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Densification process for spherical glass powders with the same particle size by hydrothermal hot pressing

KAZUYUKI HOSOI
Shiraishi Central Laboratory Co. Ltd, 4–78 Motohama-cho, Amagasaki-shi 660, Japan
SUSUMU KAWAI
Hyogo Prefectural Institute of Industrial Research, 3-1-12 Yukihira-cho, Suma-ku, Kobe-shi 654, Japan
KAZUMICHI YANAGISAWA, NAKAMICHI YAMASAKI
Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, 2-5-1 Akebono-cho, Kochi-shi 780, Japan

Low-temperature sintering of spherical glass powders with the same particle size was attempted by hydrothermal hot pressing at 260 °C. The microstructure of densified bodies was observed by scanning electron microscope and the existence of water in the surface reaction layer was confirmed by Fourier transform infrared spectroscopy. The reaction layer was formed on the surface of spherical glass particles after hydrothermal hot pressing. The thickness of the layer increased with reaction time. The layer was deformed and layers stuck together by mechanical compression. The reaction layer contained much molecular water. The kinetics of the formation rate of the reaction layer was agreed with Kondo's equation, $[1 - (1 - X)^{1/3}]^N = kt$ where t = reaction time, X = reaction ratio of glass, and N = a constant. N is 1 at the initial stage and 2 at the secondary stage. These values show that hydration on to the surface at the initial stage, and diffusion of water in the reaction layer at the secondary stage, are the rate determining steps.

1. Introduction

The hydrothermal hot-pressing technique has been used to prepare tough bodies from powder at low temperatures below 350 °C [1]. This technique is characterized by the mechanical compression of powder compacts under hydrothermal conditions and has been applied to the immobilization of various radioactive wastes [2, 3]. The technique is useful for producing bonded mass at low temperature from materials containing water and/or being easily decomposed or transferred to another phase at high temperature, which cannot be sintered by conventional technique [4, 5]. The densification kinetics of glass powder by hydrothermal hot pressing were investigated, but the powder used was irregular in shape with a broad particle-size distribution [6–8]. It is difficult to study microstructural changes in the powder during hydrothermal hot pressing.

In this study, a glass powder consisting of spherical particles with uniform diameter of 30 μm was used as a starting material. Glass powder compacts containing a small amount of water were sintered by hydrothermal hot pressing at 15 MPa and 260 °C, and the densification process of the glass powder was clarified.

2. Experimental procedure

Glass powder (GB731, Toshiba Barotiini Co. Ltd, Japan), of density 2.48 g cm^{-3}, was classified by the sedimentation method. The powder used in this study consisted of spherical particles with size from 25 to 35 μm. The composition of the glass is shown in Table I.

The glass powder (5 g) was kneaded well with a small amount of water (1.2 cm^3) in a mortar and transferred into the chamber of the autoclave for hydrothermal hot pressing [8]. The degree of filling (volumetric ratio of water to open space in the chamber unoccupied by water, glass and pistons) is 50%. After cold pressing at 40 MPa, the pressure was adjusted to 15 MPa. The autoclave was heated at the rate of 26 °C min^{-1} and held at 260 °C for a fixed time (0–60 min). The pressure was kept constant at 15 MPa during the hydrothermal treatment. The autoclave was cooled down to room temperature by an electric fan after the hydrothermal treatment. The shrinkage during hydrothermal hot pressing was determined by measuring the distance change between the ends of the top and bottom push rods.

After the densified bodies were soaked in deionized water (50 cm^3) for 1 h, they were dried at 110 °C and their apparent bulk density measured. Their polished surfaces were observed by scanning electron microscope (SEM) and they were identified by X-ray powder diffraction (XRD). The bodies produced by

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TABLE I Composition of starting glass

Composition	SiO_2	Al_2O_3	Fe_2O_3	$Na_2O + K_2O$	MgO	CaO	Ig loss
Wt %	72.0	1.0	0.1	14.0	4.0	8.0	0.9

hydrothermal hot pressing within 15 min were too brittle to polish and so were embedded in epoxy resin before polishing. The elements which dissolved in the solutions expelled from the starting powder during hydrothermal hot pressing, and the solutions in which the densified bodies were soaked (for example calcium (Ca) and sodium (Na)) were analysed by atomic absorption spectrometry and silicon (Si) by X-ray fluorescence spectrometric analysis (XRF).

3. Results and discussion

3.1. Densified processing of glass powder with reaction time

In order to investigate the reaction of the glass powder and water, the dissolved components were analysed after the glass powder had been treated under hydrothermal hot-pressing conditions. Fig. 1 shows the changes in the measured shrinkage and the concentration of elements dissolved from the glass powder during hydrothermal hot pressing with reaction time. The glass powder compact began to shrink rapidly after an induction period (within 5 min), and the shrinkage was completed by 15 min. On the whole, the concentration of Ca was small (of the order of 10^{-7} molar). The concentration of Na and Si was at first increased, then decreased. Changes in Na and Si had a maximum point at 5 min, which agreed with the time when a rapid shrinkage of the glass powder started.

These results may be explained as follows. At first, the glass powder reacted with the hydrothermal solution and the alkali ions (Na^+ and K^+) were released from the surface of the glass particles into the solution, and produced OH^-. At the same time, the resulting OH^- destroyed Si–O–Si bonds, and then silicate ions dissolved in the solution. Secondly, during hydrothermal treatment, the dissolved elements were changed to their insoluble forms. The ions of Ca^{2+} reacted with silicate ions immediately after dissolution, to produce calcium silicate hydrate. The compressive strength of a densified body produced for 60 min was 270 MPa and its porosity was 1.08%.

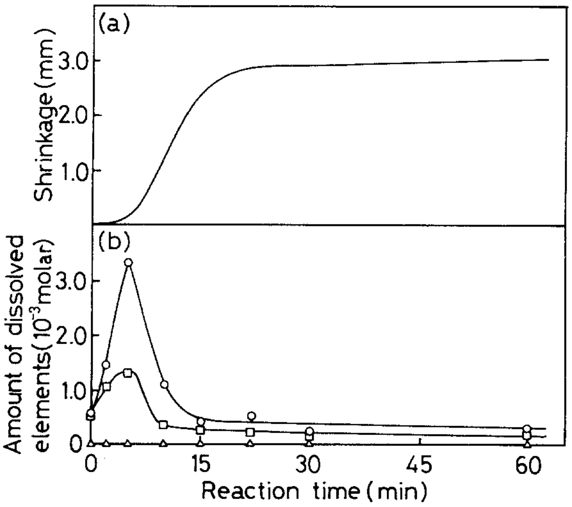

Figure 1 (a) Changes in measured shrinkage and (b) amount of dissolved elements from glass after hydrothermal hot-pressing treatment with reaction time.

3.2. Microstructural changes in densified body

Fig. 2 shows SEM photographs of the polished surface of densified bodies. A very thin reaction layer was formed on the surface of spherical glass particles for 5 min reaction time (Fig. 2a). The deformation of the layer was clearly observed as shown in Fig. 2b, and glass particles began to link with each other. These deformations may be accelerated by mechanical compression. The deformation and thickness of the layers grew up with the reaction time, and then voids among the particles disappeared. These voids completely disappeared for 30 min (Fig. 2d). Energy dispersive X-ray analysis (EDX) of the reaction layers showed that their chemical composition was the same with the starting glass. No compositional changes in the particles were detected. Fine crystals were formed on the particle surfaces and/or voids of grain boundary (Fig. 3a). The principal constituents of the fine crystals were Ca and Si (Fig. 3b).

Fig. 4 shows XRD profiles of densified bodies: the crystalline products were formed in densified bodies and their amount increased with reaction time. These products were identified to be calcium silicate hydrate (1.4 nm tobermolite) [9] and SiO_2(cristobalite) [10]. It is concluded that these products were produced by the dissolution and deposition of components of the glass powder during the hydrothermal reaction, and the fine crystals as shown in Fig. 3a were 1.4 nm tobermolite.

Molecular water diffused in the reaction layer under hydrothermal condition, and the hydrated reaction of glass network occurred in the reaction layer. Therefore molecular water and hydroxyl groups may exist in the reaction layer.

The dissolution of glass into water takes place not only in the counter-diffusion of hydronium ions and alkali ions, but also in the diffusion of molecular water as described by Doremus [11] and Smets and Tholen [12]. Ernsberger [13] and Wu [14] analysed that the manner in which water is incorporated into the silicate glasses by infrared spectroscopy (IR) and differential thermogravimetric analysis (DTG) [13–15]. They showed that the IR spectrum of hydrated glass showed a band at 1640 cm^{-1} where molecular water should be absorbed. FT–IR spectra of densified bodies obtained by hydrothermal hot pressing were very much in agreement with the IR spectrum of hydrated glass.

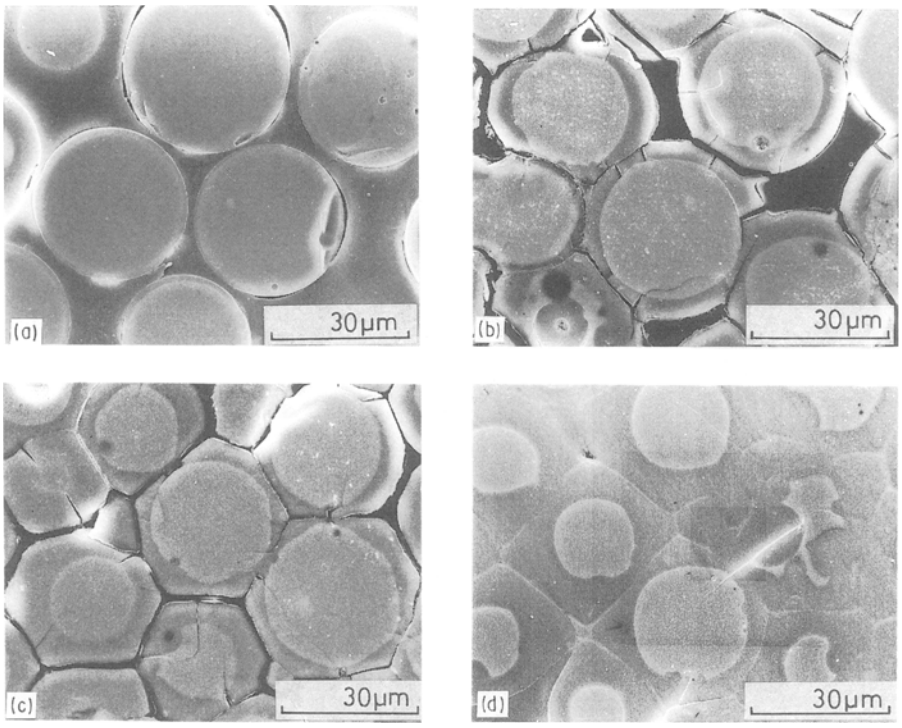

Figure 2 Scanning electron micrographs of polished surfaces of densified bodies. Specimens were produced by hydrothermal hot pressing for (a) 5; (b) 10; (c) 15; (d) 30 min. Bulk densities of samples (c) and (d) were 2.36 and 2.43 g cm^{-3}, respectively.

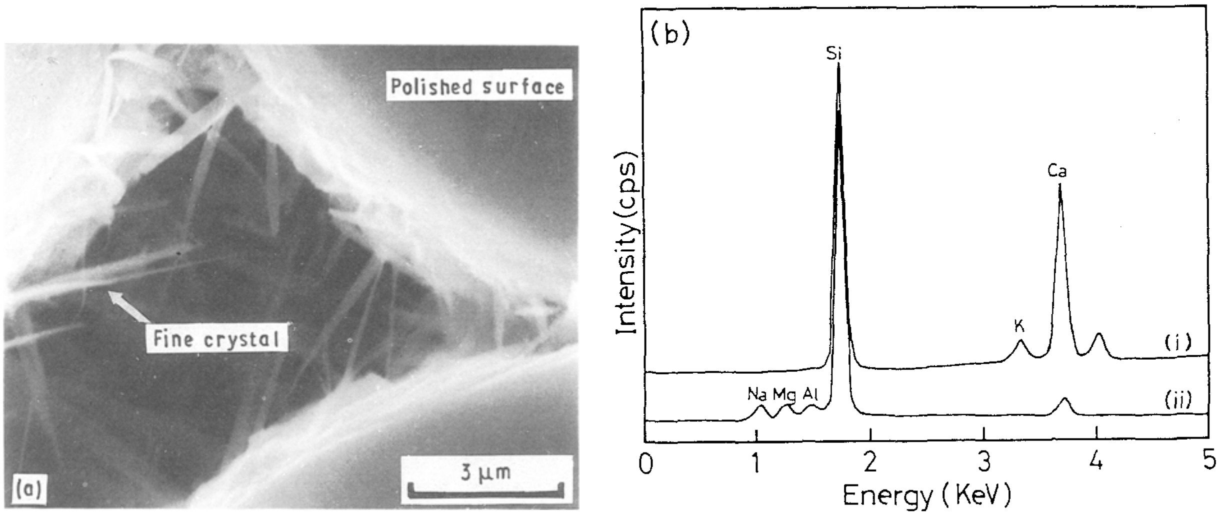

Figure 3 (a) Scanning electron micrograph of fine crystal formed on particle surface and/or void of grain boundary. (b) EDX analysis of (i) a fine crystal in Fig. 3a, and (ii) a surface of starting glass.

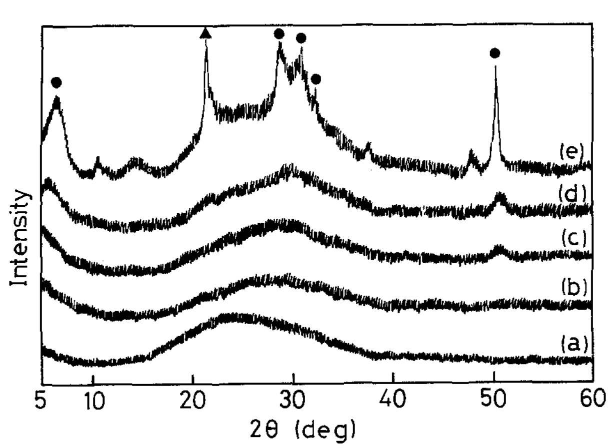

Figure 4 XRD profiles of densified bodies produced by hydrothermal hot pressing for (b) 15; (c) 30; (d) 60 min; (e) 5 h. Profile of starting glass is shown in (a). ● and ▲ are 1.4 nm tobermolite and SiO_2 (cristobalite), respectively.

Fig. 5 shows the change of absorption at 1640 cm^{-1} when the densified bodies were analysed by FT–IR spectroscopy. The amount of water in the glass increased with reaction time. This result suggests that water penetrates into the glass particle by hydrothermal treatment, and that the reaction layers containing much water were formed by a chemical reaction of glass and water.

3.3. Kinetics of densification process

We assumed that the surface reaction layer was formed by means of the hydration of glass. Kondo *et al.* [16] discussed hydrothermal reaction mechanism using the following equation

$$[1-(1-X)^{1/3}]^N = kt$$

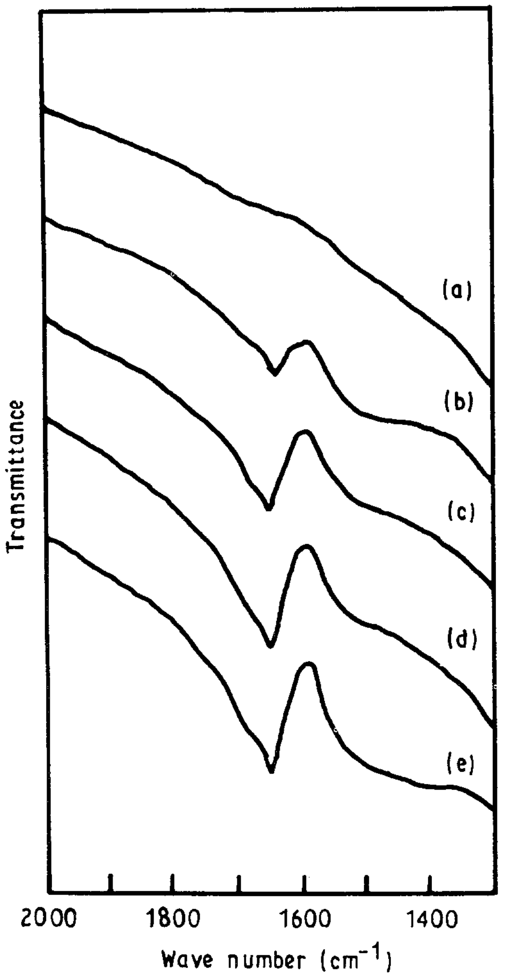

Figure 5 FT–IR spectra of densified bodies produced by hydrothermal hot pressing for (b) 5; (c) 15; (d) 30; (e) 60 min. Spectrum of starting glass is shown in (a).

where t = reaction time, X = reaction ratio, and N = a constant which is determined by the mechanism of reaction as follows:

$N = 2$, the usual diffusion rate-controlling; $N = 1$, the surface reaction rate-controlling; $N > 2$, the diffusion rate-controlling and the reaction layer spread densely with reaction time; $N < 2$, the diffusion rate-controlling and the reaction layer spread coarsely with reaction time.

In this study, the degree of the reaction of glass and water was estimated by the amount of the reaction layer. The area ratio (S/S_0), where S is the area of reaction layer and S_0 is the gross area of glass particle in Fig. 2, was calculated by an image processing technique. This value (S/S_0) was then converted into the volumetric ratio, which was used as the reaction ratio ($= X$).

Fig. 6 shows the change in reaction ratio with reaction time. Fig. 7 shows plots of $\log[1 - (1 - X)^{1/3}]$ against $\log t$. Until the reaction time reached at 20 min, the value of N was 1. The reaction rate of the glass may be controlled by the hydration rate on the surface of unreacted glass. After 20 min, the value of N was 2. The reaction rate of the glass may be controlled by the diffusion rate of water which exists in the reaction layer. In the reaction layer, molecular water may be quite mobile and could easily penetrate into the interface of unreacted glass and reaction layer. However, water could not be continuously supplied from outside the reaction layer because the layers were deformed and stuck by mechanical compression. Consequently it is considered that, in the secondary stage, the reaction rate of the glass depended on the diffusion rate of the water existing in the reaction layer.

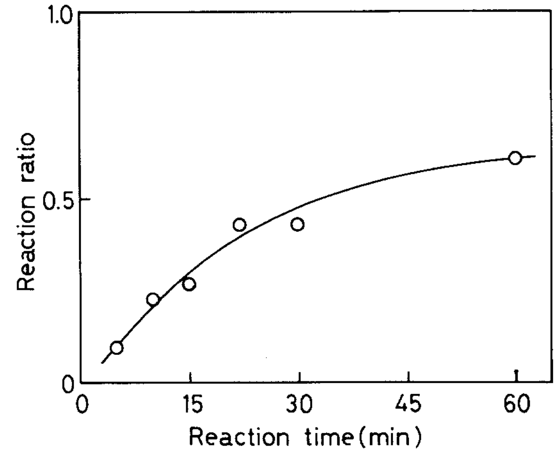

Figure 6 Change in reaction ratio of glass with reaction time.

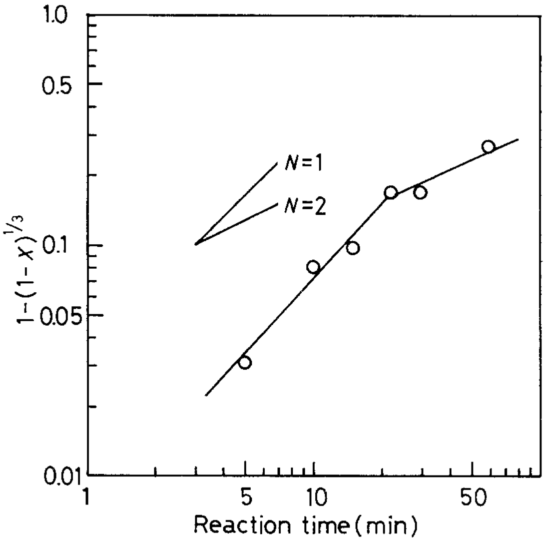

Figure 7 Plots of log $[1 - (1 - X)^{1/3}]$ against log t.

4. Conclusion

The glass powder consisting of spherical particles was densified by the hydrothermal hot-pressing technique. The shrinkage of the glass powder occurred rapidly after an induction period. The glass reacted with the hydrothermal solution and Na, Si and Ca were dissolved in water from the glass powder. In particular, the concentration of Na and Si increased during the induction period, and decreased after the rapid shrinkage started. The reaction layer was formed on the surface of glass particles by hydrothermal treatment. The layer was deformed considerably by mechanical compression, and the glass particles linked with each other.

FT–IR spectra of densified bodies indicated that the molecular water might penetrate into glass to produce the reaction layers. The formation rate of the reaction layer by hydrothermal treatment agreed with Kondo's equation, which suggested that the reaction rate of the glass powder was controlled by two mechanisms: (i) the hydration rate of glass at the initial stage (within 20 min); and (ii) the diffusion rate of water which exists in the reaction layer at the secondary stage.

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