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Microwave processing of glass matrix composites containing controlled isolated porosity

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Abstract

Porous glass matrix composites containing well-defined spherical porosity were fabricated employing microwave-assisted densification of powder compacts. The inverse thermal gradient typical of microwave heating was used to obtain a high concentration of spherical pores in the central region of the sample and a relatively dense outer shell. Pores in the central region were formed in the molten glass phase exploiting gas evolution and entrapment. The outer region, being at a lower temperature, was sintered by viscous flow. Minimal distortion of the part occurred. The diameter of the pores showed a wide size distribution, i.e. between ~5 and ~50 µm. In comparison to other methods described in the literature for the fabrication of hermetic porous materials, i.e. using hot-pressing, the present approach is advantageous due to high heating rates of microwave heating resulting in saving of time and energy. Moreover, parts of complex shape may be fabricated by this technique. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There are several application areas where ceramics and glasses containing closed, well-defined isolated pores are needed. For example, one approach proposed to decrease the dielectric constant of glasses and glass-ceramics used as substrates in electronic packaging is the incorporation of porosity.[1,2] For this application, the pores must be isolated to prevent environmental attack (hermeticity) and to allow for internal wiring network. Moreover, the porous material must retain dimensional and structural stability, and therefore the size, shape and distribution of the pores must be controlled.[2] Materials containing closed porosity of controlled size and well-defined shape are also important for the purpose of calibration and sensitivity assessment of microstructure inspection instruments and techniques, including optical microscopy and X-ray refraction analysis.[3–5] Moreover, specimens containing well-characterised porosity can be used as standards to evaluate the image quality of micrographs from microscopes, radiographs, etc.

In other application areas, porous ceramics and glasses containing closed porosity may be attractive low-weight materials when high thermal shock resistance is required. It has been shown that porous bodies can have a higher thermal shock resistance than their dense counterparts, provided the (closed) pores have a certain shape and orientation.[6–8] Also porous biomaterials (e.g. porous hydroxylapatite[9]) with controlled amount of both closed and open porosity are needed for some implant applications. Here, the closed porosity helps to match the elastic constants of the implant to that of the bone.[10] Finally, model porous materials containing well-defined, closed porosity and holes in an otherwise defect-free elastic matrix are useful to carry out basic experimental studies on the fracture behaviour of such materials under different loading conditions. For example, porous glasses[11,12] have been considered with this aim. In general, the validity and prediction capability of theoretical models proposed for porous materials can only be verified rigorously by means of experimental measurements on materials with well-defined, "designed" porosity, as emphasised by Rice.[13]

The variety of application options for closed-porosity containing materials, as described above, has originated numerous processing strategies for their fabrication

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during the last years, the most significant of them are summarised in Table 1.

Recently, one of the authors has presented a new method to fabricate porous glass with controlled porosity of spheroidal shape.[27] In this method, hollow glass microspheres are mixed with glass powder and the mixture is hot-pressed. By varying the hot-pressing parameters, i.e. time, temperature and pressure, spheroidal pores with different axial ratios in a dense glass matrix were produced. The major drawback of that method is that it relies on the use of the cost-intensive hot-pressing technique, which also has limitations regarding the shape of the products that can be fabricated.

Sintering of silicate glass and glass composite materials using microwave radiation has been tried in previous studies with the aim to obtain dense bodies. For example, fumed silica powder compacts,[29,30] silica gels,[31] soda-lime glass powders,[32] powdered tile polishing silicate sludge,[33] calcium zirconium silicate glass-ceramics,[34] multilayer cordierite substrates,[35] SiC fibre reinforced borosilicate glass composites,[36] and SiC-whisker reinforced glass-ceramics[37] have been densified by microwave heating. Microwave heating has been used also for the processing of glass, including melting, refining and reheating for forming and thermal toughening,[38] as well as to assist bulk crystallisation in glass-ceramics.[39] Microwave radiation has been also employed successfully to melt and immobilise silicate fly ash.[40] However, the use of microwave heating with the specific aim of fabricating porous materials with controlled porosity has not been reported in the literature so far, except for an early report on highly porous foam-like materials.[41] In fact, uncontrolled porosity formation has been seen as one of the disadvantages of microwave densification.[29,32,33]

In the present work, we develop a novel processing technique based on microwave heating of a composite

Table 1
Overview of the processing methods used to fabricate glass and ceramic materials with (mainly) closed porosity and some of their main characteristics

Fabrication method	Main characteristics	Refs.
Addition of polymer spheres, carbon particles or carbon fibres to a matrix and their subsequent thermal decomposition (burn out) during sintering	• Limited control of the final pore microstructure (shape and orientation) • Undesirable impurities are normally left, e.g. residual carbon due to incomplete burn out of the polymer particles or due to the formation of reaction by-products • Burn-out process may contribute to the formation of internal flaws in the material • Cavities created by the fugitive particles may become partially filled with powder of the surrounding matrix, loosing their well-defined spherical or cylindrical shape	2,5,9,14, 15
Partial sintering of powder compacts by changing the powder compacting pressure, the sintering time, atmosphere and temperature	• Adequate control of the amount of porosity but the shape and orientation of pores can not be manipulated • Impossibility to obtain high concentrations of isolated pores with no open or interconnected porosity	16–18
Utilisation of hydrogen peroxide or other foaming agents	• Shape and orientation of pores can not be easily manipulated • Impossibility to obtain high concentrations of isolated pores	19,20
Sol-gel technique	• Presence of a large fraction of open porosity, highly fragile and low structural integrity products	18,21
Incorporation of metallic particles with a higher thermal expansion than the matrix (e.g. Ni spheres in borosilicate glass). On cooling from the fabrication temperature and in absence of interfacial bonding, the spheres shrink away from the matrix, developing pores	• Difficulty to vary the shape of the pores, which normally remain spherical • Almost impossible to achieve complete separation of the metallic spheres from the matrix due to difficulties in tailoring the glass/ceramic-metal bond during processing	22
Direct sintering or chemical bonding of hollow microspheres, including microspheres produced as by-product (flyash) in coal combustion plants	• Suitable for highly porous, light-weight insulating materials with open, interconnected porosity • Difficulty to achieve solely closed porosity	23,24
Hollow glass and ceramic microspheres used as fillers in glass, ceramics, refractory bricks and castables	• Excellent control of porosity content and pore structure (shape, orientation) • Limitation due to restricted chemical composition of available microspheres • Cost-intensive process (in case of using hot-pressing technology)	25–27
Plasma-spraying process	• Anisotropic porosity structure • Difficult control of pore shape • Mainly used for ceramic coatings	28

powder compact to prepare porous borosilicate glass matrix composites containing molybdenum inclusions and spherical isolated porosity. Molybdenum particles were incorporated with the aim to increase the fracture toughness and fracture strength of the glass matrix, following our previous study on molybdenum particle reinforced glass matrix composites[42] and taking into account recent literature results.[43]

2. Experimental procedure

2.1. Materials

The glass used for the matrix was a commercially available borosilicate glass powder (DURAN®, Schott Glas, Mainz, Germany), which has the following chemical composition (in wt.%)[42]: SiO_2 (81%), B_2O_3 (13%), Al_2O_3 (2%), Na_2O (2%) and K_2O (2%). This glass powder has been also used previously to prepare dense particle reinforced glass matrix composites, both with metallic[42] and ceramic inclusions[44] by hot-pressing technique. The temperature-viscosity dependence and the sintering behaviour of this glass are well-known.[45] Other relevant properties of the DURAN® glass used are given in Table 2. The metal inclusions were molybdenum particles of guaranteed minimum 99.9% purity (Alfa Products, Johnson Matthey GmbH, Karlsruhe, Germany), and were used in the as-received state. The average particle size of primary particles was < 3 μm, but particle agglomeration occurred during processing. Relevant properties of the Mo particles are given in Table 2.

Table 2
Physical properties and characteristics of the composite constituents[42]

	Borosilicate glass DURAN®	Molybdenum inclusion
Average particle size (μm)	8	< 3
Density (g/cm^3)	2.22	10.22
Thermal expansion coefficient (10^{-6} K^{-1})	3.3	5.1
Young's modulus (GPa)	63	336
Poisson's ratio	0.22	0.31
Fracture strength (MPa)	56	466
Yield strength (MPa)		437
Hardness (GPa)	5	150 (HV10)

Mixtures containing 5 vol.% molybdenum particles were prepared. The powders were dry mixed in a polypropylene bottle for 5 h to ensure thorough mixing. The mixed composite powder was pressed uniaxially at room temperature to obtain small cylindrical samples (diameter: 10 mm, height: 2 mm) with green densities of ~60% of the theoretical density. Three sets of samples were prepared using an hydraulic press operated for 5 s at the maximum pressure of 36.9 MPa. 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.

2.2. Microwave processing

The microwave heating process was carried out in a self constructed single mode microwave applicator operating at the 2.45 GHz ISM frequency. The microwave apparatus mainly consists of a generator (magnetron), a transmission line (waveguide), a tuneable applicator and dedicated control systems, as shown in Fig. 1. The magnetron output power can be continuously varied from 50 to 650 W. In case of low 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. This is particularly useful since it has been demonstrated[46] that a magnetron operating at

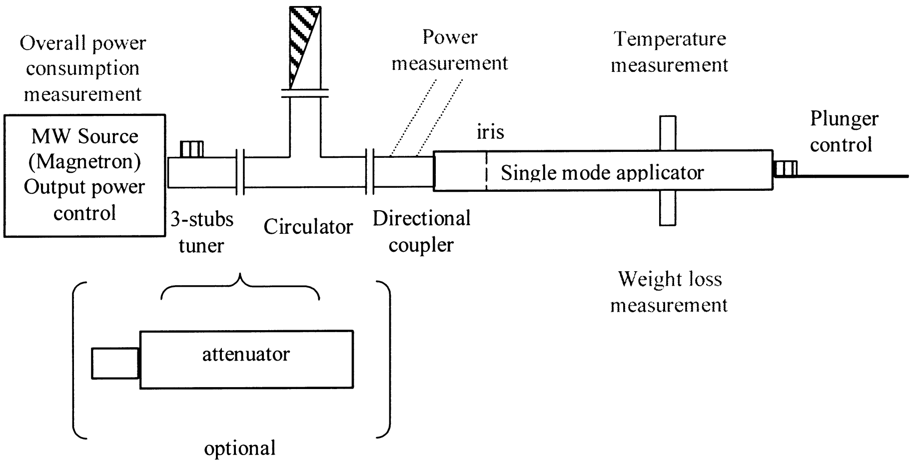


Fig. 1. Single mode microwave apparatus consisting of a generator (2.45 GHz magnetron), a transmission line (wave guide), a tuneable applicator and dedicated control systems.

less than 30% of its maximum power output is subject to frequency shifts which affect the distribution of the electromagnetic field inside the applicator and consequently, the heating process.

The Mo/glass samples were positioned, one per run, on a cylindrical silicon carbide element surrounded by an aluminosilicate fabric lining, and the whole assemblage was inserted in the single mode 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 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 sample integrity strictly depends on the temperature gradient, imposing an upper limit to how fast the load can be heated up.

As far as the heating schedule is concerned, preliminary tests on the pressed discs lead to the identification of 400 W as the maximum magnetron power output bearable by the samples without cracking during the 1.5 to 2 min-time of microwave exposure. The final step of the heating treatment consisted of 5 min air cooling by natural convection outside the applicator. The procedure was repeated on three different sets of samples to verify its reproducibility.

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, significantly cooler than the opposite side. In order to have an estimation of the temperature, however, a heating test was run with the single mode 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 waveguide. Temperatures above 1000°C were detected so that a heating ramp of at least 500°C/min for the SiC element can be assumed. Continuous tuning of the cavity was needed due to important changes of the dielectric properties of the silicon carbide and of the samples as the organic binder was removed and/or the temperature increased.

2.3. Characterisation techniques

The density of samples after processing was determined geometrically and using the Archimedes' principle. Selected samples were prepared for microscopic observation and quantitative microstructural analysis. These samples were cut, embedded in resin and polished using SiC paper of different granulometry and diamond paste (up to 1 μm). The porous microstructure was analysed by optical and scanning electron microscopy (SEM). Quantitative microstructure analysis (Quantimet 570, Cambridge Inst.) was employed to measure the pore shape. By measuring the lengths of the major (b) and minor *(a)* axes of the ellipses on plane sections and averaging, the mean axial ratio (a/b) of the cross-sectional ellipses was obtained for each sample analysed. At least 100 pores were measured. This was necessary to minimise the error in the averaging procedure. Fracture surfaces were observed by scanning electron microscopy (SEM).

3. Results

Macroscopic visual examination revealed that after microwave processing the samples retained the cylindrical shape with minimal distortion. However, a symmetric layered structure on sections perpendicular to the sample axis, as schematically shown in Fig. 2, was evident. This structure, consisting of a porous interior and a dense surface layer or shell, was also present on longitudinal sections, as revealed by optical macrographs (Fig. 3). As explained further below, this structure is a direct consequence of microwave heating processing, where heat is generated internally within the material. The total porosity determined by the Archimedes' principle was 38 vol.%, and the mean axial ratio of the pores, as determined by quantitative image analysis, was 0.98±0.04, meaning that essentially spherical porosity was achieved.

The structure of the porosity in the central region of the samples, as observed by optical microscopy examination of polished sections and by SEM examination of fracture surfaces, is shown in Fig. 4a and b, respectively.

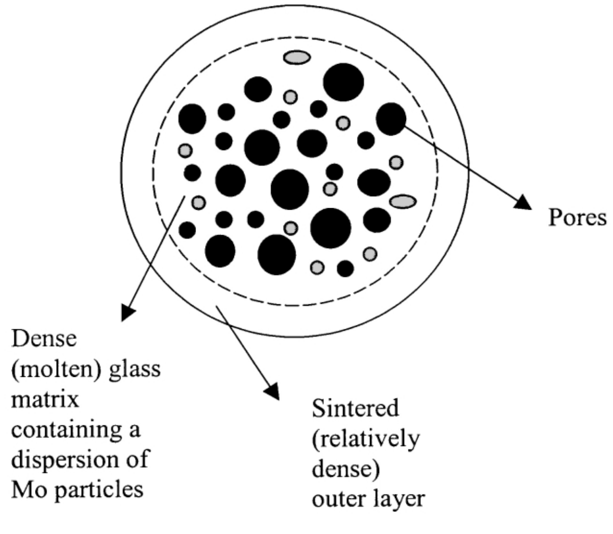


Fig. 2. Schematic diagram showing the layered structure of microwave processed cylindrical glass samples on sections perpendicular to the sample axis.

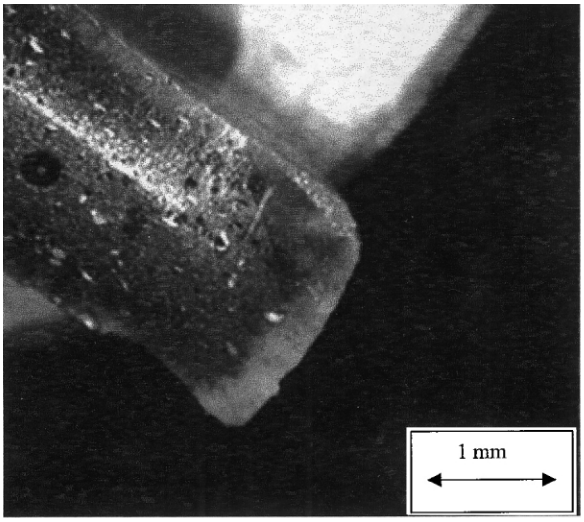
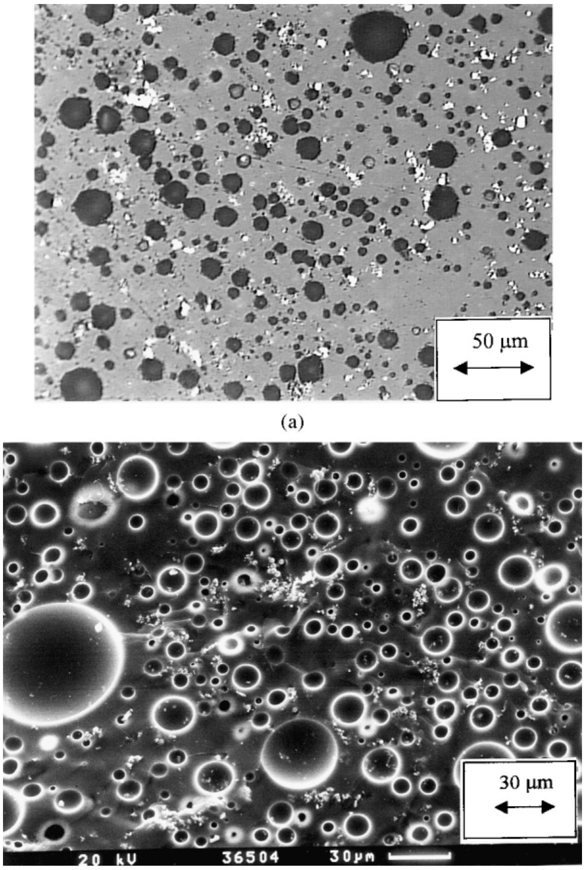


Fig. 3. Macrograph showing the typical sample structure on longitudinal sections, consisting of a porous interior and a dense surface layer or shell.



(a)

(b)

Fig. 4. Micrographs showing the porous structure of the central region of a microwave processed glass sample: (a) optical microscopy image of a polished section and (b) SEM image of a fracture surface. The fairly homogeneous distribution of both spherical porosity and Mo particles is seen.

A high concentration of spherical pores embedded in a dense glass matrix is observed. The pores are homogeneously distributed and they exhibit a wide diameter size distribution, which is in the range ~5 to ~50 μm. The fairly homogeneous dispersion of the Mo particles in the glass matrix is also evident. Some large agglomerates of Mo primary particles were present, however, as also shown in Fig. 5. This figure is an optical micrograph of the interfacial region of the sample, i.e. the region comprising the transition from the highly porous core to the denser outer region or shell. A micrograph of the denser outer region of the samples taken at a higher magnification is shown in Fig. 6. In this region the pores have a diameter of < 10 μm and a lower concentration of Mo particles than in the sample centre was detected.

It is interesting to note that besides the well-defined spherical pores, no other flaws or defects are seen in the glass matrix, as for example thermal stress induced microcracks or residual, irregular porosity left by incomplete densification. In a previous investigation on the same composite system, but using hot-pressing,[42] it

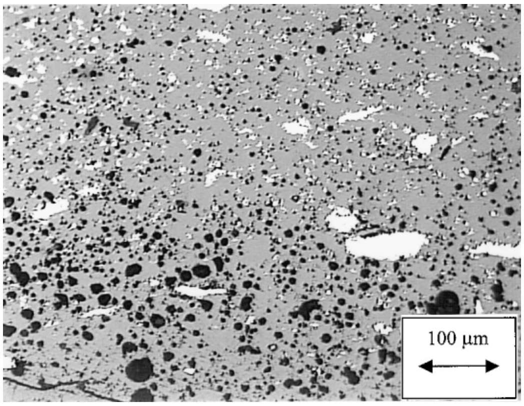


Fig. 5. Optical microscopy image showing the transition region from the highly porous central zone to the denser outer zone according to the schema of Fig. 2.

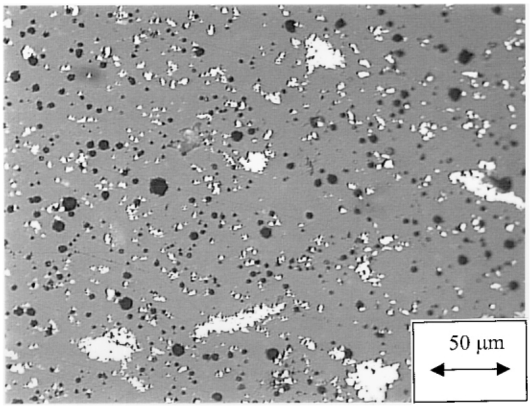


Fig. 6. Optical microscopy image of the outer region of a sample showing low porosity and pore diameters < 10 μm.

was shown that due to the relatively close match of thermal expansion coefficients between the glass matrix and Mo particles, and due to the small size of the particles, residual thermal stresses which develop upon cooling from the fabrication temperature did not lead to microcracking at the particle/matrix interfaces. This behaviour is also confirmed in the present microwave processed samples.

4. Discussion

As mentioned above, the particular microstructure of the samples, comprising a highly porous central region containing well-defined spherical pores and a denser outer layer, is a direct consequence of the microwave heating process used. In the microwave process, heat is homogeneously generated in the bulk of the sample by dielectric relaxation. As a consequence, thermal gradients reverse to those occurring in conventional heating develop, i.e. the surface is cooler than the interior of samples. In other words, if no isolation of the sample is used, heat is lost at the surface of the specimens resulting in an inhomogeneous heating. This inverse temperature profile has been seen as a problem when the aim was to obtain fully dense, crack-free sintered glass articles[32] or bubble-free molten glasses.[38] However, this phenomenon has been used advantageously in other materials, notably to control the microstructure of YBCO ceramic superconductors.[47] In the present study, the occurrence of the inverse thermal gradient was used to fabricate porous bodies with the structure schematically shown in Fig. 2.

The structure of the specimens strongly suggests that the temperature in the central region was high enough to induce melting of the glass. The temperature of the sample in this region could have reached values well above 1000°C, as mentioned above. At this temperatures, the viscosity of the DURAN® borosilicate glass used is $<10^5$ dPa s,[48] which is much lower that the viscosity at which viscous flow assisted sintering would occur under conventional heating (about 10^9 dPa s).[45] Under these conditions, the central region of the specimen behaves as a partially molten glass confined by a rigid outer layer or "shell", which is at a lower temperature due to heat loss. In this region, the glass powder particles reach however temperatures sufficiently elevated to sinter by viscous flow. In the used DURAN® borosilicate glass, viscous flow densification occurs, under conventional heating, at temperatures of ~900°C at relative high viscosities, i.e. at about 10^9 dPa s.[45] Therefore densification (shrinkage) in the outer sample layer takes place without (or with minimal) shape distortion of the body. Extensive gas evolution in the central molten glass region creates bubbles, which, on rapid cooling, remain in the structure thus forming the spherical pores.

Thus, the development of high amount of closed porosity in the molten central part of the sample is ascribed here to gas evolution and entrapment, and not to a solid matter transport mechanism where the pores are seen as sites of enhanced material transport, as suggested to explain porosity evolution during microwave sintering of polycrystalline ceramics.[49] It should be noted that Andreola et al.[33] have also indicated the presence of higher porosity in the central part of their samples fabricated by microwave heating of tiles polishing sludge, in agreement with the present experimental results. However, those authors did not consider exploiting this phenomenon to fabricate porous bodies with controlled porosity, as attempted here.

It is worthwhile to point out that under hot-pressing conditions (at pressures of 20 MPa), DURAN® glass powder compacts can densify at relatively low temperatures (740°C).[45] Since the temperature of the sample was not directly measured in the present investigation, it is not possible to assess if microwave heating has an equivalent effect to an external mechanical pressure in lowering the sintering temperature of glass.

For comparison purposes, Fig. 7 shows the typical microstructure of a porous glass sample fabricated by hot-pressing using the same DURAN® glass but incorporating hollow borosilicate glass microspheres, as described elsewhere.[27] The main difference between both samples is the level of densification of the residual glassy phase achieved. In order to retain spherical porosity in the hot-pressed sample without deformation of the microspheres (Fig. 7), relatively low pressures and temperatures had to be used, which apparently were not enough to promote complete densification of the glass matrix. Thus, residual, intergranular porosity remained. On the contrary, in the microwave processed samples, the partial melting of the glass in the central part of the

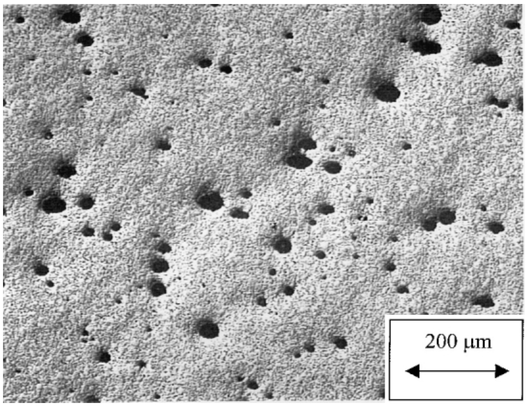


Fig. 7. Optical microscopy micrograph of a glass sample containing spherical pores fabricated by hot-pressing of a mixture of glass powder and hollow glass microspheres (from Ref. 27). Note the presence of residual matrix porosity as a result of incomplete densification, which is not observed in the microwave processed material (Figs. 4–6).

sample led to total elimination of such undesired intergranular pores, as Figs. 4–6 clearly show.

A final remark is necessary concerning the effect of the embedded Mo particles on the microwave heating process of borosilicate glass. The particles seem to migrate far from the outer dense "shell" towards the interior of the bulk. A tentative explanation of this migration can be found in the theory of the coaxial lines, being the geometry of the present test very close to that commonly used for dielectric properties measurements by the Roberts and von Hippel method.[50] The two coaxial conductors of the microwave line, in this particular case the waveguide used as applicator and the Mo particles present in the material, induce the arrangement of any dielectric material positioned in the hollow space so that to cover the central conductive material. So it is suggested that the glass powder will tend to migrate towards the surface of the sample, trying to fill in the space between the Mo-containing sample core and the metallic wall of the waveguide. This matter transportation process should enhance simultaneously the agglomeration of the Mo particles left in the central part of the sample. Indeed this hypothesis requires further verification by conducting experiments in a different microwave applicator, for example in a multimode cavity.

Another possible explanation for the depletion of Mo in the dense surface layer may be sublimation of Mo particles before densification of the glass. Again further experiments are required to verify this suggestion, which are the focus of on-going research.

Summarising, the use of microwave heating is a very attractive approach to fabricate porous glass composite compacts containing high concentrations of well-defined spherical pores. It is possible to exploit both gas evolution (foaming) in a glass melt to produce the pores and the presence of a reversed thermal gradient in the sample to create a rigid outer layer. This rigid sintered layer allows the retention of the specimen shape with minimal distortion despite the internal molten phase formed during microwave heating. The in-depth study of the effect of a metallic particle dispersion on the microwave heating of silicate glass is the matter of on-going research. For example, both the effect of particle volume fraction and particle size distribution are being considered.

5. Conclusions

A processing technique for the fabrication of glass composite specimens containing porosity of well-defined spherical shape is presented, which does not require the use of organic additives to create porosity. It is based on the use of microwave heating. Spherical pores are obtained in the central region of the sample by producing a molten glass phase and exploiting gas evolution and entrapment in a confined environment. The outer region, being at a lower temperature, sinters by viscous flow without significant deformation, and thus no (or minimal) shape distortion of the part occurs. The pore size distribution achieved was wide, i.e. between 5 and 50 μm. Further optimisation experimental work would be necessary for achieving a narrower pore size distribution, if desired. The presence of the metallic inclusion phase during microwave process appears to facilitate the formation of an outer dense shell enhancing the natural effect of inversion of the temperature profile. In comparison to the hot-pressing based method described earlier for the fabrication of similar porous materials,[27] the present approach is advantageous due to high heating rates in microwave heating resulting in saving of time and energy. Moreover, the fabrication of parts with complex shapes may be also possible. Porous, however hermetic, glass specimens as produced here may find applications in a variety of research and industrial areas, which were summarised in the introduction of this paper. In particular, the presence of both closed porosity and metallic particles in a glass matrix should lead to a lightweight material with high thermal shock resistance.

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