Growth Mechanism and Structure Evolution during Nucleation of Calcium Borosilicate Crystal in CaO–SiO₂–B₂O₃ Based Fluorine-free Mold Flux

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(Received on August 15, 2018; accepted on December 28, 2018)

Growth mechanism and structure evolution during nucleation of Calcium borosilicate (Ca₁₁Si₄B₂O₂₂) crystal in CaO–SiO₂–B₂O₃ based fluorine-free (F-free) mold flux have been investigated in this article. The results suggested that during nucleation, the existed free oxygen ions tend to depolymerize Si–O–B units and break down borosilicate structure. Then, the transformation between [BO₄]-tetrahedral and [BO₃]-triangular would further depolymerize borosilicate structure. Next, the decomposed borosilicate will connect with the formed Q²(Si) and the existed dissociative Q¹(Si), and finally form a long-range ordered borosilicate structure with a certain symmetry. Finally, Ca²⁺ ions would associate with the borosilicate structure to form Calcium borosilicate crystal nucleus. With the formation of the crystal nucleus, the crystals first precipitated at the boundary of the thermocouple and exhibited grain-shape particles orientated in a line dispersively. Then, the grain-shape crystals at the boundary became thicker and formed dendrite structure. Subsequently, the secondary dendrites were observed to form and grew on the primary dendrites axis. Ultimately, Calcium borosilicate crystals were well distributed. The precipitated crystal phase of the F-free mold flux was β -polymorphs Calcium borosilicate. The kinetics of the isothermal crystallization at 1373 K is constant number of nuclei, 3-dimensional growth by diffusion control.

KEY WORDS: mold flux; crystallization; calcium borosilicate; melt structure.

1. Introduction

Mold flux plays many significant roles during the process of continuous casting, in which the heat transfer ability of mold flux directly determines the surface defects of as-cast slabs. The precipitated Cuspidine (Ca₄Si₂O₇F₂) crystal phase in conventional mold flux is a very vital crystal phase to effectively control the heat transfer between the mold and solidified shell,^{1,2)} as it can resist the in-mold ferrostatic pressure and produce air gaps between the mold and initial solidified shell to increase the interfacial thermal resistance. In order to ensure the precipitation of Cuspidine crystal phase, a certain amount of fluorine need to be added to the mold flux. However, fluorine tends to volatilize when the mold flux is added to the mold and get in contact with high temperature molten steel, which will introduce a series of problems of environmental pollution and casting machine corrosion, etc.^{3–6)} Therefore, it is necessary to develop low-fluorine or fluorine-free (F-free) mold flux and find a substitute crystal phase of Cuspidine therein.

Recently, Wei *et al.*⁷⁾ developed a new low-fluorine mold flux by adding B₂O₃, Na₂O, Li₂O and optimizing a suitable basicity (mass ratio of CaO/SiO₂); their research reported that the crystallization behavior of Calcium borosilicate

(Ca₁₁Si₄B₂O₂₂) in low-fluorine mold flux is very similar to Cuspidine. Subsequently, research of Zhou *et al.*^{8,9)} also reported that a F-free mold flux system has been successfully developed based on the previous study of Wei *et al.*, in which the heat transfer and crystallization behaviors of the designed mold flux system is very similar to a conventional mold flux. The X-ray diffraction (XRD) analysis of their research has claimed that the main crystal phase of the designed F-free mold flux is Calcium borosilicate, and they concluded that Calcium borosilicate has the potential to replace Cuspidine to be used for controlling the heat transfer behavior in the mold.

However, for the crystal phase of calcium borosilicate, the first time to report it is in 1971 by Suzuki *et al.*,¹⁰⁾ and there is only little research available in the current ceramic material research field.^{11,12)} With the report of Calcium borosilicate in the study of low fluorine and F-free mold flux, it obtains more and more attentions recently. Although most studies regarding to the low-fluorine and F-free mold fluxes have proved that Calcium borosilicate is the main crystalline phase precipitated in the mold flux,^{7–9,13–17)} there is still no any report regarding to the formation and growth mechanism of this crystal. Therefore, the detailed crystallization process of Calcium borosilicate phase in the designed F-free mold flux would be conducted in this article, due to the significant importance of this phase for the replacement of Cuspidine.

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DOI: <https://doi.org/10.2355/isijinternational.ISIJINT-2018-560>

2. Experimental Apparatus and Method

2.1. Samples Preparation

Based on previous study,^{8,9,18)} the major composition of the designed mold flux that shows the best comprehensive performances to replace fluorine is listed in **Table 1**. First, the raw materials were prepared with the reagent grade chemicals of CaO, SiO₂, B₂O₃, etc. according to the designed percentage. Then they were fully mixed, and heated to 1 773 K for 5 mins in an induction furnace to homogenize their compositions. Subsequently, the molten slag was quickly poured onto a water-cooled copper plate to quench for achieving a fully glassy phase. Finally, the glassy sample was dried and ground into powder samples for the following Single Hot Thermocouple Technology (SHTT) tests.

2.2. Experimental Process

The in-situ observation of the Calcium borosilicate precipitation process in the molten slag was studied by using SHTT in this article. The schematics of hot thermocouple technology are given in **Fig. 1(a)**.^{19,20)} In this experiment,

Table 1. The chemical component of the experimental sample.

Component	CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	B ₂ O ₃	Li ₂ O	MgO
Contents/Wt%	41.72	36.28	4	8	6	2	2

Fig. 1. (a) The schematic of hot thermocouple technology; (b) The thermal profile for the experiment. (Online version in color.)

the powder sample was firstly mounted on a B-type thermocouple, and then it was heated to 1 773 K at the heating rate of 15 K/s for melting. After holding for 5 minutes, the thermocouple was quenched to 1 373 K with a cooling rate of 40 K/s by control the hot thermocouple drive, at which the calcium borosilicate is easy to precipitate without other crystals.⁷⁾ When the crystallization process is holding for 600 s to get the completion of crystallization, the sample was quenched by turn off the power and moved out from the B-type thermocouple for further analysis. The thermal profile was shown in **Fig. 1(b)**. And the whole process was simultaneously recorded through the CCD camera connecting with a high temperature optical microscope.

The snapshots of crystallization process could be obtained by analyzing the video of the isothermal crystallization at 1 373 K and it was shown in **Fig. 2**. It could be found that the complete crystallization time was about 70 s, and the incubation time was about 30 s. To certify the precipitated crystal phase is single Calcium borosilicate crystal in the slag sample, the sample was analyzed by X-ray Diffraction (XRD) test (D8 discover; Bruker AXS GmbH, Karlsruhe, Germany). The result was shown in **Fig. 3**, where the pattern of XRD peaks was identified as Calcium borosilicate according to JCPDS (Joint Committee on Powder Diffraction Standards) card No. 48-0953. It also could be found from the XRD results that the cell parameters of Calcium borosilicate crystal are $a=2.861$ nm, $b=1.5974$ nm, $c=0.6874$ nm, $\alpha=\beta=90^\circ$, $\gamma=104.1^\circ$, and it is monoclinic belonging to β -polymorphs.¹⁰⁾

2.3. Kinetics Study of the Crystallization Process

The kinetics of isothermal crystallization are usually related to nucleation and growth mechanism; therefore, the Johnson-Mehl-Avrami (JMA) model has been applied in this study.^{21,22)} and it is shown as following:

$$X = 1 - \exp \left\{ -[k(t - \tau)]^n \right\} \dots \dots \dots (1)$$

where X is the volume fraction of crystals, k is the constant of effective crystallization rate, t is the crystallization time, τ is the incubation time, and n is the Avrami exponent related to the nucleation and growth mechanism.

In this study, the incubation time (τ) is defined as the time of the crystalline fraction of 5% and it is 30 s. The volume fraction of crystallization (X) obtained at a certain temperature is defined as the ratio of the corresponding crystal area at a holding time over the total area of the sample, which could be obtained by analyzing video images. Thus, Eq. (1) could be converted to Eq. (2) by taking twice logarithms. And the values for k and n could be acquired from the slope and the intercept of the fitting lines of $\ln \ln(1/(1-X))$ vs $\ln(t - \tau)$, respectively.

$$\ln \ln \left(\frac{1}{1-X} \right) = n \ln k + n \ln(t - \tau) \dots \dots \dots (2)$$

2.4. Analysis Method

In order to study the structure variation of molten slag during the formation process of Calcium borosilicate, the samples crystallized for 0 s, 10 s, 20 s and 30 s as the holding time were quenched and analyzed by using Fourier

Fig. 2. The snapshot of the whole crystallization process. (Online version in color.)

Fig. 3. XRD pattern of the sample for isothermal crystallization at 1373 K. (Online version in color.)

Table 2. Assignments of FTIR bands.

Wavenumber (cm ⁻¹)	Assignments	References
400–600	T–O–T bond bending vibrations (T denotes Si or B elements <i>et al.</i>).	[25]
600–800	Bending vibrations of Si–O–B bonds.	[26]
800–1 200	[SiO ₄]-tetrahedral and [BO ₄]-tetrahedral stretching vibrations.	[25, 27–31]
1 200–1 450	[BO ₃]-triangular stretching vibrations.	[28–30]
~1 250	B–O stretching vibration of [BO ₃]-triangular in boroxol rings.	[28–31]
~1 400	Stretching mode of [BO ₃]-triangular and [BO ₂ O ⁻]-triangular in boroxol rings.	[28–31]

Transform Infrared (FTIR, Nicolet 6700) spectroscopy. 2.0 mg of above quenched sample powders mixed with 200 mg KBr (reagent grade) were pulverized and pressed into a thin section disk with the size less than 100 μm diameters for FTIR test. The tested wavenumber range was from 4 000 to 400 cm^{-1} with a resolution of 2 cm^{-1} by using a spectrophotometer equipped with a KBr detector. The wavenumber region of the samples in FTIR spectra was mainly between 1 600 to 400 cm^{-1} , and the assignments of each band were summarized in Table 2.

To semi-quantitatively identify the silicate structure, the above quenched samples were directly measured by Raman (LabRAMHR Evolution, HORIBA Jobin Yvon, Paris, France) spectroscopy with a 532-nm line of frequency-doubled Nd:YAG laser as excitation source. Raman spectra were recorded from the solid samples between 200 and 1 600 cm^{-1} for the silicate structure at spectral resolutions

Fig. 4. The isothermal crystallization evolution process of the sample at 1373 K and its crystalline fractions with different holding time. (Online version in color.)

ranging from 2 to 3 cm^{-1} . The baseline was subtracted by using the Labspec software and the wave number was corrected by using single crystal silicon wafer (520 cm^{-1}). The tested Raman spectra shifts were ranged between 200 and 1 600 cm^{-1} , but only shifts from 750 to 1 150 cm^{-1} was mainly attributed to the stretching vibration of $\text{Q}^i(\text{Si})$ ($i=0, 1, 2, 3$), in which the bands at ~ 870 , ~ 960 , ~ 990 , and $\sim 1 050$ cm^{-1} are usually assigned to $\text{Q}^0(\text{Si})$, $\text{Q}^1(\text{Si})$, $\text{Q}^2(\text{Si})$, and $\text{Q}^3(\text{Si})$,^{30–34} respectively. The Raman spectra shifts from 750 to 1 150 cm^{-1} were undergone consecutive curve fitting in by using Gaussian functions of Origin Microcal Software, until the fitting of R^2 is beyond 0.95. The characteristic peaks for $\text{Q}^i(\text{Si})$ structural units were deconvoluted at ~ 870 , ~ 960 , ~ 990 , and $\sim 1 050$ cm^{-1} from the fitting curve to obtain the corresponding peak and its parameters (wave-number, peak area, *et al.*) for further analysis.

Besides, the morphology of each sample to illustrate the growth process of the crystalline phase was analyzed through Scanning Electron Microscope (SEM) images. The samples crystallized for 30 s, 40 s, 50 s, 60 s and 70 s as the holding time in the TTT tests were quenched and observed by SEM. The obtained samples were embedded into a polyester resin and subjected to a standard metallographic polishing procedure. Then, the samples were coated by Au evaporation for SEM observation, in which the crystalline phase was confirmed by Energy Dispersive Spectrometer (EDS).

3. Results and Discussion

3.1. Kinetics of Isothermal Crystallization of Calcium Borosilicate

Figure 4 shows the isothermal crystallization process of the sample at 1373 K. It is obviously observed that at 30 s, Calcium borosilicate crystals begin to precipitate at the boundary of the thermocouple, and then they grow toward the central part. Meanwhile, some Calcium borosilicate crystals were found to precipitate in the central part of the

sample. With the prolongation of the holding time, Calcium borosilicate crystals further grow up from the boundary and central part. Thus, the liquid zone becomes very narrow in the central part, and a complete crystallization is found when the holding time reaches 70 s. The corresponding crystalline fractions with different holding time are also shown in Fig. 4 by analyzing of the snapshots.

It can be obtained from the linear relationship between $\ln\ln(1/(1-X))$ and $\ln(t-\tau)$ as shown in Fig. 5. It can be seen that the slope *i.e.* the Avrami exponent n is 1.29519. The corresponding relationship between the Avrami exponent n and the nucleation and growth mechanism of crystals are summarized in Table 3.³⁵⁾ The value of the Avrami exponent n for the sample is between 1 and 1.5, by comparing the values of the Avrami exponent n in Table 3, it may be concluded the nucleation and growth mode of the crystal for isothermal crystallization at 1 373 K is constant nucleation rate, 1-dimensional growth and diffusion control, or constant number of nuclei, 3-dimensional growth and diffusion control. With further observation of the crystallization process images in Fig. 4, it can be seen that all the crystal nucleus have already formed when the holding time is 30 s; then, the crystals grow up in 3- direction as the crystals appear equi-axial structure and they finally merge together. Thus, it can be speculated that the kinetics of this crystallization is ‘constant number of nuclei, 3-dimensional growth and diffusion control’, which could be further confirmed by the following SEM results.

3.2. Evolution of the Melt Structure during Nucleation of Calcium Borosilicate Crystal

Figure 6 shows the FTIR spectra of the samples crystallized for 0 s, 10 s, 20 s and 30 s as the holding time, and the structural units corresponding to each characteristic pattern are listed in Table 2. The vibration range between 400 to 600 cm^{-1} is assigned to the T–O–T bond bending vibrations (T denotes Si or B elements *et al.*), 600 to 800 cm^{-1} represents the bending vibrations of Si–O–B bonds, 800 to 1 200 cm^{-1} corresponds to the $[\text{SiO}_4]$ -tetrahedral and $[\text{BO}_4]$ -tetrahedral stretching vibrations, and 1 200 to 1 450 cm^{-1} stands for the $[\text{BO}_3]$ -triangular stretching vibration. Besides, the $[\text{BO}_3]$ -triangular stretching vibration can be

characteristically distinguished by the stretching vibration of B–O bonds in boroxol rings at approximately 1 250 cm^{-1} and the stretching mode of $[\text{BO}_3]$ -triangular and $[\text{BO}_2\text{O}^-]$ -triangular (O^- means non-bridged oxygen atom) in boroxol rings at 1 400 cm^{-1} .

It can be observed from Fig. 6 that comparing the FTIR spectra for the samples crystallized at 0 s to 10 s as the holding time, $[\text{SiO}_4]$ -tetrahedral and $[\text{BO}_4]$ -tetrahedral stretching vibrations at 800–1 200 cm^{-1} and the asymmetric stretching mode of $[\text{BO}_3]$ -triangular and $[\text{BO}_2\text{O}^-]$ -triangular in boroxol ring at 1 400 cm^{-1} are substantially constant. However, the T–O–T bond bending vibrations at 400–600 cm^{-1} become more pronounced, while the B–O asymmetric stretching vibration of $[\text{BO}_3]$ -triangular in boroxol rings at 1 250 cm^{-1} and the bending vibrations of Si–O–B bonds at 600 to 800 cm^{-1} attenuate. It suggests the B–O band of $[\text{BO}_3]$ -triangular in boroxol rings has been broken down and meantime the Si–O–Si or B–O–B bonds increase.

When the crystallization time reaches 20 s, it is observed that the T–O–T bond bending vibrations at 400–600 cm^{-1} , the bending vibrations of Si–O–B bonds at 600 to 800 cm^{-1} and $[\text{SiO}_4]$ -tetrahedral and $[\text{BO}_4]$ -tetrahedral stretching vibrations at 800–1 200 cm^{-1} decompose; while the spectra in range between 1 200 to 1 450 cm^{-1} standing for the $[\text{BO}_3]$ -triangular stretching vibration keeps constant.

Table 3. The value of n with different nucleation and growth mechanism.

		Diffusion	Interface Reaction
Constant nucleation rate	1-dimensional growth	1.5	2
	2-dimensional growth	2	3
	3-dimensional growth	2.5	4
Constant number of nuclei	1-dimensional growth	0.5	1
	2-dimensional growth	1	2
	3-dimensional growth	1.5	3
Surface nucleation		0.5	1

Fig. 5. The relation of crystalline volume fraction with function of time. (Online version in color.)

Fig. 6. The FTIR spectra results of the samples crystallized for 0 s, 10 s, 20 s, and 30 s as the holding time. (Online version in color.)

Therefore, it indicates that the T–O–T bond and Si–O–B bonds have been disrupted, resulting in the reduction of [SiO₄]-tetrahedral and [BO₄]-tetrahedral units.

When the holding time further goes to 30 s, the bond bending vibrations of all structural units become stronger, which indicates that borosilicate structure units have reconnected with each other and simultaneously new boroxol rings with [BO₃]-triangular and [BO₂O[−]]-triangular structure have built up.

Because the FTIR spectra of [SiO₄]-tetrahedral and [BO₄]-tetrahedral structure overlap with each other, Raman spectroscopy has been adopted to further analyze the silicate structure of above samples. The fitting and deconvoluting results of the Raman curves for the samples are presented in Fig. 7, and the wavenumber and the peak area for the characteristic peak are listed in Table 4. It can be seen from Table 4 that the Raman shift of Q¹(Si), Q²(Si) and Q³(Si) have some deviations comparing with the literature, it's probably because Q¹(Si), Q²(Si) and Q³(Si) structural units are in the case of borosilicate system, which is different from the traditional single silicate system. Also, the different bond force and distance between Si–O and B–O are different from each other, leading to the shifts in Raman spectrum. As one of the main objectives of this study is to quantify the glass structure, the mole fraction (X_i) ($i=0, 1, 2, 3$) of the four [SiO₄]-tetrahedral units have been further derived according to the following Eq. (3):^{12,34,36}

$$X_i = \frac{\left(\frac{A_i}{S_i}\right)}{\left(\sum_{i=0}^3 \frac{A_i}{S_i}\right)} \dots\dots\dots (3)$$

Where, S_i is the Raman scattering coefficient, and S_0, S_1, S_2, S_3 equal to 1, 0.514, 0.242, and 0.09, respectively. A_i ($i=0, 1, 2, 3$) is respective corresponding the peak areas of Q⁰(Si), Q¹(Si), Q²(Si) and Q³(Si) structural units and the results are shown in Table 4. The calculated mole fraction results are given in Fig. 8.

It can be observed, the samples crystallized for 10 s, the

Table 4. The parameters for the characteristic peak of Qⁱ(Si) structural units.

		Q ⁰ (Si)	Q ¹ (Si)	Q ² (Si)	Q ³ (Si)
0 s	Raman shift/cm ^{−1}	860.04	900.68	952.66	1 025.54
	Peak area	7 831	15 127	26 991	10 668
10 s	Raman shift/cm ^{−1}	863.33	901.20	934.02	1 010.42
	Peak area	4 966	11 619	10 178	20 953
20 s	Raman shift/cm ^{−1}	852.75	906.25	992.32	1 058.31
	Peak area	2 760	24 264	13 561	1 744
30 s	Raman shift/cm ^{−1}	865.03	913.31	981.57	1 034.64
	Peak area	5 456	17 002	11 306	3 307

Fig. 7. Deconvolution of Raman spectra of the samples crystallized for (a) 0 s, (b) 10 s, (c) 20 s and (d) 30 s as the holding time. (Online version in color.)

mole fraction of $Q^3(\text{Si})$ increases significantly while $Q^1(\text{Si})$ and $Q^2(\text{Si})$ decrease slightly, which suggests the T–O–T bond of the FTIR spectra for 10 s become more pronounced due to the augment of Si–O–Si bond. For 20 s sample, the mole fraction of $Q^3(\text{Si})$ decreases significantly, while $Q^1(\text{Si})$ and $Q^2(\text{Si})$ increase, which indicates silicate structure has been depolymerized as suggested by the FTIR results. When crystallization time goes to 30 s, the mole fraction of $Q^3(\text{Si})$ increases again, while $Q^1(\text{Si})$ and $Q^2(\text{Si})$ decrease, which suggests that the new borosilicate structure forms with the variation of $[\text{SiO}_4]$ -tetrahedral units. The mole fraction of $Q^0(\text{Si})$ is within 5% and could be neglected in the whole process. So, it can be concluded that there exists an equilibrium reaction between $Q^3(\text{Si})$ and $Q^1(\text{Si})$ and $Q^2(\text{Si})$ as follows:

Fig. 8. Mole fractions of various $Q^i(\text{Si})$ units in the networks versus time. (Online version in color.)

Therefore, it is inferred by combining above FTIR and Raman analysis results that originally there are the long-range disordered borosilicate structure, the dissociative silicate structural units ($Q^1(\text{Si})$, $Q^2(\text{Si})$, $Q^3(\text{Si})$, *et al.*) and free oxygen ions (O^{2-}) in melt slag before cooling, as shown in Fig. 9(a).

At the initial crystallization state (Fig. 9(a)), the existed O^{2-} (the blue ball) ions tend to depolymerize the Si–O–B bonds (the purple dotted lines), which results in the disruption of the B–O band of $[\text{BO}_3]$ -triangular in boroxol rings and the decomposition of boroxol rings. Simultaneously, the dissociative $Q^2(\text{Si})$ structural units will connect with the $[\text{SiO}_4]$ -tetrahedral in the decomposition of boroxol rings to form $Q^3(\text{Si})$ and increase Si–O–Si bond (as indicated by the purple dotted arrow). So, the structural model at the holding time of 10 s is shown in Fig. 9(b).

When the sample is further crystallized from 10 s toward 20 s (Figs. 9(b) to 9(c)), the B–O bond in $[\text{BO}_4]$ -tetrahedral as well as the Si–O–Si bond in silicate structures (the purple dotted lines in Fig. 9(b)) will be disrupted, which is caused by the equilibrium reaction between $[\text{BO}_4]$ -tetrahedral and $[\text{BO}_3]$ -triangular as follows.³⁷⁾ Thus, the $[\text{BO}_4]$ -tetrahedral (or $[\text{BO}_3\text{O}^-]$ -tetrahedral, O^- atom is represented by the sky-blue ball) structure transforms into $[\text{BO}_3]$ -triangular (or $[\text{BO}_2\text{O}^-]$ -triangular). Besides, $Q^2(\text{Si})$ units change to $Q^1(\text{Si})$ structural units, and $Q^3(\text{Si})$ units change to $Q^2(\text{Si})$ structural units. So, the structural model at the holding time of 20 s is shown in Fig. 9(c).

With the further crystallization of sample from 20 s to 30 s, the $Q^1(\text{Si})$ unit (linked with $[\text{BO}_3]$ -triangular or connected with $[\text{BO}_2\text{O}^-]$ -triangular) will connect with the adjacent $[\text{BO}_3]$ -triangular units to form new boroxol rings (the process as shown with the purple dotted lines ① in Fig. 9(c)). Then, the $Q^1(\text{Si})$ units also will connect with the depolymerized

Fig. 9. The evolution of borosilicate structure during nucleation of Calcium borosilicate.

$Q^2(\text{Si})$ units to form $Q^3(\text{Si})$ structural units (the purple dotted lines ② in Fig. 9(c)). Besides, the $Q^2(\text{Si})$ structural units (linked with $[\text{BO}_3]$ -tri-hedral and $[\text{BO}_2\text{O}^-]$ -tri-hedral or $[\text{BO}_3]$ -tri-hedral) will connect with dissociative $Q^1(\text{Si})$ to extend the length of the structure and increase the symmetry of the structure (the purple dotted lines ③ in Fig. 9(c)), which has been illustrated from Figs. 9(c) to 9(d).

Therefore, the final structure (Fig. 9(d)) is the long-range ordered borosilicate structure with a certain symmetry. And alkali ions (Ca^{2+}) will associate with the long-range ordered borosilicate structure to form Calcium borosilicate crystal nucleus. The schematic process of the formation of borosilicate structure is described in Fig. 9.

3.3. Calcium Borosilicate Crystal Growth Observed by SEM

Figure 10 shows the SEM images of the samples isothermally crystallized for 30 s, 40 s, 50 s, 60 s and 70 s. It can be seen that for the sample at 30 s, when the temperature rapidly drops to target value 1373 K and hold for 30 s, the boundary temperature of molten slag is lower than the center part, leading to a higher degree of undercooling of the boundary. Thus, it will promote the precipitation of fine crystals within micron at the boundary. Thus, the crystals mainly precipitate at the boundary of the thermocouple and exhibited grain-shape particles orientated in a line dispersively (Fig. 10(a)). The crystals formation and the dissipation of latent heat of solidification can increase the peripheral temperature, and the degree of undercooling decreases, which results in the formation of dendrites parallel to each other. Figure 10(b) shows that the grain-shape crystals at the boundary become thicker and formed dendrite structure. With the crystallization time went to 50 s, more crystals are formed in the sample, and more and more

dendrite structure are formed as shown in Fig. 10(c). When the temperature of primary dendrites is higher than the temperature between dendrites, this negative temperature gradient causes secondary dendrites to be formed and grew on the primary dendrites axis. Then, the dendrite crystals grow up with the development of secondary dendrite along the primary ones (Fig. 10(d)). Finally, the sample is fully crystallized at 70 s, and the dendrite crystals are further grown into a large size, as shown in Fig. 10(e). It also can be

Fig. 10. The SEM images for the growth process of Calcium borosilicate. (Online version in color.)

Fig. 11. The EDS results of corresponding the marked position of SEM images. (Online version in color.)

observed from the SEM images that the growth mode of the crystal is 3-dimensional growth and diffusion growth, which is consistent with the conclusion in Part III, Section 3.1.

In order to certify the precipitated crystals in the slag sample is Calcium borosilicate, the EDS was applied for the base (Position I) and the precipitated crystals (Position II) when the sample begins to crystallize (30 s as the holding time), and the precipitated crystals at the boundary (Position III) as well as in the central part of the sample (Position IV) where the sample has been fully crystallized. The EDS results are given in Fig. 11. As the atoms with atomic number less than oxygen cannot be detected in EDS, B and Li atoms are failed to show in the EDS results. The EDS result of Position I shows the base mainly contains Ca, Si, Al, Mg and Na atoms, which is fully consistent with the chemical component of the experimental sample. The EDS results of Position II and III and IV suggest the crystalline phase only contains Ca and Si atoms where the Ca/Si atomic ratio is around 3 that is close to the ratio of the Calcium borosilicate. It can be inferred that the precipitated crystals are Calcium borosilicate, which is in agreement with XRD results.

4. Conclusions

The mechanism of Calcium borosilicate ($\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$) crystal nucleation and growth were studied through SHTT combined with the kinetics and SEM. Besides, the evolution of the melt structure during nucleation of Calcium borosilicate crystal also was discussed by using FTIR and Raman. And the specific conclusions are summarized as follows:

(1) The mold flux for isothermal crystallization at 1 373 K is single β -polymorphs Calcium borosilicate crystal phase and its cell parameters are $a=2.861$ nm, $b=1.5974$ nm, $c=0.6874$ nm, $\alpha=\beta=90^\circ$, $\gamma=104.1^\circ$.

(2) The kinetics results suggest the nucleation mode of Calcium borosilicate crystal for isothermal crystallization at 1 373 K is a constant number of nuclei, and the growth mode is 3-dimensional growth by diffusion control.

(3) Originally, the existed free oxygen ions tend to depolymerize the long-range disordered borosilicate structure and then the depolymerized borosilicate structure will connect with the dissociative $\text{Q}^2(\text{Si})$ structural units. When the holding time from 10 s toward 20 s, the $[\text{BO}_4]$ -tetrahedral will transform into $[\text{BO}_3]$ -triangular, which results in the disruption of Si–O–B bond in $[\text{BO}_4]$ -tetrahedral and the $\text{Q}^3(\text{Si})$ unit is depolymerized to form $\text{Q}^2(\text{Si})$. Subsequently, the decomposed borosilicate will connect with the formed $\text{Q}^2(\text{Si})$ and the dissociative $\text{Q}^1(\text{Si})$, and finally form a long-range ordered borosilicate structure with a certain symmetry.

(4) With the formation of Calcium borosilicate crystal nucleus, the crystals first precipitate at the boundary of the thermocouple and exhibited grain-shape particles orientated in a line dispersively. With the further crystallization, the grain-shape crystals at the boundary become thicker and formed dendrite structure, also the crystals precipitate at the central part. Then, the secondary dendrites are observed to

form and grow on the primary dendrites axis. The dendrite crystals grow up with the development of secondary dendrite along the primary ones. Finally, Calcium borosilicate crystals become very thick.

Acknowledgments

The financial support from National Science Foundation of China (U1760202, 51661130154) and the Newton Advanced fellowship (NA150320) is great acknowledged.

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