

Preparation of glass ceramics from sludge bottom ash and waste glass

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Glass ceramics are prepared by milling and firing at various temperatures using sludge bottom ash from incinerators and waste glass as starting materials. The FE-SEM observations of glass ceramics indicated that with an increase of the firing temperature from 850 °C to 1050 °C, acicular type crystals were grown to about 11 μm in length. A specimen fired at 1050 °C showed the optimum formation of acicular type crystals as well as their best mechanical properties. Crystallinity, morphological properties and chemical compositions were examined using 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, Sludge bottom ash, Waste glass, Milling.

Introduction

The large amount of sludge bottom ash generated from solid waste incineration plants has been and is still posing a weighty problem to the environment and economic growth all over the world [1] since much less is recycled today than is produced. Currently, only a small percentage of this waste is recycled, mainly in the cement industry [2]. Sludge bottom ash from solid waste incineration plants contains a variety of hazardous materials such as dioxins and heavy metals [3]. Therefore, further management is necessary for it to become reasonably harmless to the environment. Sludge bottom ash containing large amounts of CaO, SiO₂, and Al₂O₃ may be a potential raw material for the production of CaO-Al₂O₃-SiO₂ system glass ceramics [2]. Regulating the raw materials composition and preferable heat treatment temperatures may produce glass-ceramics that possess various new crystalline phases and properties [4]. A number of studies have focused on new ceramics and glass-ceramics using waste materials such as coal ash, sewage sludge ash, and other materials [4-6].

Glass ceramics are of particular interest because of their high melting temperature, low thermal expansion, good oxidation resistance, and low dielectric constant [7].

To solve the environmental problems caused by waste materials and to prepare high mechanical strength materials, we fabricated glass ceramics from waste glass and sludge bottom ash from incinerators. The starting materials were

thoroughly ground to increase the interaction between the powders of raw materials, which can yield glass ceramic products of various new crystalline phases and properties by heat treatment. Although recent papers have reported on the use of incinerator sludge bottom ash and glass cullet for the production of glass-ceramics [6, 8], there are many problems such as economic loss due to double thermal steps. The purpose of this study is to fabricate glass ceramics by means of mechanical grinding that applies a disk type ball mill and a cost-effective single thermal step.

The changes in crystallinity and morphological properties of the specimens were examined using field emission-scanning electron microscopy (FE-SEM) and by varying the heat treatment temperature. The chemical composition was analyzed using an energy dispersive X-ray spectrometer (EDS). Mechanical properties of the specimens were also measured as a function of the heat treatment temperature.

Experimental Procedures

Dry sludge bottom ash from municipal waste incinerators (Yeocheon, South Korea) and waste glass cullet mixed with various types of waste glass (bottle, automobile window shield, plate, etc.) were used in this study as raw materials. The chemical compositions of the raw materials, dry bottom ash and waste glass cullet are listed in Table 1. A chemical analysis showed that the dry sludge bottom ash consists of oxides (in wt%); 42.48% SiO₂, 26.31% CaO, 6.48% MgO, 20.09% Al₂O₃, and 4.64% Fe₂O₃. Fine scale powder (–150 mesh) of the dry sludge bottom ash from the municipal waste incinerators was used in these experiments. Glass cullet was carefully washed in a water bath to remove the contaminants, and dried in a dry oven at 80 °C for 24 h.

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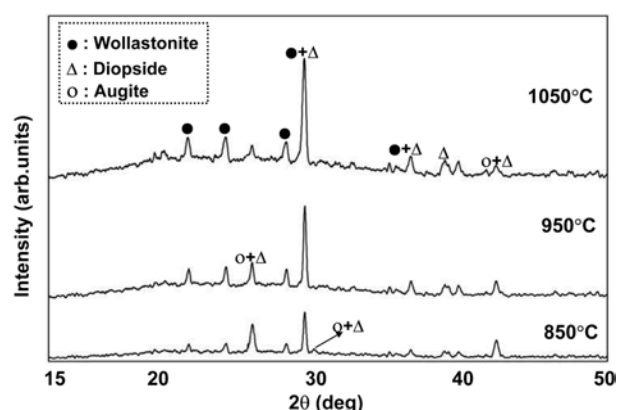
Table 1. Chemical composition (wt.%) of the raw materials used in this study

Oxide	Sludge bottom ash	Waste glass
SiO ₂	42.48	72.45
Na ₂ O	-	13.29
CaO	26.31	8.21
MgO	6.48	1.98
Al ₂ O ₃	20.09	2.04
K ₂ O	-	2.03
Fe ₂ O ₃	4.64	-

Glass powder was obtained by grinding the glass cullet in a disk type ball mill (Retsch GmbH & Co.KG, D-42781 HAAN, TYPE:RS1, Germany) for 30 minute (700rpm).

The glass powder and sludge bottom ash powder were fixed at a weight ratio of three parts waste glass powder to one part bottom ash powder. About 60 g of the mixture of the two different powders, glass and sludge bottom ash, was mechanically ground in a disk type ball mill for 4 h (700 rpm). The particle size was determined by a particle size analyzer (PSA, Malvern Ins. Lab., MS 1002). Most of the particles fell in the range of 0.1-1 μ m. The ground mixture was pressed into a cylindrical shape having a diameter of 10 mm and length of 30 mm without using any binder. The formed specimens were fired to 850 °C, 950 °C and 1050 °C with a heating rate of 5 °C·minute⁻¹ for 1 h in air (flow rate: 150-200 ml minute⁻¹), respectively, in a box-type SiC furnace and allowed to cool inside the furnace. After firing, the specimen was cleaned with ethyl alcohol in an ultrasonic bath and dried at 70 °C for 10 h.

The crystalline phases in the glass ceramics specimens were analyzed by X-ray diffraction (XRD, Rigaku Co., D-Max-1200, Jpn.) with CuK α radiation generated at 40 kV and 30 mA, in the 15° < 2 θ < 50° range at a scan speed of 2° 2 θ minute⁻¹. The morphology and surface composition of the specimens were evaluated using field emission - scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Jpn.) equipped with an energy dispersive X-ray spectrometer (EDS) that had a Robinson type backscattered electron detector. Various properties such as density, compressive strength, bending strength, and chemical durability were also examined. Density was measured using an electronic densimeter (ED-120T, MFD BY A&D CO., LTD, Japan). The compressive strength was investigated on 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 observed by measuring weight changes. To investigate the chemical durability, the specimens were immersed in 15 ml acidic solution (1 N H₂SO₄) at 60 °C for 48 h. After immersing, specimens were washed with distilled water and dried at 80 °C for 12 h.

**Fig. 1.** XRD patterns of the glass-ceramics fired at 850 °C, 950 °C and 1050 °C.

Results and Discussion

Fig. 1 shows the XRD patterns of specimens fired at various temperatures (850 °C, 950 °C and 1050 °C). The XRD study revealed the diopside [Ca (Mg,Al)(Si,Al)₂O₆], augite [Ca(Mg,Fe)Si₂O₆] and wollastonite [CaSiO₃] phases. The crystalline phases present in the specimens correspond to diopside [Ca (Mg,Al)(Si,Al)₂O₆], augite [Ca(Mg,Fe)Si₂O₆] and wollastonite [CaSiO₃].

The peak intensities corresponding to the diopside + wollastonite crystal line phases, the wollastonite crystal line phase gradually increased, and the augite + diopside crystal line phases were decreased with an increase of the heat treatment temperature from 850 °C and 950 °C to 1050 °C. When the firing temperature was increased at 950 °C, the peak intensities corresponding to the diopside + wollastonite crystal line phases, the wollastonite crystal line phase increased. With an increase of the heat treatment temperature from 950 °C to 1050 °C, the peaks at 2 θ = 29.9° and 36° were identified as the diopside + wollastonite crystal line phases gradually increased and the peak intensities at around 2 θ = 27°, 30° and 42.5° corresponding to augite + diopside were decreased. As the firing temperature reached 1050 °C, the small intensities of the peaks at around 2 θ = 23°, 25° and 28° corresponding to wollastonite were increased. However, the peaks at around 2 θ = 38.8°, which correspond to diopside, was decreased with an increase of heat treatment temperature to 1050 °C. These findings indicate that the decreases in diopside + augite crystal line phases are caused by the formation of the wollastonite crystal line phase, and the increase of heat treatment temperature to 1050 °C brought about the growth of the wollastonite crystal line phase.

Fig. 2 shows FE-SEM images of surface morphology of the glass ceramics fired at various temperatures. A morphological analysis of the specimens heat treated at 950 °C and 1050 °C (Fig. 2(b) and Fig. 2(c)) shows an acicular type of grains in the matrix. However, the structure of the specimen fired at 850 °C (Fig. 2(a)) was porous with round-shaped grains with large particles in the specimen.

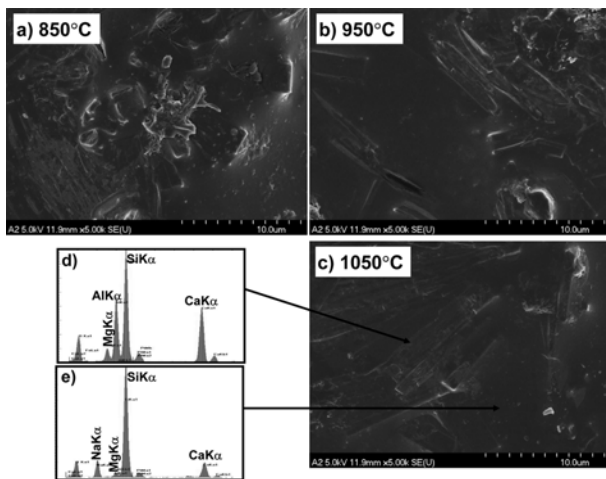


Fig. 2. FE-SEM images of the glass-ceramics fired at 850 °C (a), 950 °C (b) and 1050 °C (c) EDS analysis (d) and (e) of the specimen fired at 1050 °C.

This means that the porous and round-shaped structure was caused by the vaporization of organics during heat treatment or by insufficient annealing. As the heat treatment temperature was increased to 950 °C and 1050 °C, the round-shaped grains dramatically disappeared, and acicular type crystals were generally aggregated in the matrix ranging from about 5 μm to 11 μm in size. This is a typical SEM micrograph of wollastonite-type glass-ceramics with a heat treatment temperature at 1000 °C-1050 °C, and the XRD and FE-SEM results showed a surface crystallization mechanism while acicular-type crystals of wollastonite were formed [9]. This suggests that the mechanical strength of our specimens heat treated at a higher temperature is sufficiently strong, since specimens reinforced by the acicular type wollastonite generally show a high mechanical strength [10]. To investigate the crystal composition of well-grown acicular-type crystals and the matrix, an EDS analysis was carried out for the specimen fired at 1050 °C (Fig. 2(d) and (e)). As shown in Figs. 2(d) and (e), the amount of calcium ions in the acicular-type crystals investigated by EDS at 1050 °C (Fig. 2(d)) was significantly larger than that of the matrix (Fig. 2(e)). This is consistent with the acicular-type crystals being wollastonite. Figs. 1-2 show the XRD, FE-SEM, EDS of the glass ceramics fired at 850 °C, 950 °C and 1050 °C. The results revealed that the specimen fired at 1050 °C consists mainly of wollastonite crystals of whisker type acicular grains. As shown in Fig. 1-2, the progressive increase in heat treatment temperature causes changes in the crystal shape of specimens, demonstrating that the heat treatment temperature is an important factor in the crystal formation.

Table 2 shows the chemical durability (weight change%) of the specimens heat treated at 850 °C-1050 °C. To calculate the weight changes, we defined the degree of chemical durability as follows:

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

Table 2. Properties of glass-ceramics fired at 850 °C, 950 °C and 1050 °C

Properties	850 °C	950 °C	1050 °C
Compression Strength (MPa)	209.65 \pm 17.39	245.07 \pm 15.86	269.93 \pm 13.27
Bending Strength (MPa)	118.63 \pm 16.53	142.59 \pm 17.55	156.07 \pm 14.59
Weight-change(%) (1 N H ₂ SO ₄)	0.127 \pm 0.031	0.130 \pm 0.039	0.141 \pm 0.059

where m_1 and m_2 are the weights of the samples before and after immersing in the acidic solution [11]. The chemical durability of these specimens was not significantly affected by the heat treatment temperatures, although the weight loss of the sample heat treated at 850 °C exhibited a small but significant increase. Since it is difficult to analyze the exact chemical durability of the specimens because of the small weight changes before and after immersing, we were not able to explain the variations in the chemical durability by measuring weight gains alone.

As listed in Table 2, the compressive strength and bending strength of the specimens at 850 °C, 950 °C and 1050 °C were investigated. All the tests were done 10 times for each specimens. The compressive strength increased from 209.65 to 269.93 MPa as the heat treatment temperature was increased from 850 °C to 1050 °C. The bending strength was also increased from 118.63 to 156.07 MPa. It was quite evident as shown in Fig. 2(c) that the increase in the compressive and bending strength at 1050 °C is caused by the increase in acicular-type crystals in the glass-ceramics. Generally, the acicular-type crystals included in the glass-ceramics gave a good mechanical strength.

Fig. 3 shows the Vickers hardness measurements of glass ceramics fired at various temperatures. The hardness value clearly increases with a heat treatment temperature increase from 850 °C to 1050 °C as shown in Fig. 3. Therefore, the acicular-type crystal growth at the highest temperature accounts for the increase in hardness value. The specimen

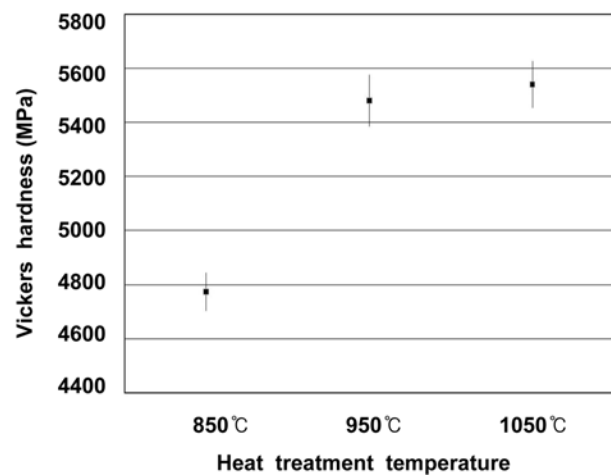


Fig. 3. Vickers hardness values of the glass-ceramics fired at 850 °C, 950 °C and 1050 °C.

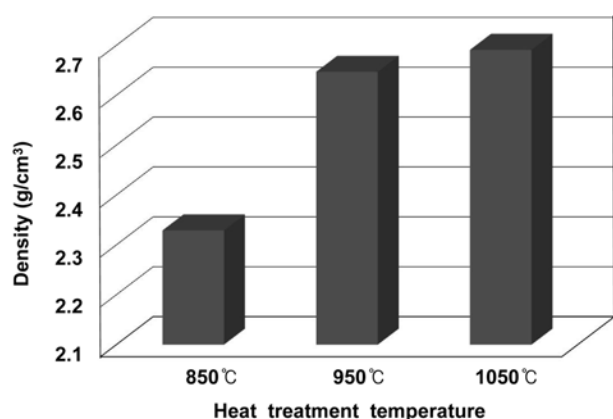


Fig. 4. Density of the glass-ceramics fired at 850 °C, 950 °C and 1050 °C.

heat treated at 1050 °C has the maximum hardness value of 5540 ± 85 MPa. In this study, the development of acicular type crystals in the glass ceramics improved the compressive and bending strength at 1050 °C. These findings led us to conclude that specimens throughout all the heat treatment temperature range are sufficient in mechanical strength for practical usage.

Fig. 4 shows the densities of glass ceramics fired at 850 °C, 950 °C and 1050 °C. As shown in Fig. 4, it is difficult to obtain a high density compact by firing at 850 °C. When the firing temperature was increased to 950 °C and 1050 °C, the density of the specimens increased from 2.329 to 2.647 and 2.691 g/cm³, respectively. We assume the existence of another effect on the mechanical strength of our specimens because the density and mechanical strength of the specimen fired at 850 °C were lower than those of the specimens fired at 950 °C and 1050 °C. These findings about the density and mechanical strength led us to conclude that as the firing temperature was increased, the pores in the specimens probably remaining in the matrix at a low temperature gradually disappeared at 950 °C and 1050 °C, resulting in the high density and mechanical strength. Furthermore, the relationships revealed by FE-SEM observations between the pores in the matrix and the firing temperature are consistent with our conclusion.

Conclusions

High grade acicular-type glass ceramics were prepared using milling and firing methods with sludge bottom ash and waste glass for raw materials. This paper makes two main contributions: first, the mechanical process of disk

type ball milling was developed which recycles raw materials, sludge bottom ash and waste glass, and second, a cost-effective single thermal step was developed.

The XRD, FE-SEM and EDS analyses results confirmed that with an increase of the heat treatment temperature from 850 °C to 1050 °C, the round shape grains in the glass matrix decreased and/or disappeared, but glass ceramics fired at 1050 °C were mainly composed of the well-crystallized acicular type grains. Suitable heat treatment temperatures are the most important issue in generating reinforced glass ceramics containing an acicular type crystalline phase with good mechanical properties. The experimental investigation showed that the compressive and bending strength of the glass ceramics possess sufficient mechanical strength for all conditions [compressive strength (850 °C : 209.65 ± 17.39 MPa, 950 °C : 245.07 ± 15.86 MPa, 1050 °C : 269.93 ± 13.27 MPa) ; bending strength (850 °C : 118.63 ± 16.53 MPa, 950 °C : 142.59 ± 17.55 MPa, 1050 °C : 156.07 ± 14.59 MPa)].

The quality of the glass ceramics prepared in this study is good enough to be applied for various purposes such as industrial building materials, outside and inside facings of walls and pavement materials.

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