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Hot-Pressing Behaviours of the Gel and Melt-Derived Sodium-Borosilicate Glass Powders

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Abstract: Na-borosilicate glasses are used widely in glass-matrix composites which are produced by slurry or sol–gel infiltration followed by hot-pressing. The hot-pressing behaviours of the glass powders are an important parameter in the preparation of the glass-matrix composites. The densification and crystallization of the gel and melt-derived Na-borosilicate glass powders under hot-pressing were studied. Gel-derived powders crystallized faster than the melt-derived powders. Cristobalite was the crystalline phase in both powders. The crystallization of the gel and melt-derived powders inhibited the viscous sintering during hot-pressing. Viscosities of the powders were calculated at various temperatures under isothermal hot-pressing conditions. Melt-derived powders had lower viscosities then the gel-derived powders. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Glass and glass-ceramic matrix composites, reinforced with continuous C or SiC fibres have been studied over the last 25 years. The main aim of the development of fibre reinforced ceramics has been material which has the advantages of a ceramic combined with much increased toughness. Improvement in fracture toughness can lead to improved strength and damage tolerance and, equally importantly, reduce variability in strength.

Early works in the area of glass matrix composites were carried out in the UK in the late 1960s and early 1970s.[1–3] In these studies, sodium borosilicate glass powders (7740. Pyrex, Corning Glass) was the most used matrix material. In the 1980s work which was similar to the work in Harwell, UK, was carried out using Pyrex with SiC (Nicalon) reinforcement and very promising results were reported.[4]

Glass matrices, compared with other ceramic matrix candidates, probably offer the greatest commercial potential because of their ease of densification (via viscous flow), low cost and high performance at temperatures up to 1000 °C.

The important parameter in glass matrix composites is that; the ability to control the viscosity of glasses for flow under pressure permits the physical densification of fibre reinforced composites without mechanical damage to the fibres and the composite densification process can be rapid since glass matrix flow is all that is required.

The preparation of the glass matrix composites is usually carried out by employing slurry infiltration of fibre tow followed by hot-pressing at high temperatures. Also, the use of sol–gel processing in glass matrix composites have been reported.[5–7] In both techniques, the matrix material is a glass powder before hot-pressing derived either by melting or sol–gel processing.

Na-borosilicate glasses are known to be resistant to crystallization during heat treatments but this behaviour is affected by the particle size of the glass powder.[8] Also, it was reported that there is a crystallization of Pyrex matrix in Pyrex–SiC composites.[7,9] The crystallization of the Na-borosilicate glass matrix in C- and SiC-reinforced composites

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was also observed.[7] It was reported that the presence of the fibres enhanced the crystallization of the glass matrix. As mentioned above the particle size of the glass powders is an important parameter. There is not any report about the behaviour of gel or melt-derived glass powders which were hot-pressed in similar conditions to the glass matrix composites. In the present work, the hot-pressing behaviour of gel and melt-derived Na-borosilicate glass powders was reported and their viscosities were calculated and compared to the commercial borosilicate glass.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

TEOS ($Si(OC_2H_5)_4$), EtOH (ethanol, C_2H_5OH), H_2O, Al-*sec*-Butoxide ($Al(OC_4H_9)_3$), Na-methoxide ($NaOCH_3$), TMB ($B(OCH_3)_3$) trimethyl borate, Boric acid (H_3BO_3), Na-acetate (CH_3COONa) were used in the sol–gel processing and $Al(OH)_3$, LA-sand (low alkali), Na_2CO_3 and H_3BO_3 were used in melting of Na-borosilicate glasses.

2.2 Sol–gel preparation

Multicomponent gels of a composition close to that of commercial Pyrex (7740, Corning Glass), composition 81 SiO_2–13 B_2O_3–4 Na_2O–2 Al_2O_3 as wt%, were prepared at room temperature using metal alkoxides, acetates and nitrates as precursors to oxides of SiO_2, Al_2O_3, B_2O_3 and Na_2O. The detailed explanation of the preparation of gel and melt-derived Na-borosilicate glass powders were given elsewhere.[7]

Gelling of the solutions and drying and aging of the gels were carried out in an oven at 50 °C, until no further weight loss was observed. In the powder preparation the heating rate was not very critical during the calcination of the resultant gels and further heat treatments up to 400 °C for 24 h were carried out. This calcined gel powder was used to study the crystallization and hot-pressing behaviours of the gel-derived Na-borosilicate glass powder (gel-derived powder).

2.3 Glass melting

A composition which was similar to the commercial Pyrex (7740, Corning Glass) composition was melted using $Al(OH)_3$, LA-sand, Na_2CO_3 and H_3BO_3 as starting materials for Al_2O_3, SiO_2, Na_2O and B_2O_3, respectively. The batch was prepared by mixing the required amounts of the starting materials manually. The batch was melted in a gas fired furnace at 1600 °C in a Pt-crucible which was encapsulated in an alumina outer crucible with an alumina lid in order to protect the Pt-crucible. The melt could not be stirred because of the lid arrangement. The batch was melted for 6 h and then poured into a pre-heated steel mould in spite of its high viscosity which made pouring difficult. The glass was allowed to cool down in air, though it appeared reasonably homogeneous it was observed to contain a considerable number of bubbles. This melted glass was used to compare the chemical compositions of the gel with the melt-derived glasses, especially in the case of B_2O_3 losses.

In the hot-pressing study, commercial Na-borosilicate glass powder was used as "melt-derived" powder throughout this article.

2.4 Powder preparation

Gel and glass powders were prepared either using a mechanical mortar or ball-mill and sieved to below a certain particle size. The ball-milling was carried out in a dry state using alumina balls as the milling media, for 24–72 h. In the mechanical mortar (agate), crushing was carried out for 1–3 h in a dry state. Sieving of the powders was performed using Cu grid sieves.

2.5 Hot-pressing

The hot-pressing of powders was carried out using a split furnace and the details about this furnace are given elsewhere.[7] The pressure was applied using a manually controlled hydraulic pressure unit. The sample temperature was monitored by using a Pt:Pt–13%Rh thermocouple which was placed into a hole in the die, near the sample. The pressing unit (die and plungers) was made from graphite with an inner diameter of 22 mm. The heating rate was 15 °C/min. up to 900 °C, then 10 °C/min. heating rate was applied until the desired temperature. The atmosphere was a controlled a flow of N_2 gas into the chamber in order to protect the graphite dies and plungers.

Usually 3 g powder were used in hot-pressing. The powders were first compressed to 25 MPa pressure in the cold state before commencing the heating. After 10 s the pressure was released and the heating started. The full pressure, up to 25 MPa, was applied when the desired temperature was reached. The operating temperature was maintained for 30 min., then the pressure was released and the sample was cooled down in the furnace.

3 RESULTS AND DISCUSSIONS

Similar Na-borosilicate glasses have been prepared by others[10] with the aim of producing monolithic glasses and heating and refluxing were usually employed during the preparation of the solutions. The aim of the present work was to prepare gel-derived powders with desired Na-borosilicate composition, not to prepare monolithic glasses. For this reason, attention was only paid to the preparation of a clear solution and after gelation, the gel was dried and calcined at 400 °C for 20 h. During drying and calcining the gel fragmented into small pieces or powders.

The nominal composition of the commercial 7740 Pyrex glass and the chemical analysis results of the gel and melt-derived glasses are given in Table 1. There is a loss of B_2O_3 from the gel and from the melted glass, but the loss is higher for the gel-derived glass. This could be attributed to the loss of some B_2O_3 precursor during the drying and heat-treatment of the gel. Also, during melting at 1600 °C, some volatilization of B_2O_3 is expected. Although there is a loss of B_2O_3 from the gel, the borosilicate gel-derived glass could be prepared with a reasonable level of B_2O_3. In fact, the B_2O_3 losses in the present work were less than those reported in other studies. In the sol–gel preparation of borosilicate system, with an expected composition of (wt%) 80.9 SiO_2–12.7 B_2O_3–3.6 Na_2O–2.2 Al_2O_3–0.6 K_2O, Dislich[10] obtained much higher losses of B_2O_3. He found that after heat-treatment at 650 °C the B_2O_3 content was 5.0 wt%. One difference from the present work was that Dislich employed heating and refluxing of the solution during processing.

Table 1. Chemical analysis of Na-borosilicate powders

	Composition (wt%)					
	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	CaO
Gel	85.0	8.7	1.7	4.6	—	—
Melt-derived	84.5	10.1	1.7	3.7	—	—
Commercial glass	80.0	13.7	2.3	4.0	0.02	0.01

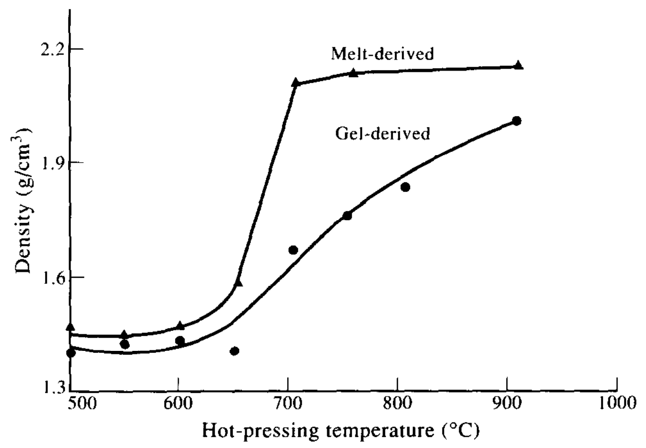

Fig. 1. Density vs hot-pressing temperature: heating rate, 15 °C/min.; holding time, 30 min.; pressure, 22 MPa; ● gel-derived powder; ▲ melt-derived powder.

The thermal behaviour of the gel-derived powders (DTA/TG traces) was reported in detail elsewhere[6,7] and will not be given in this paper again. The *Tg* (glass transition temperature) of the gel-derived glass powder was not easy to determine from the DTA trace.

The melt-derived glass particles were very fine and had an average particle size of 4.3 μm and the gel-derived powders had an average particle size of 8.4 μm. One possible reason for these differences could be the milling time. The gel-derived powders were ball-milled for 24 h, but the melt-derived powders were ball-milled for 96 h. Both powders were sieved to below 53 μm.

Models of densification under load based on a viscous flow mechanism have been developed and successfully applied to the densification of glasses and gels.[11] A simplification of the model developed by Mackenzie and Shuttleworth[12] was used by Murray *et al.*[13] to describe the hot-pressing densification process. The equation derived was:

$$dD/dt = 3P/4\eta(1 - D)$$

where $D = \rho/\rho_s$ (ρ is the measured density and ρ_s is the theoretical density) which may be integrated to

$$\ln(1 - D) = -3P/4\eta t + \ln(1 - D_i)$$

where D is the relative density and D_i is the initial relative density. The slope of the $\ln(1-D)$ vs t curve is used to calculate the viscosity for a given temperature.

The hot-pressing densification of the gel and melt-derived powders were investigated at a series of temperatures. The results are shown in Fig. 1. The rate of densification of the melt-derived glass powders appeared to be considerably faster than that of the gel-derived powders at all temperatures studied. The melt-derived powder also exhibited a much sharper increase in densification at 650–700 °C, than observed for the gel-derived powder. This was a somewhat suprising result since normally gel derived glass powder might be expected to sinter faster and easier at lower temperatures than melt-derived glass powder of a similar composition because of the high surface area of the gel-derived powder and the occurrence of residual hydroxyl in the dried gel, which would reduce its viscosity.

To investigate the origin of this difference in densification behaviour, an XRD study of the hot-pressed samples was carried out. Also, the viscosities of the gel and melt-derived powders were determined under isothermal hot-pressing conditions. Table 2 gives the results of the isothermal hot-pressing of both the gel and melt-derived powders at 625 and 675 °C. D is the relative density of the hot-pressed sample. Figure 2 shows the $\ln(1-D)$ vs t curves of the gel and melt-derived powders at 625 and 675 °C. Using the relationship of Murray *et al.*,[13] and the slope of the $\ln(1-D)$ vs t curves, the viscosity values for the given hot-pressing temperatures were calculated. The slope is equal to $3P/4\eta$, where P is pressure (N/m^2) and η is viscosity (Pa.s). Viscosity was calculated using the equation:

$$\eta = 0.75P/\text{slope}$$

The calculated viscosity values for the hot-pressed gel and melt-derived powders are given in Table 3.

Table 2. Isothermal hot-pressing results of gel and melt-derived glass powders

Time (min)	Ln(1/D)			
	Gel-derived powder		Melt-derived powder	
	625 °C	675 °C	625 °C	675 °C
15	—	—	—	−1.93
30	−1.2	−1.43	−1.39	−2.91
40	—	—	—	−3.31
45	—	−1.97	−1.56	—
60	−1.35	−2.41	−1.83	—
90	−1.47	−3.22	−2.20	—
120	−1.58	—	—	—

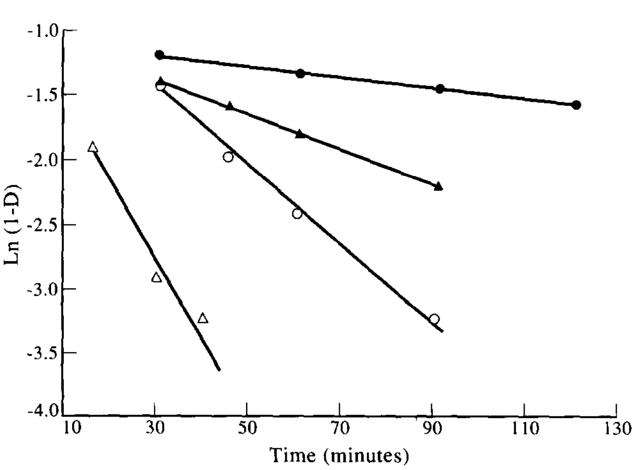

Fig. 2. $\ln(1-D)$ vs t curves of gel and melt-derived powders under isothermal hot-pressing. t, time; D, relative density. Δ-gel-derived powder at 625 °C, ▲ gel-derived powder at 675 °C, ○ melt-derived powder at 625 °C, ●-melt-derived powder at 675 °C.

The viscosity of the gel-derived powder was higher than that of the melt-derived powder at both temperatures. Viscosity values for commercial borosilicate glass (Pyrex) at temperatures of 625 and 675 °C were calculated from Fig. 3,[14] and these values were compared with the viscosity values of hot-pressed gel and melt-derived powders. Viscosities of the melt-derived powders were close to the values of the commercial Pyrex glass (Table 3).

The XRD results of the hot-pressed samples are shown in Fig. 4(a) and (b). There was no evidence of crystallization at 700 °C or below after 30 min. for the gel-derived samples. Only amorphous peaks were observed [Fig. 4(a)]. However, the sample hot-pressed at 750 °C exhibited some crystallization, and the sample hot-pressed at 800 °C showed extensive crystallization. Similar, but not identical, effects were observed for the melt-derived powders. After hot-pressing at 750 °C or below no crystallization peaks were observed, whereas at 800 °C extensive crystallization was observed, but somewhat less than in the gel-derived samples. The crystalline phase was cristobalite[15] in both powders at all temperatures. As an additional experiment, a compact of the melt-derived powders with an

Table 3. Viscosity values of gel and melt-derived glass powders.

	Viscosity (Pa.s)	
	625 °C	675 °C
Gel-derived powder	2.45×10^{11}	3.5×10^{10}
Melt-derived powder	7.77×10^{10}	1.69×10^{10}
Pyrex glass*	2.5×10^{10}	10^9

*Determined from Fig. 3.

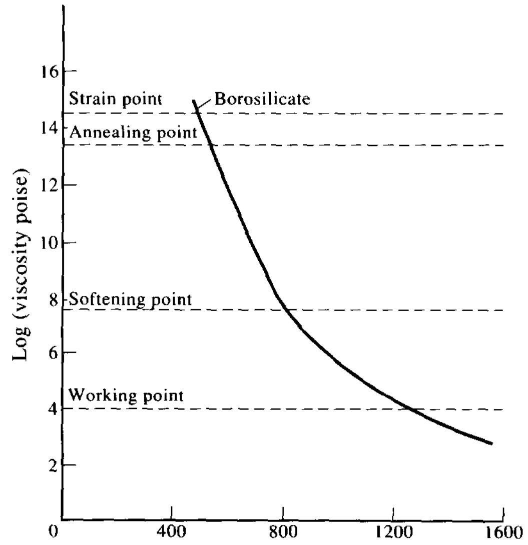

Fig. 3. Variation of viscosity with temperature for commercial borosilicate glass (Pyrex) (from Ref. 14).

organic binder was prepared by dry pressing, heat-treated at 500 °C for 30 min. to remove binder and then heat-treated at 800 °C for 30 min. Similar crystallization was observed.

These results indicate that crystallization occurred in both the gel and melt-derived powders during hot-pressing. Moreover, this crystallization probably inhibited the viscous sintering, particularly in the case of the gel-derived powders where the rate of crystallization was higher at 750 °C and 800 °C. The densification results could also be partly explained by the differences in chemical composition between the gel and melt-derived powders, leading to a difference in viscosities which was also shown by the isothermal hot-pressing results. Clearly both the greater viscosity of the gel-derived powders compared with the melt-derived powders and also the enhanced rate of crystallization of the gel-derived powders contribute to the lower densification rate of the gel-derived powder.

The hot-pressing results showed that the crystallization of the gel-derived powders was the main obstacle to achieving full density. This is because crystallization and viscous sintering are two competing processes during the densification of the gel and melt-derived powders.

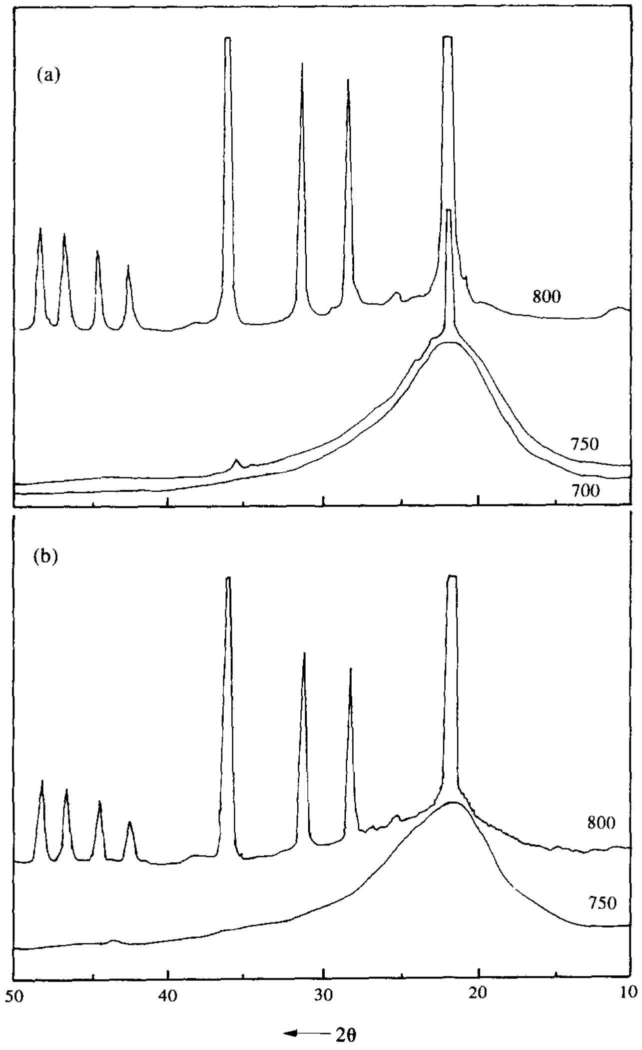

Fig. 4. XRD traces of hot-pressed gel and melt-derived powders: (a) gel-derived; (b) melt-derived powders.

4 CONCLUSIONS

Viscosity values of the melt-derived powders measured by the isothermal hot-pressing were closer to that of the commercial Pyrex glass but the viscosity values of the gel-derived powders at 625 °C and 675 °C were higher than those of the melt-derived and commercial Pyrex glasses. These differences in viscosities could be the result of the differences in chemical compositions of the gel and melt-derived powders. The gel-derived powders being the richest in SiO_2 content.

Crystallization of gel and melt-derived Na-borosilicate glass powders occurred during hot-pressing. The gel-derived powders crystallized at 750 °C after 30 min., but the melt-derived powders crystallized at 800 °C after the same heat-treatments. Cristobalite was the crystalline phase in both powders.

Crystallization of both the gel-derived and the melt-derived glass powders during hot-pressing inhibited the densification via viscous flow mechanism. This was especially effective in the gel-derived powders because the greater viscosity and the enhanced rate of crystallization of the gel-derived powders contributed to the lower densification rate. During densification of the glass powders via viscous flow, crystallization and viscous flow are two competing processes.

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