Journal of Ceramic Processing Research. Vol. 14, No. 1, pp. 51~55 (2013)

J O U R N A L O F
Ceramic Processing Research

Fracture toughness of glass-ceramics produced from power plant fly ash

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The fracture toughness of glass ceramics produced from the fly ash of the Seyitömer power plant of Turkey has been investigated using an indentation fracture technique. In this process, fly ash was melted and cast as a glass. The glass materials produced were heat treated at 1073 K, 1123 K and 1173 K for 30-240 minutes in order to obtain glass-ceramics. X-ray diffraction analysis (XRD) showed that the phases formed in the glass ceramics were diopsite and augite. Atomic force microscope (AFM) images were used for the examination of the surface structure of the glass ceramics. The fracture toughness of the glass ceramics ranged from 1.80 ± 0.15 MPa.m$^{1/2}$ to 2.92 ± 0.65 MPa.m$^{1/2}$ depending on the treatment temperature and time. The higher the crystallization temperature and the longer the treatment time, the higher the fracture toughness became.

Key words: Fly ash, Glass-ceramics, Fracture toughness, Hardness.

Introduction

Increasing demands for the generation of more electric power has resulted in construction of coal-fired thermal power plants worldwide. Thus, coal consumption and generation of combustion wastes have increased [1]. Significant amounts of solid wastes are produced during combustion of coal in thermal power plants. This residue is known as ash (unburned material) and can be classified with respect to the zone where it is recovered from. Thus, two types of ash are distinguished: fly ash (FA) and bottom ash (BA). Bottom-ash is collected at the base of the combustion chamber and consists of a slag-type material. However, fly ash is the finer fraction, collected from the flue gas by an air pollution control (APC) device that poses the more serious environmental problems. Fly ash consists of fine particles that contain leachable heavy metals, and is therefore classified as a toxic waste [2, 3]. A large amount of information is available on the application of wastes such as coal fly ash, or blast furnace slag. Each potential application of fly ash results in three main advantages: first, the use of a zero-cost raw material, secondly, the conservation of natural resources, and thirdly, the elimination of waste [2]. At present, there is an intensive search to increase their uses, although they are utilized as raw materials in the cement industry [3]. The potential uses of fly ash are as follows; construction materials, geotechnical uses, agriculture and miscellaneous uses [4].

Glass-ceramic production is an alternative for the reuse of coal fly ash [5, 6]. Fly ash contains valuable mineral resources such as SiO_2, Al_2O_3, Fe_2O_3, CaO, etc. The chemical composition of fly ash makes it quite suitable for use as the raw material for structural glass-ceramics [7-9]. In recent years, much research and many investigations have been conducted in its utilization as a starting material for glass-ceramic production [10, 11]. Glass-ceramics, which have unique mechanical properties such as a high mechanical strength, good dimensional stability and abrasion resistance, are not only suitable for replacing more traditional materials in many applications, but can be used in entirely new fields where no alternative material can satisfy the technical demands [8]. Typically, glass-ceramics obtained from fly ash are produced by a combination of a melting process and one or two-stage heat treatment for crystallization, nucleation and crystal growth [7].

In the present study, fly ash obtained from the Seyitömer power plant in Turkey was used as the raw material to produce glass-ceramic materials. Grain growth kinetics of these glass-ceramics has been investigated in our previous study [1]. The main aim of this study is to investigate the fracture toughness of the fly ash based glass ceramics depending on the process parameters such as the treatment temperature and time.

Experimental

Seyitömer power plant fly ash in Turkey was used as a raw material in the present study. The chemical composition of the fly ash is given in Table 1. Glass samples were prepared by melting the fly ash in a platinum-2% rhodium crucible at 1773 K for 2 h using an electric furnace (HERAUS). To ensure homogeneity, the melt was poured into water. The cast was crushed,

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Table 1. Chemical composition of the Seyitömer thermal power plant's fly ash.

Compounds (Wt. %)								
SiO_2	Al_2O_3	Fe_2O_3	K_2O	ZnO	CaO	MgO	Na_2O	Loss on ignition
55.67	11.67	11.90	1.71	0.01	4.75	4.40	0.70	9.19

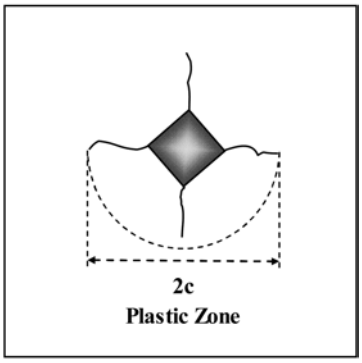

Fig. 1. Schematic view of the indentation mark and crack length.

pulverised and remelted at the same temperature for 2 h to achieve homogeneity. The refined and homogenized melt was cast into a preheated stainless steel rectangular mould with the dimensions of $1 \times 3 \times 0.5$ cm^3.

Crystallization heat treatments of the glass produced were performed in an electric furnace with a heating rate of 10 K $minute^{-1}$ at 1073 K, 1123 K and 1173 K for a period of 30-240 minutes to obtain the glass ceramic by a single stage method and to promote internal crystallization. The samples were cooled down to room temperature in the furnace. The samples were then ground, polished and etched, metallographically. An etchant of a 10% HF solution of was used for etching. The samples were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) analysis. The AFM images were obtained using a Quesant AFM at 3 Hz scanning rate. X-ray diffraction (XRD) analysis was conducted on a Rigaku D/MAX-2200/PC type difractometer with Cu K_α radiation, which has a wavelength of 1.5418 Å to analyze the phases present in the glass-ceramic materials. The hardness and indentation fracture toughness tests were performed on the polished surface of the samples using a Vickers microhardness tester (FutureTech FM 700) under a load of 100 gf for 15 s.

The fracture toughness of a material is of critical importance in mechanical applications [12, 13]. The use of the Vickers indentation method to assess fracture toughness of brittle materials such as glasses and ceramics has been developed [14]. The Vickers diamond indenter is a standard item used on a dedicated hardness tester or on a universal testing machine. In many instances, the crack length can be measured optically [15-17]. The equation used for calculating the fracture toughness is as follows:

$$K_c = X\frac{P}{c^{3/2}} \quad (1)$$

where X is the residual-indentation coefficient, P is the load and c is half of the indentation crack length as dened in Fig. 1 [11]. Crack lengths were immediately measured by an optical micrometer attached to the optical microscope. Tests were repeated three times under the same conditions to ensure the reproducibility of the fracture toughness data. The formula used in the calculation of the present study was [18, 19]:

$$K_c = 0.0824\frac{P}{c^{3/2}} \quad (2)$$

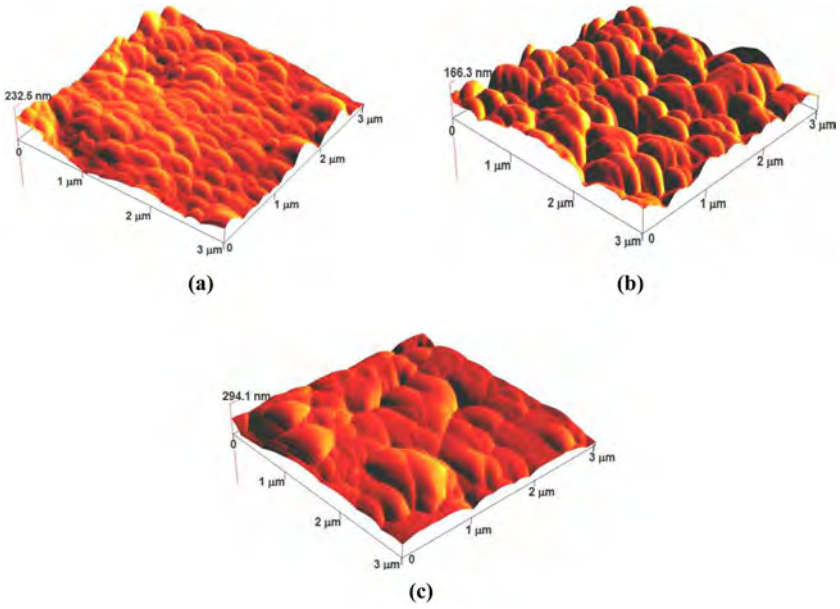

Fig. 2. AFM images of glass ceramics produced from fly ash heat treated at (a) 1073 K, (b) 1123 K and (c) 1173 K for 120 minutes.

Results and Discussion

Fig. 2 shows AFM images of glass ceramics from the surfaces depending on crystallization heat treatment temperatures. Glass ceramics produced from the fly ash have an almost homogeneously distributed and equiaxed grain structure and the grain size increases with an increase in the crystallization temperature as shown from these figures. Fig. 3 shows the grain size of the glass ceramics depending on the crystallization time and temperatures. The higher the crystallization temperature and the longer the treatment time, the coarser the grain size became.

The phases present within the glass ceramic were determined by X-ray diffraction (XRD) analysis. XRD analysis of the glass-ceramics heat treated at 1073 K, 1123 K and 1173 K for 120 minutes are seen in Fig. 4. X-ray diffraction analysis showed that the phases formed in the glass ceramics are diopsite and augite besides the minor phase lisetite (see Fig. 4). These phases are usually referred to as one phase named diopsitic-augite in the literature [8, 9, 20, 21]. The intensity of the diopsitic-augite peaks in the X-ray diffraction analysis increases with an increase in the crystallization treatment temperatures. The result is good agreement with the study of Erol et al. [6]. The diopsitic-augite provides superior abrasion and chemical resistance to glass-ceramics [20-22]. The degree of crystallinity of the glass produced from fly ash increases with an increase in the crystallization temperature as shown in Fig. 4.

The hardness of the glass ceramics obtained varies between 506 ± 12 $HV_{0.1}$ and 696 ± 46 $HV_{0.1}$ depending on crystallization temperature and time, see Fig. 5 (a) and (b). The contour diagram is very important for practical applications in scientific research. Thanks to the contour diagram, either process parameters can be calculated for a predetermined hardness value or a hardness value can be predicted depending on the process parameters [23]. An increase in the crystallization temperature and time results in a higher hardness because of the increased hard diopsitic-augite phase in

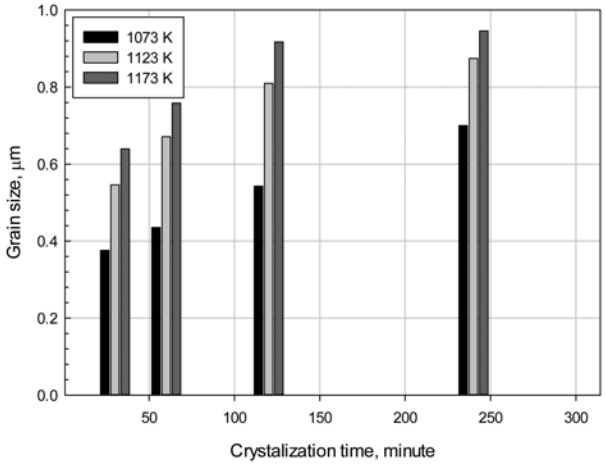

Fig. 3. Variation of grain size of the glass-ceramics produced from fly ash depending on the crystallization time and temperature.

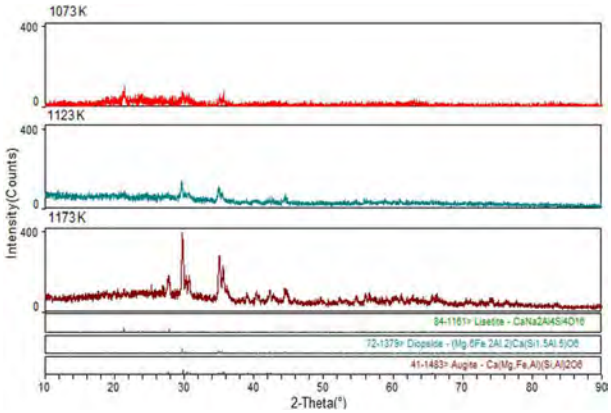

Fig. 4. XRD patterns of glass ceramics produced from fly ash heat treated at (a) 1073 K, (b) 1123 K and (c) 1173 K for 120 minutes.

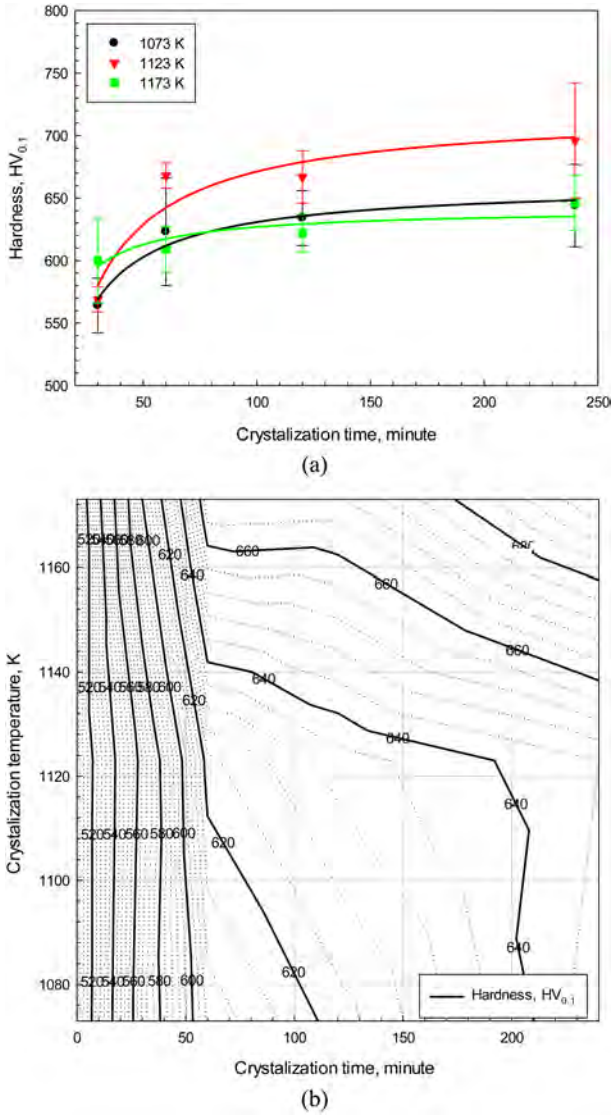

Fig. 5. (a) Hardness curves as a function of crystallization time and temperature, (b) Iso-harness diagrams.

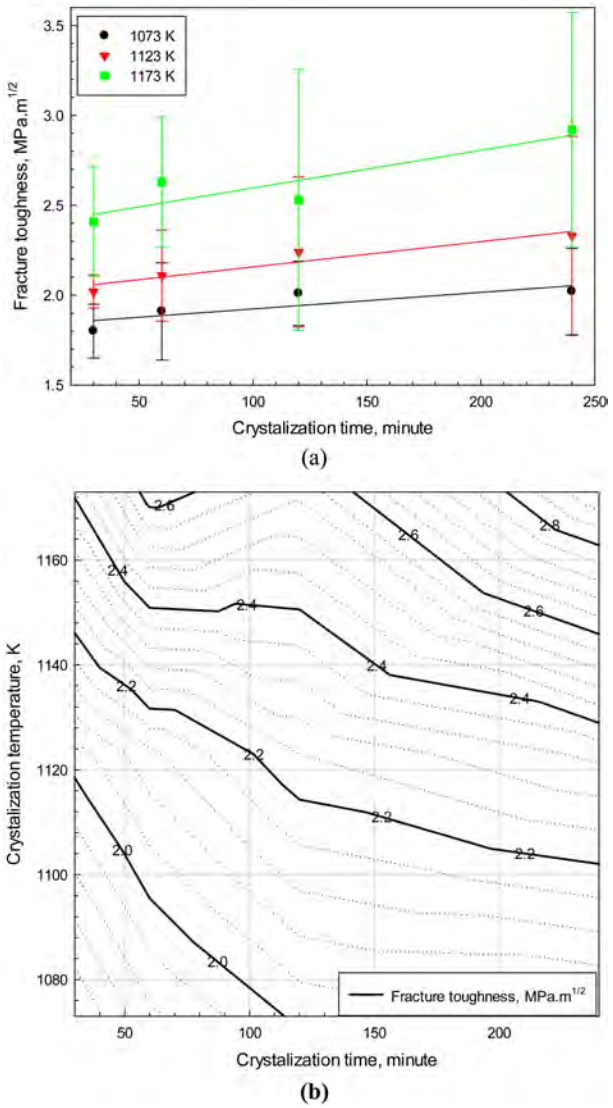

Fig. 6. (a) Fracture toughness curves as a function of crystallization time and temperature, (b) Iso-fracture toughness diagrams.

the glass ceramic (see Fig. 4). In the literature, the hardness values of fly ash based glass-ceramics ranges between 440 $HV_{0.1}$ and 730 $HV_{0.1}$ [7, 24, 25].

Fig. 6 presents the variation of fracture toughness of the glass-ceramics depending on the crystallization time and temperature. Fracture toughness of the glass ceramics produced from fly ash ranges between 1.80 ± 0.15 MPa.m$^{1/2}$ and 2.92 ± 0.65 MPa.m$^{1/2}$. The fracture toughness value of the glass ceramics produced increases with an increase in the crystallization time and temperature as shown in Fig. 6.

The fracture toughness value increased 12.22% when the crystallization time was increased 700% at 1073 K process temperature. The increment in fracture toughness value of glass ceramics depending on crystallization time at 1123 and 1173 K was approximately 15.35% and 21.16%, respectively. When increasing the crystallization temperature from 1073 to 1173 K, a 44.55% increment in the fracture toughness value of the glass ceramic was recorded for a 240 minute crystallization treatment. This indicates that the fracture toughness of the glass ceramics increases with increasing treatment time and temperature. Furthermore, the crystallization temperature has a considerable effect on the increment of fracture toughness of glass ceramics. Fracture toughness values of some fly ash based glass ceramics are given in Table 2. These values agree with the present study as shown in Table 2.

Table 2. Fracture toughness values of the some fly ash based glass ceramics [26-28].

Authors	Fracture Toughness (MPa.m$^{1/2}$)	Ref.
Y.J. Parka and J. Heo	1.86	[26]
E. Furlani et al.	0.9 ± 0.1 1.7 ± 0.25 2.9 ± 0.3 2.1 ± 0.1	[27]
A.R. Boccaccini et al.	0.7-1.7	[28]
Present study	1.80 ± 0.15 and 2.92 ± 0.65	

As a result, an increment in the crystallization time and temperature not only increases the fracture toughness and hardness values but also the grain size and crystallization degree.

Conclusions

The following conclusions can be drawn from the present study;

(i) Glass ceramics produced from fly ash of the Seyitömer power plant of Turkey have augite and diopside phases.
(ii) Higher treatment temperatures cause an increase in peak intensities of the X-ray diffraction patterns.
(iii) An increase in the crystallization temperature and time resulted in a coarser grain size of the glass ceramics.
(iv) The hardness of the glass ceramics varies between 506 ± 12 $HV_{0.1}$ and 696 ± 46 $HV_{0.1}$ depending on the crystallization temperature and time.
(v) The values of fracture toughness of the glass ceramics were between 1.80 ± 0.15 MPa.m$^{1/2}$ and 2.92 ± 0.65 MPa.m$^{1/2}$ depending on the process parameters.
(vi) Increasing the crystallization time and temperature causes the fracture toughness of the glass ceramics to increase.

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