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Sintering of glass matrix composites containing Al_2O_3 platelet inclusions

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The effect of alumina platelet inclusions on the sintering behaviour of a commercial aluminosilicate glass powder has been investigated by means of a heating microscope at 850 °C. For platelet volume fractions $\leqslant 0.15$, no significant influence of the inclusions on the densification behaviour of the composite was found. Scherer's model for viscous sintering with rigid inclusions, which uses the Hashin–Shtrikman approximation for the composite shear viscosity, can be conveniently used to interpret the experimental results. However, the composite densification rate and the stresses caused by the inclusions can be correctly predicted using this model only for inclusion volume fractions lower than a critical value, given by the percolation threshold. For platelet volume fractions $\leqslant 0.15$, high-density glass matrix composites can be fabricated by simple pressureless sintering.

1. Introduction

There is significant current research activity to develop strong, tough, and reliable glass and glass-ceramic for structural applications. These materials possess a lower density than the majority of structural metals, being hard and highly resistant to compressive stresses. Their electrical and thermal insulating properties, as well as their resistance to chemical attack, are additional attractive characteristics of these materials.

On the contrary, the brittleness and flaw sensitivity of glass and glass-ceramics, which result in a high susceptibility to catastrophic failure, are the main disadvantages limiting their use in structural applications. One approach to the improvement of the modulus of rupture and the fracture toughness of glass and glass-ceramics is the composite approach, where the low-modulus, low-strength matrix material is reinforced by a high-modulus, high-strength second phase.

An alternative to the incorporation of continuous silicon carbide and graphite fibres in glass and glass-ceramic matrices [1], which requires the application of cost-intensive production processes, is the addition of discontinuous particulate dispersions. Silicon carbide and silicon nitride whiskers [2, 3], and particles [3], and zirconia particles [4] have been used with different results for glass and glass-ceramic reinforcement. Although the improvement of the fracture behaviour of these last composites is not so spectacular as that achieved using continuous fibre reinforcement [1], the use of less-expensive powder technology preparation techniques makes the dispersion reinforcement an attractive alternative. The application of whiskers as reinforcement, however, is critical not only because their presence has a detrimental effect on the densification processes but also because inhalation of these fine needle-shaped particles is hazardous to health [5]. Platelets are thought to offer a similar reinforcing capability with higher thermal stability, easier powder-metallurgical-processing methods, and no health hazards.

Silicon carbide and alumina platelets have been applied for strengthening and toughening different ceramic matrices as mullite [6], cordierite [7], zirconia, silicon nitride and alumina [5]. Use of platelet reinforcement in glass matrices has not been reported.

The presence of heterogeneities in the structure of a green compact has a significant influence on the densification behaviour during sintering. These heterogeneities sinter at different rates than the surrounding matrix and they create internal stresses, that may cause structural damage in the compacts such as internal cracks or pores [8, 9]. Ceramic platelets dispersed in a glass matrix are, in this context, a special kind of heterogeneities because they are rigid, i.e. non-sintering, inclusions at the sintering temperature of glass. The sintering of a glass matrix containing rigid inclusions has not been investigated experimentally very exhaustively. It has only been considered a soda–lime glass containing rigid inclusion of silicon carbide [10], and a borosilicate glass with inclusions of boron carbide [11] and spherical aluminosilicate inclusions [12]. A recent work has considered the sintering of a soda–lime glass containing spherical nickel inclusions [13]. The theoretical predictions of Scherer's self-consistent model [14] for the viscous sintering with rigid inclusions has been frequently used [10–13] to interpret the experimental results. In the present work, the effect of alumina platelets addition on the pressureless densification of a commercial aluminosilicate glass was investigated by means of heating microscopy. This experimental technique to study the sintering kinetic has been recently introduced [12] and conveniently applied for investigating the sintering of glass [15]. The experimental values are

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compared with the theoretical predictions of the Scherer's model [14]. Conclusions about the possibility of pressureless processing of platelet-containing glass matrix composites are drawn. The present work is part of a wider study which addresses the feasibility of glass toughening by the incorporation of alumina platelets.

2. Experimental procedure

The glass matrix material investigated is a commercial aluminosilicate alkali-free glass powder (N.8409, Schott Glaswerke, Mainz). The mean particle size is 8 μm and the theoretical density 2.57 $g\,cm^{-3}$. The transformation temperature of the glass is 745 °C [16]. The powder was used in the as-received condition and the particle morphology was analysed using SEM. Alumina platelets (Lonza-Werke, Waldshut-Tiengen), with major axes between 5 and 25 μm, were used as reinforcement material and they were used as-received. The physical and chemical stability of the platelets at the processing conditions were tested by heating them for several hours in air at 850 °C.

The following volume fractions of inclusions were chosen: $F = 0$, 0.05, 0.15 and 0.30. The powders were dry-mixed without the addition of any binder in a rotating mixer for 5 h. Complications which arise due to binder removal of the samples was therefore avoided. Green cylindrical compacts (5 mm diameter by 5 mm) were obtained by uniaxial pressing at room temperature. Pressures of 25 MPa were used to reach relative green densities of ≈ 0.60. On the contrary to previous similar works, in which dilatometric measurements were used [10, 11], the samples here were sintered in a standard heating microscope. This allows axial and radial shrinkages to be measured without the exertion of any external force, which would influence the sintering process. Thus, complications concerning external forces or friction between the pushrods and the sample (that may lead to deviation from cylindrical geometry) are obviated.

The compacts were isothermally sintered in the heating microscope for 2 h at 850 °C in air. At this temperature the glass should have a viscosity, $\eta = 1.6 \times 10^9$ dPas [16]. After heating the furnace to the sintering temperature the compacts were set in quickly, in order to provide isothermal conditions for the whole period of sintering. The axis of the cylindrical samples coincided with the vertical direction. At prechosen time intervals during the sinter process, photographs of the samples were made to measure the change of length and diameter and hence to calculate the axial and radial shrinkage.

The mass and dimensions of the pressed and sintered compacts were measured and the geometrical densities determined. Whilst the final density of the sintered pellets was also measured using Archimedes' principle, the density as a function of time during sintering was determined from the green density and the measured shrinkage.

Scanning electron microscopy was used to investigate the microstructure of sintered compacts with different volume fractions of platelets.

3. Data analysis

The data analysis was performed following a procedure already used [10, 12]. From the experimental data for the axial and radial shrinkages during sintering, the density of the composite, ρ_c, at any time can be calculated from the expression

$$\rho_c = \rho_{c0} \Big/ \left[\left(1 - \frac{\Delta D}{D}\right)^2 \left(1 - \frac{\Delta L}{L}\right) \right] \quad (1)$$

where ρ_{c0} represent the green density of the composite, $\Delta D = D_0 - D$ and $\Delta L = L_0 - L$. D_0, L_0 are the initial sample diameter and length, respectively, and D, L are the instantaneous diameter and length, respectively.

The instantaneous absolute density of the matrix, ρ_m, can be expressed as [10]

$$\rho_m = \frac{(\rho_{c0} - \rho_i f_0)\,\rho_c}{(\rho_{c0} - f_0 \rho_c)} \quad (2)$$

where ρ_i is the density of the inclusion phase (platelets) and f_0 is the volume fraction of platelets in the initial compact. From Equation 2 and its time derivative follows the volumetric strain rate of the glass matrix as

$$\frac{\dot{\rho}_m}{\rho_m} = \frac{\left(\frac{\dot{\rho}_c}{\rho_c}\right)\rho_{c0}}{(\rho_{c0} - f_0 \rho_c)} \quad (3)$$

At this point, it is useful to make a remark about the computation of the volume fraction of inclusions. As already noticed, f_0 represents the volume fraction of platelets in the initial compact, the pore phase included. As the pore phase disappears during sintering, the instantaneous volume fraction of platelets inclusions, f, increases. As suggested by Rahaman and De Jonghe [10], it is practical to use the volumetric fraction, F, which corresponds to the fully dense composite. The instantaneous volume fraction of inclusions, f, the relative density of the matrix, ρ_m, and F are related by the expression

$$f = \frac{\rho_m}{\rho_m + (1 - F)/F} \quad (4)$$

4. Results

Fig. 1a and b show scanning electron micrographs of the aluminosilicate glass and the alumina platelets used. The non-spherical character of the glass particles is evident as well as the definite platelet-like geometry of the inclusions.

Fig. 2 shows the density of the composite, ρ_c, as function of sintering time, t, for the different volume fractions of platelets inclusions, F; ρ_c was calculated using Equation 1, the data for radial and axial shrinkage, and the green density. The data shown are an average of two or three runs under the same conditions and have a maximum relative error of 4%. Good agreement exists between the final densities calculated from the shrinkage measurements and the values determined using Archimedes' principle. The moment of introduction of the sample into the heating microscope which was already at the sintering temperature, was taken as $t = 0$.

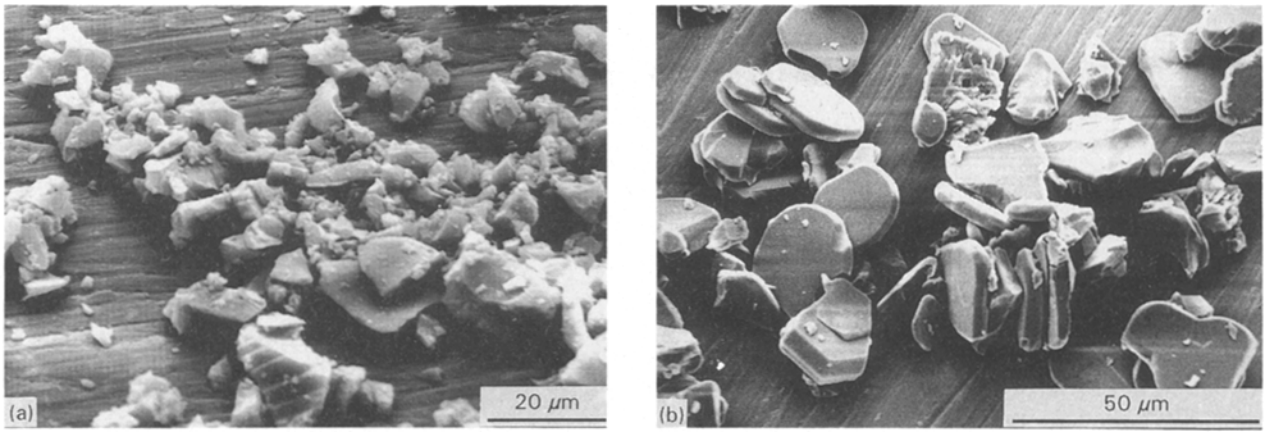

Figure 1 Scanning electron micrographs of the materials investigated: (a) aluminosilicate glass powder, and (b) alumina platelets.

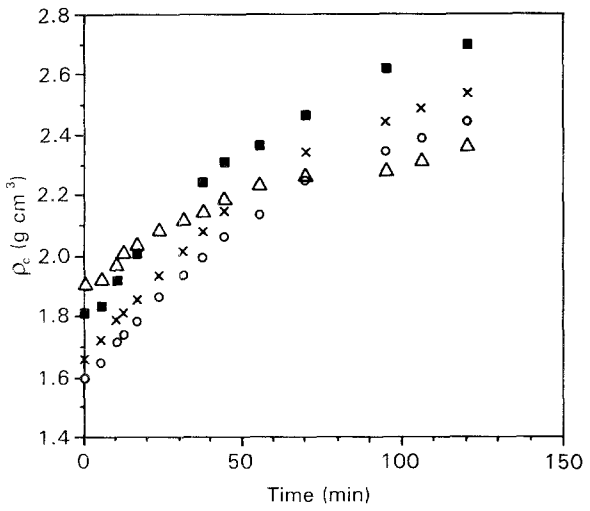

Figure 2 Density of the composite, ρ_c, versus sintering time for different volume fractions of platelets, F: (×) 0.05, (■) 0.15, (△) 0.30, (○) 0.

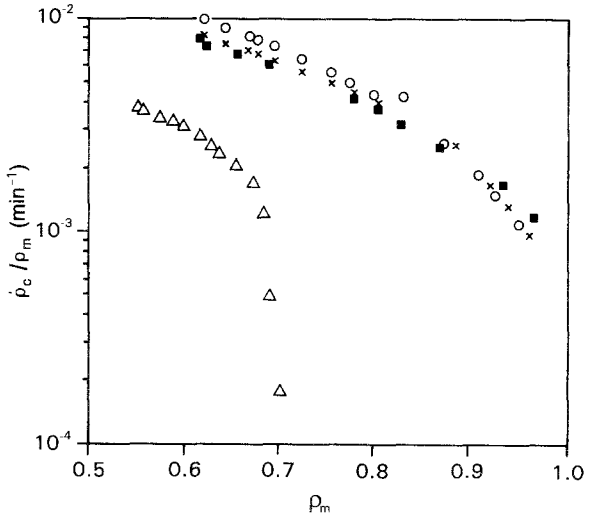

Figure 4 Volumetric strain rate of the composite $\dot{\rho}_c/\rho_c$ versus relative density of the matrix for indicated volume fractions of platelets. F: (×) 0.05, (■) 0.15, (△) 0.30, (○) 0.

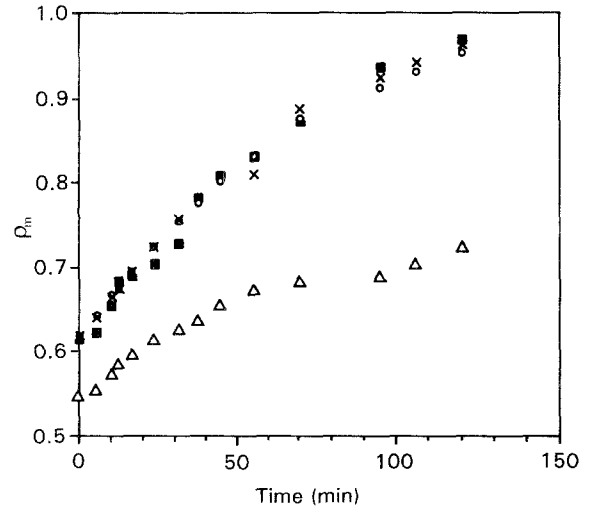

Figure 3 Relative density of the glass matrix, ρ_m, versus sintering time for different volume fraction of platelets, F: (×) 0.05, (■) 0.15, (△) 0.30, (○) 0.

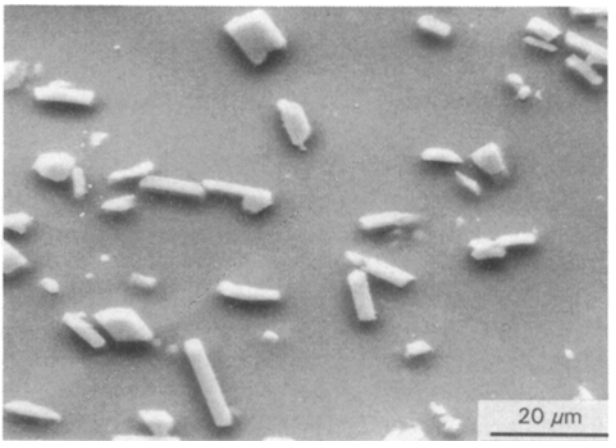

Figure 5 Scanning electron micrograph of a polished surface of the composite containing 15 vol % platelets inclusions.

The relative matrix density, ρ_m, was calculated using the values represented in Fig. 2, Equation 2, and the theoretical density of the glass matrix. Fig. 3 shows the results obtained for different values of F.

The composite densification rate, $\dot{\rho}_c/\rho_c$, was obtained by fitting smooth curves to the data of Fig. 2 and differentiation. The results for $\dot{\rho}_c/\rho_c$ versus ρ_m for different values of F are shown in Fig. 4. Fig. 5 shows a

scanning electron micrograph of a polished section of a sample containing 15 vol % platelets. An homogeneous distribution of the platelets inclusions in the glass matrix can be seen.

5. Discussion

As shown in Figs 2–4, the presence of the platelets inclusions for $F = 0.05$ and 0.15 has a relatively small effect on the densification kinetics of the composite and the glass matrix. The effect of the inclusions is seen to be significant when the inclusions volume fraction increases ($F = 0.30$).

The experiments provide data which can be compared with the predictions of theoretical models for the sintering of a matrix containing rigid inclusions. The self-consistent model of Scherer [14], derived for an isotropic, linearly viscous material, will be considered here. Considering the effect of the stresses exerted by the inclusions, Scherer [14] showed that the hydrostatic component of the stress field retards the densification of the matrix even more than a simple prediction from the rule of mixtures. According to this rule, the linear strain rate of a composite is

$$\dot{\varepsilon}_c^{rm} = (1-f)\dot{\varepsilon}_{fm} + f\dot{\varepsilon}_i \quad (5)$$

where $\dot{\varepsilon}_c^{rm}$, $\dot{\varepsilon}_{fm}$ and $\dot{\varepsilon}_i$ are the linear strain rates of the composite, the matrix and the inclusions, respectively. For rigid inclusions, $\varepsilon_i = 0$, thus

$$\dot{\varepsilon}_c^{rm} = (1-f)\dot{\varepsilon}_{fm} \quad (6)$$

This indicates that the strain rate of the composite is slower than the strain rate of the free matrix. According to Scherer's self-consistent model, the composite should sinter even more slowly than a mixture. Thus the relation between the real strain rate of the composite, $\dot{\varepsilon}_c$, and that predicted from the rule of mixtures, $\dot{\varepsilon}_c^{rm}$ (Equation 6), can be expressed by

$$\frac{\dot{\varepsilon}_c}{\dot{\varepsilon}_c^{rm}} = \left\{1 + \frac{2\rho_m(1-A)}{(\rho_m + r)(1+0.5A)}\left[1 + \frac{7.5\rho_m(1-0.5A)}{r(4-2.5A)}\right]\right\}^{-1} \quad (7)$$

where $r = (1-F)/F$ and $A = [\rho_m/(3-2\rho_m)]^{1/2}$.

To calculate the composite strain rate, the shear viscosity of the composite, G_c, must be known as a function of the matrix density. Equation 7 was obtained using the lower bound of the Hashin–Shtrikman equation [17] for G_c, as already proposed [10].

The experimental values of $\dot{\varepsilon}_c/\dot{\varepsilon}_c^{rm}$ can be obtained from the values of $\dot{\rho}_c/\rho_c$ in Fig. 3 knowing that

$$\dot{\varepsilon}_c = -\frac{1}{3}\frac{\dot{\rho}_c}{\rho_c} \quad (8)$$

Using Equations 6 and 8 and the following relation valid for the matrix without inclusions

$$\dot{\varepsilon}_{fm} = -\frac{1}{3}\frac{\dot{\rho}_{fm}}{\rho_{fm}} \quad (9)$$

we obtain

$$\frac{\dot{\varepsilon}_c}{\dot{\varepsilon}_c^{rm}} = \frac{\dot{\rho}_c/\rho_c}{(1-f)\,\dot{\rho}_{fm}/\rho_{fm}} \quad (10)$$

The values of $\dot{\rho}_{fm}/\rho_{fm}$ correspond to the case $F = 0$ in Fig. 4. As a function of ρ_m and F, this equation can be written as

$$\frac{\dot{\varepsilon}_c}{\dot{\varepsilon}_c^{rm}} = \frac{\dot{\rho}_c/\rho_c[1 + F\rho_m/(1-F)]}{\dot{\rho}_{fm}/\rho_{fm}} \quad (11)$$

Fig. 6 shows the theoretical values predicted by Scherer's model (Equation 7) and the experimental values obtained from the measurements and Equation 11 for $F = 0.15$ and 0.30. The values for $F = 0.05$ are not shown for clarity. Good agreement between the experiment and theory is seen for $F = 0.15$ and the

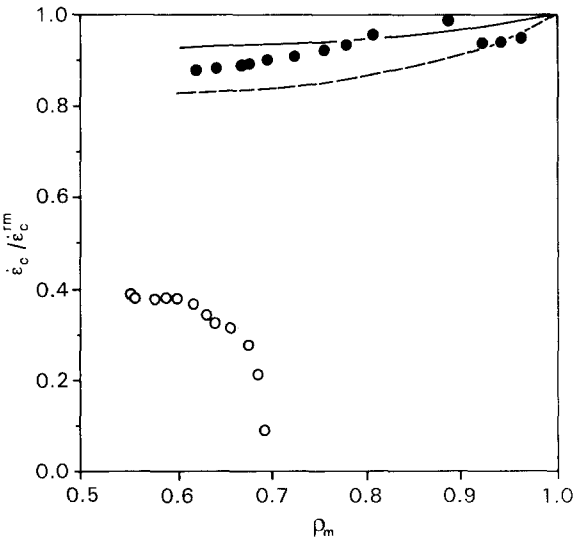

Figure 6 Linear strain rate of the composite referred to the strain rate from the rule of mixtures, $\dot{\varepsilon}_c/\dot{\varepsilon}_c^{rm}$, versus relative density of the matrix for (●, ——) 0.15, platelet volume fractions (○, – – –) 0.30, (●, ○). Experimental values and (——, – – –) theoretical values are from Scherer's model (Equation 7).

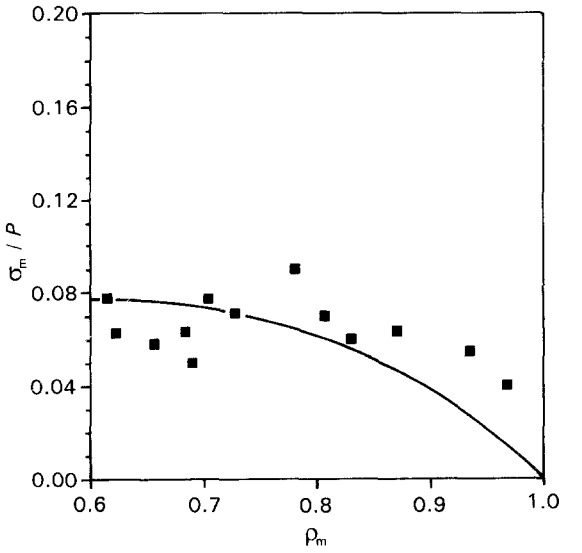

Figure 7 Hydrostatic stress in the matrix normalized to the sintering stress, σ_m/P, versus relative density of the matrix for $F = 0.15$. Comparison of (■) experimental values with (——) the prediction of Scherer's theory (Equation 13).

same can be said for $F = 0.05$. For $F = 0.30$, the deviation of the experimental data from the theoretical predictions is quite spectacular. As earlier suggested [10, 18] one factor which may give rise to the large deviations between theory and experiment above a certain volume fraction of inclusions is interaction between particles. Percolation theory [19] indicates that there is a percolation threshold at a certain volume fraction of inclusions above which the inclusions will form a contiguous network, affecting the rigidity of the composite. As shown by finite element method calculations [18] at this critical volume fraction of inclusions the shear viscosity of the composite, G_c, increases dramatically, a fact which is not taken into account by the Hashin–Shtrikman approximation used in Equation 7. Thus, this increase in G_c above the percolation threshold will cause a corresponding drop in the densification rate, which is not predicted by Equation 7. In the recent investigation of nickel inclusions in soda–lime glass [13], measured values for the shear viscosity were used to obtain the strain rate of the composite and excellent agreement between theory and experiment was found, even at high volume fractions of inclusions ($F = 0.20$).

The percolation threshold is dependent on the aspect ratio and orientation of the inclusions [20]. As pointed out by Scherer [18], however, the rigidity threshold occurs at a higher volume fraction than predicted from percolation theory because usually the matrix wets the inclusions, providing a lubricating layer at the points of contact. For randomly oriented platelet inclusions, as investigated here, this rigidity threshold is greater than $F = 0.15$. From the experimental values it is also possible to determine the hydrostatic component of the stress in the matrix, σ_m, caused by the inclusions normalized to the sintering pressure, P[10, 12]

$$\frac{\sigma_m}{P} = 1 - \frac{\dot{\rho}_m/\rho_m}{\dot{\rho}_{fm}/\rho_{fm}} \tag{12}$$

According to Scherer's model, the relation σ_m/P can be expressed as

$$\frac{\sigma_m}{P} = \frac{\rho_m/r}{\left\{\rho_m/r + \dfrac{1 + 0.5A}{2(1-A)\left[1 + 7.5(\rho_m/r)\left(\dfrac{1-0.5A}{4-2.5A}\right)\right]}\right\}} \tag{13}$$

where A and r have the same meaning as in Equation 7.

In Fig. 7 the experimental and theoretical values of σ_m/P are plotted versus the relative matrix density for a volume fraction of inclusions $F = 0.15$. For $F = 0.05$ the results are similar. As observed earlier for the $\dot{\varepsilon}_c/\dot{\varepsilon}_c^{rm}$ results, there is good agreement between theoretical and experimental values for inclusion volume fraction until $F = 0.15$. The data for $F = 0.30$ have been omitted because of the large deviations found for the strain-rate calculations. The relative low values of σ_m/P for $F \leqslant 0.15$ ($\sigma_m/P \leqslant 0.08$) cannot lead to high shear stresses at the platelet–matrix interface, which could cause the formation of cracks.

This absence of interfacial cracks for $F = 0.05$ and $F = 0.15$ was confirmed by examination of polished sections of the samples by SEM (see Fig. 5).

6. Conclusion

Using the heating microscope provides an advantageous experimental method to study the pressureless sintering behaviour of composite materials. It allows monitoring of the densification process without the exertion of external forces, which could influence the sintering kinetics.

The effect of platelets inclusions on the sintering behaviour of the glass matrix can be predicted by the Scherer's model for volume fractions of inclusions lower than the rigidity threshold, if the Hashin–Shtrikman approximation for the composite shear viscosity is used.

The calculated composite strain rate and the hydrostatic stress in the matrix caused by the platelet inclusions are in good agreement with the experimental values. For platelets inclusion volume fractions $\leqslant 0.15$, there is no significant effect of the inclusions on the densification behaviour of the composite and the stresses caused by the inclusions are low enough, without leading to the formation of cracks at the interface. This result suggests that high-density platelet-reinforced glass matrix composites can be fabricated by simple pressureless sintering for platelet volume fractions of $\leqslant 0.15$.

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