Research Article

Yi-Ci Wang*, Pei-Jun Liu, Guo-Ping Luo, Zhe Liu, and Peng-Fei Cao

Optimization of heat treatment of glass-ceramics made from blast furnace slag

Abstract: CaO–MgO–Al2O3–SiO2 glass-ceramics with diopside as the main crystalline phase were prepared by melting blast furnace slag obtained from Baotou Iron and Steel Company. The effect of heat treatment on the crystallization behavior of glass-ceramics, containing a large proportion of melted blast furnace slag, was studied by means of differential thermal analysis and scanning electron microscopy. The optimum heat-treatment regime was obtained by orthogonal experimental results for glass-ceramics in which blast furnace slag comprised 70% of the composition and 1% Cr2O3 and 4% TiO2 were used as nucleating agents. The nucleation temperature was 750°C for 2.5 h and the crystallization temperature was 930°C for 1 h. Under this regime, the performance of the glass-ceramic was better than that of other groups in the orthogonal experiment.

Keywords: blast furnace slag, glass-ceramic, heat treatment, crystallization

1 Introduction

The water-quenched slag of Baotou Iron and Steel Company (Inner Mongolia, China) is mainly used to produce cement and slag powder. This utilization has disadvantages of high capital cost, low added value of products, and inefficient utilization of slag heat. The main chemical components of the blast furnace slag are CaO, SiO2, MgO, and Al2O3, which account for about 90% of the total slag and contain less harmful impurities [1,2]. This is an ideal raw material for decorative glass-ceramics of the CaO–SiO2–MgO–Al2O3 system, and also an effective economic way to increase value added to the blast furnace slag.

Glass-ceramics prepared with large-scale molten blast furnace slag can not only greatly improve utilization of the slag but also make full use of its heat energy [3]. Diopside and melilite are the main crystalline phases of glass-ceramics developed by the Turkish steel producer, Erdemir, using their blast furnace slag [4], with up to 50% of slag in the formulation. In research on glass-ceramics carried out by Weifeng [5,6], the proportion of blast furnace slag was up to 60%, but higher proportions are not reported in the literature. In this study, the proportion of blast furnace slag was 70%, which makes full use of the slag and its heat energy. Owing to the higher addition of blast furnace slag, the crystallization behavior of the glass-ceramics is strongly affected, and their physicochemical properties deteriorate. Defects caused by the high addition of blast furnace slag can be remedied by optimizing the heat-treatment parameters.

Baowei et al. [7] and Xueli [8] studied the effect of nucleation and crystallization temperature and time on the bending strength of slag glass-ceramics through orthogonal experiments and then determined an appropriate heat-treatment system that enabled their flexural strength to exceed 100 MPa and achieve excellent physical and chemical properties. Bochen [9] studied the heat treatment system of glass-ceramics from blast furnace slag of Baotou Iron and Steel Company by orthogonal test. The influence of selected factors on the properties of glass-ceramics was found out. The flexural strength of glass-ceramics under the optimum heat treatment system was determined to be 221.7 MP. Yang and Hanning [10] optimized the heat treatment system of glass-ceramics by means of orthogonal experiment and determined the optimum technological parameters as follows: the nucleation temperature is 840°C, holding for 1 h; the crystallization temperature is 910°C, holding for 1 h. Under the same experimental method, Xin [11] optimized the heat treatment system by orthogonal design and obtained the best technological parameters and glass-ceramics samples with good properties. Therefore, proper heat treatment is an important condition to ensure good microstructure and properties of glass-ceramics [11].
In this study, flexural strength was considered as the main examination index of glass-ceramics, and the heat-treatment system was optimized using an orthogonal experimental method to determine the best heat-treatment parameters.

2 Materials and methods

2.1 Raw materials

Blast furnace water-quenched slag from Baotou Iron and Steel Company, which is shown in Figure 1, was used as the main raw material. Its proportion in the ceramic formulation was up to 70%. The chemical composition of the slag is shown in Table 1. The other raw materials were quartz sand and purification reagents, CaO, MgO, and Al₂O₃. The nucleating agents were Cr₂O₃ and TiO₂. The purities of the raw materials are shown in Table 2.

2.2 Procedures

2.2.1 Preparation of glass-ceramics

Glass-ceramics were prepared by melting the blast furnace slag. The slag was ground in a ball mill and passed through a screen with a diameter of 0.074 mm.

Table 1: Chemical composition of blast furnace slag from Baotou Iron and Steel Company (mass%)

| Chemical components | SiO₂ | CaO | MgO | Al₂O₃ | FeO | Na₂O | K₂O | F | TiO₂ | Loss on ignition |
|---------------------|------|-----|-----|-------|-----|------|-----|---|------|----------------|
| Mass percentage     | 34.06| 37.79| 9.67| 13.08 | 1.65| 0.34 | 0.31| 0.27| 0.93 | 1.90           |

The slag and other raw materials were accurately weighed, mixed evenly, placed in a corundum crucible, and melted in a high-temperature furnace using a Si–Mo rod as the heater. The mixture was held at 1,500°C for 3 h to obtain a uniform glass liquid. The molten glass liquid was then poured into steel molds for natural cooling and annealed at 600°C for 2 h to eliminate internal stress. Samples of glass-ceramics were obtained after nucleating and crystallizing heat treatment.

The steps of the operation were as follows: batching → mixing → melting → molten glass casting → annealing → nucleating and crystallizing heat treatment → glass-ceramic.

2.2.2 Detection and analysis methods

Differential thermal analysis (DTA) of glass powders was carried out using a STA + PT1600 pressurized simultaneous thermal analyzer (Linseis, Germany) to determine the heat-treatment temperature [12]. The glass sample was ground to below 0.074 mm diameter, and α-Al₂O₃ was used as the reference sample. The heating rate was 10°C/min. Argon was used as protective gas. The microstructure was determined using a JSM-6510 scanning electron microscope (SEM; Jeol, Japan).

The measured physical and chemical properties of the glass-ceramics included flexural strength, density, and acid and alkaline corrosion resistance. Flexural strength was measured using a three-point bending method on a universal testing machine, the standard of the test sample is 40 mm long, 3 mm wide, and 4 mm high. Three or four samples were calculated according to formula (1), and the average flexural strength was obtained; the volume density of the samples was measured by Archimedes’ method; the acid and alkaline corrosion resistance tests were carried out by immersing...
samples for 15 days in 3% H₂SO₄ and 3% NaOH solution, respectively, and measuring their mass change.

\[ \sigma = \frac{3FL}{2bh^2} \]  

(1)

In formula (1), \( \sigma \) – flexural strength of specimens (MPa), \( F \) – the maximum load beared by a specimen at fracture (N), \( b \) – fracture width (mm), \( h \) – fracture height (mm).

2.3 Determination of heat-treatment temperature

Glass-ceramics were prepared by introducing 70% blast furnace slag and 1% Cr₂O₃ and 4% TiO₂ as nucleating agents to the composition. The differential scanning calorimetry (DSC) curve of the glass sample was carried out by DTA, as shown in Figure 2, and used to determine the nucleation and crystallization temperatures.

According to the crystallography theory [13], the precipitation of crystal nuclei needs some energy from the environment, which is an endothermic process; in contrast, crystallization is a phase transformation from unsteady state to steady-state, which is an exothermic process. The endo- and exothermic peaks in the DSC curve, therefore, respectively, represent the nucleation and crystallization processes of the glass. An exiguous endothermic peak occurred at about 710°C, and there were two obvious exothermic peaks at 944.7°C and 988.8°C [14].

To further determine the crystallization temperature, the glass sample was heat-treated at the temperatures of the two exothermic peaks. The microstructures of the samples after heat treatment are shown in Figure 3(a) and (b), and their flexural strengths were measured, as shown in Table 3.

SEM micrographs showed that the overall crystallization degree is relatively high in Figure 3(a), the grain distribution is uniform and compact, the grain growth degree is reasonable, the grain size is distributed in 10–30 microns, and the shape is mostly long columnar and massive crystals, as shown in point A; the crystallization temperature in Figure 3(b) is 989°C, and the grain size increases at higher temperatures. The grain size is distributed in 30–45 microns, as shown in point B. Most of them are massive crystals, some of them are even connected into flakes. The overall microstructure of grain distribution is sparse, and the residual glass phase is obvious.

![Figure 2: DTA curve of the glass sample.](image)

![Figure 3: Microstructures of glass samples after heat treatment at crystallization peak temperatures: (a) 945°C and (b) 989°C.](image)
The grain size, quantity, and distribution determine the physical and chemical properties of glass-ceramics [15,16]. The selection of an appropriate heat-treatment regime is a prerequisite for ensuring the good microstructure and properties of these materials. The average flexural strengths of the samples after heat treatment and the heat-treatment parameters used are shown in Table 3, in which $T_n$ and $T_c$ are nucleation and crystallization temperatures, respectively, and $t_n$ and $t_c$ are nucleation and crystallization times, respectively.

The average flexural strength of the glass-ceramic was 96.14 MPa when the crystallization temperature was 945°C, and it was 57.43 MPa when the crystallization temperature was 989°C. Therefore, the exothermic peak temperature at 945°C was determined to be the optimum crystallization temperature.

### 2.4 Optimization of heat-treatment parameters

Heat treatment is a key step in the preparation of glass-ceramics from blast furnace slag [17,18]. Its main

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**Table 3: Flexural strength at different crystallization temperatures**

| No. | $T_n$ (°C) | $t_n$ (h) | $T_c$ (°C) | $t_c$ (h) | Average flexural strength (MPa) |
|-----|------------|------------|------------|------------|-------------------------------|
| 1   | 770        | 1.5        | 945        | 1.5        | 96.14                         |
| 2   | 770        | 1.5        | 989        | 1.5        | 57.43                         |

**Table 4: Levels and factors of orthogonal test**

| Factors | Levels | $T_n$ (°C) | $T_c$ (°C) | $t_n$ (h) | $t_c$ (h) |
|---------|--------|------------|------------|-----------|-----------|
| 1       | 1      | 750        | 930        | 1.0       | 1.0       |
| 2       | 2      | 770        | 945        | 1.5       | 1.5       |
| 3       | 3      | 790        | 960        | 2.0       | 2.0       |
| 4       | 4      | 810        | 975        | 2.5       | 2.5       |

**Table 5: Flexural strength and orthogonal experimental design for different heat-treatment systems**

| No. | $T_n$ (°C) | $T_c$ (°C) | $t_n$ (h) | $t_c$ (h) | Flexural strength (MPa) |
|-----|------------|------------|-----------|-----------|-------------------------|
| 1   | 750        | 930        | 1.0       | 1.0       | 84.15                   |
| 2   | 750        | 945        | 1.5       | 1.5       | 96.14                   |
| 3   | 750        | 960        | 2.0       | 2.0       | 79.51                   |
| 4   | 750        | 975        | 2.5       | 2.5       | 61.46                   |
| 5   | 770        | 930        | 1.5       | 2.0       | 88.62                   |
| 6   | 770        | 945        | 1.0       | 2.5       | 54.52                   |
| 7   | 770        | 960        | 2.5       | 1.0       | 82.31                   |
| 8   | 770        | 975        | 2.0       | 1.5       | 48.06                   |
| 9   | 790        | 930        | 2.0       | 2.5       | 89.06                   |
| 10  | 790        | 945        | 2.5       | 2.0       | 92.36                   |
| 11  | 790        | 960        | 1.0       | 1.5       | 46.38                   |
| 12  | 790        | 975        | 1.5       | 1.0       | 68.82                   |
| 13  | 810        | 930        | 2.5       | 1.5       | 89.58                   |
| 14  | 810        | 945        | 2.0       | 1.0       | 87.84                   |
| 15  | 810        | 960        | 1.5       | 2.5       | 69.44                   |
| 16  | 810        | 975        | 1.0       | 2.0       | 44.61                   |

**Table 6: Range analysis of orthogonal experimental results for different heat-treatment systems**

| No. | $T_n$ (°C) | $T_c$ (°C) | $t_n$ (h) | $t_c$ (h) | Flexural strength (MPa) |
|-----|------------|------------|-----------|-----------|-------------------------|
| 1   | 750        | 930        | 1.0       | 1.0       | 84.15                   |
| 2   | 750        | 945        | 1.5       | 1.5       | 96.14                   |
| 3   | 750        | 960        | 2.0       | 2.0       | 79.51                   |
| 4   | 750        | 975        | 2.5       | 2.5       | 61.46                   |
| 5   | 770        | 930        | 1.5       | 2.0       | 88.62                   |
| 6   | 770        | 945        | 1.0       | 2.5       | 54.52                   |
| 7   | 770        | 960        | 2.5       | 1.0       | 82.31                   |
| 8   | 770        | 975        | 2.0       | 1.5       | 48.06                   |
| 9   | 790        | 930        | 2.0       | 2.5       | 89.06                   |
| 10  | 790        | 945        | 2.5       | 2.0       | 92.36                   |
| 11  | 790        | 960        | 1.0       | 1.5       | 46.38                   |
| 12  | 790        | 975        | 1.5       | 1.0       | 68.82                   |
| 13  | 810        | 930        | 2.5       | 1.5       | 89.58                   |
| 14  | 810        | 945        | 2.0       | 1.0       | 87.84                   |
| 15  | 810        | 960        | 1.5       | 2.5       | 69.44                   |
| 16  | 810        | 975        | 1.0       | 2.0       | 44.61                   |

**Notes:** $\Sigma(1)$: sum of flexural strength of level 1; $\Sigma(2)$: sum of flexural strength of level 2; $\Sigma(3)$: sum of flexural strength of level 3; $\Sigma(4)$: sum of flexural strength of level 4; $\Sigma(1)/4$: average flexural strength of level 1; $\Sigma(2)/4$: average flexural strength of level 2; $\Sigma(3)/4$: average flexural strength of level 3; $\Sigma(4)/4$: average flexural strength of level 4; $R$: range of flexural strength.

**Figure 4:** Optimal heat-treatment system.
The purpose is to transform the glass into a polycrystalline solid material containing a large number of crystalline phases. The main technical parameters include nucleation and crystallization temperature and time. In this study, the flexural strength was taken as the comparative index, and an orthogonal experiment was designed to determine the optimum parameters. The ranges of nucleation and crystallization temperatures were determined from the DSC curve.

The endothermic peak at 710°C on the DSC curve represents the glass transition temperature \( T_g \). According to the literature, the nucleation temperature is generally higher than the glass transition temperature by about 40–80°C [19,20] and the crystallization temperature is generally the peak exothermic temperature – of 945°C, in this case. In this study, an orthogonal experimental design using four factors and four levels of \( k (4^4) \) was carried out for the main heat-treatment parameters of nucleation temperature, nucleation time, crystallization temperature, and crystallization time. The nucleation temperature range was 750–810°C, and the crystallization temperature ranged from 930 to 975°C. The time intervals for nucleation and crystallization were 0.5 h, ranging from 1.0 h to 2.5 h. The levels and factors of the orthogonal test are listed in Table 4; the flexural strength and orthogonal experimental design are listed in Table 5; the results are listed in Table 6.

Tables 5 and 6 indicate that the range of crystallization temperature \( T_c \) was largest \( (R = 32.27) \), the range of nucleation time \( t_n \) was second-largest \( (R = 24.01) \), and those of nucleation temperature \( T_n \) and crystallization time \( t_c \) were almost the same \( (11.94 \text{ and } 12.01, \text{ respectively}) \). Therefore, crystallization temperature had the greatest influence on the flexural strength, followed by nucleation time. The nucleation temperature and crystallization time had the least influence on the flexural strength of the blast furnace slag glass-ceramic.

### 2.5 Determination of optimal heat-treatment system and properties of glass-ceramic

The optimum heat-treatment parameters to prepare these glass-ceramics were determined by orthogonal experiment using a nucleation temperature of 750°C for 2.5 h and crystallization temperature of 930°C for 1 h. The heating rate was 5°C/min before nucleation and 3°C/min before crystallization. After heat treatment, the samples were cooled in the furnace. The optimum heat-treatment system is shown in Figure 4. Properties of this glass-ceramic prepared under the optimum heat-treatment system, such as flexural strength, density, porosity, acid resistance, alkali resistance, and water absorption, are compared with those reported for marble, granite, and similar materials in Table 7. The flexural strength of the blast furnace slag glass-ceramic under the optimum heat-treatment regime reached 102.2 MPa, which is superior to that of 16 points in the orthogonal experiment. Compared with other studies, the other physical and chemical properties of the glass-ceramic were also reasonably superior, ranking in the upper-middle level [21–23].

### 3 Conclusions

(1) Using a 70% blast furnace slag from Baotou Iron and Steel Company as the main raw material and 1% \( \text{Cr}_2\text{O}_3 \) and 4% \( \text{TiO}_2 \) as nucleating agents, an orthogonal experiment was carried out to optimize the heat-treatment process for preparing \( \text{CaO–SiO}_2–\text{MgO–Al}_2\text{O}_3 \) glass-ceramics. The results showed that the crystallization temperature had the greatest influence on the flexural strength of the glass-ceramics, followed by nucleation time; nucleation temperature and crystallization time had the least influence.
(2) The optimum heat-treatment system for preparing glass-ceramics from this large-scale blast furnace slag comprised a nucleation temperature of 750°C for 2.5 h and a crystallization temperature of 930°C for 1 h. Under these conditions, the flexural strength of the glass-ceramics reached 102.2 MPa.

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