Crystallization Kinetics of CaO-SiO₂(CaO/SiO₂=1)-TiO₂-10 mass%B₂O₃ Glassy Slag by Differential Thermal Analysis

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Crystallization characteristics of the CaO-SiO₂-TiO₂-10%B₂O₃ glassy slag at w(CaO)/w(SiO₂)=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 TiO₂ content is within 10–18%, the crystal phase precipitated is mainly CaSiO₃, and the effective activation energies for crystal growth increase with the increase of TiO₂ content. Crystallization mechanism for CaSiO₃ shifted from surface crystallization to one-dimensional growth with increase of TiO₂. As the TiO₂ content in slag further increases to 22% and 26%, CaTiSiO₅ becomes the predominant crystal phase precipitated, and the effective activation energies for crystal growth decrease with the increase of TiO₂ content. Crystallization mechanism for CaTiSiO₅ is mainly surface crystallization. Therefore, with the increase of TiO₂ content, the crystallization ability of the CaO-SiO₂-TiO₂-10%B₂O₃ 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.^{3,6,8,10–14)} 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.^{1–9)} 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;¹²⁾ (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.⁸⁾ 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,^{15,16)} 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.^{1–4)} Some reports have shown that B₂O₃ and/or TiO₂ may become most promising substitute for fluorides in traditional mould fluxes.^{1–7)} According to some previous studies,^{1,3,6,7)} the existence of TiO₂ in mould fluxes can easily lead to the formation of some crystals (*e.g.* CaTiO₃ or CaTiSiO₅) 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, B₂O₃, 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.^{2,4,5)} Accordingly, it is important to investigate the properties of slag containing B₂O₃ and/or TiO₂ for the development of optimal fluorine free mould fluxes.

CaO-SiO₂ slag is the basic system in most of the metallurgical slags. Thus, in our work, the CaO-B₂O₃-SiO₂-TiO₂ system is selected as the basic system for the further development of fluorine free mould fluxes bearing some other oxides. To the best of our knowledge, there are only limited investigations on the physio-chemical properties of the CaO-B₂O₃-SiO₂-TiO₂ system. Thus, in the present work, the method of differential thermal analyses (DTA) has been

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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 1273 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 1623 K in air atmosphere. The samples were held at 1623 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 M21XRF22 (21KW) X-ray diffractometer with Cu K α 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 1000°C in each DTA curve, and the peak temperature increases with increase of heating rate. The strong exothermic peaks between 800°C and 1000°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.

Sample number	Chemical compositions				
	CaO	SiO ₂	B ₂ O ₃	TiO ₂	B ₂ O ₃ (analyzed)
1	40	40	10	10	11.342
2	38	38	10	14	11.2
3	36	36	10	18	10.16
4	34	34	10	22	10.411
5	32	32	10	26	10.414

Fig. 1. XRD pattern of the quenched samples with different contents of TiO₂ in CaO–SiO₂–TiO₂–10%B₂O₃ system.

Fig. 2. Continued.

Fig. 2. Results of DTA measurements for glass samples with $R=1.0$ at different heating rates.

Fig. 3. XRD phase identification for the glass samples of different TiO_2 content.

results for the $\text{CaO-SiO}_2\text{-TiO}_2\text{-10%B}_2\text{O}_3$ glass samples of different TiO_2 contents heat treated at peak temperature determined by DTA curves (10 K/min). The SEM micrographs for the $\text{CaO-SiO}_2\text{-TiO}_2\text{-10%B}_2\text{O}_3$ 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

Fig. 4. SEM phase identification for the glass samples of different TiO_2 content, (a) 10%- TiO_2 , (b) 14%- TiO_2 , (c) 18%- TiO_2 , (d) 22%- TiO_2 , (e) 26%- TiO_2 and 1 represents CaTiSiO_5 phase, 2 represents CaSiO_3 phase.

18%, the XRD intensity of CaSiO_3 becomes weak obviously, with CaTiSiO_5 being the predominant crystallization product of the system. As the content of TiO_2 increases to 22% and 26%, there is no CaSiO_3 crystal, and CaTiSiO_5 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 CaSiO_3 by EDS and light grey crystal as CaTiSiO_5 could be found in samples with TiO_2 content less than 18%, whereas only light grey crystal could be found in samples with TiO_2 more than 18%. Thus, combined the XRD and SEM analysis results, it can be concluded that, as the TiO_2 content within 10–18%, there are two crystal phases CaTiSiO_5 and CaSiO_3 in the chosen system, and with the increase of TiO_2 content, the crystallization of CaSiO_3 becomes weak, while the crystallization of CaTiSiO_5 is enhanced so as to become the only crystal phase when the TiO_2 content increases to 22% and 26%.

Since there is no phase diagram reported on $\text{CaO-TiO}_2\text{-SiO}_2\text{-B}_2\text{O}_3$ system, phase diagram of $\text{CaO-TiO}_2\text{-SiO}_2$ system¹⁷⁾ shown in Fig. 5 was employed to interpret the crystal phase formation. It could be seen from Figure that CaSiO_3 precipitates as primary crystal for samples with low TiO_2 content, and CaTiSiO_5 precipitates instead at higher TiO_2 content. Therefore, at low TiO_2 content, thermodynamic condition is favorable to crystallization of CaSiO_3 . At higher TiO_2 content, CaTiSiO_5 is more likely to crystallize than CaSiO_3 due to more favorable thermodynamic condition. According to XRD and SEM-EDS analysis, CaSiO_3 and CaTiSiO_5 were determined to be crystalline phases precipitated at low TiO_2 content. CaSiO_3 could be primary crystalline phase and CaTiSiO_5 could precipitate secondly. At higher TiO_2 content, CaTiSiO_5 were determined to be sole crystalline phases precipitated by XRD and SEM-EDS. Thus, the predicted crystalline phases by thermodynamic phase diagram 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 CaSiO_3 precipitates in samples with TiO_2 content lower than 22% and CaTiSiO_5 precipitates in samples with TiO_2 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 (α), and time, t , as follows:^{18–21)}

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

Where α is the volume fraction of crystals crystallized at a given temperature at time t , n is the Avrami exponent, depending on the mechanism of growth and dimensionality of the crystal. 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-workers^{29–31)} 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 a 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 β is the heating rate of crystallization process; E_G 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, $n=m+1$.^{22,32–36)} Table

Fig. 5. Phase diagram of $\text{CaO-TiO}_2\text{-SiO}_2$ 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.³⁷⁾

$$\frac{d(\ln[-\ln(1-\alpha)])}{d\left(\frac{1}{T}\right)} \Big|_{\beta} = -1.052 \frac{mE_G}{R} \quad \dots\dots\dots (4)$$

mE_G/n could be determined by modified Ozawa-Chen method using multiple DTA curves:^{38,39)}

$$\frac{d(\ln \beta)}{d\left(\frac{1}{T}\right)} \Big|_{\alpha} = 1.052 \frac{m}{n} \frac{E_G}{R} \quad \dots\dots\dots (5)$$

$\ln \beta$ 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, α , 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 α to determine the values of mE_G/n . Figure 7 shows the plots of $\ln \beta \sim 1000/T$ 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 $\ln[-\ln(1-\alpha)] \sim 1000/T$ 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.

Table 2. Values of n and m for different crystallization mechanisms.

Crystallization mechanism	n	m
<i>Bulk crystallization with a constant number of nuclei (i.e., a well nucleated sample with the number of nuclei being independent of the heating rate)</i>		
Three-dimensional growth	3	3
Two-dimensional growth	2	2
One-dimensional growth	1	1
<i>Bulk crystallization with an increasing number of nuclei (i.e., the number of nuclei is inversely proportional to the heating rate)</i>		
Three-dimensional growth	4	3
Two-dimensional growth	3	2
One-dimensional growth	2	1
Surface crystallization	1	1

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.⁴⁰⁾ 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, α . T_x and T_l are the onset temperature and end temperature of exothermic peak, respectively; A is the total area of crystallization exothermal peak; A_T is partial area at the temperature of T . And α is the ratio of A_T/A .

Fig. 7. $\ln \beta$ vs. $1/T$ for glass samples of different TiO_2 content to determine the values of mE_G/n , according to the Ozawa-Chen method.

Fig. 8. $\ln[-\ln(1-\alpha)]$ vs. $1/T$ at heating rate of $\beta=10$ K/min for glass samples of different TiO_2 content, to determine the values of mE_G according to the Šatava method.

Table 3. Crystal phases and crystallization kinetics parameters of the $\text{CaO-SiO}_2\text{-TiO}_2\text{-10%B}_2\text{O}_3$ glass system.

	samples	n	m	mE_G	E_G	Crystal phases
1	$\text{TiO}_2\text{-10\%}$	1.47	1	508.23	508.23	$\text{CaSiO}_3(\text{CaTiSiO}_5)$
2	$\text{TiO}_2\text{-14\%}$	1.66	1	645.57	645.57	$\text{CaSiO}_3(\text{CaTiSiO}_5)$
3	$\text{TiO}_2\text{-18\%}$	1.94	1	704.79	704.79	$\text{CaSiO}_3(\text{CaTiSiO}_5)$
4	$\text{TiO}_2\text{-22\%}$	1.53	1	569.38	569.38	CaTiSiO_5
5	$\text{TiO}_2\text{-26\%}$	1.46	1	507.91	507.91	CaTiSiO_5

the proportion of Q_2 structure unit in structure of glass decreases in the system.⁴¹⁾ Then, the increase of TiO_2 produces negative effects on the Q_2 structure unit in glassy slag, and therefore formation of CaSiO_3 is retarded.

As the content of TiO_2 increases to 22% and 26%, CaTiSiO_5 is the predominant crystal phase, so crystallization ability of the glass system is reflected by the crystallization of CaTiSiO_5 . The increase of TiO_2 content would lead to increase of activity of TiO_2 in slag. Since TiO_2 is main component of CaTiSiO_5 phase, thermodynamics driving force

(Q_2) is the main component to build structure of CaSiO_3 . A Raman spectra study on the $\text{CaO-SiO}_2\text{-TiO}_2\text{-B}_2\text{O}_3$ glass system has shown that, with the increase of TiO_2 content,

Fig. 9. Relationship between E_G and TiO_2 content for the CaO-SiO₂-TiO₂-10%B₂O₃ glass system.

for CaTiSiO₅ precipitation is increased with increase of TiO₂ content. Thus, when CaTiSiO₅ 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 TiO₂ content for development of fluoride free mould fluxes. It was observed in microstructure and phase analysis that two kinds of crystals as CaSiO₃ and CaSiTiO₅ could precipitate during heating of glassy slag with TiO₂ content lower than 18%, whereas only one kind of crystal as CaSiTiO₅ could precipitate in sample with higher TiO₂ 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 with highly crystallization. According to the present kinetic analysis, crystallization rates decreases first, then increase with increase of TiO₂ content. To maintain fast crystallization and one kind crystal precipitation, mould flux with 26% TiO₂ content is the best choice. Therefore, we suggest that the larger addition of TiO₂ (as large as 26%) could be suitable to get a solid layer with larger crystallinity and good strength.

4. Conclusions

Crystallization characteristics of the CaO-SiO₂-TiO₂-10%B₂O₃ 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 TiO₂ content is within 10–18%, crystal phases precipitated in the CaO-SiO₂(CaO/SiO₂=1)-TiO₂-10%B₂O₃

glassy slag are CaTiSiO₅ and CaSiO₃. With further increase of TiO₂ content to 22% and 26%, only CaTiSiO₅ crystals precipitate in the glassy slag.

The activation energy for crystal growth increases first and then decrease with increase of TiO₂ content in slags, indicating that crystallization ability of the CaO-SiO₂(CaO/SiO₂=1)-TiO₂-10%B₂O₃ glass slag decreases initially and then increases with the increase of TiO₂ content.

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