

# Densification process of borosilicate glass powders under hydrothermal hot-pressing conditions

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Borosilicate glass powders containing  $\text{Li}_2\text{O}$  over 3.3 wt% were densified by the addition of water under hydrothermal hot-pressing conditions at 25 MPa below 300°C. The initial shrinkage proceeded by a viscous flow mechanism. The glass powders with a high concentration of network-modifying oxides had high densification rates. At low temperature, the glass powders were gently densified after an induction period in which shrinkage was very slow. During the induction period, the glass powders reacted with water and lithium in the glass structure was dissolved in water.

## 1. Introduction

Linkage of particles by means of dissolution and deposition is usually observed when a large amount of silica powder is hydrothermally treated in a small amount of alkaline solution. In order to enhance the densification of the powder, the solution should be removed from grain boundaries. In the hydrothermal hot-pressing method [1], mechanical compression of the starting powder under hydrothermal conditions from outside an autoclave accelerates compaction of the powder, and the solution is expelled from the powder into space for water retreat. Thus, low-quartz powder was converted to a solid body with high mechanical strength over 300 MPa by hydrothermal hot-pressing at 300°C and 28 MPa [2]. The hydrothermal hot-pressing temperature was much lower than that for ordinary sintering. The result suggests that the hydrothermal solution acts as an accelerator for the linkage of particles.

Recent papers [3, 4] revealed that borosilicate glass powders containing network modifying oxides could be densified by the addition of pure water under hydrothermal hot-pressing conditions below 300°C and 30 MPa. On the other hand, concentrated NaOH solution was necessary to densify quartz glass powder containing no network-modifying oxides. In the case of hydrothermal hot-pressing of a glass powder, the concentration of network-modifying oxides might affect the densification process. That means that the glass powder might react with water during hydrothermal hot-pressing.

In this paper, borosilicate glass powders with various concentrations of network-modifying oxides were densified by hydrothermal hot-pressing. The effect of composition of the glass powders on densification rate by hydrothermal hot-pressing, and the relation between the densification and the dissolution of the glass powders into hydrothermal solution, were investigated.

## 2. Experimental procedure

### 2.1. Materials

Four borosilicate glass powders with various concentrations of network-modifying oxides were used as starting materials (Table 1). Glass B (PF700P, density  $2.51 \text{ g/cm}^3$ , particle diameter  $< 40 \mu\text{m}$ ) was procured from Nihon Denki Garasu Co. Ltd, Japan. Glasses A, C and D were prepared by melting Glass B with  $\text{Li}_2\text{CO}_3$  or quartz glass powder at 1200 to 1400°C. They were crushed and passed through a 300 mesh. These glass powders contained only lithium in alkali metals.

### 2.2. Densification method

The autoclave for hydrothermal hot-pressing used in this study is shown in Fig. 1. It was a cylinder made of steel with a cylindrical chamber, 2 cm in diameter. A starting sample in the chamber was compressed by pistons from above and below. The pistons had a space for water retreat ( $1.2 \text{ cm}^3$ , each), into which water including in the starting sample was released. Gland packing made of Teflon between piston and push rod prevented leakage.

A glass powder (5 g) was kneaded with distilled water ( $0.6 \text{ cm}^3$ ) and transferred into the chamber. After the powder was cold-pressed at 100 MPa for 10 min, the pressure was adjusted to 25 MPa. Under these conditions, the degree of filling (volumetric ratio

TABLE I Composition of starting glass powders (wt %)

	A	B	C	D
$\text{SiO}_2$	57.06	58.50	62.65	70.95
$\text{B}_2\text{O}_3$	18.05	18.50	16.65	12.95
$\text{Li}_2\text{O}$	7.00	4.66	4.19	3.26
CaO	3.93	4.03	3.63	2.82
ZnO	3.84	3.94	3.55	2.76
$\text{Al}_2\text{O}_3$	4.43	4.54	4.09	3.18
BaO	3.81	3.91	3.52	2.74
$\text{SnO}_2$	1.32	1.35	1.22	0.95

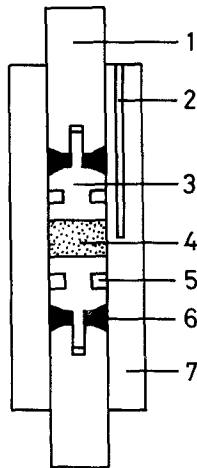


Figure 1 Autoclave for hydrothermal hot-pressing. (1) Push rod, (2) thermocouple well, (3) piston, (4) sample, (5) space for water retreat, (6) gland packing, (7) piston.

of water to open space in the chamber unoccupied by water, glass and pistons) was 18%. The autoclave was heated to a desired temperature from 260 to 300°C by an induction heater at the rate of 75°C min<sup>-1</sup>. The temperature and the pressure were kept constant for 0 to 30 h. During hydrothermal hot-pressing, the shrinkage of the starting powder was determined by continuous measurement of the distance between top and bottom push rods. The densification rates were compensated by blank tests for thermal expansion of pistons and gland packings.

### 2.3. Dissolution method

A glass powder (23.8 g) was kneaded with distilled water (2.8 cm<sup>3</sup>) and transferred into an autoclave lined with titanium (28 cm<sup>3</sup> in inner volume). The degree of filling was 18%, the same value as in the case of hydrothermal hot-pressing. The autoclave was heated by the induction heater at the rate of 75°C min<sup>-1</sup>. After the hydrothermal treatment without mechanical compression for 0 to 40 min, the autoclave was quenched by putting it into cold water. The glass powder taken out of the autoclave was ground in a mortar, and soaked in distilled water (200 cm<sup>3</sup>) at 40°C for 4 days. The solid was washed with distilled water and removed by a centrifugal separator. The solution (500 cm<sup>3</sup>) was analysed by atomic absorption spectrometry. Concentrations of lithium, silicon and

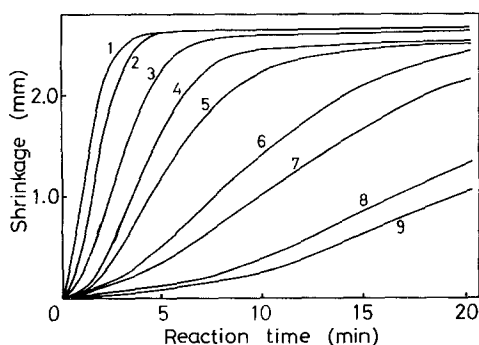


Figure 2 Measured shrinkage of Glass B at various temperatures. (1) 300°C, (2) 295°C, (3) 290°C, (4) 285°C, (5) 280°C, (6) 275°C, (7) 270°C, (8) 265°C, (9) 260°C.

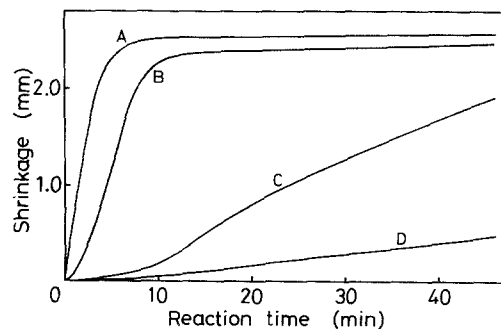


Figure 3 Effect of glass composition on measured shrinkage at 280°C.

calcium appeared in figures expressed those of this solution.

## 3. Results and discussion

### 3.1. Densification of glass powders

Measured shrinkage of Glass B at various temperatures is shown in Fig. 2. Shrinkage occurred after the temperature at the autoclave reached a desired value. The glass powder was densified in a short time at high temperature. At low temperature, it was gently densified after an induction period in which the shrinkage was very small. The total shrinkage of the powder was equal to 0.29 cm in all runs after hydrothermal hot-pressing for 30 h.

Figure 3 shows the effect of glass composition on measured shrinkage. High concentration of network-modifying oxides in the starting glass powders gave high shrinkage rate.

Fractured surfaces of the specimens produced from Glass B at 280°C are shown in Fig. 4. Linkage of grains was observed even in the specimen (Fig. 4b) produced by cooling as soon as the temperature reached 280°C. Porosity measurement by a porosimeter (American Institute Co. Inc.) using the mercury intrusion technique, showed that pore distribution of this specimen was in a small range of about 1 μm. As the reaction time was increased, pores decreased in volume and size. No pores were detected in the specimen (Fig. 4e) produced by hydrothermal hot-pressing for 20 min. The long reaction time made the fractured surface smooth, like a fused glass (Fig. 4f).

The linkage of grains, observed in the specimens produced by hydrothermal hot-pressing, gives an assumption that shrinkage of the glass powders by this method is similar to that obtained by ordinary pressure sintering. Murray *et al.* [5] showed a rate equation for hot-pressing based on flow characteristics of a Bingham solid.

$$\ln(1 - \rho) = -(3\sigma/4\eta)t + c \quad (1)$$

where  $\rho$  is the relative density,  $\sigma$  the pressure,  $\eta$  the viscosity,  $t$  the time and constant  $c$ . This equation has been found to agree with experiments on aluminium oxide [6] and metal powders [7]. Vasilos [8] has pointed out that the equation also agrees with shrinkage of fused silica, which behaves essentially as a viscous fluid at temperatures below vitrification.

Plots of  $\ln(1 - \rho)$  against time for Glass B are shown in Fig. 5. A linear relationship between these

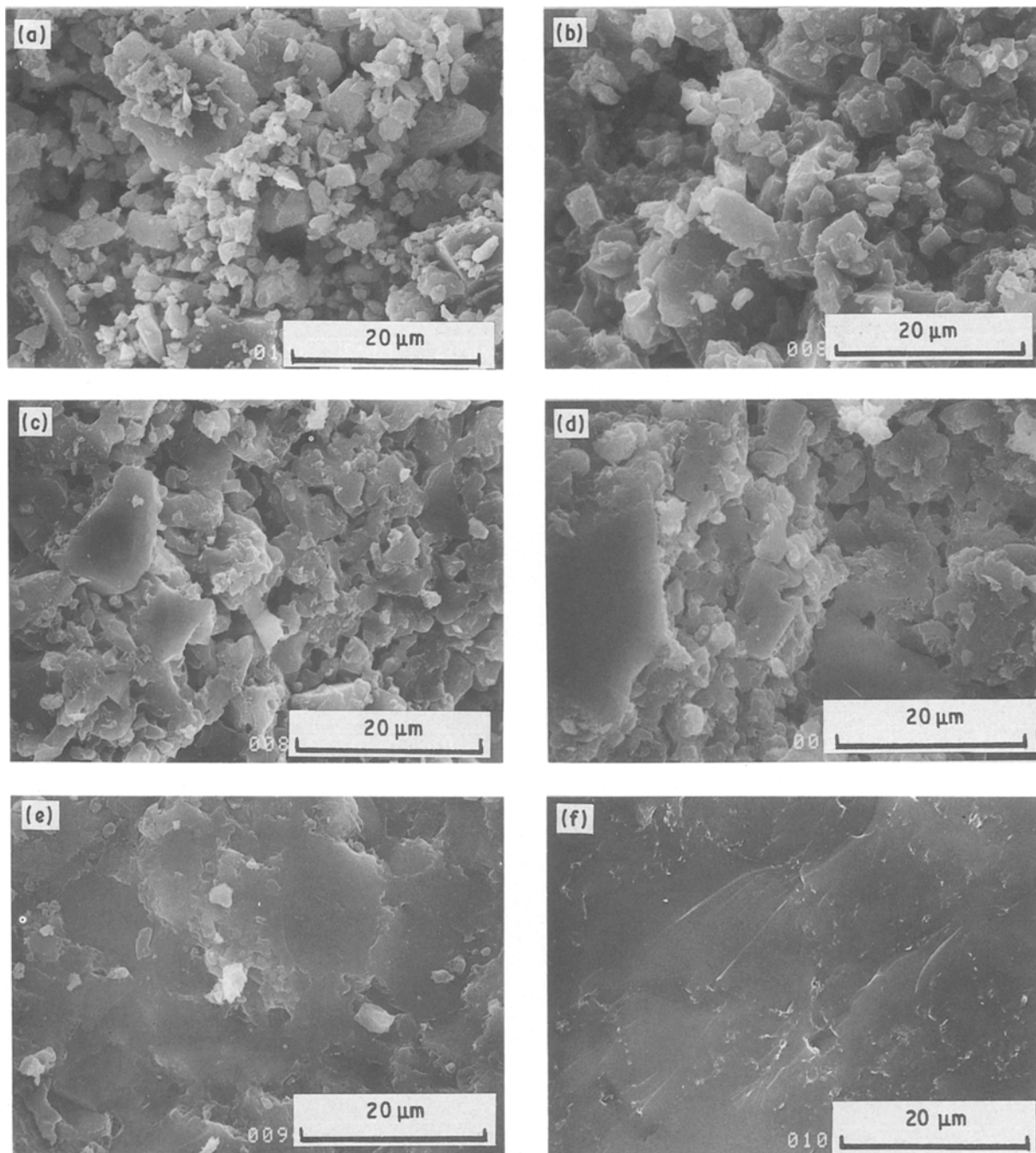


Figure 4 Fractured surfaces of densified bodies. Specimens were produced from Glass B by hydrothermal hot-pressing at 280°C for (b) 0 min, (c) 5 min, (d) 10 min, (e) 20 min, (f) 30 min. Starting powder of Glass B is shown in (a).

two quantities was observed until the shrinkage reached 0.24 cm, regardless of differences in reaction temperature. The same linear relationship was observed for other glass powders. It is concluded that the initial shrinkage of the glass powders during hydrothermal hot-pressing may proceed by viscous flow.

Since the slope of the straight line plots of  $\ln(1 - \rho)$  against time at a constant temperature is equal to  $-(3\sigma/4\eta)$ , the viscosity of the glass powder may be calculated for various temperatures employed. The plots of  $\log \eta$  against the reciprocal temperature (the Arrhenius plots) in Fig. 6 show straight lines. The activation energy can be calculated from the slope of these lines. The values of the activation energy for Glass A, B, C and D were 32, 43, 47 and 53 kcal mol<sup>-1</sup>, respectively. The glass powder with a high concentra-

tion of network-modifying oxides had a low value of activation energy. The result suggests that a glass powder with a high concentration of network-modifying oxides reacts easily with water under hydrothermal conditions.

### 3.2. Dissolution of glass powders

In order to investigate the reaction of the glass powders with water, dissolved components were analysed after the glass powders were treated under hydrothermal conditions without mechanical compression from outside the autoclave. The hydrothermally treated glass powders were loosely aggregated. When they were soaked in distilled water at 40°C, the concentration of dissolved components was increased with an increase in soaking time up to 4 days. It

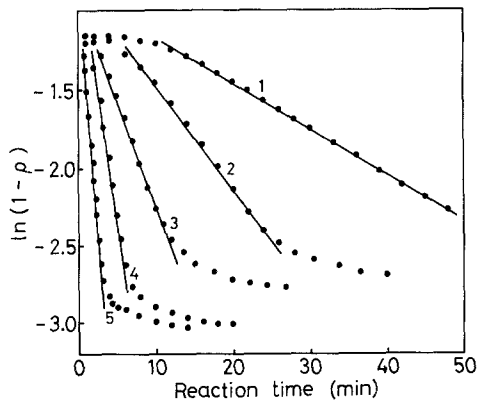


Figure 5 Plots of  $\ln(1 - \rho)$  against time for Glass B. (1) 260°C, (2) 270°C, (3) 280°C, (4) 290°C, (5) 300°C.

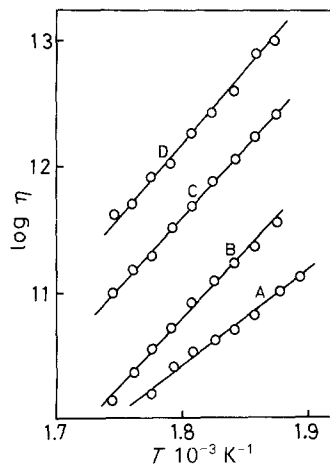


Figure 6 Plots of  $\log \eta$  against  $1/T$  for Glass A, B, C and D.

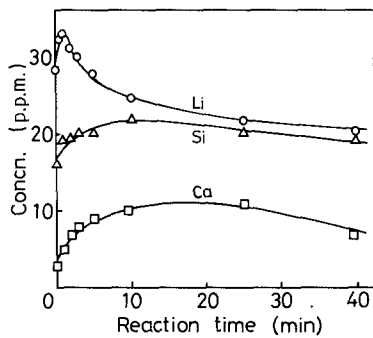
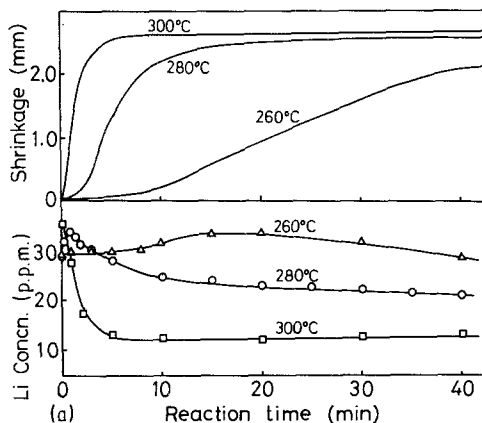


Figure 7 Concentration of dissolved elements from Glass B after hydrothermal treatment at 280°C for various reaction times.



is considered that water may diffuse into the glass particles from their surfaces by the hydrothermal treatment and produce reaction layers in which soluble components in the glasses are easily washed out by soaking in water. It has been confirmed by other experiments that a surface layer is produced on the bulk of Glass B by hydrothermal treatment at 280°C.

The concentration of dissolved elements from Glass B by hydrothermal treatment at 280°C, is shown in Fig. 7 against reaction time. The concentration of all elements was at first increased, then decreased. Especially, changes in lithium concentration had a maximum point at 1 min, which agreed with the time when shrinkage of the glass started.

The relationship between the shrinkage during hydrothermal hot-pressing and the concentration of lithium dissolved by hydrothermal treatment, is shown in Fig. 8. Glass B was rapidly densified as soon as the temperature reached 300°C, and the lithium concentration was also rapidly decreased with the increase in time (Fig. 8a). At low temperatures below 280°C, Glass B began to shrink rapidly after an induction period, and changes in lithium concentration had a maximum point at the end of the induction period. A similar relationship between the shrinkage and lithium concentration was also observed by experiments using different glasses (Fig. 8b). It is concluded that a glass powder may begin to shrink by hydrothermal hot-pressing after an induction period, during which the glass reacts with hydrothermal solution to make the glass components with a high solubility to dissolve into the solution. During rapid shrinkage of the glass powder, dissolved elements are changed to their insoluble forms.

#### 4. Conclusion

The initial densification rate of borosilicate glass powders by hydrothermal hot-pressing agreed with Murray's equation, which suggested that the shrinkage proceeded by viscous flow mechanism. The glass powders with high concentration of network-modifying oxides had high densification rates and low values of the activation energy calculated from Murray's equation. The shrinkage of glass powders occurred rapidly at high temperature. At low temperature, the

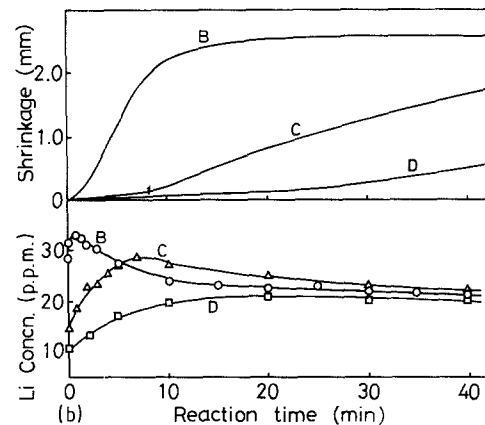


Figure 8 Relationship between measured shrinkage and lithium concentration. (a) Effect of reaction temperatures for Glass B. (b) Effect of glass composition at 280°C.

glass powders were gently densified after an induction period in which the shrinkage was very slow. The concentration of lithium dissolved in water from the glass powders after hydrothermal treatment was increased during the induction period, and decreased after the rapid shrinkage started. It was considered that the rapid shrinkage might occur after soluble components in glass powders were dissolved in water by a hydrothermal reaction. The rapid shrinkage of the glass powders with the high concentration of network-modifying oxides suggests that they reacted easily with water under hydrothermal conditions.

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