Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 1141–1149

UNIQUE MICROSTRUCTURE OF GLASS-METAL COMPOSITES OBTAINED BY MICROWAVE ASSISTED HEAT-TREATMENTS

P. Veronesi [1*], *C. Leonelli* [1], *G. C. Pellacani* [1] *and A. R. Boccaccini* [2]

[1]Department Materials and Environmental Engineering, University of Modena and R. Emilia, Via Vignolese 905/A, 41100 Modena, Italy
[2]Department Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BP, UK

Abstract

The present study deals with the computer-aided simulation of the microwave heating of metal/glass composites in single mode applicator and the rapid densification of borosilicate glass matrix composites containing molybdenum particle inclusions. The selective and penetrating microwave heating led to a layered porous structure of the samples. They consisted of a highly porous core containing spherical pores and a relatively dense outer shell. Pores in the central region were formed in the molten glass phase due to gas evolution and entrapment. The outer region of the sample remained at lower temperature and it sintered by viscous flow with minimal distortion.

Keywords: composite, glass/metal, microwave, porous, sintering

Introduction

Microwave heating

Microwaves are electromagnetic waves having a frequency ranging from 300 MHz and 0.3 THz. Most of the existing apparatuses, however, operate between 400 MHz and 60 GHz, using well defined frequencies, allocated for Industrial, Scientific and Medical (ISM) applications. Among them, the 2.45 GHz is widely used for heating applications, since it is allowed world-wide and it presents some advantages in terms of costs and penetration depth.

Quantitative information regarding the microwave-material interaction can be deduced by measuring the dielectric properties of the material, in particular of the real and imaginary part of the relative complex permittivity, $\varepsilon=\varepsilon'-j\varepsilon''_{\text{eff}}$, where the term $\varepsilon''_{\text{eff}}$ includes conduction losses, as well as dielectric losses. The relative permittivity is not a constant and strictly depends on frequency and temperature. A different and more practical way to express the degree of interaction between microwaves and ma-

* Author for correspondence: E-mail: paolov@unimo.it

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

terials is given by two parameters: the power penetration depth (*Dp*) and the power density dissipated in the material (*P*), defined in a simplified version as follows:

$$Dp=(\lambda_0\sqrt{\varepsilon'})/2\pi\varepsilon'' \quad P=2\pi f\varepsilon_0\varepsilon''_{\text{eff}}E^2_{\text{rms}}$$

where $\varepsilon=\varepsilon'-j\varepsilon''_{\text{eff}}$ is the complex permittivity of the material under treatment, λ_0 is the wavelength of the radiation, f is its frequency, $\varepsilon_0=8.854\cdot10^{-12}$ F/m is the permittivity of empty space and E_{rms} is the electric field strength inside the material itself [1]. *P* and *Dp* can only give qualitative and often misleading information, especially when it is critical to determine the temperature profiles inside the material. Others are the variables involved, however from this two parameters can be deduced most of the peculiarities which make the microwave heating a unique process.

First of all, it can be noticed the existence of temperature profile inversion with respect to conventional heating techniques. The air in proximity of the materials during the heat treatment, in fact, is not a good microwave absorber, so that it can be considered that the atmosphere surrounding the material is essentially at low temperature. Viceversa, the material under treatment, interacting in a stronger way with the electromagnetic field, heats up and reaches higher temperature. The result is that, in most cases, the surface temperature of the sample is lower than inside the material itself [2]. This effect is more pronounced for poor heat conducting materials.

Since the given formulations for *Dp* and *P* show a strong dependence upon the real and imaginary part of the materials permittivity, for multiphase systems having components with quite different permittivities, it is expected a strong selectivity of the microwave heating process. Power, in fact, is transferred preferentially to lossy materials (high $\varepsilon''_{\text{eff}}$), so that it can be possible to rise the temperature of just a single phase or component, or to spatially limit the heat treatment to the material, without involving the surrounding environment. This peculiarities can be particularly useful when treating composite materials.

The rapid variations of the permittivity as a function of temperature is responsible for a not always desirable phenomenon, the thermal runaway, that is to say the rapid and uncontrollable overheating of parts of the material under processing. Considering a low thermal conductivity material, whose permittivity increases as the temperature rises, in particular ε'' increasing as the temperature growing, it will be subject to a gradient of temperature, being colder in the regions where heat is rapidly dissipated or the field strength is lower, and hotter in the remaining zones. These zones, presenting higher values of ε'', and thus of *P*, will start absorbing microwaves more than the cold ones, further rising their temperature and consequently the local value of ε'', strengthening the phenomenon [3].

Finally, dielectric heating is penetrating, depending on the operating wavelength, and permits to directly heat treat the surface and the core of the body, without waiting for the heat to reach the core of the sample by means of conduction, particularly time-taking for low thermal conductivity materials, like most of ceramics and polymers are. In these materials, the penetration depth is high, of the order of some tens of centimetres, thus facilitating the processing of large bodies, too.

Sintering of glass composites

Sintering of glass and glass composite materials using microwave radiation has been investigated by many authors in previous studies, with the aim to obtain dense bodies. For example, fumed silica powder compacts [4, 5], silica gels [6], soda-lime glass powders [7], powdered tile polishing silicate sludge [8], calcium zirconium silicate glass-ceramics [9], multilayer cordierite substrates [10], SiC fibre reinforced borosilicate glass composites [11], and SiC-whisker reinforced glass-ceramics [12] have been densified by microwave heating.

In the present work, we develop a novel processing technique based on microwave heating of a composite powder compact to prepare porous borosilicate glass matrix composites containing metal inclusions (Mo and W) and presenting a peculiar microstructure. Molybdenum particles were incorporated with the aim to increase the fracture toughness and fracture strength of the glass matrix, following previous studies on molybdenum particle reinforced glass matrix composites [13] and taking into account recent literature results [14].

The choice of adding tungsten particles, instead, was made considering both the thermal and electrical properties of W, with the aim of achieving a certain control on the microwave absorption capabilities of the resulting composite material. The thermal expansion of tungsten is about the same of borosilicate glass; this guarantees dilatometric compatibility between the matrix and the metal powders. As far as electrical properties are concerned, the conductivity of tungsten ranges from 15 to 33% that of copper, depending on the microstructure. This implies a skin depth of few μm at the most used microwave ISM frequencies, that is to say, of the same order of magnitude of the average particles size of the tungsten powders used. The skin depth indicates the degree of interaction of the electromagnetic field at a given frequency with a non-ideal conductor medium, being the skin depth the distance at which the field is attenuated by 1/e factor of its value at the surface. Moreover, varying the percentage of metal particles, the maximum conductive path length is affected, until complete percolation is achieved and the whole sample becomes electrically conductive, so its permittivity can be described by Drude dispersion model [15].

Experimental

Materials

Mo/glass composite

The glass used for the matrix was a commercially available borosilicate glass powder (DURAN®, Schott Glas, Mainz, Germany). The temperature-viscosity dependence and the sintering behaviour of this glass are well-known [16]. 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 less than 3 μm, but particle agglomeration occurred during processing. Mixtures containing 5 vol% molybdenum

particles were prepared. The powders were dry mixed and the composite powder was pressed uniaxially at room temperature for 5 s at the maximum pressure of 36.9 Mpa, in order to obtain small cylindrical samples (diameter: 10 mm, height: 2 mm). A water solution of 3 mass% PVA was added to the powder mixture in a 5 mass% concentration in order to bind the pressed particles thus allowing samples handling and transportation. The pellets were then inserted in a hot air dryer for 12 h to allow complete water removal.

W/glass composite

Commercially available borosilicate glass hollow spheres, having a diameter of 50±5 μm, were used for the matrix. The metal inclusions used in this study are tungsten particles of guaranteed minimum 99.9% purity, and were used in the as-received state. The average particle size of primary particles was less than 2 μm, but particle agglomeration occurred during processing. Mixtures containing 0, 3, 5, 10, 15, 20, 30, 50, 75 mass% of W particles were prepared. The powders were dry mixed and then formed as previously described.

Dielectric properties measurement and electromagnetic field modelling

The electromagnetic field distribution inside the microwave applicator and inside the W/glass samples was simulated using the commercially available software Concerto 2.0, which is able to provide as well the dissipated power in lossy regions and the reflection and transmission coefficient. Input data concerning dielectric properties at room temperature were measured in the microwave frequency range from 2 GHz to 12 GHz using an HP 851907B vector network analyser with dielectric probe meter HP 85070B. The measurement technique consists in converting complex reflection coefficient into complex permittivity. Calibration is achieved using distilled water, open and short circuit loads.

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 described in a previous paper [17].

This microwave applicator was operated in inert atmosphere at 400 W for 60 s to qualitatively estimate the dielectric heating of the W/glass composites, in order to indirectly validate the electromagnetic field modelling results and the microwave absorption of the different samples. The sample were positioned, one per run, in correspondence of the applicator choked opening, and the applicator was tuned during the whole heating process, in order to follow the dielectric properties changes of the material.

The Mo/glass samples were positioned, in air and one per run, on a cylindrical silicon carbide element surrounded by an aluminosilicate fibrous lining, and the whole assemblage was inserted in the single mode applicator. The silicon carbide ele-

ment 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. The samples 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 samples lead to the determination of 400 W as the maximum magnetron power output bearable by the samples without major cracking during the 90 to 120 seconds-time of microwave exposure. The final step of the heating treatment consisted of 300 s air cooling by natural convection outside the applicator. Temperatures above 1000°C were detected at the end of the 120 s heating, so that a heating ramp of at least 8.3°C s^{-1} 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, while the organic binder was removed and/or the temperature increased.

Results

Dielectric properties measurement and electromagnetic field modelling

The real and imaginary part of permittivity, at selected tungsten percentage, are shown as a function of the frequency in Fig. 1. Both real and imaginary part of complex permittivity increase with respect to the tungsten content.

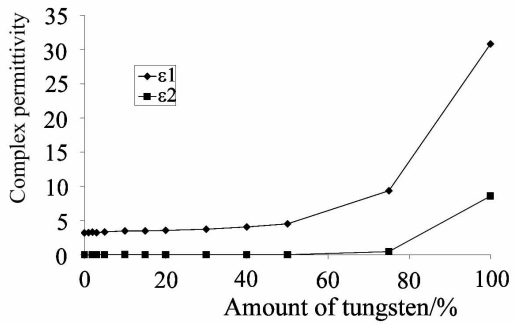

Fig. 1 Real (ε1) and imaginary part (ε2) of complex permittivity of the W/glass mixtures measured at 2.45 GHz

The simulation, after 20000 iterations, using a sinusoidally excited source, at the 2.45 GHz frequency, lead to the outputs reported in Fig. 2. Despite the scale difference, it is evident a more uniform microwave absorption for the samples containing small amounts of metal, while the higher the metal content, the less homogenous is the power dissipated in the material, and presumably the temperature distribution.

The microwave absorption behaviour was confirmed by the heating test performed in the single-mode applicator, showing a lower power reflection as the W content increases. Thermal maps of the samples during the heating process could not be directly used to investigate the dissipated power, since the thermal capacity of the samples

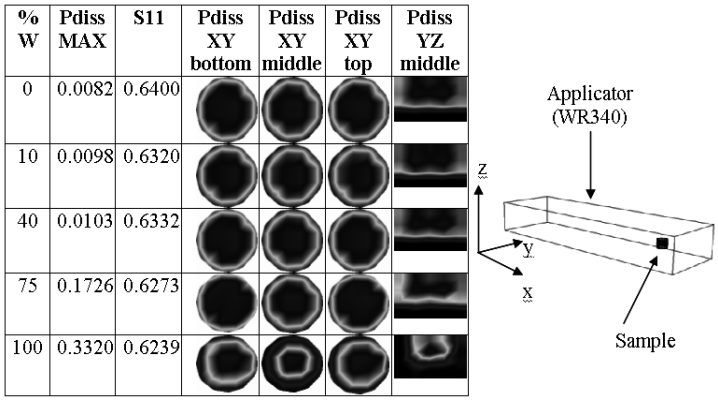

Fig. 2 Reflection coefficient (S11) and dissipated power inside the material (0, 10, 40, 75, 100% of tungsten contents, %W): darker regions: higher dissipated power

changes as the W content varies. However, the higher rate of temperature raise was measured for the samples containing 40% W, followed by the 50% and 30% ones.

Mo/Glass composite

Macroscopic visual examination revealed that after microwave processing the samples retained the cylindrical shape with minimal distortion. However, a symmetric layered structure, as schematically shown in Fig. 3 resulted after optical microscope observations.

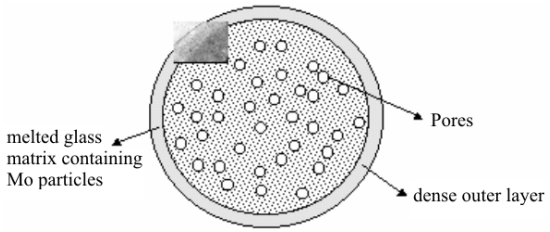

Fig. 3 Optical microscope surface photograph (top, left) and representation of the layered porous structure of microwave processed cylindrical Mo/glass samples

Samples obtained by conventional heating, under the same heating schedule and conditions, instead, presented a pronounced distortion and major cracks. Moreover, the surface was not continuous, but interrupted by open porosity. Figure 4 shows SEM micrographs of two representative samples of the microwave treated discs section and of the conventional heated ones, and measured data on pores (Archimede's law) and porosity (image analysis).

The microstructure of both samples is quite different, as depicted in Figs 4a and 4b.

Microwaved sample exhibits, in the centre, a high concentration of spherical pores embedded in a dense glass matrix. The pores are homogeneously distributed

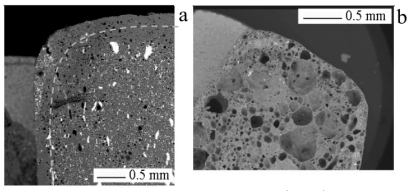

Fig. 4 SEM section micrograph of a – microwave, b – conventional-heated sample. Dashed line sketched in Fig. 4a is meant to separate the outer dense region from the inner porous one

and they present a diameter size distribution, which is in the range ~5 to ~50 μm. In the denser outer region or shell, instead, the pores are smaller than 10 μm in diameter. The complete absence of Mo particles in this region, as evident in Fig. 4a, was also confirmed by EDS analyses.

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. Conventional heat-treated samples, instead, are swelled and cracked, and they do not exhibit the presence of an outer denser shell separated from the inner core, while the porosity diameter size is distributed over a much wider range.

Discussion

The higher microwave absorption of the metal-richer samples resulting from the dielectric properties measurement and the electromagnetic field distribution simulation, leading to the reflection coefficient and the dissipated power, is in good agreement with the experimental results of the heating tests. However, the present simple model does not take into account the different thermal properties of the samples, and the dissipated power maps can be used only to determine the local heat-generation term of the heat equation [18], and not to directly visualise temperature profiles. Moreover, another phenomenon which is not taken into account by the model is that, during microwave heating, arcing and electric discharge can occur, even at a microscopic level, altering the process and the microstructure too [19]. This inaccuracies explain the reason why the higher heating rate was measured for the 40% W/metal composite, and, up to a certain extent, the reason of the absence of Mo particles in the outer layer of the Mo/glass composites sintered by microwaves.

As a matter of fact, Mo particles seem to migrate far from the outer dense 'shell' towards the interior of the sample. Arching between small conductive particles dispersed in a dielectric matrix is a phenomenon well known in the microwave thermal treatment of materials and it has been observed by the authors during the heating test conducted in the single mode applicator. Moreover, interrupting the heating treatment before full sintering occurred, it is possible to observe the formation of crystals near the surface of the sample, which, after SEM-EDS investigations, proved to be Mo-rich. A tentative explanation of

this phenomenon lies in the rapid sublimation of the Mo particles and in the subsequent crystallisation once the cooler surface is encountered.

As far as the peculiar microstructure of the microwaved samples is concerned, with respect to conventionally heated ones, it can be explained considering the thermal profile induced by the two different techniques of energy transmission. During microwave heating, benefiting of the low-metal content, heat is homogeneously generated in the bulk of the sample by interaction of the electromagnetic field with the matter. As a consequence, thermal gradients reverse to those occurring in conventional heating develop, i.e. the surface is cooler than the interior of samples. The structure of the specimens itself suggests that the temperature in the central region was high enough to induce melting of the glass matrix. At temperatures higher than 1000°C, the viscosity of the DURAN® borosilicate glass used for this work is $<10^5$ dPa s [11], which is much lower that the viscosity at which viscous flow assisted sintering would occur for this material. Under these conditions, the central region of the specimen behaves as a partially molten glass retained by a rigid outer layer, which is at a lower temperature due to heat dissipation toward the cooler surroundings. In this region, however, the glass powder particles reach temperatures elevated enough to sinter by viscous flow. In the used DURAN® borosilicate glass, viscous flow densification occurs at temperatures of ~900°C at relative high viscosities, i. e. at about 10^9 dPa s [8]. Therefore densification (shrinkage) takes place without (or with minimal) shape distortion of the body. Extensive gas evolution in the central molten glass region, instead, creates bubbles, which, on rapid cooling, remain trapped in the structure thus forming the spherical pores.

This phenomenon is not present in the samples sintered by conventional means, since the outer region is exposed to higher temperatures. Therefore, gas evolution from the central glass encounters partially molten regions in its diffusion path, thus distorting the sample's shape and being responsible for the formation of open porosity at the surface. Moreover, pore size is no longer controlled by an existing internal pressure, since gases are almost free to leave the samples, due to the absence of an outer rigid and dense shell.

Conclusions

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 set-up of an effective microwave-assisted heating process, however, requires a prior knowledge of the dielectric properties of the materials involved, and of the main characteristics of the microwave applicator which is intended to be used. It is the combination of this two issues which determines if a microwave assisted treat-

ment is feasible. Moreover, the now available computer modelling tools can provide useful information prior to experimental tests, helping, for instance, in choosing sample position, in estimating energetic yields and, if necessary, in suggesting how to alter materials properties or how a more efficient applicator should be designed.

References

1 A. C. Metaxas and R. J. Meredith, Industrial microwave heating, Peter Peregrinus Ltd, London 1993, pp. 7–24.
2 W. H. Sutton, Am. Cer. Soc. Bull., 68 (1989) 376.
3 P. Veronesi, C. Siligardi and C. Leonelli, Cer. Inf., (2000) 397. (in Italian).
4 J. Majling, P. Znasik, D. Agrawal, J. Cheng and R. Roy, J. Mat. Res., 10 (1995) 2411.
5 A. Goldstein, R. Ruginets and Y. Geffen, J. Mat. Sci. Lett., 16 (1997) 310.
6 R. R. Di Fiore and D. E. Clark, Ceram. Eng. Sci. Proc., 16 (1995) 1089.
7 L. Schenck, C. Oswald and R. Clasen, Proc. XVIII International Congress on Glass, 1998.
8 F. Andreola, C. Leonelli, C. Siligardi and A. B. Corradi, Tile and Brick Int., 16 (2000) 6.
9 C. Siligardi, C. Leonelli, F. Bondioli, A. Corradi and G. C. Pellacani, J. Europ. Ceram. Soc., 20 (2000) 177.
10 D. A. Lewis, European Patent 0538 663 A1, 2. 10. 1992.
11 Y. Zhou and O. Van der Biest, Silicates Ind., 7–8 (1996) 163.
12 L. Chen, C. Leonelli, T. Manfredini and C. Siligardi, J. Am. Ceram. Soc., 80 (1997) 3245.
13 I. Dlouhy, M. Rheinish, A. R. Boccaccini and J. F. Knott, (1997) 1235.
14 Y. Waku, M. Suzuki, Y. Oda and Y. Kohtoku, J. Mat. Sci., 35 (2000) 2955.
15 A. Sihvola, Electromagnetic mixing formulas and applications, London, IEE, 1999.
16 A. R. Boccaccini, PhD Thesis, Aachen University of Technology, 1994.
17 P. Veronesi, C. Leonelli and A. R. Boccaccini, Key Engineering Mat., (2002) 317.
18 V. Tse, Chow Ting Chan and H. C. Reader, Understanding microwave heating cavities, Artech House (2000), pp. 28–30.
19 R. J. Meredith, Engineer's handbook of industrial microwave heating, IEE, 1999.