

# Sintering of $\beta$ .q.<sub>ss.</sub> and Gahnite Glass-ceramic/ Silicon Carbide Composites

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## Abstract

The sintering of  $\beta$ .quartz solid solution,  $\beta$ .q.<sub>ss.</sub>, and gahnite glass-ceramic/particulate SiC composites has been studied by two different sintering procedures. In one procedure, the composites were fired above the melting point of the crystalline phase, identified by DTA, at a very high heating rate ( $800^\circ\text{C min}^{-1}$ ) in air, nitrogen and argon atmospheres, for 1–6 min. It was found that the reduction of ZnO constituent of the glass by SiC particles gives rise to Zn, CO, and SiO gaseous products preventing complete densification of composites. In the other procedure, sintering was done at about crystallization peak temperature of the glass phase, employing a low heating rate ( $40^\circ\text{C min}^{-1}$ ) in air for 60 min. In this case, the circumferential tensile stress in the glass-ceramic matrix phase, caused by the presence of incompressible SiC particles, retards the densification of the composites. The maximum amount of SiC particles yielding a reasonably dense composite was found to be 9 vol.%. © 1999 Published by Elsevier Science Ltd. All rights reserved

**Keywords:** glass ceramics, composites, sintering, SiC, ZnAl<sub>2</sub>O<sub>4</sub>.

## 1 Introduction

Owing to their favorable properties, i.e. low density, low cost and tailor-made thermal and mechanical properties, the glass-ceramics have been considered as a category of important engineering materials. It seems that by using glass-ceramics as the matrix phase and high strength particles as the reinforcement phase in composites, superior mechanical properties can be obtained.

However, as the preparation of the glass-ceramic matrix composites is carried out by the powder route, the parent glass composition has to have special properties such as good wettability, low viscosity and high surface energy<sup>1</sup> at the sintering temperature.

It is known that besides the above-mentioned parameters, oxidation of SiC particles and interaction of ingredients play crucial roles in complete densification of SiC-glass composites.<sup>2–5</sup> These reactions release gases and give rise to porosity and bloating in the fired composites.

The aim of the present investigation is to study the sinterability of  $\beta$ .quartz solid solution,  $\beta$ .q.<sub>ss.</sub>, glass-ceramic/SiC and gahnite, ZnAl<sub>2</sub>O<sub>4</sub>, glass-ceramic/SiC particulate composites.

It is well known that in ZnO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system by variation of nucleants and heat treatment procedure it is possible to make various glass-ceramics with thermal expansion coefficients varying in a wide range from negative to about  $70 \times 10^{-7} \text{ K}^{-1}$ . Monophase  $\beta$ .q.<sub>ss.</sub> and gahnite glass-ceramics which are both located in the above-mentioned system may provide glass-ceramic matrix phases with thermal expansion coefficients lower and higher than SiC particles, respectively. In this way it would be possible to investigate the effect of thermal expansion coefficient differences in matrix phases upon the mechanical properties of the composite material.

## 2 Experimental Procedure

The chemical composition of the glasses the sinterability of which has been discussed previously<sup>6</sup> are displayed in Table 1. Glasses were prepared by fusing reagent-grade chemicals in a platinum crucible. The glasses were melted and maintained for 2 h at  $1480^\circ\text{C}$  in an electric furnace. The molten glasses were then quenched in cold distilled water.

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**Table 1.** The chemical composition of the glasses  $\beta$ .Q and G

Glass	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZnO	ZrO <sub>2</sub>	TiO <sub>2</sub>	Li <sub>2</sub> O	As <sub>2</sub> O <sub>3</sub>
$\beta$ .Q	45.57	22.78	22.78	6.37	—	2.00	0.49
G	46.50	23.25	23.25	—	6.50	—	0.50

The particle size measurements of the powdered glasses which were carried out by a laser particle size analyser (Fritsch, analysete 22) shows a mean particle size of about 1.5  $\mu$ m. The crystallization and melting point temperatures of the crystalline phase were determined by simultaneous thermal analysis, STA (Polymer Laboratories, model 1640) at a rate of 10 °C min<sup>-1</sup>. The composite powder mixture were prepared by dispersing 47 vol% glass powder and 53 vol% of SiC Powder (400 mesh, Jean Wirtz, Germany) in acetone by hand mixing and ultrasonic vibration for 2 min. Drying was carried out by simultaneous mixing and heating of suspension. The dried, homogeneous powder mixture was pressed using laboratory uniaxial hydraulic press into 57×17×4 mm rectangular bars at initial and final pressures of 10 and 40 MPa, respectively. Carboxy methyl cellulose (0.45 wt%) was used as a binder.

Sintering was carried out in a electric tube furnace, under two different programmes. In the first program, sintering was carried out at the onset of DTA crystallization temperatures, where only one crystalline phase could be crystallized, at a heating rate of 40 °C min<sup>-1</sup>. The sintering atmosphere was air and soaking time was 60 min. In the second program, sintering was done at 1250 °C which is higher than the DTA endothermic peak temperature (which can be attributed to the solubility of gahnite into the glass phase) at a very high heating rate (800 °C min<sup>-1</sup>) for three different soaking times, i.e. 1, 3 and 6 min, in three atmospheres, nitrogen, argon and air at a pressure of 0.4 bar.

The density of sintered composites were determined by Archimedes method. The wettability of SiC powder by glass phase was determined by measuring wetting angles ( $\theta$ ) on planer, SiC polycrystalline substrates at 1250 °C by sessile drop method.<sup>7</sup>

### 3 Results and Discussion

The measured physical properties of the two glasses and their composites sintered according to the first program are summarized in Table 2. The low relative density of these glasses and their composites indicates a low sinterability of the glasses, probably due to their high viscosity.

In adopting the second firing program it was assumed that while the rapid increase of firing temperature beyond the melting point of the crystalline phase may prevent its crystallization, owing to kinetic considerations, at the same time the considerable drop in viscosity may accelerate the sintering process. According to Tables 3 and 4, although the wetting angles of the two glasses are in the limited wetting range,<sup>8</sup> i.e. 90° >  $\theta$  > 10°, and the sintering temperature is high enough for occurrence of grain rearrangement and viscous flow, only a negligible densification improvement can be seen in composites by utilizing the second firing program. It was noted that the shrinkage measurement of the glasses was not possible due to viscous deformation of the samples during rapid increasing of temperature. Moreover, it can be seen from Tables 3 and 4 that, besides crystallization of unwanted minor crystalline phases, about 3% weight loss occurred during the sintering of composites. It appears that this weight loss is independent of the sintering atmosphere, but increases with the soaking time.

A white-yellowish powder was precipitated on the surface of the composite samples after sintering

**Table 2.** Physical properties of glasses  $\beta$ .Q and G and their composites fired according to the first program

	T <sub>o</sub> <sup>*a</sup> (°C)	T <sub>c</sub> <sup>*b</sup> (°C)	Firing shrinkage (%)	Relative density	Weight loss (%)
$\beta$ .Q	775	830	4.10	0.61	—
G	750	837	1.00	—	—
$\beta$ .Q/SiC	770	873	2.01	0.59	—
G/SiC	748	828	0.30	—	—

<sup>a</sup>T<sub>o</sub><sup>\*</sup>, onset of crystallization peak temperature.

<sup>b</sup>T<sub>c</sub><sup>\*</sup>, crystallization peak temperature.

**Table 3.** Physical properties of  $\beta$ .Q/SiC composites fired according to the second program

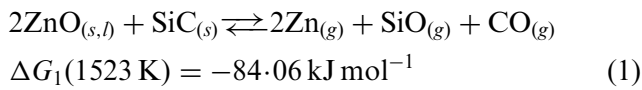
Firing atmospheres	Air			Nitrogen			Argon		
Soaking time (min)	1	3	6	1	3	6	1	3	6
Linear firing shrinkage (%)	5.20	5.33	5.30	5.31	5.33	5.33	5.30	5.26	5.28
Relative density	0.69	0.69	0.68	0.69	0.68	0.67	0.69	0.68	0.68
Weight loss (%)	2.20	2.55	2.67	2.90	3.10	3.46	3.20	3.24	3.40
DTA endothermic peak temperature	1220 °C								
Wetting angle ( $\theta$ )	75–80								
Precipitated crystalline phase	$\beta$ .q <sub>ss</sub> and gahnite (minor phase)								

**Table 4.** Physical properties of G/SiC composites fired according to the second program

Firing atmospheres	Air			Nitrogen			Argon		
Soaking time (min)	1	3	6	1	3	6	1	3	6
Linear firing shrinkage (%)	5.18	5.23	5.23	5.20	5.21	5.23	5.17	5.20	5.24
Relative density	0.68	0.69	0.68	0.69	0.69	0.68	0.69	0.68	0.68
Weight loss (%)	3.01	3.11	3.14	3.11	3.11	3.13	2.99	3.13	3.17
DTA endothermic peak temperature	1230 °C								
Wetting angle ( $\theta$ )	77–81								
Precipitated crystalline phase	gahnite and cristobalite (minor phase)								

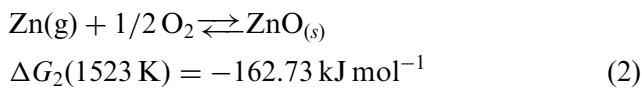
procedure. X-ray diffraction analysis of the powder indicates the presence of zinc oxide.

It seems that the following reactions can occur thermodynamically at the soaking temperatures and may be responsible for the above-mentioned phenomenon.



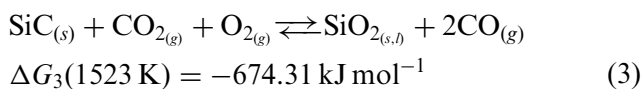
$$\text{and } k_1(1523 \text{ K}) = 10^8$$

In the presence of oxygen the oxidation of gaseous Zn takes place by the following reaction:



$$\text{and } k_2(1523 \text{ K}) = 4.64 \times 10^6$$

Another possible gas-forming reaction is



$$\text{and } k_3(1523 \text{ K}) = 3.04 \times 10^{23}$$

where  $\Delta G$  and  $k$  values are the calculated standard free energy and equilibrium constants of reactions using data from Barin and Knacke.<sup>9</sup> But it appears that the glass phase surrounding the SiC particles inhibits the occurrence of reaction (3). This is proved by the nearly constant weight loss under different sintering atmospheres. Thus the release of gaseous Zn along with  $\text{SiO}_{(g)}$  and  $\text{CO}_{(g)}$  is mainly responsible for the incomplete densification of composites at high temperatures.

According to the above results, it can be concluded that sintering of zinc aluminosilicate glasses–SiC composites using the second firing program is not an appropriate approach for obtaining a completely densified body with desired crystalline phases. Therefore, it is preferable to choose appropriate glass compositions which are sinterable at about their DTA crystal-

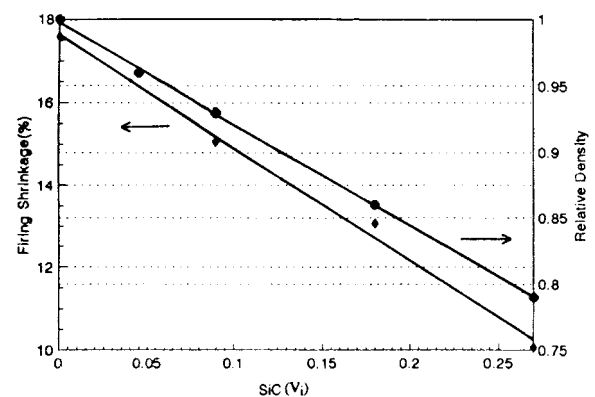
lization peak temperatures, yielding mono-crystal glass-ceramics.

Accordingly, the glass compositions of  $\beta$ .QL17.5 and GL17.5 which had been discussed previously,<sup>6,10</sup> were adopted. Table 5 shows the chemical composition of the glasses. According to our experimental results,<sup>6</sup> the thermodynamic driving force of crystallization decrease and sinterability of the glasses improve by addition of PbO to the glasses. In the case of  $\beta$ .q-ss- glass-ceramic, increase of activation energy of crystallization is another positive factor influencing the sintering of the glass. The improvement of sintering by addition of PbO shows itself as a shift in onset of crystallization peak to higher temperature, increase of dilatometric softening point-crystallization peak interval temperatures and decrease of crystallization peak intensity in the DTA results of the glasses.

Figures 1 and 2 depict the linear firing shrinkage and relative density of these  $\beta$ .q-ss and gahnite

**Table 5.** Chemical composition (wt%) of glasses

Glass	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZnO	PbO	ZrO <sub>2</sub>	TiO <sub>2</sub>	Li <sub>2</sub> O	As <sub>2</sub> O <sub>3</sub>
$\beta$ .QL17.5	45.57	22.78	5.28	17.5	6.37	—	2.00	0.49
GL17.5	38.36	19.18	19.18	17.5	—	5.36	—	0.41



**Fig. 1.** Linear firing shrinkage and relative density of  $\beta$ .QL17.5 glass-ceramic/SiC composites versus volume fraction of SiC,  $V_i$ , fired at 820 °C for 60 min.

glass-ceramic/SiC composites as a function of volume fraction of SiC particles, respectively. The firing temperatures of  $\beta$ .q.ss. glass-ceramic/SiC and gahnite glass-ceramic/SiC composites were respectively 820 and 900°C, and the firing time was 60 min. It can be seen that both the relative density and the linear shrinkage of the fired samples are gradually decreased by increasing the amount of SiC,  $V_i$ , where  $V_i$  is the calculated volume fraction of SiC for the fully dense composite. This behaviour can be explained by the Scherer models,<sup>11</sup> according to which, rigid and incompressible inclusions retard the densification of bodies by creating a circumferential tensile stress in the matrix phase. In Figs 3 and 4 the experimental linear shrinkage of these composites and the linear shrinkage predicted by the rule of mixtures<sup>11</sup> have been compared, as a function of sintering time for  $V_i = 0.09$  and  $V_i = 0.27$ .

It can be seen from Figs 3 and 4 that the deviation from the linear shrinkage predicted by the rule of mixtures increases along with an increase in the amount of SiC particles. This deviation is also observed in Figs 5 and 6 which indicates the experimental results for the linear strain rate of the

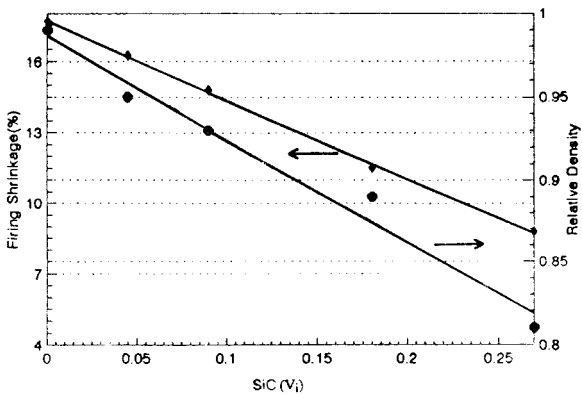


Fig. 2. Linear firing shrinkage and relative density of gahnite glass-ceramic/SiC composites versus volume fraction of SiC,  $V_i$  fired at 900°C for 60 min.

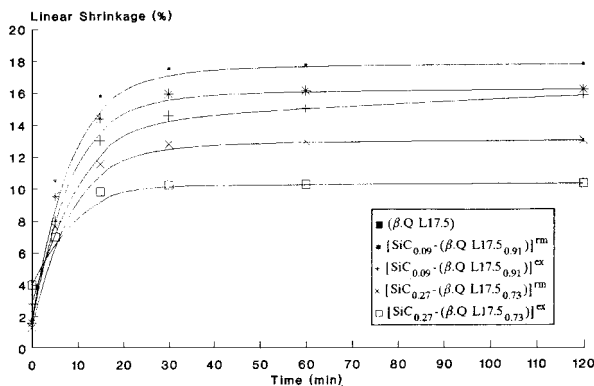


Fig. 3. Measured and predicted linear shrinkage of glass  $\beta$ .QL17.5 and their composites versus sintering time: rm, rule of mixtures prediction; ex, experimentally measured.

composites normalized by the strain rate from the rule of mixtures,  $\frac{\epsilon_c^0}{\epsilon_c^0 \rho_m}$ , versus instantaneous relative density of the glass matrix,  $\rho_m$ , for the two volume fractions.  $\rho_m$  was calculated by the following equation:

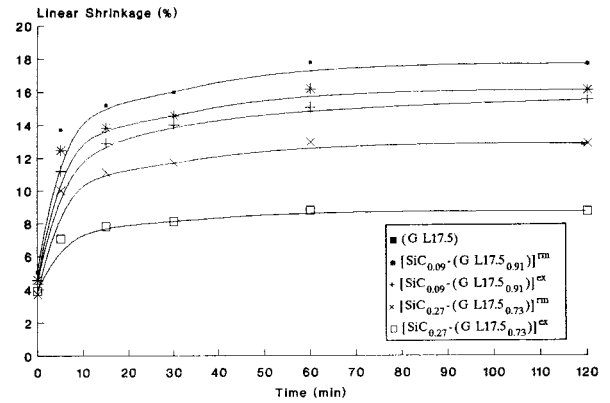


Fig. 4. Measured and predicted linear shrinkage of glass GL17.5 and their composites versus sintering time: rm, rule of mixtures prediction; ex, experimentally measured.

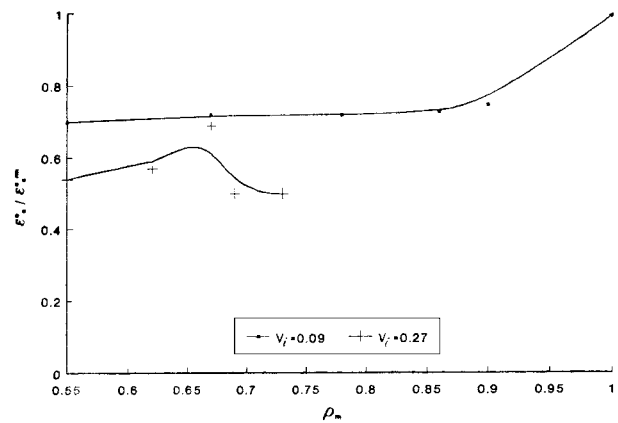


Fig. 5. Comparison of the experimental results for the linear strain rate of the  $\beta$ QL17.5 glass-ceramic/SiC composites normalized by the linear strain rate from the rule of mixtures,  $\frac{\epsilon_c^0}{\epsilon_c^0 \rho_m}$  versus instantaneous relative density of the matrix,  $\rho_m$ , for indicated volume fractions of SiC,  $V_i$ .

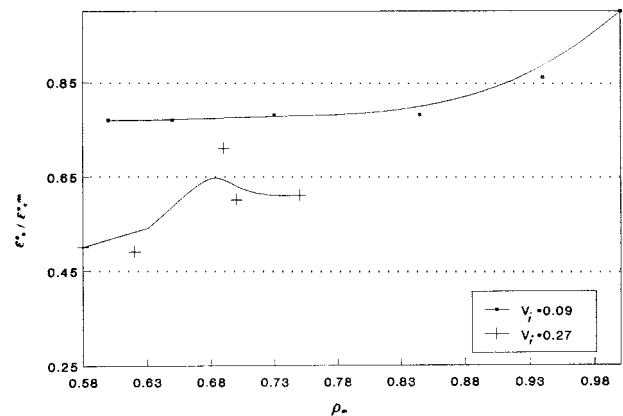


Fig. 6. Comparison of the experimental results for the linear strain rate of the gahnite glass-ceramic/SiC composites normalized by the linear strain rate from the rule of mixtures,  $\frac{\epsilon_c^0}{\epsilon_c^0 \rho_m}$  versus instantaneous relative density of the matrix,  $\rho_m$ , for indicated volume fractions of SiC,  $V_i$ .

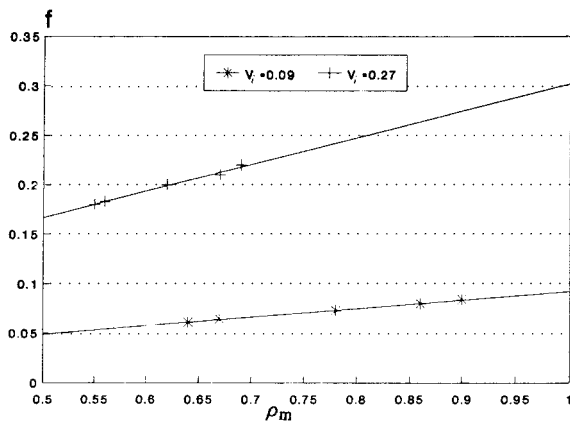


Fig. 7. Instantaneous volume fractions of SiC particles,  $f$ , versus instantaneous relative density of the matrix,  $\rho_m$ , for indicated volume fractions of SiC particles,  $V_i$ .

$$\rho_m = \frac{(m_c - m_i)}{(V_c - V)}$$

where  $m_c$  and  $m_i$  are the mass of composite sample and silicon carbide particles and  $V_c$  and  $V$  are the instantaneous volumes of composite and silicon carbide particles, respectively. Obviously, with increasing relative density of glass phase, the instantaneous volume fraction of SiC particle,  $f$ , would increase (Fig. 7). This may cause contact of SiC particles at a certain  $f$  which according to the Percolation theory<sup>12</sup> for spherical particles occurs at  $f \approx 0.16$ . The decrease in  $\frac{\epsilon_c^0}{\epsilon_{cm}^0}$  ratio, for composites with SiC amount of  $V_i = 0.27$  beyond  $\rho_m = 0.7$ , i.e. according to Fig. 7 at  $f \approx 0.22$ , as shown in Figs 5 and 6, can be attributed to the aforementioned phenomenon of particle contacts.

For the composite containing 9 vol% SiC this decrease is not observed, which indicates that in this composite the particles never come to close contact before the occurrence of complete densification.

An increase of  $\frac{\epsilon_c^0}{\epsilon_{cm}^0}$  ratio above  $\sim \rho_m = 0.9$  in this specimens can be attributed to the increase of capillary tension at this matrix density. Our results indicate that using SiC particles in any exceeding 9 vol% inhibits the complete densification of composites by the same mechanisms discussed above.

Therefore it can be concluded that the maximum allowable amount of SiC particles which can be used as a second phase in obtaining a nearly dense composite of  $\beta$ .q.<sub>ss</sub> and gahnite glass-ceramics/SiC is about 9 vol%.

## 4 Conclusions

1. The reaction of SiC particles with ZnO constituent of the glass phase was the main obstacle to complete densification of composites, when employing the high temperature sintering route.
2. Densification of the glass-ceramic/SiC composites was not influenced by firing atmosphere employed in the high temperature sintering route.
3. The low temperature sintering route was feasible only by using lead bearing glass compositions.
4. At the low temperature sintering route complete densification of the composites is delayed by the Circumferential tensile stress in the glass phase caused by the presence of SiC particles while at higher volume fractions the mutual contact of the particles is an additional hindering factor.
5. The maximum SiC amount which could be used to obtain complete densification was about 9 vol%.

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