

A preparation and performance study of glass-ceramic glazes derived from blast furnace slag and fly ash

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Glass-ceramic glazes have been prepared successfully via crystallization from blast-furnace slag (BFS), fly ash (FA) fluxed with potash feldspar and borax. The crystalline behavior of glass-ceramic glazes was investigated using differential thermal analysis and thermogravimetric analysis (DTA/TG), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results revealed that the major crystalline phases are anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and crystalline phases disperse well in glassy phases with a uniform size of $1\ \mu\text{m}$. Glass-ceramic glazes possess low density, low water absorption, perfect stain resistance, acid resistance and alkali resistance. The thermal expansion coefficient of glass-ceramic glazes is steady up to $800\ ^\circ\text{C}$ with an average value of $7.2 \times 10^{-6}/\text{K}$. Final results suggest that BFS and FA have potential to be vitrified into economically and environmentally low-cost glass-ceramic glaze materials.

Key words: Blast-furnace slag (BFS), Fly ash (FA), Glass-ceramic glazes, Anorthite, Akermanite.

Introduction

BFS and FA are two widespread industrial waste residues with large outputs. BFS is a by-product of steel enterprises discharged from blast furnaces in the steel smelting process, essentially consisting of SiO_2 , CaO , Al_2O_3 , MgO along with other compounds such as Fe_2O_3 , TiO_2 , MnO_2 . FA is a vastly produced waste in power stations, containing a large number of glass phases, a small amount of mullite and quartz crystalline phases as well as a few residual ore minerals [1]. The main components of these wastes are calcium-aluminum-silicate glass. However, FA is relatively abundant in Al_2O_3 while BFS in CaO . BFS and FA have been used for the manufacture of cements, glass-ceramics, ceramic tiles, geopolymers, paving materials, construction materials etc [2-10]. Liu *et al.* [11] prepared glass-ceramics with a major crystalline phase of gehlenite using BFS and 5 wt% potash feldspar additives. Vasilopoulos *et al.* [12, 13] synthesized bulk nucleated glass-ceramics using FA as a precursor. Dana *et al.* [14] added BFS and FA together to traditional porcelain tiles and found that microcrystallines were present. Nevertheless, a considerable amount of BFS and FA is still undisposed, which would not only occupy land and pollute the environment, but also be a waste of resources [15, 16]. Therefore, searching for new applications of BFS and FA is needed badly.

Glaze is a thin vitreous coating applied to ceramics to decorate, strengthen or waterproof them by sintering. Consisting of both glassy phases and different crystalline phases, glass-ceramic glazes can achieve the desired properties and show superior performance to traditional amorphous glazes [17, 18]. They possess good mechanical strength, chemical stability, thermal stability, beautiful appearance and easy-to-clean surfaces [19-22]. Most studies presently focus on preparing glazes from precise minerals and chemical materials, so the cost is high. However, the cost may be reduced and quality improved by combined use of BFS and FA, and in some cases, the combination is suitable for the formation of crystalline phases [14]. It would be interesting to try to produce glass-ceramic glazes with BFS and FA serving as raw materials.

In this study, BFS and FA were used to prepare glass-ceramic glazes, mixed with potash feldspar and borax for easier maturation. Moreover, the glass-ceramic glazes obtained possess many excellent properties.

Experimental Procedure

BFS came from Anyang iron Corporation (China) and FA was provided by Zhengzhou Thermal Power Plant (China). Our previous study indicated that BFS was mainly in a glassy state with a small amount of gehlenite [11]. The composition point of glass-ceramic glazes was designed to form major crystalline phase of anorthite based on the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ternary phase equilibrium diagram. Table 1 shows the chemical analyses of BFS, FA and glass-ceramic glaze by X-ray fluorescence (Model XRF-1700, Shimadzu,

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Table 1. Chemical compositions of BFS, FA and glass-ceramic glaze (parts by weight)

Composition/%	SiO ₂	CaO	Al ₂ O ₃	MgO	K ₂ O	Na ₂ O	B ₂ O ₃	TiO ₂	Fe ₂ O ₃
BFS	37.63	36.36	12.54	10.25	-	-	-	0.79	0.45
FA	55.20	4.23	26.20	1.26	1.65	0.50	-	0.98	5.06
Glass-ceramic glaze	51.51	10.25	18.85	2.91	4.73	0.83	1.46	0.54	1.93

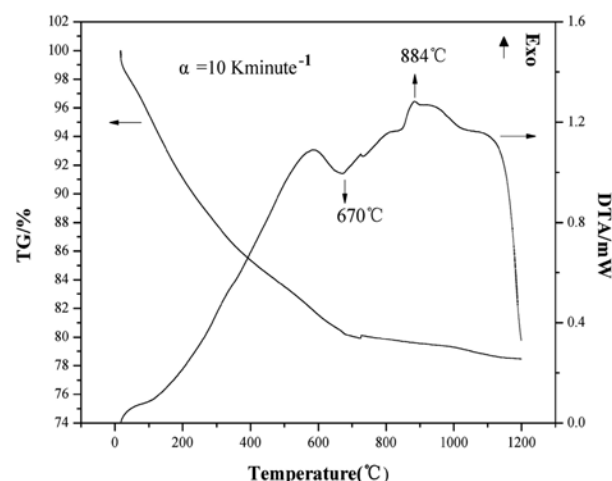
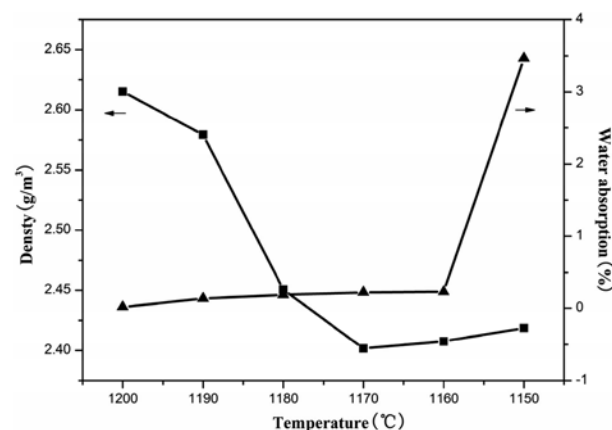
Japan). The total utilization rate of industrial waste residues was 60 wt%. Some potash feldspar and borax additives were added as fluxing agents.

BFS was pre-pulverized by ball milling and 30 μm size particles were achieved. To obtain glass-ceramic glazes, the weighed batches according to the formula were ball milled for 20 h in a porcelain mill containing 100 g alumina balls and 150 ml distilled water. The dried and thoroughly mixed powders were uniaxially pressed in a steel die at room temperature, using a hydraulic pressure of 60 MPa without any binder. The resulting green glass-ceramic glazes were sintered at different temperatures (1200 °C, 1190 °C, 1180 °C, 1170 °C, 1160 °C or 1150 °C) and held for 1 h in air, separately.

The thermal behavior of glass-ceramic glazes was studied by DTA/TG analyses (Model STA-409PC/4/H, Luxx, Germany) in air with a heating rate of 10 K·minute⁻¹ from room temperature to 1200 °C. After sintering, glass-ceramic glazes were characterized by XRD (Model XD-3, Pgeneral, China) with Cu K α radiation (0.15418 nm, 36 kV, 20 mA) at a scan rate of 2°/minute. The heat-treated glass-ceramic glazes were polished and then corroded chemically in HF (5 vol%) for 20 s, and gold coated for microstructural analysis. Microstructures of uncorroded and corroded surfaces were characterized by SEM (Model Quanta-200, FEI, Netherlands). The density and water absorption of glass-ceramic glazes were measured by the Archimedes method. The thermal expansion coefficient was measured using a ZRP-03 thermal dilatometer. Glass-ceramic glazes were corroded in a 100 g/l NH₄Cl solution for 48 h to observe the surface appearance in an acid resistance test, while in a 100 g/l KOH solution for 96 h in an alkali resistance test. Chrome green and 13 g/l iodine were used as pollutant sources in stain resistance tests.

Results and Discussion

DTA/TG curves of a glass-ceramic glaze powder are plotted in Fig. 1. The DTA result presents a clear endothermic peak at 670 °C and an exothermic peak at 884 °C corresponding to a weight loss and weight constant on the TG curve, respectively. A decrease of the base line is observed from 900 °C without a significant weight loss, which is related to a decreased density of the powder. Accordingly, crystallization occurs in glazes during heat treatments. TiO₂ and Fe₂O₃ contained in the BFS and FA act as nucleating agents and promote the formulation of glass-ceramic glazes, dynamically. The nucleation temperature is at around 670 °C, and the crystallization temperature

**Fig. 1.** DTA/TG curves of the glass-ceramic glaze powder.**Fig. 2.** Density and water absorption of glass-ceramic glazes sintered at different temperatures.

is at around 884 °C. Taking into account the DTA result, glass-ceramic glazes were obtained by nucleating at 670 °C for 1 h and crystallizing at 884 °C for 1 h. Heating rates were made to be 7 K·minute⁻¹ from room temperature to 884 °C and 4 °K·minute⁻¹ at higher temperatures, which are in accord with the general sintering rule.

The density and water absorption of glass-ceramic glazes sintered at different temperatures are presented in Fig. 2. With a sintering temperature decreasing from 1200 °C to 1150 °C, the density drops dramatically to achieve a minimum at 1170 °C and then increases slightly, while water absorption changes steadily at first but increases sharply at 1150 °C. One possible explanation may be that densification is performed more completely and bubbles are discharged more absolutely above 1160 °C to result in

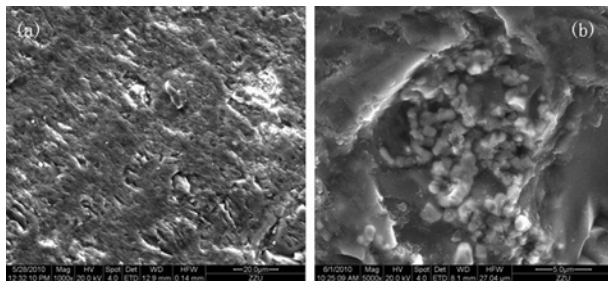


Fig. 3. SEM images of uncorroded (a) and corroded (b) glass-ceramic glaze after sintering at 1160 °C.

a higher bulk density. Of course, a low density is usually favored for decorative building materials in the case of other conditions being consistent. The structure of glass-ceramic glazes fired at 1150 °C is not dense enough so that the water absorption is a little high. To compare comprehensively, the optimum sintering temperature is 1160 °C, which endows glass-ceramic glazes with a relatively low density and water absorption.

Fig. 3 demonstrates microstructures of uncorroded and corroded surfaces of glass-ceramic glazes at different magnifications obtained by SEM after sintering at 1160 °C. The uncorroded glass-ceramic glaze shows a flat and dense texture (Fig. 3(a)), which is in accord with a low water absorption. Glass-ceramic glaze consists of a glassy matrix and crystalline particles generated by segregation of ions from the matrix. Crystalline phases dispersed in glassy phases are visible as well-shaped granular particles with a uniform size of 1 μm (Fig. 3(b)). Because this micro-crystalline dimension is close to the wavelengths of visible light, glass-ceramic glaze strongly and uniformly scatters visible light, and thus achieves a glossy surface. The existing of crystalline particles after the corrosion treatment suggests that crystalline phases can lead to a better corrosion resistance. Better mechanical properties of glass-ceramic glazes when compared with the usual vitreous glazes could also due to the presence of crystalline phases.

An XRD pattern of the glass-ceramic glaze after sintering at 1160 °C is illustrated in Fig. 4. This clearly indicates that crystallization occurs, which is in agreement with the results of DTA and SEM. Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) is crystallized and a small amount of akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) emerges also. Both of these crystalline phases possess good mechanical properties, wear resistance and corrosion resistance.

The thermal expansion coefficient (α) values at different temperatures of glass-ceramic glazes after sintering at 1160 °C are shown in Fig. 5. There are some fluctuations in the α value for each temperature, but the difference is not significant, which can be regarded as steady up to 800 °C with an average value of $7.2 \times 10^{-6}/\text{K}$. The glass-ceramic glazes are appropriate for tiles having higher α values than this. In this way, the thermal expansion coefficient mismatch between body and the glass-ceramic glaze would generate a residual compressive stress, which would do well for their interfacial adhesion and thus benefit the

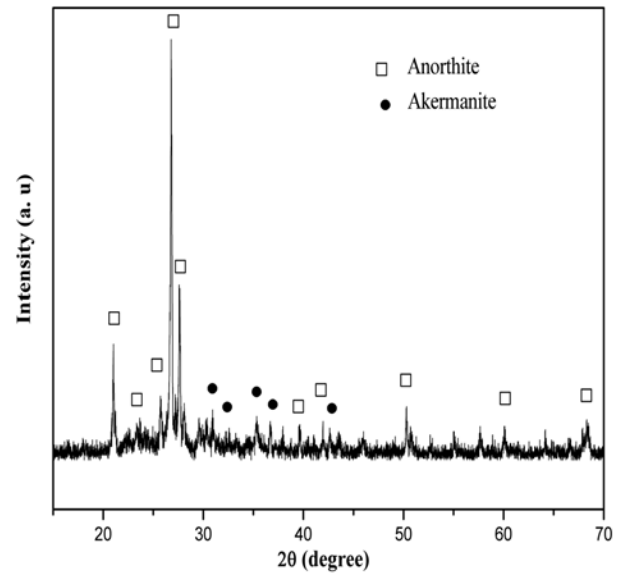


Fig. 4. XRD pattern of glass-ceramic glaze after sintering at 1160 °C.

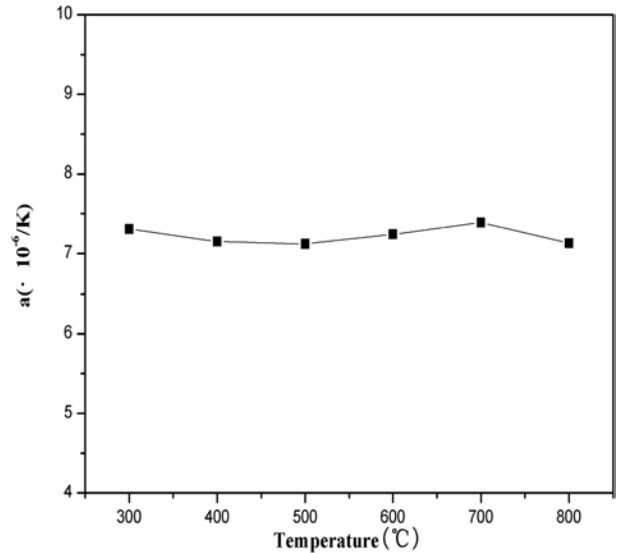


Fig. 5. Thermal expansion coefficient values at different temperatures of glass-ceramic glaze after sintering at 1160 °C.

Table 2. Properties of glass-ceramic glaze after sintering at 1160 °C

Test	Glass-ceramic glaze	Glass-ceramics	Ceramic tiles
Density/ $\text{g}\cdot\text{cm}^{-3}$	2.4076	2.36-2.65	2.3-2.4
Water absorption/%	0.2282	0.1-0.5	4-18
Acid resistance	Class A(0)	0.5	0
Alkali resistance	Class A(0)	0	0.02
Stain resistance	Class 5	-	-

overall performances of tiles.

Some properties of the glass-ceramic glaze obtained as determined by certain standard tests [23] are listed in Table 2. The glass-ceramic glaze shows a good performance and the water absorption is at a low level. The stain resistance

is Class 5, which means that it can be easily cleaned in water. The acid resistance and alkali resistance are all Class A, which indicates there is no visible difference before and after the acid or alkali treatment. In brief, the glass-ceramic glaze obtained was satisfactory in terms of density, surface texture, and met the requirement of standard tests for glazed wall tiles.

Conclusion

The present study indicated that BFS and FA can be fluxed with potash feldspar and borax to produce a glass-ceramic glaze by nucleating at 670 °C, and crystallizing at 884 °C. Experimental results can be summarized as follows.

(1) It was possible to crystallize without the addition of nucleating agents possibly due to the existence of TiO_2 and Fe_2O_3 in the raw materials. The best sintering temperature of the glass-ceramic glaze was 1160 °C.

(2) The major crystalline phase was anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and a small amount of akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) was precipitated. Granular microcrystallines with a uniform size of 1 μm were dispersed well in glassy phases.

(3) The thermal expansion coefficient value was steady up to 800 °C with an average value of $7.2 \times 10^{-6}/\text{K}$. The glass-ceramic glaze sintered at 1160 °C was satisfactory in terms of density, surface texture, and met the requirement of standard tests for glazed wall tiles.

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