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Crystallization characteristics of iron-rich glass ceramics prepared from nickel slag and blast furnace slag

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Abstract: The crystallization process of iron-rich glass-ceramics prepared from the mixture of nickel slag (NS) and blast furnace slag (BFS) with a small amount of quartz sand was investigated. A modified melting method which was more energy-saving than the traditional methods was used to control the crystallization process. The results show that the iron-rich system has much lower melting temperature, glass transition temperature (T_g), and glass crystallization temperature (T_c), which can result in a further energy-saving process. The results also show that the system has a quick but controllable crystallization process with its peak crystallization temperature at 918°C. The crystallization of augite crystals begins from the edge of the sample and invades into the whole sample. The crystallization process can be completed in a few minutes. A distinct boundary between the crystallized part and the non-crystallized part exists during the process. In the non-crystallized part showing a black colour, some sphere-shaped augite crystals already exist in the glass matrix before samples are heated to T_c. In the crystallized part showing a khaki colour, a compact structure is formed by augite crystals.

Keywords: glass ceramics; grain growth; crystallization; slag

1. Introduction

The system of SiO_2-Al_2O_3-CaO-Fe_2O_3 (FeO) is usually considered as an important system. Based on this system, a magnetic glass ceramic can be prepared, which is widely used in the realms of biology and biomedicine because of their interesting magnetic and structural properties [1-3]. In addition, most of industrial wastes belong to this system, and therefore, it is possible to prepare glass ceramics from industrial wastes [4-7]. The technology with which glass ceramics can be prepared from industrial wastes is very important not only to sustain the development of the related industries but also to solve the environmental problems caused by industrial wastes. Therefore, it is promising to develop glass ceramics from the wastes. The study on preparing glass ceramics with industrial wastes has been made since the early 1960s, and some results were widely reported [8]. Various crystallization systems are involved, for example, the system of SiO_2-Al_2O_3-CaO-MgO, SiO_2-Al_2O_3-CaO-Fe_2O_3, and SiO_2-Al_2O_3-CaO-Na_2O [9-12].

The system of SiO_2-Al_2O_3-CaO-Fe_2O_3 (FeO) has some particular crystallization characteristics. First, the melting temperature of the system is relatively low compared with those in other systems. Secondly, Fe_2O_3 (FeO) can be considered as good nucleating agents, and therefore, the crystallization for this system can be easily realized. It is known that in the SiO_2-CaO-MgO-Al_2O_3-Fe_2O_3 (FeO) system, Fe^{2+} as a net gap ion will destroy the Si–O net structure and will decrease the viscosity of glass, similar to Ca^{2+} and Mg^{2+}. Like Al^{3+}, Fe^{3+} will form FeO_4 tetrahedrons and mend the net structure causing the increase in viscosity of the glass. When the glass is short of alkali metals and alkaline-earth metals, Fe^{3+} will be located in the gaps of the glass net structure and form FeO_6 octahedrons. On the other hand, when the alkali and alkaline-earth metals are sufficient, Fe^{3+} will accommodate SiO_4 tetrahedrons and contribute to a greater viscosity of the glass melt [13-14].

There are some investigations on iron-rich glass ceramics, and the glass ceramics were mostly prepared by the sintering method and the conventional melting method [15-18].

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But there is usually a small amount of Fe_2O_3 (or FeO) as a nucleating agent in these systems. However, a large amount of Fe_2O_3 (or FeO) exists in some industrial wastes such as nickel slag and steel slag. As a result, it is necessary to investigate the crystallization characteristics of the iron-rich system to produce glass ceramics with a large quantity of wastes.

2. Experimental

2.1. Raw materials and determination of treatment temperatures

The experimental sample was composed of nickel slag (NS), blast furnace slag (BFS), and quartz sand in a mass ratio of 20:80:10 with the SiO_2 content in the quartz sand being up to 99.96wt%. NS, BFS, and quartz sand were mixed by a planet milling ball with a speed of 120 r·min^{-1} for 30 min. The major compositions of the raw material and the glass-ceramic sample are listed in Table 1.

Table 1. Major compositions of NS, BFS, and glass-ceramic samples wt%

Material	FeO	SiO_2	MgO	CaO	Al_2O_3	Others
NS	48.21	34.61	7.86	3.37	5.26	0.69
BFS	0.90	36.68	4.79	37.46	18.57	1.60
Sample	9.42	42.06	4.91	27.85	14.47	1.29

To determine the treatment temperatures, including the glass transition temperature (T_g) and crystallization temperature (T_c), differential scanning calorimetric (DSC) measurement was used.

The well-mixed raw materials (50 g) were transferred into an alumina crucible and melted in an experimental furnace at 1300°C for 2 h. Then the melt was quenched into water to form glass frits. Finally, DSC analysis can be carried out on the powder of the glass frits with sizes being less than 75 μm. The testing temperature was from 10 to 1100°C at a heating rate of 10°C/min. The DSC curve is shown in Fig. 1. It is shown in Fig. 1 that T_g and T_c of the glass ceramic sample are 717 and 918°C, respectively.

2.2. Crystallization process and analysis methods

The well-mixed raw material was melted in the experimental furnace at 1300°C for 2 h. A lot of tries to determine a proper method for controlling the glass re-crystallization process were carried out. The finally determined method, a modified melting method, was described as follows. The melt was poured into four steel moulds after the raw materials being melted at 1300°C for 2 h. Then the cooled melts along with the moulds were removed into another furnace

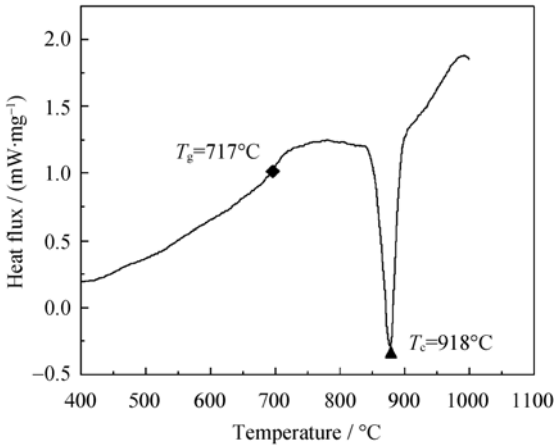

Fig. 1. DSC curve of the glass sample.

with its temperature being at T_g (717°C) and held for 15 min. Subsequently, the cooled melts were heated up to the temperature of T_c (918°C) at a heating rate of 10°C/min and also held for 15 min. Finally, the glass ceramics can be obtained after the annealing process. The time-temperature curve of the modified melting method is shown in Fig. 2.

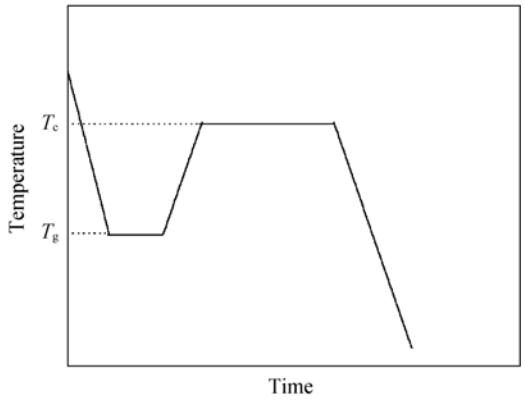

Fig. 2. Time-temperature curve of modified melting method.

To observe the crystallization process, the 4 samples were put out from the furnace and placed into the air after the samples were held for 2, 3, 4, and 5 min at T_c (918°C), respectively. The 4 samples were investigated by scanning electron microscope analysis (SEM SUPRA 55, Carl Zeiss, Germany) and X-ray diffraction analysis (XRD M21, MAC Science, Japan) to identify the crystalline phases and observe the microstructures.

3. Results and discussion

Fig. 3 shows the photographs of the sample heated at 918°C for different time. It is shown that two distinguishable parts of khaki and black occur in most of the samples but with different proportions. In Fig. 3(a), only a small portion of the khaki part occurs on the edge of the sample, and a clear boundary can be observed between the two parts. As

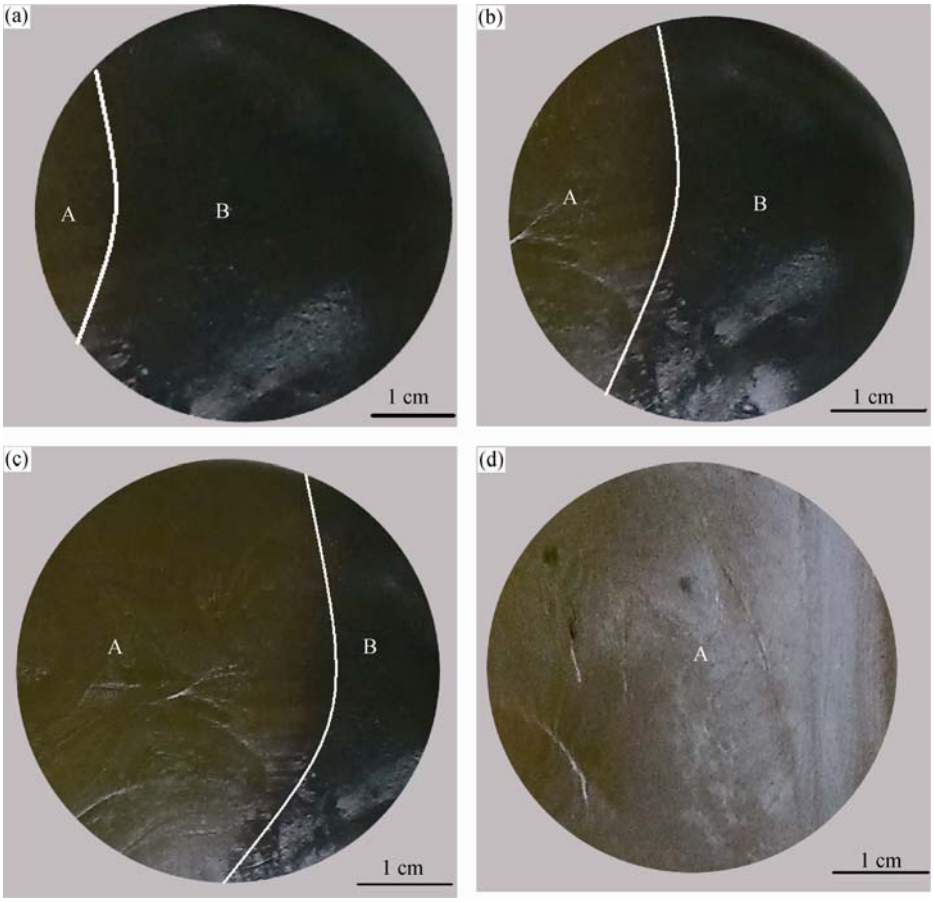

Fig. 3. Samples heated up to 918°C with different holding time: (a) 2 min; (b) 3 min; (c) 4 min; (d) 5 min.

the holding time prolonged from 2 to 5 min, the khaki part invades, and the black part retreats. The boundary moves from the left edge to the right edge of samples and finally disappeared in the 5-min sample. The colour of the whole sample becomes khaki.

XRD analysis was carried out on the powdered samples of the khaki and black parts. The results reveal that the khaki part (A) is the crystallized region, while the black part (B) is the coexisting region of the glassy phase and crystalline phase but dominated by the glassy phase. Fig. 4 shows the XRD spectra of the khaki part A and black part B in the sample heated at 918°C for 3 min. The spectrum of part A in Fig. 4 suggests that the khaki part is the crystalline phase dominated with augite ($Ca(Mg,Fe,Al)[(Si,Al)_2O_6]$) as its only crystalline phase. The spectrum of part B in Fig. 4 shows that the black part has the same crystalline phase as that of the khaki part. But the obvious swelling up background on the spectra suggests that the black part B is dominated by the glassy phase. It means that some tiny crystals of augite occur before the sample reaching the crystallization temperature. The tiny crystals which are soaked in the glass matrix may act as cores for subsequent quick crystallization.

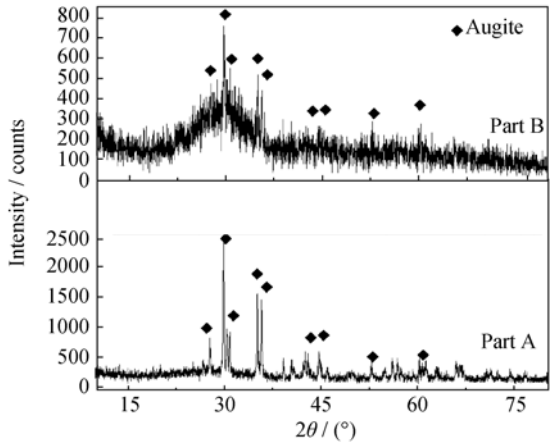

Fig. 4. XRD patterns of part A and part B in the sample heated 918ºC for 3 min.

Figs. 5(a) and 5(b) shows the microstructures of the khaki part (part A) of the sample heated at 918°C for 3 min, while Figs. 5(c) and 5(d) shows the microstructures of the black part (part B). As shown in Fig. 5(a), the khaki part has been well crystallized, which presents irregular crystal shapes with the compact structure. Fig. 5(b) shows some recognize-

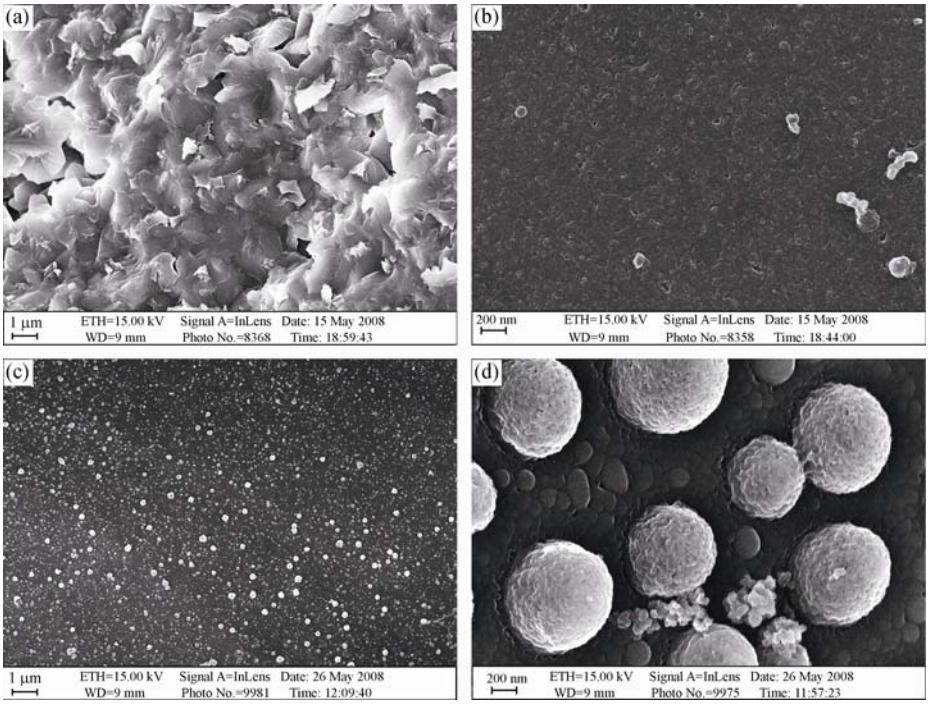

Fig. 5. SEM images of part A (a and b) and part B (c and d) in the sample heated at 918°C for 3 min.

able traces of the sphere-shaped crystals that closely join and grow with each other. In addition, most of sphere-shaped crystals are hardly recognizable. From Fig. 5(c), it is not difficult to find that a large number of sphere-shaped crystals already exist in the glass matrix. These isolated crystals intersperse in the glass matrix with the size being less than 1 μm. A magnified photograph for the sphere-shaped crystals is shown in Fig. 5(d). It is shown that a sphere-shaped crystal is probably formed by the aggregation of a great number of worm-shaped crystals being observed on the surface of the sphere-shaped crystal. The worm-shaped crystals agglomerate into the sphere-shaped tiny crystals on the early stage of crystallization, which means that the sphere-shaped crystal may not be the smallest crystalline unit.

Fig. 6 shows the microstructure of the transitional zone between the glassy part and the crystalline part. It is shown in Fig. 6 that along with the arrow direction, the khaki crystalline part invades into the black glassy part during the crystallization process. It is also shown that along with the arrow direction, the size of the sphere-shaped crystals becomes smaller and smaller, and finally, they cannot be observed on such a microscopic scale. This suggests that bigger sphere-shaped crystals are formed by the combination of smaller sphere-shaped crystals. In addition, on the top-left corner of the photograph, it shows that the bigger sphere-shaped crystals already begin to combine and grow with each other to form a compact crystalline structure. While on the bottom-right corner of the photograph, the size of the sphere-shaped crystals is so small that they hardly can be recognized.

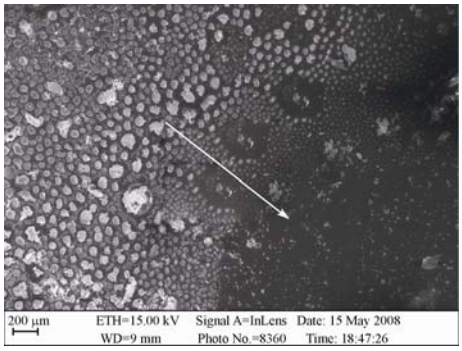

Fig. 6. SEM image of the transitional zone in the sample heated at 918°C for 3 min.

4. Conclusion

Glass ceramics can be prepared from the NS and BFS with a small amount of quartz sand with a mass ratio of 20:80:10. T_g of the glass ceramic is 717°C, and T_c is 918°C. The crystalline phase of the glass ceramics is augite. The crystallization of augite crystals begins from the edge of the sample and invades into the whole sample with a few minutes, and a distinct boundary between the crystallized part and the non-crystallized part can be observed.

Acknowledgments

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