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Fabrication of Low Temperature Foaming Glass Materials Using Hydrothermal Treatment

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In order to prepare functional porous glasses, the fabrication of low temperature foaming glass materials was achieved using a hydrothermal treatment. The hydrothermal hot pressing technique was applied to 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass at 523 K. The water releasing behavior of the glass was analyzed by TG-DTA. A macroscopic change was observed after the heat treatment at 423–673 K and foaming was exhibited at temperatures as low as 473 K. The mechanism for foaming of the hydrothermally treated glass is discussed from the microstructure change observed with laser microscopy. Furthermore, the application of hydrothermally treated glass is proposed and demonstrated.

KEY WORDS: foaming glass; water; hydrothermal treatment; porous material.

1. Introduction

As the porous glasses are attractive for using in heat-insulating, filtering materials, and catalyst support, the conversion of waste, secondary productive materials and minerals to the glasses has been attempted. Although the glasses are generally prepared through high temperature melting processes, such as gas bubbling or the addition of gas-forming agents to the glass melts, phase separations followed by acid etching, *etc.*, these processes may not be feasible when the energy consumption and CO_2 emission are considered.

Recently, hydrothermal treatment has been used for recycling waste materials as functional materials.[1–3] Materials in the hydrothermal process are exposed to water at a high reactivity with high pressure water vapor and/or high temperature aqueous solution. This takes advantage of energy costs because it can be operated at a temperature controlled by an industrial waste. Matamoros-Veloza *et al.*[4,5] introduced water to the waste glass mainly composed of SiO_2, Na_2O and CaO by hydrothermal synthesis and obtained a hydrated glass compact. When the prepared glass was heated, it started to foam around 923 K with the release of water and became a porous material. For the practical use of foaming glass, however, a foaming property at a lower temperature would be beneficial.

One of the authors[6,7] has been attempting to fabricate a lubricant for the high strain rolling of steels from waste glass using the hydrothermal treatment. When the sodium-silicate based glass was hydrothermally reacted, the constituents of the glass considerably influenced the water content of the glass under an identical hydrothermal condition. Moreover, the tendency was observed that an increase in water content lowers the glass transition temperature.[6]

Hence, for the fabrication of low temperature foaming glass, 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass, which exhibited the lowest glass transition temperature after the hydrothermal treatment in the previous study,[6] was selected in the present work. The glass was subjected to the hydrothermal treatment at 523 K and its water releasing and foaming behavior with a heat treatment at 423–673 K was investigated. Furthermore, the application of the hydrothermally treated glass was demonstrated using its foaming property.

2. Experimental

2.1. Hydrothermal Treatment of SiO_2–Na_2O–B_2O_3 Glass

The original glass sample was prepared from reagent grade quartz, Na_2CO_3 and H_3BO_3. Forty grams of mixture of these powders corresponding to a composition of 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 were melted in a Pt–20%Rh crucible at 1 473 K for 3 h in air, and then rapidly cooled on a copper cooling block.

The glass was subjected to a hydrothermal hot-pressing (HHP) technique developed by Yamasaki *et al.*[8] **Figure 1** shows a schematic diagram of the autoclave in the HHP apparatus. The autoclave is composed of a stainless steel cylinder with an inner diameter of 30 mm and stainless steel pistons, teflon packings and an external band heater, and can be heated to 623 K. Teflon packings give the air-tightness inside the autoclave by compressive modification when the vapor pressure is increased at high temperature.

Pre-melted glass was ground and sieved at 63 μm. Ten grams of glass powder were well-mixed with 4 g of purified water and charged into the autoclave. The inner surface was coated with kish graphite powder of less than 5 μm to prevent sticking between the solidified sample and the cylinder. After the mixture was pressed at 40 MPa, the autoclave

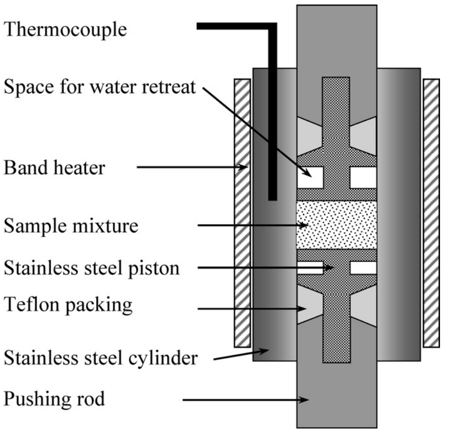

Fig. 1. Schematic diagram of an autoclave in the hydrothermal hot pressing apparatus.

was heated to 523 K within 20 min and then immediately cooled to room temperature within the same time.

2.2. Observation of Shape Change of HHP Treated SiO_2–Na_2O–B_2O_3 Glass by Heat Treatment

The HHP treated SiO_2–Na_2O–B_2O_3 glass prepared above was cut into cubic blocks of almost 6 mm. Each block was placed on a platinum pan and heated in a horizontal electric resistance furnace controlled to 423–673 K in air for 5 min. The platinum pan was chemically washed in dilute hydrochloric solution and pre-heated at 1 073 K to remove adsorbed components, prior to the experiment. The weight change in the sample was measured before and after the heat treatment. The apparent density of the sample after firing was determined by measuring its shape.

3. Results and Discussion

3.1. Characterization of Hydrothermally Hot Pressed SiO_2–Na_2O–B_2O_3 Glass

The compact obtained after the hydrothermal hot pressing of SiO_2–Na_2O–B_2O_3 glass is shown in **Fig. 2**. The glass was densified and its bulk density was determined to be 2.30 g/cm^3 by Archimedes' method.

Figure 3 shows the X-ray diffraction patterns for the glass sample before and after the hydrothermal hot pressing. As no crystalline phase is observed after the hydrothermal treatment, the HHP treated glass is regarded as keeping a glass state. The shoulder appearing around 21 degree in the original glass is strongly reduced in the HHP treated glass, which may correspond the modification of silicate network by water dissolution into glass. Further spectroscopic analysis, however, should be carried out for the discussion on the structure of water-containing glass.

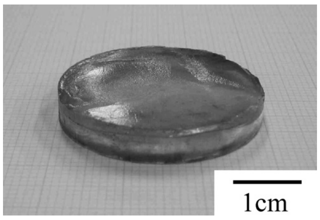

Fig. 2. Obtained compact of the 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass powder after the hydrothermal hot pressing at 523 K.

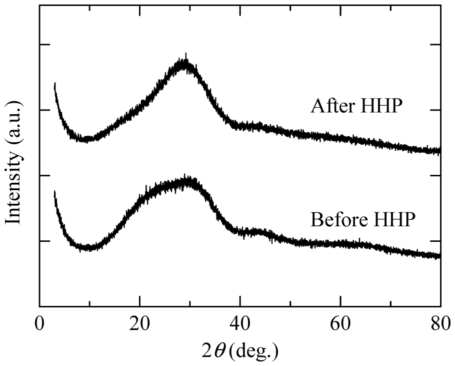

Fig. 3. XRD patterns of the 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass powder before and after the hydrothermal hot pressing at 523 K.

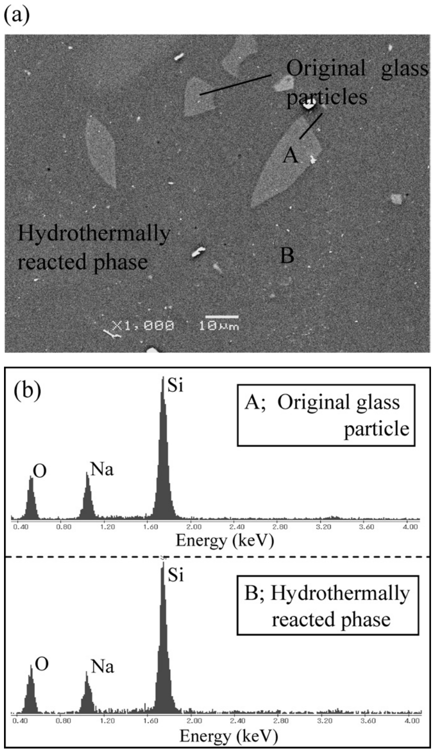

Fig. 4. (a) SEM micrograph of the HHP treated 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass, and (b) EDX profiles for the original glass particle and the hydrothermally reacted phase.

Figure 4(a) shows the microstructure of the HHP treated glass compact observed by scanning electron microprobe analysis. White-colored particles are unreacted original glass particles, and the gray-colored region is the hydrothermally reacted phase connecting thoroughly in the sample. An energy dispersive X-ray spectrometry profile suggests no significant difference in compositions between the glass particle and the reacted phase as shown in Fig. 4(b) although hydrogen cannot be detected in EDX analysis. Hence, the hydrothermally reacted phase is speculated to be the hydrated glass that is formed by water dissolution into the original glass under the hydrothermal condition,$^{9–11)}$ in view of the entirely glass structure of the HHP treated glass. The densification process of glass powder during the hydrothermal hot pressing is expected: (1) water dissolves into the original glass to form the hydrated glass

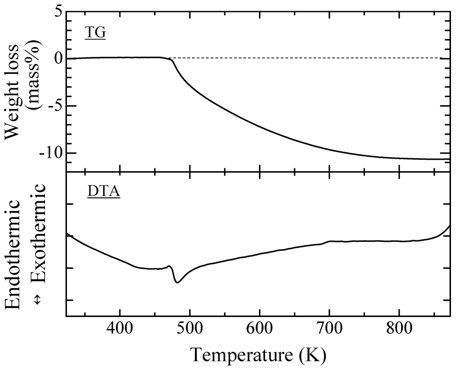

Fig. 5. TG-DTA profiles for the hydrothermally treated 63 mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass.

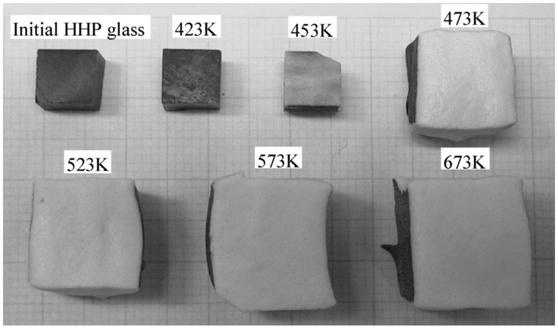

Fig. 6. Change in macroscopic shapes of the HHP treated 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass after firing at 423–673 K.

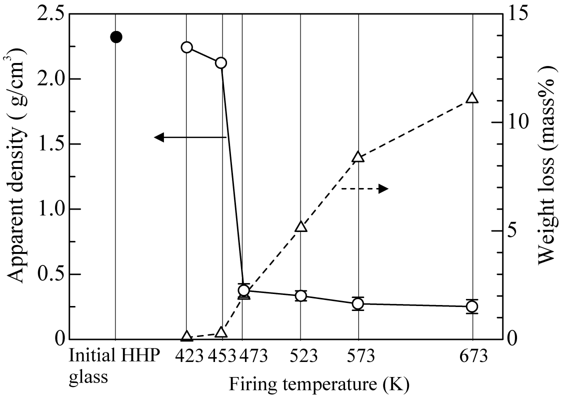

Fig. 7. Apparent densities and weight loss after firing of the HHP treated 63mass%SiO_2–27mass%Na_2O–10mass% B_2O_3 glass.

at the surface of glass particles, (2) the hydrated glass phases connect with one another due to their viscous motion under compression and fill the intragrain spaces of glass particles.

To determine the tendency for the HHP treated glass to release water through heating, the sample was subjected to TG-DTA analysis at a heating rate of 10 K/min in an argon atmosphere. The result is shown in **Fig. 5**. From the thermogravimetric profile, the sample weights started to decrease around 473 K, where the weight loss corresponds to water release from the hydrated glass. The water content in the HHP treated glass was determined to be 10.8 mass% from the final weight loss at 873 K. The profile for the differential thermal analysis exhibits a shallow endothermic peak at 450 K and a larger endothermic peak starting at around 473 K. The lower temperature peak would correspond to the glass transition as indicated in the previous work.[6)] On the other hand, the larger endothermic peak is dominated by the vaporization heat of water in the hydrated glass, taking the weight loss into account at the corresponding temperature in the TG profile. Therefore, the HHP treated glass obtained from SiO_2–Na_2O–B_2O_3 glass demonstrated the beginning of water release at a low temperature of around 473 K, and can be expected to foam at that temperature.

3.2. Change in Hydrothermally Hot Pressed SiO_2–Na_2O–B_2O_3 Glass with Heat Treatment

To determine the macroscopic change in the HHP treated SiO_2–Na_2O–B_2O_3 glass, blocks of the glass were heat treated at 423–623 K in air. The samples after the heat treatment are shown in **Fig. 6**. Although no apparent change was observed when heated at 423 K, the sample heated at 453 K appeared to be whitened. Macroscopic expansion, namely foaming, of hydrated glass was observed for the samples heated over 473 K, which corresponds to the starting temperature for water release observed by the TG-DTA analysis mentioned before. A higher firing temperature resulted in a larger expansion of the glass materials. Here, a low temperature foaming was successfully obtained compared with the previously reported temperature of around 923 K by Matamoros-Veloza *et al.*[4)] with soda-lime silicate glass. It was confirmed by XRD analysis that the foamed glass at any temperature possesses the glass structure.

Apparent densities of the foamed glasses were determined from the sample shapes under the assumption of isotopic expansion, and are summarized in **Fig. 7**, with the weight losses during the heat treatment. The apparent density decreases dramatically at 473 K due to foaming, and continues to decrease gradually as the firing temperature increases. The lowest apparent density of 0.25 g/cm^3 was obtained when the heat treatment was conducted at 673 K. The weight loss was larger at a higher firing temperature, and the value of 11% at 673 K was almost in accordance with the water content of the HHP treated glass. The relationship between the weight loss and firing temperature indicates the possibility for the control of the porosity of the foamed glass by changing the heating process.

To understand the foaming behavior of the HHP treated glass, its structural change during heating was observed *in-situ* using a laser microscope. The sample was polished to a thin film with a thickness less than 100 μm using SiC emery paper #2000, and placed in an alumina crucible. Observations were made during heating at a rate of 10 K/min to 523 K under an argon atmosphere. **Figure 8** shows the morphology during the heating operation. Below 453 K, the surface structure did not appear to change. When heated to 458 K, the start of an undulation can be seen especially in the right portion. The undulation grows as the temperature increases in the entire view. When the temperature reaches 472 K, the formation of several holes that are likely due to gas bubbles are observed with further undulation. Above 493 K, the holes expand and the surface becomes dramatically uneven. Importantly, the starting temperatures of undulation and hole formation are in accordance with the

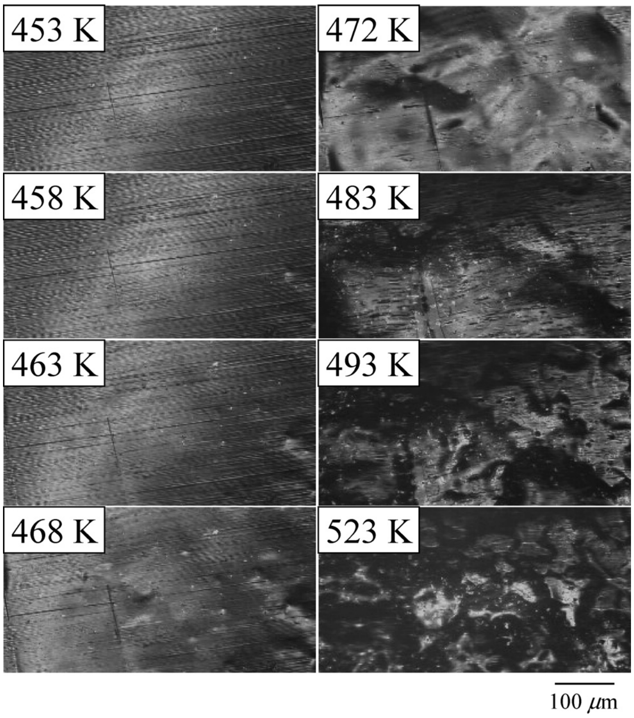

Fig. 8. Change in surface structure of the HHP treated 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass observed by laser microscope.

glass transition temperature around 450 K and starting temperature of water release around 473 K, suggested by TG-DTA analysis, respectively. From this observation, the mechanism for the foaming process of the HHP treated glass during the heating process is speculated as: (1) the glass begins to soften at 453–458 K, and (2) the internal water vapor pressure increases as the temperature increases, and a bubble forms and expands the softened glass due to its viscous motion above 472 K.

3.3. Application of Hydrothermally Hot Pressed SiO_2–Na_2O–B_2O_3 Glass

One of the applications of the foaming glass material is expected to be a filtering material. HHP treated SiO_2–Na_2O–B_2O_3 glass was crushed to 2–5 mm sized particles and charged in a glass tube with an inner diameter of 6 mm. The tube was heated externally by a gas burner. **Figure 9** shows the glass tube before and after the heat treatment. HHP treated glass foamed and filled the tube without any shape change of the tube. This demonstration indicates that the use of hydrated glass materials is a convenient method for the fabrication of an impurity filtering tube. In addition, the glass can be applied in a complex-shaped container using the spontaneous foaming by heating at a low temperature of 473 K.

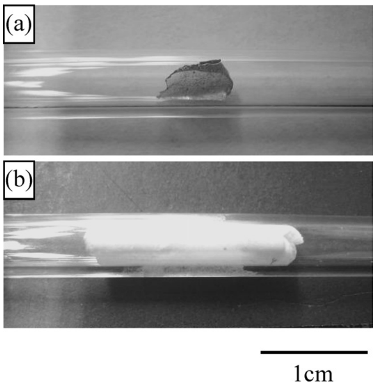

Fig. 9. Change in shapes of the HHP treated 63mass%SiO_2–27mass%Na_2O–10mass%B_2O_3 glass particles in the glass tube; (a) before, (b) after firing by gas burner.

4. Summary

In order to prepare functional porous glasses, the fabrication of low temperature foaming glass materials was achieved by the hydrothermal treatment of 63mass% SiO_2–27mass%Na_2O–10mass%B_2O_3 glass in the present work. The results obtained are as follows.

(1) Pre-melted SiO_2–Na_2O–B_2O_3 glass was subjected to hydrothermal hot pressing under a condition of 40 MPa loading pressure and heating to 523 K. The obtained material contained 10.8 mass% water and began to release water from 473 K during the TG-DTA analysis.

(2) The HHP treated SiO_2–Na_2O–B_2O_3 glass was heated at 423–673 K in air to determine its macroscopic change by firing. A foaming behavior was observed even at 473 K and this foaming temperature was much lower than that of hydrated glass reported previously.

(3) A microstructure change in the HHP treated glass during heating was observed by laser microscope up to 523 K. From the observation, the foaming of the glass was speculated to be due to softening, followed by bubble formation from the increased water vapor pressure.

(4) Application of the HHP treated glass was demonstrated. An impurity filtering tube was conveniently prepared by heating the HHP treated glass inside a glass tube.

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