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Control of pore size by metallic fibres in glass matrix composite foams produced by microwave heating

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Abstract

The application of microwave radiation as the heating source for the fabrication of glass foams reinforced with metallic fibres has been investigated. A soda-borosilicate glass powder was chosen for the matrix. The metal fibres were Hastelloy X fibres in volume concentration of 0, 2 and 10%. The fibre diameter was 8 μm and length was 100 μm. The microwave heating process was carried out in a self constructed over-moded microwave applicator operating at the 2.45 GHz ISM frequency. The glass foamed during processing leading to greater than 50 vol.% of spherical pores. The samples were characterised in terms of pore size and distribution, density, metal fibre distribution and interface characteristics. Adding stainless steel fibres to the glass composite prevented the glass from fracturing during processing and resulted in a more even distribution of finer pores. It is proposed that porosity formed during microwave heating as a consequence of localised glass matrix overheating in correspondence with the presence of metal fibres, caused by the preferential microwave absorption exhibited by the Hastelloy X fibres themselves and by the micro-regions of the matrix heated well above the glass softening temperature.

Keywords: Composites; Foams; Glass foams; Microwave processing; Porosity; Sintering

1. Introduction

Sintering of silicate glass and glass composite materials with microwave radiation has been attempted in a number of cases with the aim to obtain dense bodies. For example, fumed silica powder compacts,[1,2] silica gels,[3] nanoscaled glass powder compacts,[4] powdered tile polishing silicate sludge,[5] calcium zirconium silicate glass-ceramics,[6] multilayer cordierite substrates,[7] SiC fibre reinforced borosilicate glass composites,[8] and SiC-whisker reinforced glass-ceramics[9] have been densified by microwave heating. Microwave heating has been used also for other processing methods with glass, including melting, refining and reheating for forming and thermal toughening,[10] as well as to assist bulk crystallisation in glass-ceramics[11] and to melt silicate ashes.[12] The use of microwave heating with the specific aim of fabricating porous materials with controlled porosity has been also reported in the literature, including the fabrication of highly porous foam-like materials,[13] graded porous glass/metal composites[14] and sodium silicate-ortodibasic calcium phosphate foams.[15] In other papers, uncontrolled porosity formation has been seen as one of the disadvantages of microwave densification.[1,3,4] The interrelationship between the processes of pore formation and crystallisation in glass-ceramics heated under microwaves has been also investigated.[16]

Some of the main advantages of using microwave radiation include very short processing times obtainable due to rapid, selective and volumetric heating. In particular for composites, short processing times can prevent any undesirable reactions between the glass matrix and the reinforcing phases (particles or fibres), while selective microwave absorption by one of the two phases can lead to the formation of peculiar interfaces.[17–19] Moreover, the inverse temperature profile in microwave heating can be used to obtain porous bodies with accurate dimensional tolerances (no shape distortion).[14]

In the present work, we explore for the first time the application of microwave radiation as the heating

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source for the processing of glass matrix composite foams containing metallic fibres that act as reinforcement. The addition of metallic fibres to a glass matrix has the aim to increase fracture toughness exploiting several mechanisms such as ductile deformation and crack bridging.[20,21] The fibres are also thought to control the pore size and distribution of porosity in the material. Glass foams are useful for their thermal and acoustic insulating properties and their low densities;[22–25] moreover, by tailoring the dielectric properties of foamed composites, it can be possible to produce building materials able to attenuate the EM fields in a wide range of frequencies, or low-thermal capacity heating elements to be used as "grilling plates" in microwave ovens. A soda-borosilicate glass powder was chosen for the matrix and the volume fraction of metallic (Hastelloy X) fibres was varied in the composite. The main goals of the experimental research were: (i) to determine the effect of the metallic fibres on the structural integrity and distortion of the glass composites during processing and (ii) to determine the effect of the metallic fibres on the size and distribution of pores. Moreover, the mechanism of pore formation in the present composites during microwave heating is discussed.

2. Experimental procedures

2.1. Materials

The glass used for the matrix was a soda-borosilicate glass named VG98, which has the following chemical composition (in wt.%):[26] SiO_2 (56.7%), B_2O_3 (12.4%), Al_2O_3 (2.6%), Na_2O (17.5%), CaO (4.1%), MgO (2.1%) and TiO_2 (4.6%). This glass was originally developed for immobilisation of nuclear waste,[26] but in the last 10 years has been considered frequently as the matrix for fabrication of glass matrix composites.[27–29] The Hastelloy X fibres (Bekaert, Belgium) were of composition (in wt.%) Ni (51%), Cr (22%), Mo (9%) and Fe (18%) and were received chopped at 1 mm length in polyvinlyalcohol binder. Table 1 gives a selection of the properties of the glass matrix and of the Hastelloy X fibres.

After washing the Hastelloy X fibres with water to remove the binder, mixtures containing 2 and 10 vol.% metallic fibres were prepared. The fibres and glass powder were mixed in water in an ultrasonic bath for 15 min. Any remaining lumps were removed and the slurry was dried and dispersed by sieving through a sieve with and aperture of 0.25 mm. After this treatment the fibres had an average length of 100 μm. Similar mixtures have been used in a previous investigation to prepare dense fibre reinforced glass matrix composites by hot pressing.[25] Cylindrical samples (diameter: 10 mm, height: 2 mm) were obtained by uniaxial pressing the mixed composite powders at room temperature. A water solution of 3 wt.% PVA was added to the powder mixture in a 5 wt.% concentration in order to bind the pressed particles thus allowing samples handling and transportation. Three sets of samples were prepared using an hydraulic press operated for 5 seconds at the maximum pressure of 36.9 MPa. Green densities of ~60% of the theoretical density were achieved. Samples of glass powder containing no fibres were prepared in an identical manner for comparison.

2.2. Microwave processing

The microwave heating process was carried out in a self constructed over-moded microwave applicator operating at the 2.45 GHz ISM frequency. The microwave apparatus mainly consists of a remote controlled power supply (SM1150T, Alter), a generator (magnetron TM030, Alter), a transmission line (WR340 + 3-stubs tuner), a tuneable applicator (variable height) and dedicated control system, as shown in Fig. 1.

The magnetron output power can be continuously varied from 300 to 3000 W. In case of lower power requirements, an adjustable attenuator can be mounted along the transmission line, so that the magnetron can be operated at higher power levels, maintaining the correct power output towards the load.

The glass/metal fibre composite samples were positioned, one per run, on a disc-shaped silicon carbide element surrounded by an aluminosilicate refractory lining belonging to the JM26 class, having an average thickness of 30 mm. The whole assemblage was axially inserted in the cylindrical applicator. The silicon carbide element is used to absorb microwaves and to develop heat in the first stages of the heating process, when the dielectric properties of the samples alone do not allow a fast and effective heating. Once the sample, heated by the silicon carbide element, reaches a temperature corresponding to higher dielectric losses, it starts

Table 1
Properties of the VG98 borosilicate glass and Hastelloy X fibres.[27]

Material	Density ($g\ cm^{-3}$)	Mean particle size (μm)	CTE ($10^{-6}\ ^{\circ}C^{-1}$)	E (GPa)
Glass, VG98	2.57	5.5	10.65	74.8
Hastelloy X fibre	8.22	8 (diameter) × 100 (length)	15	221

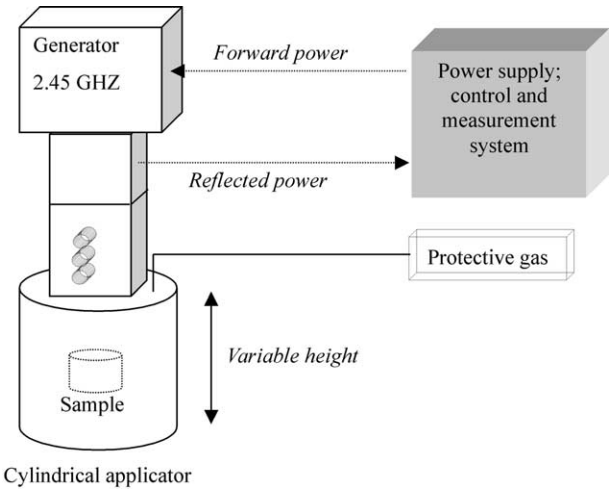

Fig. 1. Microwave sintering apparatus and control/measuring system.

coupling with the microwaves to a larger extent and the power transfer from the electromagnetic field proceeds more rapidly, leading to sintering or, eventually, melting. However, the samples integrity strictly depends on the temperature gradient, imposing an upper limit to how fast the load can be heated up.

Regarding the heating schedule, preliminary tests on the pressed discs lead to the identification of 800 W as the maximum magnetron power output bearable by the samples without cracking during the 2 min-time of microwave exposure. Under these conditions, a reflected power of 150–200 W was measured, leading to 600–650 W dissipated in the system. The final step of the heating treatment consisted of 5 min cooling by forced convection in the applicator. Heating and cooling were performed in Ar flux of 30 Nml/min. The complete densification process took 7 min for each sample. The procedure was repeated on three different sets of samples to verify its reproducibility.

The temperature was not monitored since metallic thermocouples, even if shielded, positioned in or near such small samples would affect the process. Moreover, optical pyrometer data could report only the temperature of the surface of the sample side exposed to air, which remains most of the time significantly cooler than the opposite side facing the SiC. In order to have an estimation of the temperature, however, a heating test was run with the cylindrical applicator loaded only with the silicon carbide element. Soon after the heating schedule, the same used for the samples, the surface temperature of the SiC element was rapidly measured by inserting a thermocouple in the applicator. Temperatures above 800 °C were detected so that a heating ramp of at least 400 °C/min for the SiC element can be assumed. Continuous tuning of the cavity was needed due to significant changes of the dielectric properties of the load. From previous experiences on similar composite systems,[14,18] microwaves absorption from the load increases during the treatment. This can be explained considering the increasing loss factor of the SiC as a function of temperature, the lower electrical conductivity of the metal reinforcement as a function of temperature and, most important of all, the higher ion mobility in the matrix at temperatures higher than the glass transition temperature.

2.3. Characterisation

The density of samples after microwave processing was determined using the Archimedes' principle. The macrostructure and external appearance of the samples was characterised by low magnification optical microscopy and a digital camera. Selected samples were prepared for microscopic observation and quantitative microstructural analysis. These samples were cut, embedded in epoxy resin and polished using SiC paper and diamond paste (up to 1 μm). The microstructure of selected samples, both fracture surfaces and polished sections, was analysed by scanning electron microscopy (SEM) using a Jeol LV5160 SEM equipped with a backscattered detector.

3. Results and discussion

Macroscopic visual examination revealed that during microwave processing the samples containing no Hastelloy X fibres swelled and distorted and during cooling they cracked into several pieces. The samples containing only 2 vol.% Hastelloy X fibres swelled and distorted but remained in one piece. The samples containing 10 vol.% Hastelloy fibres underwent the least amount of swelling and distortion and also remained in one piece.

All samples contained high levels of closed porosity. It was not possible to measure the density of the samples containing 0 vol.% and 2 vol.% fibres using the Archimedes' principle as the density was less than that of water. The relative density is therefore less than ~32% for the 2 vol.% fibre containing samples (i.e. the samples contained > 68% porosity). For the samples with 10 vol.% Hastelloy X fibres, swelling was less severe and the density was measured as 1.39 g/ cm^3, which corresponds to a relative density of 45% (55% porosity). Fig. 2 shows a macrograph of a cylindrical sample containing 10 vol.% fibres which indicates low dimensional distortion.

The porosity levels achieved are considerably higher than those obtained in a previous investigation, where a different borosilicate glass matrix with a higher sintering temperature and Mo inclusions were used for microwave fabrication of porous glass matrix composites containing up to 38% porosity.[14] This is despite the fact that in the present case the power density in the cylindrical applicator was kept significantly lower. Moreover,

in the present case, sintering occurred in argon flux and not in oxidising atmosphere (air), as it was the case in the previous work, where oxidation products were observed.[14]

A visual examination of the sectioned samples revealed a highly irregular distribution of large pores in the samples without fibre addition and with 2 vol.% Hastelloy X fibres; some pores were greater than 1 mm in diameter. In contrast the pore distribution in the composite containing 10 vol.% fibres was more even, and the pores were much smaller in size, the largest pores having a diameter of less than 0.2 mm.

Typical SEM micrographs of the foam composites containing 10 vol.% and 2 vol.% Hastelloy fibres are shown in Fig. 3a and b, respectively. These are secondary electron images in which the position of the stainless steel fibres has been artificially coloured black for clarity. The samples contained closed pores with high sphericity. The Hastelloy X fibres were distributed in the glass matrix between the pores. The interface between the fibres and the glass was sharp and the wetting appeared good with no cracking observed at the interface. A high magnification micrograph focusing on the fibre matrix interface is shown in Fig. 4. Little agglomeration of the Hastelloy X fibres was observed. It is interesting to note that the fibres frequently appear to be in positions where the spherical shape of the pores is distorted indicating that the fibres may be pinning the expanding pores. Several sites where the fibres appear to have prevented growth of pores in the 10 vol.% fibre sample are marked with arrows in the SEM micrograph shown in Fig. 5. This indicates the mechanism by which increasing the volume fraction of the Hastelloy X fibres controls pore growth and leads to a more even

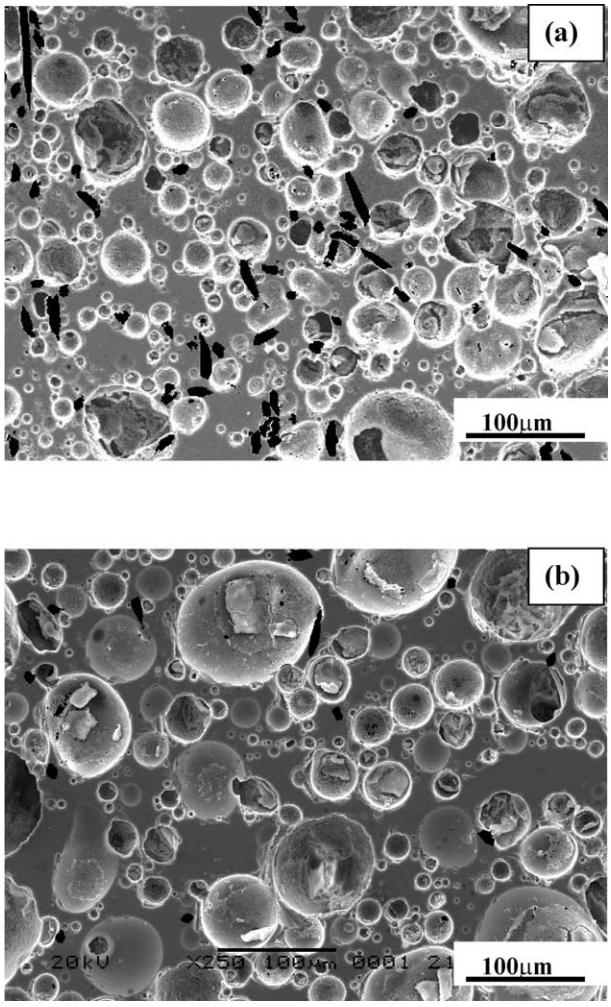

Fig. 3. Foamed samples of Hastelloy X fibre reinforced borosilicate glass fabricated by microwave heating: (a) fibre volume fraction = 10%, (b) fibre volume fraction = 2%.

Fig. 2. Macrograph showing final shape of a foam borosilicate glass sample containing 10 vol.% Hastelloy X fibres after microwave processing.

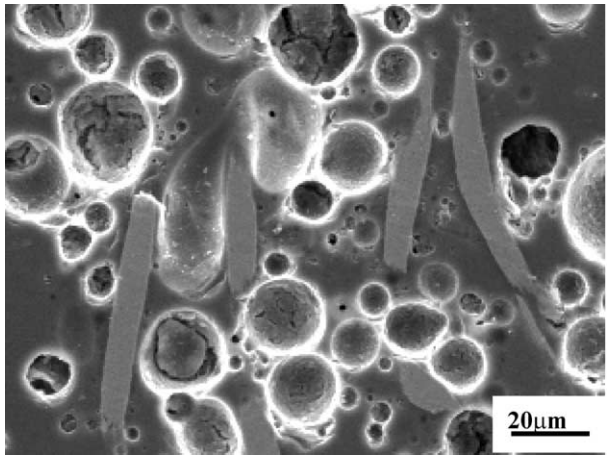

Fig. 4. SEM micrograph showing the sharp Hastelloy X fibre/glass matrix interfaces and absence of microcracking or other defects at the interfaces.

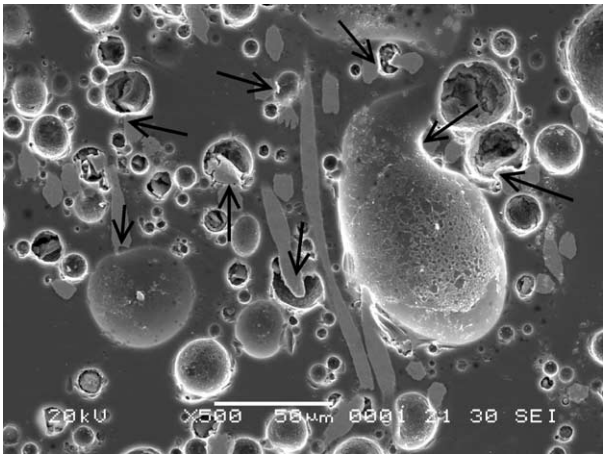

Fig. 5. SEM micrograph of foamed glass containing 10 vol.% Hastelloy X fibres. Arrows indicate areas where the stainless steel fibres are pinning the pores causing them to become less spherical in shape.

distribution of smaller pores in the glass foam composite. Moreover the higher volume fraction of fibres led to more dimensionally stable samples during microwave heating. The samples with 10 vol.% fibre retained their cylindrical shape (Fig. 2), whereas samples with 0 and 2 vol.% fibres deformed severely during heating.

The formation of porosity in the present composites may be explained following similar arguments as those presented in our previous investigations on porous Mo particles reinforced borosilicate glass matrix composites.[14]

Foaming could be ascribed to gas evolution from the molten glass matrix, which, above the glass softening temperature ($T_s = 620$ °C),[26] undergoes thermal runaway, that is to say, increasingly absorbs microwaves, becoming more and more "microwave active" as its temperature increases. This phenomenon occurs locally, since it depends on the local electric field strength and on the dielectric properties of the material, which, being multi-phased, vary locally too. Thus, in the sample without fibre addition, the portion in contact with the SiC element is heated first, and as it reaches the T_s of the glass, it undergoes thermal runaway, swelling and foaming, while the cooler surface layers, exposed to air, remain almost unaltered. Due to the low thermal conductivity of the samples, bubbles tend to form only in a relatively small region, which absorbs most of the microwaves. Thus, large pores are formed, the pore distribution is inhomogeneous and the sample shape is lost due to the low viscosity of the melt. The 2 vol.% samples exhibit a similar behaviour, due to the small amount of fibre reinforcement. By increasing the fibre content up to the 10 vol.% the system drastically changes its behaviour: the electric field is concentrated in proximity of the fibers' tips, the overall composite loss factor becomes higher and its thermal conductivity increases. The combination of these factors should cause the sample to absorb more homogeneously the microwaves, and to better conduct the heat generated from the SiC susceptor. Moreover, the fibres' tips should act as "nucleating agents" for pores, since the higher local electric field strength in their vicinity, connected with their pronounced radius of curvature should lead to higher power dissipation in the surrounding glass matrix, which overheats. An evidence of this phenomenon can be seen in Fig. 5, where pores seem to be situated preferentially closed to fibre's tips. It has to be noticed that the Hastelloy X fibre used proved to be non reactive in the soda-borosilicate glass system investigated, as no indication of interfacial reactions or secondary phases formed at the fibre/matrix interfaces were detected by SEM (see Fig. 4). The fibres seem to act as a barrier to pore growth, since they form a kind of random network, leaving small free space for the pores to expand and coalesce.

Thus the presented fabrication method based on microwave heating may open possibilities for making highly porous glass foams with metal fibre reinforcement and controlled microstructure. Current research is focussed on measuring the thermal and mechanical properties of the produced foams.

4. Conclusions

The application of microwave radiation as the heating source for processing glass matrix composite foams reinforced by metallic fibres has been demonstrated for the first time in this study. Soda-borosilicate (VG98) glass matrix composite foams with 2 and 10 vol.% Hastelloy X fibres were produced. The higher volume fraction of Hastelloy X fibres led to an improved distribution of smaller pores in the material. Porosity levels of $>50\%$ were achieved in all composites. The best composites in terms of an even pore distribution and shape retention were achieved with the higher volume fraction of Hastelloy X fibres. The reason for this is related to the fibres being pushed by the pores during foaming and hindering pore agglomeration and growth, as ascertained by microscopy. The pore formation is attributed to gas evolution from the molten glass matrix, which probably is subjected to microwave thermal runaway due to localised overheating. The present results suggest that glass matrix overheating depends on the volume percentage of added fibres, which act as a "nucleating agents" for the formation of pores.

The combination of high porosity and metal fibre toughening should lead to composites of high thermal shock resistance and thermal stability suitable for thermal protection systems. This has been demonstrated in the present study by the Hastelloy X fibres preventing cracking and disintegration of the composites during processing. Other possible applications of the foams are in the area of sound absorption and as lightweight

components for electromagnetic interference shielding. Current research focuses on the evaluation of the thermomechanical properties of the foams.

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