

Effect of reducing agent on the crystallization characteristics and properties of Baiyunebo east mine tailing glass-ceramics

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Ingredient manipulations of raw materials were always an important issue in the field of recycling silicate solid wastes of mining and metallurgy processes. For this purpose, glass-ceramics of CaO-MgO-Al₂O₃-SiO₂ quaternary system were successfully produced by the method of melting, using Baiyunebo east mine tailing and fly ash as main sources of raw materials. The effect of carbon powder variation on the crystallization, and properties of the glass-ceramics were systematically investigated by differential thermal analysis (DTA), X-ray diffraction (XRD), Raman microscopy, scanning electron microscope (SEM) and mechanical testing. The results showed though carbon powder addition cannot change the formation of main crystal phase (augite), the concentration of this primary crystalline phase can be enhanced with the increase of the carbon powder addition to 5.6 wt%. As a result, the density, bending strength, acid-resistance and activation energy of the materials can be manipulated accordingly. And the mechanism of our manipulating process was close related to the reduction effect of carbon powder on decreasing the valence and concentration of iron ion within the studied glass ceramics.

Key words: Glass ceramics, Baiyunebo east mine tailing, Iron, Augite, Carbon powder.

Introduction

Industrial residues, such as tailing, fly ash, aluminum refining red mud, steel slag, etc., always discarded by land filling and considered as various wastes, have aroused wide concerns all over the world because of their hazardous effects on the environment. Lately, accumulated studies have shown all these wastes can be used as the main starting materials in the production of glass-ceramics which can have been applied in the fields of construction industry with high abrasion, high mechanical strength and high resistance to corrosion [1-4]. Especially, glass-ceramics prepared by using ferrous tailing and slag exhibit useful mechanical, thermal and magnetic properties since iron play an important role in phase separation, nucleation and crystallization process of glass-ceramics [5-8]. Our previous studies have shown that no additional nucleant agents are added for the crystallization of the glass-ceramics due to the fact that the Baiyunebo east mine tailing contains a significant amount of iron oxide which could act as nucleant agents for crystallization [9].

As a usual component of so many tailings and an effective nucleating agent of glass-ceramics, iron has

attracted much attention. Generally speaking, in glass network structure, Fe²⁺ can form [FeO₆] octahedrons which can break the [Si-O] net structure and decrease the viscosity. Where, the Fe³⁺ can form the [FeO₄] tetrahedrons which mend the silicate skeleton with [SiO₄] tetrahedrons [10]. Thus, the Fe³⁺/Fe²⁺ ratio can effective influence the nucleation and crystallization of glass-ceramics. The oxidizing or reducing agents can be considered as an effective method to change the Fe³⁺/Fe²⁺ ratio. A.Karamanov *et al.* [11] investigated the influence of the Fe³⁺/Fe²⁺ ratio on the crystallization of iron-rich glasses made with industrial wastes. The carbon powder was used as a reducing agent in the batch. Their results showed that decreasing the Fe³⁺/Fe²⁺ ratio can increase the crystallization rate.

At present, glass-ceramics in the CaO-MgO-Al₂O₃-SiO₂ (CMAS) system using the Baiyunebo east mine tailing and fly ash as main raw material have shown good mechanical properties in our work. However, the effect of valence and concentration of iron on crystallization kinetics and properties of glass-ceramics using the Baiyunebo east mine tailing has not been reported. In this work, the valence and concentration of iron in glass-ceramics are controlled by the presence of reducing agents in the batch. The purpose of this study is aimed at investigating the influence of valence and concentration of iron on nucleation mechanism, crystallization behaviors and mechanical properties of Baiyunebo east mine tailing glass-ceramics.

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Experimental Procedure

Samples preparation

Baiyunebo east mine tailing and fly ash were used to synthesise the glass-ceramic samples in present study in addition to small amount of quartz sand, potassium nitrate and other necessary chemicals. The major chemical compositions of Baiyunebo east mine tailing and fly ash were showed in our previous study [12]. The basic composition of the parent glass, 42.60% SiO₂, 27.20% CaO, 2.36% MgO and 6.50% Al₂O₃ (all the compositions are referred to wt.%) was selected. In order to provide reducing conditions, fine carbon powder was added in different percentages to batch compositions. Glass-ceramics 1, 2, 3, 4 and 5 with carbon powder content 0, 5.6, 8.1, 10.6 and 12.9 (wt.%) respectively, were melted in an electric furnace at 1450 °C for 3h using corundum crucible. The melts then were cast into preheated stainless steel moulds and subsequent annealing at 600 °C for 2 h. Then the annealed glass samples were placed in a muffle furnace for the nucleation and crystallization treatments, whose temperatures were kept at 720 °C and 850 °C respectively [12]. Both of the soaking time of above two continuous heat-treatment was 2 h. After the crystallization treatment, all five samples were furnace cooled to room temperature before the property and the microstructure examinations.

Techniques of characterization

In order to determine the crystallization products, the heat-treated samples were subjected to XRD analysis (Bruker diffractometer, AXS D8 ADVANCE) using Cu K α radiation at 40 kV and 80 mA setting and in 2 θ range from 20 to 80. The samples after polishing and etching in 3% HF solution for 30s, were coated with a thin film of gold and subjected to microscopic examination by a scanning electron microscope (HITACHI S-3400). In order to research the crystallization kinetics, thermo behaviors of the parent glasses were examined by a differential thermal analysis (DTA) measurement (NETZSCH STA 449C) at the heating rates of 5, 10, 15 and 20 °C/min. The Raman spectra was performed by using a Raman microscope (Jobin Yvon, HR800) consisting of an Ar⁺ laser (514.5 nm). The laser power was 20 mW and the integration time was 20s. The three-point bending strength of rectified parallelepiped bars (3 mm $\times$ 4 mm $\times$ 40 mm) of glass-ceramics was tested by the CSS-88000 electronic universal testing machine. Each value is the mean value of measurements made with five samples. The corrosion test was measured according to the cast stone standard JC/T258-1993, with a concentration of 20% H₂SO₄, and diameter of 0.5 mm-1.0 mm glass-ceramic pellets for water bath heating of 100 °C. The densities were measured by Archimedes method. The ratio of Fe³⁺/Fe²⁺ of glass-ceramic was evaluated by the spectrophotometric method.

Results and Discussion

Ratio and concentration of Fe³⁺/Fe²⁺ in glass-ceramics

Fig. 1 shows the result for the ratio and concentration of Fe³⁺/Fe²⁺ in glass-ceramics as a function of the percentage of carbon powder in the batch. The weight losses of TFe in samples 3-5 can be observed from Fig. 1 and the direct experimental evidence is that irons are precipitated by reduction reaction during the melting process [13]. The recovered spherical metallic iron sunk at the bottom of the crucible because of the gravity and the energy dispersive spectrometer (EDS) spectrum analyses (Fig. 2) discovers the presence of Fe as major constituent element. The metallic iron can be obtained using the reactions:



Moreover, it can be evaluated that the Fe³⁺/Fe²⁺ ratio is about 4 for sample 1 and about 1 for samples 2-5. That is, a decrease in the Fe³⁺/Fe²⁺ ratio occur with the addition of carbon powder according to Eq. (1). However, the Fe³⁺/Fe²⁺ ratio is not modified with increasing carbon powder content, which indicate a dynamic balance of oxidation-reduction reaction may exist. Generally, the Fe³⁺/Fe²⁺ ratio in a glass depends on the oxidizing or reducing agents in the batch. In our experiment, certain amounts of carbon powder can play a role in the reducing agent and the Fe³⁺ can be reduced to Fe²⁺.

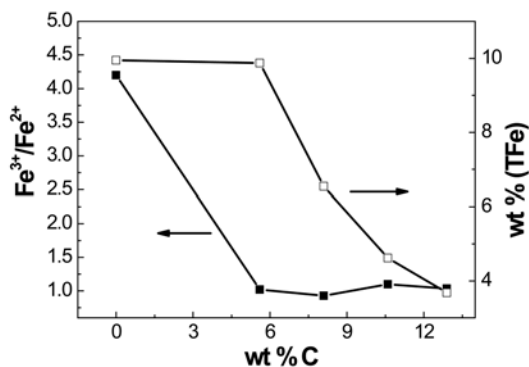


Fig. 1. Fe³⁺/Fe²⁺ ratio and concentration for glass-ceramics with different carbon powder.

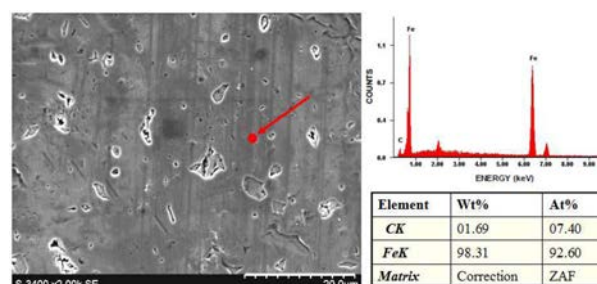


Fig. 2. EDS analyses of recovered iron.

However, the Fe^{2+} can be reduced to metallic iron by adding excess of carbon powder, such as samples 3-5. Meanwhile, an oxidizing agent can be created since the samples are heat-treated in air atmospheres and some amount of Fe^{2+} can be oxidized to Fe^{3+} in the melting process. As a result, a dynamic balance of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in glass-ceramics can exist.

Crystallization characteristics

DTA curves for the different ratio of carbon powder glass samples are shown in Fig. 3. The crystallization temperature (T_p) at which a glass experiences its most intensified crystallization, can be determined according to the exothermic peak on the DTA curve. The results show that with the increase of carbon powder ratio the crystallization temperature of as-cast glasses first decrease and then increase. It is also noticeable that the intensity of exothermic peaks is generally weak when the carbon powder ratio exceed 8.1, indicating the crystallization process is less intense. The reason of above phenomenon is determined mainly by the nucleation agent and high temperature viscosity. The nucleation agent of iron ions in glass-ceramics can not be changed for samples 1-2 and gradually decrease for samples 3-5. Therefore, the increase of crystallization temperature for samples 3-5 can be interpreted as a decrease of the iron oxide. However, the decrease of crystallization temperature for sample 2 can be mainly related to high temperature viscosity. That is, the increase of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio may account for the broken of the glassy network structure, which is evidenced by shift the crystallization temperature to lower temperatures [14-15].

In order to quantitatively describe the crystallization kinetics for crystal growth in glass-ceramics, the activation energy of crystal growth, E_c , can be estimated by using the Ozawa equation [10] on the basis of DTA experiments at different heating rates:

$$\ln \alpha = -\frac{E_c}{R} \cdot \frac{1}{T_p} + \text{Const} \quad (3)$$

where E_c is the activation energy of crystallization [KJ/mol], α is the heating rate [K/min], R is the

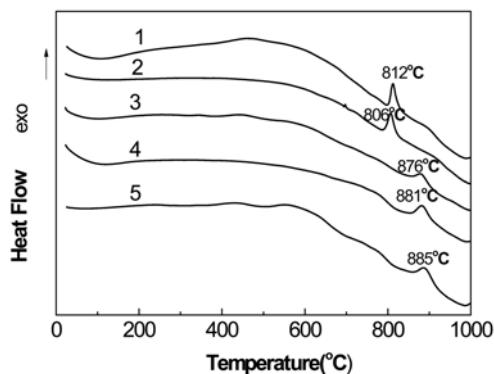


Fig. 3. DTA curves of the as-cast glasses with different carbon powder.

Table 1. the values of T_p (K) at different heating rates α of DTA.

Sample no.	T_p (°C)					$\text{Fe}^{3+}/\text{Fe}^{2+}$
	5 (°C/min)	10 (°C/min)	15 (°C/min)	20 (°C/min)	E (kJ.mol ⁻¹)	
1	799	812	820	475	828	4.2
2	792	806	818	391	826	1.0

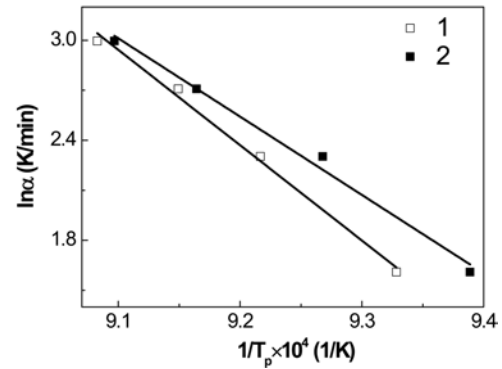


Fig. 4. the plots of $\ln \alpha \sim 1/T_p$ for the glass samples 1-2.

universal gas constant [J/(k·mol)] and T_p is the crystallization peak temperature [K]. Tab.1 shows the values of the T_p of DTA experiments of samples 1-2 at different heating rates. According to Equation (3), a linear relationship between $\ln \alpha$ and $1/T_p$ (Fig. 4) give a slope of $-E_c/R$ and the energy of activation can be obtained (Tab. 1). It is found to be about 475 KJ/mol for sample 1, which is higher than the dissociation energy of [Si-O] bonds (452 KJ/mol). Generally speaking, when the glass phase transforms to crystalline, it must overcome a certain energy barrier, which corresponds to the dissociation energy of [Si-O] bonds. The reason for the higher E_c in sample 1 can be attributed to large numbers of Fe^{3+} in sample 1 since Fe^{3+} can form the $[\text{FeO}_4]$ tetrahedrons in glass phase and mend the [Si-O] net structure. Through a comparison, the activation energy of sample 2 (391 KJ/mol) is relatively small, which means that the increase of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can effectively reduce E_c and promote crystallization.

Phase formation and morphological characterization

Fig. 5 shows the powder XRD pattern of CMAS system with different amount of carbon powder, respectively. It can be found that the predominant crystalline phase in samples 1-4 are augite ($\text{Ca}(\text{Mg,Fe,Al})_2(\text{Si,Al})_2\text{O}_6$, JCPDS 89-5691), while no significant peaks can be found in sample 5. The above phenomenon is mainly determined by the content of carbon powder since it can change the ratio and concentration of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in glass-ceramics. Generally, iron can act as nucleant agents for crystallization and greatly affect the formation of crystalline phase, rate of crystallization [16]. As a result, crystalline phase gradually decreases in samples 3-5 with the decrease in iron content.

Fig. 6 shows the SEM micrographs of the glass-

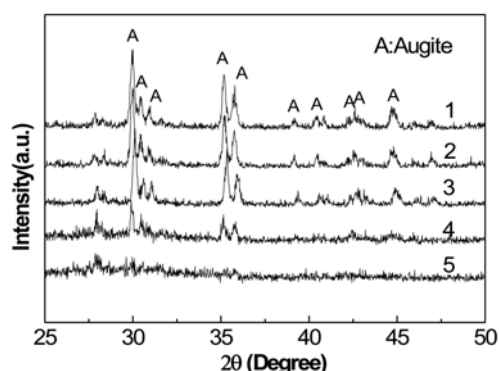


Fig. 5. XRD spectra of different carbon powder samples after crystallization process.

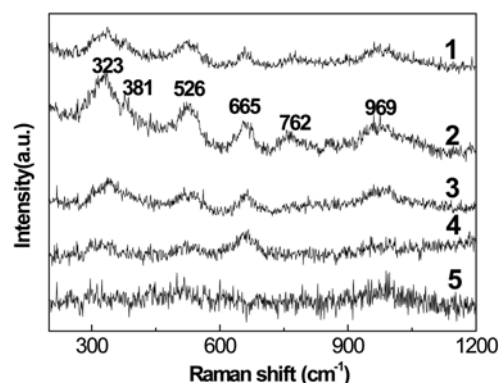


Fig. 7. Raman spectra of different carbon powder samples after crystallization process.

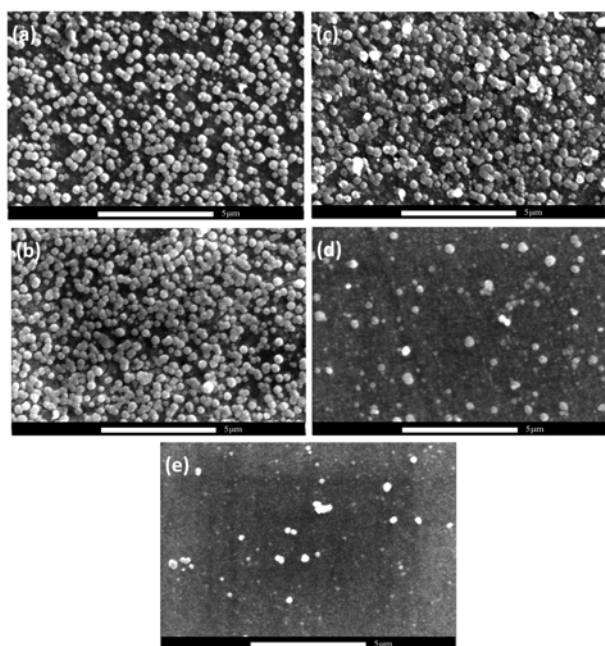


Fig. 6. SEM microstructures after crystallization process of different carbon powder samples; (a) 0, (b) 5.6, (c) 8.1, (d) 10.6, (e) 12.9 wt.%

ceramics treated at different content of carbon powder. A great number of crystallites with the size of 200–300 nm in diameter distributed homogeneously among the glass matrix appear in samples 1–3. The formation of above morphology may relate to the valence and concentration of iron since phase separation occurs firstly in the iron-rich region in the initial stage of nucleation and it can provide the core of nucleation for the consequent precipitation of augite crystalline. The minimum grain size and the highest degree of crystallization are found to occur in sample 2 with 5.6 wt% carbon powder addition, which can be explained as the more Fe^{2+} present in the glass network. With the carbon powder content further increase, the numbers of crystals and degree of crystallization are significantly reduced, which is consistent with the XRD results.

Raman spectra analysis

Fig. 7 demonstrates the Raman spectra of glass-ceramics with different carbon powder. The spectra show a good agreement with the reported main spectra of augite at 323, 381, 526, 665, 762, and 969 cm^{-1} despite little differences in peak positions [17]. In the Raman spectra of the glass-ceramics, the bands below 400 cm^{-1} are attributed to the metal-oxygen translation modes, which reflect the long-range order of silicate structure and only appear in the crystal. In our experiments, the bands observed at 323 and 381 cm^{-1} can be reasonably assigned to M–O (M = Mg, Fe) and Ca–O stretch. It can be found that the intensity of Raman spectra in sample 2 is always greater than those from other samples, which represents a higher degree of crystallinity. The bands of the O–Si–O and Si–O–Si bend are assigned to be 526 and 665 cm^{-1} . Meanwhile, the band of the Si–O stretching modes of the bridging O atoms (Si-O_{br}) is assigned to 969 cm^{-1} .

Physical and mechanical properties

In order to evaluate the effect of the carbon powder adding on the physical and mechanical properties of the glass ceramics, the density, bending strength and acid-resistance of all five sets of samples are systematically tested accordingly.

The influence of carbon powder ratio on density is plotted in Fig. 8. It can be found that the densities after crystallization treatment are higher than the densities after nucleation treatment, which can be attributed to the improvement in the degree of the crystallization. Furthermore, with the increase of carbon powder ratio the densities for crystallized samples and nucleated samples all first increase and then decrease, which can be proved by the SEM results.

Fig. 9 shows the influence of carbon powder ratio on the bending strengths of glass-ceramics. The difference in mechanical properties may be attributed to the crystallite size and degree of crystallization. Generally, more fine grain size and higher degree of crystallization can improve the mechanical properties. The properties

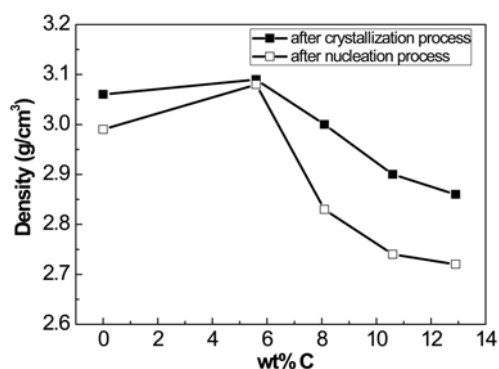


Fig. 8. Density of different carbon powder samples after nucleation and crystallization process.

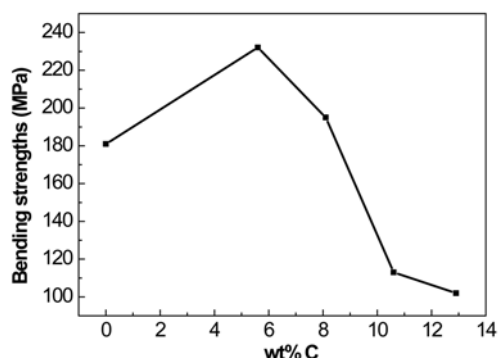


Fig. 9. Bending strengths of different carbon powder samples after crystallization process.

variations of a material are always the result of its microstructure changes. In the present study, both DTA and SEM examinations confirmed that with the increase of carbon powder ratio, the microstructure of the samples firstly changed from low degree of crystalline of sample 1, to a composed of well crystallized spherical nano grains of sample 2, then to barely crystallized samples with an only small amount of roundish crystals embedded within the glass matrix in samples 3-5. It is, therefore, the sample with 5.6 wt% carbon powder addition have a higher value of bending strengths compared with other samples.

The chemical durability of glass-ceramics, especially for acid solution, is important if the materials are to be considered as potential building materials, because acid rain is becoming an increasingly serious problem in number of countries. It can be found from Fig. 10 that the variation of acid-resistance with carbon powder addition is consistent with the results of bending strengths. The highest alkali-resistance of sample 2 is derived from the high degree of crystalline. That is, with the increase of the degree of crystalline further crystalline phase can form and more iron ions can enter into the crystalline phase of the glass-ceramics. As a result, the free iron ions in glass phase become relatively reduction and the acid-resistance of glass-ceramics increase.

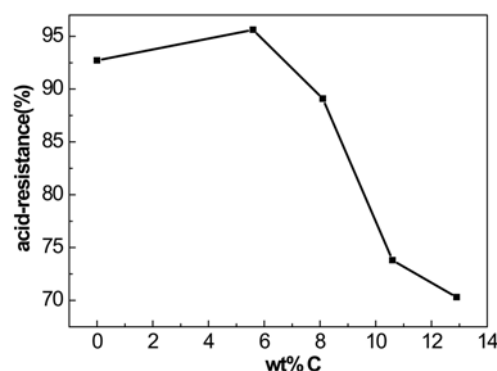


Fig. 10. Acid-resistance of different carbon powder samples after crystallization process.

Conclusions

The influence of carbon powder adding on crystallization, structure and properties of glass-ceramics were systematically researched and discussed. The result confirmed the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in glass-ceramics decreased significantly with the carbon powder added. The activation energy in sample 1 was higher than the dissociation energy of [Si-O] bonds, which indicated that Fe^{3+} can mend the [Si-O] net structure. With the increase of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, the activation energy was greatly reduced and the crystallization characteristics of the glass-ceramic were improved. However, iron ions can be reduced to iron and separated from the glass-ceramic by reduction reaction with the carbon powder content further increase. Thus, the crystallization ability of glass-ceramic reduced accordingly. The change of crystallization characteristics directly affected the acid-resistance and bending strength of the glass-ceramic. The best performance of the glass-ceramic, a bending strength of 232 MPa and a acid-resistance of 95.6% can be obtained when the ratio of carbon powder is 5.6 wt.%.

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