ELSEVIER

Ceramics International 32 (2006) 603–608

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Glass foams from dismantled cathode ray tubes

Enrico Bernardo*, Francesca Albertini

Dipartimento di Ingegneria Meccanica, Settore Materiali, Università di Padova, via Marzolo 9, 35131 Padova, Italy

Received 25 January 2005; received in revised form 15 April 2005; accepted 28 April 2005
Available online 18 July 2005

Abstract

Glasses from dismantled cathode ray tubes (CRTs) represent a pressing environmental problem, since their direct reutilization in manufacturing the original glass components is very difficult. The most hardly recycled glass, panel glass, has been employed for the manufacturing of glass foams, intended for thermal and acoustic insulation, by sintering of a mixture of glass and calcium carbonate powder mixture. In this work, we illustrate the effects of the heating rate, the holding time and the concentration of carbonate, employed as foaming agent, in the same sintering process, on the relation between density and crushing strength. Due to the observed mechanical properties and the results of preliminary thermal conductivity tests the obtained materials were found to approach commercial glass foams.

Keywords: A. Sintering; C. Mechanical properties; D. Glass; E. Thermal applications

1. Introduction

It is well known that in glasses several inorganic wastes can be easily dissolved and almost definitely immobilized [1,2], since the obtained glasses generally exhibit a remarkable chemical stability; however, the vitrification treatment, i.e. the formation of a new glass from wastes, is extremely energy-consuming and may be economically advantageous only in the case of the re-employment of the glasses in the manufacturing of new glass-based articles, like glass fibres [3], glass ceramics [4], glass or glass-ceramic matrix composites [5,6] or glass foams [7,8]. The same applications are suitable also for glasses which represent by themselves a kind of industrial waste, as their direct recycling in the manufacturing of the original glass articles is complicated by risks of contamination and loss of qualitative requirements. A fundamental example of such glasses is represented by the glasses employed in cathode ray tubes (CRTs). In a CRT, different types of heavy metal containing glasses, lead- or barium-based, are employed to absorb the UV and X radiations escaping from the electron gun [9]. Our investigation considered essentially the panel glass, that corresponding to the front part (i.e. the ‘‘screen’’), which is a barium-strontium glass; the usage of expensive oxides like BaO and SrO, instead of PbO, prevents the precipitation of metallic clusters from easily reducible oxides (like PbO), induced by high-energy electrons, which in turn may cause an undesirable darkening effect of the screens (the effect being known as ‘‘solarization’’) [10]. It must be noted that the lower specific absorption of radiations of Ba–Sr glasses, compared to Pb glasses, is compensated by the relevant thickness of the screens, resulting in the fact that almost two thirds of the total weight of the glass components of a typical CRT are attributable to panel glass. Panel glass, unlike the other glasses in a CRT, is hardly employed in the manufacturing of new CRTs (the weight percentage of ‘‘used’’ glass being lower than 15% [11]), since only high-quality pristine glass, from selected raw materials and with no lead contaminations (for example, coming from the glass-to-glass joining of panel glass to Pb glasses in a CRT), is desirable.

Glass foams, intended for thermal and acoustic insulation, represent an interesting application for waste glasses from an economic and environmental point of view. In fact, their processing route consists of the foaming, i.e. the formation of gaseous species, in a pyroplastic mass of softened glass powders undergoing viscous flow sintering.

---

* Corresponding author. Tel.: +39 049 8275510; fax: +39 049 8275505.
E-mail address: enrico.bernardo@unipd.it (E. Bernardo).

0272-8842/$30.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.04.019

Unlike the first experiences, dating back to 1930s [12–14], there is no need of introducing gasses within molten glass, but foaming gasses come from some chemical reactions simultaneous to sintering. The lacking of a melting process leads to a certain production economics and prevents from the volatilisation of some oxides. The foaming may be caused by an oxidation process, which is typical for C-based ‘‘foaming agents’’, namely C (graphite, coal, carbon black, pyrolytic residues in fly ashes, etc.) and SiC, or by a decomposition process, as for minerals like carbonates (Na_2CO_3, $CaCO_3$, $MgCO_3$, etc.) or sulphates ($CaSO_4$, i.e. gypsum) [12]. As previously reported [12,15], decomposition processes are more suitable for glasses containing remarkable amounts of heavy metals, since they do not bring the risk of oxidation reactions of carbonaceous substances by the reduction of easily reducible oxides, like those of some heavy metals. In this paper we present the foaming of panel glass by using $CaCO_3$, following different processing conditions, which in turn may be useful for an actual industrial application.

2. Experimental

The chemical composition of panel glass is shown in Table 1 [9,16].

The glass, available as granules with a diameter in the range 5–10 mm, was dry ball milled and sized in order to obtain grains <37 μm. The glass powders were ground in a tungsten carbide vibratory mill for 10 min, producing smaller glass particles (about <25 μm). The fine glass powders were added with $CaCO_3$ (reagent grade, Sigma–Aldrich) and water (in a concentration of about 15 wt.%), then mixed in the same ball mill for 1 h. The proportions in weight of $CaCO_3$ were 3, 5, 7%. The glass/carbonate mixtures were uniaxially pressed at 40 MPa in a cylindrical steel die with a diameter of 31 mm, by using a hydraulic press at room temperature. The obtained discs were dried at 80 °C overnight, then subjected to heat treatment at 725 °C. The processing temperature was that employed in [15], and it represents the optimum temperature since the decomposition of $CaCO_3$ begins at about 700 [15] and 725 °C is far beyond the (dilatometric) softening temperature of panel glass (see Table 1), thus leading to low viscosity, essential for foaming. In the present investigation several processing conditions were considered, since the heating rate and the holding time varied from 5 to 20 °C/min and from 5 to 30 min, respectively. All the samples were drastically cooled (more than 10 °C/min) from the foaming temperature to 600 °C, in order to ‘‘freeze’’ the microstructural evolution for the selected holding time, then slowly cooled (~1 °C/min) to 500 °C, in order to perform a sort of ‘‘annealing’’ treatment, in a temperature range close to the transformation temperature ($T_g \sim 530$ °C) and again quickly cooled (~5 °C/min) to room temperature.

Table 1
Chemical and physical properties of panel glass from dismantled CRTs

Chemical composition	
Oxide	wt.%
SiO_2	60.7
Al_2O_3	1.70
Na_2O	7.50
K_2O	6.90
CaO	0.10
BaO	9.90
SrO	8.60
ZnO	0.20
PbO	0.01
ZrO_2	5.50
Sb_2O_3	0.45
Fe_2O_3	0.05
TiO_2	0.55
Transformation temperature T_g (°C)	525.7
Dilatometric softening temperature (°C)	592.8
Density (g/cm^3)	2.71

The obtained foams were subjected to compression tests by using an Instron 1121 UTS machine, with a crosshead speed of 2 mm/min, employing samples of about 15 mm × 15 mm × 10 mm, cut from larger specimens (the appearance of the obtained foams is illustrated by Fig. 1). Each data point represents the average of 5–10 individual tests.

The morphology of the foams was investigated by scanning electron microscopy (Philips XL 30 ESEM). Samples in powder form were subjected to X-ray diffraction analysis (XRD, Philips PW3710), by using Cu Kα radiation (0.15418 nm). The thermal conductivity of selected samples was measured by means of non-steady-state hot disk method on disks of 8–10 mm thickness and 22 mm diameter.

3. Results and discussion

The mechanical properties of the obtained glass foams are illustrated in the graphs of Fig. 2.

The compression resistance (i.e. crushing strength) of foams, σ_f, is generally expressed by the Gibson–Ashby equation [17], as follows:

$$\frac{\sigma_f}{\sigma_{bend}} = C\Phi\rho_{rel}^{3/2} + (1 - F)\rho_{rel}$$

where σ_{bend} is the bending strength of the employed glass; C, a dimensionless constant (being ~0.2) and ρ_{rel} is the relative

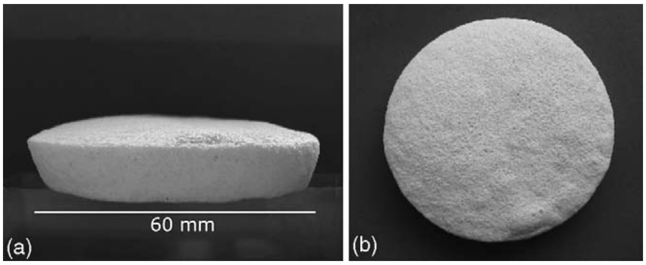

Fig. 1. Images of the glass foams (*a*: side view, *b*: upper view).

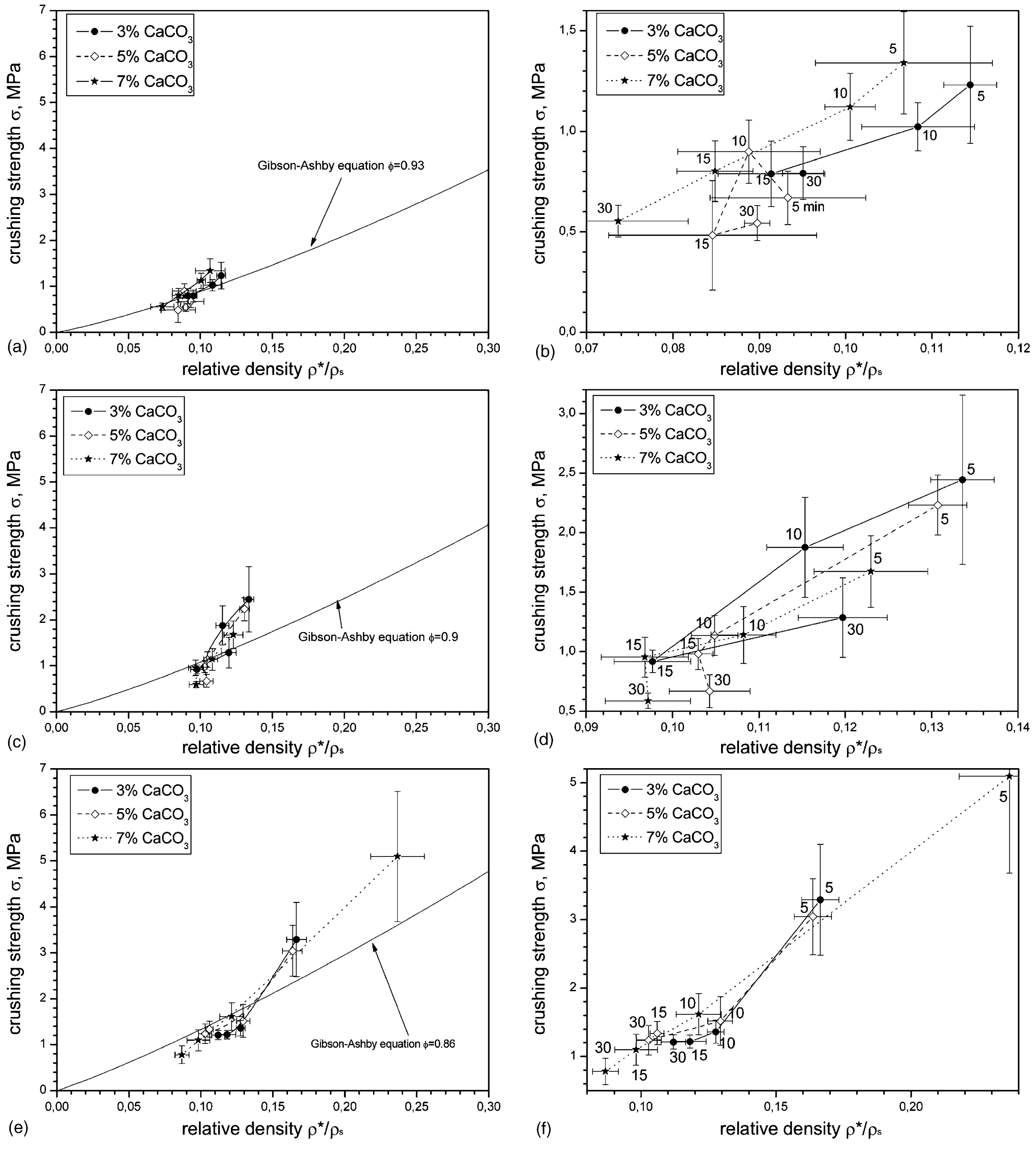

Fig. 2. Crushing strength of the foams as a function of their relative density and heat treatment: (a, b) 5 °C/min; (c, d) 10 °C/min; (e, f) 20 °C/min; on the left, graphs reported with the same scale in order to facilitate the comparison between different conditions; on the right, graphs with expanded scales, with the holding time reported near each data point.

density (the ratio between the measured density of the foams and the density of the employed glass). Φ is a correction factor $(1 - \Phi)$ expressing the fraction of glass being in the cell walls; if the foam is open-celled, the pores are fully interconnected, with no material in the hypothetical walls, so that $\Phi = 1$ $(1 - \Phi = 0)$; on the contrary, for a closed-cell foam, $\Phi = 0$. It was found that the correction factor is close to unity for all the processing conditions, and this is coherent with the findings in the literature [12], predicting a tendentially open-celled morphology for foaming agents operating by decomposition, like carbonates and sulphates. However, this was not confirmed by the morphology of the foams, discussed later on. Moreover, a certain progression of the correction factor was revealed, since Φ slightly varied from

0.93 for a 5 °C/min heating rate, to 0.9 for 10 °C/min and 0.86 for 20 °C/min.

The foams obtained with a heating rate of 5 °C/min or 10 °C/min exhibited a similar low density. The relative density is in the range 0.07–0.12 (the density of the foams being in the range 0.19–0.35 g/cm^3); the crushing strength is around 1 MPa, thus configuring foams with similar mechanical properties than commercial foams [18]. However, some features are particularly interesting. The increase of the duration of the holding time generally caused a decrease in the relative density (see Fig. 2b, d and f), probably due to the more extensive decomposition of $CaCO_3$. For some samples heated at 5 °C/min (3, 5 wt.% $CaCO_3$) and for all the samples at 10 °C/min, a certain anomaly was revealed, since the extension of the holding time from 15 to 30 min did not cause a decrease of the relative density, but caused the density to be stationary, with a remarkable decrease of the crushing strength, or increase (3%, 10 °C/min, Fig. 2d). One likely reason is that with the extension of the heating rate secondary effects of "coalescence" of pores occurred; after foaming, smaller pores likely dissolved in larger pores, favoured by the decrease of the surface energy of the system. This phenomenon, widely reported in the literature [12], has a secondary effect in the increase of the thickness of the cell walls, with a certain increase of density; the crushing strength does not increase, since the enhanced thickness of the cell walls provides an enhanced probability of finding critical flaws. The effect is particularly remarkable for a low content of the foaming agent, since probably almost all $CaCO_3$ decomposed during the first minutes.

The limited density range, for the foams obtained by 5 and 10 °C/min heating rate, was attributed to the fact that the foaming was probably active before reaching the processing temperature: slower rates allow a longer "exposition" of the glass/carbonate system to the temperature range in which $CaCO_3$ decomposed. Prolonged foaming treatments did not cause a more extensive foaming, but favoured coalescence. It must be noted (see Fig. 2d) that the samples maintained only 5 min at 725 °C exhibited a remarkable crushing strength (much superior to that predicted by the Gibson–Ashby equation).

The hypothesis of foaming during heating, prior to the holding time, was confirmed by the data obtained from samples heated at 20 °C/min, shown in Fig. 2e and f. The fast heating rate was thought to limit the foaming upon heating and cause the density to be related only to the holding time. A direct correlation between crushing strength and relative density is effectively visible, with no anomalies. The crushing strength can be reasonably "tailored", as a function of the relative density, with the concentration of $CaCO_3$. The increase of the content of foaming agent led to lower densities. The only anomaly is represented by the samples maintained for 5 min, for a 7 wt.% $CaCO_3$, probably due to incomplete decomposition.

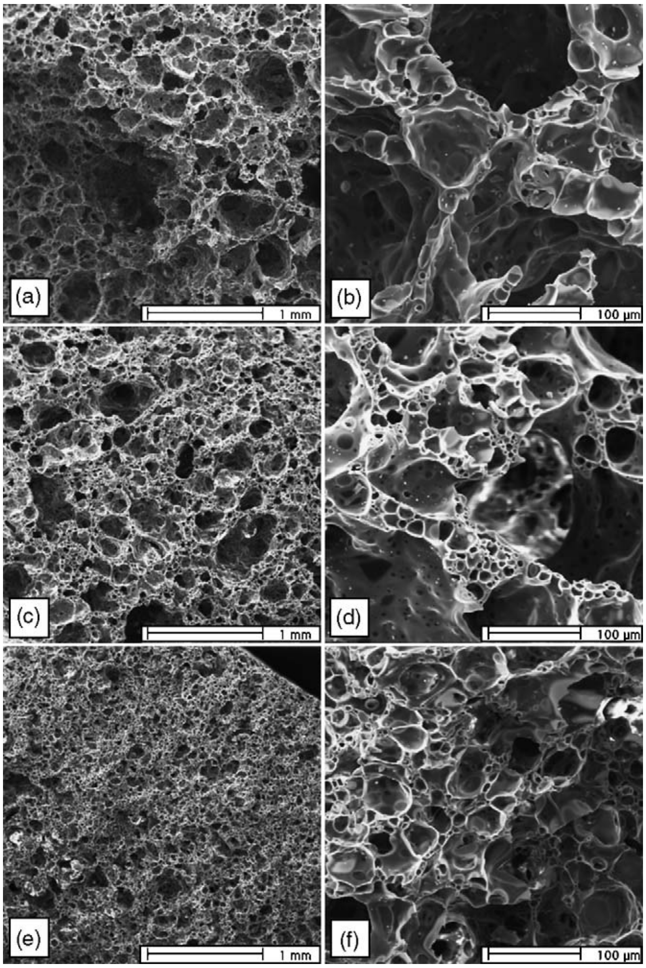

Fig. 3. Microstructures of selected glass foams (5% $CaCO_3$, 5 min holding time at 725 °C).

As illustrated in Fig. 3, for the same concentration of foaming agent and the same holding time, the dimension of the cells drastically decreases with increasing heating rate. Foams from slow heating are quite not homogeneous and exhibit large pores, surrounded by walls in turn containing small cells (see Fig. 3b and d). One likely reason for such morphology is the foaming, in a limited number of points, prior to the reaching of the processing temperature. On the contrary, the pores in the foams from fast heating remain small (smaller than 100 µm), with very thin separation walls, since the foaming was concentrated in the holding time. The foams are tendentially closed-cells, but the presence of pores in the separating walls may have a weakening effect, thus configuring foams with a mechanical behaviour similar to open-celled foams. In addition, the observed modification in the correlation factor Φ in the Gibson–Ashby equation may come from the modification of the structure upon cell separations. A further investigation on the porosity/strength relation is undoubtedly needed and will be the object of our future studies.

The above-mentioned effect of "coalescence" is illustrated by Fig. 4.

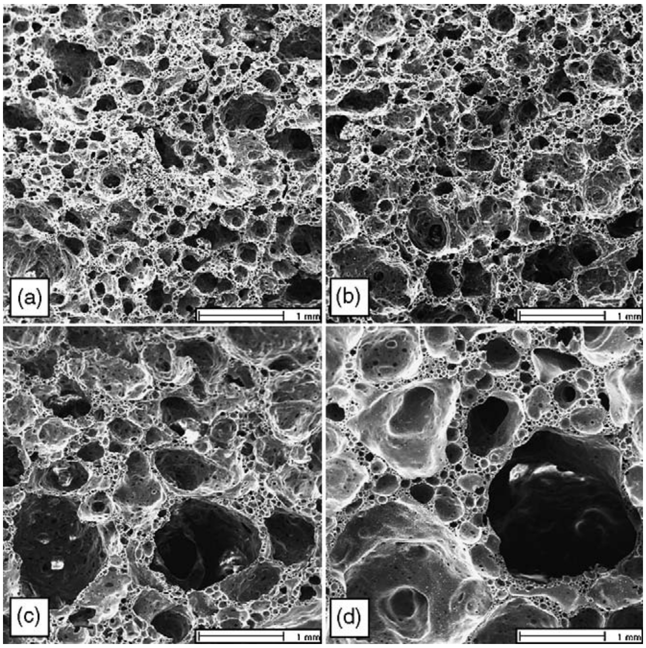

Fig. 4. Glass foams (3% $CaCO_3$, 10 °C/min) at different holding times: (a) 5 min; (b) 10 min; (c) 15 min; (d) 30 min.

The foams exhibit an effective coarsening of the microstructure with increasing holding time. The foams maintained at 725 °C for 30 min (Fig. 4d) show very large pores (1 mm diameter) but also very large walls, thus confirming the considerations about Fig. 2d. Only for a limited holding time, 5 min (see Fig. 4a), the microstructure is rather homogeneous, resulting in the above mentioned remarkable crushing strength (foams with more than 2 MPa crushing strength, see Fig. 2c and d).

The glass foams were amorphous, all with spectra analogous to those reported in Fig. 5. The observed microstructure was due only to the particular thermal treatments, not to any crystallization phenomenon. No peak corresponding to metallic inclusions was revealed.

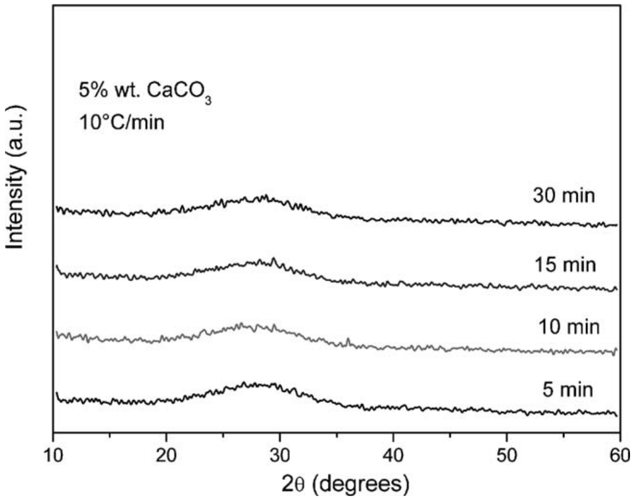

Fig. 5. XRD spectra of selected glass foams.

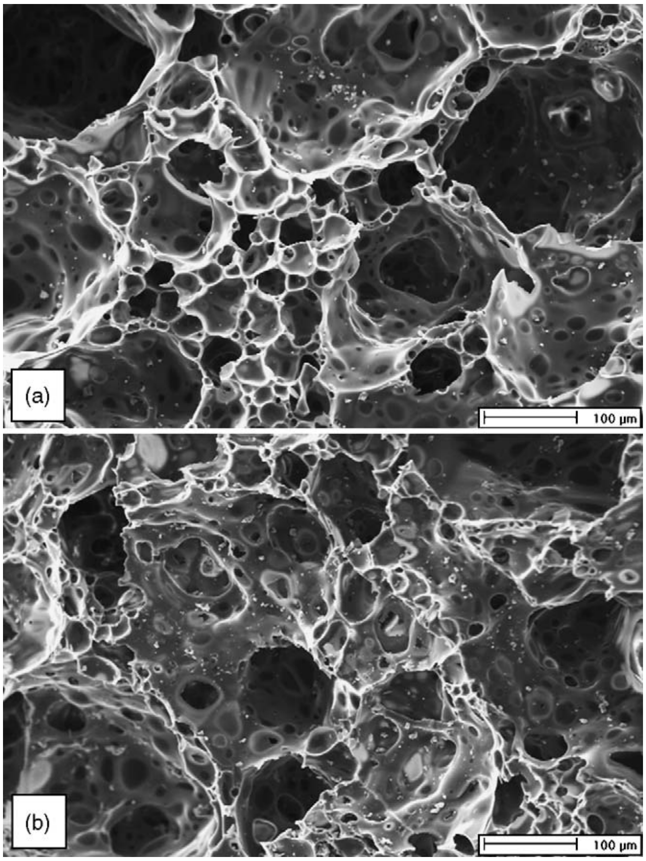

Fig. 6. SEM micrographs of the foams subjected to thermal conductivity analysis (5 wt.% $CaCO_3$, 15 min holding time): (a) 20 °C/min; (b) direct insertion at the foaming temperature.

The fact that fast heating rate promoted a fine microstructure of the foams (see Fig. 3e and f) was confirmed by a validation test, in which foams were prepared by direct heating of the glass/carbonate mixture at 725 °C, for the same concentration of $CaCO_3$, 5 wt.%, and the same holding time, 15 min. The results from fast heating and direct insertion are compared in Fig. 6. The densities are similar (0.25 ± 0.02 g/cm^3 for the conventionally heated sample and 0.27 ± 0.02 g/cm^3 for the sample from direct insertion) and both the foams consists of pores with about 100 μm diameter surrounded by smaller pores (10 μm), with very thin separations. It must be noted, however, that in the foams from conventional heating many small pores lay in the separating walls of main pores.

The last samples were subjected to thermal conductivity tests. The foams showed a low thermal conductivity, being 0.060 ± 0.004 W/m K for the sample heated at 20 °C/min and 0.068 ± 0.002 W/m K for the sample from direct insertion at the foaming temperature. Even if thermal test need to be extended to all the processing conditions, the achieved values are promising, since they are close to the values reported in the literature for commercial foams [12]. The small pores in the cell walls had probably an advantageous effect, by reducing the fraction of solid between the main cells, leading to lower conductivity.

4. Conclusions

Glass foams may be considered a promising way to re-employ panel glass from the dismantled cathode ray tubes. Several processing conditions were evidenced, leading to various combinations of density and crushing strength, which might be useful in industrial applications, as follows:

- Fast heating rates promote a direct correlation between crushing strength and relative density, so that they may be tailored in function of the holding time and the concentration of foaming agent;
- The microstructures from fast heating treatments are generally finer than those available from slow treatments, since the foaming is concentrated in the holding time at the foaming temperature;
- Slow heating rates do not allow a wide range of density and crushing strength; the foaming prior to reaching the processing temperature causes poor homogeneity and coalescence of pores for prolonged treatments; only in the case of short holding time the microstructure is acceptable, yielding to remarkable crushing strength (>2 MPa, for a relative density of about 0.13);
- The lightest foams (~0.10 relative density) exhibit a crushing strength of about 1 MPa, thus being comparable to commercial foams;
- Preliminary tests showed that the achieved foams possess a low thermal conductivity, 0.060–0.070 W/m K, again comparable to that of commercial foams.

Acknowledgements

The authors would like to thank Prof. Nikolay Maliavski of the Department of General Chemistry of the Moscow State University of Civil Engineering (MGSU) and the Russian State Research Institute of the Physico-Technical and Radio-technical Measurements (VNIIFTRI) for performing thermal conductivity tests and C. Furlan for SEM micrographs.

References

[1] P. Colombo, G. Brusatin, E. Bernardo, G. Scarinci, Inertization and reuse of waste materials by vitrification and fabrication of glass-based products, Curr. Opin. Solid State Mater. Sci. 7 (3) (2003) 225–239.
[2] R. Gutman, Thermal technologies to convert solid waste residuals into technical glass products, Glastech. Ber. Glass Sci. Technol. 69 (9) (1996) 223.
[3] G. Scarinci, G. Brusatin, L. Barbieri, A. Corradi, I. Lancellotti, P. Colombo, S. Hreglich, R. Dall'Igna, Vitrification of industrial and natural wastes with production of glass fibers, J. Eur. Ceram. Soc. 20 (2000) 2485–2490.
[4] P.D. Sarkisov, The modern state of technology and application of glass-ceramics. Glass'89 Survey Papers of the XVth International Congress on Glass Leningrad, 1989, pp. 411–441.
[5] A.R. Boccaccini, M. Bücker, J. Bossert, K. Marszalek, Glass matrix composites from coal flyash and waste glass, Waste Manage. 17 (1) (1997) 39–45.
[6] P.A. Trusty, A.R. Boccaccini, Alternative uses of waste glasses: issues on the fabrication of metal fibre reinforced glass matrix composites, Appl. Composite Mater. 5 (4) (1998) 207–222.
[7] G. Bayer, S. Koese, Reaction of foaming additives with waste glass powders in the preparation of lightweight materials, Riv. Staz. Sper. Vetro 5 (1979) 310–320.
[8] V. Ducman, M. Kovačević, The foaming of waste glass, Key Eng. Mater. 132–136 (1997) 2264–2267.
[9] S. Hreglich, R. Falcone, M. Vallotto, The recycling of end of life panel glass from TV sets in glass fibers and ceramic productions, in: Proceedings of the International Symposium "Recycling and Reuse of Glass Cullet", University of Dundee, UK, 19–20 March 2001, pp. 123–134.
[10] J.S. Nordyke, Lead in the World of Ceramics, The American Ceramic Society, Westerville, OH, USA, 1984.
[11] L.A.R. Siikamaki, End of life cathode ray tube glass as a raw material for hollow ware glass product, in: R.K. Dhir, M.D. Newlands, J.E. Halliday (Eds.), Recycling and Reuse of Waste Materials, Thomas Telford Publishing, London, 2003.
[12] G. Scarinci, G. Brusatin, E. Bernardo, Production technology of glass foams, in: M. Scheffler, P. Colombo (Eds.), Cellular Ceramics. Structure, Manufacturing, Properties and Applications, Wiley-VCH, Weinheim, Germany, 2005.
[13] B. Long (Saint Gobain, France), US Patent 1,945,052, 30 January 1934.
[14] W.O. Lytle (Pittsburgh Plate Glass, USA), US Patent 2,215,223, 17 September 1940.
[15] E. Bernardo, G. Scarinci, S. Hreglich, Foam glass as a way of recycling glasses from cathode ray tubes, Glass Sci. Technol. (Glastechnische Berichte) 78 (2005) 7–11.
[16] E. Bernardo, G. Scarinci, S. Hreglich, Development and mechanical characterization of Al_2O_3 platelet-reinforced glass matrix composites obtained from glasses coming from dismantled cathode ray tubes, J. Eur. Ceram. Soc. 25 (9) (2005) 1541–1550.
[17] L.J. Gibson, M.F. Ashby, Cellular solids, in: Structure and Properties, second ed., Cambridge University Press, Cambridge, UK, 1999 , pp. 209–214.
[18] Pittsburgh Corning Foamglas Insulation, www.foamglasinsulation.com.