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Film blowing of ceramics

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Thin, flat, sintered ceramic sheets of thicknesses down to 50 μm were made by the tubular film blowing of a suspension consisting of 50 vol % alumina powder. This represents the transfer of a well-established method for the manufacture of thermoplastic polymer films to the engineering ceramics arena.

1. Introduction

The procedures that are currently used for the manufacture of thin ceramic sheet are drawn from polymer processing. They include calendering and solvent casting, which has been renamed "tape casting" by the ceramics industry. The products of these technologies find application *inter alia*, in thick-film circuits, multilayer ceramic devices and fuel cells. It is the purpose of this work to transfer another polymer processing method, that of tubular film blowing, to the ceramics arena.

The first commercial cellulosic plastic, cellulose nitrate, became available in 1833 and because of its flammability and its tendency to decompose excessively in melt processing it was fabricated by solvent casting [1]. Polyvinyl chloride and its copolymers are also sometimes manufactured by solvent casting but the process is expensive, there is an explosion hazard and a necessity to handle and recover solvent vapour [2, 3]. It is not anticipated that the process will see growing application in the future [3].

In solvent casting, the polymer solution is poured on to a moving endless belt which passes into an oven where temperatures are controlled to prevent bubbling and the solvent is recovered [2]. If ceramic powder is incorporated into this mixture the film can be pyrolysed and sintered to produce ceramic wafers [4]. Tape casting of ceramics suffers the same disadvantages as the solvent casting of polymers in addition to difficulties of controlling the suspension viscosity.

Blown tubular film extrusion emerged in 1949 as a means of mass producing polymer film for packaging. In recent years, 300 000 tonnes per annum of low-density polyethylene are produced by this method ([2] p. 4). It is a process that involves extremely large extensional strains and, therefore, presents considerable problems for ceramic manufacturing. However, previous work has shown how extensional flow processes can be used to achieve vacuum forming [5] and blow moulding [6, 7] of ceramic suspensions. The resulting particle assemblies can be sintered to produce intricate shapes in thin-walled ceramic structures. A particular advantage of these processes is that the removal of the organic vehicle which fills interparticle space is less problematic than is the case in ceramic injection moulding where thicker components are made [8]. Another advantage is that high initial ceramic volume fractions can be used. In ceramic tape casting, large amounts of solvent are needed to keep the suspension viscosity low. Substantial shrinkage then occurs before the firing as the tape dries. This results in shrinkage cracks and deformation.

In the present work, a ceramic–polymer composite based on polystyrene, similar to those used for vacuum forming and blow moulding [5, 7], was employed. The experimental arrangement was a grossly simplified version of the apparatus conventionally used for tubular film blowing of polymers. The work is therefore an investigation of the feasibility of the process and does not demonstrate perfection, but the fact that it was successful in producing ceramic wafers of a minimum of 50 μm thickness after sintering on the first attempt, is an indication that this method has a promising future.

2. Experimental details

2.1. Materials

The alumina powder was grade RA6 kindly donated by Alcan Chemicals (Gerrards Cross, UK). It has a mean particle size of 0.9 μm. The polystyrene was grade HF555 from BP Chemicals (Grangemouth, UK), and the diluent was a trimellitate ester, grade Hexaplas OTM supplied by ICI Chemicals and Polymers (Middlesbrough, UK); stearic acid was obtained from BDH Chemicals (Poole, UK).

2.2. Compounding

The mixture was compounded by twin-screw extrusion using a Betol TS40 machine (Luton, UK) with a screw speed of 60 r.p.m. and a temperature profile of 170–180–190–200 °C feed to exit. The machine was starve fed and the extrudate was water cooled, dried under vacuum at 40 °C for 24 h before being granulated and re-extruded under the same conditions. The second extrusion was done to eliminate slight variations in volume loading of ceramic from beginning to end of the first pass.

The composition (Table I) was checked by loss on ignition up to 650 °C in air and gave 79.43 wt %

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alumina corresponding to 50.0 vol % ceramic as desired.

2.3. Tubular film blowing

A specially constructed die (Fig. 1) was fitted to a Davenport Capillary Rheometer with the gas inlet attached to a nitrogen cylinder set at 14 kPa gauge. The granulated material was dried overnight under vacuum at 40 °C and the barrel temperature was set at 120 °C, the actual temperature being 117.2 °C. A period of 10 min elapsed after charging the barrel. The die temperature, which was not independently controlled, was approximately 105 °C. The extrusion rate was $7.1 \times 10^{-8} m^3 s^{-1}$.

The extruded tube was 10 mm o.d. with a 1.5 mm wall thickness. When it emerged from the die in the vertically downwards extrusion mode, it was clipped with a metal "bulldog" clip and the parison was inflated with manual gas control.

2.4. Binder removal and sintering

Several methods were used to flatten and pyrolyse the film; they are discussed below. The most successful method was to sandwich the film between layers of paper (Whatman hardened ashless, W and R Balston, UK) stacked between two 115 mm × 115 mm × 1 mm alumina plates (Vesuvius Zyalon, Tonyrefail, Glamorgan, UK). This arrangement was heated at 2 °C h^{-1} to 200 °C and furnace cooled. The paper was then removed by soaking in distilled water with a few drops of surfactant (Ilftol, Ilford, Cheshire, UK). The film was fired to 1600 °C on alumina tiles lightly dusted with LG20 grade alumina powder (Alcan Chemicals, Gerrards Cross, UK). The heating schedule is shown in Fig. 2.

An initial presintering of 10 min at 1600 °C was employed. Some films were sintered for 2 h at 1600 °C. A Cambridge stereoscan S250 electron microscope was used for observation of the film after mounting in an araldite resin and polishing, or as fracture surfaces.

TABLE I Composition of ceramic–polymer suspension

Materials	(wt %)
Alumina powder	79.43
Polystyrene	14.40
Trimellitate ester	4.11
Stearic acid	2.06

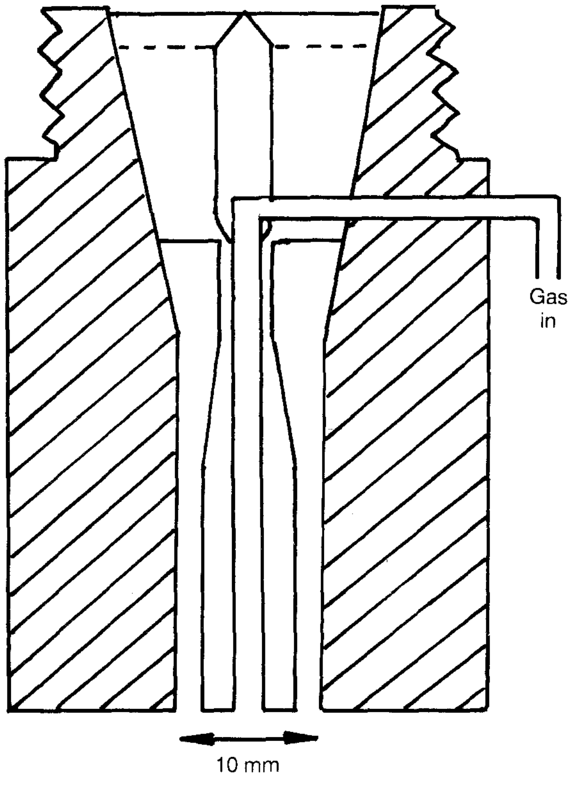

Figure 1 Schematic diagram of the die used for tubular film blowing.

3. Results and discussion

3.1. Tubular film blowing

The ceramic volume loading selected for this work is conservative for a powder which can be injection moulded at 60 vol %. The caution is attributable to the requirement of achieving high extension prior to melt fracture. The importance of uniformity of volume loading has been discussed before [5] and arises because of the strong volume loading-dependence of viscosity of crowded suspensions. In the present context, this is essential for the achievement of uniform film thickness. For this reason, two passes of the twin-screw compounding extruder were used.

Fig. 3 shows the first blown films that were produced by the method described above. The blow-up ratio (BUR) is defined as the ratio of final to initial tube diameter. The average BUR was 5.8 and the maximum was 6.3. To compare this with polymer film blowing, a B45 Samafor small-scale production machine with a 4.5 m tower and 75 mm diameter annular die operates with a BUR of 6, although larger production machines may exceed this.

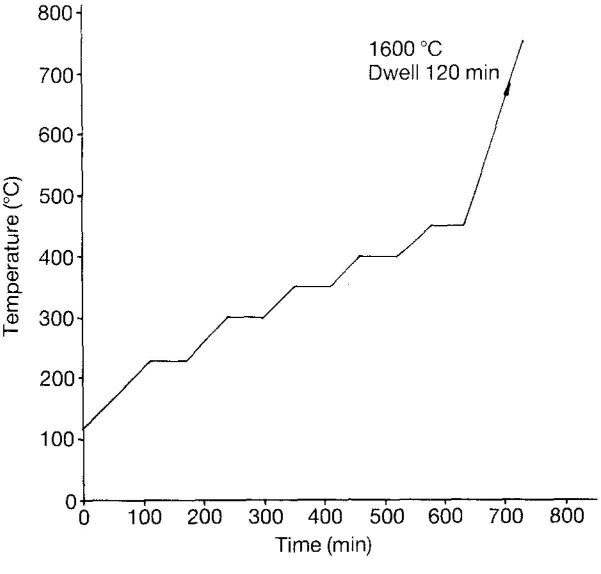

Figure 2 Heating schedule for pyrolysis and sintering.

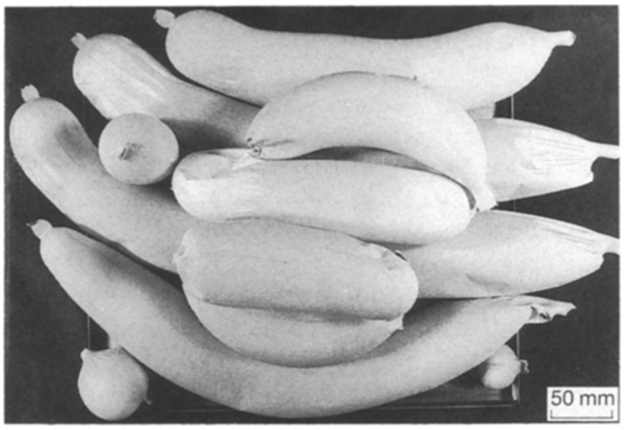

Figure 3 The first film-blown tubes.

The limit on the blow-up ratio is set by melt fracture of the film and also by a crazing phenomenon witnessed at film thickness of less than approximately 50 μm. The film becomes whitish, suggestive of particle–matrix separation. However, this effect appears to be the result of imposing high extensions when the film has left the die and is chilled.

Fig. 3 shows that the initial tubes are not straight. This arises because of slight misalignment of the core. It illustrates the precision that is needed if the film is to be pressed flat after blowing. This also means that the variation in wall thickness around a section is artificially large. Thus for film of about 115 μm thickness before firing, the 95% confidence limits for thickness fell between 10 and 17 μm. This is obviously not inherent in the process. The 95% confidence limits from measurements in the longitudinal direction were 7 μm and the variability here results from manual gas control.

The strain in the circumferential direction is given by

$$\begin{aligned} \varepsilon_\theta &= \frac{r'_0}{r_0} - 1 \\ &= \mathrm{BUR} - 1 \qquad (1) \end{aligned}$$

where the subscript indicates the outside radius and the prime distinguishes the blown condition. Conservation of volume indicates that the longitudinal strain is given by

$$\varepsilon_{\mathrm{L}} = \frac{\bar{r}t}{\bar{r}'t'} - 1 \qquad (2)$$

where $\bar{r}$ is the average of the internal and external radii and t is the wall thickness. While the average value of ε_θ was 4.8, the average of ε_{L} was zero. The longitudinal strain caused by the weight of the extrudate in the downward film blowing process is negligible. This means that the process involves strip-biaxial stretching, also known as planar elongational flow, immediately after the fluid leaves the die.

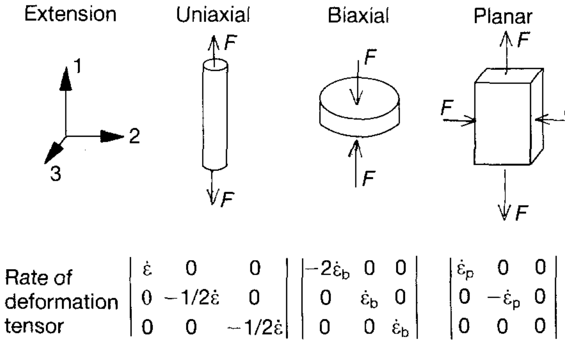

Figure 4 Geometry of elongational flow modes and their rate of deformation tensors.

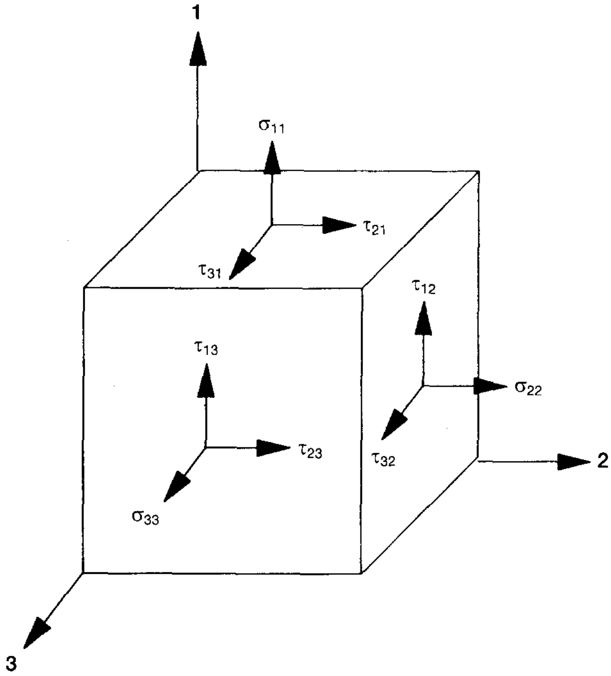

Figure 5 Stresses acting on an elemental cube.

The three modes of elongational deformation are uniaxial, biaxial and planar (pure shear) flow (Fig. 4). The deformation of the material can be described in terms of a Cartesian coordinate system (Fig. 5) using axes orientated such that they coincide with the principal directions of the strain-rate tensor

$$\dot{\varepsilon} = \begin{vmatrix} \dot{\varepsilon}_{11} & 0 & 0 \\ 0 & \dot{\varepsilon}_{22} & 0 \\ 0 & 0 & \dot{\varepsilon}_{33} \end{vmatrix} \qquad (3)$$

In uniaxial flow, the material is stretched in one principal direction, ε_{11}, and contracts in the remaining two. In biaxial flow the rate of strain is equal in two orthogonal directions and the material contracts in the third. In planar flow, the strain is restricted in the x_3 direction while the material is elongated in the x_1 direction and contracts in the x_2 direction. A summary of the rate of deformation tensors is shown in Fig. 4.

In polymer film blowing practice, the haul-off speed is regulated to give a longitudinal strain so that polymer orientation can be controlled and this gives a biaxial mode of deformation.

Gas control was manual and this limited consistency of thickness in the longitudinal direction. In the circumferential direction, the thickness uniformity is sensitive to die alignment. In polymer film blowing, a steady state is reached because the film is folded on

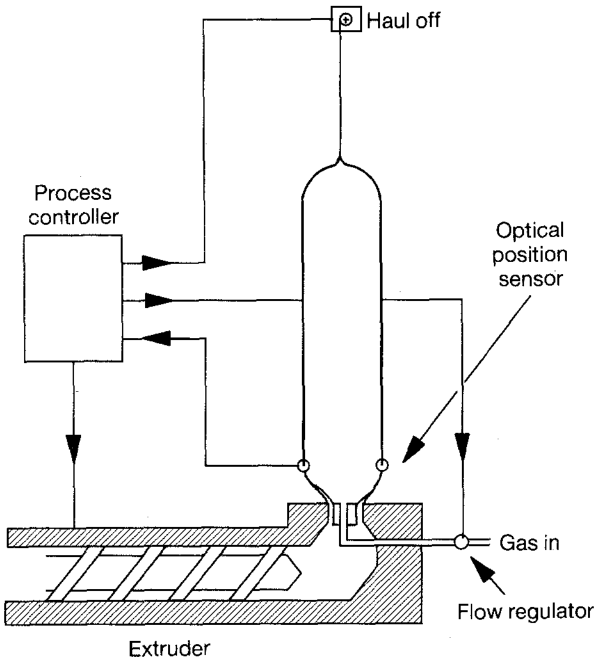

Figure 6 Proposed three-channel process control mode with vertical upwards extrusion.

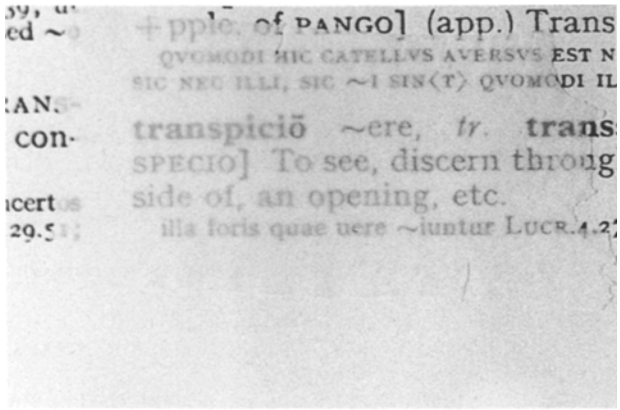

Figure 7 Translucent partially sintered alumina film of thickness 50 μm.

to take-up rollers and the bubble is trapped. This is not possible in ceramic tubular film blowing because the film would fracture when chilled. A simple three-channel process control system would be needed to achieve exact control and the authors would recommend a vertical upwards extrusion mode (Fig. 6).

3.2. Pyrolysis and sintering

The film was easily cut with a pair of scissors but difficulty was experienced in obtaining flatness. Heating the film to 60 °C on a tile caused shrinkage and wrinkling probably due to the relaxation of polymer orientation. Flatness could not be obtained when the film was placed on a powder bed with powder on top and heated to 60 °C. The film was placed between two alumina tiles, pyrolysed to 450 °C at 2 °C hr^{-1} in nitrogen and sintered to 1600 °C. It adhered to the tiles, shrinkage was prevented and tearing ensued.

Flat, sintered film was obtained by the method described in Section 2.4. After heating to 200 °C between paper, the film was flat but could still be separated without fracture by immersion in water. It was then placed on an alumina tile which had been lightly dusted with alumina powder and partially sintered at 1600 °C. Fig. 7 shows that despite the absence of efforts to maintain high purity or to employ special sintering conditions, the partially sintered film is translucent at thicknesses of 50 μm.

Fig. 8 shows a polished section of film displaying three types of defect. There are several large pores which, because they show no signs of elongation and have caused local bloating, have occurred during pyrolysis of the binder. They may be caused by the collection of organic impurities during mixing. Relics of undispersed agglomerates appear as rounded protrusions on the surface. Indeed film blowing offers an effective and quantifiable method for the detection of residual agglomerates. The measurement of shear stress during mixing followed by assessment of dispersion by the back-scattered electron image technique has shown that applied shear stress should be five to ten times the agglomerate strength in order to promote dispersion [9].

Fig. 8 also shows lack of flatness. This is dependent on technique, although the selection of paper for stacking also plays a part. The ashless filter paper used is extremely coarse (Fig. 9) on a scale compatible to film thickness. It may not, therefore, be ideal; however, finer papers of writing quality showed staining from the transfer of diluent from the suspension and could

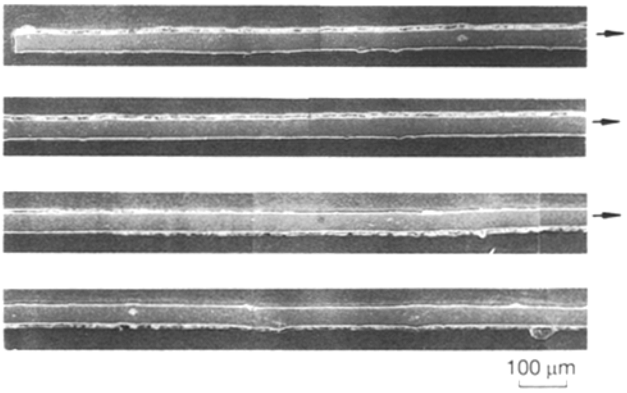

Figure 8 Polished sections of sintered film – blown alumina of thickness approximately 50 μm (zero tilt). Three defect types are shown; large pores, agglomerate relics and deviation from flatness.

Figure 9 Scanning electron micrograph of the ashless filter paper used to stack and press film before pyrolysis.

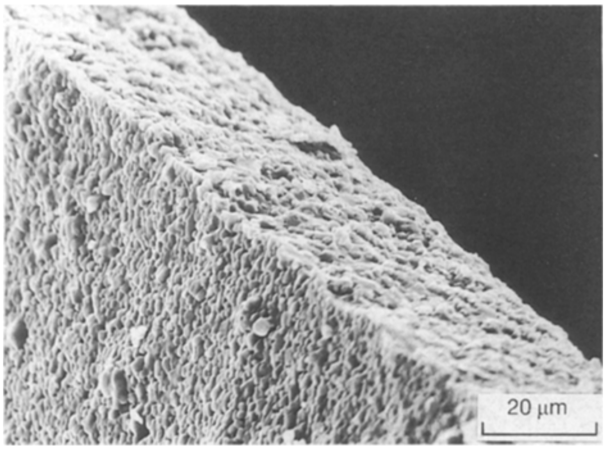

Figure 10 Fracture surface of sintered alumina film.

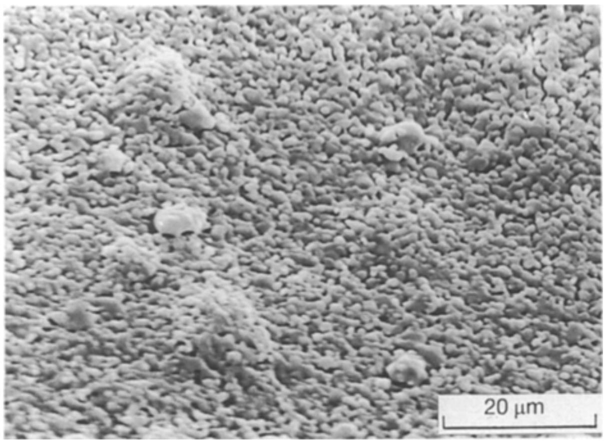

Figure 11 As-sintered surface of alumina film showing relics of undispersed agglomerates.

not be removed after pressing at up to 200 °C. The mineral content of paper, in addition to fibre size and packing also restricts selection for high-purity alumina applications.

When the film was sintered for 2 h at 1600 °C it adhered strongly to the supporting powder and to the alumina tiles. Fig. 10 shows a fracture surface of the material sintered for 2 h. It retains a surprising degree of apparent porosity but no attempt was made to measure apparent density. The incomplete removal of organic vehicle at heating rates of 3 °C min^{-1} has been held responsible for low sintered density in ZrO_2 ceramic [10] but the restriction on sintering could also be due to the restraint of the surrounding powder to which the film was firmly attached and which shows limited shrinkage itself. The sintered surface of the film is shown in Fig. 11. The relics of undispersed agglomerates are clearly seen at the surface.

4. Conclusions

An initial laboratory-scale process for the film blowing ceramic suspensions was successful. The film can be flattened, pyrolysed and sintered to produce ceramic film down to 50 µm thickness. The partially sintered film is translucent without taking any special precautions on powder, purity or sintering conditions. Considerable scope for improvement and automation of the process can be identified. The process avoids many of the operational difficulties and solvent hazards of tape casting.

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References

1. C. G. CHANDLER, in “Basic Principles of Thermoforming”, edited by P. F. Bruins (Gordon Breach, New York, 1973) pp. 223–40.
2. J. H. BRISTON, “Plastic Films”, 2nd Edn (Goodwin/P.R.I., New York, 1983) pp. 81–2.
3. Radion Corporation, “Plastic Processing”, Noyes Data Corporation, NJ (1986) pp. 50–2.
4. E. P. HYATT, *Bull. Am. Ceram. Soc.* **65** (1986) 637.
5. K. M. HAUNTON, J. K. WRIGHT and J. R. G. EVANS, *Br. Ceram. Trans. J.* **89** (1990) 53.
6. K. KOBAYISHI, M. FURUTA and Y. MAENO, Eur. Pat 0034056, 19th August 1981.
7. P. HAMMOND and J. R. G. EVANS, *J. Mater. Sci. Lett.* **10** (1991) 294.
8. J. R. G. EVANS, M. J. EDIRISINGHE, J. K. WRIGHT and J. CRANK, *Proc. R. Soc. A* **432** (1991) 321.
9. J. H. SONG and J. R. G. EVANS, *J. Euro. Ceram. Soc.*, in press.
10. J. WANG, *J. Am. Ceram. Soc.* **75** (1992) 2627.

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