Waste glass and fly ash derived glass-ceramic

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Crystallization behavior of a waste-based glass-ceramic was studied by means of X-ray diffraction analysis, and the surface morphological observations and chemical compositions were evaluated by field emission-scanning electron microscopy and energy dispersive X-ray spectrometry. Applying the mechanical milling method, the glass-ceramic was prepared by using fly ash from a thermal power plant mixed with waste glass cullet. Powder mixtures consisting of waste glass powder (70 wt%) and fly ash (30 wt%) were used to make glass-ceramic. Various heat treatment temperatures [900, 925, 950, 975, 1000 and 1025°C] were used to obtain a glass-ceramic of the optimum crystal phase, mechanical properties and chemical durability. The X-ray diffraction analysis showed that the crystalline phases in the glass-ceramic were diopside [Ca(Mg, Al)(Si, Al)$_2$O$_6$], augite [Ca(Mg, Fe)Si$_2$O$_6$] and wollastonite [CaSiO$_3$]. The crystallization of an acicular phase in the matrix was achieved in the heat treatment temperature range of 1000–1025°C, and the acicular type main crystal phase in the glass-ceramic was wollastonite [CaSiO$_3$]. The heat treatment temperature range [1000–1025°C] also showed much better mechanical properties.

1. Introduction

Recent industrial developments have drastically increased the amounts of waste materials [1], and many concerns have been raised regarding the treatment and disposal of waste materials. Fly ash produced in thermal power plants poses serious environmental problems. In 1999 about 3.9 million tons of fly ash was generated in Korea to become a topic of the environmental and social interest [2]. Fly ash has been recycled through thermal treatment to be used for construction materials as aggregates, bricks, tiles and eco-cement [3,4].

The massive amount of industrial and domestic waste glass without proper management and disposal continues to pose one of the most challenging problems. More than 0.6 million tons of waste glass is generated per annum in South Korea including glass containers, light bulbs, plate glass, and automobile window glass [9]. Many research and development investigations have been conducted on its utilization as a starting material for glass-ceramic production [5–8].

In this study, glass-ceramic was prepared by using fly ash from the thermal power plant and waste glass cullet. It is important to note that waste materials such as fly ash and glass are recycled, and many recycling problems such as chemical bonding by heat-treatment and economic loss caused by several thermal steps are solved by mechanical processing by disk type ball milling. In the present work, crystallinity and morphological properties were analyzed by varying the heat-treatment temperatures. Energy dispersive X-ray spectrometer (EDS) was used to observe and analyze the chemical composition. Mechanical properties of the glass-ceramic have been studied.

2. Experimental procedure

Fly ash from thermal power plants (Yeocheon, Chonnam) in South Korea and waste glass cullet mixed from all kind of waste glass (bottles, automobile windows, plates, etc.) were used to prepare the glass-ceramic. The composition of the fly ash and waste glass cullet is shown in Table I.

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TABLE I. Chemical composition (wt%) of the raw materials used in this work

Oxide	Waste glass	Fly ash
SiO_2	73.17	44.38
Na_2O	12.29	–
CaO	7.91	24.69
MgO	2.07	4.93
Al_2O_3	2.85	21.97
K_2O	1.71	–
Fe_2O_3	–	4.03

Fly ash (−150 mesh) from the thermal power plant was used in the as-received condition. Waste glass cullet was washed and dried in a dry oven at 60°C for 12 h. Waste glass powder was obtained by grinding the waste glass cullet in a disk type ball mill (Retsch GmbH & Co. KG., D-42781 HAAN, TYPE:RS1, Germany) for 30 min (700 rpm). The powder size of the obtained waste glass was about −150 mesh.

To make glass-ceramic, powder mixtures consist of waste glass powder (70 wt%) and fly ash (30 wt%). Two different powder mixtures, about 60 g of waste glass and fly ash, were mechanically ground in a disk type ball mill for 4 h (700 rpm). After milling, the mixture was pressed into cylindrical shape having a diameter of 10 mm and length of 30 mm without using any binder. The formed disks were heated up to 900°C, 925°C, 950°C, 975°C, 1000°C and 1025°C at the rate of 5°C/min for 1 h in a box-type SiC furnace and allowed to cool inside the furnace. After the heat treatment, the glass-ceramic specimens were cleaned with ethyl alcohol in an ultrasonic cleaner and dried at 70°C for 10 h. Fig. 1 shows the experimental procedure in this work.

Crystallinity of the glass-ceramic specimens was measured by X-ray diffraction (XRD, Rigaku Co., D-Max-1200, Jpn.) with CuKα radiation generated at 40 kV and 30 mA, in the $5^\circ < 2\theta < 55^\circ$ range at a scan speed of 2° 2θ/ min. The crystallized phases were identified by comparing the peak positions and intensities with those in the JCPDS data files. The changes in crystallinity, the morphological properties of crystal, and the matrix structures with variation of the heat-treatment temperatures were investigated using field emission – scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Jpn.) equipped with an energy dispersive X-ray spectrometer (EDS) that has a Robinson type backscattered electron detector. Density, compressive strength, bending strength and chemical durability were also investigated. Density was measured using an Electronic Densimeter (ED-120T, MFD BY A&D CO., LTD, Japan). The compressive strength was examined with a universal tester (Instron 4302, Instron Co., England), and the bending strength was determined from the 4-point bending strength test in a Shimadzu Universal Testing Machine model Autograph AG-A series. The chemical durability was analyzed by the measurement of weight change resulting from immersing in 15 mL acidic solution (1 N H_2SO_4) at 60°C for 48 h. After immersing, specimens were washed with distilled water and dried at 80°C for 12 h.

3. Results and discussion

A glass-ceramic was prepared using fly ash and waste glass cullet for raw materials. Fig. 2 gives the XRD pattern of fly ash powder (−150 mesh) used in this study. The FE-SEM morphological analysis of the fly ash powder is shown in Fig. 3. The fly ash contained 44.38:SiO_2, 24.69:CaO and 21.97:Al_2O_3 consisting of silicate minerals that are spherically and irregularly round-shaped powder particles with an agglomerate size of 1.2–7.3. As shown in Fig. 2, the mineral phases of the fly ash powder are identified as α-quartz (SiO_2), mullite ($Al_6Si_2O_{13}$) and enstatite [(Mg, Fe)SiO_3]. The peaks are typically detected in the XRD pattern of the fly ash powder [10].

The XRD results on the glass-ceramic heat-treated at various temperatures (900°C, 925°C, 950°C, 975°C, 1000°C and 1025°C) show that their crystal structures are mixed with various crystals (Fig. 4). The crystalline phases present in the glass-ceramic correspond to diopside [Ca (Mg, Al)(Si, Al)$_2O_6$], Augite [Ca(Mg, Fe)Si_2O_6] and wollastonite [$CaSiO_3$]. Peak intensities corresponding to the diopside + wollastonite crystal and wollastonite crystal gradually increased, and the augite + diopside, diopside and augite crystals decreased with the increase of heat-treatment temperature from 900°C to 1025°C. As shown in Fig. 4, the peaks at $2\theta = 27^\circ$, 30° and 42° corresponding to augite + diopside, the peak at $2\theta = 29.8^\circ$ corresponding to augite, and the peak at $2\theta = 39^\circ$ corresponding to diopside decreased with an increase of heat-

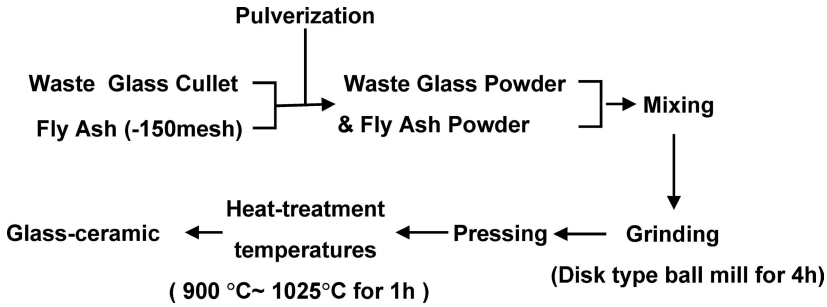

Figure 1 Scheme of the experimental procedure.

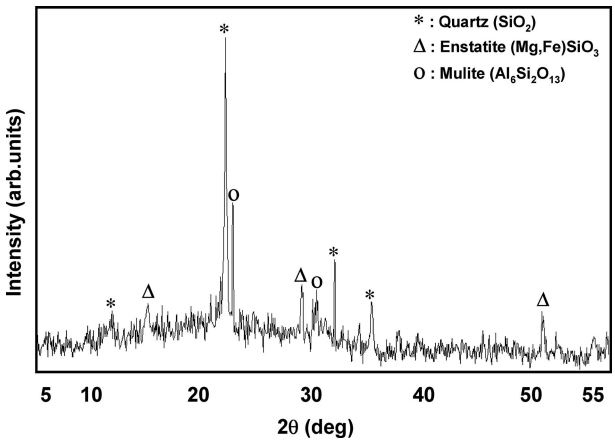

Figure 2 XRD pattern for the fly ash used in this study.

treatment temperature. In contrast, when heat-treatment temperature was increased as shown in Fig. 4, a distinct increase of peak intensity was identified, for the peaks at around $2\theta = 23°$, 25°, 26° and 28° corresponding to wollastonite crystals, and newly formed peaks at around $2\theta = 23°$ and 26° corresponding to wollastonite were also identified. The peak at 29.9° corresponding to wollastonite + diopside showed an increase of intensity from 900°C to 1025°. At 1025°C, the highest crystallized wollastonite peak appeared. As the heat-treatment temperature increased, the formation of the wollastonite became easier because it was affected by the decrease of the augite, diopside crystals.

Fig. 5 shows the surface morphology of the glass-ceramics at various heat-treatment temperatures [900°C (a), 925°C (b), 950°C (c), 975°C (d), 1000°C (e) and 1025°C (f)]. As shown in Figs 5a–c, the specimens heat-treated at 900°C, 925°C and 950°C was analyzed by observing surface morphology with field emission-scanning electron microscopy. The surface of the specimens annealed at 900°C (a), 925°C (b) were porous with various particles throughout the specimens. It is clearly that the

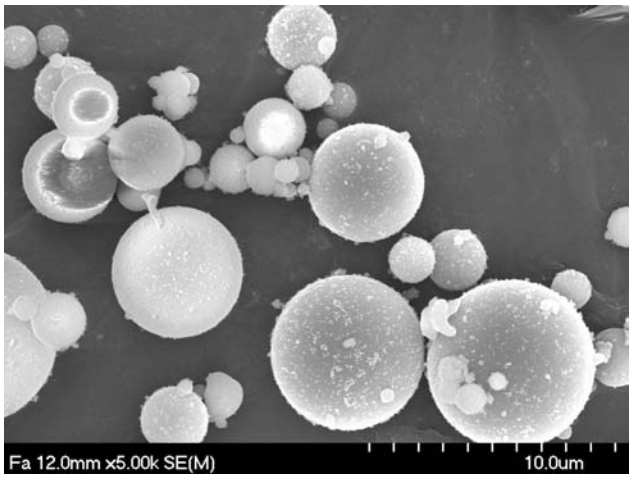

Figure 3. FE-SEM image for the fly ash from thermal power plant (Yeocheon, Chonnam) in South Korea.

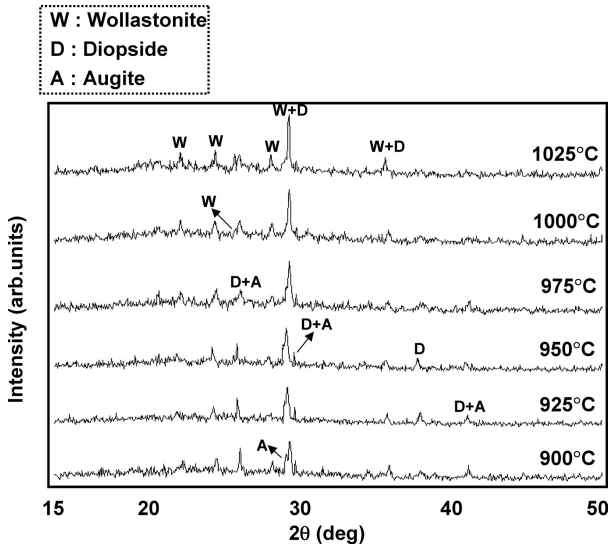

Figure 4 XRD patterns for the glass-ceramic heat-treated at 900–1025°C.

porous of surface is caused by the vaporization of organics during heat treatment or insufficient annealing.

Figs 5a–c show that many round-shaped grains and acicular type grains are irregularly distributed in the matrix. However, as the heat-treatment temperatures are increased to 1000°C and 1025°C (Fig. 5e, f), the round-shape grains disappeared, and a high density of well-crystallized acicular type grains are generally aggregated in the matrix from about 7 μm to 13 μm in size. This is typical of the wollastonite type glass-ceramic formed at heat treatment temperatures of 1000°C and 1025°C, and the XRD and FE-SEM results showed a surface crystallization mechanism with the formation of acicular type grains of wollastonite [11].

To investigate the crystal composition, we performed EDS analysis on the same area used in the morphological analysis. Chemical compositions of the surface for the glass-ceramic heat-treated at 1025°C (a, c) and 900°C (b, d)]are shown in Fig. 6. The calcium ion content in the acicular type grain (Fig. 6c) in the glass matrix confirmed by EDS is significantly larger than that in the round shape grain (Fig. 6d). This is consistent with the acicular crystals being wollastonite. The XRD, FE-SEM, EDS results revealed that the glass-ceramic heat-treated at 1025°C consists mainly of wollastonite crystals of whisker type acicular grains.

As shown in Figs 4–6, progressive increase in heat-treatment temperature causes changes in the crystal shape condition of specimens, demonstrating that heat-treatment temperature is an important factor in the crystal formation.

Table II shows the chemical durability (weight change%) of the specimens heat treated at 900–1025°C. To calculate the weight change, we defined the degree of the chemical durability as follows:

Chemical durability (weight change%) $= (m_1 - m_2)/m_1 \times 100$ where m_1 and m_2 are the weights of the specimens before and after immersing in acidic solution [12].

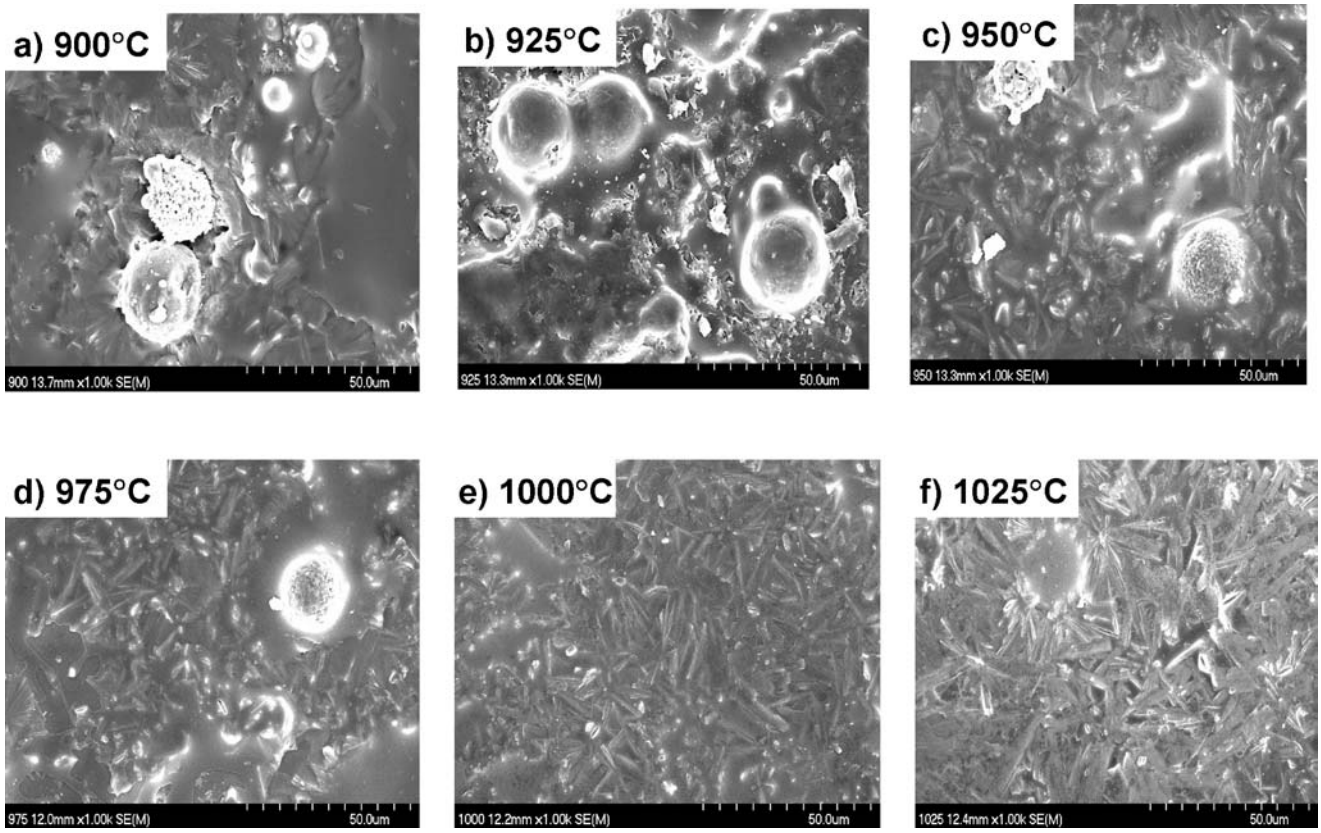

Figure 5 FE-SEM images for the glass-ceramic heat-treated at 900°C (a)–1025°C (f).

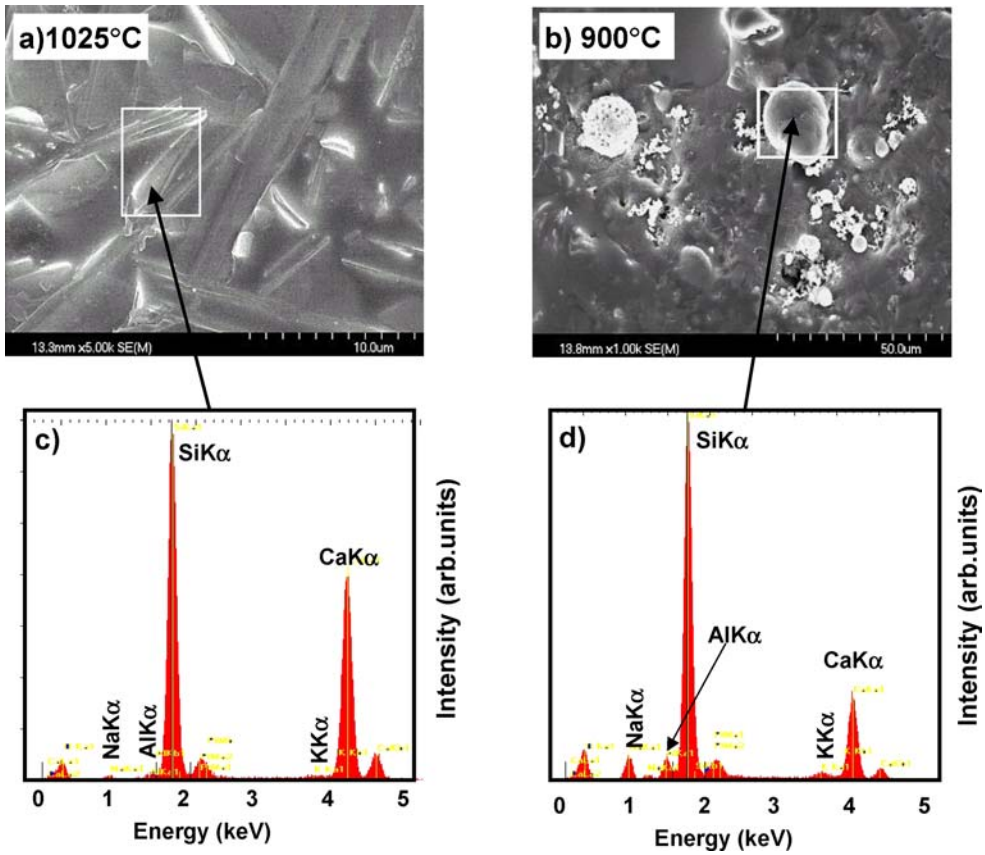

Figure 6 FE-SEM images and chemical compositions of surface from EDS for the glass-ceramic heat-treated at 1025°C (a), (c) and 900°C (b), (d).

TABLE II. Density and weight change% for the glass-ceramic heat-treated at 900–1025°C

	900°C	925°C	950°C	975°C	1000°C	1025°C
Density (gcm^{-3})	2.610	2.748	2.712	2.699	2.709	2.693
Weight change%	0.149	0.138	0.145	0.140	0.137	0.141

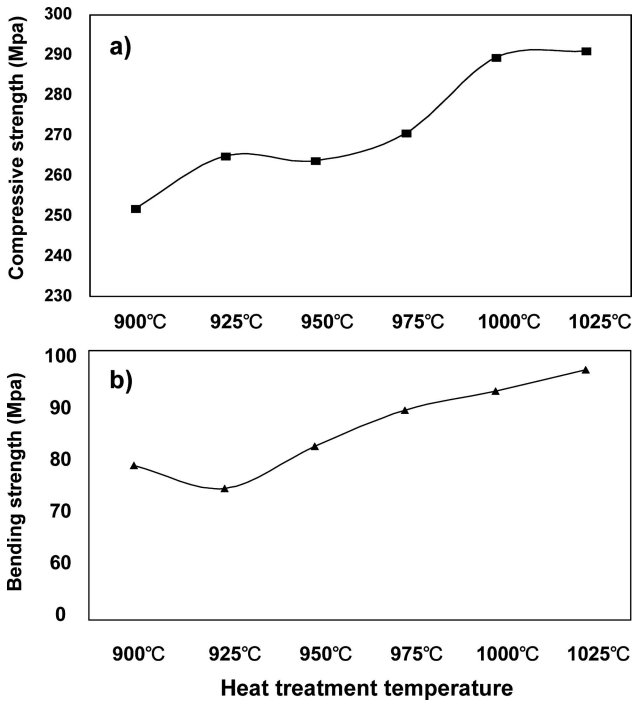

Figure 7 Compressive strength (a) and bending strength (b) for the glass-ceramic heat-treated at 900–1025°C.

The weight changes in the specimens are not affected by the increasing heat-treatment temperatures, and it is difficult to investigate the exact chemical durability of the specimens due to their small weight changes before and after immersing.

Fig. 7 shows the results of our investigation on compressive strength and bending strength of the specimens at various temperatures. The data points are the average from tests on 5 samples. The compressive strength (Fig. 7a) increased from 251.9 to 291.1 MPa as the heat treatment temperature increased from 900°C to 1025°C, and the bending strength (Fig. 7b) also improved from 74.4 to 96.4 MPa.

It is evident as in Fig. 5f that the increase in the compressive and bending strength at 1025°C is due to the increasing acicular type grains, wollastonite crystals, in the glass-ceramic. Generally, the more the acicular type grains are included in the glass-ceramic, the greater the mechanical strength. We conclude that they have sufficient mechanical strength for practical usage.

4. Conclusions

Glass-ceramics were produced using Fly ash from thermal power plants and waste glass cullet mixed from various waste glass to resolve their environmental and recycling problems. The XRD, FE-SEM and EDS analyses results demonstrated that with an increase of the heat-treatment temperature from 900 to 1025°C, the round-shape grains in glass matrix decreased and/or disappeared, but glass-ceramic heat-treated at 1025°C was mainly composed of the wollastonite crystals with well-crystallized whisker type acicular shape. Proper combination ratio of waste glass and fly ash and suitable temperature for heat treatment are the most important issue in generating glass-ceramic containing acicular type crystalline phase with good mechanical property. The compressive strength and the bending strength of the glass-ceramics were proven to have good mechanical strength [compressive strength (900°C:251.9 MPa-1025°C:291.1 MPa); bending strength (900°C:78.7 MPa-1025°C:96.4 MPa)]. The Compressive strength and the bending strength of the glass-ceramic through all the heat-treatment temperatures exhibited sufficient mechanical strength for practical usage.

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