

The characterization of glass-ceramics made from waste glass and fly ash

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Glass-ceramics with well-crystallized whisker-type crystals were prepared by milling and heat treatment using fly ash from a thermal power plant and waste glass cullet. Various heat treatment temperatures [850, 900, 950 and 1000 °C] were used to obtain a glass-ceramics that have the optimum crystal phase and mechanical properties. The crystallization of a whisker-type phase in the matrix was achieved in the heat treatment temperature range of 950-1000 °C, and the whisker-type main crystal phase in the glass-ceramics was wollastonite [CaSiO₃]. The heat treatment temperature range [950-1000 °C] also brought about much better mechanical properties. Crystallinity, morphological properties, and chemical compositions were observed by X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), and an energy dispersive X-ray spectrometer (EDS). Various properties such as density, compressive strength, bending strength and chemical durability were also examined.

Key words: Glass-ceramics, Milling, whisker type crystal, Wollastonite.

Introduction

Fly ash containing a large amount of CaO, SiO₂, and Al₂O₃ can be a good raw material for the production of glass ceramics in the CaO-Al₂O₃-SiO₂ system [1]. Glass-ceramic systems have been used to extend recycling to several types of by-products such as fly ash from coal- and oil-fired electric power stations and urban solid waste incinerators [2]. Moreover, glass-ceramics are of particular interest because of their high melting temperature, low thermal expansion, good oxidation resistance, and low dielectric constant [3]. Although there are many ways of utilizing glass ceramics, fly ashes and blast furnace slags are being mainly used now for the production of building materials [4-6]. Glass ceramic production has been developed mainly from waste materials. Many researchers have reported the use of fly ashes combined with waste glass for the production of glass ceramics for potential architectural and decorative applications [7-8].

In this study, glass-ceramics was prepared using fly ash from a thermal power plant and waste glass cullet. Although recent papers have reported the use of fly ashes and waste glass cullet for the production of glass-ceramic [9, 10], there are many problems such as high cost of a dual thermal step. The purpose of this study is to obtain glass-ceramics by means of mechanical grinding that applies a disk-type ball mill and one time

thermal step. Throughout our study, crystallinity and morphological properties were analyzed at various heat-treatment temperatures. An energy dispersive X-ray spectrometer (EDS) was used to analyze and characterize the chemical compositions. Mechanical properties were also investigated on glass-ceramics synthesized from fly ash and waste glass cullet.

Experimental Procedure

Glass-ceramics was prepared using fly ash and waste glass cullet as raw materials. Fly ash from a thermal power plant (Yeocheon, Chonnam) in South Korea and waste glass cullet mixed with various kinds of waste glass such as bottles, automobile window shields, and plates were used. The chemical compositions of the raw materials, fly ash and waste glass cullet, are shown in Table 1.

Very fine powder (-200 mesh) fly ash from the thermal power plant was used in the experiment. Waste glass cullet was washed and dried in a dry oven at 60 °C for 8 h. Waste glass powder (-150 mesh) 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 20 minutes (700 rpm).

Waste glass powder and fly ash powder were mixed at a weight ratio of three parts waste glass powder to one part fly ash powder. Two different powder mixtures, about 80 g of waste glass and fly ash, were mechanically ground in a disk type ball mill for 6 h (700 rpm). After milling, the mixture was pressed into a cylindrical shape 10 mm in diameter and 30 mm in length

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Table 1. Chemical composition (wt.%) of the raw materials used in this study

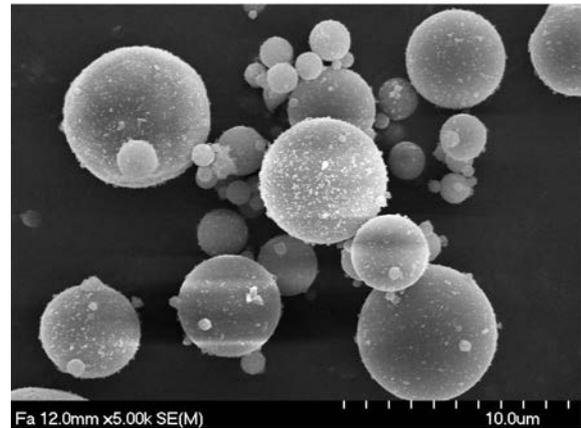
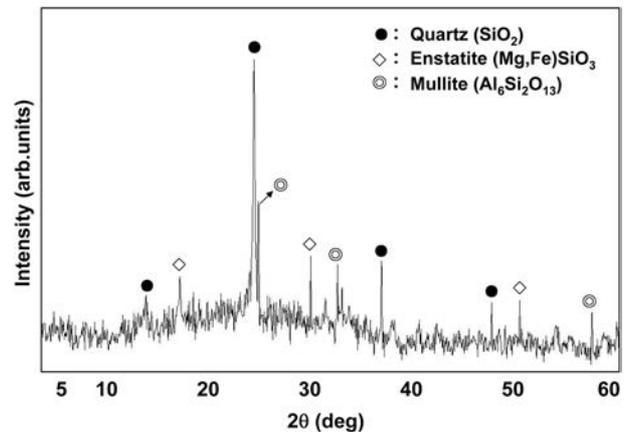
Oxide	Waste glass	Fly ash
SiO ₂	76.24	45.23
Na ₂ O	11.60	–
CaO	5.24	23.62
MgO	2.98	5.34
Al ₂ O ₃	2.21	20.69
K ₂ O	1.73	–
Fe ₂ O ₃	–	5.12

without using a binder. The specimens formed were annealed at 850 °C, 900 °C, 950 °C, 1000 °C for 1 h in a tube-type furnace and allowed to cool inside the furnace. The heat-treated specimens were cleaned with ethyl alcohol in an ultrasonic cleaner and dried at 110 °C for 12 h.

The crystalline phases of the specimens were established by X-ray diffraction (XRD, Rigaku Co., D-Max-1200, Jpn.) with CuK α radiation generated at 40 kV and 30 mA, in the 5° < 2 θ < 60° range at a scan speed of 2° 2 θ /minute. 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 the crystals, and the matrix structures with the variations induced by heat-treatment 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. The density, compressive strength, bending strength and chemical durability of the specimens were also investigated. The density was measured using an Electronic Densimeter (ED-120T, MFD BY A&D CO., LTD, Japan). The compressive strength was investigated by a universal tester (Instron 4302, Instron Co., England), and the bending strength was determined by a 3-point bending strength test in a universal tester (Instron N8872, Instron Co., England). The Vickers hardness was estimated using a Vickers' hardness tester (Shimadzu Co., HMV-2 series, Japan). The chemical durability was analyzed by the measurement of weight changes resulting from immersing in 15 ml acidic solution (1 N H₂SO₄) at 60 °C for 48 h. After immersing, the specimens were washed with distilled water and dried at 80 °C for 12 h.

Results and Discussion

Glass-ceramics was obtained by mixing fly ash from the thermal power plant and waste glass cullet made up of all types of waste glass. Figure 1 presents a FE-SEM morphological analysis of the fly ash sample, showing spherical and irregular round-shaped powder particles with an agglomerate size of 1.0 μ m~7.8 μ m (a typical particle morphology for fly ash powders). Figure 2

**Fig. 1.** FE-SEM image of the fly ash from the thermal power plant (Yecheon, Chonnam) in South Korea.**Fig. 2.** XRD pattern for the fly ash used in this study.

shows an XRD pattern of the fly ash powder (~200 mesh) used in our study. As is clearly seen in Fig. 2, the mineral phases of the fly ash powder are identified as α -quartz (SiO₂), mullite (Al₆Si₂O₁₃) and enstatite [(Mg,Fe)SiO₃]. These peaks are detected in the XRD pattern of the fly ash powder [11].

The XRD results on the glass-ceramic heat-treated at various temperatures (850 °C, 900 °C, 950 °C and 1000 °C) show that their crystal structures are mixed with various crystal types (Fig. 3). The crystalline phases present in the glass-ceramic correspond to diopside [Ca(Mg,Al)(Si,Al)₂O₆], augite [Ca(Mg,Fe)Si₂O₆] and wollastonite [CaSiO₃]. The peak intensities corresponding to the wollastonite + diopside crystals and wollastonite crystals gradually increased, and the augite + diopside, diopside and augite crystals decreased with an increase of heat-treatment temperature from 850 °C to 1000 °C.

As clearly shown in Fig. 3, the peaks at 2 θ =27°, 30° and 42° correspond to diopside + augite. The peak at 2 θ =29.8° corresponding to augite decreased with an increase of heat-treatment temperature, and the peak at 2 θ =39° corresponding to diopside was still identified in the specimen after annealing at 1000 °C. By contrast,

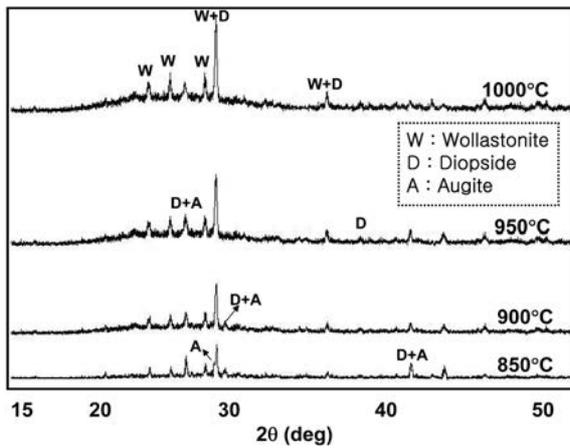


Fig. 3. XRD patterns for the glass-ceramics heat-treated at 850 °C~1000 °C.

with an increase of heat-treatment temperature to 1000 °C, a distinct increase of peak intensity was identified, and the small intensities of the peaks at around $2\theta=23^\circ, 25^\circ$ and 28° corresponding to wollastonite crystals were increased. The peak at 29.9° corresponding to wollastonite + diopside showed an increase of intensity from 850 °C to 1000 °C. At 1000 °C, the highest crystallized wollastonite peak appeared. However, the peaks, which correspond to diopside + augite and augite, decreased with an increase of heat-treatment temperature at 1000 °C. These decreases in the diopside + augite and augite crystals are caused by the formation of wollastonite crystals and by the increase of heat-treatment temperature to 1000 °C that brought about the

growth of the wollastonite crystals.

Figure 4 shows the surface morphology of these glass ceramics at various heat-treatment temperatures [850 °C(a), 900 °C(b), 950 °C(c) and 1000 °C(d)]. A morphological analysis of the specimen heat treated at 850 °C(a) and 900 °C(b) shows that the well-crystallized whisker-type crystals are partially aggregated in the matrix. However, with an increase of heat-treatment temperature to 950 °C(c) and 1000 °C(d), a high density of well-crystallized whisker-type crystals is generally aggregated in the matrix which are about 50-70 μm in size. This is typical of the wollastonite type glass-ceramic formed at heat treatment temperature of 1000 °C, and the XRD and FE-SEM results showed a surface crystallization mechanism that is capable of forming whisker-type crystals of wollastonite [10].

To investigate the crystal composition, we performed an EDS analysis on the same area used in the morphological analysis. Chemical compositions of the surface for the glass-ceramic heat-treated at 1000 °C [(a), (b) and (c)] are shown in Fig. 5. The calcium ion content in the whisker type crystal [Fig. 5(b)] in the glass matrix confirmed by EDS is significantly larger than that in the matrix [Fig. 5(c)]. This is consistent with the acicular crystals which are wollastonite. The XRD, FE-SEM, EDS results revealed that the glass-ceramic heat-treated at 1000 °C consists mainly of wollastonite crystals of whisker-type acicular grains. As clearly shown in Figs. 3-5, progressive increases of heat-treatment temperature cause changes in the surface condition and the crystalline shape in the specimens. There-

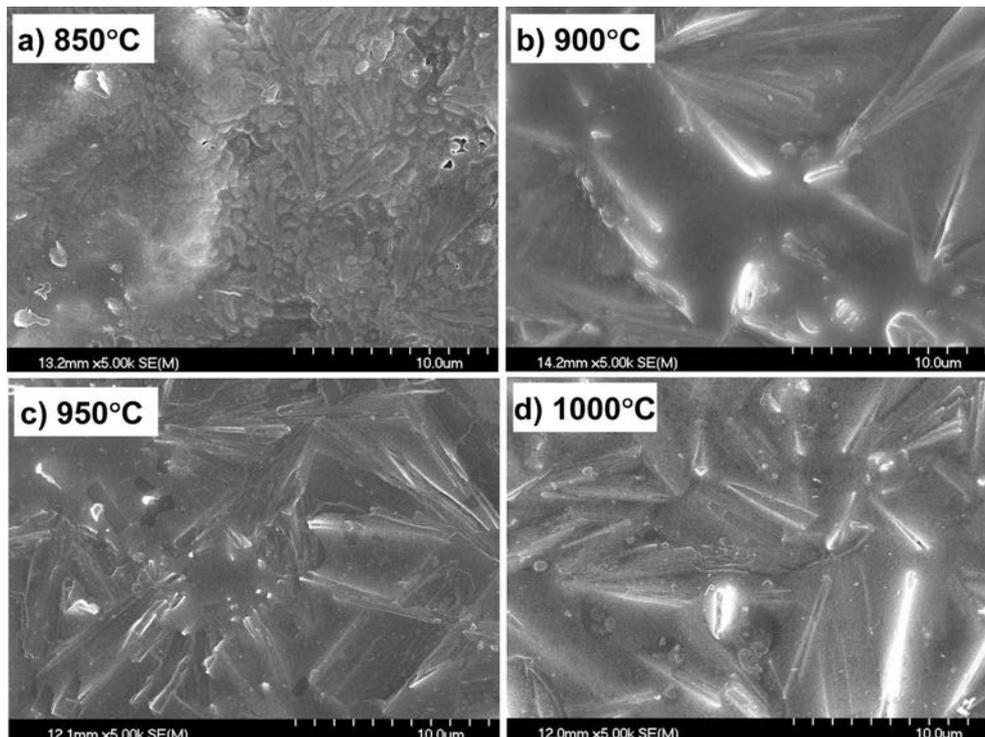


Fig. 4. FE-SEM images for the glass-ceramics heat-treated at 850 °C (a)~1000 °C (d).

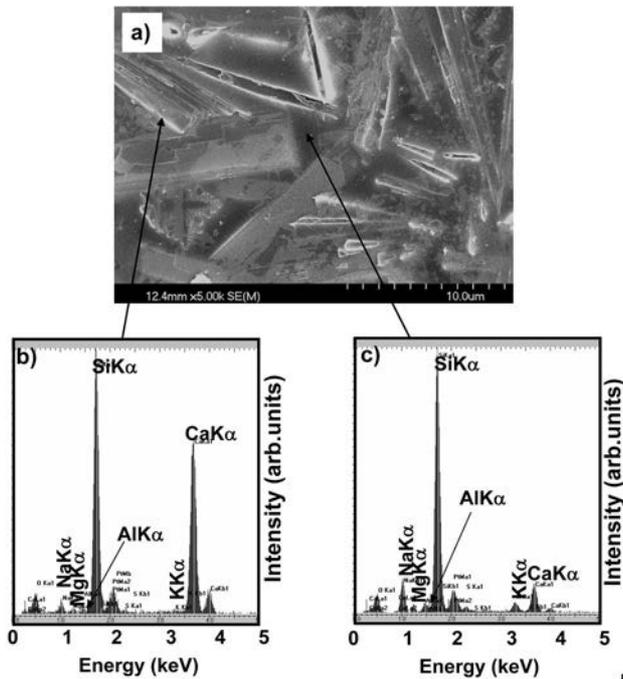


Fig. 5. FE-SEM images and chemical compositions of surface from EDS for the glass-ceramics heat-treated at 1000 °C (a), (b) and (c).

fore, the important factor in the crystal formation is the heat treatment temperature.

The compressive strength and bending strength of the specimens at 850 °C, 900 °C, 950 °C and 1000 °C were investigated. All the tests were done with 7 times/each specimens, and the results are shown in Table 2. The compressive strength increases from 229.2 to 272.8 MPa as the heat treatment temperature increases from 850 °C to 1000 °C. The bending strength also changed from 119.6 to 156.8 MPa. It is quite evident from Figs. 4(d) and Fig. 5(a) that the increase of the compressive and bending strength at 1000 °C is attributed to the increase in whisker-type crystals, wollastonite crystals, in the glass-ceramic. Generally, the whisker-type crystals included in the glass-ceramic showed good mechanical strength.

Table 2 shows the chemical durability (weight change %) of the specimens heat-treated at 850 °C, 900 °C, 950 °C and 1000 °C. The weight change values were evaluated according to the following equation:

$$\text{Chemical durability (weight change \%)} = (m_1 - m_2) / m_1 \times 100$$

where m_1 and m_2 are the weights of the samples before

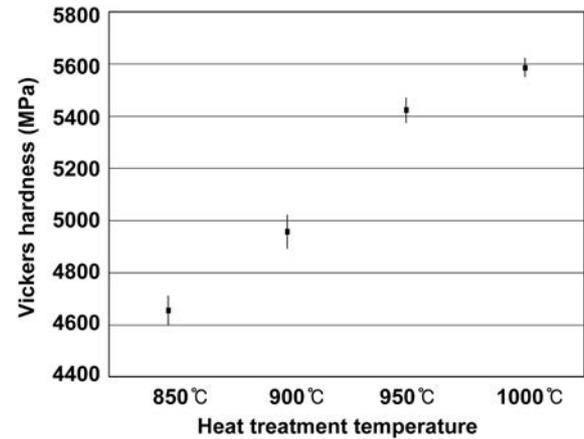


Fig. 6. Vickers hardness values of the glass-ceramic specimens heat-treated at 850 °C~1000 °C.

and after immersing in the acidic solution [12]. The weight change of the specimens are not affected by the increase of the heat-treatment temperature, and it is hard to suggest any relation between weight change and heat treatment temperature.

Figure 6 represents the Vickers hardness measurements of the glass-ceramic specimens heat-treated at various temperatures. It is clear from Fig. 6 that the hardness value increases with the heat treatment temperature from 850 °C to 1000 °C. Therefore, the whisker-type crystal growth at the highest temperature accounts for the increase in hardness value. As shown in Fig. 6, the glass-ceramic specimen heat-treated at 1000 °C has a maximum hardness value of 5587 ± 35 MPa. In this study, the development of well-crystallized whisker-type crystals in the glass-ceramic was found to improve the compressive and bending strength by heat treatment at 1000 °C. Consequently, these findings led us to conclude that our specimens through all the heat-treatment temperature-range are sufficient in mechanical strength for practical usage.

The mechanical properties and chemical durability of the specimens in this study should be further researched for practical applications. Our future investigations will focus on the environmental and recycling problems such as an advanced technique of producing glass-ceramics which have the proper ratios of used wastes such as fly ash, sludge and waste glass.

Conclusions

Glass-ceramics were produced using fly ash from a

Table 2. Properties of glass-ceramics heat-treated at 850 °C, 900 °C, 950 °C and 1000 °C

Properties	850 °C	900 °C	950 °C	1000 °C
Density (gcm ⁻³)	2.457 ± 0.021	2.729 ± 0.005	2.531 ± 0.006	2.653 ± 0.011
Compression Strength (MPa)	229.2 ± 11.3	249.1 ± 13.9	267.9 ± 15.8	272.8 ± 13.5
Bending Strength (MPa)	119.6 ± 18.7	129.3 ± 15.6	150.7 ± 16.2	156.8 ± 17.1
Weight-change (%) (1 N H ₂ SO ₄)	0.132 ± 0.042	0.149 ± 0.039	0.156 ± 0.021	0.150 ± 0.026

thermal power plant and waste glass cullet mixed with various waste glass to resolve their environmental and recycling problems. The results of XRD, FE-SEM and EDS analyses revealed that glass-ceramics containing well-advanced whisker-type crystals with good mechanical properties are significantly crystallized by increasing the heat-treatment temperature from 850 °C to 1000 °C. The most suitable glass-ceramic specimen was acquired by controlling the heat treatment temperature and the ratio of the waste materials utilized. The compressive strength and bending strength of the glass-ceramics were proven to be good [compressive strength (850 °C: 229.2 MPa-1000 °C: 272.8 MPa); bending strength (850 °C: 119.6 MPa-1025 °C: 156.8 MPa)].

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