

Porous ceramics fabricated from waste resources (waste glass and fly ash)

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We prepared porous ceramics by mixing the fly ash from a thermal power plant with waste glass to resolve the environmental waste recycling problems. Applying the mechanical milling method and annealing procedure, powder mixtures consisting of waste glass powder (70 wt%) and fly ash (30 wt%) were used at various heat treatment temperatures of 600, 650, 675 and 700 °C to obtain porous ceramics with a variety of structural and mechanical properties. The pore structure was substantially affected by the starting raw materials and annealing temperatures. The pore formation mechanism is discussed in relation to these effects. In the present study, the crystallinity and morphological properties were observed by X-ray diffraction (XRD) and field emission-scanning electron microscopy (FE-SEM). Various properties, such as bending strength and Brunauer-Emmett-Teller (BET) absorption were also examined.

Key words: Porous ceramics, Fly ash, Milling method.

Introduction

Fly ash is produced as a by-product of coal- and oil-fired electric power stations and thermal power plants all over the world, and much less fly ash is recycled today than is generated. Currently, only a small percentage of this waste is utilized, mainly in cement-based materials [1-4], so development of new technologies to recycle and convert waste materials into reusable materials is important for environmental protection and sustainable improvement of our society. Recently, porous ceramics have found growing significance due to their various applications such as in membranes [5], filters [6], and catalyst controls [7], and commercial porous ceramics have been effectively produced using different pure starting materials such as Al₂O₃, ZrO₂ or SiC [8]. In the past few decades, there has been a great deal of research effort dedicated to porous ceramics, including various fabrication techniques using different starting materials. These materials bear high costs because of both expensive starting materials and high heat-treatment temperatures. To solve this problem, researchers have manufactured new porous ceramics using waste materials [9, 10].

In this study, porous ceramics that have interesting properties were prepared using fly ash and waste glass cullet. It is significant to note that the waste material such as fly ash and waste glass are recycled, and many

recycling problems such as chemical bonding by high heat-treatment and economic loss caused by several thermal steps are solved by mechanical processing with the milling method. The present study focuses on the development of a pore structure at various reaction temperatures to fabricate porous ceramic materials.

The crystallinity, morphology and physical properties of waste resources based porous ceramics materials prepared were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), bending strength measurements and Brunauer-Emmett-Teller (BET) absorption experiments.

Experimental Procedure

Porous ceramics was prepared from fly ash and waste glass which were used as raw materials. Fly ash from a thermal power plant (Yeosu, Jeonnam) in South Korea and a variety of waste glass (bottles, automobile windows, plates, etc.) were used. The chemical compositions of the raw materials, fly ash and waste glass, are listed in Table 1. 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 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 powder size of the waste glass obtained was about -150 mesh. To make porous ceramics, powder mixtures consist of waste glass powder (70 wt%) and fly ash (30 wt%) were used. Two different powder mixtures, about 80 g of waste glass and fly ash were mechanically ground in

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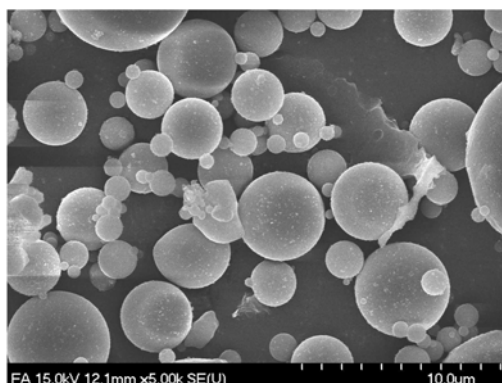
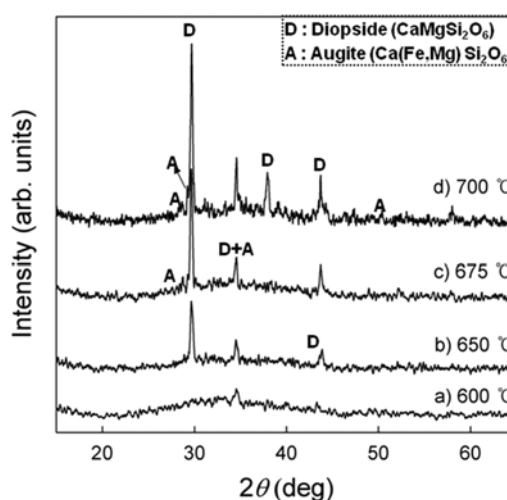
Table 1. Chemical composition (wt.%) of the raw materials used in this study.

Oxide	Waste glass	Fly ash
SiO ₂	73.55	46.91
Na ₂ O	5.53	-
CaO	11.68	25.62
MgO	5.61	11.43
Al ₂ O ₃	1.95	7.31
K ₂ O	1.68	-
Fe ₂ O ₃	-	8.73

a disk type ball mill for 140 minutes (700 rpm). The mechanical processing by the milling method is an efficient technique for preparing porous ceramics using fly ash and waste glass. 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 formed disks were heated up to 600, 650, 675 and 700 °C at a rate of 5 K minutes⁻¹ for 1 h, in a box-type SiC furnace and allowed to cool inside the furnace. X-ray diffraction analysis for specimens using Cu K_α radiation was performed with scanning at a rate of 2 degrees minutes⁻¹ with a diffractometer (XRD, Rigaku Co., D/MAX Ultima III, Japan). The scan speed was 2° minutes⁻¹, and the scan range of the diffraction angle (2θ) was 15° ≤ 2θ ≤ 65°. The surface morphology of the specimens was also observed by scanning electron microscopy (FE-SEM, Hitachi Co., S-4700, Japan). The bending strength was determined from a 3-point bending strength test in a universal tester (Instron N8872, Instron Co., England). The nitrogen adsorption and desorption isotherms at 77 K were measured in the relative pressure (P/P₀) range of 10⁻⁵ to 0.99, using a volumetric adsorption analyzer (Micromeritics, ASAP 2020) to characterize the geometrical structures of the specimens with/without heat curing. Prior to the measurements, about 0.2 g of a sample was outgassed at 373 K under vacuum for 24 h to remove the moisture contents as well as the impurities. The textural properties such as the specific surface area (Brunauer-Emmett-Teller, BET), pore volume (total pore volume at P/P₀ = 0.99 and Barrett-Joyner-Halenda, BJH, for mesopore size distribution) were calculated from the nitrogen adsorption isotherm data.

Results and discussion

Porous ceramics were achieved by mixing fly ash from the thermal power plant and waste glass cullet made up of all types of waste glass. Fig. 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 0.7 μm ~ 9.8 μm (a typical particle morphology for fly ash powders). Four representative heat treated specimens ((a) 600 °C, (b) 650 °C, (c) 675 °C and (d) 700 °C) were charac-

**Fig. 1.** FE-SEM image of the fly ash from the thermal power plant (Yeosu, Jeonnam) in South Korea.**Fig. 2.** XRD patterns for the porous ceramics heat treated at (a) 600 °C (b) 650 °C (c) 675 °C (d) 700 °C.

terized by XRD phase analysis. As shown in Fig. 2, they had very similar features in both peak positions and peak intensities in the XRD spectra [(b) ~ (d)]. Based on the data gathered, diopside [CaMgSi₂O₆] and augite [Ca(Fe Mg)Si₂O₆] are the major components found in the porous ceramic materials. The intensity peaks of the crystalline phase were sharp, and higher peaks of the diopside were formed after synthesis at a high reaction temperature (700 °C) when compared with 600 °C. This is attributed to the development of the diopside crystalline phase with an increasing heat treatment temperature.

Figure 3 shows SEM micrographs of specimens heat treated at different temperatures ((a) 600 °C, (b) 650 °C, (c) 675 °C and (d) 700 °C). It can be seen clearly that the microstructure changes with an increase in the heat treatment temperature from 600 °C to 700 °C, and there are many closed pores in the matrix of specimens, whose pore size decreases with an increase in temperature from 600 to 700. This procedure results in a gradual reduction in pore size and continuous variations in surface shape that should become fine until the pores are mainly removed.

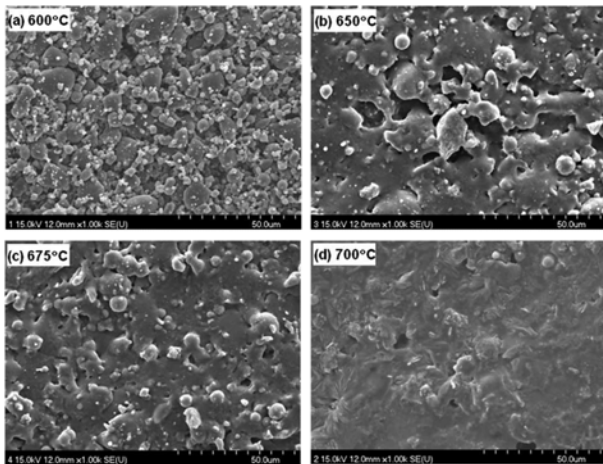


Fig. 3. FE-SEM images for the porous ceramics heat treated at (a)600 °C ~ (d)700 °C.

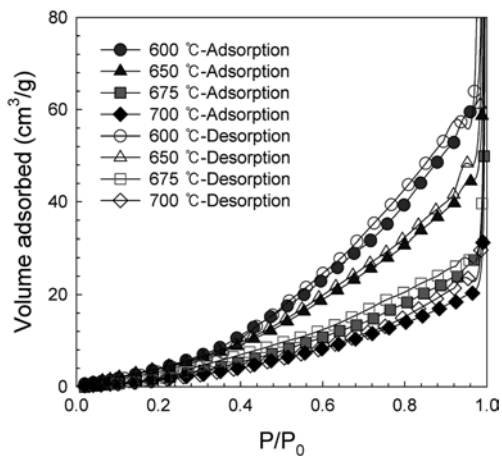


Fig. 4. The nitrogen adsorption and desorption isotherms of the porous ceramics heat treated at 600 °C ~ 700 °C.

Figures 4 and 5 show the results of the nitrogen (N_2) adsorption, desorption isotherms and pore size distributions on the waste resources based porous ceramics prepared. The nitrogen adsorption and desorption isotherms of the porous ceramics seem to belong to type V according to the IUPAC classification. The amount of N_2 adsorbed and desorbed of the porous ceramics prepared decreased with an increase of the temperature of the heat treatment. This means that the formation of pores is hindered by the heat treatment. As can be seen in the result of pore size distributions (Figure 5), the average pore size of the porous ceramics prepared also decreased by increasing the heat treatment temperature. Table 2 lists the detailed properties of the heat treated porous ceramics such as the surface area, pore volume, and average pore size.

The mechanical properties such as Vickers hardness or bending strength for porous ceramics are related to the pore size or generation of pores of porous ceramics. In other words, when a number of variables such as the heat treatment temperature or holding time are causing the pore size to grow bigger or the pores to grow in

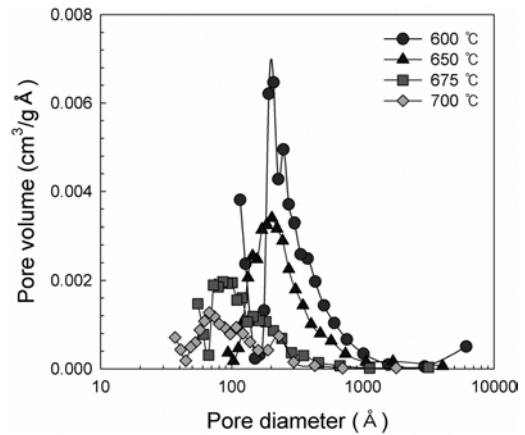


Fig. 5. Pore size distributions of the porous ceramics heat treated at 600 °C ~ 700 °C.

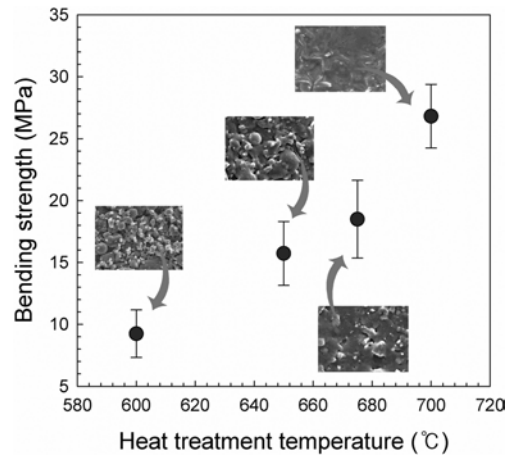


Fig. 6. Bending strength of porous ceramics heat treated at 600, 650 °C, 675 °C and 700 °C.

Table 2. Comparison of the specific surface area, pore volume, and pore diameter with the heat treatment temperature

Heat treatment temperature	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (Å)
600 °C	50.4	0.324	30.06
650 °C	49.5	0.135	20.65
675 °C	25.2	0.108	15.36
700 °C	22.8	0.084	12.99

number, the mechanical properties of porous ceramics become such that ceramics having a small pore sizes or small pore volumes yield a better result than ceramics having large pore sizes or greater pore volumes. Our investigation of the bending strength of the porous ceramics prepared indicated that with an increase in the heat treatment temperature from 600 °C to 700 °C, the bending strength improved from 9.25 to 26.81 MPa as shown in Figure 6. The porous ceramic specimens exhibited a decreasing tendency of strength with increasing pore size and pore volume, which may be attributed to defect formation. The porous ceramic specimens at all the annealing temperature range used are strong enough for practical usage.

Conclusions

Porous ceramics were fabricated from waste glass and fly ash using the milling method and annealing procedures. This manufacturing technique is effective in changing waste materials into valuable porous ceramics by mechanically applying a disk type ball milling and one time firing process. This research developed an easy method for controlling the pore size and pore volume of porous ceramics utilizing waste resources (waste glass and fly ash). The FE-SEM and BET results indicated that an irregular pore size in the ceramics matrix decreased and disappeared, because the pores kept on shrinking as the heat treatment temperature was increased from 600 °C to 700 °C. Consequently, a more compact porous ceramic was produced at 700 °C than at 600 °C.

600 °C is the most suitable heat treatment temperature for generating a porous ceramic containing the proper pore size and pore volume with good physical properties. Our future studies will concentrate on the environmental and recycling problems, such as an advanced technique of producing a porous ceramic

which has the best ratios of used wastes (fly ash and waste glass). We will also explore the possibility of applying porous filter ceramic to waste water absorption.

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