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Micro- and macro-cellular sintered glass-ceramics from wastes

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Abstract

Glass obtained from melting a mixture of industrial wastes (panel glass from dismantled cathode ray tubes, mining residues from feldspar excavation and lime from fume abatement systems of the glass industry) has been employed for manufacturing micro- and macro-cellular sintered glass-ceramics. Micro-cellular glass-ceramics, with a closed porosity, were prepared by the direct foaming of the glass mass, determined by viscous flow sintering of fine powders (<37 μm), due to addition of a SiC-based waste (from the polishing of glass articles). The surface crystallization of glass, upon sintering, limited the porosity (being about 50%), but imparted a remarkable crushing strength to the products (up to about 80 MPa), useful for construction applications. Micro- and macro-cellular glass-ceramics, with an open porosity and very low relative density (from 40 to less than 10%), were prepared by the sintering of fine glass powders mixed with sacrificial poly-methyl methacrylate microbeads or deposited on sacrificial poly-urethane sponges. The crystallization, besides imparting a good mechanical strength, allowed the maintenance of the open-celled morphology, useful for filtering applications.

Keywords: Sintering; Mechanical properties; Glass; Glass ceramics; Structural applications; Waste materials

1. Introduction

Sintering treatments represent an undoubtedly interesting method for the manufacturing of glass-ceramics.[1,2] The products generally possess a very pleasant aesthetic appearance, unavailable for glass-ceramics obtained by the traditional nucleation/crystal growth procedure and comparable to that of natural stones and traditional ceramics. A very important example is that of "Neoparies" glass-ceramics, based on β-wollastonite, which represent a well established commercial product in Japan since 1970s.[3] The process is based on the surface crystallization of glass powders, with concurrent viscous flow densification ('sinter-crystallization'), and features remarkable economic advantages. Due to the rapid crystallization of glass particles, compared to bulk pieces with the same composition,[4–7] nucleating agents in the glass formulation are not essential and the processing times are very limited. These features are very profitable for glasses obtained by melting mixtures of wastes, to be converted into low-cost glass-ceramics, typically for building applications.[8–10] It must be noted that the sintering approach may have a positive influence on reducing the (usually high) costs of waste vitrification: as the glasses are employed in powdered form, there is no need to perform an extensive refining (generally required to remove some defects, like gas bubbles from vitrification reactions), with a limited holding time of glass at high temperatures. A short vitrification process is also useful for impeding the volatilisation of certain dangerous oxides (like PbO), which remain immobilized in the glass structure.[8] A wide range of sintered glass-ceramics from waste glasses has been reported.[11–18]

The sintering approach has recently led to significant innovations, applied to fine glass powders (typically <37 μm).[14,15,17,18] Firstly, the same enhancement of crystallization, provided by the high specific surface of fine powders, may lead to the development of phases which are hardly found by applying the traditional procedures. Feldspar and feldspathoid crystals (like sanidine, trikalsilite, nepheline), known to give notably stable glasses, practically unable to crystallize, have been recently found as the main crystal phase of several sintered glass-ceramics.[15,17,18] Secondly, using fine glass powders may allow the incorporation of secondary phases, like alumina platelets,[14,15] useful for the preparation of strong glass-ceramic matrix composites. Finally, the fine powders may be useful for the preparation of cellular glass-ceramics, deposited on

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polymeric foams, by the so-called “replication process” (the polymeric foam models the solid fraction of the final cellular material),[19] or mixed with “foaming agents”, i.e. additives originating gaseous species (from combustion or decomposition reactions) embedded in the pyroplastic mass provided by the sintering of the same glass powders.[20] Also an “indirect replication” method (with the pores modelled by sacrificial organic materials), has been recently reported.[21] Porous glass-ceramics are of remarkable interest, especially in the field of biomaterials (employed for the regeneration of trabecular bone)[21] or in filtering applications (open-celled glass-ceramics are permeable to fluids and may act as substrates for catalysts).[19]

In this work we illustrate the production of cellular sintered glass-ceramics, both by direct foaming (exploiting a SiC-based waste) and by the usage of sacrificial polymeric materials. The surface crystallization, already experienced with the employed glass formulation for the development of monolithic glass-ceramics,[17,18] was found to be even enhanced in porous bodies (due to the relevant specific surface), impeding an extensive “direct” foaming but imparting to the related cellular glass-ceramics a notable mechanical strength. In the case of the usage of polymeric templates, the crystallization was useful for imparting, in addition to mechanical strength, a defined pore morphology, by counteracting the viscous flow of glass.

2. Experimental

Panel glass, corresponding to the front part of CRTs (hardly recyclable, due the high quality requirements for the same CRTs), was added with residues from feldspar excavation (fractions of feldspar minerals not employed in the ceramic industry due to their high silica content) and calcium hydroxide from fume abatement systems of the glass industry (after reaction with acidic fumes, this waste contains several pollutants, like nitrates, sulphates, fluorides, etc.). Details about the composition of the starting wastes and the melting process are reported in a previous paper,[18] focused on the preparation of monolithic sintered glass-ceramics. The chemical analysis of the investigated glass is shown in Table 1. The transition temperature is 595 °C and the dilatometric softening point is 680 °C.[18]

For direct foaming experiments, glass powders (maximum size of 37 μm) were added with a SiC-based polishing waste, whose composition is also illustrated in Table 1. This waste corresponds to the residues from the polishing of artistic glass articles; the main constituent is SiC, the abrasive material, coupled with the abraded glass. The relatively high content of Fe_2O_3 is due to the fact that SiC powders (with a maximum dimension of about 50 μm) are generally deposited on cast iron discs, which are subjected to a certain abrasion during the polishing of glass. The current production of polishing waste from glass abrasion, in factories near Venice, is about 200 t per year, and represents a pressing environmental problem, since no application is available; moreover, the disposal of this kind of waste is complex and expensive, due to the presence of significant traces of heavy metal oxides, from the formulation of the abraded artistic glasses. The SiC-based waste was employed in concentrations of 5, 10 and 15 wt.%. Some samples featured a further addition of MnO_2 powders (reagent grade, 10 μm, Sigma–Aldrich Co. Ltd., Gillingham, UK), for a ratio between MnO_2 and SiC-based waste equal to 1/5. The SiC waste-glass mixtures were homogenized in a ball mill for 30 min and subsequently gently pressed in a rectangular die. Glass sinter-crystallization and foaming were achieved by subjecting the mixtures to a thermal treatment at 880 and 950 °C, with a heating rate of 10 °C/min and a holding time of 1 h.

Table 1
Chemical analysis of the starting materials

	Glass	Polishing waste
SiO_2	51.9	25.0
Al_2O_3	9.5	
Na_2O	7.1	5.0
K_2O	3.2	2.0
CaO	16.2	2.0
MgO	0.8	1.1
BaO	3.1	
SrO	1.3	
Fe_2O_3	0.7	15.0
Cr_2O_3		0.3
MnO		0.2
CuO		0.2
TiO_2	0.2	0.2
ZrO_2	0.2	
PbO	0.4	0.3
ZnO	0.1	0.6
As_2O_3	0.2	
Sb_2O_3	0.6	1.0
P_2O_5	0.1	
B_2O_3	1.5	
F	2.4	0.1
Cl	0.1	
SO_3	0.4	
SiC		48.0

For indirect replication experiments, fine glass powders were dispersed in a solution of commercial silicone resin (MK, Wacker-Chemie GmbH, München, Germany) in acetone (in the proportions 8 g glass/0.8 g resin/100 cc acetone) under magnetic stirring; after drying (60 °C, overnight), the dispersion was ground, thus producing glass particles covered by a thin layer of silicone resin, subsequently mixed with poly-methyl methacrylate microbeads (with a diameter of about 190 μm, Cray Valley Waterborne Polymers Department, Atofina Italia, Milan, Italy) in the volume proportions 30% glass/70% polymer. In some formulations a slight amount (5 wt.%) of α-SiC (HC Starck Inc., Newton, MA, <1 μm) was added to the glass powders to promote gas formation and provide additional porosity. The glass-polymer mixture was pressed in a steel die at 30 MPa and treated at 300 °C for 2 h (0.5 °C/min heating rate) to eliminate the microbeads and cause the cross-linking of the silicone resin (acting as a binder). Sintering treatments, for 0.5 or 1 h, were performed at 880 and 950 °C, with a heating rate of 20 °C/min or by direct insertion of green bodies in the furnace.

Finally, for direct replication experiments, the glass powders (additionally sized to a dimension <25 μm) were dispersed in an aqueous solution (18 g of glass for 30 cc of solution) of poly-vinyl-alcohol (1.7 wt.%, employed as viscosity modifier), added with bentonite (5 wt.%, employed as binding agent). The components were homogenised by magnetic stirring (for 30 min) and ultrasonication (for 10 min). Commercial poly-urethane sponges (Bulpren S 28280 – cell size ~2800 μm – Recticel IDC, Wetteren, Belgium) were subjected to 3 or 6 cycles of immersion in the obtained slurry, centrifugation (15 min at 300 rpm) to prevent excessive impregnation and drying (60 °C, 1 h); after the last impregnation cycle the sponges, coated with glass particles, were dried overnight and heat treated at 880 °C for 1 h, causing both the burn-out of the polymeric substrate and the sinter-crystallization of glass powders in the form of open-celled foams.

The density measurements were performed both geometrically and by using a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA), operating on bulk and powdered samples.

The crushing strength of the foams was measured at room temperature by compression testing, using an Instron 1121 UTM (Instron Danvers, MA) with a cross-head speed of 1 mm/min, on samples of a nominal size of about 8 mm × 8 mm × 3 mm (for foams from direct foaming) or 10 mm × 10 mm × 8 mm (for foams from indirect replication), cut from larger specimens. Each data point represents the average value of 5–10 individual tests.

The morphology of the porous glass-ceramic samples was studied by means of optical and scanning electron microscopy (Philips XL 30 ESEM, Eindhoven, The Netherlands). Powdered samples were investigated by X-ray diffraction (Philips PW 3710, Eindhoven, The Netherlands), employing Cu Kα radiation (0.15418 nm).

3. Results and discussion

The porous structure had a remarkable effect on crystallization. As shown in Fig. 1, cellular glass-ceramics exhibited, for sintering treatments of only 1 h at 880 °C, practically the same diffraction pattern as monolithic glass-ceramics from the same powders (and the same maximum dimension of 37 μm) sintered at 880 °C, for 2 h. The holding time of 2 h, for monoliths, as reported by Bernardo et al.,[18] corresponds to the condition of maximum crystallization. The phase assemblage consists of an alkali feldspar, i.e. sanidine $(K, Na)AlSi_3O_8$[22] (the main crystal phase), mixed with feldspathoids crystals corresponding to trikalsilite[23] and panunzite,[24] both represented by the same formula $(K, Na)AlSiO_4$ (the crystals are polymorphs, and a clear distinction is difficult, except for a few peaks in the XRD pattern); traces of Ca alumino-silicate $Ca_3Al_6Si_2O_{16}$[25] and Ca-K silicate $K_4Ca(SiO_3)_3$[26] are also present. Some unreacted SiC[27] was found in samples from direct foaming.

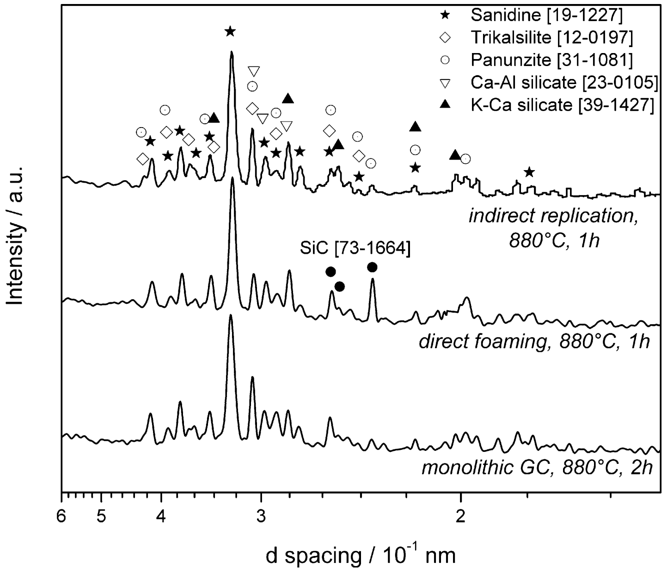

Fig. 1. XRD patterns of cellular glass-ceramics (methods of direct foaming and indirect replication) compared to that of a monolithic sintered glass-ceramic with the same parent glass composition.

The unusual crystallization of feldspar crystals (feldspar minerals are known to give excellent glasses, but unable to crystallize in practical times),[1] for monoliths, had been attributed to the high nucleation activity of fine glass powders, upon sintering. At the surface of glass powders, the crystal nuclei are not completely surrounded by the parent glass, so that the volume variations, typical of crystallization, are less impeded than in the bulk (where the nuclei are completely surrounded by residual glass).[4–7] Fine glass powders, by maximizing the specific surface, i.e. maximizing the content of "free" glass surfaces, significantly promote nucleation, even for phases which are hard to precipitate. Precisely, for the monoliths, feldspathoid crystals (the first to be developed, according to Bernardo et al.)[18] were susceptible to surface crystallization in limited times, like in another work, focused on nepheline glass-ceramics.[15] In the case of porous bodies, the precipitation of crystals is even accelerated, likely due to the high specific surface of cellular materials: in a monolith, the progression of sintering gradually reduces the "free glass surfaces", i.e. the nucleation sites; in a foam, every cell wall may be useful for surface crystallization.

The enhanced crystallization in porous glass-ceramics is evident also from their morphology. Fig. 2a and b illustrates the morphology of a cellular sintered glass-ceramic from direct foaming. Several pores in the 200–300 μm range are visible, surrounded by a number of smaller micro-pores. The surface of cell walls, as shown in Fig. 2b, features the presence of a number of crystal "protrusions", consistent with the above described mechanism of crystallization.

Although SiC is well known to be an excellent "foaming agent" for the production of cellular glasses, due to its oxidation (with formation of CO and CO_2 gases),[28] the cellular glass-ceramics from direct foaming process (see Fig. 3) did not exhibit a particularly low relative density (i.e. the ratio between the "apparent" density of the cellular material, determined geometrically, and the "true density", or density of the solid phase, easily measured by pycnometry on finely powdered samples), not lower than 30%; this is confirmed by the relatively thick struts in Fig. 2a. It is well known, from the literature,[29] that elongated crystal inclusions, embedded in a glass matrix, greatly increase the viscosity of the system. The viscosity of the pyroplastic mass determined by the sintering of glass was reasonably enhanced by the concurrent crystallization, so that the gas formation did not cause a relevant foaming. The best expansion was reached

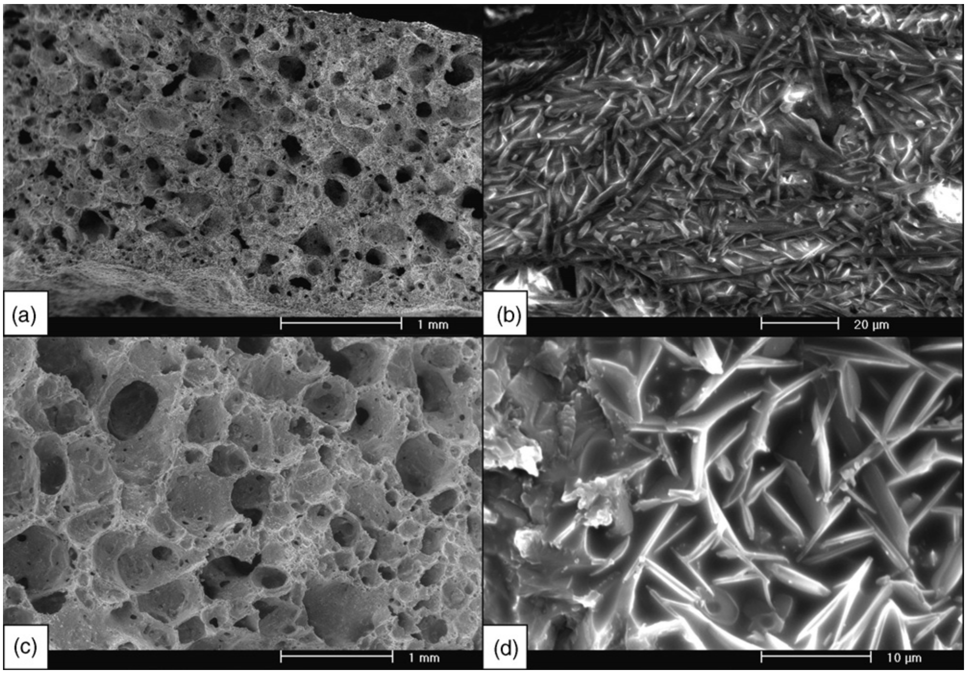

Fig. 2. Morphology of cellular glass-ceramics: (a, b) direct foaming (10% SiC-based waste, 2% MnO_2, sintered at 880 °C); (c, d) indirect replication (direct insertion at 950 °C, for 1 h).

with treatments at 950 °C, with the highest content of SiC-based waste (15 wt.%); in this case a certain decrease of crystallization was observed (the intensity of diffraction peaks, at 950 °C, decreased about 50%), thus favouring the expansion. It must be noted, in addition, that 950 °C has already been evidenced as the optimum temperature for the preparation of cellular glass with SiC employed as foaming agent.[30] Finally, a certain improvement of expansion is visible for samples made with the addition of MnO_2. This behaviour, as previously observed for cellular glasses foamed with the same SiC-based waste,[31] is attributable to the improved oxidation of SiC (MnO_2 decomposes into MnO and some oxygen), leading to an enhanced amount of "expanding" gas and to a more uniform distribution of gas bubbles.

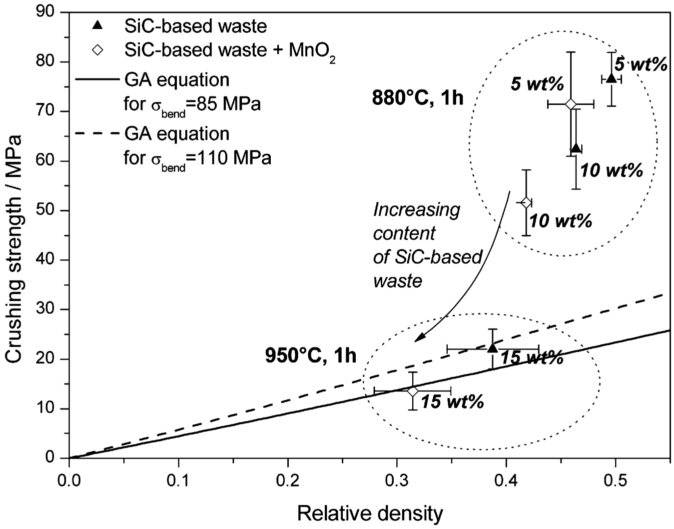

Fig. 3. Plot of crushing strength vs. relative density for cellular glass-ceramics produced by the direct foaming method.

The crushing strength of cellular glass-ceramics foamed with SiC-based waste, illustrated by the same Fig. 3, is relevant. In general, the crushing strength of a porous material is ruled by the relative density ρ_{rel}, following the well-known equation developed by Gibson and Ashby (GA)[32]:

$$\sigma_{\text{f}} = \sigma_{\text{bend}}[C(\Phi\rho_{\text{rel}})^{3/2} + (1-\Phi)\rho_{\text{rel}}] \tag{1}$$

where σ_{bend} is the bending strength of the solid phase and the Φ parameter rules the pore distribution (open or closed porosity). In fact, the quantity $(1-\Phi)$ expresses the fraction of solid at the cell faces; if the foam is open-celled, with fully interconnected pores, the solid phase is only at cell edges, so that Φ tends to unity $(1-\Phi=0)$; on the contrary, for a closed-cell foam, Φ is lower, since some material constitutes the separation walls between the pores. C is a dimensionless calibration constant, being ~0.2. In the present case, the Φ parameter was estimated to be equal to 0.5 (the same quantity of solid at the cell edges than at the cell walls); the bending strength of the solid phase was considered to be equal to 85 or 110 MPa, corresponding to the bending strength of monoliths from the same glass powders (not pressed), sintered at 880 °C for 1 and 2 h,[17] respectively. From Fig. 3 it is evident that the crushing strength (especially for samples sintered at 880 °C, with 5 and 10 wt.% SiC-based waste) largely exceeds that predicted from Eq. (1), even for a bending strength of 110 MPa. This means that the solid phase, in a cellular body sintered for 1 h, is stronger than a monolith sintered for 2 h. This substantially confirms the observations from the diffraction patterns: the increased specific surface (due to porosity) corresponds to an increased "intrinsic" strength, induced by the enhanced crystallization. Finally, it should be noted that the strength of cellular glass-ceramics (up to about 80 MPa) is comparable to that reported for conventional clay bricks,[33] with a lower density (the density of the present cellular glass-ceramics was in the range of about 0.82–1.36 g/cm^3, while the density of clay bricks is higher than 1.5 g/cm^3).[34] This makes the glass-ceramic products useful in applications as structural panels. In addition, applications as lightweight (thermally and acoustically insulating) aggregates in concrete are possible: the usage of drastically weaker glass foams as aggregates has already been reported.[35,36] However, while glass foams may experience alkali-silica reaction with concrete[36] (it is well known that alkali-silica reaction in concrete is based on the availability of amorphous silica in the aggregates), cellular glass-ceramics are expected to be less reactive. Moreover, the recent findings about cellular glasses foamed with the SiC-based waste[31] suggest that the chemical stability of the cellular glass-ceramics could be good. All these conditions are positive for the investigated materials to enter the market of construction materials, which in turn, due to its huge dimension, could be highly advantageous for a large absorption of wastes.

Replication methods were useful for the preparation of drastically more porous glass-ceramics. The "indirect replication" process caused an open-celled porosity, shown in Fig. 2c, determined by the packing of glass powders around PMMA microbeads and stabilized by the silicone binder after the burn-out of the polymer. The formation of gases, due to the addition, in some cases, of fine commercial SiC (the SiC-based waste is rather coarse, so that it was thought to be hardly homogenized in the glass/silicone/PMMA mixture) and to the oxidation of the silicone resin (this kind of polymers is subjected to ceramic conversion at about 570 °C, with the development of a silica-based residue and the evolution of gases, due to burn-out of carbon)[37] determined a certain expansion (it can be seen that the pores are generally larger than the PMMA microbeads); in any case, the microstructure was generally more homogeneous than in the porous glass-ceramics from direct foaming (typically, as shown in Fig. 2c, there was a number of pores in the 300–400 μm range, coupled with some smaller micro-pores and openings between adjacent cells). The relative density, as shown in Fig. 4, was in the range 0.12–0.30 (the density varied from 0.38 to 0.84 g/cm^3). The open-celled morphology was confirmed by pycnometry measurements, from which it was inferred that the open porosity (due to the several openings between adjacent cells) varied from 94 to 97%.

From Fig. 4, it is interesting to note the modification of both strength and relative density with the conditions of thermal treatment. The treatment at 880 °C, due to the relevant crystallization ability of glass at this temperature, minimizes the porosity (and maximizes the strength) by limiting viscous flow expansion; the increase of sintering temperature to 950 °C (at which crystallinity is lower) and the SiC addition reduce the relative density to values commonly reported for glass foams ($\rho_{\mathrm{rel}} \sim 0.15$, corresponding to a porosity of about 85%).[28] Conventional heating causes a low expansion and the best crushing strength values; direct insertion at the sintering temperature is useful for reducing the density. This condition is reasonable, since the samples from conventional heating are "exposed" for a longer time at high temperatures, at which crystallization occurs, with the above described increase of viscosity. The presence of "pre-existing" pores from PMMA burn-out, however, led to a remarkable porosity even with limited viscous flow; the same increase of viscosity is thought to be advantageous in counteracting any collapse of the PMMA-modelled porosity. Direct insertion at 950 °C, at which the crystallization ability is lower, slightly favours the viscous flow, with a certain expansion effect, maximized by the addition of SiC (a certain flow effect is evident by considering the sintering time: the expansion decreased by decreasing the sintering time from 1 h to 30 min).

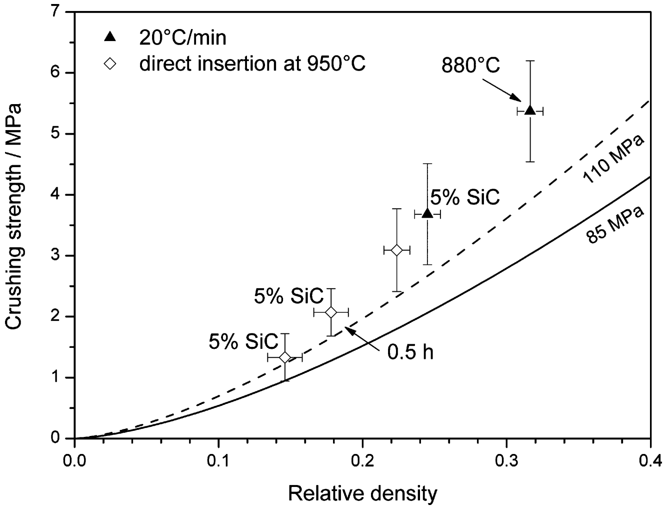

Fig. 4. Plot of crushing strength vs. relative density for cellular glass-ceramics produced by the indirect replication method; reference lines refer to $\Phi = 1$, typical for open-celled foams.

The crushing strength, as shown in the same Fig. 4, is well fitted by Eq. (1) (with $\Phi = 1$, typical for open-celled foams) for a bending strength of the solid phase equal to 110 MPa. This means that the "intrinsic" strength of porous bodies, i.e. the strength of the solid phase, after sintering treatments of 1 h, is comparable to the strength of monoliths sintered for 2 h. Like in the previous cellular glass-ceramics, the enhanced crystallization, due to porosity, caused an enhanced mechanical strength. It must be noted that the achieved open-celled glass-ceramic foams are stronger than commercial closed-celled glass foams, which for a relative density of about 0.15 possess a crushing strength of about 1 MPa.[28,38]

Surface crystallization, with the formation of protrusions at the cell walls, is visible from Fig. 2d. The protrusions greatly enhance the specific surface of glass-ceramic foams, already remarkable for highly porous bodies; this feature, coupled with the open-celled morphology, makes the materials obtained by indirect replication promising for applications as catalyst support or in gas filtering.

The fact that crystallization counteracts viscous flow is even more evident with macro-cellular foams made by direct replication of PU sponges. As shown in Fig. 5, the morphology of PU sacrificial substrates was maintained in the cellular glass-ceramics. In general, while for direct foaming the high viscosity of a glass embedding elongated crystals had the negative effect of limiting the expansion (the crystallization limits the development of porosity), in replication processes it

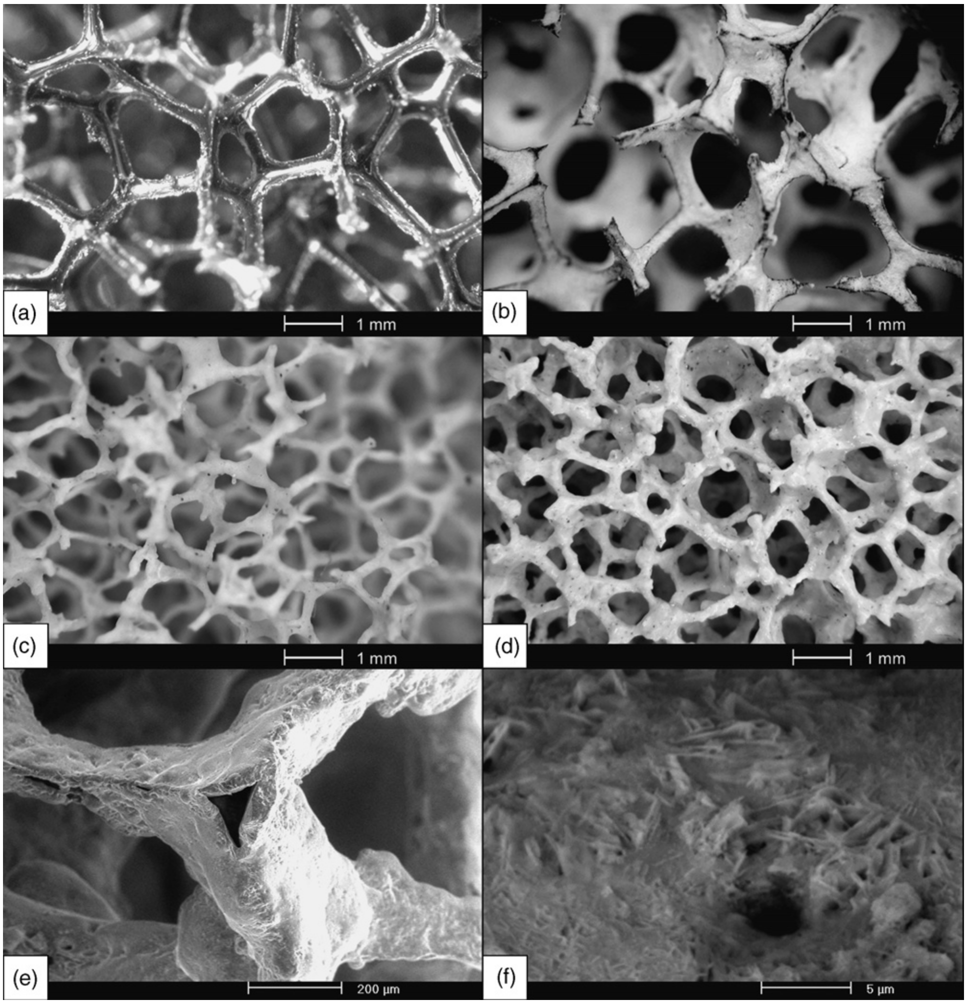

Fig. 5. Optical and SEM micrographs of macro-cellular foams from direct replication of PU sponges: (a) PU substrate; (b) PU substrate coated by glass powders (six cycles); (c) cellular glass-ceramic (three cycles); (d) cellular glass-ceramic (six cycles); (e) example of hollow strut; (f) crystals at the surface of struts.

has the positive effect of maintaining the pore shape (the crystallization limits the viscous flow, i.e. the collapse of the cellular structure). Although the replication process could be improved, by employing even finer glass particles (mainly in order to expedite the impregnation), after some preliminary tests (on samples of a nominal size of about 15 mm × 15 mm × 10 mm), the foams exhibited a promising crushing strength, consistent with recent findings about analogous cellular glass-ceramics[19]: for three cycles of impregnation, the relative density was 0.06 (6% of solid) and the strength was of 40 kPa; six cycles led to a limited increase of relative density, equal to 0.11, compared to the increase of strength, which reached 120 kPa (0.12 MPa). The crushing strength of the foams from direct replication is reasonably lowered by the presence of hollow struts, as evidenced by Fig. 5e (if the viscous flow of glass is impeded by crystallization, the porosity induced by the burn-out of the polymeric substrate is hard to be removed in limited times). The effect of the number of depositions is mainly due to the continuity and thickness of the glass coating (it can be seen, from Fig. 5d, that six deposition cycles led to a more homogeneous and defined morphology of struts). The surface crystallization is visible also for these foams, as evidenced by Fig. 5f. Due to the relevant porosity, the macro-cellular foams could be applied in fluid filtering or as catalytic support. Further studies will be dedicated, besides to the improvement of the deposition (by modifying the particle size of the starting glass powders), to reinforcement techniques; Duke et al.[39] demonstrated that feldspathoid crystals, like nepheline, are suitable for ion strengthening (replacement of sodium ions with potassium ions, by immersion of glass-ceramics in fused potassium salts), with a notable increase of bending strength (nepheline glass-ceramics exhibited a spectacular strength increase from 58 to 1300 GPa).[1,39] The variation of the sodium/potassium balance could be reasonably applied to the feldspar and feldspathoid crystals developed in the present glass-ceramics; the increase of bending strength of the solid phase should produce, with the same porosity content, a relevant increase of crushing strength, according to Eq. (1).

4. Conclusions

In this investigation, a glass obtained by employing wastes (panel glass from dismantled CRTs, mining residues and lime from fume abatement systems) as raw materials, was successfully converted into sintered cellular glass-ceramics, by simple and economic treatments, starting from fine particles. The main features of the obtained products may be summarized as follows:

1. the enhanced specific surface of porous bodies causes the enhancement of surface nucleation, which is the key point for a rapid crystallization and the precipitation of particular crystal phases (feldspar and feldspathoid crystals, hardly found in conventional glass-ceramics);
2. cellular glass-ceramics made by a direct foaming process, focused on the oxidation of a SiC-based waste, added to the fine glass powders, did not exhibit a very low density, due to the increase of viscosity caused by the crystallization; the same crystallization led to a remarkable crushing strength, which could constitute the basis for applications of the porous glass-ceramics in the construction industry;
3. lightweight open-celled micro-cellular glass-ceramics were prepared by exploiting the burn-out of PMMA microbeads (indirect replication), eventually coupled with a SiC addition; the enhanced crystallization was the origin of both a relevant crushing strength and an enhanced specific surface (see crystal protrusions at the cell walls);
4. Highly porous macro-cellular glass-ceramics were obtained by direct replication of PU sponges; although improvements of the deposition technique are expected, the surface crystallization was useful for avoiding any collapse of the cellular structure caused by the viscous flow of glass; the crystal phases of the investigated glass-ceramics could be useful for chemical strengthening treatments.

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References

1. Höland, W. and Beall, G., *Glass-Ceramic Technology*. The American Ceramic Society, Westerville OH, USA, 2002.
2. Strnad, Z., *Glass-Ceramic Materials*. Elsevier Science Publishers, Amsterdam, 1986.
3. Tashiro, M., Crystallization of glasses: science and technology. *J. Non-Cryst. Sol.*, 1985, **73**, 575–584.
4. Gutzow, I., Pascova, R., Karamanov, A. and Schmelzer, J., The kinetics of surface induced sinter-crystallization and the formation of glass-ceramic materials. *J. Mater. Sci.*, 1998, **33**, 5265–5273.
5. Clark, T. J. and Reed, J. S., Kinetic processes involved in the sintering and crystallization of glass powders. *J. Am. Ceram. Soc.*, 1986, **69**, 837–846.
6. Müller, R., Zanotto, E. D. and Fokin, V. M., Surface crystallization of silicate glasses: nucleation sites and kinetics. *J. Non-Cryst. Sol.*, 2000, **274**, 208–231.
7. Prado, M. O. and Zanotto, E. D., Glass sintering with concurrent crystallization. *C R Chimie*, 2002, **5**, 773–786.
8. Colombo, P., Brusatin, G., Bernardo, E. and Scarinci, G., Inertization and reuse of waste materials by vitrification and fabrication of glass-based products. *Curr. Opin. Solid State Mater. Sci.*, 2003, **7**, 225–239.
9. Sarkisov, P. D., The modern state of technology and application of glass-ceramics. In *Glass '89 Survey Papers ot the XVth International Congress on Glass*, 1989, pp. 411–441.
10. Davies, M. W., Kerrison, B., Gross, W. E., Robson, M. J. and Witchall, D. F., Slag ceramics: a glass ceramic from blast-furnace slag. *J. Iron Steel Inst.*, 1973, **208**, 348–370.
11. Karamanov, A., Taglieri, G. and Pelino, M., Iron-rich sintered glass-ceramics from industrial wastes. *J. Am. Ceram. Soc.*, 1999, **82**, 3012–3016.
12. Karamanov, A., Pisciella, P., Cantalini, C. and Pelino, M., Influence of Fe^{3+}/Fe^{2+} ratio on the crystallization of iron-rich glasses made with industrial wastes. *J. Am. Ceram. Soc.*, 2000, **83**, 3153–3157.
13. Karamanov, A., Pelino, M. and Hreglich, S., Sintered glass-ceramics from municipal solid waste-incinerator fly ashes-part I: the influence of the heating rate on the sinter-crystallization. *J. Eur. Ceram. Soc.*, 2003, **23**, 827–832.
14. Brusatin, G., Bernardo, E. and Scarinci, G., Sintered glass-ceramics from waste inert glass. In *In Proceedings of IV International Workshop VARIREI (Valorization and Recycling of Industrial Residues)*, 2003.
15. Bernardo, E., Andreola, F., Barbieri, L. and Lancellotti, I., Sintered glass-ceramics and glass-ceramic matrix composites from CRT panel glass. *J. Am. Ceram. Soc.*, 2005, **40**, 5259–5264.
16. Barbieri, L., Corradi, A., Lancellotti, I., Pellacani, G. C. and Boccaccini, A. R., Sintering and crystallization behaviour of glass frits made from silicate wastes. *Glass Technol.*, 2003, **44**(5), 184–190.
17. Bernardo, E., Castellan, R. and Hreglich, S., Sintered glass-ceramics from mixtures of wastes. *Ceram. Int.*, 2005, **33**, 27–33.
18. Bernardo, E., Castellan, R., Hreglich, S. and Lancellotti, I., Sintered sanidine glass-ceramics from industrial wastes. *J. Eur. Ceram. Soc.*, 2005, **26**, 4017–4023.
19. Sousa, E., Silveira, C. B., Fey, T., Greil, P., Hotza, D. and Novaes de Oliveira, A. P., LZSA glass ceramic foams prepared by replication process. *Adv. Appl. Ceram.*, 2005, **104**, 22–29.
20. Wu, J. P., Boccaccini, A. R., Lee, P. D., Kershaw, M. J. and Rawlings, R. D., Glass ceramic foams from coal ash and waste glass: production and characterisation. *Adv. Appl. Ceram.*, 2006, **105**, 29–32.
21. Kasuga, T., Bioactive calcium pyrophosphate glasses and glass-ceramics. *Acta Biomater.*, 2005, **1**, 55–64.
22. JCPDS, International Centre for Diffraction Data (ICDD), Powder Diffraction File (PDF) # 19-1227.
23. JCPDS – ICDD, PDF # 12-0197.
24. JCPDS – ICDD, PDF # 12-1081.
25. JCPDS – ICDD, PDF # 23-0105.
26. JCPDS – ICDD, PDF # 39-1427.
27. JCPDS – ICDD, PDF # 73-1664.
28. Scarinci, G., Brusatin, G. and Bernardo, E., Production technology of glass foam. In *In Cellular Ceramics. Structure, Manufacturing, Properties and Applications*, ed. M. Scheffler and P. Colombo. Wiley-VCH Verlag GmbH & CO., Weinheim, 2005, pp. 158–176.
29. Boccaccini, A. R., On the viscosity of glass composites containing rigid inclusions. *Mater. Lett.*, 1998, **34**, 285–328.
30. Brusatin, G., Scarinci, G. and Bernardo, E., Foam glass from recycled glass. In *In Sustainable Waste Management and Recycling of Glass Waste*, ed. M. C. Limbachiya and J. Roberts. Thomas Telford Ltd., London, 2004, pp. 67–82.
31. Bernardo, E., Cedro, R., Florean, M., Hreglich, S., Reutilization stabilization of wastes by the production of glass foams, *Ceramics International*, 2006, doi:10.1016/j.ceramint.2006.02.010.
32. Gibson, L. J. and Ashby, M. F., *Cellular Solids and Structure and Properties (2nd ed.)*. Cambridge University Press, Cambridge, UK, 1999.
33. Karaman, S., Gunal, H. and Ersahin, S., Assessment of clay bricks compressive strength using quantitative values of colour components. *Constr. Build. Mater.*, 2006, **20**(5), 348–354.
34. Demir, I., An investigation on the production of construction brick with processed waste tea. *Build. Environ.*, 2006, **41**, 1274–1278.
35. Fotiadou, S., Limbachiya, M. C., Fried, A. N. and Roberts, J. J., Use of foamed glass gravel in construction. In *In Sustainable Waste Management*

and Recycling of Glass Waste, ed. M. C. Limbachiya and J. Roberts. Thomas Telford Ltd., London, 2004, pp. 305–312.

36. Moons, M. J. M. and Van Breugel, K., Application of expanded glass (Misapor) in concrete susceptibility fro alkali silica reaction (ASR). In *In Sustainable Waste Management and Recycling of Glass Waste*, ed. M. C. Limbachiya and J. Roberts. Thomas Telford Ltd., London, 2004, pp. 197–204.
37. Harshe, R., Balan, C. and Riedel, R., Amorphous Si(Al)OC ceramic from polysiloxanes: bulk ceramic processing, crystallization behavior and applications. *J. Eur. Ceram. Soc.*, 2004, **24**, 3471–3482.
38. Pittsburgh Corning Foamglas Insulation, www.foamglasinsulation.com.
39. Duke, D. A., MacDowell, J. F. and Karstetter, B. R., Crystallization and chemical strengthening of nepheline glass-ceramic. *J. Am. Ceram. Soc.*, 1967, **50**, 67–74.