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Expanded ceramic foam

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A method for manufacturing low-density ceramic foam by applying the procedures used for expanded polystyrene is described. Alumina powder was incorporated into polystyrene at 50 vol % by high shear mixing and the pelletized product was immersed in pentane. Low-density foam mouldings were then produced by single-stage steam treatment. These mouldings retained their shape during pyrolysis of the polystyrene. The foams were then sintered to give a porous ceramic with a void content of about 84%. This process offers an inexpensive route for the manufacture of moulded porous ceramics, for example in refractory applications, and is expected to be able to serve a wide range of high-performance ceramic powders.

1. Introduction

Porous ceramics are used in exhaust filters, molten metal filtration, catalyst supports, refractories and lightweight structures [1]. Ceramic foams are made by immersion of a polymeric open cell foam in a ceramic slurry such that the internal surfaces are coated. The porous ceramic results from pyrolysis of the organic matter and sintering [2]. Alternatively, an aqueous polyurethane suspension can be foamed [3]. Other methods include the foaming of a conventional polyol-isocyanate mixture in which ceramic particles are suspended [4], the use of fugitive porosifiers and the foaming of aqueous suspensions with gases [2].

Large quantities of polystyrene are expanded using blowing agents such as pentane to produce foams for use in thermal insulation and packaging [5]. The main mode of deformation is biaxial elongational flow. Previous work has shown that polymer–ceramic suspensions can be subjected to this mode of deformation to give blow-moulded [6], vacuum-formed [7] and tubular film-blown [8] ceramic components. In these processes, the polymeric vehicle is expelled by controlled thermolysis before sintering the assembly of ceramic particles.

There is an intuitive objection to applying this technique to ceramic foam manufacture. During reheating to expel the organic vehicle it might reasonably be anticipated that the foam would collapse. The driving forces for collapse are the entropic relaxation of chain-extended molecules and the reduction in excess surface energy. The surprising result of this work is that such foams do not collapse but retain most of their macropore fraction after sintering.

The procedures for preparing polystyrene foams have been reviewed by Ingram and Fogel [5], Ferringo [9], Benning [10] and Suh [11]. Suitable low boiling point organic liquids for use as blowing agents have been discussed by Ferringo [9] and include paraffins C_5–C_7, of which *n*- or *iso*-pentane are commonly used. It is suggested that expandable polystyrene does not accept high concentrations of colouring pigments and that plasticizers such as phthalate esters are sometimes added to compensate for such additions.

Commercially, a two-stage foaming process is employed in which steam, radiant heat or hot air prefoamers are used to pre-expand polystyrene beads. The pre-expanded beads are then conditioned to allow air to be established as the cell gas. In the conventional manufacture of mouldings, the pre-expanded beads are introduced into a steam chest mould in which superheated steam completes the expansion and fuses the beads into a shape [9]. Prefoaming is essential if uniform low density is required but appropriate equipment was not available in the present work which instead used a single-stage expansion.

The blowing agent can be incorporated into polystyrene granules by immersion in the liquid or vapour phase and uptakes are typically 6.3–7.3 wt %. The upper limit is 7.5 wt % based on a free volume in the polystyrene of 14% on the assumption that the pentane occupies existing intermolecular spaces in the matrix rather than inducing swelling [5]. The microstructure of such foams is illustrated by Ingram and co-workers [5, 12].

2. Experimental procedure

The alumina was grade A16SG from Alcoa GB Ltd (Droitwich, UK). This has a particle size in the 0.3–0.5 μm region and a specific surface area of 9.5 $m^2 g^{-1}$. The polystyrene was grade HF555 from BP Chemicals (Grangemouth, UK) and the stearic acid was grade GPR from BDH-Merck (Lutterworth, UK).

The planned composition contained 79.1 wt % alumina (density 3987 $kg m^{-3}$), 18.8 wt % polystyrene (density 1065 $kg m^{-3}$) and 2.1 wt % stearic acid (density 941 $kg m^{-3}$) giving 50 vol % ceramic. It was mixed on a twin-roll mill (J. Robinson and Co. Ltd, Manchester, UK) for 15 min with oil heating set at

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170 °C. The mixture was removed from the rolls and re-fed four times to ensure lateral mixing. The exact ceramic content was obtained from loss on ignition.

The solid ceramic suspension was granulated on a machine (Cumberland ex USI Eng., Warrington, UK) fitted with a 9 mm sieve and fines were removed by allowing them to pass a 16 mesh sieve thus removing particles <1.5 mm diameter. The ceramic–polymer granules and as-received granules of unfilled polystyrene, employed as a comparison, were stored under *n*-pentane at room temperature for a minimum period of 50 days before a single-stage expansion and moulding in steam at 100 °C. The expansion was carried out in high-density polyethylene (HDPE) moulds made from microscope sample mounting pots with a 6 mm steam entry hole and five 3 mm outlets on the opposite face. Granules were placed in these moulds within 30 s of removal from the pentane and steam was admitted.

The expanded ceramic–polymer foam was heated in air or in oxygen-free nitrogen at 5 °C h^{-1} to 450 °C. It was furnace cooled to room temperature and then sintered at 1600 °C for 2 h after heating at 5 °C min^{-1}. The density of the sintered foam was measured by mercury immersion (Doulton Industrial Products, Stone, UK) and, in the case of mouldings which formed complete cylinders, checked from the dimensions of weighed samples.

3. Results and discussion

3.1. Foam expansion

The alumina is a fine submicrometre-sized powder which is representative of the particle size and size distribution of modern ceramic powders suitable for engineering components. Polystyrene was selected as the organic vehicle because the foaming process has been well established with polystyrene for non-chlorofluorocarbon blowing agents such as pentane. Stearic acid was added to assist in the mixing process.

The ceramic volume fraction was selected according to the following guidelines. The maximum packing fraction for which viscosity approaches infinity, deduced from apparent viscosity measurements, is approximately 73% for this powder in a polymeric vehicle [13]. In processes which rely mainly on shear flow, such as injection moulding, the maximum ceramic volume fraction is about 0.60. For processes that require high elongational strains the ceramic volume fraction needs to be 5–10 vol % lower than this value [8]. Loss on ignition indicated that the actual ceramic volume fraction after mixing was 0.516.

Initial experiments showed that individual pellets of this mixture, which had been immersed in pentane, expanded when placed in water at 90–100 °C. Satisfactory expansion was obtained after immersion times of 100 h at room temperature. Preliminary experiments using a composition which contained a phthalate diluent and hence presented a lower glass transition temperature, T_g, did not blow uniformly and tended to collapse quickly, so such compositions were abandoned.

Because a single-stage expansion was used to prepare mouldings rather than the more complex two-stage process employed commercially, the maximum possible voidage was not attained. This is reflected in the high measured density for the unfilled polystyrene reported below. Similarly, steam at 100 °C was used rather than superheated steam which is used commercially. The method of foaming was insufficiently sophisticated to ensure uniform expansion, throughout the mould and, in some cases, the expanding foam blocked the steam exit ports in the mould. The foaming technique also prevented complete granule adhesion seen in commercially made expanded polystyrene. However, despite imperfect technique, high-voidage mouldings were made and the resistance to collapse, as well as the resulting microstructure, could be studied.

In order to observe the resistance to collapse on reheating, identical mouldings of unfilled polystyrene and polystyrene–50% alumina were placed on an alumina tile and heated in a glass-fronted oven. Once the T_g for polystyrene was passed, the polystyrene moulding began to expand (Fig. 1a) as a result of residual pentane, air and steam that had entered the cells by that time under their own partial pressures [5]. This confirms that the single-stage expansion did not develop full porosity. The ceramic–polystyrene moulding, on the other hand, showed no dilation. Fig. 1b shows the situation at 147 °C. The polystyrene moulding had, by this stage, substantially collapsed. The ceramic–polystyrene mould still remained unchanged.

There are two driving forces for collapse of the thermoplastic foam: the relaxation of chain-extended molecules which result from deformation near T_g and the reduction in surface excess free energy by pore shrinkage.

The implication is that the filled polystyrene has a yield stress for elongational flow which is sufficiently low to allow the initial expansion but sufficiently high to resist collapse under these two driving forces. It is therefore likely to be strongly dependent on ceramic volume fraction, the optimum value of which may be unique for each powder.

Failure to collapse raises some interesting questions about the molecular conformation adjacent to the high-energy surface of filler particles. Adsorbed layer thicknesses are generally of the same order as the random coil dimensions for solution studies and, for high molecular weight polystyrene, can be up to 100 nm [14]. The situation in the melt is believed to be similar [15]. In the present work, inter-particle distances are in the 33 nm region and the possibility exists for a proportion of coils to adopt the bridge configuration with adsorption sites on two particles. Bridging molecules behave as springs with a minimum energy at an equilibrium particle spacing [16, 17]. The suspension may thus have a "structure" as a result of physical adsorption which contributes to yield stress.

The mouldings were then fully pyrolysed in air and sintered at 1600 °C for 2 h which is sufficient to bring the ceramic skeleton to nearly full density. Provided

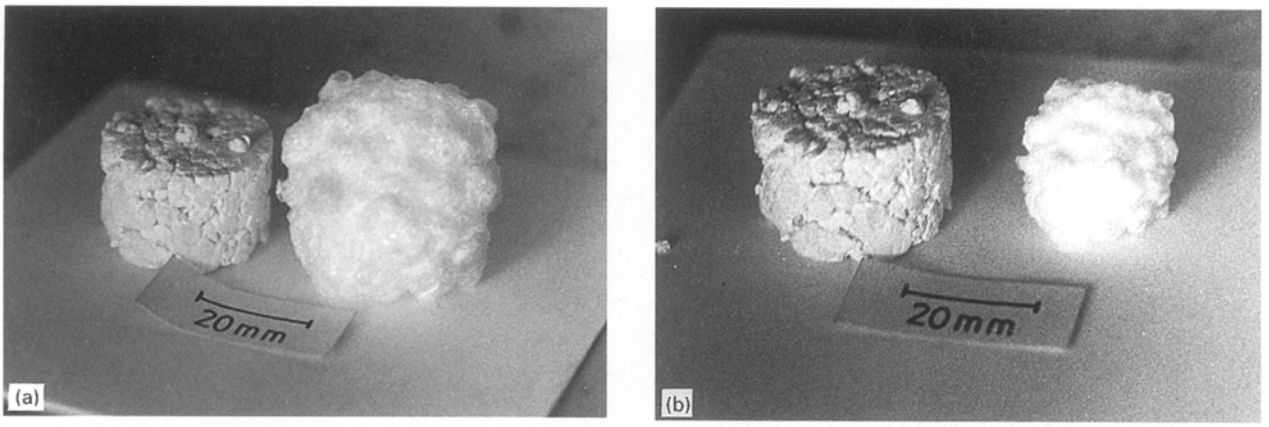


Figure 1 Expanded polystyrene (on the right) and expanded polystyrene–50 vol % alumina (on the left) mouldings at (a) 110 °C and (b) 147 °C.

the pores introduced by the blowing agent are large compared with the interparticle pores, the initial macro-porosity should be retained. Sintered mouldings are shown in Fig. 2.

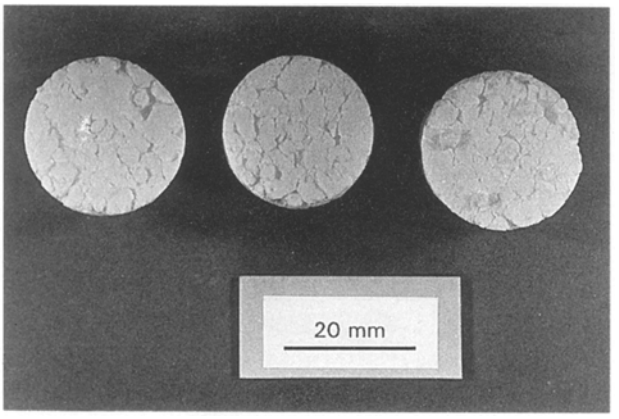


Figure 2 Sintered expanded alumina foam mouldings.

3.2. Shrinkage and density measurements

The average linear shrinkage after removal of the organic phase, measured with a travelling microscope, was 2.8 ± 0.7% (95% confidence limits). This shrinkage is related to the approach of particles as the organic matter is displaced from junctions. Interparticle distance, x_0, can be estimated from an expression deduced from ordered arrays of monodisperse spheres of diameter d_0, as [18]

$$\frac{x_0}{d_0} \approx 0.4\left(1 - \frac{V}{V_0}\right) \qquad 0 < \frac{x_0}{d_0} < 0.15 \qquad (1)$$

where V is the initial ceramic volume fraction and V_0 is the volume fraction after binder removal. The latter is always less than the maximum packing deduced from relative viscosity measurements because particles cannot rotate as they approach. The value for A16SG alumina has been found to be 0.65 [13] giving $x_0/d_0 = 0.082$ or $x_0 = 33$ nm for 0.4 μm diameter particles. During pyrolysis in air, the full shrinkage is not reached because of the non-uniform removal of the organic phase. Thus the ceramic skeleton that develops during pyrolysis inhibits shrinkage.

In previous work, binder removal in air at 50 vol % initial loading of ceramic gave a shrinkage of about 1% for a bulk sample [13]. For the foam, the structural resistance to shrinkage is expected to be less and this accounts for the higher observed shrinkage. The overall linear shrinkage from moulded to sintered states was 20.1 ± 0.7% (95% confidence limits) giving an actual linear sintering shrinkage of 17.8%. This corresponds to an overall volumetric shrinkage of 49% and a final relative density close to 100% for the ceramic skeleton which is compatible with the microstructure of the observed skeleton discussed below.

Table I shows that the macroporosity for unfilled polystyrene obtained by the expansion technique used here is significantly less than that obtained for a range of commercial expanded polystyrenes. The porosity of the ceramic–polystyrene foam mouldings was very similar to that for the unfilled polystyrene mouldings, indicating that the presence of the alumina did not inhibit expansion. The expanded beads which were unconstrained by the mould reached a higher porosity of about 90% which was largely retained during pyrolysis and sintering. The voidage of 84% obtained for the sintered expanded ceramic foam mouldings was the same as that for the unfired mouldings, confirming that collapse of the structure had not taken place to any significant extent during pyrolysis or during sintering. This porosity is comparable to that seen in low-density alumina fibre board for high-temperature refractory applications.

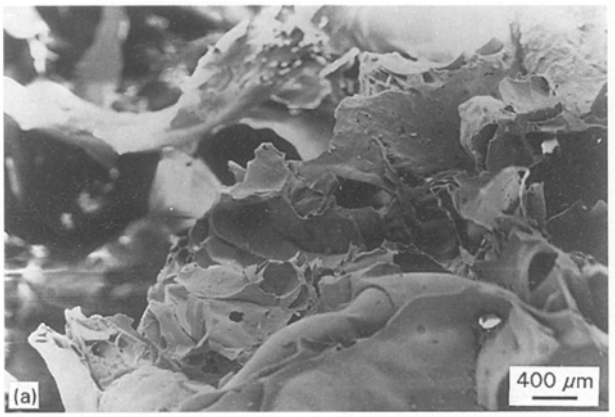
3.3. Microstructure

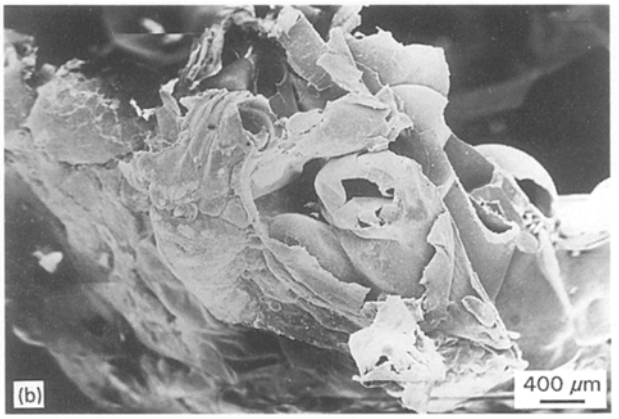
Fig. 3a shows a representative region of the disordered structure of the polystyrene foam. This is a fracture surface and therefore does not disclose the extent of closed cell porosity. The ceramic–polystyrene foam is shown in Fig. 3b and is indistinguishable from the unfilled foam, confirming that ceramic powder has not impaired the expansion process. Similarly, the final microstructure of the sintered foam (Fig. 3c) is almost indistinguishable from the filled polymer foam. The lack of a regular cell structure as seen in Ingram and co-workers' micrographs [5, 12] may be due to the

TABLE I Apparent density and porosity of foams (95% confidence limits and number of samples tested are given)

	Apparent density ($kg\,m^{-3}$)	True density ($kg\,m^{-3}$)	Porosity[a] (%)
Range of commercial PS foams	9–28	1065	97–99
Polystyrene foam mouldings (this method)	174 ± 57 (4)	1065	83.7 ± 3.4 (4)
Polystyrene–ceramic beads	226 ± 40 (8)	2566	91.2 ± 1.6 (8)
Polystyrene–ceramic mouldings	406 ± 25 (3)	2566	84.2 ± 0.9 (3)
Sintered ceramic beads	396 ± 28 (4)	3987	90.1 ± 0.7 (4)
Sintered ceramic foam	621.5 ± 97 (6)	3987	83.2 ± 2.5 (6)

[a] Calculated assuming the cell gas is air.





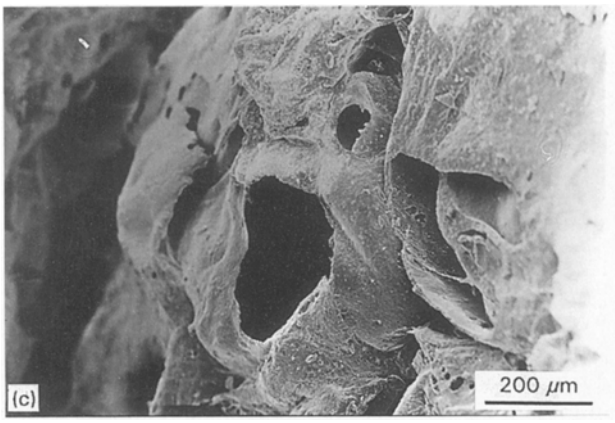


Figure 3 Microstructure of (a) expanded polystyrene, (b) expanded polystyrene–50 vol % alumina, and (c) sintered expanded ceramic foam.

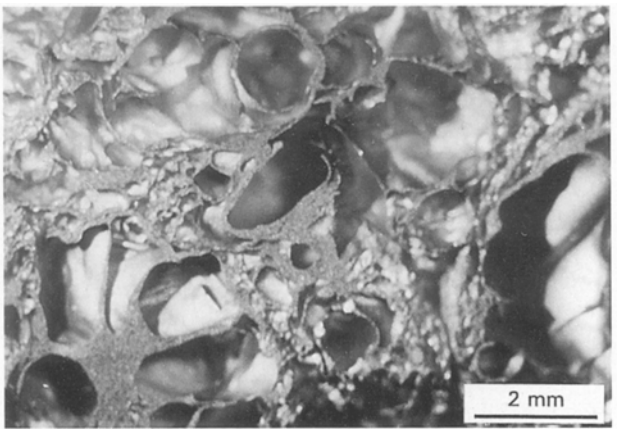


Figure 4 Optical micrograph of sintered expanded ceramic foam after polishing on silicon carbide powder (400 grade) to reveal a random section and then sputter-coated with gold to enhance reflectivity.

crude single-stage expansion and to excess blowing agent, resulting from the long sorption time employed. This is thought to cause irreparable cell damage [5]. However, optical microscopy on a sintered moulding which had been polished on silicon carbide powder to reveal a random section (Fig. 4) shows that many cell walls are largely undamaged. The structural feature highlighted in Fig. 5 is sintered alumina at nearly full density and indicates the extent to which elongational flow of a ceramic–polymer suspension can produce thin ceramic film. The wall thickness is as low as 6 μm.

3.4. Thermal properties

There was insufficient sintered foam to measure thermal conductivity with the guarded hot plate available. However, estimates can be made using the best model equations from an extensive assessment of such expressions [19]. At 84% porosity, with air as the cell gas (conductivity $0.0263\ W\,m^{-1}\,K^{-1}$), the room-temperature conduction contribution to apparent thermal conductivity of the alumina foam is predicted to be $2.5\ W\,m^{-1}\,K^{-1}$ using the method of calculation presented by Batty *et al.* [20]. Using their calculation for the radiation contribution, the room-temperature radiation transfer is insignificant. This calculation takes the conductivity of alumina as $36\ W\,m^{-1}\,K^{-1}$ at 25 °C [21].

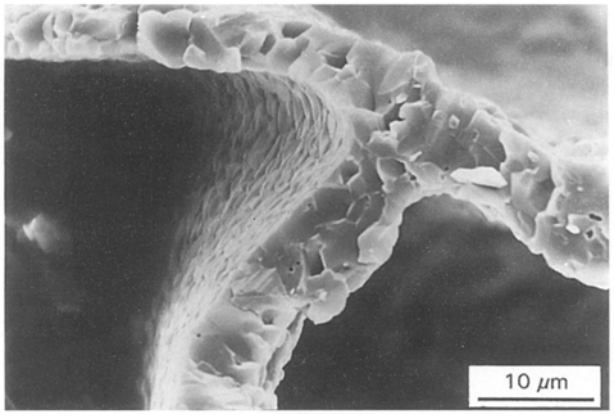


Figure 5 A structural feature of the sintered ceramic foam showing cell wall thickness as low as 6 μm.

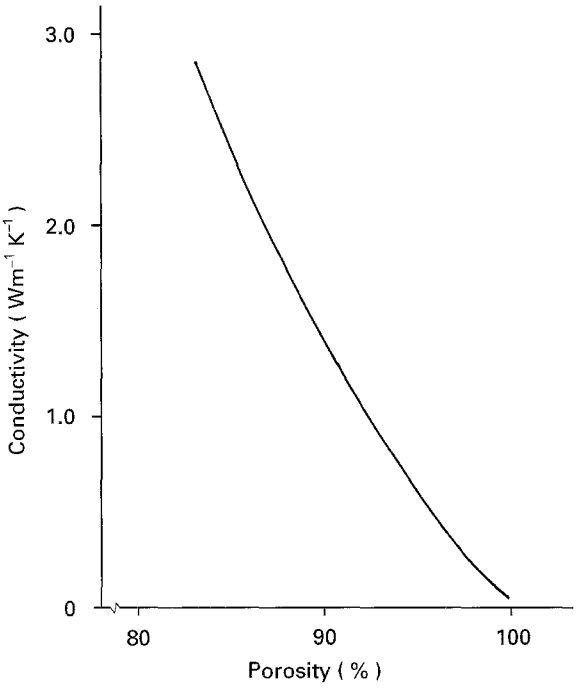


Figure 6 The relationship between conduction contribution to apparent thermal conductivity of porous alumina at 25 °C, ($k_s = 36$ W $m^{-1} K^{-1}$, $k_g = 0.0263$ W $m^{-1} K^{-1}$) deduced from Batty *et al.* [20].

If it were possible, by deploying the two-stage commercial blowing technique, to attain porosities as high as in the most dense polystyrene foams (97%), the room-temperature conductivity would be 0.3 W m^{-1} K^{-1}. Fig. 6 shows the relationship between conduction contributions to apparent thermal conductivity and porosity deduced from Batty's equation [20]. At higher temperatures, the radiation contribution becomes significant but the emissivity and thermal conductivity decrease substantially [21].

Clearly, the application of this technique to diverse high-purity ceramic powders would allow high thermal resistance refractories to be constructed which could withstand high working temperatures. Thus refractories could be made free from siliceous components and could, in principle, be moulded into diverse shapes as practised for expanded polystyrene.

4. Conclusion

The conventional method for preparing expanded polystyrene foam mouldings can be used to make porous ceramics for refractory applications by the appropriate selection of ceramic volume loading. Such mouldings do not collapse on reheating to expel the organic vehicle by pyrolysis. A single-stage expansion procedure allowed porosity of 84% to be retained in the sintered foam.

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