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Ceramics International 29 (2003) 223–227

CERAMICS INTERNATIONAL

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Crystalline phase control of glass ceramics obtained from sewage sludge fly ash

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Received 27 February 2002; received in revised form 15 March 2002; accepted 2 May 2002

Abstract

Different types of glasses and glass-ceramics were made using fly ash from sewage sludge incinerators. The optimum nucleation condition was heating at 760 °C for 1 h. Crystallization of the nucleated specimen in the region of 1050–1200 °C resulted in the formation of two crystalline phases, i.e. anorthite and diopside. The relative fractions of these two phases changed with crystallization temperature. Specimens heat-treated for 2 h at 1050 °C consisted mainly of diopside crystals with a minor proportion of anorthite. On the other hand, those heat-treated at 1150 °C were primarily composed of anorthite. Glass-ceramics containing large amounts of diopside (1050 °C/2 h) generally displayed better physical and chemical properties than their anorthite counterparts (1150 °C/3 h) due to the interlocking microstructure of diopside crystals.

Keywords: D. Glass ceramics; Crystal phases; Sewage sludge fly ash

1. Introduction

Most sewage sludge is buried in landfills or dumped in the ocean without any specific treatment for environmental protection. However, the high concentration of organic substances in sludge creates many environmental concerns such as leachate and soil contamination. In addition, these organic matters lead to the excessive propagation of microorganisms such as red tides in the ocean; therefore, an effective stabilization and incineration method must be discovered and put in place [1,2]. Incineration can effectively decompose organic substances and furthermore, it sharply reduces the volume and weight of original wastes [1].

On the other hand, incineration leaves behind ashes that need to be disposed of. Up to the present, ashes from incinerators have been solidified by mixing them with cements. This method, though economical and well-established, resulted in a large volume increase of the wastes to be disposed. Further, the final composites are not chemically durable against water. To the contrary, vitrification of ashes can sharply reduce the volume of wastes. This technique can also detoxicate or volatilize hazardous constituents in wastes during the high-temperature melting stage. Despite these advantages, however, it is not a very economical technique due to the consumption of large amounts of thermal energy. Therefore, it is desirable to recycle the products either in a glassy state or a crystallized form if one can fulfill the requirements for their ruggedness and environmental safety.

Several works have been reported concerning the characteristics of glass-ceramics made of sewage sludge ashes [2], coal ash [3] and ashes from municipal solid waste incinerators [4]. Glass ceramics prepared from sewage sludge ash [2] consisted of anorthite as a main crystalline phase. They showed a hardness of 5000–6000 MPa and a rupture modulus of 500 kg cm^{-2}. However, these previous works only focused on the properties of glass-ceramics prepared from the ash itself and no attempt was made to control the types and amount of crystalline phases [4,5]. In many cases, the composition of wastes is complex and therefore, various crystalline

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0272-8842/03/$22.00
PII: S0272-8842(02)00109-8

phases can be formed unless a certain degree of control is applied. This study focused on the control of crystalline phases in glass-ceramics made of sewage sludge fly ash. Two strategies were employed; adjusting the chemical composition of ash with additives and controlling the crystalline phases by monitoring the heat-treatment schedule. The physical and chemical properties of the glass-ceramics thus prepared were evaluated and optimum conditions for ceramic process were suggested.

2. Experimental

Sewage sludge fly ash used for the experiments was sampled from the bag filter in a fluidized bed incinerator. Fly ash appeared as fine brown powders with diameters of several micrometers. The chemical composition of as-received ash analyzed by X-ray fluorescence spectroscopy (XRF) is shown in Table 1. Since ash contains more than 60 wt.% of glass-formers and intermediates, it was possible to form a glass by melting the as-received ash only. However, approximately 10 wt.% CaO to the total amount of ash was added to obtain the desired crystalline phases by subsequent heat-treatment. Target crystalline phase was anorthite ($CaAl_2Si_2O_6$) and diopside ($Ca[Mg, Fe, Al][Si, Al]_2O_6$) which have chemical compositions close to that of the as-received ash. In addition, it is known that anorthite and diopside can provide high mechanical strength and toughness [2,6]. Simultaneously, the addition of CaO decreases the melting temperature which provides additional economical benefits. Glasses were prepared by melting in an alumina crucible at 1500 °C for 1 h after which melts were poured onto a copper plate preheated at 400 °C to reduce thermal shock. Following this, these glasses were annealed at 700 °C for 1 h and slowly cooled to room temperature.

It is important to determine nucleation and crystal growth temperatures precisely for effective conversion of glasses to glass-ceramics. Nucleation temperature was determined to be 760 °C which is 30 °Cabove the dilatometric softening point (T_{ds}) measured from the thermomechanical analyzer (TMA) [7]. To determine optimum nucleation duration, the glass samples ($12\times12\times12$ mm^3) were nucleated for 0.5–2 h at 760 °C and crystallized for 2 h at 1100 °C. The duration for the most effective nucleation was determined from the intensity ratio between the three large peaks and the total XRD peak intensities. The initial crystallization temperature (1100 °C) used for this experiment was determined by a differential thermal analyzer (DTA). Determination of the crystal growth temperature was somewhat complicated since the final crystalline phases changed depending on the crystallization temperature. Therefore, XRD patterns were recorded to identify the crystalline phases after heat treatment in the 1050–1200 °C range. In addition, the crystallinity of the specimens and the relative amount of each crystalline phase were calculated from the peak areas in the XRD patterns using Williams' method [8]. The morphology of the crystalline phases was investigated using a scanning electron microscope (SEM).

Several techniques were used to evaluate the properties of glasses and glass-ceramics. Density was measured by the Archimedes' method using water as a medium. Hardness and fracture toughness were measured by an indentation method using the Vickers indenter [9]. Vickers hardness was measured with loads of 100–1000 g with loading times of 10 s. Bending strength was obtained from a four-point method with spans of 20 and 40 mm at a cross-head speed of 100 μm/min, as designated by American Society of Testing Materials (ASTM) E855-90 [10]. The thermal expansion coefficient (α) was measured by TMA with a heating rate of 10 °C/mm in air atmosphere. Acid resistance was measured following the designation of ASTM C279–88 [11]. First, powdered specimens were prepared in particle sizes of 4.75–6.75 mm. Twenty grams of the powder were then immersed into 100 ml of sulfuric acid (78 wt.%) and boiled on a hot plate for 48 h. The specimens were dehydrated and acid resistance was estimated by measuring the weight loss of powders.

Table 1
Chemical composition of fly ash from a sewage sludge incinerator

Component	wt.%	Component	wt.%
SiO_2	39.52	MgO	2.13
Al_2O_3	17.17	SO_3	1.97
Fe_2O_3	11.91	Na_2O	1.23
P_2O_5	7.55	TiO_2	0.81
CaO	7.16	ZnO	0.52
K_2O	2.72	Others (containing L.O.I.)	7.31

3. Results and discussion

Ashes produced by incinerating sewage sludge can be vitrified without addition of glass-forming agents such as SiO_2 and B_2O_3. However, a small amount of CaO ($\sim$10 wt.%) was added to obtain the target crystalline phases. Up to 30 wt.% of CaO can be added to ash without crystallization. The crystallization sample had a composition of 90 fly ash-10 CaO in wt.%.

As explained previously, nucleation temperature was 760 °C, 30 °C higher than the measured dilatometric softening point [7]. After nucleating for different time duration, all specimens were crystallized at 100 °C for 2 h. The optimum duration for nucleation was determined from the maximum in the ratio between the sum of the intensity of the largest peaks (I_3) to that of all peaks (I_{total}) in the XRD pattern. Fig. 1 shows that crystallization was most effective when the nucleation duration

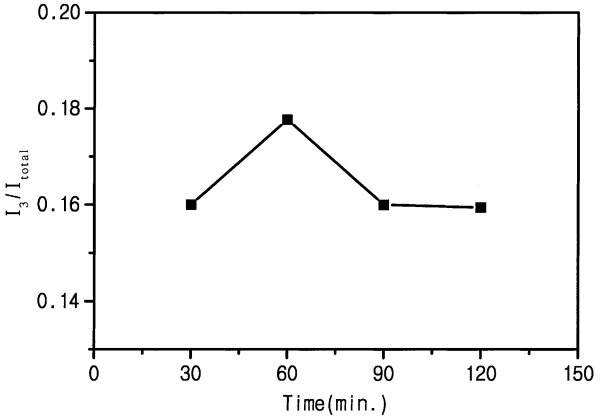

Fig. 1. Determination of the optimum nucleation duration. Nucleation temperature was 760 °C and crystallization was performed at 1100 °C for 2 h.

is 1 h. Therefore, all samples in this study were nucleated for 1 h at 760 °C.

The DTA curve of the glass sample showed an exothermic peak in the temperature range of 1020–1200 °C due to crystallization. The specimens were first nucleated at 760 °C for 1 h and then heat-treated for another 2 h in the range of 1050–1200 °C at a 50 °C interval. Crystals formed during heat treatment were identified as shown in Fig. 2. At first, when the glasses were crystallized at 1050 °C, a major crystalline phase was diopside with a small amounts of anorthite. However, when the heat-treatment temperature increased, relative amount of anorthite increased until it became a major crystalline phase. Changes in crystallization duration did not affect the formation of crystalline phases and the major crystalline phases remained similar to those in Fig. 2. When the crystallization temperature reached 1050 °C, diopside crystals were observed even after heat treatment of

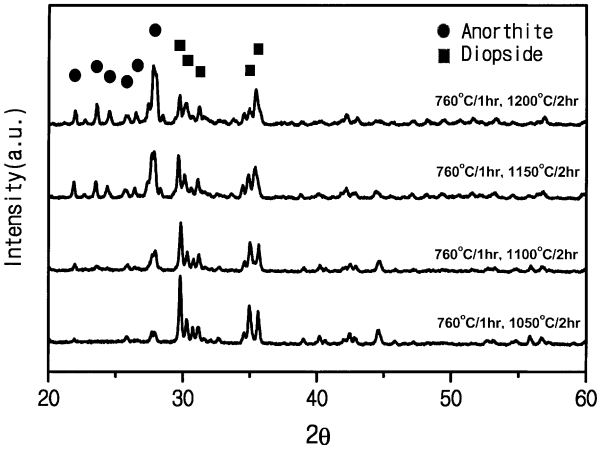

Fig. 2. X-ray diffractograms of glass-ceramics produced after heat treatment at various crystallization temperatures for 2 h. Each diffractogram was shifted for clarity.

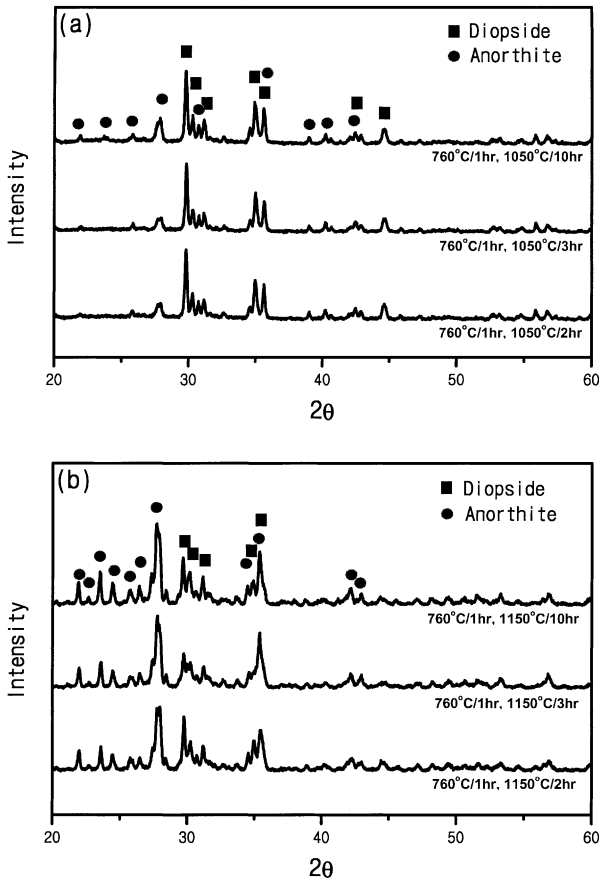

Fig. 3. X-ray diffractograms of glass-ceramics after heat treatment at 1050 °C (a) and 1150 °C (b) for various time durations.

10 h [Fig. 3(a)]. Similarly, at 1150 °C, a major portion was occupied by anorthite crystals [Fig. 3(b)]. The microstructure of crystalline phases observed by SEM also confirmed the formation of two distinct crystalline phases (Fig. 4). When the specimen was crystallized for 2 h at 1050 °C, square pillar-like crystals were formed [Fig. 4(a)] while the specimen crystallized for 3 h at 1150 °C had typical layered structures of anorthite [Fig. 4(b)]. Crystallinity and the relative fraction of both crystalline phases were investigated using Williams' method [8]. The crystallinities of specimens crystallized at 1050 °C/2 h and 1150 °C/3 h were approximately 80% in both cases. The specimen heat-treated at 1050 °C for 2 h (1050 °C/2 h) consisted of 37% anorthite and 43% diopside while the 1150 °C/3 h specimen contained 54% anorthite and 24% diopside.

The properties of the glass and glass-ceramics are summarized in Table 2. Glass-ceramics were prepared under two different crystallization conditions, 1050 °C/2 h and 1150 °C/3 h after nucleation at 760 °C for 1 h, as explained previously. Improvement was observed after conversion of the glass to glass-ceramics. The Vickers hardness of the glass was 4590 MPa and increased up to 6230 MPa in glass-ceramics. This microhardness is

Table 2
Properties of glasses and glass-ceramics

	Glass	Glass-ceramics	
		760 °C/1 h, 1050 °C/2 h	760 °C/1 h, 1150 °C/3 h
Vickers micro-hardness (MPa)	4590	6230	5860
Bending strength (MPa)	70	92	75
Thermal expansion coefficient (α)	88×10^{-7}/K	83×10^{-7}/K	74×10^{-7}/K
Density (g/cm^3)	2.83	2.87	2.93

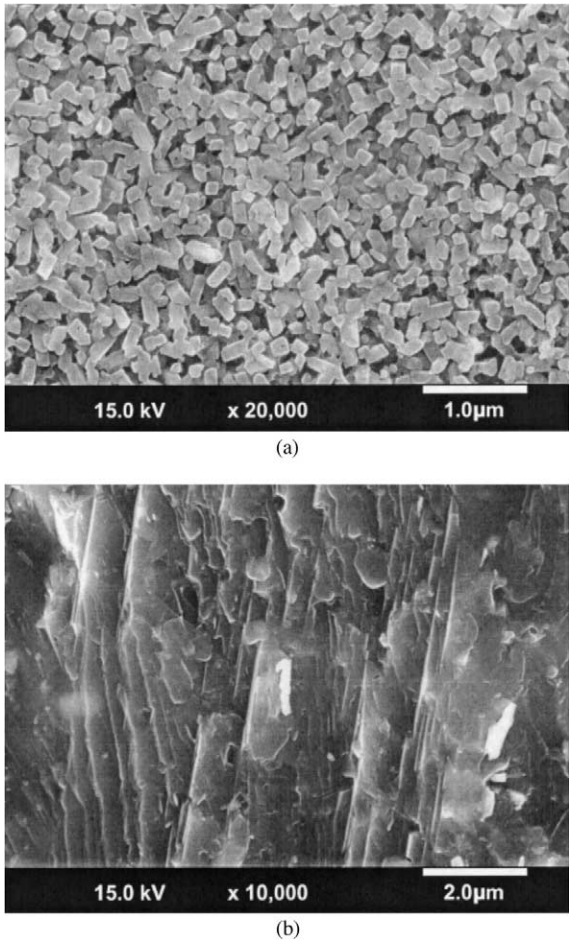

Fig. 4. Scanning electron micrograph of glass-ceramics. Heat treatment schedules were 1 h/760 °C for nucleation, (a) 2 h/1050 °C and (b) 3 h/1150 °C for crystallization.

comparable to the values found in $MgO–Al_2O_3–SiO_2$ glass-ceramics (6180 MPa) [13] or granites (5500 MPa) [14]. Bending strength also improved from 70 MPa in glass to 92 and 75 MPa, respectively, in glass-ceramics. These values again are similar to those of $CaO–MgO–SiO_2$ glass-ceramics (90–130 MPa) and $Li_2O–Al_3–SiO_2$ glass-ceramics (100–130 MPa) [6]. The thermal expansion coefficient (α) decreased slightly upon crystallization with a small increase in densities. In addition, an acid resistance test (ASTM C279-8) was performed to evaluate chemical durability. The glass-ceramics showed a weight loss of less than 2 wt.% after boiling for 48 h in sulfuric acid. Weight loss of a marble was approximately 2.5 wt.%. The results of various properties and acid resistance measurements indicate that glass-ceramics heat-treated at 1050 °C for 2 h are better than those heat-treated at 1150 °C. The difference in physical and chemical properties may be due to the different crystalline phases and microstructures of glass-ceramics. Interlocked diopside structures are more advantageous compared with layered anorthite structures.

4. Conclusions

Glasses and glass-ceramics were prepared from ash collected from sewage sludge incinerators. The optimum nucleation condition was heating at 760 °C for one hour. Crystallization of the nucleated specimen in the 1050–1200 °C region resulted in the formation of two crystalline phases, i.e. anorthite and diopside. Specimens heat-treated for 2 h at 1050 °C consisted mainly of diopside crystals with a minor proportion of anorthite. On the other hand, those heat-treated at 1150 °C were composed mainly of anorthite. Glass-ceramics crystallized at 1050 °C for 2 h showed a microhardness of 6230 MPa and a bending strength of 92 MPa. Glass-ceramics containing large amounts of diopside (1050 °C/2 h) generally showed better physical and chemical properties than their anorthite counterparts due to the interlocking microstructures of diopside crystals.

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