Journal of Non-Crystalline Solids 380 (2013) 103–108

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Structure and performance of glass–ceramics obtained by Bayan Obo tailing and fly ash

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ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form 5 September 2013
Available online 29 September 2013

Keywords:
Glass ceramic;
Bayan Obo tailing;
Fly ash

ABSTRACT

Glass in the $CaO–Al_2O_3–MgO–SiO_2$ quaternary phase system has been obtained by the Bayan Obo tailing and fly ash as main raw materials. On the basis of differential scanning calorimetry (DSC) analyses, this article took the glass and glass–ceramic samples which the Bayan Obo tailing and fly ash added respectively to 50% and 20% as the object of study. Nucleation experiment was carried out at 720 °C for 2 h whereas crystallization experiment was performed at 880 °C for 2 h. The phases and microstructure of glass and glass–ceramic samples were characterized by X-ray diffraction (XRD), Raman spectra, transmission electron microscopy (TEM) and scanning transmission electron microscope (STEM). In addition, physical and mechanical properties of the produced glass–ceramics have been examined. The results demonstrate that the glass–ceramics have potential for a wide range of construction application.

1. Introduction

Glass–ceramics, which have unique physical and mechanical properties such as high bending strength and hardness, good corrosion resistance and abrasion resistance, are fine-grained polycrystalline materials formed when glasses of suitable composition are heat treated and thus undergo controlled crystallization [1,2]. Plenty of silicate-based wastes, such as fly ash from power plants, filter dusts from waste incinerators, slag from steel production, mill tailings from mineral separation, different types of sludge as well as glass cullet or mixtures of them have been considered for the production of glass–ceramics [3]. The first and most important instance was certainly that Russian Slagsitalls produced the slag glass–ceramics from several slags from metal hydrometallurgy, ashes and wastes from mining and chemical industries as early as the 1960s [4]. Then, more and more scholars of different countries began to research on glass–ceramics by all kinds of slag and wastes. Bernardo et al. [5] obtained glass–ceramics with a bending strength exceeding 100 Mpa by employing panel glass, lime and mining residues. Jae-Myung and Hyung Sun [6] prepared glass–ceramics, by using a municipal waste incinerator fly ash with high Cl content. Khater [7] investigated the manufacture of glass–ceramics prepared with silicon manganese slag and steel slag. Of course, those samples came from just a handful of the research scholars abroad.

In recent years, with the rapid development of industrialization, a lot of industrial wastes have been produced in China, especially fly ash from power plants, slag from steel production and tailings from mineral separation. It is reported that the power plants in China annually consume a total of about 305 million tons of coal, resulting in combustion waste of about 86 million tons[8]. The Bayan Obo in China produces approximately 8.0 million tons of tailings each year [9]. At present, most of the fly ash is used for producing bricks, cement, concrete, and so on. Moreover, a large amount of the rare earth tailings of Bayan Obo is piling up in the tailings dam. Therefore, how to reuse, recycle fly ash and tailings has become an increasing economic and environmental burden.

Recently, considerable research has been focused on utilization of fly ash or tailing as the raw materials to produce glass–ceramics because fly ash and tailing contain a large amount of SiO_2 and Al_2O_3, which are main glass network formers [10–12]. In this study, the possibility of using Bayan Obo tailing and fly ash as raw materials in glass–ceramics has been investigated. Moreover, we report the result of production and properties of a glass–ceramic without the addition of an extra nucleating agent during its preparation.

2. Experiment procedure

2.1. Starting materials and parent glass produced

In this paper, glass–ceramic material was prepared from Bayan Obo tailing and fly ash as the main raw materials by the melting method. The chemical compositions of as-received Bayan Obo tailing and fly ash were listed in Table 1. Figs. 1 and 2 show the X-ray diffraction patterns of the fly ash sample and the Bayan Obo tailing sample. As seen in Fig. 1, the Bayan Obo tailing sample comprised the mineral phases: quartz (SiO_2, JCPDS 85-1054), fluorite (CaF_2, JCPDS 75-97), hematite (Fe_2O_3,

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http://dx.doi.org/10.1016/j.jnoncrysol.2013.09.012

JCPDS 72-469) and silicon oxide (SiO_2, JCPDS 80-2148). From Fig. 2, the mineral phases of silicon oxide (SiO_2, JCPDS 81-65) in the fly ash sample are shown. In accordance with the features of the composition and phase of fly ash and Bayan Obo tailing, fly ash consists of high SiO_2 and Al_2O_3, but the Bayan Obo tailing consists of high SiO_2 and CaO, which could refer to CaO–Al_2O_3–MgO–SiO_2 phase diagram during parent glass production. In addition, Fe_2O_3 and CaF_2 were considered as suitable nucleating agents in the heat treatment process of crystallization. Al_2O_3 of the parent glass mainly derived from the fly ash and fly ash addition was (wt.%) 20%. The added amounts of Bayan Obo tailing were respectively (wt.%) 10%, 20%, 30%, 40% and 50%, and five samples were named as sample wk10%, wk20%, wk30%, wk40%, wk50%, respectively. Moreover, we calculated five different batches based on the chemical composition of different parent glasses (Table 2) by adding the right amount of quartz, calcium, magnesium oxide and soda ash. Glass batches packing in corundum crucibles was melted in a high temperature electric furnace at 1470 °C for 4 h, after which melts were poured onto an iron mold preheated at 350 °C to reduce thermal shock. Following this, these glasses were annealed at 600 °C for 3 h and slowly cooled to room temperature. Then the annealed glasses were produced through the nucleation and crystallization treatments according to the DSC result.

2.2. Differential scanning calorimetry analysis (DSC)

The thermal behavior of the glass sample, a less than 20 mg (grain size < 45 μm), was put into a Al_2O_3 crucible and then heated at 5 °C/min from room temperature to 1000 °C through differential scanning calorimetry (DSC) equipment (STA 449C-1600 °C, NETZSCH), which adopted an empty Al_2O_3 crucible as reference material and a sensitivity of 20 μV/in.

2.3. X-ray diffraction analysis (XRD)

Powder X-ray diffraction investigations were obtained using a Bruker D8 Advance with Cu Kα radiation, operated at 40 Kv and 40 mA in the 2θ from 20° to 80° at the rate of 2° min^{-1}. The crystalline phases were identified by comparing the peak intensities and positions in the spectrum with those in the Joint Committee on Powder Diffraction Standards data files.

2.4. Raman spectra

Raman spectra measurements were made with a Raman microscope (Jobin Yvon, HR 800) equipped with an Ar^+ laser (514.5 nm). The laser power was 20 mW at the sample and the instrumental resolution was 1 cm^{-1}. All of the experiments were performed at room temperature in a dark room. The measurements were performed on the annealed sample and crystallization sample.

2.5. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX)

The microstructure characterization of glass–ceramics produced from Bayan Obo tailing and fly ash was performed by transmission electron microscopy (TEM) and scanning transmission electron microscope (STEM). The TEM and STEM characterizations of the side-projected phlogopite plates were performed on a Tecnai G2 F20 S-Twin electron microscope operated at 200 kV acceleration voltage. EDX was employed to analyze the chemical composition of the crystal and glass phase observed in the glass–ceramic sample.

2.6. Physical and chemical property tests

For glass–ceramic samples, the physical and chemical properties including three-point bending strengths, density, acid resistance and alkaline resistance were also investigated. The volumetric density was measured by the Archimedes method using distilled water as medium. Hardness was analyzed by the Vickers indentation method. Vickers hardness was measured with a load of 300 g and loading time of 30 s on Vmht Mot. Bending strengths were obtained using the 3-point method with spans of 3 mm × 4 mm × 40 mm at a cross-head speed of 0.5 mm/min on a Universal Testing Machine (DSS-25T). Glass–ceramic samples of 1 g were treated at 98 °C for 1 h in a 50 ml leaching solution (20% (wt.%) NaOH and 20% (wt.%) H_2SO_4). Residual weight was then measured for the chemical durability evaluation.

3. Results

3.1. DSC results

Fig. 3 shows the DSC thermogram of the five different specimens. With the added amount of Bayan Obo tailing increased, the temperatures of the shallow endothermic peaks start and the exothermic peaks decreased. In addition, the temperatures of exothermic peaks were 967 °C, 962 °C, 932 °C, 902 °C, and 887 °C, respectively. Moreover, when the amounts of Bayan Obo tailing at (wt.%) 50% and 40% were added, there were obviously endothermic valleys. With a comprehensive consideration of the viscosity, the mobility, the formability and the thermal stability, we took wk50% as the object of study. For the heat treatment, we adopt the conventional method by two-stage heat treatment. The first stage is a low temperature heat treatment at a temperature that gives a high density of nuclei throughout the interior of the glass. The second stage is a higher temperature heat treatment at around temperature Tg to produce growth of the nuclei at a reasonable rate [3]. Therefore, in this work, a sample of the bulk glass was heat treated at 720 °C for 2 h for the nucleating stage and at 880 °C for up to 2 h for the crystallization stage.

3.2. XRD results

Fig. 4 shows the XRD result of the annealed glass sample and glass–ceramic sample. For the annealed glass sample, XRD confirmed the amorphous glass structure. For the glass–ceramic sample, it can be seen from the flat baseline that, the content of the glass phase is low. Calcium magnesium aluminum iron silicate and diopside, Ca (Mg, Fe, Al) $(Si, Al)_2O_6$ (JCPDS 25-1217), which has a monoclinic structure with lattice parameters $a = 0.9679$ nm, $b = 0.8812$ nm, $c = 0.5284$ nm and $\beta = 106.22°$, were identified as a major phase. Second

Table 1
The chemical composition of the Bayan Obo tailing and fly ash (wt.%).

Raw materials	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	FexOy*	BaO	MnO	Nb_2O_5	Cr_2O_3	CaF_2	REO**	LOI***	Total
The Bayan Obo tailing	27.56	7.20	20.23	5.32	0.50	1.84	19.84	2.28	1.36	0.20	0.05	10.35	1.25	2.02	100
Fly ash	51.68	30.70	3.89	0.76	1.62	1.84	7.43	–	–	–	–	–	–	2.08	100

* FexOy: FeO and Fe_2O_3.
** REO: rare earth oxides.
*** LOI: loss on ignition at 1000 °C.