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Effect of particle size on the sintering of Li_2O–Al_2O_3–$4SiO_2$–borosilicate glass composites

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The effect of spodumene particle-size on the sintering of spodumene-borosilicate glass composites was investigated. The results can be explained by a particle-size dependence of the extent of reaction between spodumene and glass. For samples fabricated with fine spodumene particles (1.5–3 μm), a reactive liquid-phase sintering behaviour was observed. Smaller particle size resulted in a higher sintered density and coarser microstructure. For samples fabricated with coarse spodumene particles (3–7 μm), a non-reactive liquid-phase sintering behaviour was observed when a high-viscosity glass, a lower initial glass content, and a lower sintering temperature were used. A larger particle size resulted in a higher sintered density and coarser microstructure. If a low sintering temperature or a coarse (e.g., 7 μm) particle size were used, the dissolution of the glass into spodumene was reduced which resulted in an increased amount of glass crystallization.

1. Introduction

Several new systems that consist of a glass added to a crystalline ceramic have been recently developed [1–5] to replace conventional alumina as a substrate for high-performance large scale integrated (LSI) packaging [6]. To fulfill the high speed signal-propagation requirement, the substrate material should have a low dielectric constant, a thermal expansion coefficient near that of Si ($3.0 \times 10^{-6}\ K^{-1}$), and a low sintering temperature (< 1000 °C) to enable co-firing with low-resistance metals such as copper, silver, or gold. Vitreous silica and some borosilicate glasses have often been used as the glass phase because of their low dielectric constant (< 4). In addition borosilicate glasses, have especially, low softening points and thus enable sintering. The ceramic phase in these glass + ceramic composites acts mainly as a fillter that inhibits curling when the glass is soft. The ceramic phases which have the potential to meet substrate requirements are α-cordierite ($2MgO$–$2Al_2O_3$–$5SiO_2$), β-spodumene (Li_2O–Al_2O_3–$4SiO_2$), celsian (BaO–Al_2O_3–$2SiO_2$), mullite ($3Al_2O_3$–$2SiO_2$), alumina, and α-quartz [6]. The formation and properties of composites consisting of borosilicate glass added to α-cordierite [1–4], alumina [1,2,5], mullite [1], and α-quartz [2] have been reported. However, few investigations on the spodumene–borosilicate glass composites have been performed. It is known that particle size has a significant influence on the formation of a ceramic + glass composite. Therefore, the intention of this study is to investigate the effect of spodumene particle size on the sintering, crystallization of the glass additive, and microstructure of spodumene–borosilicate glass composites.

2. Experimental Procedure

2.1. Sample preparation

Three glasses based on B_2O_3–SiO_2 compositions were prepared before adding to the stoichiometric β-spodumene composition (Li_2O–Al_2O_3–$4SiO_2$). The compositions of the glasses, denoted by B, C, and D, are listed in Table I. The sequence of glass viscosity is B < C < D, according to the modifier (Na_2O and CaO) content. The glasses were prepared by mixing powders containing appropriate amounts of reagent-grade SiO_2, B_2O_3, Na_2CO_3, and $CaCO_3$, melting in a platinum crucible and then quenching into deionized water to form glass frits. The dried frits were crushed in an alumina-lined mortar grinder (Model RMO, F. Kurt Retsch GmbH & Co. KG, Germany) until the powder passed through 80 mesh. The crushed glass powders were then milled for about 20 h in alumina-lined mills containing alumina balls and ethanol until an average particle size of about 3 μm was obtained (measured with a particle-size analyser, Model MSE02SM, Malvern Instruments Ltd., Worcestershire, UK).

The β-spodumene ceramic powder was prepared by a standard ceramic procedure. Well-mixed powder

TABLE I Glass compositions studied

	Composition (wt %)			
Glass	B_2O_3	SiO_2	Na_2O	CaO
B	15	65	10	10
C	20	70	5	5
D	25	70	2.5	2.5

containing appropriate amounts of reagent-grade Li_2CO_3, Al_2O_3, and SiO_2 was calcined at 1300 °C for 10 h. Then, the powder was ground by hand and recalcined at 1350 °C for 4 h. The X-ray diffraction pattern of the resultant powder was characteristic of a pure β-spodumene phase. The powder was then milled for appropriate periods in alumina-lined mills containing alumina balls and ethanol until average particle sizes of 1.5, 3, and 7 μm were obtained.

Spodumene–glass composite powder mixtures were prepared by mixing the above β-spodumene and glass powders in ethanol for 4 h, using Teflon balls. The slurry was mixed with polyvinyl alcohol as a binder, dried, and screened (< 80 mesh). The green compacts were uniaxially pressed at 70 MPa in a 10 mm diameter steel die lubricated with a thin layer of stearic acid. The green densities were about 50% of theoretical densities. The green compacts were prefired at a heating rate of 2 °C K per min to 500 °C and held for 1 h. The samples were then sintered in air at 700–1000 °C for 2 h, at a heating rate of 10 °C per mim, and furnace cooled. The samples containing glass B, glass C and glass D are denoted as L × B, L × C and L × D, respectively, where × is the glass fraction (wt%).

2.2. Characterization

The densities of the sintered bodies were measured by the Archimedes method. The theoretical densities of the sintered bodies were calculated, using a mixing rule, using densities of 2.45 $g\,cm^{-3}$ for glass B, 2.41 $g\,cm^{-3}$ for glasses C and D, and 2.375 $g\,cm^{-3}$ for β-spodumene. Phase identification was conducted by X-ray diffraction (XRD) analysis using polished samples. Measurements were performed on a diffractometer (Model D5000, Siemens, Germany) with CuK_α radiation and a Ni filter. The operating power was 40 kV and the current was 15 mA. Continuous scanning was used with a scan speed of 2° per min and a sampling interval of 0.01° (2θ). The sintered bodies were polished, etched (1 wt % HF, 10–30 s, 25 °C), and then coated with a thin film of gold for scanning electron microscopy (SEM) observations.

3. Results and discussion

3.1. Sintering

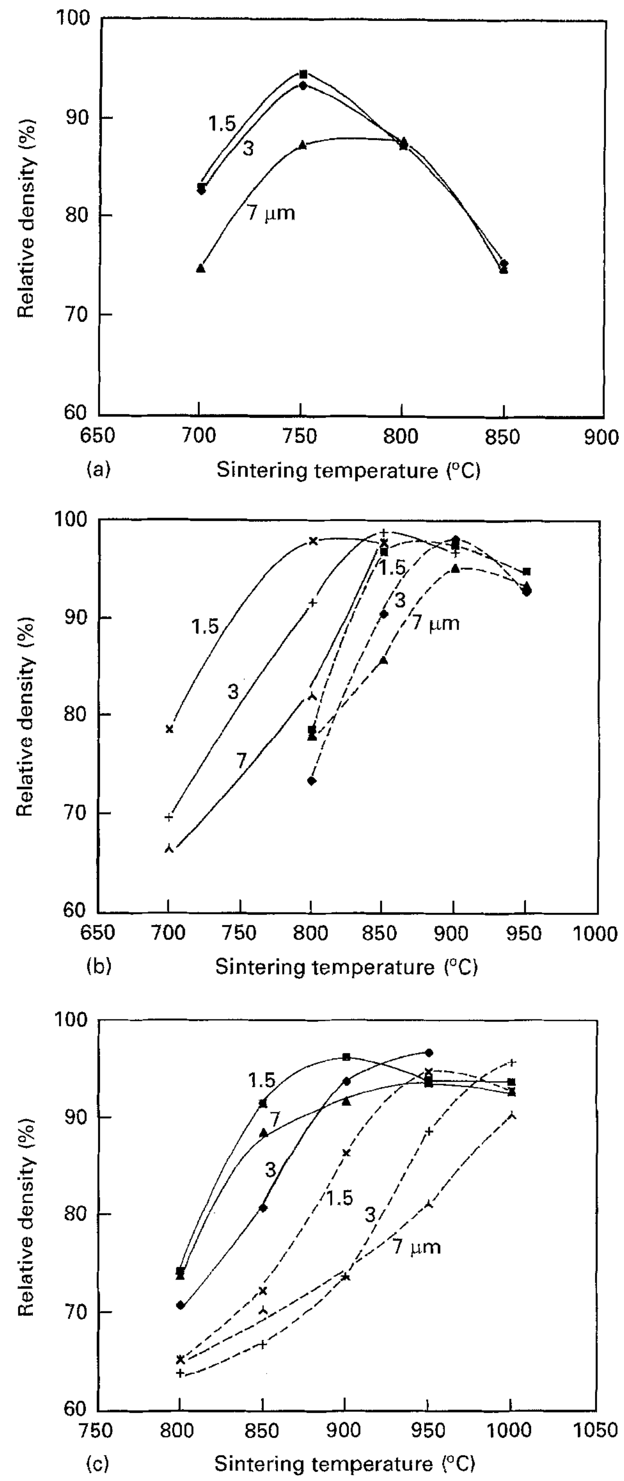

Figure 1 Relative density of composites containing (a) glass B (—) in sample L50B (b) glass C in samples; (—) L60C and (–––) L50C and (c) glass D, in samples; (—) L60D and (---) L50D.

Fig. 1(a–c) shows the variation of relative density of the sintered samples with sintering temperature. Relative densities higher than 90% could be obtained for appropriate sintering temperatures. It can be seen that several curves show density reduction at higher sintering temperatures. This trend becomes less significant as a high-viscosity glass (i.e., glasses C and D) is used. It has been shown that this density reduction can be attributed to coalescence of the neighbouring closed pores and/or closed pore expansion as a result of pressure developed by the expansion of the gases trapped in the pores [7]. It was found that in this higher temperature range in which density reduction occurred, no clear relationship between density and particle size could be obtained. However, in the lower temperature range in which density reduction did not appear, the effect of the spodumene particle-size can be divided into two categories:

i) 1.5–3 μm: for all compositions, the density for the 1.5 μm sample is higher than that for the 3 μm sample. Namely, fine spodumene powder increases the sintered density.

ii) 3–7 μm: for L50B and L60C, the density for a 3 μm sample is higher than that for a 7 μm sample. This is also true for L50C, L50D, and the L60D samples sintered at higher temperatures. However, for L50C, L50D, and L60D samples sintered at lower temperatures the density for the 3 μm sample is lower than that for the 7 μm sample. In other words, coarse spodumene powder tended to improve sintering as a high-viscosity glass (i.e., glass C and, especially, glass D), lower initial glass content (cf., L50C and L60C), and a lower sintering temperature were used.

Since a liquid phase would form (from the glass phase) during sintering of the glass + ceramic composites, either liquid-phase sintering or a non-reactive liquid-phase sintering mechanism should be considered. It is known that a liquid-phase sintering mechanism can be divided into rearrangement, solution–precipitation, and coalescence processes [8], in which dissolution of the solid particles into the liquid phase is important. Moreover, densification can be improved by using a smaller particle-size. For samples fabricated with fine spodumene particles (1.5–3 μm, category i), the higher specific area increased the degree of reaction between spodumene and glass, thus a liquid-phase sintering behaviour was observed. Therefore, the sintered density increased with the decreasing spodumene particle-size. A non-reactive liquid phase-sintering mechanism for the sintering of borosilicate glass + alumina composites has been proposed by Ewsuk and Harrison [9]. It is assumed that the liquid phase does not react with the ceramic particles to create additional liquid to aid densification. Glass redistribution, grain rearrangement, and viscous flow are considered as the three stages. They found that higher composite densities are achieved more quickly when a coarse rather than a fine particle size alumina filler was used. For samples fabricated with coarse spodumene particles (3–7 μm, category ii) in this study, the lower specific area decreased the degree of reaction between spodumene and glass and thus a non-reactive liquid-phase sintering mechanism is also possible. This is particularly true as the degree of reaction between spodumene and glass can be decreased (i.e., when high-viscosity glass, a lower initial glass content, and a lower sintering temperature were used).

3.2. Microstructure

Fig. 2 shows a typical micrograph to illustrate the pore morphology observed in the present study. Pores with a round shape were seen. Fig. 3(a–c) shows the enlarged microstructure for the L50C composition sintered at 900 °C to illustrate the typical morphology of spodumene particles. It can be seen that the spodumene particles have an angular shape with smooth, straight sides. This indicates that a solution–precipitation process occurred. Particles of α-quartz can also be seen in the 7 μm sample. Moreover, it can be seen that the average size of spodumene particles in the 7 μm sample is larger than that in the 3 μm-sample. However, the average size in the 3 μm sample is smaller than that in the 1.5 μm sample. Since fine spodumene powder would result in a higher degree of reaction between spodumene and glass, an accelerated coarsening rate for spodumene particles would be expected. Therefore, the largest final particle size of the 7 μm sample should be caused by the largest

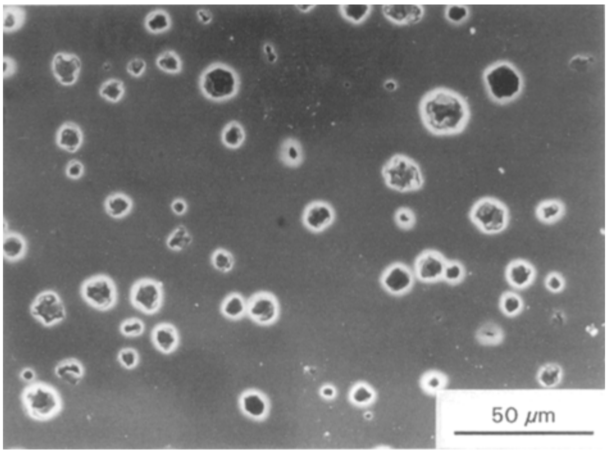

Figure 2 Microstructure of the L60D sample made with 1.5 μm spodumene particle-size to illustrate the typical pore morphology. The sintering temperature was 900 °C.

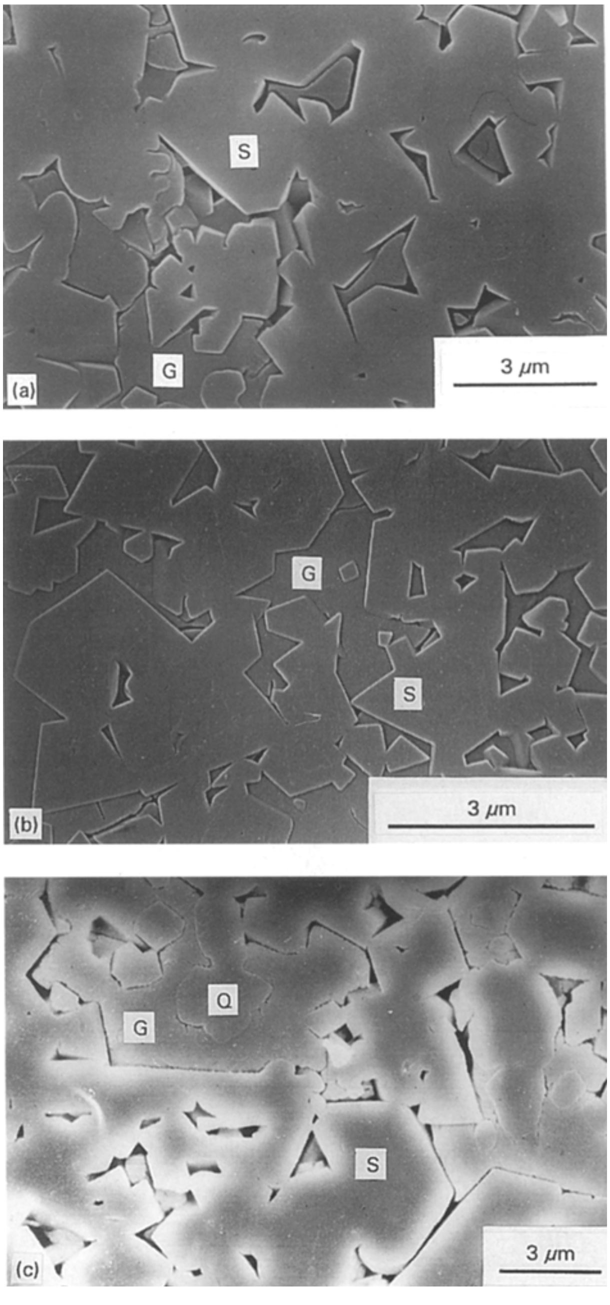

Figure 3 Microstructures of the L50D samples made with an (a) 1.5, (b) 3, and (c) 7 μm spodumene particle-size and sintered at 900 °C. (S: β-spodumene, G: glass, Q: α-quartz)

initial particle size and/or the smallest degree of reaction between spodumene and glass. On the other hand, the smallest initial particle-size of the 1.5 μm sample resulted in more significant coarsening of spodumene particles than that in the 3 μm-sample, thus a larger final size for the 1.5 μm sample than that for the 3 μm sample was obtained. The other compositions also showed a similar trend.

3.3. X-ray diffraction

It was found that the sintered samples showed crystallization of glass: anorthite ($CaO–Al_2O_3–2SiO_2$) and α-quartz for L50B, α-quartz for L50C and L60C, and α-quartz and cristobalite for L50D and L60D. The formation of anorthite in composition L50B is probably caused by the dissolution of Al^{3+} ions from spodumene into glass B, which contained a higher calcium concentration. It was found for all compositions that the total crystallized amount decreased with increasing sintering temperature. The typical XRD patterns are shown in Fig. 4 for composition L50C sintered at 800–950 °C. It can also be seen that, although the crystallized amount decreased with increasing sintering temperature, the broad scattering intensity associated with a glass phase was not obviously increased and was lower than that for the unfired sample. This indicates that there were remarkable reactions between glass and spodumene, i.e., the glass can partially dissolve into spodumene. As the sintering temperature was increased, the increased degree of glass dissolution resulted in a decreased amount of crystallization. The typical effect of particle size on the glass crystallization is shown in Fig. 5 for the L50C composition. It can be seen that the 7 μm sample showed higher crystallized concentrations than did the 1.5 and 3 μm samples which agrees with the SEM observations (Fig. 3c). Due to the reduced total contact area between spodumene and glass particles in the 7 μm sample, the amount of glass dissolution into spodumene decreased and thus the amount of residual glass increased, resulting in a higher crystallized amount. Other compositions also showed a similar trend.

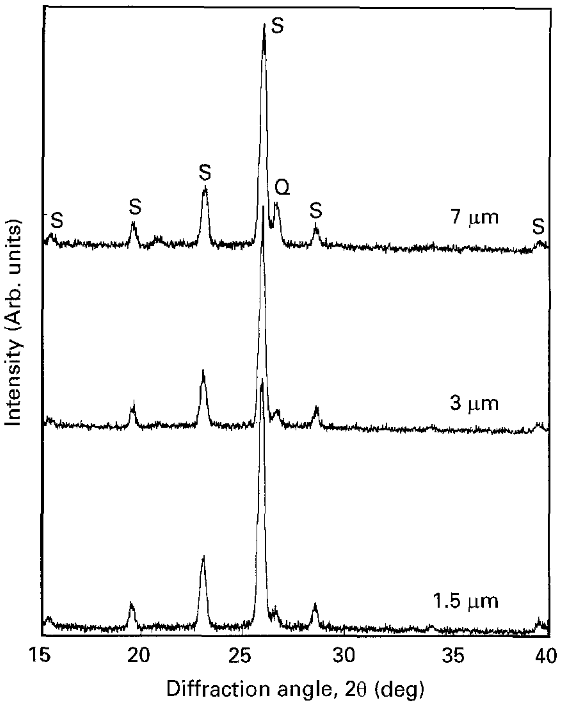

Figure 5 Effect of spodumene particle-size on the XRD pattern of the L50C sample sintered at 900 °C. (S: β-spodumene, Q: α-quartz).

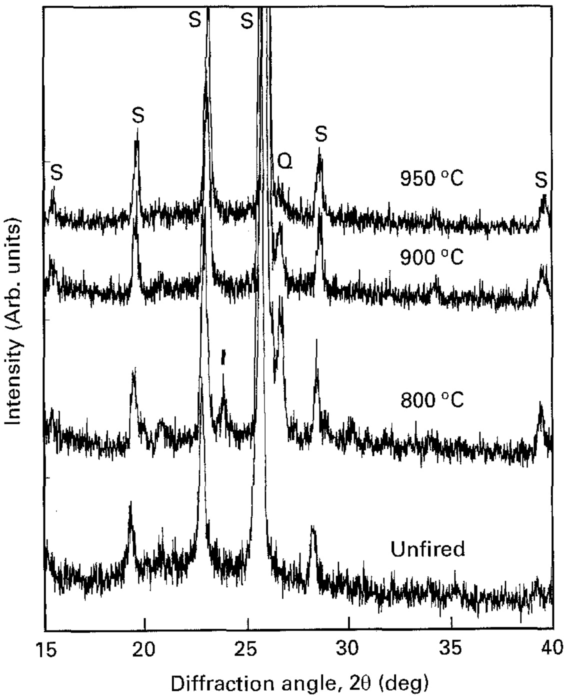

Figure 4 Effect of sintering temperature on the XRD pattern of the L50C sample. The starting spodumene particle-size is 3 μm. (S: β-spodumene, Q: α-quartz, 1: unknown).

4. Conclusions

The effect of spodumene particle-size on the sintering, glass crystallization, and microstructure of spoumene–borosilicate glass composites were investigated. Densities > 90% could be obtained for samples sintered at appropriate temperatures. For samples fabricated with fine spodumene particles (1.5–3 μm), a reactive liquid phase sintering behaviour was observed. A smaller particle size resulted in higher sintered density and a coarse micorstructure. For samples fabricated with coarse spodumene particles (3–7 μm), a non-reactive liquid-phase sintering behaviour was observed as a high-viscosity glass, a lower initial glass content, and a lower sintering temperature were used. Larger particle sizes resulted in a higher sintered density and coarser microstructure. The above results can be explained by the particle-size dependence of the extent of reaction between spodumene and glass. Moreover, if a low sintering temperature or a coarse (e.g., 7 μm) particle size were used, the dissolution of the glass into the spodumene was reduced which resulted in an increased amount of glass crystallization.

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