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Preparation and properties of glass–ceramics derived from blast-furnace slag by a ceramic-sintering process

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Abstract

Glass–ceramics were synthesized using ground blast-furnace slag and potash feldspar additives by a conventional ceramic-sintering route. The results show 5 wt% potash feldspar can enhance the sintering properties of blast-furnace slag glass and the results glass–ceramics have desirable mechanical properties. The main crystalline phase of the obtained glass–ceramic is gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$). A high microhardness of 5.2 GPa and a bending strength higher than 85 MPa as well as a water absorption lower than 0.14% were obtained.
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Keywords: Blast-furnace slag; Sintering process; Glass–ceramics; Crystallization

1. Introduction

Glass–ceramics are fine-grained polycrystalline materials formed when glasses of suitable compositions are heat-treated and thus undergo controlled crystallization to reach a lower energy crystalline state [1]. Since the early 1960s, using waste to prepare glass–ceramics has been developed in Russia, by employing slag of ferrous and non-ferrous metallurgy, ashes and wastes from mining and chemical industries [2]. Lately, the waste of coal combustion ash, fly ash and filter dusts from waste incinerators, mud from metal hydrometallurgy, pass cement dust, different types of sludge and glass cullet or mixtures of them have been considered for the production of glass–ceramics [3–7]. Using waste to prepare glass–ceramics is significant for industrial applications as well as for environment protection [8].

The conventional approaches to sinter glass–ceramics usually include two steps: first vitrifying raw materials at a high temperature (1300–1500 °C) and then following a nucleation and crystal growth step. The disadvantage of the conventional route is that it is difficult to vitrify the raw materials and the high energy consumption in this step. An alternative manufacturing method to produce sintered glass–ceramics, in which sintering and crystallization of fine glass powders take place simultaneously, has recently been reported [9]. In such route fine glass powders are pressed and sintered, and the crystallization occurs with densification. However, this route also needs a short time to vitrify raw materials at high temperature for preliminary glass-making.

The blast-furnace slag is formed in the processes of pig iron manufacture from iron ore, contains combustion residue of coke, fluxes of limestone or serpentine, and other materials. If the molten slag was cooled quickly by high-pressure water, fine grain glass of vitreous Ca–Al–Mg silicate can be formed [10]. This suggests the blast-furnace slag can be used as a glass source to make sintered glass–ceramics and vitrifying raw materials at high-temperature step can be omitted. The free glass surfaces are preferable sites for devitrification and thus crystallization may occur without any nucleating agent. Therefore, the finely ground slag powder can used as the main component of parent glass. Comparing with the two sintered methods mentioned above, a remarkable advantage of the present study is absent of vitrification step because of the using of blast-furnace slag. Thus a low energy cost and manufacture simplicity can be expected. However, in our previous studies glass–ceramics prepared with pure blast-furnace slag show poor properties [11]. Therefore, some sintering additives are needed. In this study, we show when using blast-furnace slag to prepare glass–ceramics by a conventional ceramics route, if suitable amount of potash

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feldspar is added. Glass–ceramics with high microhardness and bending strength as well as lower water absorption can be obtained.

2. Experimental procedure

The slag (provided by Anyang iron Corporation of China) was pulverized by ball milling for about 24 h (size in the range of 10–20 μm), and then blended with 5–10 wt% potash feldspar powder. The mixtures were ball milling for 2 h. We use K5, K8 and K10 to denote the weight percent of potash feldspar in the samples.

The process used in our study is illustrated in Fig. 1. The blended powders were uniaxially pressed in a steel die at room temperature, using a hydraulic pressure of 40–60 MPa without any binder. The obtained green bodies were sintered in air at nucleation temperature of 720–760 °C and crystallization temperature of 800–900 °C for different times (from 20 to 60 min), with heating rates of 2–5 °C/min, followed by a high-temperature treatment at 1200 °C.

The blended powders were examined by differential scanning calorimetry (DSC) (Labsys, Setaram, France) in air with a heating rate of 10 °C/min from room temperature to 1100 °C. The phase of the blast-furnace slag and obtained glass–ceramics were examined by X-ray diffraction (XRD) (Model D/MAX-3B, RIGAKU, Japan). The samples surfaces were polished and corroded in HF (5 vol%) for 20 s and then observed by scanning electron microscopy (SEM) (Model JSM-5610LV, JEOL, Japan). The density of the samples was measured by the Archimedes method. The microhardness was measured by a microhardness-tester (Model HX-1000TM, Taiming, China) with a measuring force of 9.807 N and a load time 20 s. Samples for bending strength tests with dimensions of 3 mm × 4 mm × 30 mm were carefully polished and tested by a universal testing machine (Zwick/Roell Z030, Germany). The chemical resistance of glass–ceramics was tested by a chemical etch method. The samples were corroded in the HCl (0.5 vol%) and NaOH (0.5 vol%) solution for 95 h and then the residual rate was calculated.

3. Results and discussion

Table 1 shows the chemical composition of blast-furnace slag obtained by X-ray fluorescence. The nominal composition

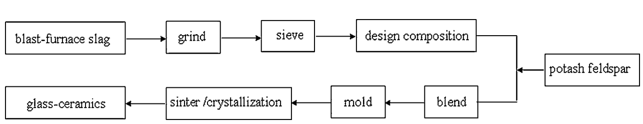

Fig. 1. Flow chart of the ceramics sintering method.

Table 1
Chemical composition of blast-furnace slag.

Oxide	SiO_2	CaO	Al_2O_3	MgO	TiO_2	Fe_2O_3	MnO
Content (wt%)	37.63	36.36	12.54	10.25	0.79	0.45	0.26

Table 2
Chemical composition of glass–ceramics.

Oxide (wt%)	SiO_2	CaO	Al_2O_3	MgO	TiO_2	MnO	Fe_2O_3	K_2O
K5	39.22	34.58	12.67	9.78	0.75	0.25	0.43	0.48
K8	40.19	33.49	12.78	9.48	0.73	0.24	0.42	0.76
K10	40.84	32.76	12.85	9.27	0.71	0.24	0.41	0.96

of the blended mixture is given in Table 2. Fig. 2 shows the XRD patterns of the blast-furnace slag.

It can be seen that the chemical composition of the slag involves SiO_2, CaO, Al_2O_3, and MgO as its major components. Fe_2O_3 and TiO_2 that act as nucleating agents can greatly enhance the crystallization. Due the presence of Fe_2O_3 and TiO_2, other nucleating agents are not needed. A small amount of gehlenite exists in the amorphous glass (Fig. 2). The primary-precipitated phase can act as heterogeneous nucleating centers. In fact, crystallization is favored at the surface of glass particles and primary-precipitated phase, since nuclei may be formed without the impedance of the surrounding materials, taking into account the volume variation from glass to crystal.

Fig. 3 shows the DSC curves of the blended mixture. The small endothermic peak (737–741 °C) indicates the molecular rearrangement in this temperature. The exothermic peak (800–900 °C) corresponds to the crystallization reaction of the glass. With 5 wt% potash feldspar additive, the glass powders have an intense exothermic effect at 840 °C, indicating the formation and growth crystals. With more potash feldspar additive, the exothermic peak increases slightly. Therefore, a nucleation temperature in the range of 720–760 °C and a crystallization temperature in the range of 800–900 °C were employed, respectively.

Fig. 4 shows the SEM images of the samples. The results show that crystallization is mainly induced by surface nucleation in samples K8 and K10, but by both surface and bulk nucleation in sample K5 since crystallization take place throughout the entire volume in the sample. Uniform, ultrafine crystalline grains with sizes of 2–5 μm exist in sample K5. In contrast, there are only small amounts of crystalline phases in K8 and K10 as shown by

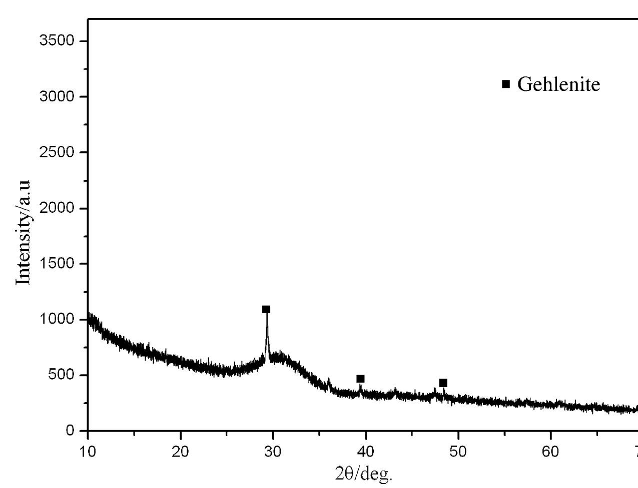

Fig. 2. X-ray diffraction pattern of the blast-furnace slag.

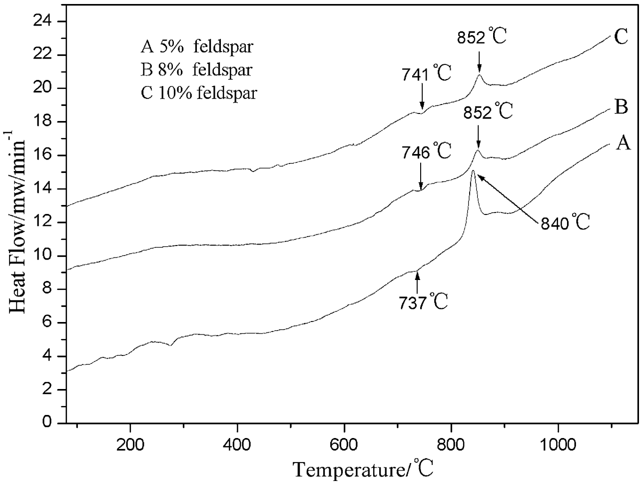

Fig. 3. Differential scanning calorimeter patterns of the glass.

XRD patterns (Fig. 5). Alkali feldspar crystals are known to give excellent glasses but they are unable to be crystallized in practical periods of time. They have been successfully developed by exploiting the tendency of powdered glass to devitrify during appropriate heat treatments in recent works [12]. Our results show glass powder with 5 wt% potash feldspar can be successfully devitrified during the heat treatment because potash feldspar can act as fluxing agents during sintering process thus decrease the sintering temperature and reduce the viscosity of glass. The value of viscosity during sintering and crystallization is very important. If the value of viscosity is too low, crystallization will be too fast, which can hinder sintering and creates a large amount of porosities. On the other hand, if the value of viscosity is too high, crystallization is difficult. Therefore, controlling the glass viscosity is very important. With more potash feldspar additive, the crystallization rate of the glass will decrease. According to our experimental data add 5 wt% potash feldspar will be an appropriate amount.

Fig. 5 shows the XRD patterns of K5, K8 and K10 samples, obtained by heat-treating at 1200 °C for 1 h. In the fully

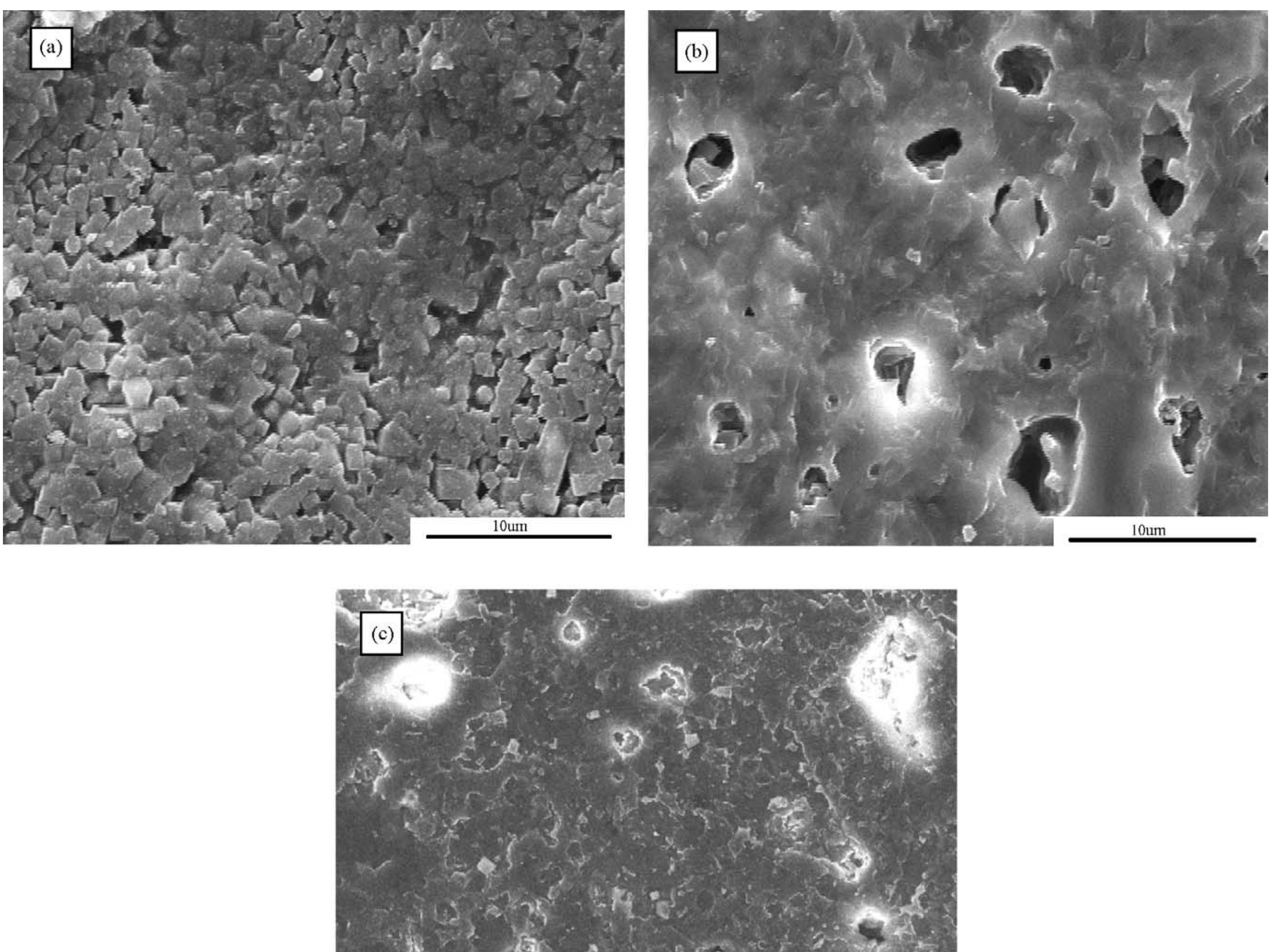

Fig. 4. SEM images of the samples: K5 (a), K8 (b) and K10 (c).

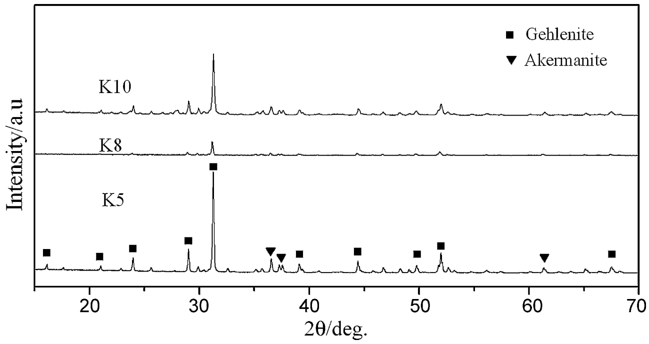

Fig. 5. X-ray diffraction patterns of glass–ceramics.

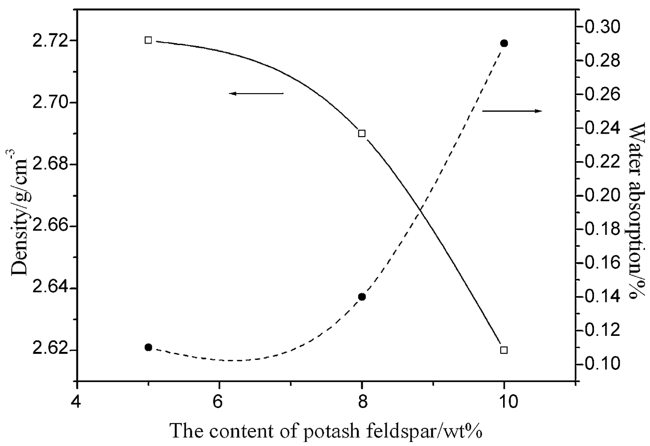

Fig. 6. Density and water absorption of glass–ceramics.

crystallized specimens K5, the gehlenite ($Ca_2Al_2SiO_7$) is the main. But thin akermanite ($Ca_2MgSi_2O_7$) phase is also present. Both gehlentie and akermanite belong to the melilite group, which possesses good wear resistance and corrosion resistance. The sample K5 contains more crystalline phases than K8 and K10 under the same heat treatment from the diffraction peak intensity. It is obvious that the diffraction peak intensity of K5 is higher than those of K8 and K10. The glass particles with an appropriate amount of potash feldspar once submitted to an effective heat treatment can be transformed into crystalline phases as shown by SEM images (Fig. 4).

Fig. 6 shows the density and water absorption of K5, K8 and K10 samples. By increasing the amount of potash feldspar, the density trends to decrease while the water absorption increases. The possible explanation is that there are lots of uniform, ultrafine micro-crystals in K5 sample, while only a small amount of crystals is formed in K8 and K10 samples. In addition, the pore also plays an important role on density and water absorption. There are few pores in K5, but many pores in K8 and K10 samples. These result in low density and high water absorption of K8 and K10. Best values of other properties of K5 sample are as follows: (i) microhardness 5.2 GPa; (ii) bending strength exceeds 85 MPa; (iii) the chemical resistance near 100%. In general, slag-based glass–ceramics obtained show mechanical and physicochemical properties that are superior to the clay bricks.

4. Conclusion

Glass–ceramics with good properties have been successfully synthesized from blast-furnace slag with 5 wt% potash feldspar additive by the conventional ceramic-sintering process. The 5 wt% potash feldspar additive can greatly improve the sintering properties of blast-furnace slag glass. Glass–ceramics obtained show good mechanical and physicochemical properties. The present method can enhance the utilization ratio of blast-furnace slag and drastically reduced the cost, and will be an effective manufacturing process for large industrial applications.

Acknowledgement

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