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Preparation and Properties of Blast Furnace Slag Glass Ceramics Containing Cr_2O_3

<https://doi.org/10.1515/htmp-2019-0029>

Received May 09, 2018; accepted December 09, 2018

Abstract: In this study, the blast furnace slag of the Baotou Steel and Iron Company was used as the main raw material to prepare glass ceramics with diopside as the main crystal phase. The composition of the parent glass was designed by thermodynamic calculations with FactSage software. Small amounts of the nucleation agent Cr_2O_3 were then added to the parent glass to induce crystallization. Differential thermal analysis was used to determine the nucleation and crystallization temperatures of the glasses, and scanning electron microscopy and X-ray diffraction were adopted to determine the microstructures and phase compositions of the glasses after heat treatment, respectively. The results showed that glass ceramics of the diopside phase can be prepared with up to 73 wt% blast furnace slag when 1.44–1.91 wt% Cr_2O_3 is added, and the ceramics have uniform compact grains and a high bending strength of about 84.6–101.7 MPa. In addition, the mechanical properties are better than those of natural marble and granite. These results provide basic information and a scientific basis for industrial production of diopside glass ceramics using molten blast furnace slag as the main raw material.

Keywords: glass ceramics; blast furnace slag; nucleation agents; Cr_2O_3

Introduction

The blast furnace (BF) slag is the highest quantity metallurgical slag in the iron and steel industry, which has been used as the main raw material to produce cement.

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Although its utilization ratio has reached 78% in China, its additional value is rather low [1, 2]. In recent years, investigation of glass ceramics prepared from solid waste, such as BF slag, tailings, and fly ash, has gradually become an important issue [3, 4]. It is important to prepare glass ceramics using molten BF slag to improve utilization and the added value of iron smelting slag, reduce energy consumption, increase the economic benefit, and alleviate environmental pollution. In BF slag, the mass percentage of CaO , SiO_2 , Al_2O_3 and MgO is about 90%, which is the ideal raw material for preparing glass ceramics. Glass ceramics with diopside or wollastonite as the main crystal phase have high strength and good chemical resistance. Therefore, they are widely used as building decoration materials [5, 6]. Because of the low crystallization capacity of the glass [7], it is necessary to add a small amount of nucleating agents to promote precipitation of diopside and wollastonite. Omara et al. [8] suggested that addition of Cr_2O_3 as a nucleating agent can promote precipitation of diopside or wollastonite from the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ glass system. However, Erkmen et al. [9] showed that the crystalline phases only exist on the surface of the sample, and akermanite ($2\text{CaO}\cdot\text{MgO}\cdot2\text{SiO}_2$) and gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) are the main crystallization phases when glass ceramics produced from BF slag are added with 5 wt% TiO_2 , 10 wt% TiO_2 , and 5 wt% $\text{TiO}_2 + 5$ wt% Cr_2O_3 . Yang et al. [10] found that when a high proportion of BF slag is introduced, scum is generated in the liquid glass surface layer during the melting process and both phase separation and crystallization of the glass are difficult. Similar problems have also been encountered in many other studies. Therefore, the mass ratio of BF slag should be limited to less than 50%, which leads to lower utilization efficiencies for the slag and its latent heat. Thus, it will lead to high cost and energy consumption for industrial production of glass ceramics when molten blast BF slag is used as the main raw material. To overcome the above problems, in this study, preparation and the properties of BF slag glass ceramics containing Cr_2O_3 were investigated for mixtures containing of more high proportion of molten slag. The results will provide a scientific basis for industrial production of diopside glass ceramics using molten BF slag as the main raw material.

Materials and methods

Raw materials

The main raw materials for preparation of the parent glass were BF slag, quartz sand, and small amounts of the analytical reagents CaO, MgO, and Al_2O_3 . Table 1 presents the chemical composition of BF slag used. CaO and Al_2O_3 powder were provided by the third chemical reagent plant (Tianjin, China), MgO powder was provided by Yongda chemical reagent company (Tianjin, China). First, the particles of each raw material were ground to sizes smaller than 0.074 mm. The raw materials were then completely mixed with addition of a small amount of Cr_2O_3 as a nucleating agent to promote crystallization of the glass. The added amount of Cr_2O_3 in each sample is shown in Table 2.

Preparation of the parent glass

Mixtures were prepared according to the ratios in Table 2. The mixtures were then completely mixed, placed in corundum crucibles, and melted in a furnace at 1450°C for 3 h using Si–Mo rods as heaters. The furnace was heated from room temperature to 200°C at a heating rate of 10°C/min, from 200 to 1000°C at a heating rate of 8°C/min, and from 1000 to 1450°C at a heating rate of 4°C/min. The melts were then poured into steel molds. The molds containing the cooled melts were placed in another furnace and held at 600°C for 2 h. The glasses were obtained after the annealing process.

Detection and analysis methods

Differential thermal analysis

Differential thermal analysis (DTA) was performed to determine the nucleation and crystallization temperatures of the glasses. The thermal variations of the phase transformations were analyzed using about 10–15 mg powdered glass samples. The $\alpha\text{-Al}_2\text{O}_3$ powder was used as a reference material in the temperature range from room temperature to 1250°C in an argon atmosphere at a heating rate of 10°C/min.

X-ray diffraction

An X-ray diffractometer (D8 ADVANCE, Germany) was used to identify the crystalline phases present in the glass samples after heat treatment. The particle sizes of the samples were ground to sizes less than 200 mesh and the experimental conditions were a copper target, a working voltage of 40 kV, a working current of 80 mA, a scanning angle range of 20°–80°, and a scanning angular velocity of 3°/min.

Scanning electron microscopy

Scanning electron microscopy (SEM) was performed with an S-3400 scanning electron microscopy (Japan) to observe the microstructures of the glass samples after heat treatment. The polished surfaces of the samples

Table 1: Chemical composition of the BF slag provided by the iron plant of the Baotou iron and steel company (wt%).

SiO_2	CaO	MgO	Al_2O_3	FeO	Na_2O	K_2O	F	TiO_2	Others
34.06	37.79	9.67	13.08	1.65	0.34	0.31	0.27	0.93	1.90

Table 2: Mass percentage of raw material for the six samples containing Cr_2O_3 and the prepared glass composition (wt%).

No.	Mass percentage of raw material							Chemical composition of the prepared glass							
	BF slag	Quartz sand	CaO	Al_2O_3	MgO	Cr_2O_3	CaO	SiO_2	Al_2O_3	MgO	Cr_2O_3	FeO	Na_2O	K_2O	Others
1	72.96	22.78	1.84	0.89	1.53	0.00	29.41	47.63	10.43	8.59	0.00	1.20	0.25	0.23	2.26
2	72.97	22.54	1.68	0.84	1.49	0.48	29.26	47.39	10.38	8.55	0.48	1.20	0.25	0.23	2.26
3	72.99	22.30	1.53	0.78	1.44	0.96	29.11	47.16	10.33	8.50	0.96	1.20	0.25	0.23	2.26
4	72.98	22.07	1.38	0.73	1.40	1.44	28.96	46.93	10.28	8.46	1.44	1.20	0.25	0.23	2.26
5	73.00	21.83	1.24	0.67	1.35	1.91	28.83	46.69	10.22	8.41	1.91	1.20	0.25	0.23	2.26
6	72.96	21.59	1.14	0.62	1.31	2.37	28.71	46.44	10.16	8.37	2.37	1.20	0.25	0.23	2.26

were corroded by hydrofluoric acid (4 vol%) for 40 s and then observed after gold sputtering treatment.

Determination of the flexural strength

The flexural strengths of the samples after heat treatment were determined using an electronic universal testing machine (CSS-88000) by the three-point bending method. The sizes of the samples were 40 mm (length) $\times$ 4 mm (width) $\times$ 3 mm (height). The reported flexural strengths are the average of measurements for 3–6 samples.

Results and discussion

Thermodynamic prediction of the crystallization mineral composition of the parent glass

FactSage software contains a thermodynamic database with rich information and it has a powerful calculating function under the Windows operating system [11]. First, the Equilib module of the software was used to calculate the amounts of the crystallization minerals if the parent glass sample was heat treated in the temperature range 1000–1100°C. The calculated results are given in Table 3. If the parent glass containing 31 wt% CaO, 49 wt% SiO₂, 11 wt% Al₂O₃, and 9 wt% MgO in Table 3 completely changes into crystallization minerals, the mass percentages of the different minerals are 50.3–51.2 wt% diopside (CaMg(SiO₃)₂), 23.7–24.2 wt% wollastonite (CaSiO₃), 7.0–7.2 wt% akermanite (Ca₂Mg(Si₂O₇)), and 18.1–18.3 wt% anorthite (Al₂Ca(SiO₄)₂) when the parent glass is heat treated at 1000–1100°C, in which the main crystal phases were diopside and wollastonite phase. Chemical composition design of the parent glass can ensure that diopside and wollastonite are the main crystal phases, so the chemical composition in Table 3 was selected to prepare the glass ceramics.

Nucleation and crystallization temperatures of the glasses containing Cr₂O₃

Precipitation of a new phase (crystal nucleus) from the parent glass is an endothermic process, but transformation of the glass from amorphous to crystalline is an exothermic process [12]. According to the Tammann curves, the endothermic and exothermic peaks in the DTA curve represent nucleation and crystallization of glass, respectively. That is, the crystal nuclei will precipitate close to the temperature corresponding to the endothermic peak and crystals will grow at the temperature corresponding to the exothermic peak. In addition, the sharper the exothermic peak, the higher the crystallization rate.

The DTA curves of the glasses containing different mass percentages of Cr₂O₃ as a nucleating agent are shown in Figure 1. It can be seen that there is an inconspicuous endothermic peak and obvious clear exothermic peak in each DTA curve. The temperatures corresponding to the inconspicuous endothermic peaks in the DTA curves (765–768°C) are the glass transition reactions. This shows that the added amount of Cr₂O₃ hardly affects the nucleation temperature of the glass, but it has a clear influence on the crystallization

Figure 1: DTA curves of the glass samples containing Cr₂O₃.

Table 3: Mass percentages of the crystallization minerals for the parent glass calculated by Factsage (wt%).

Chemical composition of the parent glass				Calculated crystallization minerals			
CaO	SiO ₂	Al ₂ O ₃	MgO	Diopside	Wollastonite	Akermanite	Anorthite
31	49	11	9	50.3–51.2	23.7–24.2	7.0–7.2	18.1–18.3

temperature. The significant exothermic peaks at 1113, 1109, 1061, 1068, 1028, and 1008°C for samples 1–6, respectively, are the crystallization temperature, which clearly decreases as the amount of Cr_2O_3 gradually increases from 0 to 2.37 wt%. When the amount of Cr_2O_3 is less than 0.48 wt% (samples 1 and 2), the crystallization peak temperatures are higher than 1100°C, the peak areas are small, and the peak shapes are not sharp. Thus, crystallization is difficult when the glass samples are heat treated at their exothermic peak temperatures. However, when the amount of Cr_2O_3 is 0.96, 1.44, 1.91, or 2.37 wt%, the exothermic peaks are sharper and their peak temperatures are lower than 1100°C. The DTA results show that the nucleating agent Cr_2O_3 promotes crystallization of the glass. Cr^{3+} in the glass attracts non-bridged oxygen atoms and makes peripheral cations form an oriented arrangement. Furthermore, it makes heterogeneous nucleation of the Cr-enriched phase easy, which induces crystals to form. Therefore, the crystallization peak temperature decreases [13].

Mineral composition of the glasses containing Cr_2O_3 after heat treatment

According to related studies [14–16], the optimum nucleation temperature is usually 30–70°C higher than the glass transition temperature and the crystallization temperature is close to the exothermic peak temperature in the DTA curve. In this study, the nucleation temperature of the glass is determined to be 60°C higher than its glass transition temperature. The six glass samples (1–6) were heat treated for 1 h at their nucleation temperatures (827°C, 825°C, 827°C, 828°C, 827°C, and 826°C) and crystallization temperatures (1113°C, 1109°C, 1061°C, 1068°C, 1028°C, and 1008°C). The XRD patterns of the glass samples after heat treatment are shown in Figure 2.

From the thermodynamic calculation, when the designed parent glass is heat treated at a temperature of 1000–1100°C, the mineral mass percentages are 50.3–51.2 wt% diopside ($\text{CaMg}(\text{Si}_2\text{O}_6)$), 23.7–24.2 wt% wollastonite (CaSiO_3), 7.0–7.2 wt% akermanite ($\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$), and 18.1–18.3 wt% anorthite ($\text{Al}_2\text{Ca}(\text{SiO}_4)_2$). It can be seen that diopside and wollastonite are the main crystal phases. However, the XRD pattern of the sample without Cr_2O_3 (sample 1) in Figure 2 shows that $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ is the main crystal phase that precipitated from the glass sample, and there are also peaks for $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ and $\text{Al}_2\text{Ca}(\text{SiO}_4)_2$. $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ and $\text{CaMg}(\text{Si}_2\text{O}_6)$ have a

Figure 2: XRD patterns of the glass samples containing Cr_2O_3 after heat treatment.

similar structure and properties, and they can be regarded as the same type of mineral. Therefore, the detected mineral species are consistent with the calculated results. However, based on the estimation of XRD peak intensity, the amounts of the $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ phase ranges from 74.5 to 80.0 wt%, different from its thermodynamic calculated value of 50.3–51.2 wt%.

The glass includes the four chemical components CaO , SiO_2 , Al_2O_3 , and MgO , with 73 wt% of the chemical components coming from BF slag. According to many studies [17, 18], most of the chemical components exist as $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ complex oxides in the slag. Although 27% of these chemical components are introduced as free oxides, they hardly affect precipitation of $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ from the glass. Therefore, the main crystal phase of the glass samples after heat treatment is $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ rather than $\text{CaMg}(\text{Si}_2\text{O}_6)$.

When the mass percentage of Cr_2O_3 is in the range 0.48–1.91 wt% (samples 2–5), $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ becomes the main crystal phase, which can be regarded as $\text{CaMgSi}_2\text{O}_6$, but the $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ phase are not detected revealed by the XRD patterns in Figure 2. Thus, the nucleating agent affects the mineral composition of the glass after heat treatment. When the mass percentage of Cr_2O_3 is 2.37 wt%, from the XRD pattern of sample 6, the diffraction peaks of $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ become weaker, but those of $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ appear again. Therefore, Cr_2O_3 can promote generation of heterogeneous nucleating positions and improve nucleation of glass, which can promote precipitation of $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ crystals. However, the mass percentage of Cr_2O_3 should be controlled in the range 0.48–1.91 wt% to obtain the expected main crystal phase.

Microstructures of the glass ceramics containing Cr_2O_3

SEM images of the glass ceramic samples containing 0, 1.44, 1.91, and 2.37 wt% Cr_2O_3 (samples 1, 4, 5, and 6) are shown in Figure 3. For sample 1 without any nucleating agent, there are many microcracks and a few unevenly distributed large crystal grains. This is because of the higher crystallization temperature and weaker crystallization ability of the glass. The irregular grains of samples 4 and 5 are dense and uniform and the grain size is about 2–3 μm . Because it contains more nucleating agent, the grains of sample 5 are more compact than those of sample 4. However, precipitation of grains is unfavorable if the glass contains a large amount of Cr_2O_3 . For sample 6 containing 2.37 wt% Cr_2O_3 , neither the distribution of the grains nor their sizes are uniform, because a large amount of Cr_2O_3 makes the molten glass glutinous, which inhibits precipitation of crystals [19]. Therefore, the mass percentage of Cr_2O_3 should be controlled in the range 1.44–1.91 wt% to obtain a green glass ceramic with an ideal microstructure. According to the above analysis, the high field strength chromium ions (Cr^{3+}) obtained from Cr_2O_3 in an oxidizing atmosphere make the ambient ions order. In addition, the solubility of Cr_2O_3 is very low and most of the Cr_2O_3 will exist as

solid particles in the molten glass and form many tiny crystal nuclei [20]. Therefore, Cr_2O_3 promotes precipitation of diopside crystals when its mass percentage is lower than 1.91 wt%.

Flexural strengths of the glass ceramics containing Cr_2O_3

The flexural strength is a very important factor for the performance of glass ceramics. The flexural strengths of the glass ceramic samples were determined by the three-point bending method, and the results are given in Figure 4. It is seen that the flexural strength firstly increases and then decreases with increasing amount of Cr_2O_3 . The flexural strength of the sample containing 1.91 wt% Cr_2O_3 is the highest (101.7 MPa), followed by the sample containing 1.44 wt% Cr_2O_3 (84.6 MPa). The flexural strength of the sample containing 2.37 wt% Cr_2O_3 is even lower (56.5 MPa) than the sample containing 1.44 wt% Cr_2O_3 .

The flexural strengths of the samples are closely related to their microstructures. The higher flexural strengths of samples 4 and 5 (containing 1.44 and 1.91 wt% Cr_2O_3 , respectively) are because of the uniformly distributed compact grains. For samples 1 (containing no

Figure 3: SEM images of the samples after heat treatment: (a) sample 1, (b) sample 4, (c) sample 5, and (d) sample 6.

Figure 4: Flexural strengths of the samples after heat treatment.

nucleating agents) and 6 (containing 2.37 wt% Cr_2O_3), the flexural strengths are lower because they have microcracks, a low crystallization rate, or a heterogeneous crystal grain distribution. The flexural strength of natural granite is 15–38 MPa and that of natural marble is 7–19 MPa [21]. In comparison, the glass ceramics reported in this study have good mechanical properties, with flexural strengths of 84.6–101.7 MPa for mass percentages of Cr_2O_3 of 1.44–1.91 wt%. Thus, the mechanical strengths of the glass ceramics are much higher than those of natural granite and natural marble [21].

It is feasible that a technique can be developed to produce glass ceramics with high added value using molten BF slag as the main raw material. This is of great significance for improving utilization and the added value of iron smelting slag and reducing environmental pollution.

Conclusions

- (1) Parent glass composed of 31 wt% CaO, 49 wt% SiO_2 , 11 wt% Al_2O_3 , and 9 wt% MgO has been designed by thermodynamic calculations. Among the raw materials, the mass percentage of the BF slag is up to 73%, and the other raw materials are quartz sand and small amounts of pure chemical reagents. When the mass percentage of Cr_2O_3 is 1.44 or 1.91 wt%, glass ceramics of the diopside phase with uniform crystal grains can be prepared.
- (2) The nucleating agent Cr_2O_3 has a clear effect on the crystallization temperature of the parent glass, which gradually decreases with increasing mass percentage of Cr_2O_3 , and Cr_2O_3 also promotes crystallization of the glass.
- (3) In the process of preparing glass ceramics from BF slag, Cr_2O_3 promotes precipitation of diopside crystals. When the mass percentage of Cr_2O_3 is in the range 0.48–1.91 wt%, the expected main crystal phase $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$ precipitates from the parent glass.
- (4) When the mass percentage of Cr_2O_3 is controlled within the range 1.44–1.91 wt%, a microstructure composed of compact uniform grains can be obtained. The sizes of the crystal grains are about 2–3 μm . The flexural strengths of the glass ceramics are 84.6–101.7 MPa and their mechanical strengths are much higher than those of natural granite and natural marble.

Acknowledgements: This work was financially supported by the Natural Science Foundation of Inner Mongolia (Grant No. 2018LH05026), National Natural Science Foundation of China (Grant No. 51364030) and Key Research Projects of Inner Mongolia Colleges and Universities (Grant No. NJZZ16153 and Grant No. NJZZ157).

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