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Ceramics International 39 (2013) 7089–7095

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Processing, structures and compressive properties of porous glass-ceramic composites prepared from secondary by-product materials

A.A. Francis*, M.K. Abdel Rahman, A. Daoud

Central Metallurgical Research and Development Institute–CMRDI, P.O. Box 87 Helwan, Cairo, Egypt

Received 31 December 2012; accepted 16 February 2013
Available online 6 March 2013

Abstract

Glass cullet and blast furnace slag represent two particularly high volume by-products coming from the metallurgical and glass industries. The conversion of these wastes into porous glass-ceramics has been performed by the powder technique. The influence of temperature, SiC concentration and reaction time on the physical and mechanical property of porous glass-ceramics has been developed in three-dimensional representation. The load–displacement curves of porous glass-ceramics having densities between 0.95 and 1.15 g/cm^3 were smoother, presenting no serrations at the initial stage, than the ones having densities less than 0.95 g/cm^3. The deformation mode for these porous materials was mainly due to layer crushing process. The obtainment of this smooth shape was attributed to the formation of more glassy silica that leads to stronger bonding and pores sealing. The present technology does not require big investment and is suitable for the large scale manufacturing of a wide range of porous glass-ceramics for fire resistant, thermal and structural applications.

Keywords: Industrial wastes; Porous glass-ceramics; Load–displacement curves

1. Introduction

The steady increase in the total amount of wastes being generated, the rapid urbanization as well as the consumption patterns of people are emerging concerns demanding the attention of scientists and specialists. The adoption of recycling concept in the framework of a global and integrated approach would lead to obtain not only high quality products from industrial wastes but also to consider and manage wastes as a resource.

The iron and steel industry is a highly material and energy intensive industry as more than half of the mass input becomes outputs in the form of off-gases and solid wastes by-products. Blast furnace slag (BFS) represents one of the many types of wastes resulting from this metallurgical industry. The re-use of silica-rich wastes, including glass cullet and slag from iron and steel processes, for the production of porous glass-ceramics is a promising approach to increase the value of these waste materials. Porous glass is a lightweight construction material suitable for thermal and acoustic insulation, since they possess a low thermal conductivity, good mechanical property, high permeability and chemical inertness. It is worth mentioning that the successful implementation of the powder technique to produce foam/porous glass will also act to reduce the environmental impact of slag and the amount of cullet glass deposited in landfill sites. A large number of experiments have been conducted on the use of slag and fly ash as a filler in the fabrication of cements [1], including the fabrication of glass-ceramics with interesting properties for building, architectural and other technical applications [2–7], or the use of mixtures of glass cullet and fly ash to form the matrix of particle reinforced glass matrix composites [8].

The mechanical properties of porous materials prepared from pure components have been tackled in many articles but, to the best of the authors' knowledge, the compressive strength of porous glass-ceramics made from various waste materials has not been so much considered. There is, however,

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*Corresponding author. Tel.: +20 22 5010642; fax: +20 22 5010639.
E-mail address: adel_francis@hotmail.com (A.A. Francis).

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http://dx.doi.org/10.1016/j.ceramint.2013.02.048

an investigation carried out by Wu et al. [9] on the compressive strength of glass-ceramic foams prepared at 1000 °C from waste glass and coal ash with incorporation of 2 wt% SiC. A compressive strength equal to 1.5 MPa was obtained with an apparent density between 0.2 and 0.4 g/cm^3. Fernandes et al. [10] produced glass-based foams at 850 °C with relatively high compressive strength (2.40–2.80 MPa) from a mixture of sheet glass and fly ash generated from coal thermal plant. On the other hand, the development of foam glasses by thermal treatment of a mixture of glass micro-balls waste and aluminum nitride as foaming agent has been demonstrated by Lebullenger et al. [11], where steel-making dusts were used as additive to improve the foaming process.

In recent research, it has been shown that humidity-controlling porous ceramics can be fabricated by sintering a mixture of volcanic ash soil and waste glass at 800–815 °C [12]. These results indicate that useful porous ceramic products with attractive properties for building and other environmental applications can be obtained from such silica–alumina rich wastes.

This paper is an experimental contribution toward implementing the sintering technique in the presence of SiC to prepare porous glass-ceramics from a mixture of silica-rich wastes as well as investigates the relationship between the porosity, water absorption and compressive strength of the final products. This porous glass-ceramic can be considered as candidate for the production of catalytic supports and others structural materials for the civil construction industry.

2. Experimental procedure

The Blast furnace slag (BFS) composition was determined by means of an X-ray fluorescence (PANanalyticalXRF-AXIOS advanced). Table 1 shows the composition of the investigated slag expressed as weight percent of the oxide. The particle size distribution of slag was determined by means of laser particle size analyzer (Fritsh analysett 22).

X-ray diffraction (XRD) analysis (Brucker D8 Diffractometer, Cu Kα radiation, and Ni-filter) was used to identify the crystalline phases present in the sintered glass-ceramics. The microstructure of porous glass-ceramics was determined by scanning electron microscopy (SEM-Jeol). Differential scanning calorimetry analysis (DSC) was performed on the Setaram model in air up to 1000 °C. As a result of preliminary experiments, the specimen containing 30 wt% slag was selected for this study. The slag was crushed, milled, pressed uniaxially at room temperature with the addition of 70% glass cullet and various concentrations of SiC (1–10 wt%). The powder compacts were sintered at 900, 950 and 1000 °C for 1 h. The density of sintered samples was determined from measurements of mass and dimensions. The glass-ceramic foams then underwent series of tests, including compressive strength, water absorption, and bulk density measurements, to determine their physical and mechanical properties. The water absorption was calculated according to the following equation: Water absorption $= (W_2 - W_1/W_1) \times 100$, where W_1 is the dry weight of the foam and W_2 is the weight of the foam impregnated with boiling water for 3 h.

Table 1
Chemical analysis of blast furnace slag.

Element	wt%
SiO_2	37.2
CaO	31.2
Al_2O_3	13.6
MgO	6.4
P_2O_5	0.14
K_2O	1.18
Na_2O	0.76
TiO_2	0.23
BaO	2.14
MnO	6.45
FeO	0.52

Compression tests were performed at a fixed crosshead speed of 0.5 mm/min using a universal testing machine (Shimadzu-UH-F1000 kNI). Compression experiments were carried out under displacement control. The load was applied to the specimen via two thick and parallel plates and the typical load–displacement curve of each glass-ceramic foam was automatically constructed. The compression test was continued until there was a break point of the specimens. Stress is evaluated as the load per total area of the specimen.

3. Results and discussion

Fig. 1 shows the particle size distribution of slag powder which has an average particle size of 50 μm. The XRD pattern of the sintered specimen showed the presence of both $CaSiO_3$ and $Ca_2Mg_{0.75}Al_{0.25}Si_{1.75}O_7$, Fig. 2. These crystalline phases were identified in all samples sintered within 900–1000 °C. The amorphous nature of the as-received blast furnace slag was also included.

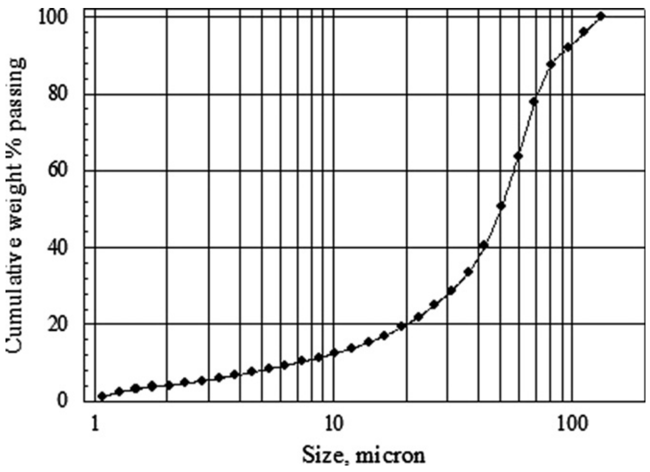

Fig. 1. Particle size distributions of blast furnace slag.

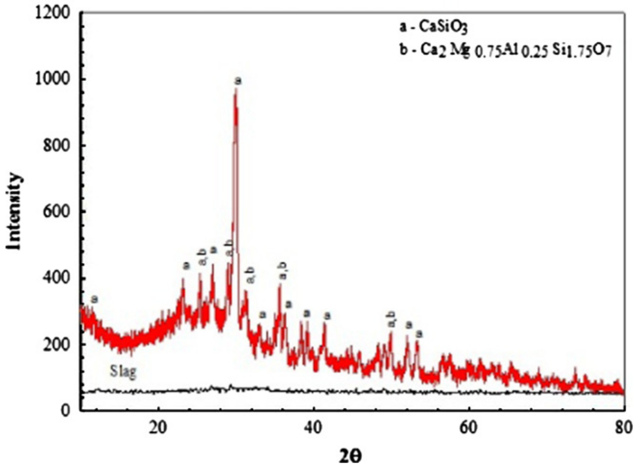

Fig. 2. XRD of the amorphous structure of slag and crystallized mixture (slag + glass + 5% SiC) at 950 °C.

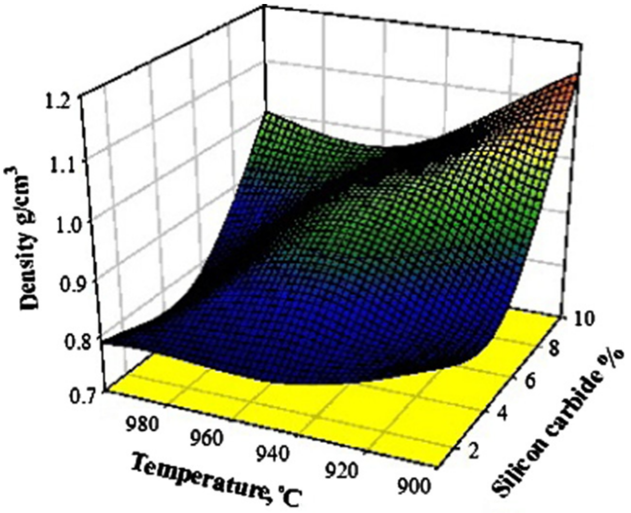

Fig. 3. Effect of temperature and SiC percentage on the density of glass-ceramic foam.

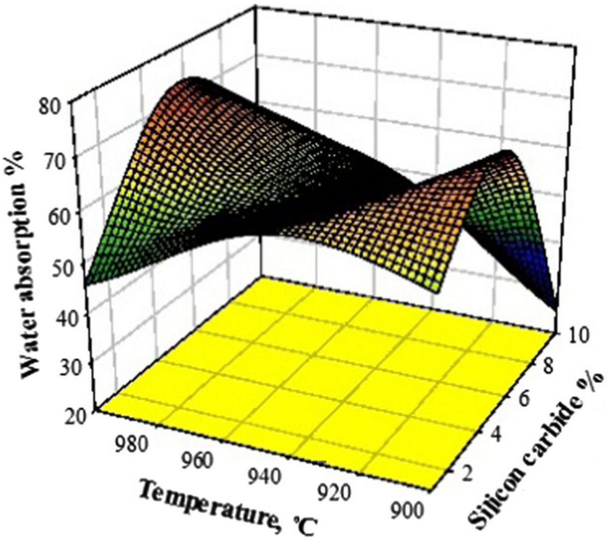

Fig. 4. Effect of temperature and SiC percentage on the water absorption capacity of glass-ceramic foam.

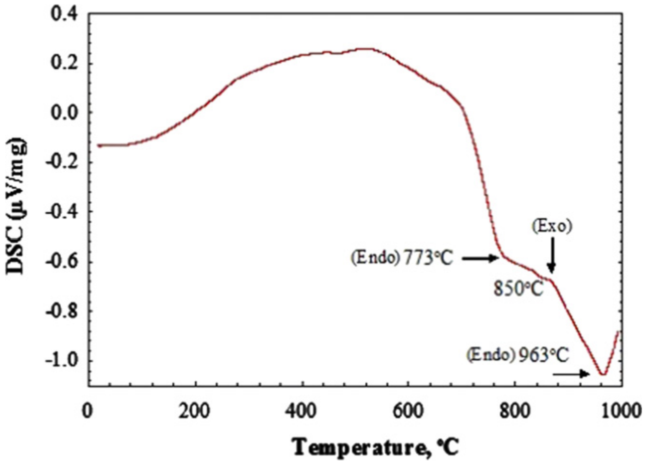

Fig. 5. DSC plot at a heating rate 10 °C/min for a mixture of BFS and glass cullet containing 5 wt% SiC.

Figs. 3 and 4 show the influence of temperatures and concentrations of SiC on the physical property of glass-ceramic foams after sintering for a constant time period (60 min). It is obvious that the density decreases slightly with increasing concentration of SiC (up to 5%) and sintering temperature, reaching minimum values of 0.837 and 0.76 g/cm^3 at 900 and 1000 °C respectively. However, the density increases again by adding 10% SiC and this might be due to the release of more silica as a result of SiC oxidation, which sealed the surface pores of porous glass-ceramics. These findings can be explained in the light of the water absorption (WA) capacity which also increased up to the incorporation of 5% SiC and decreases again by adding much more SiC (10%). These large concentrations of SiC lead to the presence of higher amount of SiO_2 that has the tendency to the formation of glassy phase at 1000 °C. This trend cannot be seen at 950 °C, but a gradual and slight increase in the density was observed up to 10% SiC, which is explained by the incomplete oxidation of SiC.

An evidence can be brought from the DSC of a mixture (BFS + Glass cullet) containing 5% SiC and heated up to 1000 °C, Fig. 5, where an apparent endothermic peak was observed at ~960 °C caused by the low viscosity of the sample which closes the pores and enhances the densification. In the light of the above results, the trend of the water absorption capacity can be understood as demonstrated in Fig. 4. The black or shadow side in the middle of the 3D representation indicates the steady state of WA capacity over the whole concentration range of SiC at 950 °C.

In general, the compressive strength depends on the structure and density of glass or glass-ceramic foams. It is well known that the increase in compressive strength is accompanied with porosity reduction. Fig. 6 showed the variation in compressive strength with sintering temperatures of glass-ceramic foams, containing different percentages (1%, 5%

and 10%) of SiC. As noticed the porous glass-ceramic containing 1% SiC showed increase in compressive strength with increasing temperatures. By increasing the SiC concentration to 5%, the compressive strength decreases at 900 and 1000 °C. The trend is completely different at 950 °C, where the compressive strength increases till reaching 7.1 MPa at 5% SiC and then decreases slightly to 4.6 MPa at higher content of SiC. We have to take into consideration that the viscosity is low at 963 °C which is very close to the sintering temperature 950 °C.

It is seen that the sintering temperature affected the glass-ceramic foam structures and final physical and mechanical properties of interest in this study, namely density and compressive strength. Photographs of porous glass-ceramics obtained at 900, 950 and 1000 °C,while keeping constant the SiC concentration at 5% and the reaction period for 1 h, are shown in Fig. 7. The role of temperatures on the extent of average pore diameter and densification degree in particular at higher temperatures can be clearly observed. Specimens containing 5 wt% SiC and sintered at 950 °C exhibited the best combination of properties, i.e. relatively low density (0.95 g/cm^3) and good compressive strength. However, specimens containing 10 wt% SiC were dense but the compressive strength was better due to the release of more silica content from the oxidation of SiC. A microstructural investigation was performed on selected specimens containing 5 wt% SiC sintered at 1000 and 900 °C for 1 h in Figs. 8 and 9. The image reveals the existence of significant porosity and densified structure in accordance with the density and the compressive strength. The difference in texture and densification degree between the 2 specimens can also be noticed, where melting has occurred due to the lower viscosity at 1000 °C. However, the walls of the porous glass-ceramic at 900 °C are not homogenous and are closed with unreacted remnant materials (bright clusters).

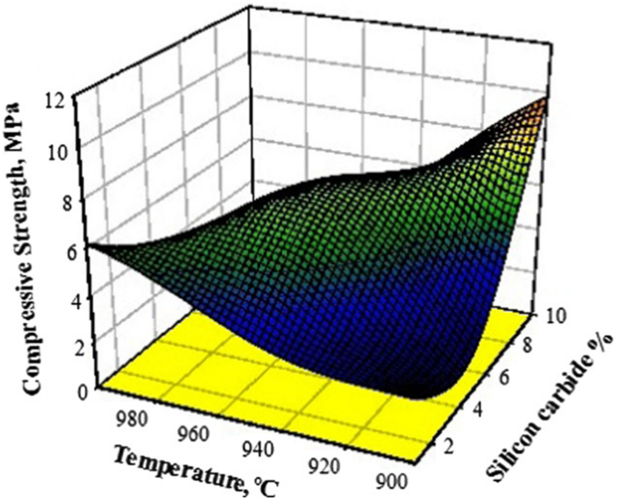

Fig. 6. Effect of temperature and SiC percentage on the compressive strength of glass-ceramic foam.

Representative compressive load–displacement curves at different temperatures and various concentrations of SiC for the glass-ceramic foams were illustrated in Fig. 10. The compressive strength was determined from the point in the compressive load–displacement curves where the load reached its maximum. Generally, the shapes of the investigated porous glass-ceramics exhibited typical behavior of brittle foams. It is apparent that the load increases almost linearly in the initial stage, corresponding to the linear elastic behavior for the typical fracture of brittle foams. During the compression test of samples, the strain tends to localize into a thin band, which causes cracking of cell walls. When the compressive load surpasses a certain value, the porous sample begins to crush before reaching the maximum compressive stress. Upon increasing load level, serration is observed which is typically associated with brittle foam failure. This means that the present foams behave like brittle foams, where the deformation of the sample is caused predominantly by cracking of pore walls. In other words, in the investigated foams, sudden failures of the pore walls accompanied by the load drop were occurred, leading to a zigzag behavior of the load–displacement curve Fig. 10(c, e).

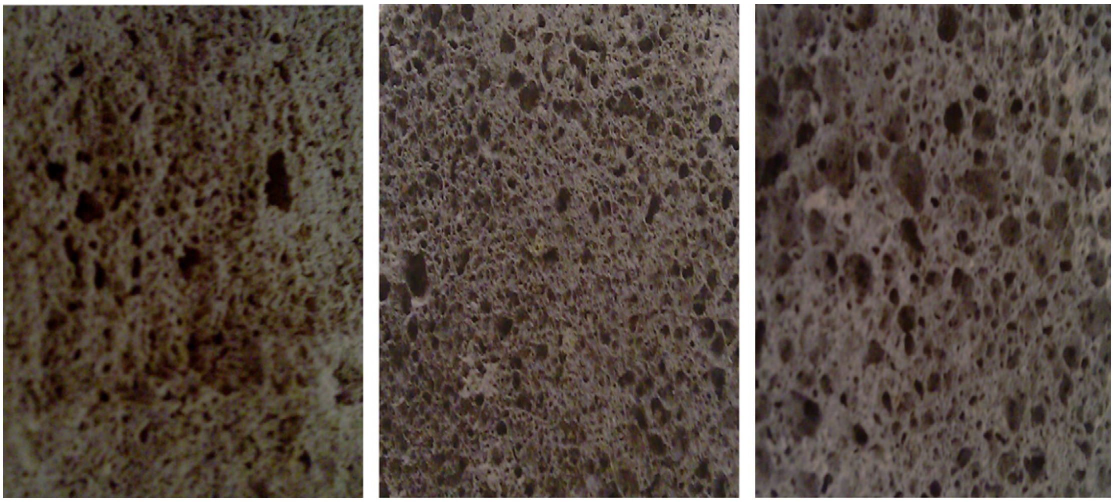

Fig. 7. Glass-ceramic foam structures containing 5% SiC and sintered at 900, 950 and 1000 °C for 1 h.

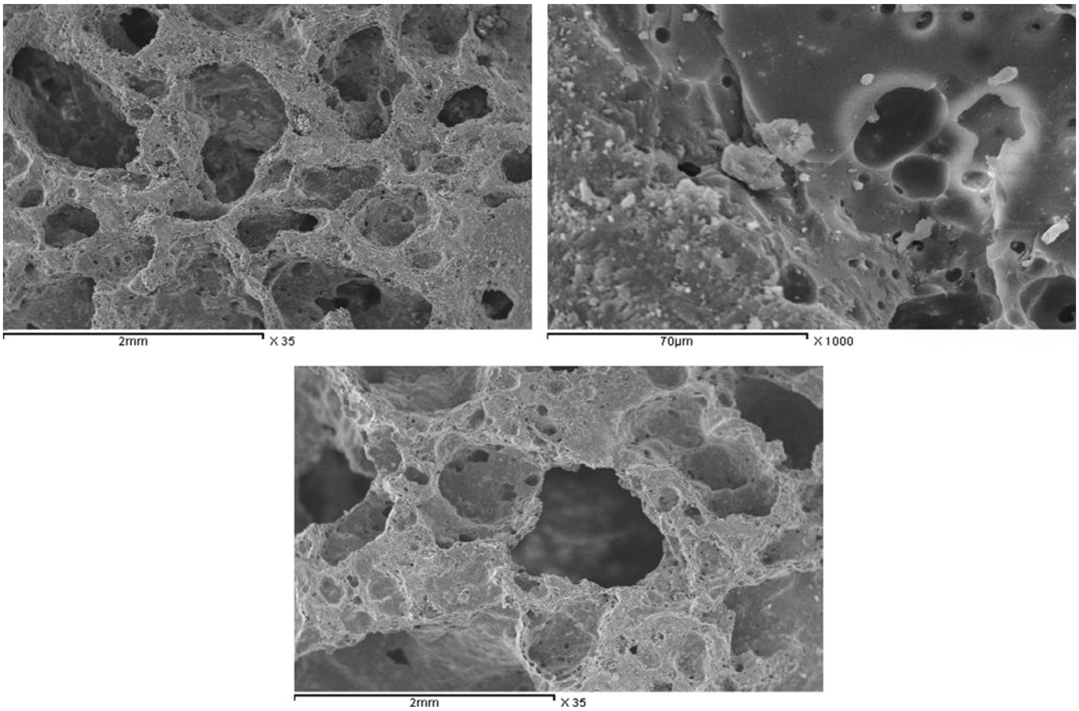

Fig. 8. SEM of sample heat-treated at 1000 °C containing 5% SiC for 1 h.

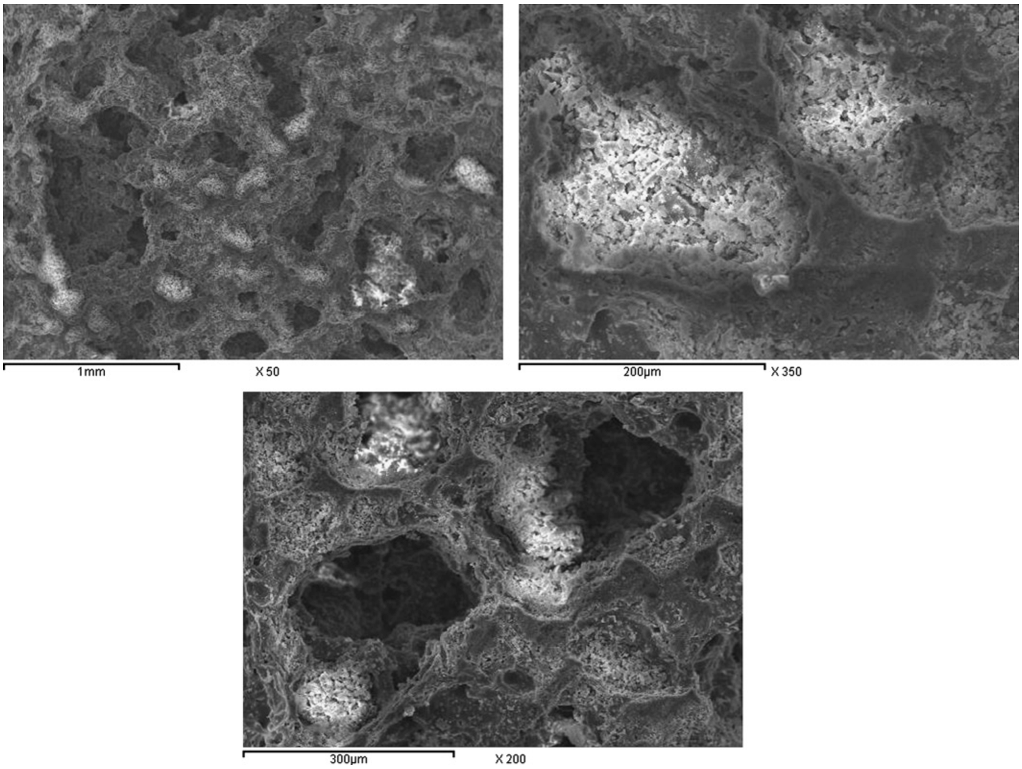

Fig. 9. SEM of sample heat-treated at 900 °C containing 5% SiC for 1 h.

With increasing the strain, the collapse propagation of foam cells occurred layer by layer from either the top or bottom successively in the direction of the compression load into the middle of the compression specimen.

It is worth noting that the porosity (cell size) or relative density is the most significant influencing structural parameters of cellular materials and foams that determine the mechanical property of these materials. Méar et al. [13] found

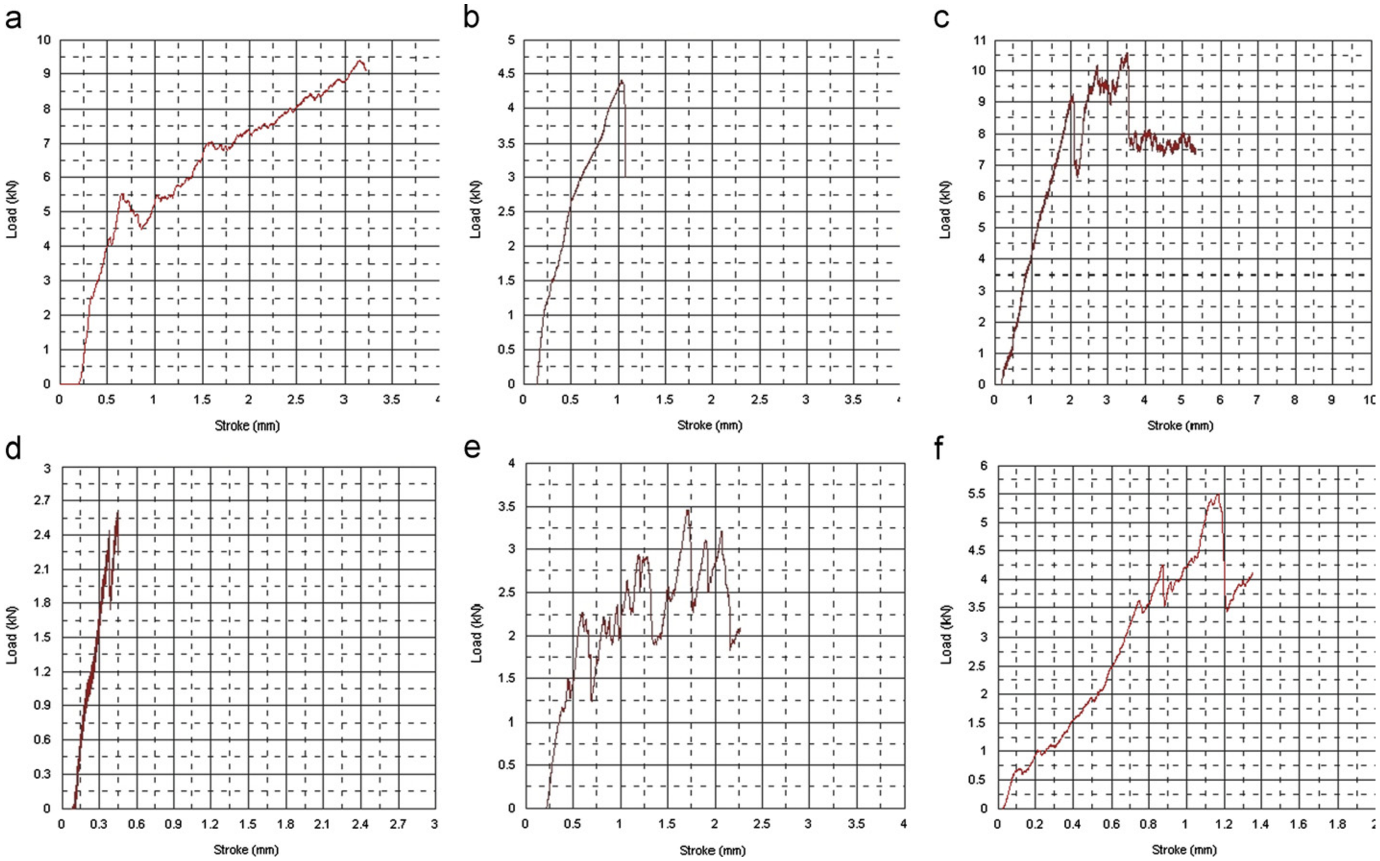

Fig. 10. Compressive load–displacement curve for glass-ceramic foams prepared at different temperatures for 60 min and containing 1, 5 and 10 wt% SiC: (a) 900 °C–10% SiC, (b) 950 °C–10%, (c) 1000 °C–10% SiC, (d) 900 °C–1% SiC, (e) 950 °C–1% SiC, (f) 1000 °C–1% SiC.

that the compressive strengths of cellular glasses, prepared from CRT with SiC or TiN, varied between 4 and 267 MPa. Other authors [10] studied the influence of type and amount of foaming agent as well as of the sintering temperature on the apparent density and compressive strength of glass foams produced from sheet glass cullet and fly ash. The compressive strength was found to vary between 2.40 and 2.80 MPa depending on relative density. Indeed, Scheffler and Colombo [14] have shown that commercial glass foams exhibit apparent density and compressive strength values of about 0.1–0.3 g/cm^3 and 0.4–6 MPa respectively. In the case of foam ceramics prepared from red mud and fly ash [15], the best mixture (40–50 wt% red mud, 26.25–40 wt% fly ash, 15–20 wt% sodium borate and 5 wt% sodium silicate) was foamed at 900 °C for 2 h, and a compressive strength in the range 4.04–10.63 MPa was achieved. The effects of different ratios of red mud and fly ash on foam ceramic properties were also investigated in terms of phase compositions, density, microstructure, and porosity.

The present results are useful, suitable and cost effective for the production of porous glass-ceramics with reasonable mechanical and physical properties by the powder technology route. Changes in the amount of foaming agent and processing can lead to a wide range of materials with different microstructures and hence physical and mechanical properties.

4. Conclusions

The development of porous glass-ceramics from different industrial sources of wastes is considered as a vital contribution toward implementing the recycling concept in the framework of a global and integrated approach that leads to the management of wastes as a resource. The compressive strength of the present materials depends on the concentration of SiC and sintering temperature. XRD results revealed the formation of both $CaSiO_3$ and $Ca_2Mg_{0.75}Al_{0.25}Si_{1.75}O_7$ in the sintered compacts which could be useful for thermal and structural applications. The relatively smooth shape of the load–displacement curves of porous glass-ceramics at higher concentrations of SiC was attributed to the formation of more glassy silica that leads consequently to stronger bonding and pores closure.

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