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Effect of compaction on the sintering of borosilicate glass/alumina composites

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Abstract

The effect of initial compaction on the sintering of borosilicate glass matrix composites reinforced with 25 vol.% alumina (Al_2O_3) particles has been studied using powder compacts that were uniaxially pressed at 74, 200 and 370 MPa. The sintering behaviour of the samples heated in the temperature range 850–1150 °C was investigated by density measurement, axial and radial shrinkage measurement and microstructural observation. The density of the sintered composites increased continuously with temperature for compacts pressed at 74 MPa, while for compacts pressed at 200 and 370 MPa it reached the maximum value at 1050 °C and at higher temperatures it decreased slightly due to swelling. The results showed anisotropic shrinkage behaviour for all the samples, which exhibited an axial shrinkage higher than the radial shrinkage, and the anisotropic character increased with the initial compaction pressure.

Keywords: Al_2O_3; Borosilicate glass; Compaction; Composites; Glasses; Sintering

1. Introduction

Powder technology is the processing route most commonly used to fabricate ceramic products. Also, most composite materials with glass matrix containing a dispersion reinforcement are obtained by the powder sintering route.[1–3] Mechanical compaction of dry or semidry powders in a die is one of the most widely used methods for the consolidation of ceramic powders.[4,5] The compaction process poses complex problems because it involves the reduction of large voids by sliding and rearrangement of particles and the reduction of small voids either by fracture of the particles or by plastic deformation in the case of relatively soft ceramics.[5] Theoretical analysis of the process is very difficult and several expressions have been developed to describe it, which are often criticised as being merely curve fitting.[3,5]

Usually, in die compaction, the applied pressure is not transmitted uniformly to the powder because of friction between the particles and between the particles and the die wall, leading to stress gradients and hence density gradients. The presence of heterogeneities in the structure of a green compact can have significant effects on the sintering behaviour and consequently on the final properties of the ceramic products.[1–5]

Glass matrices exhibit a much higher sinterability compared to crystalline matrices due to the ability of the viscous glass phase to relax the shear stresses developed as a consequence of differential sintering rates.[6,7] The sintering of glass has been widely investigated providing results about densification and flow during sintering.[1,6,8] However, the sintering of glass matrix containing rigid inclusions (e.g. particles, whiskers or platelets) has not been much studied.[1,7,9] During sintering of glass powder compacts containing rigid inclusions not only the compacts usually shrink as the material densifies by viscous flow,[7,10] but also the shape of the compacts may vary as a consequence of anisotropic or non-uniform sintering shrinkage.[7]

The main objective of the present work was to study the effect of the initial compaction pressure on the sintering of borosilicate glass matrix composites containing 25 vol.% Al_2O_3 inclusions. The sintering of the composites was investigated by density measurement and by

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axial and radial shrinkage measurement. The microstructure was analysed by scanning electron microscopy (SEM) and the crystalline phases present in the sintered composites were identified by X-ray diffraction (XRD).

2. Experimental

An alumina powder (SG16 from Alcoa, UK) with a particle size range of 0.3–0.6 μm and a commercially available amorphous borosilicate glass powder (code 658909 from Corning, France) were used. The as-received glass powder had a particle size range of 80–160 μm, which was reduced by agate ball milling until a finer powder with a mean particle size ~10 μm was achieved. The composition (wt.%) of the glass was as follows: 79.8SiO_2, 12.3B_2O_3, 2.3Al_2O_3, 4.8Na_2O and 0.8K_2O.

A powder mixture, containing the required amounts of glass and alumina, was uniaxially pressed in a hardened steel die at 74, 200 and 370 MPa to make cylindrical compacts with 13 mm diameter and about 5 mm height, but it was very difficult to handle these compacts as they crumbled very easily. Therefore, for the preparation of the powder mixture compacts, the glass and alumina powders were mixed with 5 wt.% polyethylene glycol and diluted with ethanol. The suspension was deagglomerated in an ultrasonic bath and this was followed by mixing using a mixer/mill. The powder mixture was dried, ground in an agate mortar and then uniaxially pressed at the selected pressure.

The heating profile for binder burnout was determined by thermogravimetric analysis at a heating rate of 10 °C/min in air using a Rigaku thermobalance, model 8504B1. As the total weight loss occurred below 400 °C, before the sintering experiments all the samples were heated at 1 °C min^{-1} from room temperature up to 400 °C and then held for 60 min at this temperature in order to ensure complete binder burnout. The samples were sintered in an electric furnace at a heating rate of 5 °C min^{-1} from room temperature up to 850–1150 °C, held during 30 min at the selected temperature, and then the furnace was switched off and the samples were cooled in the furnace.

The mass, diameter and length of the samples were measured before and after the sintering process. Geometrical densities were determined for the powder compacts in the green state, after binder burnout and after sintering. If the geometrical relative density of the sintered composite samples was higher than 95% the density was also measured using the Archimedes' principle. The open porosity of the sintered samples was determined using an immersion process, where the open pores were filled with boiling water for 30 min. The theoretical density of the composites was calculated by the rule of mixtures taking into account the glass and alumina densities, which were respectively, 2.23 and 3.91 g cm^{-3}. From the previous data, the relative density, the total and closed porosities of each sintered composite sample were calculated.

The linear shrinkage exhibited by the compacts during the sintering process was calculated in terms of the radial shrinkage, $\Delta r/r = (r_o - r)/r_o$, where r_o and r are the initial and the final sample radius, respectively, and in terms of the axial shrinkage, $\Delta l/l_o = (l_o - l)/l_o$, where l_o and l are the initial and the final sample length, respectively.

The microstructure of sintered compacts was observed with a scanning electron microscope (Zeiss, model DSM962) using polished sample surfaces coated with a thin film of gold. XRD analysis was performed using powdered samples in a Rigaku Dmax III-C 3 kW diffractometer, with CuK_α radiation and a Ni filter, at 40 kV and 20 mA. Continuous scanning was used with a scan speed of 2° min^{-1} and a sampling interval of 0.01° (2θ).

3. Results and discussion

Table 1 shows the effect of the applied compaction pressure on the initial relative density of the powder mixture compacts both in the green state (ρ_g) and after binder burnout (ρ_o). All the density values represent the average from at least three samples. It was observed that the compacts did not change dimensions during binder burnout. For every sample, the initial density increased with the compaction pressure and $\rho_g > \rho_o$ due to the increase in porosity caused by the burning of the binder.

From the linear regression analysis performed on the plots of the initial relative densities as function of the applied compaction pressure (P) the following relations were obtained: $\rho_g = 0.68 + 10^{-3}$ P and $\rho_o = 0.64 + 10^{-3}$ P. The correlation coefficient was 0.99 for the samples in the green state and 0.93 for the samples after binder burnout. This lower value was due to the higher experimental difficulty in handling the samples after binder burnout.

Fig. 1 shows the change of relative density with sintering temperature for the composites obtained at different compaction pressures. All the density values represent the average from at least three samples. As the

Table 1
Effect of compaction pressure on the relative density of powder compacts in the green state (ρ_g) and after binder burnout (ρ_o)

Pressure (MPa)	Relative density (%)	
	ρ_g	ρ_o
74	69	65
200	71	67
370	73	68

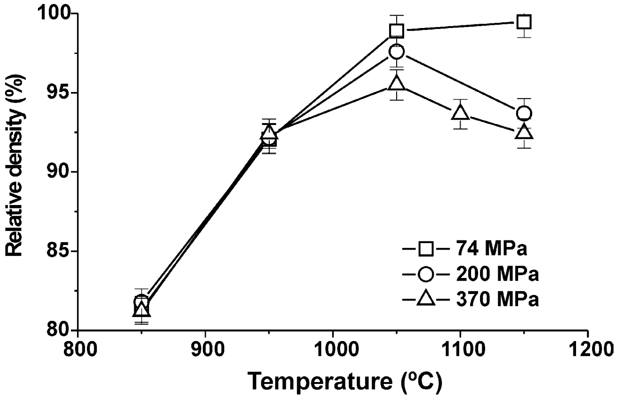

Fig. 1. Effect of temperature on the relative density of borosilicate glass–Al_2O_3 composites obtained at different compaction pressures.

temperature increased from 850 to 1050 °C, the sintered density of all the samples increased from about 81 to 95–98%, reaching values that indicate a sintering stage where only isolated porosity is present,[5] and above 1050 °C, samples pressed at 200 and 370 MPa showed a reduction in density with increasing temperature.

Figs. 2 and 3 show the open porosity and closed porosity, respectively, of the composites as a function of sintering temperature. At 850 °C, the samples exhibited an open porosity within the range 12–15% (Fig. 2), and at this temperature, samples that have been pressed at the highest pressure showed the highest closed porosity (Fig. 3), suggesting that less pores remained connected with the sample surface as the packing pressure increased. Taking into account that usually, in die compaction, the applied pressure is not transmitted uniformly to the powder and that density gradients are present in the compacts,[5] it is considered that sintering at the sample surface might occur faster in compacts pressed at the highest pressure, where some of the original open pores from the surface will be isolated and converted to closed pores.

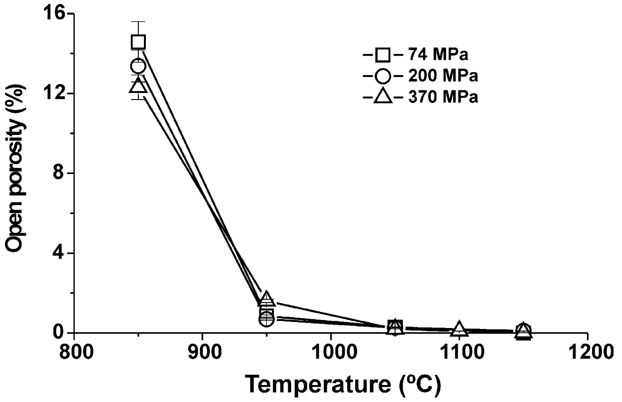

Fig. 2. Effect of temperature on the open porosity of borosilicate glass–Al_2O_3 composites obtained at different compaction pressures.

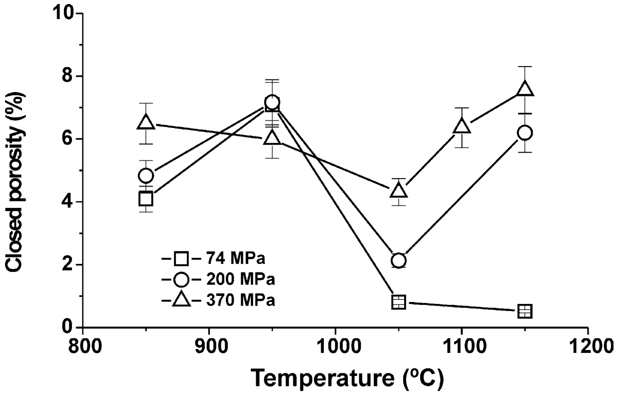

Fig. 3. Effect of temperature on the closed porosity of borosilicate glass–Al_2O_3 composites obtained at different compaction pressures.

From Fig. 2 it is observed that for all the samples the open porosity decreased sharply between 850 and 950 °C, i.e. at sintering temperatures higher than the softening point of the borosilicate glass,[11] and it approached zero at 1050 °C. The closed porosity of samples pressed at 74 MPa increased up to 950 °C and then decreased above this temperature with a consequent improvement in density.

Whatever the applied pressure, all composite samples had similar density when sintered at 850 °C (Fig. 1), although the highest open porosity was exhibited by samples pressed at 74 MPa (Fig. 2). Thus, when these samples were treated at higher temperatures, where the borosilicate glass softened, viscous flow occurred more easily, and therefore, the glass–Al_2O_3 compacts pressed at 74 MPa densified better than the compacts pressed at higher compaction pressures. For samples pressed at 200 and 370 MPa, the minimum closed porosity was achieved at 1050 °C, temperature corresponding to the maximum density, and an increase in closed porosity was found at higher temperatures, which is associated to the reduction in density observed in Fig. 1.

It is suggested that the density reduction might result from the occurrence of the following processes with an increase in temperature:[5,12] (1) expansion of the closed pores caused by an increase in the pressure of the gases trapped in the pores or by a decrease in gas solubility within glass, (2) coarsening of the closed pores due to pore coalescence or Ostwald ripening.

In order to identify which process caused the swelling of the samples, the microstructural development of the sintered composites was analysed by SEM. Fig. 4 shows the micrograph of a sample sintered at 1050 °C, where the maximum density was achieved, and the micrograph of a sample sintered at the highest temperature (1150 °C), where reduction in density was detected. The micrographs show clearly that both samples contained only isolated pores, which appear white or to have a dark colour, according to the smaller or higher deepness below the polished surface.

By comparison of the SEM photographs presented in Fig. 4, the increase in pore size with the increased sintering temperature is evident. In fact, pore growth had

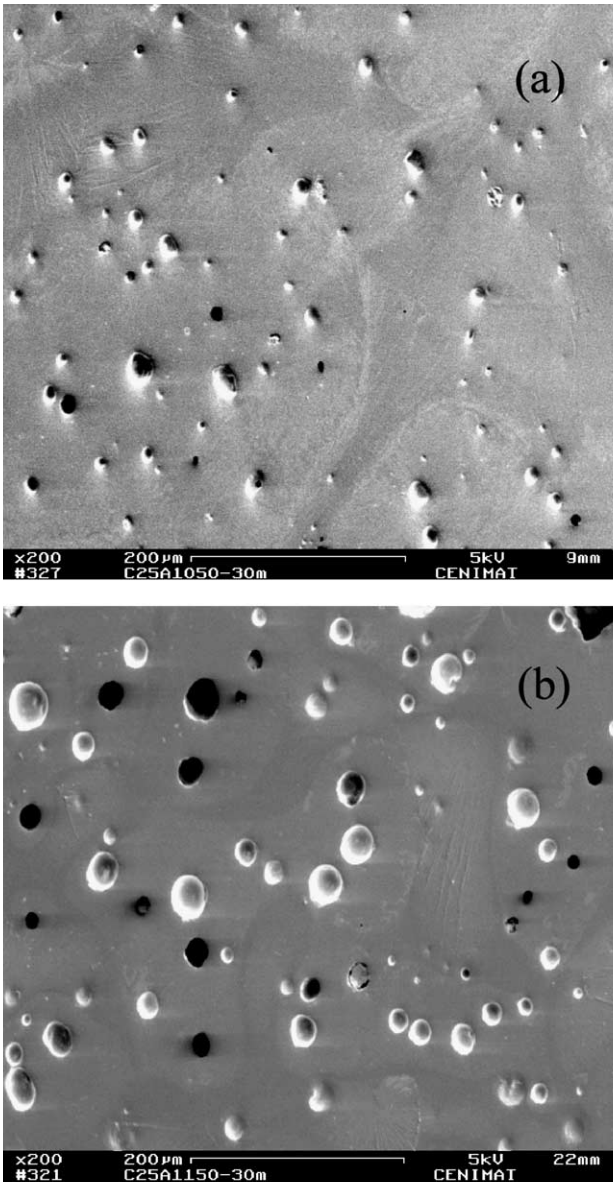

Fig. 4. SEM micrographs of borosilicate glass–Al_2O_3 samples pressed at 370 MPa and sintered for 30 min at (a) 1050 °C and (b) 1150 °C.

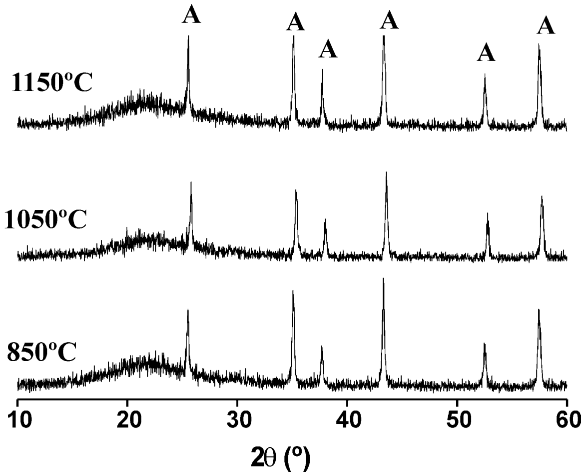

Fig. 5. XRD of borosilicate glass–Al_2O_3 composites sintered for 30 min at different temperatures. ($A = Al_2O_3$)[16].

occurred in the sample sintered at the highest temperature, but the number of closed pores exhibited by this sample did not decrease, which indicates that pore coalescence or Ostwald ripening was not the cause for the coarsening of the pores. These results suggest that, in the present study, the density reduction was possibly caused by process (1) instead of (2). Since the solubility of gases (e.g. nitrogen) in oxide glasses generally increases with temperature,[12] it is more likely that pore expansion was caused by the increase in the pressure of the gases trapped in the pores.

It has been reported that residual binder can apparently play a part in this swelling phenomenon, as in the sintering process of some systems, incomplete binder burnout can also lead to an increase in gas pressure and, hence, to swelling at the highest temperatures.[12,13] Although in the present study, a significant amount of binder (5 wt.%) was used in the die pressing experiments, it has been observed that the mass of the samples did not change during the sintering process. This suggests that complete binder burnout had been achieved by the pre-sintering treatment, and therefore, the gases trapped in the pores should not result from the decomposition of residual binder during densification. In fact, it is considered that the increase in sintering temperature caused an increase in the pressure of the gases occluded in the closed pores, resulting therefore in an increase in pore size, i.e. decrease in density of the sintered compacts, at the highest temperature, where the glass matrix softened and had sufficient fluidity to allow swelling of the samples.

The formation of mullite, caused by the reaction between Al_2O_3 and the glass during the sintering process, was investigated by XRD. In fact, mullite formation has been detected in borosilicate glass–Al_2O_3 composites containing an Al_2O_3 content $\geqslant 10$ vol.% and sintered at temperatures from 1200 to 1400 °C during 5 h[13] or during 8 h.[14] XRD analysis performed on the composites sintered under the conditions studied in this work (850–1150 °C for 30 min) indicated that unreacted Al_2O_3 is the only crystalline phase present in the composites, as illustrated by the diffractogram shown in Fig. 5.

The formation of cristobalite resulting from the devitrification of the borosilicate glass has been observed,[11,14,15] particularly when the alumina content in the composites was <10 vol.% (lower than in the present work) and the firing temperature range was 700–1200 °C. Precipitation of cristobalite has not been detected under the present experimental conditions, indicating that the amount of added Al_2O_3 (25 vol.%) inhibited the crystallization of cristobalite, which is in agreement with the results reported in previous works.[14,15,17]

The XRD results also contribute to exclude any possible association between the density reduction observed in some samples sintered at the highest temperatures and the formation of a crystalline phase with a higher specific volume than alumina.

The sintering behaviour of the composites obtained at different packing pressures was also analysed in terms of the linear shrinkage exhibited by the compacts sintered in the temperature range 850–1150 °C. It was observed that for a given sintered compact the axial shrinkage ($\Delta l/l_o$) was always higher than the radial shrinkage ($\Delta r/r_o$) and that the increase in the compaction pressure favoured the anisotropic shrinkage behaviour as illustrated in Fig. 6. The slopes of the curves adjusted to the experimental data obtained for the samples pressed at 74, 200 and 370 MPa were 1.23, 1.37 and 1.69, respectively, indicating a higher shift from the isotropic behaviour as the compaction pressure increased.

Shrinkage anisotropy has also been reported in some sintering studies on glass powders[8,18–20] and on glass matrix composites containing rigid inclusions,[7] where different experimental conditions have been used. Rahaman et al.[8] used the loading dilatometer technique to investigate the creep and densification behaviour of soda-lime glass powder compacts and found that shrinkage was greater in the axial direction. Giess et al.[18,19] investigated the free sintering of cordierite-type glass cylindrical compacts, uniaxially pressed from nonspherical crushed glass particles,[18] or from spheroidized particles,[19] and observed that the compacts shrank more in the radial direction. Boccaccini[20] and Boccaccini et al.[7] used a heating microscope to investigate the isothermal sintering behaviour, without the exertion of any external load, of a borosilicate glass powder especially developed for the immobilization of nuclear wastes,[20] and of the same glass reinforced with vanadium particles,[7] and in both cases it was verified that the shrinkage was less in the axial than in the radial direction.

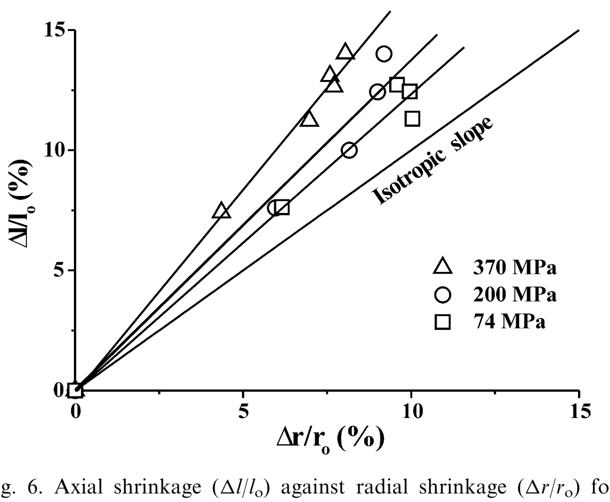

Fig. 6. Axial shrinkage ($\Delta l/l_o$) against radial shrinkage ($\Delta r/r_o$) for sintered borosilicate glass–Al_2O_3 composites obtained at different compaction pressures.

In the present work, the die pressed glass–Al_2O_3 powder compacts were pressureless sintered during 30 min between 850 and 1150 °C. In this temperature range, the used borosilicate glass softened[11] and compacts prepared from the glass powder (without Al_2O_3 inclusions) warped and glued to the furnace at the highest temperatures. If the powder glass compacts were sintered at temperatures lower than 850 °C, cristobalite precipitation was observed,[11] and this has not been detected in the present study, where 25 vol.% Al_2O_3 was added to the glass (Fig. 5). Taking into account the present experimental results, it is suggested that the higher the applied pressure in the compaction of the powders the higher the density gradients in the compacts and therefore, non-uniform shrinkage on sintering the borosilicate glass matrix composites with Al_2O_3 inclusions was promoted. It is possible that the applied pressure might provide some microstructural anisotropy in the glass–Al_2O_3 compacts that gave rise to the observed shrinkage anisotropy.

The assessment of occurrence of shrinkage anisotropy is an important practical issue in the fabrication of compacts by sintering.[7] Anisotropic shrinkage may result on the formation of undesired cavities and other microstructural damage in sintered compacts.[4,5,7] Expensive and time-consuming post-densification machining of dense, sintered products can be avoided or minimised, if it is possible to predict the final dimensions and shape of the sintered products from the dimensions and shape of the initial green bodies.[7]

Further experimental work is in progress to determine how the pressing process (uniaxial vs. isostatic), sintering time and inclusion content influence the densification of borosilicate glass matrix composites reinforced with Al_2O_3 particles.

4. Conclusions

The results showed that an increase in the compaction pressure resulted in an increase in the initial relative density of the compacts both in the green state and after binder burnout. Within the temperature range 850–1150 °C, compacts uniaxially pressed at 74 MPa exhibited a continuous increase in density with sintering temperature, while compacts uniaxially pressed at higher pressures, 200 and 370 MPa, reached a maximum sintered density (95–98% theoretical density) at 1050 °C, which decreased slightly at higher temperatures. The increase in sintering temperature caused an increase in the pressure of the gases occluded in the closed pores, which resulted in pore expansion at the highest temperatures, where the glass matrix softened and had enough fluidity to allow swelling of the samples. Crystallization of the glass and/or formation of mullite were not found in the composites sintered under the studied conditions. The composites exhibited anisotropic sintering behaviour, showing a radial shrinkage smaller than the axial shrinkage, and increasing the initial compaction pressure promoted microstructural anisotropy in the glass–Al_2O_3 compacts leading to enhanced anisotropic shrinkage.

References

1. Rahaman, M. N. and De Jonghe, L. C., Effect of rigid inclusions on the sintering of glass powder compacts. *J. Am. Ceram. Soc.*, 1987, **70**, C348–C351.
2. Boccaccini, A. R. and Conradt, R., Isotropic shrinkage of platelet containing glass powder compacts during isothermal sintering. *Int. J. Inorg. Mater.*, 2001, **3**, 101–106.
3. Ray, A. and Tiwari, A. N., Compaction and sintering behaviour of glass-alumina composites. *Mater. Chem. Phys.*, 2001, **67**, 220–225.
4. Reed, J. S., *Principles of Ceramic Processing*, 2nd edn. John Wiley and Sons, New York, 1995.
5. Rahaman, M. N., *Ceramic Processing and Sintering*. Marcell Dekker, New York, 1995.
6. Jeng, D.-Y. and Rahaman, M. N., Effect of inclusions on the sintering of mullite synthesized by sol-gel processing. *J. Mater. Sci.*, 1993, **28**, 4421–4426.
7. Boccaccini, A. R., Conradt, R. and Olevsky, E. A., Anisotropic effects during sintering of particle reinforced glasses. In *Proceedings of the 5th European Society of Glass Conference*, ed. A. Helebrant, M. Maryska and S. Kasa. Prague, 1999, pp. C3.50–C3.57.
8. Rahaman, M. N., De Jonghe, L. C., Scherer, G. W. and Brook, R. J., Creep and densification during sintering of glass powder compacts. *J. Am. Ceram. Soc.*, 1987, **70**, 766–774.
9. Pascual, M. J., Pascual, L. and Durán, A., Sintering behaviour of borosilicate glass/zirconia fibres composites. In *Proceedings of the 5th European Society of Glass Conference*, ed. A. Helebrant, M. Maryska and S. Kasa. Prague, 1999, pp. C2.63–C2.70.
10. Lima, M. M. and Monteiro, R., Pressureless sintering of alumina-glass composites. In *Ceramics-Processing, Reliability, Tribology and Wear, Euromat 99, Vol. 12*, ed. G. Muller. Wiley-VCH, Weinheim, 2000, pp. 178–183.
11. Lima, M. M. R. A. and Monteiro, R. C. C., Characterisation and thermal behaviour of a borosilicate glass. *Thermochim. Acta*, 2001, **373**, 69–74.
12. Shyu, J.-J. and Wang, J.-K., Sintering of cordierite-borosilicate glass composites. *J. Mater. Res.*, 2000, **15**, 1759–1765.
13. Mattox, D. M., Gurkovich, S. R., Olenik, J. A. and Mason, K. M., Ceramic substrates and packages for electronic applications. In *Advances in Ceramics, Vol. 26*, ed. M. F. Yan, K. Niwa, H. M. O' Bryan Jr and W. S. Young. The American Ceramic Society, Westerville, OH, 1987, pp. 431.
14. Imanaka, Y., Aoki, S., Kamehara, N. and Niwa, K., Cristobalite phase formation in glass/ceramic composites. *J. Am. Ceram. Soc.*, 1995, **78**, 1265–1271.
15. Jean, J.-H. and Gupta, T. K., Devitrification inhibitors in borosilicate glass and binary borosilicate glass composite. *J. Mater. Res.*, 1995, **10**, 1312–1320.
16. *Powder Diffraction File, Card No. 10-173*, 1967, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA.
17. Park, J.-H. and Lee, S.-J., Mechanism of preventing crystallization in low-firing glass-ceramic composite substrates. *J. Am. Ceram. Soc.*, 1995, **78**, 1128–1230.
18. Giess, E. A., Fletcher, J. P. and Herron, L. W., Isothermal sintering of cordierite-type glass powders. *J. Am. Ceram. Soc.*, 1984, **67**, 549–552.
19. Giess, E. A., Guerci, C. F., Walker, G. F. and Sheree, H. W., Isothermal sintering of spheroidized cordierite-type glass powders. *J. Am. Ceram. Soc.*, 1985, **68**, C328–C329.
20. Boccaccini, A. R., Anisotropic densification during sintering of glass powder compacts. *J. Mater. Sci. Letters*, 1993, **12**, 943–945.