

EFFECT OF CaO/SiO₂ AND HEAT TREATMENT ON THE MICROSTRUCTURE OF GLASS-CERAMICS FROM BLAST FURNACE SLAG

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Glass-ceramics, with molten blast furnace (BF) slag as the major raw material, were prepared successfully by the melting method. The effect of the CaO/SiO₂ ratio in the molten BF slag and heat treatment on the viscosity and microstructure of glass-ceramics produced from BF slag were traced using the melt property tester, DSC, XRD and SEM. The results showed that increasing the CaO/SiO₂ ratio of BF slag caused a decrease not only in the viscosity of the BF slag at high temperature but also in the nucleation and crystallization temperature for the preparation of glass-ceramics. The content of akermanite-gehlenite increased as the CaO/SiO₂ ratio increased from 0.30 to 0.63. With increasing nucleation and crystallization temperature, the crystalline phases remain unchanged, but the crystal shape changes from granular to flaky. The optimum CaO/SiO₂ ratio was found to be 0.44, resulting in diopside as the main crystalline phase, augite as the secondary crystalline phase and a small amount of akermanite-gehlenite after appropriate heat treatment i.e. nucleation at 775°C and crystallization at 920°C.

INTRODUCTION

China's steel production exceeded 770 million tons in 2013, and continues to comprise 49.1 % of the world's total production [1]. With each ton of pig iron, 300 - 600 kg of blast furnace slag (hereafter referred to as BF slag) is produced as a by-product. Therefore, 230 - 460 million tons of BF slag are produced every year. At this time, most of the BF slag is piled into slag yards without utilization, which is not only a serious problem in terms of environmental pollution, but also a waste of resource [2].

BF slag, which consists mainly of CaO, SiO₂, MgO and Al₂O₃, can be regarded as a raw material for the production of glass-ceramics. In fact, in the last few decades considerable attention has been paid to utilizing BF slag as a raw material for glass-ceramics [3-5]. However, the usual raw material for fabricating BF glass-ceramics is not molten BF slag, but water-granulated slag, which leads to an enormous waste of heat [6]. In order to reduce the waste of this latent heat, BF slag in the molten state is directly used as a raw material for the manufacturing of glass-ceramics in this work.

Melting and sintering methods are the two most practical ways of making glass-ceramics. The processes of making glass-ceramics include melting, refining, forming, nucleation and crystallization, and each process is strongly dependent on the viscosity of the molten parent glass. The diffusion velocity of the solute is

greatly related to the viscosity at the glass melt. A non-uniform diffusion of solute will undoubtedly lead to a non-uniform chemical composition distribution within the glass melt. The viscosity of the parent glass melt has also an obvious impact on the temperature of nucleation and crystallization of the resulting glass-ceramics [7-8]. CaO and SiO₂, as glass network modifier and glass network former, respectively, are the main ingredients of glass. Therefore, it is necessary to study the effect of the CaO/SiO₂ ratio in the BF slag and the influence of the heat treatment on the viscosity of the molten slag as well as the crystalline phase of glass-ceramics produced from BF slag.

EXPERIMENTAL

The raw materials used to synthesize glass-ceramics were original BF slag from an iron-making plant and pure commercial chemical agents. The chemical composition of the BF slag used, which is listed in Table 1, was analyzed with X-ray fluorescence spectroscopy (ZSX Primus II, Rigaku, Japan).

Table 1. Chemical composition of BF slag used to produce glass-ceramics (wt. %).

CaO	MgO	SiO ₂	Al ₂ O ₃	TiO ₂	K ₂ O
40.57	7.88	34.15	15.88	0.95	0.57

According to the chemical composition of the BF slag used, the system belongs to CaO–SiO₂–MgO–Al₂O₃ glass-ceramics. The design of chemical composition for the parent glass was based on the phase triangle of CaO–SiO₂–Al₂O₃ system with 10 % MgO. Three glass-ceramics (labelled A, B and C) in different chemical composition, as listed in Table 2, were designed in order to explore the influence of the CaO/SiO₂ ratio on the microstructure of glass-ceramics produced from BF slag.

The BF slag was pre-pulverized in an enclosed sample preparation crusher and then powders with a particle size less than 100 µm were achieved. A certain amount of pulverized BF slag, as listed in Table 3, was weighed accurately and put into a graphite crucible prior to melt BF slag each time. The BF slag together with graphite crucible was heated up to 1500°C, which was used to simulate molten BF slag. The crucible was hold at 1500°C for 30 min for the purpose of obtaining a uniform melt composition distribution, after the other chemical reagents required to fabricate each glass-ceramic listed in Table 3 had been added into the molten BF slag. Melt viscosity measurements were performed on a melt properties tester (RTW-10, Northeast University, China) using a rotating cylinder method. A viscometer is connected to a molybdenum spindle immersed into the melt through a corundum rod. The viscosity value of the melt was converted by software according to the detected instant torque value. A higher torque need to be given when the viscosity of the melt increases to maintain molybdenum spindle rotating in a uniform velocity. Finally, a viscosity-temperature curve is be obtained with decreasing temperature of the melt in the crucible.

After finishing the viscosity measurement, the melt was heated up to 1500°C again. Then the molten glass was quickly poured into a stainless steel mold, which had been preheated to 600°C. After the glass cooled down to room temperature, it was placed into a muffle furnace and heated up to 600°C, then cooled down to room temperature again in order to decrease internal stress.

The thermal behavior of the glass samples was examined by DSC (STA449F3, Netzsch, Germany) in order to assist the selection of suitable nucleation and crystallization temperatures. The powder of the parent glass was heated in a Al₂O₃ holder against another Al₂O₃ holder containing Al₂O₃ as a reference material (heating rate 10 K·min⁻¹). Three glass-ceramics were produced by parent glass undergoing reasonable heat treatment.

The crystalline phase of the obtained glass-ceramics was examined by X-ray diffractometer (Model D8 ADVANCE, Bruker, Germany) after grinding into a fine powder in an enclosed test sample preparation crusher. The glass-ceramics were polished and corroded in HF solution (10 vol. %) for 15 s, and then gold coated. The microstructures of the glass-ceramics were characterized by SEM (Model S-4800, Hitachi, Japan).

RESULTS AND DISCUSSION

Determination of high-temperature viscosity of BF slag glass melts

Figure 1 shows the high-temperature viscosity of three BF slag glass melts with different CaO/SiO₂ ratio. According to these results, the viscosity of the BF slag glass melt is lowest when the CaO/SiO₂ ratio is 0.63. Another phenomenon is that the viscosity increases as the CaO/SiO₂ ratio is lowered. When the temperature is higher than 1425°C, the viscosity does not exhibit a clear increase with decreasing temperature. However, at lower temperatures (< 1425°C), the viscosity increases strongly as the temperature decreases. This phenomenon is more obvious when the CaO/SiO₂ ratio is low. Si and O exist in the form of [SiO₄] tetrahedra in the molten glass. CaO is the main network modifying oxide. There is an ionic bond between Ca and O. This forms Ca²⁺ and O²⁻, which move freely when the ionic bond fractures at high temperature. These free O²⁻ lead to rupture of the Si–O bonds. Thus, the [SiO₄] network is damaged.

Table 2. Chemical composition of the parent glass (wt. %).

Sample label	CaO	SiO ₂	CaO/SiO ₂	MgO	Al ₂ O ₃	K ₂ O	ZnO	Na ₂ SO ₄	TiO ₂
A	15	50	0.30	10	12	3	3	2	5
B	20	45	0.44	10	12	3	3	2	5
C	25	40	0.63	10	12	3	3	2	5

Table 3. Weight of each component in parent glass (g).

Sample label	BF slag	SiO ₂	MgO	Al ₂ O ₃	K ₂ O	ZnO	Na ₂ SO ₄	TiO ₂
A	37.0	37.4	7.1	6.1	2.7	3	2	4.6
B	49.3	28.2	6.1	4.2	2.7	3	2	4.5
C	61.6	19.0	5.2	2.2	2.6	3	2	4.4

At the same time, Ca^{2+} can lead to a polarization of the Si^{4+} cation, weakening the covalent bonds between Si and O and making them easier to break [9]. Basic oxide (CaO) can form compounds with low melting point. Therefore, the high-temperature viscosity of the glass melts is lower and the fluidity improves as the CaO/SiO_2 ratio increases. At the same temperature, the diffusion velocity of particle can be increased if the amount of CaO increased, making the mixing time shorter. If the viscosity is the same, the melting temperature can be lower, meaning that much energy can be saved.

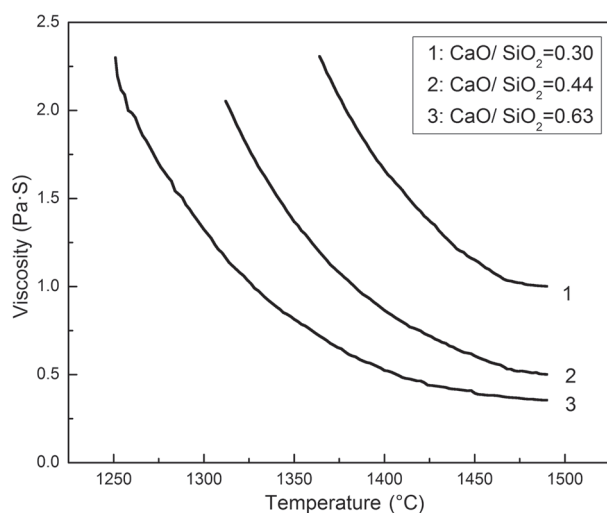


Figure 1. Viscosity curves of glass melt with different CaO/SiO_2 ratio.

DSC data of the studied glass

DSC curves of the glass powder are plotted in Figure 2. The endothermic peaks are in the temperature range 736 - 763°C. The crystallization reaction of the glass occurs at the exothermic peak temperature. With increasing CaO/SiO_2 ratio, the temperature of nuclea-

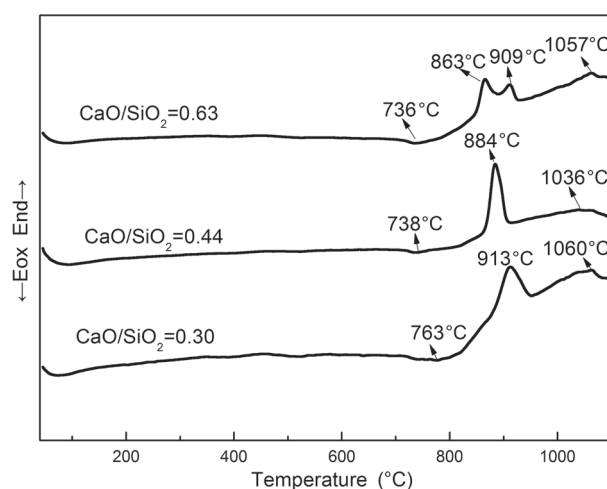


Figure 2. DSC curves of the parent glass powder with different CaO/SiO_2 ratio.

tion and crystallization is lower, which is in agreement with the measurements of glasses with different CaO/SiO_2 ratio. In order to increase the nucleation rate, the nucleation temperature was chosen slightly higher than the endothermic peak, while the crystallization temperature was around the exothermic peaks.

In the light of the DSC results, the following heat treating regimes were designed to examine the impact of heat treatment on crystalline phase constituent of glass-ceramics. The parent glass samples of the three chemical compositions labelled A, B, C, as listed in Table 2, were first nucleated and then crystallized, respectively, for one hour. The nucleation and crystallization temperatures were 750°C and 900°C, 775°C and 920°C, 800°C and 940°C, respectively.

Effect of the CaO/SiO_2 ratio and process temperature on crystalline phases

Figures 3-5 show the X-ray diffraction (XRD) patterns of glass-ceramics after completed nucleation and crystallization at different temperatures. These results clearly indicate that the main crystalline phase of the glass-ceramics is diopside (PDF card 41-1370), followed by augite (PDF card 78-1392) and a small amount of akermanite-gehlenite (PDF card 79-2423), when the CaO/SiO_2 ratio is 0.30 and 0.44. When the CaO/SiO_2 ratio increases to 0.69, the akermanite-gehlenite content increases. The two main crystalline phases of glass-ceramics are diopside and akermanite-gehlenite, but there is some augite when the CaO/SiO_2 ratio is up to 0.69.

For the glass melt containing a TiO_2 content up to 5 %, quadridentate titanium is dominant from the combination of Ti^{4+} and O^{2-} in the parent glass [10, 11]. Accordingly, during the preparation of the parent glass from the melt, quadridentate titanium is relatively easy to generate. However, when the parent glass is heated again to crystallization temperature, the quadridentate titanium tends to transform into sexadentate titanium which is more stable. However, the newly formed stable sexadentate titanium is incompatible with the glass matrix network. It naturally becomes a crystal nucleus or reacts with other oxides in the glass to grow into a new crystalline phase. At the crystallization temperature, a solid solution of diopside, augite and akermanite-gehlenite finally occurs. Ti mainly occurs in this solid solution of diopside, augite and akermanite-gehlenite, which may also contain K, Na and Zn. The d-spacings (Bragg reflections in XRD) of the solid solutions formed are similar as for the pure crystal phases.

The XRD patterns for the three samples prepared at different nucleation and crystallization temperatures were analyzed. As the temperature of nucleation and crystallization increased, both sample A and sample B exhibited almost no change in the content of the main

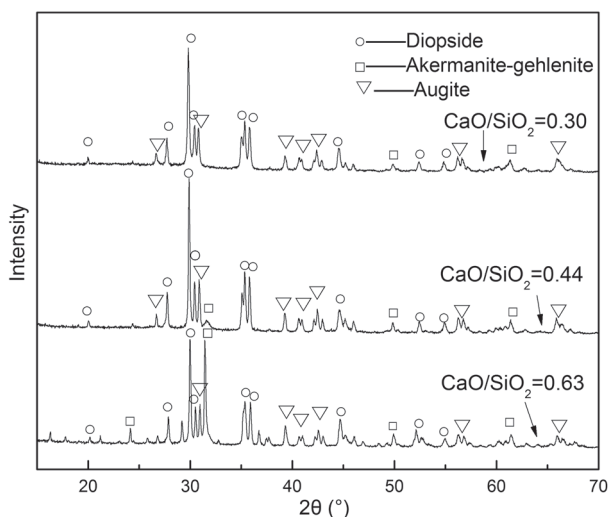


Figure 3. XRD patterns of three glass-ceramics after nucleation at 750°C and crystallization at 900°C.

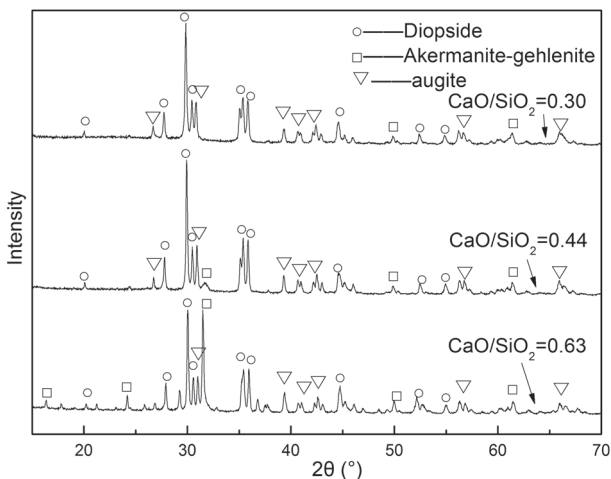


Figure 4. XRD patterns of three glass-ceramics after nucleation at 775°C crystallization at 920 °C.

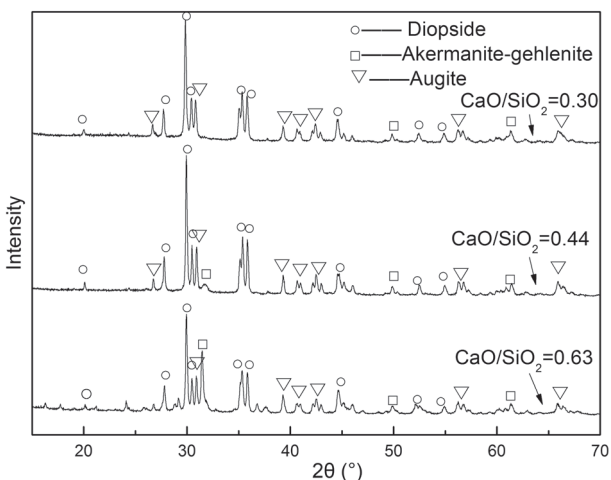


Figure 5. XRD patterns of three glass-ceramics after nucleation at 800 °C and crystallization at 940°C.

crystal phase diopside and the second phase augite. Therefore, the temperature appears to have little effect on diopside and augite at the test temperature. As for the sample C, it is evident that for nucleation temperatures 750°C or 775°C and crystallization temperatures 900°C or 920°C, the main crystalline phases are diopside and akermanite-gehlenite. As the temperature of nucleation and crystallization are increased to 800°C and 940°C, respectively, the content of akermanite-gehlenite decreased. Therefore, raising the temperature is shown to be unfavorable to the formation of akermanite-gehlenite.

Analysis of the microstructure of glass-ceramics

Effect of CaO/SiO₂ ratio on the microstructure of glass-ceramics

Figure 6-8 show SEM micrographs of the three samples nucleated at 775°C and crystallized at 920°C. Using BF slag, with the addition of other chemical agents to adjust the chemical composition, glass-ceramics can be successfully prepared after a proper temperature of nucleation and crystallization. Figure 6 shows that diopside and augite are granular and staggered within the glass phase matrix. The crystal phase exhibits good growth features.

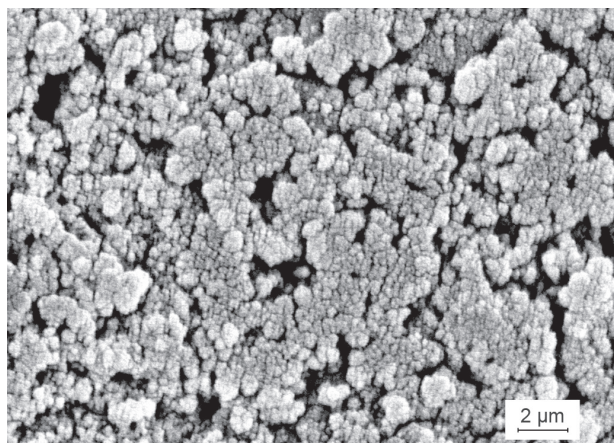


Figure 6. SEM micrograph of glass-ceramics A after nucleation at 775°C crystallization at 920°C.

Figure 7 shows that the grain size of diopside and augite increases and the crystal morphology changes from granular to flaky. In the SEM, bulk crystallization is noticeable and only a little glass phase is scattered among the crystallites. This is because with increasing CaO/SiO₂ ratio, the viscosity is lower and the speed of the particle growth was quicker, faster diffusion resulting in bigger crystals. Diopside and augite crystals are dispersed randomly throughout the ceramic matrix, which has the further effect of increasing the strength of the microstructure. Pyroxenes have excellent mecha-

nical properties and outstanding corrosion resistance to acid [12, 13]. Thus, the glass-ceramic B nucleated at 775°C and crystallized at 920°C should have prominent mechanical properties and resistance to acid corrosion.

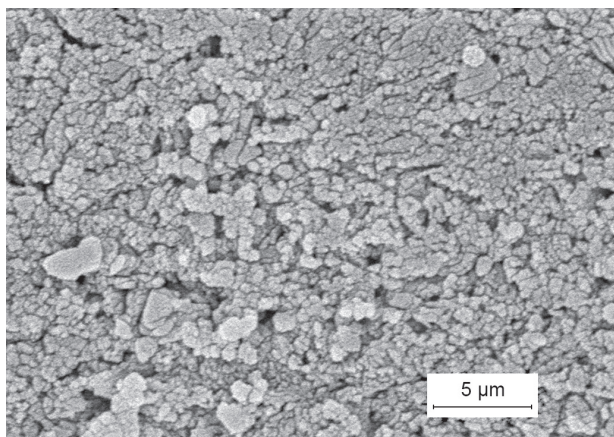


Figure 7. SEM micrograph of glass-ceramics B after nucleation at 775°C crystallization at 920°C.

Figure 8 shows bulky “snowflake” crystals distributed uniformly in the glass-ceramic, with only a small amount of glass phase. Also, these results indicate that a higher CaO/SiO₂ ratio can promote crystallization within the glass-ceramic, resulting in larger crystals.

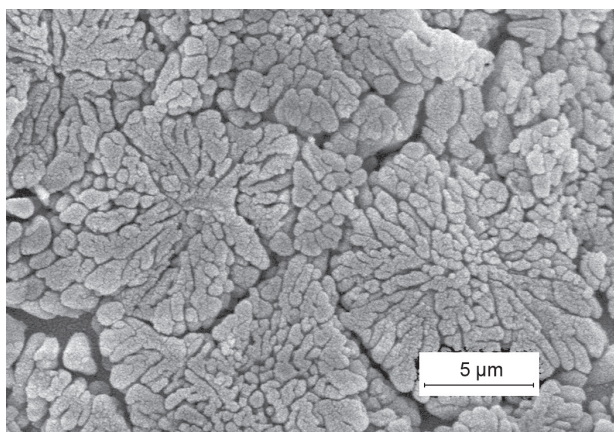


Figure 8. SEM micrograph of glass-ceramics C after nucleation at 775°C crystallization at 920°C.

Figures 7, 9 and 10 demonstrate the microstructure of glass-ceramic B prepared at different nucleation and crystallization temperatures. Spherical crystalline particles are generated from the matrix after nucleation at 750°C and crystallization at 900°C. However, this also results in a high amount of glass phase (Figure 9). When the temperature of nucleation and crystallization is raised to 775°C and 920°C, respectively, the amount of glass phase is reduced and the small amount of crystallites changes shape from the spherical to flaky (Figure 7).

When the base glass is heat treated by nucleation at 800°C and crystallization at 940°C, the size of crystal particle increases again, and some crystal particles even link together to form larger crystal blocks, resulting in rather non-uniform crystallites.

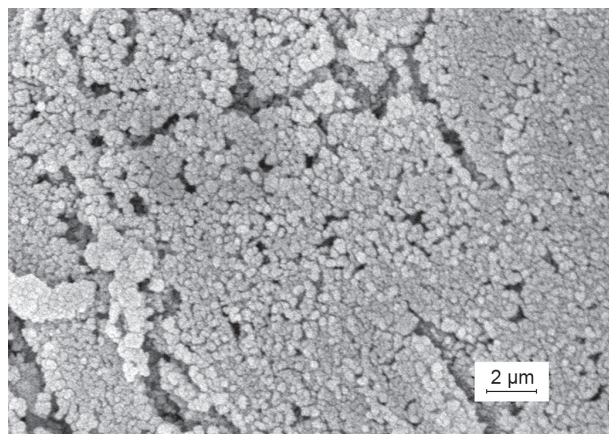


Figure 9. SEM micrograph of glass-ceramics B after nucleation at 750°C crystallization at 900°C.

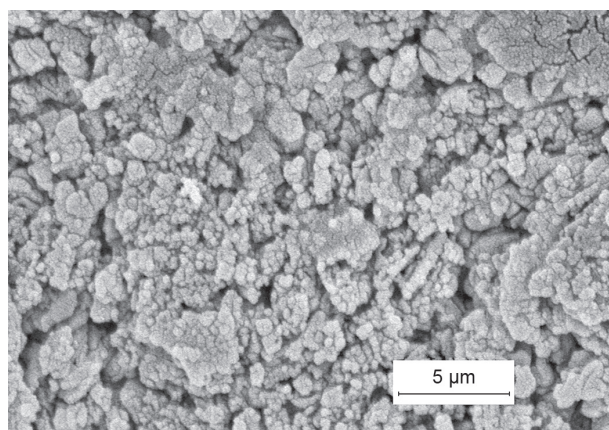


Figure 10. SEM micrograph of glass-ceramics B after nucleation at 800°C crystallization at 940°C.

CONCLUSIONS

- The technique of using molten BF slag with added chemical agents to adjust the composition of the BF slag to fabricate glass-ceramics is feasible.
- The crystalline phases of glass-ceramics change with the CaO/SiO₂ ratio. When the CaO/SiO₂ is 0.30 or 0.44, glass-ceramics with diopside as the main crystalline phase, augite as the second crystalline phase and a small amount of akermanite-gehlenite are obtained, and the crystallite shape is granular. The content of akermanite-gehlenite increased when the CaO/SiO₂ ratio was up to 0.63, and the crystallite shape is flaky

in this case. In other words, the crystalline phases are directly influenced by the chemical composition of the parent glass. In order to take full advantage of BF slag and reduce the use of chemical agents, the favorable ratio of CaO to SiO₂ in glass-ceramics fabrication should be 0.44, in which case the glass-ceramic is expected to have good mechanical properties and corrosion resistance.

- When the temperature of nucleation and crystallization is increased, the crystal shape changes from granular to flaky.

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REFERENCES

1. Chi H.: *Macroeconomic Management* 1, 86 (2014).
2. Das K., Raha S., Chakraborty D., Burhanuddin, Saheb Ali SK.: *Transactions of the Indian Ceramic Society* 71, 137 (2012).
3. Francis A. A.: *Journal of the European Ceramic Society* 24, 2189 (2004).
4. Liu Y., Xiao H. N.: *Ceramics* 6, 17 (2003).
5. Yang S. M., Zhang W., Dai H.: *Bulletin of the Chinese Ceramic Society* 33, 86 (2014).
6. Luo S. Y., Yi C. J., Zhou Y. M.: *Renewable Energy* 50, 373 (2013).
7. Zhang S. X., Yue Q. Y., Yu H., Xie J. K., Wang X. N.: *Journal of Shandong University* 41, 129 (2006).
8. Karamanova E., Avdeev G., Karamanov A.: *Journal of the European Ceramic Society* 31, 989 (2011).
9. Duan F.: *Journal of Non-Crystalline Solids* 357, 1494 (2011).
10. Yue Q. Y., Zhang S. X., Yu H., Gao B. Y., Wang X. N., Xie J. K.: *Chinese Journal of Process Engineering* 7, 327 (2007).
11. Wu J. F., Zhang Y. T., Xu X. H., You D. Q., Yin Y. P., Li P.: *Journal of Wuhan University of Technology* 28, 10 (2006).
12. Toya T., Tamura Y., Kameshima Y., Okada K.: *Ceramics International* 30, 983 (2004).
13. Zhao L. H., Li Y., Zhou Y. Y., Zhang D. Q.: *Materials & Design* 64, 608 (2014).