

Chemical durability of glass-ceramics obtained from waste glass and fly ash

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Applying the mechanical milling method and annealing procedure, we prepared glass-ceramics using fly ash from a thermal power plant mixed with waste glass cullet to resolve the environmental waste recycling problem and find out the optimum crystallizing mechanism. The chemical durability of the heat-treated specimens [850°C, 950°C and 1000°C] was investigated by measuring the weight changes, morphological properties, and chemical composition at the sample surfaces before and after acid immersion by field emission-scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectrometry (EDS). Various properties, such as density, compressive strength, bending strength and Vickers hardness of specimens [before and after acid immersion] were observed. Regardless of chemical treatment, glass-ceramics heat-treated at 850°C, 950°C and 1000°C showed sufficient mechanical properties for practical usage.

Key words: Glass-ceramics, Chemical durability, Milling method, Mechanical properties.

Introduction

Fly ash is a by-product of coal-, oil-fired electric power stations and thermal power plants. An increasing amount of fly ash from power plants and urban solid waste incinerators has caused an environmental problem with technological and economic damages all over the world.

Recently, by properly selecting raw materials and other wastes in the forms of bottom ash, fly ash, slag and mining residue, new products have been developed such as glass fibers and glass-ceramics for potential architectural and decorative applications which have chemical and mechanical properties comparable to, if not better than, commercial ones [1-2].

The production of glass-ceramic materials has found their applications in the field of abrasion-resistant materials, that is, industrial floor coverings, wall facings, abrasion-resistant linings and high temperature insulators. Moreover, developing appropriate methods of new glass-ceramic materials from recycling fly ash has acquired particular importance [3-6]. However, much more effort is needed in resolving environmental waste recycling problems for the life and health of future generations. Many researches have been conducted on the utilization of fly ash as a starting material for glass-ceramic production [7-9].

Glass-ceramics have been prepared using fly ash from a thermal power plant and waste glass [10]. It is

important to note that the waste materials such as fly ash, and glass are recycled, and that many recycling problems such as chemical bonding by heat-treatment and economic loss caused by several thermal steps are solved by a mechanical processing method. In the present study, we investigated the chemical durability and mechanical properties of glass-ceramics.

Experimental procedures

The experimental procedure and the starting materials used in this study have been reported on previously [10].

Briefly, fly ash and waste glass were used as starting materials to prepare glass-ceramics. Fly ash (–200 mesh) from a thermal power plant was used in its raw state in these experiments. Waste glass powder was obtained by grinding the raw material, waste glass cullet, in a disk type ball mill (Retsch GmbH & Co.KG, D-42781 HAAN, TYPE : RS1, Germany) for 20 minutes (700 rpm). The powder size of the waste glass obtained was about –150 mesh to produce the glass-ceramic. Table 1 shows

Table 1. Chemical composition (wt.%) of the raw materials.

Oxide	Waste glass	Fly ash
SiO ₂	73.36	40.47
Na ₂ O	13.01	-
CaO	6.43	25.04
MgO	3.02	6.52
Al ₂ O ₃	2.49	21.48
K ₂ O	1.69	-
Fe ₂ O ₃	-	6.49

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the composition of the raw materials, fly ash, and waste glass powder used in this study. 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 mixtures were pressed into cylindrical shapes having a diameter of 10 mm and length of 30 mm without using any binder. The glass disks formed were annealed at 850°C, 950°C, and 1000°C at a rate of 5 K minute⁻¹ for 1 h, in a tube-type 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.

To investigate the chemical durability, heat-treated samples were immersed in a 20 ml acidic solution (1N H₂SO₄) at 60°C for 48 h. After immersion, the samples were successfully washed with distilled water and dried at 80°C for 12 h in air. The chemical durability was analyzed by measurement of weight change and by observation of the surface morphology by field-emission scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Japan). The variation of the chemical composition at the sample surfaces before and after acid immersion was also evaluated by energy-dispersive X-ray spectrometry (EDS) with a Robinson-type backscattered electron detector.

Furthermore, various properties such as density, compressive strength and bending strength were also investigated. Density was measured using an Electronic Densimeter (ED-120T, MFD BY A&D CO., LTD, Japan). The compressive strength was examined by a universal tester (Instron 4302, Instron Co., England) and the bending strength was determined from 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).

Results and discussion

Table 2 shows the density and weight change (%) of the specimens heat treated at 850°C~1000°C. To calculate the weight change, we defined the degree of the weight change (%) as follows:

$$\text{Weight change (\%)} = (m_1 - m_2) / m_1 \times 100 \quad (1)$$

where m_1 and m_2 are the weights of the specimens before and after immersing in the acidic solution, respectively. The weight changes in the specimens are affected neither by immersing in the acidic solution nor by increasing the heat-treatment temperature. Because it was difficult to examine the exact chemical durability of the specimens owing to their small weight changes before and after immersing, we could not clearly explain the variation of the chemical durability of the specimens by weight gain alone.

Table 2. Weight change(%) of the glass-ceramics heat-treated at 850°C, 950°C and 1000°C before acid immersion and after acid immersion

Properties	850°C	950°C	1000°C
Density(gcm ⁻³)	2.469	2.583	2.591
Weight-change(%) (1 N H ₂ SO ₄)	0.104	0.097	0.093

To obtain sound information about the chemical durability of the samples before and after immersion, the surface morphology and chemical composition were evaluated by FE-SEM and EDX.

Fig. 1(a, b), 2(a, b) and 3(a, b) show the surface morphologies and chemical compositions for the glass ceramics heat-treated at 850°C, 950°C and 1000°C before acid immersion, respectively. In all the specimens, silicon, calcium, aluminum and alkali ions such as sodium, magnesium, and potassium were detected on the surface grains for the samples before acid immersion. A morphological analysis of the specimen heat-treated at 950°C and 1000°C [Fig. 2(a) and Fig. 3(a)] using FE-SEM shows that well-crystallized acicular type crystals are generally aggregated in the matrix. The acicular crystals are typical SEM results from a Wollastonite [CaSiO₃] type glass-ceramic heat treated at 1000°C. As clearly shown in Fig. 3(b), for the sample heat-treated at 1000°C, relatively strong peak intensities corresponding to calcium were identified at a whisker type crystal area, which probably were caused by the formation of highly crystallized Wollastonite [CaSiO₃]. Moreover, the calcium content of the grain shown in Fig. 1(b) at 850°C was smaller in grain area than at 1000°C [Fig. 3(b)]. This is additional evidence of the growth of acicular type Wollastonite crystals in the specimen heated at 1000°C, since the formation of Wollastonite needs more calcium ions. Therefore, the important factor in the surface crystallization mechanism of the acicular type crystals is the heat treatment temperature.

Fig. 1(c, d), 2(c, d) and 3(c, d) show the surface morphologies and chemical compositions for the glass-ceramics heat treated at 850°C, 950°C and 1000°C, respectively, after acid immersion. As shown in Figs. 1(b) and 1(d), for the sample heat-treated at 850°C, it is difficult to identify the variation of calcium ion content in the grains by EDX. At 950°C and 1000°C, as seen in Figs. 2(d) and 3(d), the calcium ion content in the acicular-type grains decreased slightly after treatment in the acidic solution [compare with Figs. 2(b) and 3(b)]. The calcium ion content of the acicular-type grain of all specimens [850°C, 950°C and 1000°C] was not affected significantly by the chemical treatment in the acidic solution, although there was a small decrease of the specimen heat-treated at 950°C and 1000°C.

Fig. 4 shows the variations in the sodium contents by weight ratio (Na/Si) of the glass-ceramics surface [grain] at various temperatures [850°C, 950°C and 1000°C]

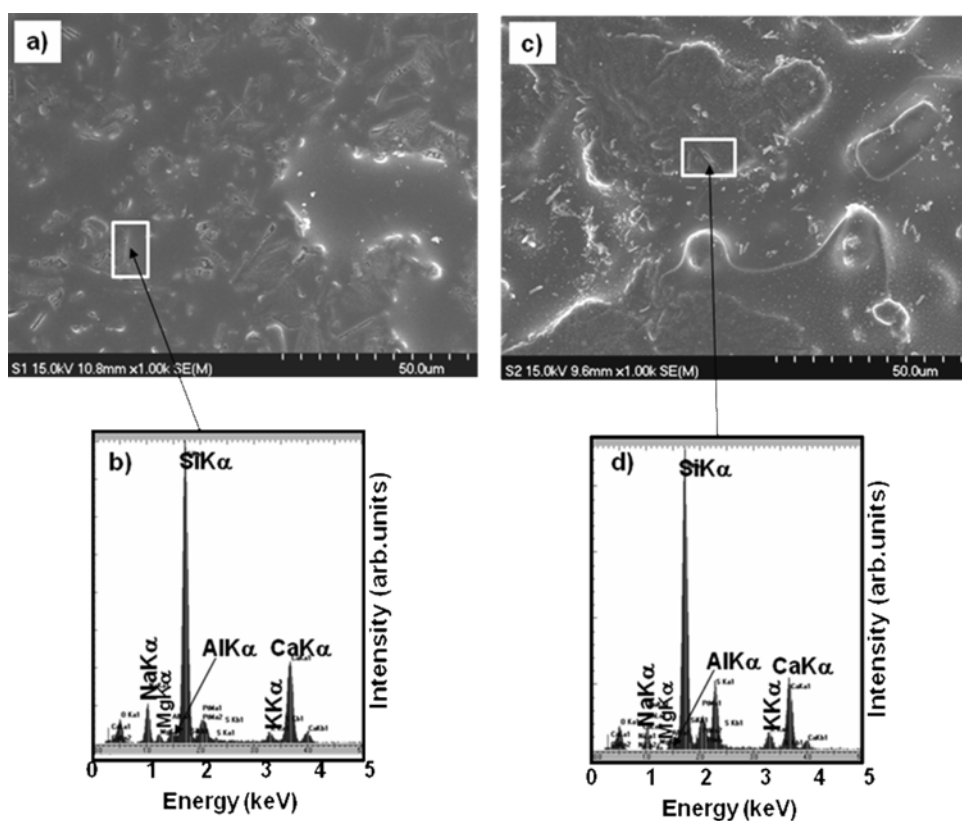


Fig. 1. FE-SEM image and chemical composition of the surface from EDS for the glass-ceramic heat-treated at 850°C, before acid immersion (a), (b) and after acid immersion (c), (d).

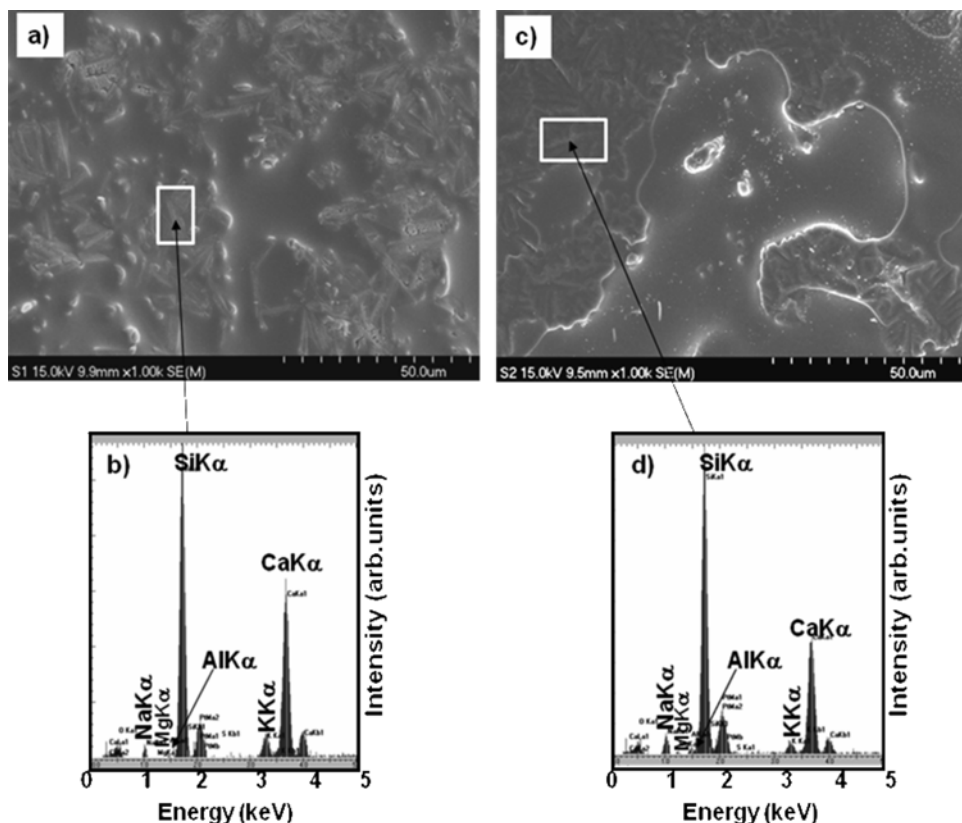


Fig. 2. FE-SEM image and chemical composition of the surface from EDS for the glass-ceramic heat-treated at 950°C, before acid immersion (a), (b) and after acid immersion (c), (d).

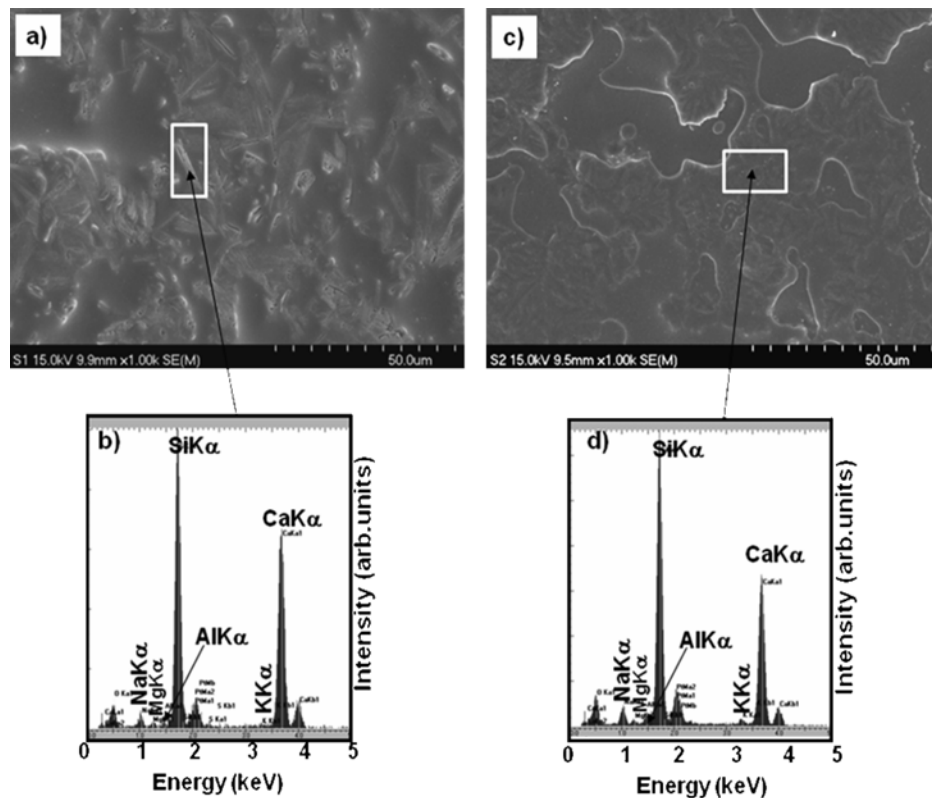


Fig. 3. FE-SEM image and chemical composition of the surface from EDS for the glass-ceramic heat-treated at 1000°C, before acid immersion (a), (b) and after acid immersion (c), (d).

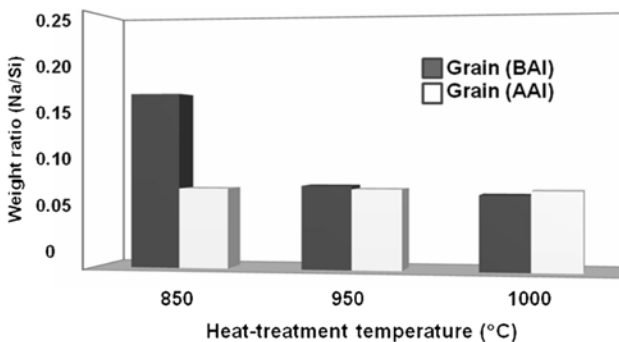


Fig. 4. Variation in the sodium contents of the glass-ceramic surfaces at various temperatures between before (BAI) and after acid-immersion (AAI).

between before and after acid-immersion. The data values are the average of sodium contents by weight ratio (Na/Si) on 5 specimens by EDS. In the specimen heat-treated at 850°C, sodium ions showed a larger ion variation in grain areas between before and after acid-immersion. However, owing to chemical stability of well-crystallized grains, the crystalline phase of the grain areas of the specimen heat-treated at 950°C and 1000°C exhibited a smaller sodium ion variation between before and after acid immersion. Generally, the chemical stability of glass-ceramic materials is affected by the composition of the crystalline phase and also by the composition and amount of the residual glass phase and its morphology. Alkali ions are much more stable in the crystalline

phase than in the residual glass phase. Consequently, for glass-ceramic materials to have good chemical resistance, it is necessary that the crystalline phase contains high concentrations of alkali metal oxide [11].

From the result of the EDS analysis of the surface grains for the specimens before acid immersion and after acid immersion, we can conclude that the specimens heat-treated at 950°C and 1000°C were favorable for good chemical durability, since their crystalline phase (grain) slightly changed the amount of alkali ions (such as Na) as compared with the specimen heat-treated at 850°C.

Table 3 shows the results of investigation on compressive strength and bending strength of the specimens at various temperatures [before and after acid immersion]. All the tests were done with 5 times/each specimens. The data values are the average from tests on specimens. The compressive strengths are 236.4-279.7MPa(before acid immersion) and 192.1-248.6 MPa (after acid immersion) and the bending strength also improved from 72.8 to 94.9 MPa (before acid immersion) and from 55.3 to 72.6 MPa (after acid immersion) as the heat treatment was temperature increased from 850°C to 1000°C. The mechanical strength of all the specimens was not influenced by the increase of heat-treatment temperature not by the chemical treatment in acidic solution.

Vickers hardness measurements of the specimens heat-treated at various temperatures [before and after acid immersion] were also investigated. As shown in

Table 3. Various properties of the glass-ceramic heat-treated at 850°C~1000°C, Before Acid Immersion (BAI) and After Acid Immersion (AAI).

Properties	850°C		950°C		1000°C	
	BAI	AAI	BAI	AAI	BAI	AAI
Compression Strength(MPa)	236.4	192.1	266.1	227.8	279.7	248.6
Bending Strength(MPa)	72.8	55.3	79.1	62.5	94.9	72.6
Vickers Hardness(GPa)	4.8	4.1	5.1	4.6	5.3	4.7

table 3, the glass-ceramic specimen heat-treated at 1000°C [before and after acid immersion] has the maximum hardness value of 5.3 GPa (before acid immersion) and 4.7 GPa (after acid immersion). Generally, glass-ceramics of the well-crystallized whisker grain type showed good mechanical properties. In this study, the acicular-type crystals in the glass-ceramic specimen heat-treated at 1000°C improved the compressive strength, bending strength and Vickers hardness, and these findings led us to conclude that, throughout the temperature range and chemical treatment in acidic solution, our specimens showed sufficient mechanical properties and chemical durability for practical usage. The future work will focus on the environmental and recycling problems, such as an advanced technique of glass-ceramic formation which has proper ratios of the wastes used (sludge, waste-incinerator fly ash, coal fly ash and waste glass) and employs a filter ceramic for waste water absorption.

Conclusions

Glass-ceramics were synthesized from fly ash of a thermal power plant and waste glass cullet as starting materials. The FE-SEM and EDX analyses revealed that glass-ceramics heat-treated at 950°C and 1000°C exhibited favourable improvements in chemical durability, since their crystalline phases of grain areas maintained the amount of alkali ions, such as sodium ions, and showed a smaller calcium ion variation between before and after acid immersion. The compressive strength and the bending strength of the glass-ceramics were proven to be good, regardless of whether before or after immersion

in the acidic solution. The compressive strengths were 236.4-279.7 MPa (before acid immersion) and 192.1-248.6 MPa (after acid immersion) and the bending strengths were 72.8-94.9 MPa (before acid immersion) and 55.3-72.6 MPa (after acid immersion) as the heat treatment temperature increased from 850°C to 1000°C. Throughout all the heat-treatment temperature range [before and after acid immersion], the specimens showed mechanical properties strong enough for practical use.

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