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Preparation and characterization of foams from sheet glass and fly ash using carbonates as foaming agents

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Abstract

Glass foams were produced using sheet glass cullet and fly ashes from thermal power plant with added carbonates (commercial dolomite- and calcite-based sludges) as foaming agents. The influence of type and amount of carbonates as well as of the sintering temperature on the apparent density, compressive strength, microstructure and crystalline phases was evaluated. The experimental results showed that homogenous microstructures of large pores could be obtained by adding just 1–2 wt.% carbonates and using low sintering temperature (850 °C), leading to foams presenting apparent density and compressive strength values of about 0.36–0.41 g/cm^3 and 2.40–2.80 MPa, respectively. Good correlations between compressive strength, apparent density and microstructure (pore size, struts' thickness and internal porosity) were observed.

Keywords: Glass foams; Glass wastes; Fly ashes; Carbonates; Recycling

1. Introduction

In the light of the rapid technological development and the consequent increase of commercial exchanges, recycling has been emerged as a very important environmental issue nowadays due to the diminishing natural resources and the increasing amount of solid wastes. Glasses are among the materials which attract great interest in the recycling concept. In many developed countries there are already systematic community projects for collecting and recycling the waste glasses.

A Report to DGXI European Commission [1] defines ‘‘core’’ C&DW (Construction and Demolition Wastes) as the mix of materials obtained when a building or piece of civil engineering infrastructure is demolished, including under this same heading waste materials arising as a result of construction. ‘‘Core’’ C&DW alone amounts to around 180 million tonnes each year (excludes road planning, excavated soil – whether clean or contaminated – external utility and service connections—drainage pipes, water, gas and electricity and surface vegetation). This is over 480 kg per person per year, and only about 28% is re-used or recycled. Landfilling the other 72% (some 130 million tonnes a year) at a density of 1.0 requires the equivalent of a brand new landfill 10 m deep and roughly 13 square km in surface area every year. Glass wastes correspond to 0.5 wt.% of ‘core’ C&DW, which means that EU produces about 900,000 tonnes of glass wastes every year [2]. In Portugal this value is about 15,000 tonnes/year.

On the other hand, the increasing demand of energy production leads to the world production of about 600 million tonnes of fly ashes in the thermal power plants, and this value tends to increase in the next future [3]. As an example, a 1000 MW power plant uses about 12,000 tonnes of coal and produces about 2000 tonnes of fly ashes per day. The reutilization of these wastes is variable according to the countries, changing from 100% in Netherlands to lower than 20% in other EU countries [4]. In Europe, a minor part of the fly ashes produced have found applications in cement industry as additives, in road construction, in the production of structural materials and as soil additives [5]. Nevertheless, the major part of the produced fly ashes (more than 60 wt.%) is directly putted in landfill. This represents a huge negative environmental impact including the leaching of potentially toxic substances into soils and groundwater, the changes in the elemental

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composition of vegetation growing close to the ashes, and the accumulation of toxic elements in the food chain [6].

Foam glass is a porous heat-insulating and soundproof material, with true porosity up to 90 vol.%. In its physical aspect, foam glass is a heterophase system consisting of the gaseous and the solid phases. The solid phase is glass that forms thin walls of single cells several micrometers thick. The cells are filled with the gaseous phase. Depending on destination, heat-insulating and soundproof foam glass can have predominantly closed or intercommunicating pores, respectively. Over the past few years there has been an increasing interest in the production and use of glass foams. This interest is mainly associated with the properties that these materials offer, such as high surface area, high permeability (intercommunicating pores), low density, low specific heat, high thermal and acoustic insulation and high chemical resistance. Glass foams are resistant to water and water vapor and do not burn [7–9]. Commercial glass foams exhibit porosity, apparent density and compressive strength values of about 85–95 vol.%, 0.1–0.3 g/cm^3 and 0.4–6 MPa, respectively [8].

All glass foams are currently produced by the powder method. The essence of this method consists in sintering a mixture of glass powders and special additives facilitating the formation of a gaseous phase upon heating. These additives introduced into a glass foam batch in small quantities are called pore-forming or gas-forming agents. Several processes take place under thermal treatment of such a mixture, resulting in the foam formation. When the temperature of the mixture exceeds the softening temperature, glass particles start sintering and form a continuous sintered body. Particles of the pore-forming agent become insulated by softening glass. After a certain temperature is reached, they start emitting gases frothing the glass melt. Due to gas emission, pores emerge in all parts of the sintered body where the particles of the pore-forming agent were blocked. The shape of pores and the properties of foam glass obtained largely depend on the concentration and type of the foaming agent used [10].

It is generally accepted that foaming agents are of two types: redox and neutralization agents. Redox foaming agents are usually carbon-containing materials: coke, anthracite, soot, graphite and silicon carbide. The reason for gas emission in these materials is the oxidation reaction of the foaming agent by gases dissolved in the glass melt. The second group usually comprises carbonates which decompose upon heating with emission of gases (CO_2). Intense gas release during their decomposition breaks the walls of individual pores, which merge and create a maze-like system of cavities in glass. Such foam glass has high water absorption and elevated soundproof parameters [10]. Our previous paper [11] reports the preparation of glass foams using redox-type foaming agents. Particularly glass foams suitable for structural and insulating applications in building constructions were produced by using recycling sheet glass cullet along with SiC powder as gasifying agent. It was demonstrated that the incorporation of an alkali earth aluminosilicate glass powder in amounts of 3–5 wt.% improved sintering ability and increased the compressive strength of glass foams (2.07–2.60 MPa). The present study aims at preparing high compressive strength foams using sheet glass wastes in combination with fly ash as main raw materials. Carbonates, namely dolomite—$CaMg(CO_3)_2$ and a sludge derived from the marble cutting process (calcite-based material comprising about 99% $CaCO_3$) were applied as foaming agents.

2. Materials and experimental procedure

Cullet of commercially produced sodium–calcium–silicate sheet glass had a chemical composition (wt.%) of 70.64% SiO_2, 0.68% Al_2O_3, 0.18% Fe_2O_3, 9.93% CaO, 3.55% MgO, 13.66% Na_2O, 0.29% K_2O and 0.21% SO_3 (the data were obtained form the manufacturer). Cullet glass was first crushed in a crushing machine, and then dry-milled using a ring mill (Retsch RS100, Germany) at 1400 rpm for 10 min. The resulting powder, named as G, presented values for mean particle size and bulk density of about 12.5 μm (Table 1) and 2.51 g/cm^3, respectively. Fly ash (A) resulting from an extinguished thermal power plant (Tapada do Outeiro, Portugal) had the following chemical composition (wt.%): 49.6% SiO_2, 20.9% Al_2O_3, 6.6% Fe_2O_3, 0.5% CaO, 1.8% MgO, 0.4% Na_2O, 2.7% K_2O, 0.9% TiO_2, 0.3% MnO and 0.5% P_2O_5, loss of ignition 15.8%.

Commercial dolomite (D), and sludge from a marble cutting–polishing plant consisting of calcite (C) were used as foaming gents. Table 1 presents some physical properties of raw materials.

With the aim to incorporate an appropriate amount of fly ash, 5 compositions free of carbonates comprising only glass and fly ash with glass/fly (G/A) ash ratios $G_{90}A_{10}$, $G_{80}A_{20}$, $G_{70}A_{30}$, $G_{60}A_{40}$ and $G_{50}A_{50}$ were prepared by dry mixing in cylindrical rotary mixer for 30 min. Pellets of cylindrical shape with diameter 20 mm and thickness 3 mm obtained by uniaxial pressing (80 MPa) were sintered at 800 and 900 °C for 20 min followed by measurements of apparent densities, shrinkage and visual observation of the samples. Subsequently, batches containing a fixed glass/fly ash ratio of 80/20 and varying added amounts of carbonates were prepared (Table 2). Appropriate

Table 1
Properties of the precursors used for preparation of the foams

	G	A	C	D
Density (g/cm^3)	2.51	2.44	2.71	2.86
Particle mean size (μm)	13.1	10.4	2.6	19.1
Surface area (m^2/g)	0.865	0.727	1.422	0.834

Table 2
Batch compositions of prepared foams

Composition	G80/A20	C	D
GAC_1	99	1	–
GAC_2	98	2	–
GAC_3	97	3	–
GAC_4	96	4	–
GAC_5	95	5	–
GAD_1	99	–	1
GAD_2	97	–	2
GAD_3	97	–	3
GAD_4	96	–	4
GAD_5	95	–	5

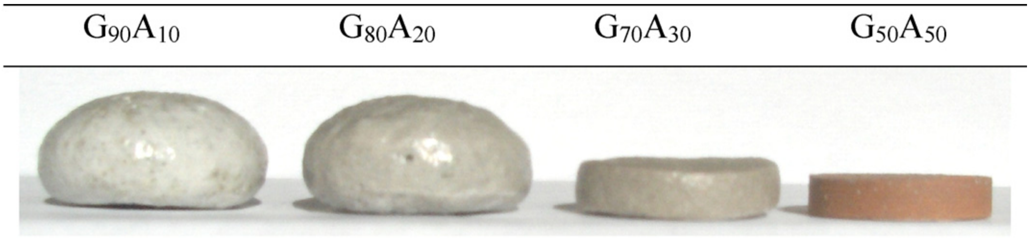

Fig. 1. Side view of pellets comprising glass and fly ash sintered at 900 °C.

amounts of the powder batches were sintered in stainless steel moulds in air. Heat treatment schedule comprised heating at 5 °C/min up to temperatures in the range of 750–950 °C with increments of 50 °C, and holding for 30 min at the heat treatment temperature. Foams were easily removed from the stainless steel moulds and cut in a universal precision cut-off machine (Struers Secotom-10, Denmark). The cutting process was performed without any difficulty and cooling of cutting disc was not essential.

The following characterization techniques were employed. The particle size distribution was measured by light scattering equipment (Coulter LS 230, UK, Fraunhofer optical model). Bulk density was measured using a He picnometer (Micromeritics Accupyc 1330, USA). The apparent density of materials was determined either by Archimedes method (immersion in ethyleneglycol) or by measuring the weight and the dimensions of the produced materials. Porosity was evaluated according to the Eq. (1), where P' is porosity (%), d_a is apparent density and d is bulk density measured by He picnometer

$$P'\,(\%) = \left(1 - \frac{d_a}{d}\right) \times 100 \qquad (1)$$

Thermal analysis of the foaming agents was performed in the interval 20–1000 °C (Setaram Labsys TG-DTA/DSC, France, $T_{\max} = 1600$ °C). The compression strength of cubic samples of ~30 mm edges, placed between parallel plates of stainless steel, was measured in a Shimadzu machine (Trapezium 2, Japan, displacement 0.5 mm/min). Five different samples from each composition were tested. The maximum load of the first plateau of the stress–strain plots divided by the cross-sectional area was considered as the crushing strength [10,11]. The use of intermediate rubber layers placed between the porous samples and the metallic plates of the apparatus did not perceptibly alter the presenting results. Standard deviation values for mechanical strength, density and shrinkage were less than 2, 0.3 and 3%, respectively. X-ray diffraction analyses (XRD, Rigaku Geigerflex D/Mac, C Series, Cu Ka radiation, Japan) and microstructure observations (SEM, Hitachi S-4100, Japan) were also carried out.

3. Results and discussion

Heat treatment at 800 °C for 20 min of pellets having glass/fly ash ratio $G_{90}A_{10}$, $G_{80}A_{20}$, $G_{70}A_{30}$ and $G_{60}A_{40}$ resulted in well-sintered bodies (shrinkage 12.65–14.25%) of dark-brownish color featuring a vitreous aspect with smooth surface. Composition $G_{50}A_{50}$ that kept the yellow-brownish color of as-pressed pellets possessed lower shrinkage as 8.35%. Heat treatment at 900 °C for 20 min caused a significant decrease in apparent densities of the samples containing 10 and 20% of fly ash to less than 50% due to the forming effect (Fig. 1). Foaming was not significant in the $G_{70}A_{30}$ and was not revealed in the compositions $G_{60}A_{40}$ and $G_{50}A_{50}$. Assuming the maximum possible incorporation of ashes into the batch and the ability to form porous structures, composition containing 80 wt.% of glass and 20 wt.% of fly ash was considered for foam production to which varying amounts of carbonates were added.

In establishing an optimal heat treatment procedure for foam production the thermal behavior of glass cullet and carbonates plays a key role. The thermal analysis of glass cullet performed earlier [11] featured a glass transition, $T_g = 540$ °C, and a softening point, $T_s = 590$ °C. The decomposition temperature range for calcite was 750–940 °C (Fig. 2) and the measured total weight loss was 43.9% that is in close agreement with the theoretical one (44%) for pure calcite (Fig. 1b) [12]. Dolomite possessed two strong endothermic peaks (Fig. 2a) corresponding to two moments of weight loss (Fig. 2b) characteristic of

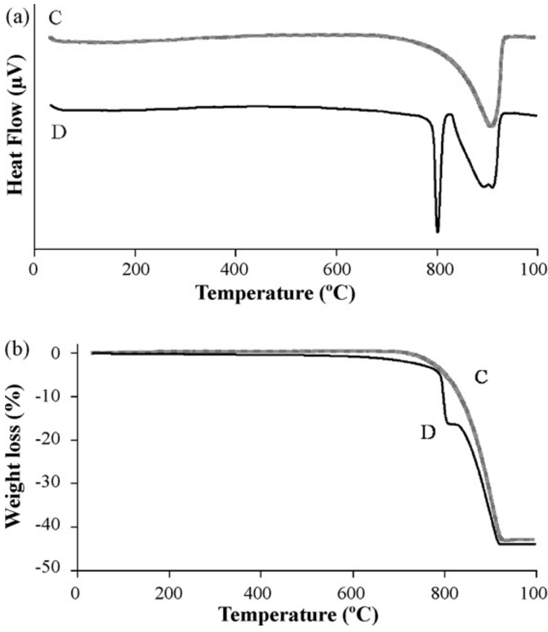

Fig. 2. Thermal analysis (heating rate 5 °C/min) of carbonates C and D: (a) DTA, and (b) TG.

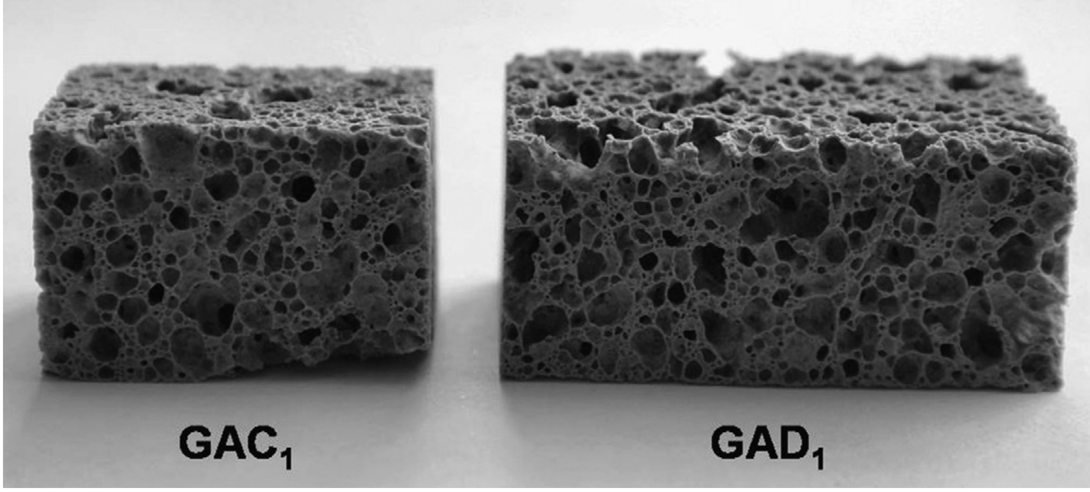

Fig. 3. The typical aspect of the glass foams after rectifying.

this material. The first endothermic peak (800 °C) was due to the decomposition of magnesium carbonate and the second one (890 °C) was attributed to decomposition of calcium carbonate with release of CO_2, according to the Eq. (2) and (3) [13,14]. The total weight loss was about 45%.

$$CaMg(CO_3)_2 \leftrightarrow CaCO_3 + MgO + CO_2 \tag{2}$$

$$CaCO_3 \leftrightarrow CaO + CO_2 \tag{3}$$

The processing temperature for carbonate-containing compositions was established in the interval of 750–950 °C since it was far beyond the dilatometric softening point of glass (590 °C) and thus leading to low viscosity essential for foaming [15] and corresponded to decomposition temperature range of foaming agents (Fig. 2). Fig. 3 shows the typical aspect of the glass foams after rectifying.

The results obtained after measurements of apparent density and compressive strength for the experimental compositions are plotted in Figs. 4–6. Generally, density decreases with increasing sintering temperature reaching minimum values within the temperature range of about 850–900 °C. Further increasing the heat treatment temperature to 950 °C caused an increase in the apparent density. A good correlation between compressive strength and apparent density was effectively visible with some anomaly in the compositions containing 5 wt.% of carbonates, i.e. in GAC$_5$ and GAD$_5$. Moreover, observation of Figs. 4 and 5 revealed that those formulations exhibited highest apparent density values in the range 800–950 °C and their properties were less sensitive to temperature variations. On the contrary, foams comprising 1 and 2 wt.% carbonates showed significant variations with increasing temperature reaching lowest apparent density (0.36–0.41 g/cm^3) among the investigated compositions after sintering at 850 °C (Fig. 6). Their compressive strength values (2.40–2.80 MPa) are superior to glass–ceramic foams from waste glass and coal ash with incorporation of 2 wt.% SiC as foaming agent [16] which exhibited compressive strength of about 1.5 MPa when apparent density ranged from 0.2 to 0.4 g/cm^3. From the study of Wu et al. [16] foams have to be processed at a higher temperature (1000 °C) that increases production costs despite to the relatively short (5 min) sintering time used. One likely reason for this is that SiC effectively acts as foaming agent at temperatures 950–1150 °C due to oxidation reactions and formation of CO_2 and CO gas bubbles [16].

The type of porous structure, namely cells size and thickness of cell walls, play an important role in the resulting mechanical

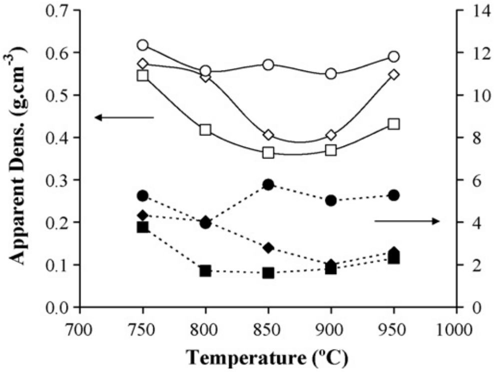

Fig. 4. Evolution of apparent density (white symbols) and compressive strength (dark symbols) with heat treatment temperature for compositions comprising calcite as foaming agent (◇, ◆: GAC$_1$; □, ■: GAC$_2$; ○, ●: GAC$_5$).

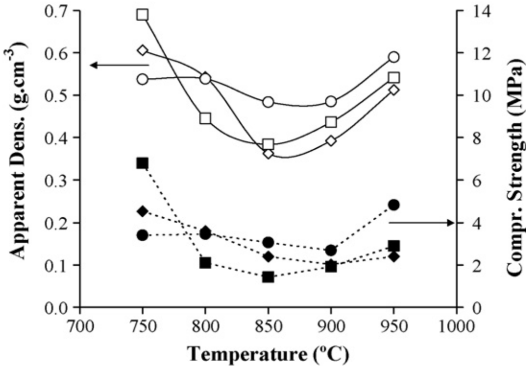

Fig. 5. Evolution of apparent density (white symbols) and compressive strength (dark symbols) with heat treatment temperature for compositions comprising dolomite as foaming agent (◇, ◆: GAD$_1$; □, ■: GAD$_2$; ○, ●: GAD$_5$).

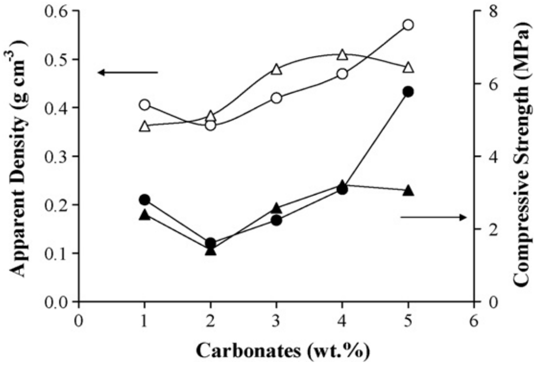

Fig. 6. Evolution of apparent density (white symbols) and compressive strength (dark symbols) with the amount of carbonates (wt.%) for samples sintered at 850 °C (○, ●: GAC; ◇, ◆: GAD).

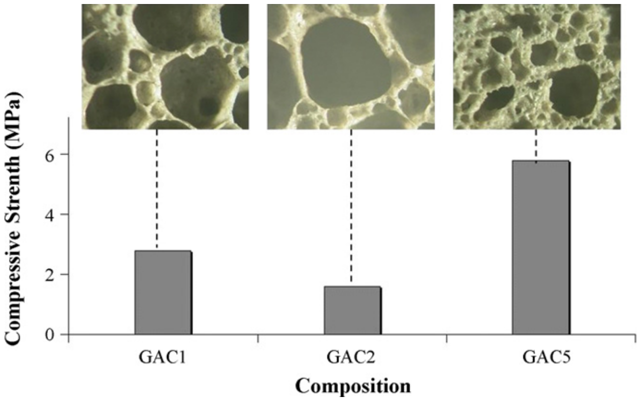

Fig. 8. Relationship between compressive strength and microstructural features for foams comprising calcite as foaming agent sintered at 850 °C.

strength [15]. As an example Fig. 7 illustrates the evolution of microstructure for the samples comprising 2 wt.% of calcite heat treated at 750–900 °C. The foam sintered at 850 °C presents round shaped large pores (1.5–2 mm in diameter), and a lower ratio between the area of the struts and the total area can easily be inferred in accordance with the results of apparent density (0.36 g/cm^3) and compressive strength (1.61 MPa). The foams sintered at lower temperatures (750 and 800 °C) showed higher values of apparent density (0.42–0.55 g/cm^3) and compressive strength (1.70–3.76 MPa) due to denser microstructure. Sintering at higher temperatures (900 and 950 °C) led to diminishing of pore sizes and to growing of cell walls (Fig. 7). This was seemingly achieved due to a lowering of liquid phase viscosity [17] and an enhancement of sintering inside of the struts with subsequent increase of the apparent density (0.37–0.43 g/cm^3) and compressive strength (1.70–2.29 MPa).

Generally, crushing strength was reasonably correlated with apparent density and with porous structure of the produced materials. Particularly, Fig. 8 schematically illustrates connectivity between microstructural features and compressive strength for foams sintered at 850 °C. Although porosity of GAC$_2$ (84%) and GAC$_1$ (82%) are in the same order of magnitude the smaller pores size and their homogeneous distribution in GAC$_1$ resulted in compressive strength 2.80 MPa that is significantly higher than that for GAC$_2$ (1.61 MPa). Composition GAC$_5$ featuring significantly denser microstructure with porosity around 75% exhibited superior values of compressive strength as 5.78 MPa, which are about twice in comparison to GAC$_1$.

The formation of crystalline phases and the extent of crystallization, as well as its dependence of starting composition and sintering temperature, are other important factors that determine the structural evolution and the final properties of glass foams, namely the apparent density and compressive strength. The evolution of crystalline regime of the glass foams over increasing temperature is shown in the X-ray diffractograms of compositions GAC$_1$ and GAD$_1$ (Fig. 9). Quartz (ICDD card 46-1045) and tridymite (ICDD card 42-1401) were revealed at 750 °C while pyroxene phase augite Ca(Mg,Fe,Al)(Si,Al)$_2$O$_6$ (ICDD card 00-41-1483) crystallized at 800 °C. The chain silicate structure of pyroxenes enables solubility of various cations in their structure [18]. Thus, calcium, magnesium, iron and aluminum might occupy octahedral sites, while silicon and aluminum might occupy tetrahedral sites in pyroxene structure. Earlier it was demonstrated [19] that the admixture of calcium carbonate, as a foaming agent, changed the phase composition of the resulting glass–ceramics by an increased rate of the crystallization process and the intensive formation of gehlenite simultaneously with diopside. Pyroxene phase augite was revealed in present study along with pargasite (ICDD card 00-41-1430), that belongs to amphibole group having formulae NaCa$_2$Mg$_4$Al(Si$_6$Al$_2$)O$_{22}$(OH)$_2$, by XRD after heat treatment at 900 °C (Fig. 9). Further temperature increase caused diminishing intensity of quartz peaks most probably due to its dissolution and partial transformation into tridymite after 900 °C. At 950 °C one can observe that the quartz peaks intensity decreased significantly while the peaks of augite and pargasite appeared well defined.

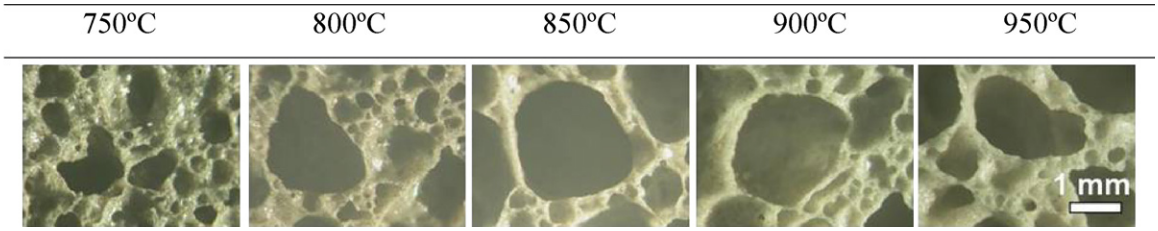

Fig. 7. Microstructural evolution upon heat treatment of composition GAC$_2$.

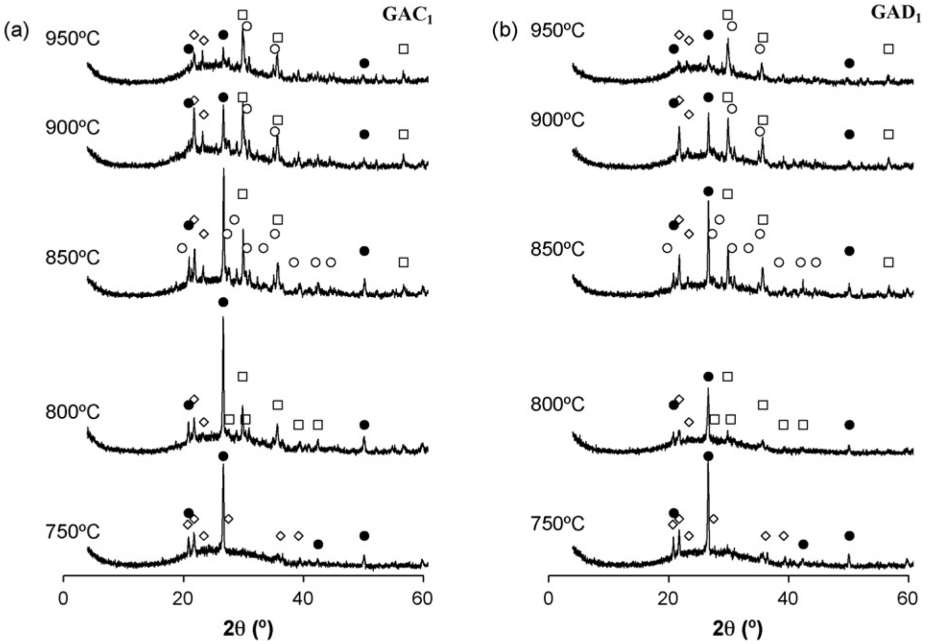

Fig. 9. Evolution of crystalline phases with sintering temperature for glass foams: (a) GAC$_1$ and (b) GAD$_1$ (●: quartz, ◇: tridymite, ○: pargasite and □: augite).

The crystalline phases formed in the samples comprising 1 and 5 wt.% carbonates after heat treatment at 850 °C are presented in Fig. 10. More extensive crystallization of pyroxene and amphibole phases occurred for the higher added amount of carbonates. This resulted in mechanically stronger glass foams (Figs. 4–6). The results of the present study demonstrated that relatively low weight foams can be produced from sheet glass and fly ash when the amount of carbonates does not exceed 2–3 wt.%. The excess amounts of foaming agents tend to limit the foaming ability of the glass/fly ash-based system. This effect is specifically attributed to the formation of crystallites at the surface of the glass particles, which, in turn, would increase the viscosity of the system, reducing its ability to expand under the internal gas pressure. This interpretation is consistent with the more extended crystallization of pyroxene and amphibole phases observed in the presence of the higher added amount of carbonates (Fig. 10) and supported by the microstructural features of the foams shown in Fig. 8.

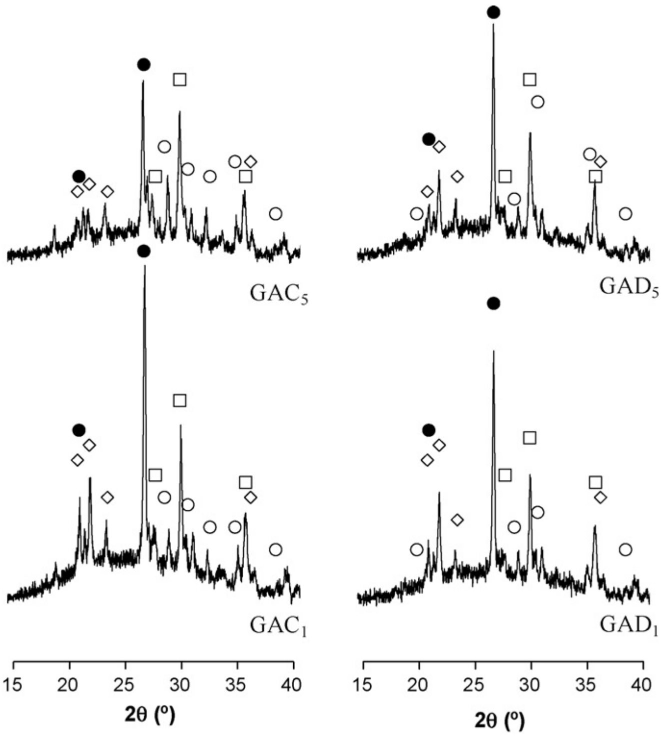

Fig. 10. XRD patterns of glass foams sintered at 850 °C (●: quartz, ◇: tridymite, ○: pargasite and □: augite).

4. Conclusions

The results presented and discussed along with this work enable to draw the following conclusions:

(1) Glass-based foams with low apparent density (0.36–0.41 g/cm^3) and relatively high compressive strength values (2.40–2.80 MPa) can be produced from a mixture containing 80% of sheet glass and 20% of fly ash with low added amounts of carbonates (1–2%) as foaming agents.
(2) Increasing the amount of foaming agents tends to enhance crystallization, which in turn is expected to increase the overall viscosity of the system, limiting the expansion and leading to higher values of apparent density and compressive strength.
(3) For each formulation, the minimum values of apparent density observed at 850 °C depend on a balance between the decrease of viscosity with temperature increase, which favors the expansion of the melt under the internal gas pressure, and the gas release accompanied by the gradual collapse of the foam.

(4) Besides the apparent density values and the extent of crystallization, the compressive strength of the foams also depends on the internal porosity and thickness of the struts.
(5) The production of glass foams is a good way to recycle glass wastes and fly ashes, allowing high incorporation percentages of 95–99 wt.%.

Acknowledgment

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