range of 10–18%, the crystal phases of the system are titanite (CaTiSiO$_5$) and wollastonite (CaSiO$_3$), and with the TiO$_2$ content increasing to
18%, the XRD intensity of CaSiO3 becomes weak obviously, with CaTiSiO5 being the predominant crystallization product of the system. As the content of TiO2 increases to 22% and 26%, there is no CaSiO3 crystal, and CaTiSiO5 becomes the only crystallization product. As can be seen from Fig. 4, SEM results agree well with the XRD results. Dark grey crystal determined as CaSiO3 by EDS and light grey crystal as CaTiSiO5 could be found in samples with TiO2 content less than 18%, whereas only light grey crystal could be found in samples with TiO2 more than 18%. Thus, combined the XRD and SEM analysis results, it can be concluded that, as the TiO2 content within 10–18%, there are two crystal phases CaTiSiO5 and CaSiO3 in the chosen system, and with the increase of TiO2 content, the crystallization of CaSiO3 becomes weak, while the crystallization of CaTiSiO5 is enhanced so as to become the only crystal phase when the TiO2 content increases to 22% and 26%.

Since there is no phase diagram reported on CaO–TiO2–SiO2–B2O3 system, phase diagram of CaO–TiO2–SiO2 system17) shown in Fig. 5 was employed to interpret the crystal phase formation. It could be seen from Figure that CaSiO3 precipitates as primary crystal for samples with low TiO2 content, and CaTiSiO5 precipitates instead at higher TiO2 content. Therefore, at low TiO2 content, thermodynamic condition is favorable to crystallization of CaSiO3, whereas only light grey crystal could be found in samples with TiO2 more than 18%. Thus, combined the XRD and SEM analysis results, it can be concluded that, as the TiO2 content within 10–18%, there are two crystal phases CaTiSiO5 and CaSiO3 in the chosen system, and with the increase of TiO2 content, the crystallization of CaSiO3 becomes weak, while the crystallization of CaTiSiO5 is enhanced so as to become the only crystal phase when the TiO2 content increases to 22% and 26%.

Thus, the predicted crystalline phases precipitated by XRD and SEM-EDS analysis agree with phases determined by XRD and SEM-EDS analysis.

As seen in Fig. 2, only single crystallization peak could be found in DTA curves for all samples. It could be due to unfavorable conditions for precipitation of the second crystal in DTA measurement. Therefore, it is proposed that CaSiO3 precipitates in samples with TiO2 content lower than 22% and CaTiSiO5 precipitates in samples with TiO2 higher than 22% during DTA measurements.

3.2. Crystallization Kinetics

3.2.1. Theoretical Basis

For isothermal crystallization, the classical Johnson-Mehl-Avrami (JMA) model has been intensively applied to describe the relationship between experimentally determined crystallized fraction ($\alpha$), and time, t, as follows:18–21)

$$\alpha(t) = 1 - \exp\left(-kt^n\right) \quad \text{........................ (1)}$$

Where $\alpha$ is the volume fraction of crystals crystallized at a given temperature at time t, n is the Avrami exponent, and k is the effective (overall) reaction rate constant, which obeys an Arrhenius expression for the absolute temperature and can be given by:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad \text{........................ (2)}$$

Where $k_0$ is the frequency factor, R is the universal gas constant, and T is the absolute temperature and $E$ is the effective (apparent) activation energy representing the kinetic barrier for crystallization and describing the overall crystallization process.

The JMA equation has been widely applied to the isothermal crystallization of inorganic glasses, bulk metal glasses and mould fluxes.22–24) The increasing use of differential thermal analysis (DTA) or differential scanning calorimetry (DSC) at non-isothermal mode has, however, required reliable methods to deal with non-isothermal kinetics. Many researchers have proposed some methods on non-isothermal crystallization kinetics.25–28) One of these methods is the well-known Matusita-Sakka model. Matusita and co-workers29–31) emphasized that the crystallization mechanism, such as bulk crystallization or surface crystallization, should be taken into consideration for acquiring the meaningful activation energy. They have proposed that if a glass is heated at an invariable heating rate, the nucleation process occurs at temperatures somewhat higher than the glass transition temperature and reaches the maximum nucleation rate, so crystal nuclei no longer increases in number during the crystal growth (forming the DTA peak) and the activation energies for crystal growth can be estimated by analyzing the DTA crystallization peak.26,29–31) Main equation that they derived is as follows:

$$\ln(-\ln(1-\alpha)) = -n \ln \beta - 1.052 \frac{mE}{RT} + \text{const} \quad \text{........ (3)}$$

Where $\beta$ is the heating rate of crystallization process; $E_0$ is the effective activation energies for crystal growth; n and m are constants, depending on the crystallization mechanism; n, m values are different for crystallization of well nucleated glass and as-quenched glass. if a large number of existing nuclei in the glass, i.e. for a crystallization of well nucleated sample, nuclei does not increase further, n=m; on the other hand, for crystallization of as-quenched glass, nucleation proceeds with constant rate, n=m+1.25,32–36)

Table

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Fig. 5. Phase diagram of CaO–TiO2–SiO2 system.
2 lists the values of n and m and associated crystallization mechanisms. Samples investigated at the present work were not heat treated between quenching and crystallization experiments and should belong to group of as-quenched glass.

In Eq. (3), \( mE_G/R \) can be determined by the Šatava method using a single DTA curve at single heating rate:

\[
\frac{d(\ln(-\ln(1-\alpha)))}{d\left(\frac{1}{T}\right)} \bigg|_{T} = -1.052 \frac{mE_G}{R} \ \\
\]

\( mE_G/n \) could be determined by modified Ozawa-Chen method using multiple DTA curves:

\[
\frac{d(\ln \beta)}{d\left(\frac{1}{T}\right)} \bigg|_{T} = 1.052 \frac{mE_G}{n \ R} \ \\
\]

\( \ln \beta \) could be plotted as a linear function of reciprocal of temperature at the same crystallization fraction for different curves.

3.2.2. Crystallization Kinetics of the CaO-SiO2-TiO2-10 mass% B2O3 Glass System

In terms of the method shown in Fig. 6, for each sample, the volume fraction of crystals crystallized at a given temperature, \( \alpha \), was calculated at different heating rates. According to the modified Ozawa-Chen method (Eq. (5)), curves of (\( \ln \beta \)) vs. (1000/T) were plotted at different given values of \( \alpha \) to determine the values of \( mE_G/n \). Figure 7 shows the plots of \( \ln \beta \) vs. (1000/T) for samples of different TiO2 contents. Then, Šatava method (Eq. (4)) was applied to calculate the values of \( mE_G \) by plotting \( -\ln[-\ln(1-\alpha)] \) vs. (1000/T) with the heating rates at 5 K/min. The plots of \( \ln[-\ln(1-\alpha)] \) vs. (1000/T) for samples of different TiO2 contents are exhibited in Fig. 8. Dividing of the values of \( mE_G \) obtained by Šatava method by the average values of \( mE_G/n \) obtained by Ozawa-Chen method provides the values of n. Based on the relationship of m and n in Table 2, m can be determined, and then the crystallization mechanism of the slag system as well as the activation energies for crystal growth \( E_G \) can be obtained. Table 3 presents crystalline phases and values of n, m, \( mE_G \) and \( E_G \) for each sample.

According to the values of n and m extracted from kinetic analysis in Table 3, we can get a general idea about the crystallization mechanisms of the present CaO-SiO2-TiO2-10 mass% B2O3 glass systems. It can be inferred that, when the content of TiO2 is low (10% and 14%), the crystallization mechanism of the present glass system is mainly surface crystallization, when the content of TiO2 is 18%, the crystallization mechanism of the present glass system is one-dimensional growth mechanism, and when the content of TiO2 increases to 22% and 26%, the crystallization mechanism of the present glass system is mainly surface crystallization.

Values of \( E_G \) can reflect the crystallization ability of the investigated glass system. Effects of TiO2 content on the crystallization performance of the glass system can be inferred from the values of \( E_G \). Based on the data in Table 3, the relationship with \( E_G \) and TiO2 content has been shown in Fig. 9. According to Fig. 9, it can be concluded that, with the increase of TiO2 content, the values of \( E_G \) for the CaO-SiO2-TiO2-10%B2O3 glass system increase initially and then decrease. When the TiO2 content is about 18%, the values of \( E_G \) reach a maximum, and further increase of TiO2 content leads to the decrease of \( E_G \).

The maximum values of \( E_G \) could be also related to change of crystal phases with the increase of TiO2 content. As the content of TiO2 within 10–18%, CaSiO3 is generally the primary crystal phase, so the crystallization ability of the glass system is mainly affected by the crystallization of CaSiO3. The decrease of crystallization ability of samples with increase of TiO2 content could be interpreted by thermodynamic and structural information of system. Firstly, the velocity of crystal growth depends on the thermodynamic driving force of crystallization. According to phase diagram of CaO–TiO2–SiO2 system shown in Fig. 5, the addition of TiO2 would decrease the liquidus temperature of slags, which leads to decrease of supercooling of slags. Thus, the thermodynamic driving force decreases and crystallization is retarded. On the other hand, from viewpoint of structure, the slag would tend to precipitate crystal which has similar structure as slag. The chain silicate structure unit...

![Fig. 6. Estimation of the volume fraction of crystals, \( \alpha \), \( T_x \), and \( T_1 \) are the onset temperature and end temperature of exothermic peak, respectively; A is the total area of crystallization exothermal peak; \( A_x \) is partial area at the temperature of T. And \( \alpha \) is the ratio of \( A_x/A \).](image-url)
(Q2) is the main component to build structure of CaSiO3. A Raman spectra study on the CaO–SiO2–TiO2–B2O3 glass system has shown that, with the increase of TiO2 content, the proportion of Q2 structure unit in structure of glass decreases in the system. Then, the increase of TiO2 produces negative effects on the Q2 structure unit in glassy slag, and therefore formation of CaSiO3 is retarded. As the content of TiO2 increases to 22% and 26%, CaTiSiO5 is the predominant crystal phase, so crystallization ability of the glass system is reflected by the crystallization of CaTiSiO5. The increase of TiO2 content would lead to increase of activity of TiO2 in slag. Since TiO2 is main component of CaTiSiO5 phase, thermodynamics driving force

![Fig. 7. ln β vs. 1/T for glass samples of different TiO2 content to determine the values of mE0/n, according to the Ozawa-Chen method.](image)

![Fig. 8. ln[-ln(1-α)] vs. 1/T at heating rate of β=10 K/min for glass samples of different TiO2 content, to determine the values of mE0 according to the Šatava method.](image)

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<tr>
<th>Table 3. Crystal phases and crystallization kinetics parameters of the CaO-SiO2-TiO2-10%B2O3 glass system.</th>
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<tbody>
<tr>
<td>samples</td>
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<tr>
<td>TiO2-10%</td>
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<tr>
<td>TiO2-14%</td>
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<td>TiO2-18%</td>
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<tr>
<td>TiO2-22%</td>
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<td>TiO2-26%</td>
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for CaTiSiO$_5$ precipitation is increased with increase of TiO$_2$ content. Thus, when CaTiSiO$_5$ becomes the main crystal phase, $E_G$ decreases and the crystallization ability of the glass system has an increase.

Combining the microstructure and phase analysis with kinetic analysis, we could get some preliminary ideas for optimizing the TiO$_2$ content for development of fluoride free mould fluxes. It was observed in microstructure and phase analysis that two kinds of crystals as CaSiO$_3$ and CaTiSiO$_5$ could precipitate during heating of glassy slag with TiO$_2$ content lower than 18%, whereas only one kind of crystal as CaTiSiO$_5$ could precipitate in sample with higher TiO$_2$ content. The fracturing of solid film of mould fluxes has a detrimental effect on continuous casting process, and could even cause the sticking of steel. Improvement of strength of solid slag film could decrease the risk of fracturing. Compared to solid slag film with several kinds of crystal precipitation, solid slag film with single kind of crystal precipitation have larger strength, therefore could be better for continuous casting practice. On the other hand, casting of some kinds of steel (e.g. peritectic steel) requires mild cooling, which could be provided by solid mould fluxes layer and then decrease with increase of TiO$_2$ content lower than 18%, whereas only one kind of crystal as CaTiSiO$_5$ could precipitate during heating of glassy slag with TiO$_2$ content. Thus, when CaTiSiO$_5$ becomes the main crystal phase, $E_G$ decreases and the crystallization ability of the glass system has an increase.

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4. Conclusions

Crystallization characteristics of the CaO-SiO$_2$-TiO$_2$-10%B$_2$O$_3$ glassy slag have been studied by non-isothermal heating DTA. Crystals precipitated in glassy slag have been identified by XRD and SEM-EDS. Matusita-Sakka method has been successfully applied to the investigation on crystallization kinetics of the chosen system. Following conclusions could be drawn:

As the TiO$_2$ content is within 10–18%, crystal phases precipitated in the CaO-SiO$_2$(CaO/SiO$_2$=1)-TiO$_2$-10%B$_2$O$_3$ glassy slag are CaTiSiO$_5$ and CaSiO$_3$. With further increase of TiO$_2$ content to 22% and 26%, only CaTiSiO$_5$ crystals precipitate in the glassy slag.

The activation energy for crystal growth increases first and then decrease with increase of TiO$_2$ content in slags, indicating that crystallization ability of the CaO-SiO$_2$(CaO/SiO$_2$=1)-TiO$_2$-10%B$_2$O$_3$ glass slag decreases initially and then increases with the increase of TiO$_2$ content.

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REFERENCES