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Development of a technique to prepare porous materials from glasses

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Abstract

A new technique to prepare porous materials has been developed for recycling of used glasses. Porous materials were produced from used glass powders by hydrothermal reaction of glass powders with water at low temperatures followed by calcination at high temperatures for expansion. The new technique does not require additional vesicants such as calcium carbonate, silicon carbide, and organic polymers that have been used in the ordinary method. In this process, the water incorporated into the glass structure by hydrothermal treatment acts as a vesicant. When the hydrothermally treated glass was heated at high temperatures around 700 °C, water was released as vapor from the softened glass to form pores. The obtained porous materials had different pore structures that were determined by the sizes of raw glass particles. Crystallization occurred during the calcination of the hydrothermally treated glass powder.

Keywords: Calcination; Shaping; Porosity; Glass; Hydrothermal reaction

1. Introduction

Material recycling is a key for a sustainable development in the world.[1,2] As for the used glass bottles, the reuse is the best way.[3,4] Returnable glass bottles for milk, beer, and so on, are available, but after using several times, they become wastes. Every year, Japan produces huge amount of used glasses, which have potential to be recycled. More than 2,500,000 tons of used glass bottles have been produced every year since 1995.[5] However, only around 60% of the total amount of used glass bottles was reused.[5] The rest, colored glass bottles in particular, is hard to be efficiently reused for glass production because of their complicated chemical compositions and requirement of additional separation in accordance with the colors.[6] Therefore, the recycling of colored glass bottles has been received increasing interest.

Porous materials have been received much attention because of their wide range of pore properties for numerous applications such as building materials, adsorbents, catalyst supports, and thermal and noise insulators, and so on.[7–10] A wide range of porous materials were produced from used glasses in both laboratory scale and industrial scale mainly by calcinations of the mixture of glass powders and additional vesicants such as calcium carbonate, silicon carbide, organic polymers, and so on.[11,12] During the calcinations, the gas, mainly CO_2, generated by the thermal decomposition of the vesicants or by chemical reactions, foams in the soften glass powders. However, this method brings us another serious environmental problem including the global warming caused by the disposal of CO_2.[13] Hydrothermal reaction of glasses can result in the formation of pores in glasses.[14–16] The reaction of glasses with water under supercritical conditions becomes extremely active, so that the high mobility of ions and molecules results in a high rate of the M^{n+}/H_3O^+ ion exchange reaction in glasses.[17–19] The solubility of silica or other components in glasses also increase. Therefore, the silica-matrix porous materials were prepared by one step under supercritical hydrothermal conditions at 450 °C.[14,16] A subsequent heat treatment at around 1000 °C then resulted in the porous silica-matrix materials with crystalline phases.[14,16] However, strictly supercritical conditions

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usually are hard to be attained for industrial productions with low cost. Hydrothermal hot-pressing combining of a subsequent calcination at 700 °C is another kind of hydrothermal methods for preparing porous materials from used glass powders at relatively low hydrothermal temperatures less than 300 °C.[20,21] A low density of 0.4 g/cm^3 for porous columns with a size less than 4 cm-scale were prepared using much fine glass powders with grain size in the range of 39–45 μm in the laboratory scale.[22] However, the large scale-preparation is hard to achieve because of the limitation of a low production efficiency of hydrothermal hot-pressing instruments.

In the present study, we develop a technology involving two steps, hydrothermal treatments of glass powders at low temperatures and calcinations of hydrothermally treated glass powders at high temperatures. In this process, the water incorporated into the glass structure acts as a blowing agent. This process has following characteristics: wide range of the expansion temperature, low expansion temperature in comparison with the ordinary method, and production of large porous materials with a fine structure.

2. Experimental

2.1. Sample preparation

A commercially available glass powder was purchased from Toyo System Plant Co., Ltd., Japan, which was produced by milling of used glass bottles. The powder has a particle size distribution as shown in Fig. 1 and a true density of 2.54 g/cm^3. In a typical experiment, a mixture of the raw glass powder with 15 mass% of water was transferred into a Teflon container with 80% volume filling, and then sealed by a stainless steel autoclave. The autoclave was put into an oven for heating and the hydrothermal reaction was conducted at 200 °C for 6 h. The hydrothermally treated glass powder was transferred into a stainless steel cylindrical case with inner diameter of 2.8 cm and height of 1 cm. A subsequent calcination was performed in a preheated electric furnace at 750 °C for 30 min. The glass powder greatly expanded by the heat treatment, and a porous block with low density of 0.35 g/cm^3 was formed.

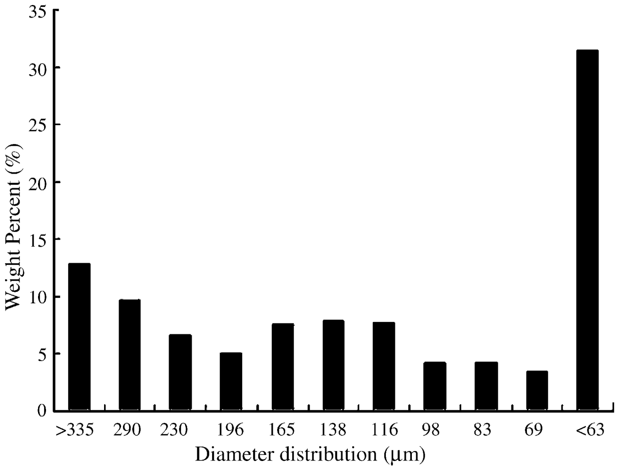

Fig. 1. Particle size distribution of the raw glass powder.

2.2. Characterizations

The crystalline phases of the samples were determined by powder X-ray diffraction (XRD) with a Rigaku Rotaflex type X-ray diffractometer (RAD-RC). The morphology and pore structure of the raw glass powder, hydrothermally treated glass powder, prepared porous materials were investigated by a Scanning Electron Microscope (SEM, S-350, Hitachi Ltd. Tokyo, Japan).

3. Results and discussion

3.1. Crystallization of glasses

Crystallinity is one of the most essential technological properties in applications of various materials.[23] Usually, glass ceramics with finely disperse volume crystallization can give enhanced mechanical and physicochemical properties. Therefore, a high crystallinity is very necessary for glass ceramics. The crystallinity of the samples was observed by XRD patterns shown in Fig. 2. A very broad peak, ranging form 10° to 40° in Fig. 2A, indicates a mainly amorphous property of the raw used glass powder. Crys-

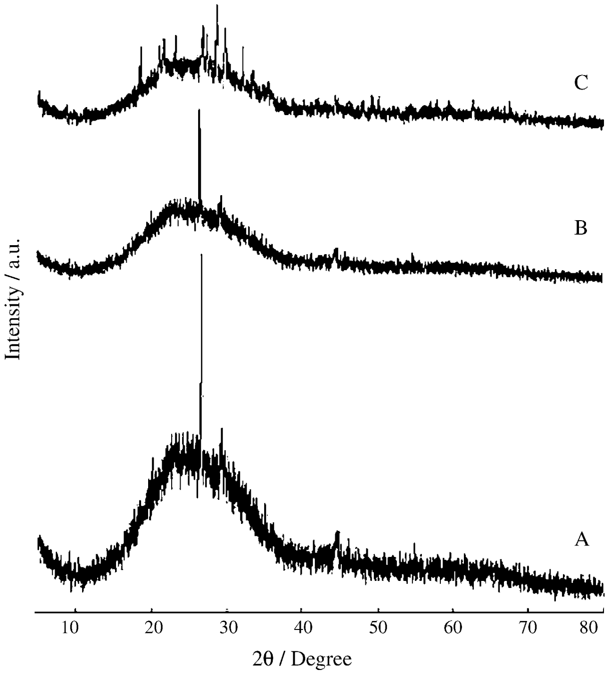

Fig. 2. XRD patterns of the raw glass powder (A); hydrothermally treated glass powder (B); and at 200 °C for 6 h, and porous materials (C) obtained by calcination of hydrothermally treated glass powders at 750 °C for 30 min.

talline calcium silicate, indicated by one, additionally, strong diffraction peak shown in Fig. 2A, is also contained in the as received glass powder. After the hydrothermal treatment, the powder still mainly consisted of amorphous materials (Fig. 2B). Additional one strong diffraction peak shown in Fig. 2B is due to the contained crystalline calcium silicate in raw glass powder. However, after the heat treatment of the hydrothermally treated glass powder at 750 °C for 30 min, we obtained porous materials with a certain crystallinity indicated by the diffraction peaks shown in Fig. 2C. The crystalline components are mainly calcium silicate ($CaSiO_3$, JCPDS 39-1425) and cristobalite (SiO_2, JCPDS 27-0088). The remaining broad XRD peak ranging from 15° to 40° indicates the existence of amorphous components in the porous materials due to an incomplete crystallization reaction.

3.2. Porous materials prepared from hydrothermally treated glass powders

Expansion of the hydrothermally treated glass powder was examined by putting the powders into the stainless steel cylindrical case. The powder volume is the same as that of the case. Therefore, we can clearly observe the expansion of the hydrothermally treated glass powder after calcination. Fig. 3A and B show top-view and side-view photographs of the expanded sample with the case, respectively. Some large pores are observed on the surface of expanded porous sample (see Fig. 3A), and the height of expanded porous sample is nearly double of the starting height of the hydrothermally treated glass powder (see Fig. 3B). Because of the limitation of the stainless steel case wall, the glass powder can only expand up out of the case. Therefore, the centre of the hydrothermally treated glass powder in the case expanded obviously, resulting in the formation of a mushroom-top-like part out of case.

Because the pores in the final porous materials belong to macropores, we can directly observe the pore morphology of the polished sample with an optical microscope. Fig. 3C shows the optical micrograph of surface morphology of the polished porous material. We find that the solid net structure of the porous material is made of three different types of pore net structures which have been marked with arrows in the inset of Fig. 3C. This is caused by the particle size distribution of the raw glass powder. For large glass particles, because the reaction time is not long enough, the hydration reaction proceeded only on the particle surface and no hydration reaction occurred deep in the inner part of particles. Therefore, the expansion reaction occurred only in the hydrated surface layer of the particles, and the inner part still did not expand, as shown by the area marked with letter “a” in Fig. 3C. According to Fig. 1, glass particles with particle size of >0.3 mm occupy over 20% of the total amount of the raw glass powder. Thus, it is still observed that a broad XRD peak, ranging form 15° to 40° indicating the existence of amorphous components, appears in the XRD pattern of the porous material (see Fig. 2C). For glass particles with a middle size, the hydration reaction occurred throughout the whole particle. As a result, during the subsequent calcination, they totally expanded to form the pore structure shown by the area marked with letter “b” in Fig. 3C. For fine particles with size of < 100 μm which consisted of over 40% of the total amount of the raw glass powder, they were totally hydrated and expanded by the calcination. However, because of the much fine size, the expanded glass particles stuck each other to form the porous net structure shown by the area marked with letter “c” in Fig. 3C. This kind of structure occupied the main part in the porous material.

3.3. Pore structure and pore formation in expanded porous materials

The pore structure was observed by SEM and the possible pore formation process was investigated by comparison of morphologies and structures of glass particles at different preparation stages.

Fig. 4A and B show SEM micrographs of the raw glass particles and hydrothermally treated glass particles, respec-

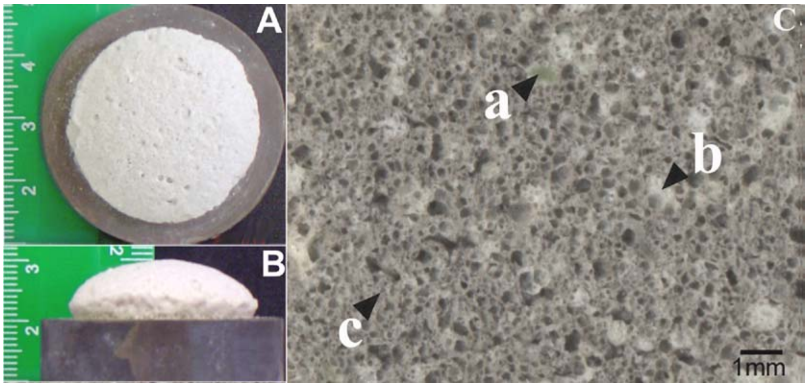

Fig. 3. Top-view (A) and side-view (B) photos of the sample with case, showing the expansion of hydrothermally treated glass powders. (C) Is the optical micrograph of surface of polished porous materials, arrows marked with a, b and c represent the large glass particle with unexpanded bulk, the pore net formed from totally expanded large glass particle, and the pore net formed from totally expanded fine glass powders, respectively.

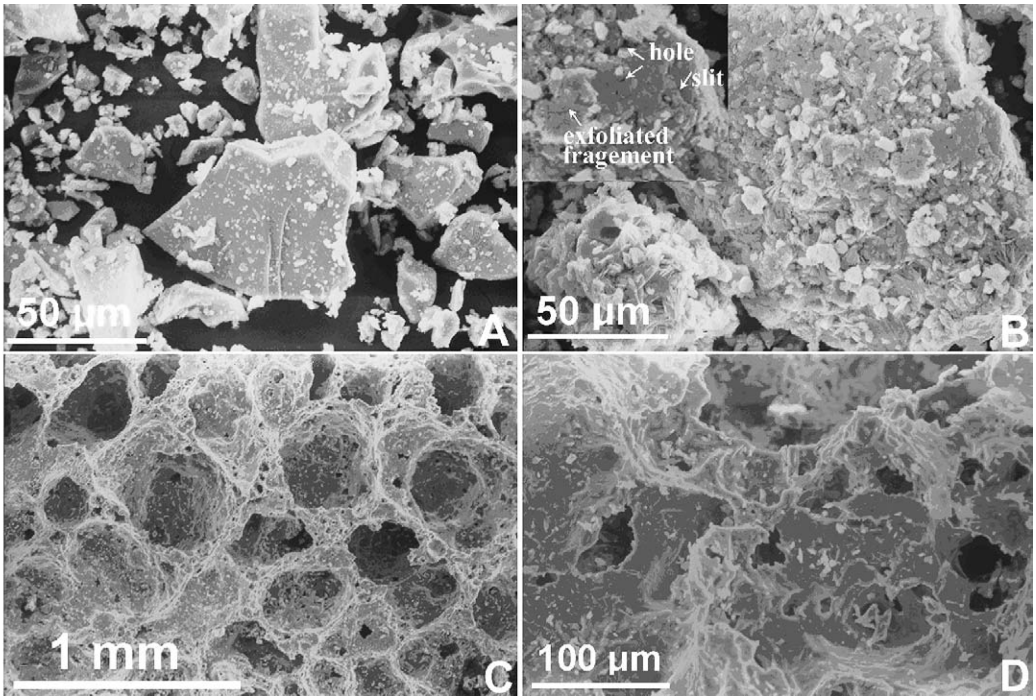

Fig. 4. SEM micrographs of the raw glass powder (A); hydrothermally treated glass powder (B); porous materials (C) obtained by calcination of hydrothermally treated glass powder, and structure of pore wall at a high magnification (D).

tively. It is observed that most of raw waste glass particles are irregular particles with smooth surface (see Fig. 4A). However, after the hydrothermal treatment, the glass surface was corroded and exfoliated fragments stuck on the surface of the large glass particles (see Fig. 4B). Pores and slits also appeared in glass particles because of the dissolution of the glass, as shown in Fig. 4B. Fig. 4C shows SEM micrograph of the polished surface of the porous material. The average diameter of large pores is around 300 μm. The structure of pore walls is further observed by SEM at a high magnification as shown in Fig. 4D. It is observed that pores with average diameter around 25 μm exist on the wall of large pores. This indicates that the pores are of a kind of interpenetrating networks.

3.4. Other properties and extended preparation of porous materials

The porous material obtained in this study has the following characteristics: 0.35 g/cm^3 of a bulk density, 1.94 g/cm^3 of a true density, 85% of water adsorption, and 65% of opening pore content. The porous materials with a large size can be produced in industrial scale by using a large case in a continuous furnace. At present, plates with 45 cm × 45 cm × 3 cm in size could be obtained. The porous materials have high machinability and enough mechanical strength to be cut. These plates may be useful as a light weighted board for thermal insulators, sound and water absorbents, floats to form floating islands, and so on.

4. Conclusions

In the present study, porous materials were prepared from used glass powders by two steps, hydrothermal reaction of glass with water at low temperatures and calcination at high temperatures for expansion. Water incorporated into the glass structure by the hydrothermal reaction acts as a vesicant in the latter calcination at 750 °C, resulting in the formation of macropores. The porous materials with a large size of 60 cm × 40 cm × 3 cm can be industrially produced by using a continuous furnace. These plates may be useful as light weighted materials.

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