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Chemical durability of wollastonite glass-ceramics derived from waste glass and sludge bottom ash

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Wollastonite glass-ceramics was prepared by using the milling and sintering process with a mixture of two different powders. As a solution to environmental and waste recycling problems, powder mixtures consisting of dry sludge bottom ash and waste glass powder were used to make Wollastonite glass-ceramics. The chemical durability, crystallinity, morphological properties and chemical compositions of the specimens before and after acid immersion were observed by field emission-scanning electron microscopy (FE-SEM) and an energy dispersive X-ray spectrometer (EDS). Various mechanical properties, such as density, compressive strength, bending strength and Vickers hardness were also investigated. Various heat treatment temperatures [850, 950 and 1050 °C] were used to obtain glass-ceramics before and after the acid immersion of the optimum chemical durability and to find adequate mechanical properties for practical usage. As the heat-treatment temperature was increased from 850 °C to 1050 °C, the mechanical properties improved, especially the glass-ceramics in a dense acicular type of crystals of the Wollastonite phase at 1050 °C, in particular, and all specimens before and after acid immersion, in general.

Key words: Wollastonite glass-ceramics, Chemical durability, Milling, Mechanical properties.

Introduction

Recent industrial developments over the last five decades have tremendously increased the amount of waste materials, and the disposal and management of bottom ash, incinerator fly ash and coal fly ash have attracted much interest [1-3]. Sludge bottom ash generated from solid waste incineration plants and thermal power plants amounts to 4.2 million tonnes per year in Korea.

The sludge bottom ash from the incineration of municipal solid wastes contains a multiplicity of hazardous materials such as dioxins and toxic heavy metals, Cd, Cr, Pb, etc., which subsist in the bottom ash as oxide and chlorides [4]. It therefore requires further treatment for it to become reasonably harmless for the environment. In recent years, new ceramic and glass-ceramic materials prepared by recycling various sludge bottom ashes have been getting much consideration from research and development [5-7]. So solving the environmental problems caused by the sludge bottom ash ensuing from the production of glass ceramics will confer the product further benefits and offer a significant prospective for profit.

Conversion or inclusion in glass-ceramic systems has been used to extend recycling to several types of by-products, such as sludge bottom ash and fly ash from coal- and oil-fired electric power stations and fly ash from urban solid waste incinerators [8-9]. Some of these glass-ceramic materials became commercial products [10, 1].

Their main applications are in the field of abrasion-resistant materials, that is, industrial floor coverings, wall facings, abrasion-resistant linings, and high-temperature insulators. Moreover, the low cost and availability of the raw materials make them very attractive economically [11]. Glass-ceramic products composed of Wollastonite crystals have excellent properties and exhibit no deterioration at high temperatures of above 1000 °C. Therefore, the products are expected to be useful as thermal insulating materials, refractories, external-internal wall facings and in-road construction compositions.

Recently, we have prepared glass-ceramics using sludge bottom ash from solid wastes incineration plants and waste glass cullet [12]. It is important to make the Woallstonite glass-ceramics by means of a mechanical grinding method, applying a disk type ball mill and one time thermal step. For recycling, it is useful to obtain a Wollastonite glass-ceramic which has great advantages in terms of mechanical and thermal properties. In this study, we investigated the chemical durability of Wollastonite type glass-ceramics by means of a mechanical grinding method to determine their mechanical properties.

Experimental procedures

The experimental procedure for preparation of the specimens and the starting materials used in this study have been reported on previously [12]. Wollastonite glass-ceramics were prepared from dry sludge bottom ash from

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municipal waste incinerators (Yeocheon, South Korea) and waste glass cullet were used as the raw materials. In these experiments, we used dry sludge bottom ash of a minute powder (−150 mesh) and waste glass cullet was washed and dried by a drying oven at 60 °C for 24 h. 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 30 minutes (700 rpm). The waste glass powder of about −150 mesh was used to produce Wollastonite glass-ceramics. Table 1 shows the composition of the raw materials, sludge bottom ash and waste glass powder used in this study. 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.

The mixture of the two different powders, about 60 g of waste glass power and bottom ash, was mechanically ground in a disk type ball mill for 4 h (700 rpm). After milling, the 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 placed in a box-type SiC furnace, and the temperature was increased at 5 °C minute^{-1}, sintered at different temperatures (850 °C, 950 °C and 1050 °C for 1 h, respectively) and then cooled to room temperature.

To analyze their chemical durability, the specimens were immersed into 20 cm^3 of an acidic solution (1*N* H_2SO_4) at 80 °C for 48 h. The chemical durability of the specimens was analyzed by both measuring the weight change and observing the surface morphology with a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Jpn.) equipped with a Robinson-type backscattered electron detector. Variations in chemical compositions at the surface of the specimens before and after immersing were evaluated by an energy dispersive X-ray spectrometer (EDS). Various properties such as density, compressive strength and bending strength of the specimens were also investigated before and after the immersion. 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).

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

Oxide	Sludge bottom ash	Waste glass
SiO_2	40.01	71.3
Na_2O	-	11.86
CaO	28.38	9.41
MgO	7.27	1.73
Al_2O_3	18.72	1.95
K_2O	-	3.75
Fe_2O_3	5.62	-

Table 2. Weight change (%) of the wollastonite glass-ceramics heat-treated at 850 °C, 950 °C and 1050 °C before acid immersion and after acid immersion.

Properties	850 °C	950 °C	1000 °C
Density(gcm^{-3})	2.349	2.502	2.586
Weight-change(%) (1 N H_2SO_4)	0.086	0.102	0.094

Results and Discussion

Table 2 shows the chemical durability (weight change%) of the specimens heat-treated at 850 °C, 950 °C, and 1050 °C. The weight change values were evaluated according to the following equation:

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

where m_1 and m_2 are the weights of the specimens before and after the immersion in the acidic solution, respectively. The chemical durability of these specimens was not considerably affected by the heat-tcreatment temperature, although the weight loss of the sample heat-treated at 850 °C exhibited a small but significant increase. Since it is hard to evaluate the accurate chemical durability of the specimens due to their small weight changes before and after the immersion, we were not able to make clear the variations in the chemical durability by measuring weight gain alone.

For more insight into the chemical durability, the morphological and chemical compositions of the grain-like acicular phase at the surface of the specimens before and after immersing in the acidic solution were examined by FE-SEM and EDS. Figs. 1, 2, and 3 show the surface morphologies and acicular phase's chemical compositions of the glass-ceramics heat-treated at 850 °C, 950 °C and 1050 °C before and after the acid-immersion. Figs. 1(a), 2(a) and 3(a) present the results of the morphological analysis of the specimen heat-treated at 850 °C, 950 °C and 1050 °C, respectively, by using FE-SEM. Fig. 1(a) shows many rough round-shape grains of a size (5 μm-18 μm) and acicular type grains about 9 μm-19 μm in the matrix and the grain's surface shape of a heterogeneous and small size. As seen in Figs. 2(a) and 3(a), as the heat-treatment temperature was increased to 950 °C and 1050 °C, the specimen's surfaces showed irregular and unsystematic acicular grains ranging from 7 μm up to 23 μm. As clearly shown in Figs. 1(a), 2(a) and 3(a), progressive increases of the heat-treated temperature cause changes in the grain shape and the surface state of specimens. Therefore, the important factor in the crystal formation is the heat treatment temperature.

In our EDS analysis, Si, Ca, Al, and alkali ions such as

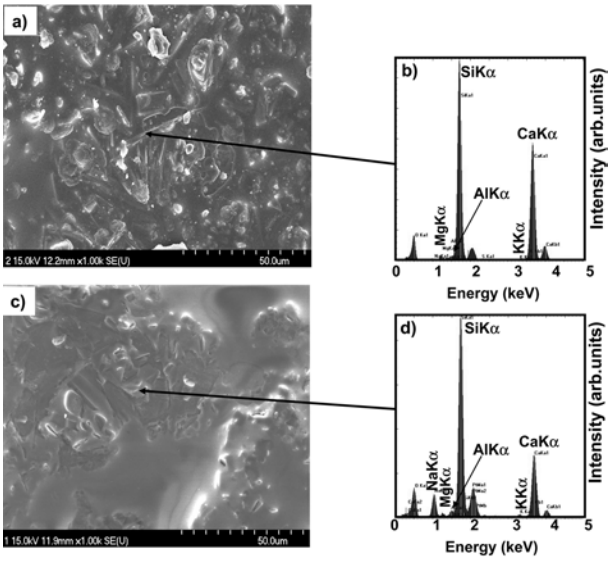

Fig. 1. FE-SEM image and chemical composition of the surface from EDS for the Wollastonite glass-ceramics heat-treated at 850 ºC, before acid immersion (a), (b) and after acid immersion (c), (d).

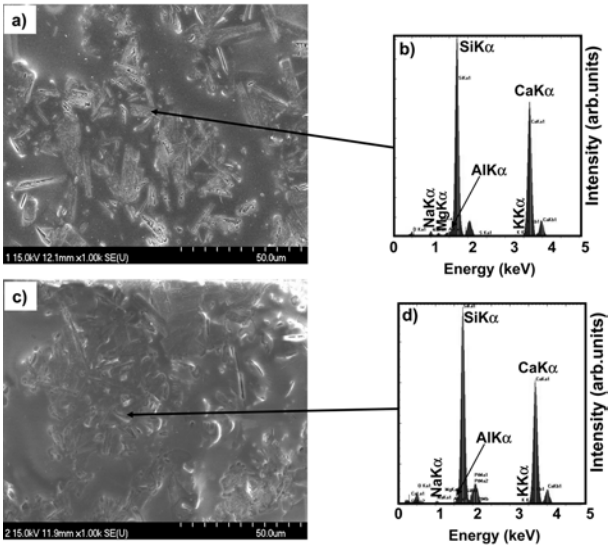

Fig. 2. FE-SEM image and chemical composition of the surface from EDS for the Wollastonite glass-ceramics heat-treated at 950 ºC, before acid immersion (a), (b) and after acid immersion (c), (d).

Na, Mg, and K were detected on the acicular phase surfaces of all specimens before and after the acid-immersion. However, as is clearly seen in Fig. 1(d), relatively small and weak peak intensities corresponding to calcium were identified on the surface grains for the specimen heat-treated at 850 ºC. As shown in Figs. 2 and 3, for specimens heat-treated at 950 ºC and 1050 ºC, it is very difficult to identify variations in the calcium peak intensities of the EDS between the before [Fig. 2(b) and 3(b)] and after [Fig. 2(d) and 3(d)] the acid-immersion. It is important to note that well-crystallized grain-like acicular crystals to withstand the acid treatment are closely aggregated in the glass-ceramic matrix for specimens heat-treated at 950 ºC

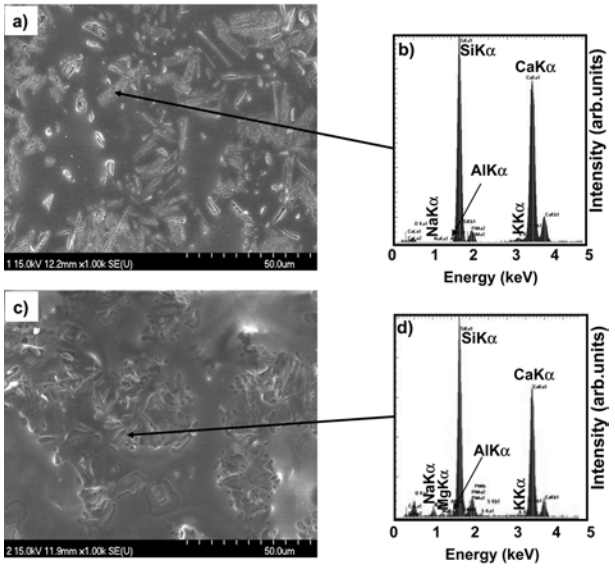

Fig. 3. FE-SEM image and chemical composition of the surface from EDS for the Wollastonite glass-ceramics heat-treated at 1050 ºC, before acid immersion (a), (b) and after acid immersion (c), (d).

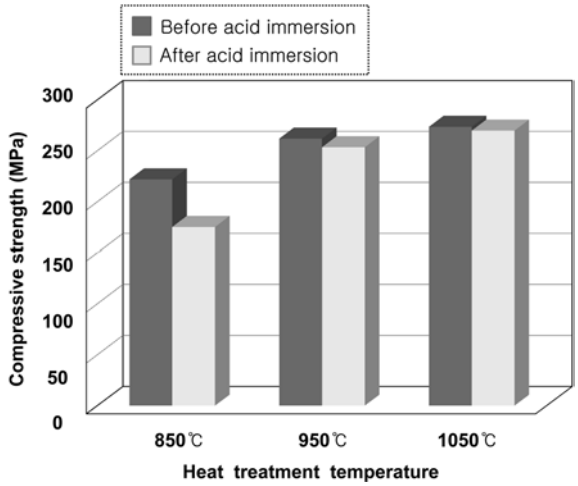

Fig. 4. Compressive strength of Wollastonite glass-ceramics heat-treated at 850 ºC, 950 ºC and 1050 ºC, before acid immersion and after acid immersion.

and 1050 ºC. The acicular type crystals are typical SEM results from a Wollastonite [$CaSiO_3$] glass-ceramic heat treated at 950 ºC-1050 ºC, and they showed a surface crystallization mechanism with the formation of acicular type grains of Wollastonite [9].

We also examined the compressive and bending strength of specimens heat-treated at 850 ºC, 950 ºC, and 1050 ºC before(BAI) and after(AAI) acid-immersion (Fig. 4 and Fig. 5). All the tests were conducted with 8 times for each specimen. The data values are averaged from tests on specimens. The compressive strengths are 221.9-273.4 MPa (BAI) and 175.3-269.7 MPa (AAI), and the bending strength also advanced from 83.5 to 96.9 MPa (BAI) and from 59.8 to 88.5 MPa (AAI) as the heat treatment temperature was increased from 850 ºC to 1000 ºC. It is quite evident from Figs. 4 and Fig. 5 that the increase of the compressive and

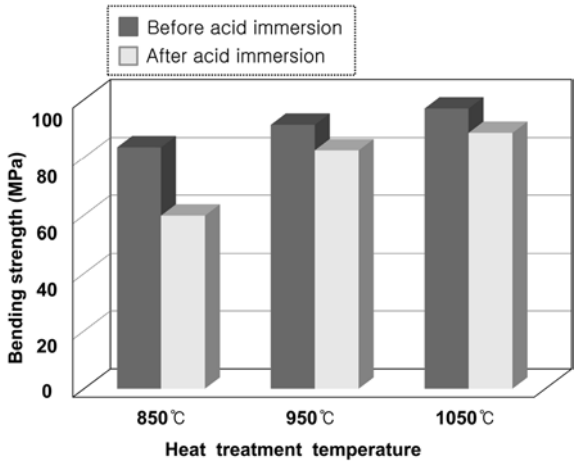

Fig. 5. Bending strength of Wollastonite glass-ceramics heat-treated at 850 ºC, 950 ºC and 1050 ºC, before acid immersion and after acid immersion.

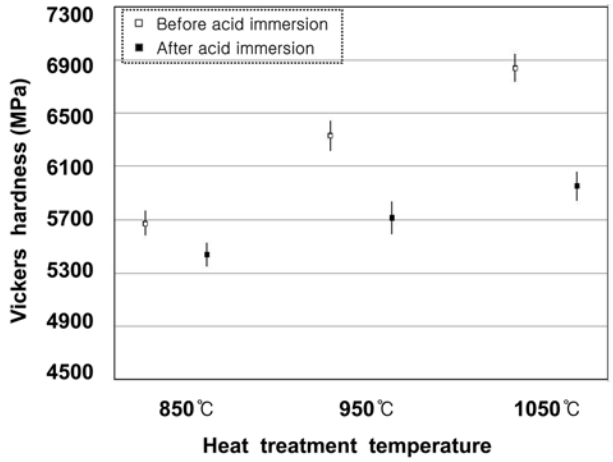

Fig. 6. Vickers hardness values of Wollastonite glass-ceramics heat-treated at 850 ºC, 950 ºC and 1050 ºC, before acid immersion and after acid immersion.

bending strength at 1050 ºC is caused by an increase in the amount of acicular- type Wollastonite crystals, in the glass-ceramic matrix. Generally, acicular type crystals included in glass-ceramics showed a good mechanical strength. In this study, glass-ceramics (heat-treated at 950 ºC, and 1050 ºC) of the acicular-type Wollastonite crystals showed a high mechanical strength which means that it is not influenced by the chemical treatment in an acidic solution.

Fig. 6 represents the Vickers hardness measurements of the Wollastonite glass-ceramic specimens heat-treated at various temperatures [before and after acid immersion]. Fig. 6 clearly shows that the hardness value increases with the heat treatment temperature from 850 ºC to 1050 ºC. Therefore, the acicular type crystal growth at the highest temperature accounts for the increase in the hardness value. As shown in Fig. 6, the Wollastonite glass-ceramic specimen heat-treated at 1050 ºC has the maximum hardness value of 6842 ± 105 MPa (before acid immersion) and 5949 ± 109 MPa (after acid immersion). In this study, we discovered that the development of well-crystallized acicular type crystals in a Wollastonite glass-ceramics can improve the compressive strength, bending strength and Vickers hardness at 1050 ºC. These findings led us to conclude that specimens that withstood all the heat-treatment temperature-ranges are sufficient in terms of mechanical properties for practical usage.

Conclusions

We prepared well-crystallized wollastonite glass-ceramics from dry sludge bottom ash from municipal waste incinerators using waste glass cullet as raw materials. From FE-SEM and EDS analyses, we found that the glass-ceramics heat-treated at 950 ºC and 1050 ºC showed cost-effective improvements in chemical durability, since their well-advanced acicular type Wollastonite crystals in the glass-ceramics matrix had a smaller calcium ion variation between before and after acid immersion, showing high mechanical properties for all conditions. Calcium content in acicular type grain of the glass-ceramics matrix has been maintained, which is an evidence of the stable chemical durability and good mechanical properties, because it is an important factor in the crystal formation. The compressive and bending strength of the specimens obtained at all heat-treatment temperatures investigated (850, 950 and 1050 ºC) is sufficient for practical usage, in all cases of before or after immersion in the acidic solution. The compressive strengths were 221.9-273.4 MPa(before acid immersion) and 175.3-269.7 MPa (after acid immersion), and the bending strengths were 83.5-96.9 MPa(before acid immersion) and 59.8-88.5 MPa (after acid immersion) as the heat treatment temperature increased from 850 ºC to 1050 ºC.

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