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Sintering Behaviour of Tape-Cast CMAS Glass–Ceramic Reinforced with Alumina Chopped Fibres

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Abstract

The sintering behaviour of CMAS glass–ceramic and CMAS glass–ceramic/alumina chopped fibre (20 wt%) composites was studied at different temperatures, ranging from 800 to 1000°C, using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and porosimetry investigations. The evaluation of linear shrinkage, density and porosity were sufficient to define the best sintering conditions, while SEM and XRD allowed the nature of the matrix/fibre interface to be studied.

Das Sinterverhalten von CMAS-Glaskeramik und eines CMAS-Glaskeramik/Aluminiumoxydfaserverbunds (20 Gew.%) wurde bei verschiedenen Temperaturen, zwischen 800 und 1000°C, mit Hilfe der Rasterelektronenmikroskopie (SEM), Röntgenbeugung (XRD) und Porosimetrie untersucht. Die Auswertung der linearen Schrumpfung, der Dichte und der Porosität erlaubte die Bestimmung der günstigsten Sinterbedingungen. Die Matrix/Faser-Grenzfläche wurde mit Hilfe von SEM und XRD untersucht.

Le comportement à la sinterization de composites vitrocéramiques CMAS/fibres courtes d'alumine (20% en poids) a été étudié à différentes températures comprises entre 800 et 1000°C. Les résultats présentés concernent des analyses par microscopie électronique à balayage (SEM), diffraction de rayons X (XRD) et porosimétrie. Les meilleures conditions de frittage ont été estimées à partir de la mesure du retrait linéaire, de la densité et de la porosité; la nature de l'interface matrice/fibre a été caractérisée par microscopie électronique à balayage et diffraction RX.

1 Introduction

Glass–ceramic matrices for composite materials provide the unique capability to tailor their compositions to meet the requirements set down by the fibre composition.[1] One of the most important matrix physical parameters is the thermal expansion coefficient, α, which is responsible for the thermomechanical behaviour of the composite. As a general observation it appears from experimental studies that when $\alpha_{\text{matrix}} > \alpha_{\text{fibre}}$ thermal cracking of either the fibres or the matrix is prevented.[2]

Another very important matrix property is the viscosity, which is related to the sintering process of the composite. The parent glass composition should be designed to have the correct viscosity, considering the fact that the densification behaviour of powdered glassy matrices is significantly retarded in presence of rigid inclusions, such as chopped fibres, whiskers, or particulates.[3]

Moreover, since most of the properties of glass–ceramic reinforced composites are widely affected by both the fabrication technique and the interface between fibre and matrix, different forming techniques and sintering conditions should be tested for each matrix-reinforcement combination.

In this paper, a new glass–ceramic composition is investigated as a matrix for alumina fibre-reinforced composites. The parent glass chemical composition is that of a CMAS glass with 5 mol% of BaO substituted for CaO.[4] The linear thermal expansion coefficient of the matrix is $\alpha = 7{\cdot}2 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ and that of the alumina fibres used as reinforcements is $\alpha = 5{\cdot}7 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$, satisfying the aforementioned condition. The viscosity of this glassy composition is such that composites with a high degree of densification are produced by the tape-casting technique.[5]

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The reactivity at the glass–ceramic/Al_2O_3 chopped fibre interface has been investigated with reference to different heating cycles.

2 Experimental

A glass with the composition (mol%) 50 SiO_2, 5 Al_2O_3, 20 MgO, 20 CaO and 5 BaO, was wet ball-milled in water using alumina-sintered balls to a powder of less than 50 μm in size. SAFFIL-RF ceramic grade Al_2O_3 chopped fibres, 200 μm long and 3 μm in diameter, were added to the glass in the proportion of 20 wt%. To avoid the breaking of the fibres the mixture was homogenized in acetone by light blending in a polyethylene container for 30 minutes. The dried powder was then mixed with 8 wt% poly(vinylbutyral) (PVB) and blended with 40 wt% of acetone to obtain a slurry of the proper density to be layered on a flat plane with doctor blade equipment.

The tape was cut into pieces of approximately 50 mm × 100 mm to make 6-mm thick plies, which were pressed at 13 MPa at a temperature of 130°C.

Sintering of both glass and composite materials was carried out in air in an electric furnace at different temperatures, ranging from 800 to 1000°C. Two different heating rates were used in order to better evaluate the sintering process: a slow cycle, with a burn-out 1 h soak at 350°C (Fig. 1), and a rapid cycle without burn-out (Fig. 2). In both cases no defects due to the decomposition of the organic matter were observed.

The linear shrinkage and the apparent density (with mercury immersion method) were measured for all the samples.

The crystallization process of the glass–ceramic matrix and the composites' microstructure were studied by X-ray diffraction analysis (Philips PW1050) and scanning electron microscopy (Philips PSEM500), respectively.

The pore size distribution and the average pore radius of the better densified composite samples were determined by mercury porosimetric measurements (Carlo Erba 2000).

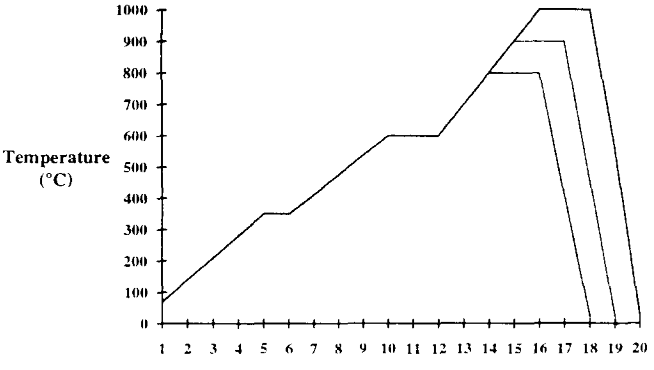

Fig. 1. Sintering schedule of the slow cycle.

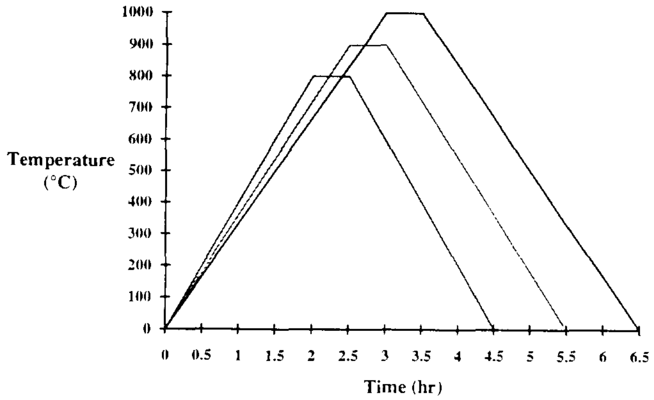

Fig. 2. Sintering schedule of the rapid cycle.

3 Results and Discussion

The sintering behaviour, that is to say densification and linear shrinkage, of the simple glass–ceramic matrix as a function of sintering maximum temperature and heating rate is shown in Fig. 3. The curves have a maximum at 900°C, after which the matrix expands, causing a swelling and a density decrease and a linear shrinkage decrease. The highest density values were found in the sample prepared at the slower heating rate. The difference in density between samples prepared with the slow cycle and those sintered with the fast cycle is about 7% at 900°C.

The XRD patterns from the polished surface of glass–ceramics crystallized in fast and slow cycles are shown in Figs 4 and 5, respectively. This CMAS composition crystallizes with different crystalline phases: diopside (JCPDS file no. 11-654) hexacelsian (JCPDS file no. 12-726) and celsian (JCPDS file no. 38-1450) starting from 900°C.[4] The crystallization process cannot be considered completed even at 1000°C, when the fast heating rate is used. The residual glassy phase, evaluated by the Ohlberg method, is about 40 vol.% for the slow cycle and 60 vol.% for the fast cycle.[6]

When 20 wt% Al_2O_3 fibres were added the sintering behaviour of the composite was similar to that of the parent glass (Fig. 6); the density at the maximum densification temperature of 900°C was a little lower (4%) than that of the simple matrix.

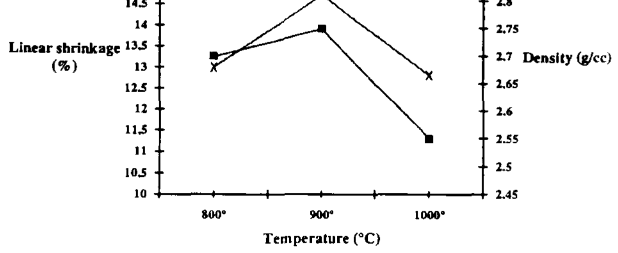

Fig. 3. Densification and shrinkage behaviour of CMAS glass–ceramic matrix. ▲, Linear shrinkage; ×, linear shrinkage (rapid cycle); ◆, density; ■, density (rapid cycle).

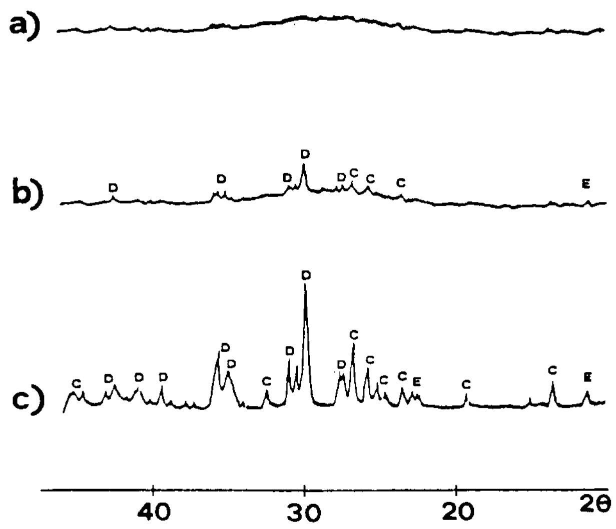

Fig. 4. XRD patterns of the polished surface of the CMAS glass ceramic matrix sintered with the rapid cycle: (a) 800°C, (b) 900°C, (c) 1000°C; D, diopside; C, celsian; E, hexacelsian.

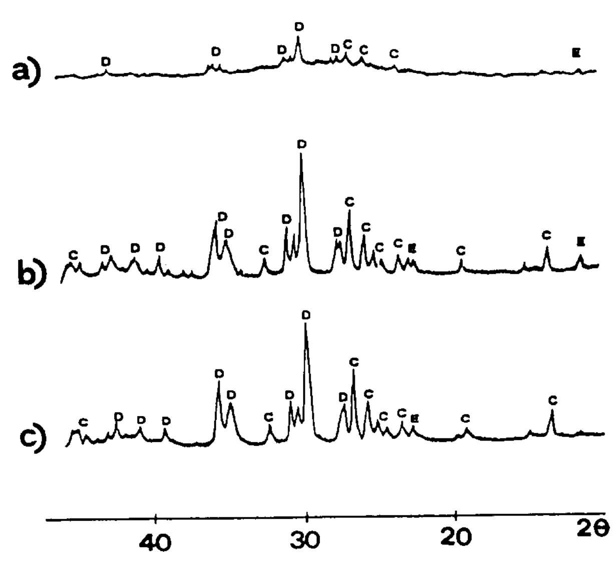

Fig. 5. XRD patterns of the polished surface of the CMAS glass–ceramic matrix sintered with the slow cycle: (a) 800°C, (b) 900°C, (c) 1000°C; D, diopside; C, celsian; E, hexacelsian.

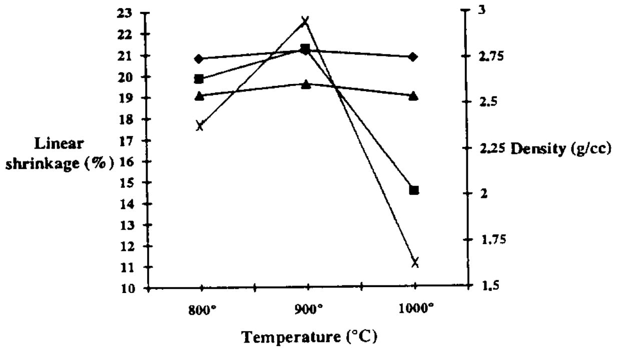

Fig. 6. Densification and shrinkage behaviour of composites. ▲, Linear shrinkage; ×, linear shrinkage (rapid cycle); ◆, density; ■, density (rapid cycle).

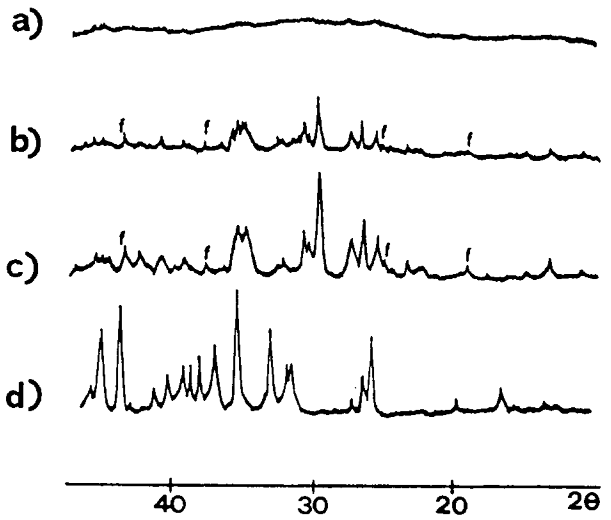

Fig. 7. XRD patterns of the polished surface of the composites sintered with the rapid cycle: (a) 800°C, (b) 900°C, (c) 1000°C; and (d) of reinforcement f, Al_2O_3 fibre.

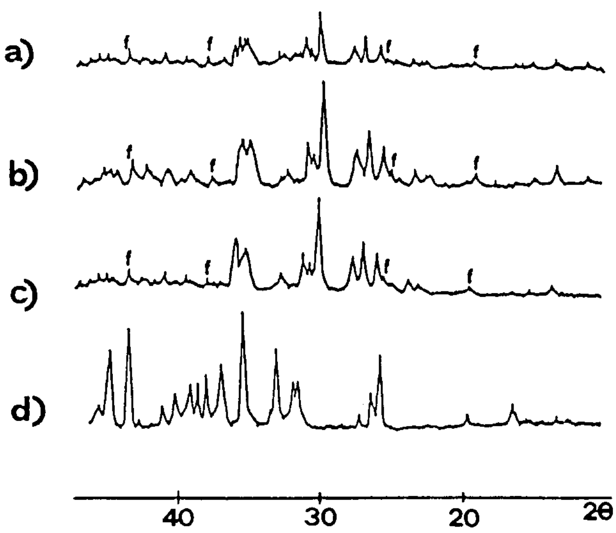

Fig. 8. XRD patterns of the polished surface of the composite sintered with the slow cycle: (a) 800°C, (b) 900°C, (c) 1000°C; and (d) of reinforcement f, Al_2O_3 fibre.

The crystallization of the polished surface of the composites has been investigated by XRD, and is shown in Figs 7 and 8, for the fast and the slow heating rate cycles, respectively. The crystalline phases are those characteristic of the glass–ceramic matrices, with some peaks due to the presence of Al_2O_3 fibres: α-alumina (JCPDS file no. 10-173), γ-alumina (JCPDS file no. 10-425) and mullite (JCPDS file no. 15-776). No new phases have been found in the composites. The percentage of residual glass in the composite is similar to that obtained for the simple matrix.

In order to better analyse the effect of the sintering cycles on composite microstructure the densified materials obtained with both cycles were tested in a mercury porosimeter. The distribution of the pore diameter is similar in the two cases (Fig. 9), but a slight difference is recorded in the total cumulative volume (TCV) values, which are 48·9 and 46·7 mm^3/g, and the total sample porosity (TSP) values, which are 13·7% and 12·9%, for fast and slow cycles, respectively. Even these measurements prove that the slowest cycle leads to better densified materials.

SEM micrographs of the polished surface of the

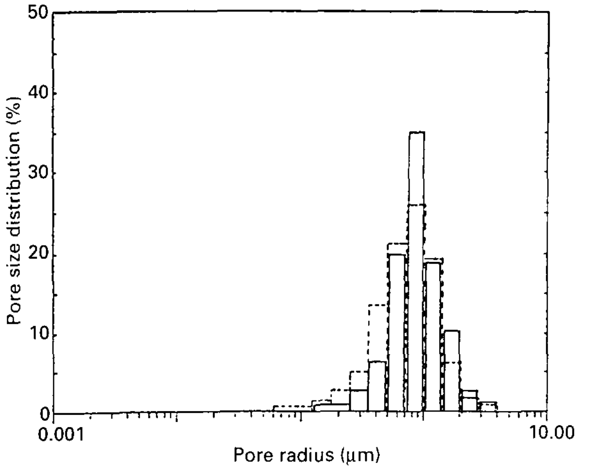

Fig. 9. Distribution of the pore diameter in the composites heated at 900°C; ——, rapid cycle; -------, slow cycle.

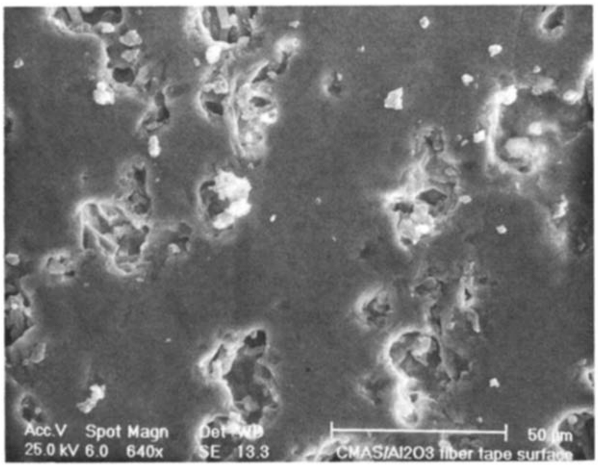

Fig. 10. SEM micrograph of the polished surface (640 ×) of the composite obtained with the slow cycle at 900°C.

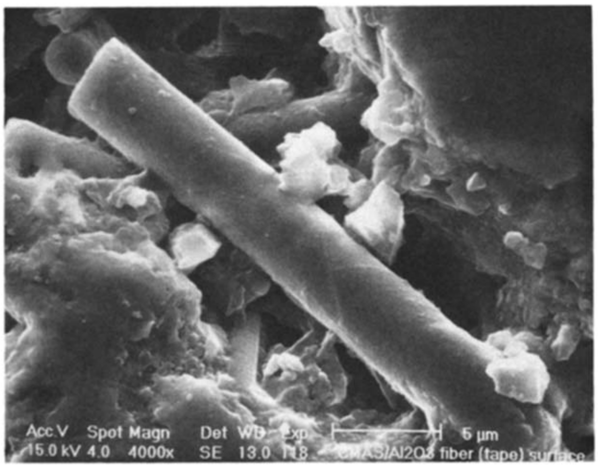

Fig. 11. SEM micrograph of the polished surface (4000 ×) of the composite obtained with the slow cycle at 900°C: particular of the fibres.

composite obtained with the slow cycle at 9000°C and of the fibres are given in Figs 10 and 11. The morphology observed is that of a glass sintered in presence of fibres and then crystallized: the pore distribution and size indicate a compaction similar to that of a composite obtained by other fabrication techniques and densified by glass sintering and devitrification.[7,8] A good orientation of the fibres was observed.

4 Conclusions

The pressing of tape-cast composite materials and sintering at a slow heating rate has proved to be a good technique for fabricating dense bodies with a porosity of about 13% and a mean pore radius of 0·8 μm. The highest densification stage of the matrix, reached at 900°C, is not retarded by the presence of 20 wt% alumina chopped fibre.

Due to the high densification reached by tape casting, the matrix crystallization, recorded at 975°C from DTA on unpressed glassy powder, has been anticipated at 800°C when prepared by tape casting, even when alumina fibres are added. The crystalline phases remain those due to the matrix or to the fibres, while no new crystalline phase is formed at the interface.

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