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Development and mechanical characterization of Al₂O₃ platelet-reinforced glass matrix composites obtained from glasses coming from dismantled cathode ray tubes

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Abstract

A cold-pressing and pressure-less viscous flow sintering treatment for the manufacturing of dense alumina platelet-reinforced glass matrix composites was proposed for the recycling of glasses coming from dismantled cathode ray tubes (CRTs). Mixtures of three different glasses from CRTs and Al_2O_3 platelets were investigated regarding the introduction in glass of rigid, non-sintering, inclusions and the nature of the matrix glasses. An innovative short-time sintering procedure was found to be advantageous, leading to significant increases in bending strength, microhardness and fracture toughness, despite the relatively low Al_2O_3 platelet addition. Both the morphology of the residual porosity, due to the sintering process and particular chemical and physical interactions within the matrix, and the crack deflection effect, due to the specific matrix-reinforcement combination, were found to be the determinant of the observed mechanical properties. The obtained bending strength, Vickers' microhardness and fracture energy are comparable to the values reported for glass-ceramics for technical applications in the building industry. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Sintering; Composites; Mechanical properties; Glass; Al2O3; Platelets

1. Introduction

The manufacturing of innovative glass-based materials may be considered as a promising way for the treatment of various types of wastes.¹ Glass fibers,² glass-ceramics,³ foam glasses^{4,5} and, mainly in the last ten years, glass or glass-ceramic matrix composites^{6,7} were developed with this aim.

A particular type of waste glasses are those coming from dismantled cathode ray tubes (CRTs). Such glasses represent a pressing environmental problem, since their direct (closedloop) recycling in the manufacture of new CRTs is very complicated. In a CRT different types of heavy metal containing glasses, lead- or barium-based, are employed.⁸ The usage of heavy metal oxides in the chemical formulation of CRT glasses is necessary for the UV and X radiation, produced by the electron gun, to be absorbed. The front part, named panel, is made of a barium–strontium glass, practically lead free, very homogeneous and thick. Lead is used in the funnel and neck part, the one hidden inside the TV set, because of its low cost. The more expensive barium is chosen, instead of lead, in order to prevent the browning of the front part due to easily reducible oxides (like PbO) caused by high-energy electrons. Such effect is known as "solarization".⁹ The closed-loop recycling could be profitable only in the case of an absolute separation of the glass components: the introduction of a small percentage of funnel or neck glass in panel manufacturing is not acceptable for the solarization effect; on the other hand, the addition of panel glass to the funnel or neck glass composition is limited, since the mixture of Pb and Ba glasses has inferior mechanical properties.⁸

Open-loop recycling, i.e. the utilization of CRT glasses as raw materials for applications independent from CRT manufacturing, may be performed. At the present time

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the open-loop recycling is mainly due to the heavy metal content which could be advantageous in applications such as laboratory equipment for radiation protection (containers, glass fibre textiles,^{10,11} etc.). Such applications, however, may absorb only a small volume of CRT glasses so that they generally end in waste combustors or landfills, with a given danger of environment pollution. In recent times it was recognized the environmental risk of PbO volatilization upon waste combustion, causing CRTs to be banned from such form of disposal.¹² Some authorities have recently banned CRT glasses also from landfills; even if the environmental risk is dramatically lower, the huge amount of the specific waste leads to the need of enhancing CRT recycling.¹² The situation is complicated, at the same time, by the replacement of standard-definition television with high-definition television (without cathode ray tube); the difficult and insufficient closed-loop recycling will be less and less suitable, since a drastic reduction of CRTs production is probable.¹³

Some recent works pointed out the feasibility of innovative glass-based materials from CRT glasses. The fundamental remark of such research is that CRT glasses possess a relatively low softening temperature, which could be particularly profitable in viscous flow sintering applications. Glass foams^{14,15} and glass matrix composites^{16–19} were successfully fabricated from CRT glasses. In the specific field of glass-matrix composites it has been shown that CRT glasses are suitable for the obtainment of highly dense composites in spite of cold pressing and pressure-less sintering (it is well known that the densest glass-matrix composites are developed by hot pressing).

In this paper we present the manufacturing of Al_2O_3 platelet-reinforced glass-matrix composites from CRT glasses. The reinforcement is low-cost and commercially available as abrasive material for polishing applications. Ceramic platelets (SiC^{20,21} and Al₂O₃^{22,23}) have been used successfully to reinforce glass and glass-matrix composites for the last ten years, after extensive applications in ceramic matrices such as mullite, zirconia, alumina.24-26 The improvement in mechanical properties is mainly related to crack deflection, caused by the introduction of residual stresses in the matrix, due to the thermal expansion mismatch with the reinforcing phases. Some work has been performed on manufacturing platelet-reinforced glass-matrix composites by cold-pressing and pressure-less viscous flow sintering, thus yielding a cost-effective processing route.^{6,27} A precise optimisation of the sintering conditions may lead to highly dense materials. Besides economic advantages, the sintering approach has an environmental benefit, since the relatively low processing temperature causes the possible volatilisation of some elements to be prevented.

The main objective of this work was to optimise the sintering behaviour of Al_2O_3 platelet-reinforced recycled glass, in order to reach high-density products, with suitable mechanical properties and with a short-time procedure, thus obtaining materials compatible for tiles applications. The employment of products from CRTs in the field of the building industry is thought to be particularly promising since the size of the relative market is suitable for a strong waste absorption. Alumina platelets have been already proposed for the reinforcement of panel glass¹⁹ by an extrusion process; in this work a simple viscous flow sintering approach was employed for a mixture of all glass components of a CRT. A certain economic benefit could be recognized, besides in the processing route, in the reduction of the costs of materials selection.

2. Experimental

A mixture of barium and lead-silicate glasses was employed as the matrix. The chemical composition and the physical properties of the investigated glass are shown in Table 1. All the glasses were ground without re-melting and making a frit like in previous works;^{16,17} the grinding was more difficult, but there was neither thermal nor chemical alteration of the CRT glasses.

A dilatometric analysis was performed to obtain the dilatometric softening point, essential for the study of the sintering behaviour. The dilatometric plots, shown in Fig. 1, illustrate that the dilatometric softening point for the investigated glass is between 512.0 and 592.8 $^{\circ}$ C.

All the CRT glasses were first dry ball milled and sized in order to obtain grains $<37 \,\mu\text{m}$. The powders were then mixed for 1 h in the same ball mill in the proportions in weight available from statistics (65.73% panel glass, 33.86% funnel glass, 0.41% neck glass).^{14,28}

 α -Alumina monocrystals (platelets) were chosen as the reinforcement (Microabrasives Co., Westfield, MA). The platelets are hexagonal-shaped, with major axes between 5 and 10 μ m and axial ratio (thickness/average diameter) ≈ 0.2 . The density of α -alumina was considered to be 3.99 g cm⁻³.²⁹ The thermal expansion coefficient of alumina platelets ($\alpha_p = 8.9 \times 10^{-6} \,^{\circ}\text{C}^{-1}$) was lower than that of CRT glasses which constitutes the matrix ($\alpha_m = 9.9 \times 10^{-6} \,^{\circ}\text{C}^{-1}$)

Table 1

Chemical composition and physical properties of the investigated glasses;⁸ the density data were measured by applying the Archimedes' principle to as-received CRT glasses

	Panel (Ba containing)	Funnel (Pb containing)	Neck (Pb containing)
Chemical c	composition in wt.%	of CRT glasses (mai	in oxides)
SiO_2	60.70	54.10	38.00
Al_2O_3	1.70	1.80	0.90
Na ₂ O	7.50	6.20	2.00
K_2O	6.90	8.20	16.50
CaO	0.10	3.50	0.10
BaO	9.90	0.80	0.70
SrO	8.60	0.70	4.80
PbO	0.01	22.00	35.00
Thermal ex	pansion coefficient ($(10^{-7} \circ C^{-1})$	
	99.0 ± 0.5	99.0 ± 0.5	99.0 ± 0.5
Density (g	cm ⁻³)		
	2.82 ± 0.01	3.03 ± 0.01	3.05 ± 0.01

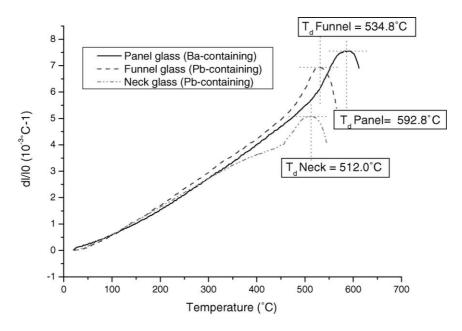


Fig. 1. Dilatometric plots of the investigated CRT glasses, with evidence of the dilatometric softening points.

for all the glasses; the identity of α being essential for an effective joining of the glasses in a CRT).

Alumina platelets in 5, 10, 15% concentrations by volume were added to the mixture of fine-powdered CRT glasses, and mixed in a dry ball mill for 1 h. Also powders of pure mixture were considered. The powders were uniaxially pressed in a steel die of rectangular section ($50 \text{ mm} \times 34 \text{ mm}$) at room temperature, by using an hydraulic press operating at 40 MPa, without any binder. The obtained green tiles were sintered in air at temperatures varying from 650 to 800 °C. A first series of samples was treated with a heating rate of 10 °C/min and a sintering time of 1 h. A second series was treated with the same firing duration, but with a heating rate of 5 °C/min. Finally, the last series was treated with a heating rate of 15 °C/min and a very short firing duration of 15 min.

The density of the sintered compacts was measured by the Archimedes' principle. At least ten fragments were analysed for each sample. The theoretical densities of composite materials were calculated by applying the rule of mixtures from the density of the constituents. The ratio measured density/theoretical density, named relative density, was chosen as a reference parameter.

Beam samples of about 3 mm \times 2 mm \times 42 mm, for bending strength (modulus of rupture) determinations were cut from sintered samples. All samples were carefully polished up to a 6 μ m finish, by using abrasive papers and diamond paste. The edges of the bars were bevelled by using fine abrasive papers and diamond paste. Four point bending tests (32 mm outer span, 8 mm inner span) were performed by using an Instron 1121 UTS (Instron Danvers, MA), with a crosshead speed of 0.1 mm/min. Each data point represents the average from 5 to 10 individual tests.

Polished samples were employed for Vickers indentation tests, from which the hardness (H_v) and the indentation fracture energy (G_{IC}) of the investigated materials were obtained by applying, respectively, low loads (500 g) and high loads (1500–2200 g). The fracture energy³⁰ was calculated by using the well-known equation of Anstis et al.,³¹ starting from the measured length of cracks emanating from the corners of the Vickers indents, originally reported for the fracture toughness parameter, as follows:

$$K_{\rm IC} = \xi \left(\frac{E}{H_{\rm v}}\right)^{0.5} \left(\frac{P}{c^{1.5}}\right)$$

$$K_{\rm IC} = \sqrt{EG_{\rm IC}}$$

$$G_{\rm IC} = \frac{K_{\rm IC}^2}{E} = \xi^2 \left(\frac{1}{H_{\rm v}}\right) \left(\frac{P^2}{c^3}\right)$$

where P is the applied load, c is the length of the emanated cracks and ξ is a calibration factor ($\xi = 0.016 \pm 0.004$). The fracture energy calculation is independent from the elastic modulus: the improvement of the fracture resistance of the glass matrix due to the reinforcement was consequently investigated neglecting the enhancement of the elastic modulus provided by the inclusions (the Young's modulus of alumina is much larger than that of glass). The fracture energy parameter is, in practice, a function only of the intrinsic crack deflection effect, due to the particular matching between the matrix and the reinforcement, whose effectiveness was one of the most important research themes of the present work. In addition, it must be noted that the size of the Vickers indents for $G_{\rm IC}$ calculations was about 80 μ m, thus being much larger than the size of the alumina inclusions; as a consequence, the $G_{\rm IC}$ evaluation could be related to the overall fracture behaviour of the composite materials.

The fracture surfaces of sintered samples were characterized by Scanning Electron Microscopy (Philips XL 30 ESEM). Powdered samples were investigated by X-ray diffraction (XRD, Philips PW3710).

3. Results and discussion

As previously reported, the fundamental aim of this work was the obtainment of materials suitable for tiles applications, developed by a particularly cost-effective method. Simple and rapid thermal treatments of glass matrix composites were therefore proposed. The latest experience with plateletreinforced glass matrix composites coming from recycled glasses and obtained by cold pressing²⁷ also constituted a reference point.

The first series of sintered products was developed, at different temperatures, with a heating rate of 10 °C/min. The relatively high heating rate was proposed to drastically shorten the processing times, when compared to the previously sintered products, based on a different glass matrix.²⁷ It had been observed that, by maintaining the holding time constant, 1 h, the processing temperature had to be increased with increasing Al₂O₃ platelet content. This fact was consistent with the findings in the literature about the retardation in viscous flow sintering of glass caused by the presence of rigid, non-sintering inclusions like the same platelets.³² However, it was also observed that the sintering temperature could not be 100 °C higher than the optimum sintering temperature for the un-reinforced glass matrix, due to a more rapid sintering occurring at the surface (nearest to the heating elements) with entrapment of gasses (the residual porosity of the green tiles) in the core, thus configuring a sort of "differential densification".

In the present work, the situation was complicated by the fact that the matrix resulted from the simultaneous sintering of three different glasses. It was widely reported^{16,33} that the optimum sintering temperature of glass can be estimated as being 50 °C higher than the dilatometric softening temperature T_d , at which the contraction of a sample due to viscous flow is exactly counterbalanced by the thermal expansion; while the lead-silicate glasses from the funnel and the neck exhibit a quite compatible dilatometric softening point (510–530 °C), the Ba-based panel glass exhibits a drastically higher softening point (about 600 °C). Since the panel glass constitutes almost two thirds of the total glass content in a typical CRT, the reference temperature for the sintering of the matrix was chosen to be 650 °C. An enhancement of the sintering temperature, from 50 to 100 °C, for every 5 vol.% addition of Al₂O₃ platelets was proposed, as an analogy with the previous studies.²⁷

As shown in Fig. 2a the materials of the first series exhibited very low relative densities and low bending strength. It must be noted that for a 15% concentration of platelets the increase of the sintering temperature from 750 to 800 °C led to a dramatic decrease of density and bending strength, which

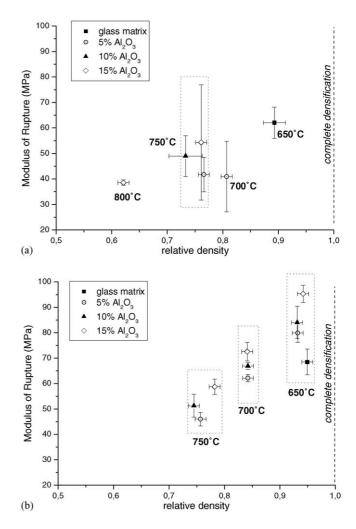


Fig. 2. Bending strength (modulus of rupture) vs. relative density plots for the first (a) and the second (b) series of sintered products.

were found to be much lower than those of the un-reinforced glass matrix. Composites sintered at 750 $^{\circ}$ C showed a certain increase in the bending strength with increasing alumina content, but they were surprisingly characterized by a similar relative density. Such anomalous behaviour was firstly attributed to the above-described differential densification. Due to the fact that the matrix was partially constituted by low temperature sintering lead glasses, the densification of the outer layer of the composites was thought to be very rapid, with the entrapment of pores. A relatively fast heating rate was thought to be detrimental, since the sintering could occur before pore evolution.

The second series of sintered products was produced with a slower heating rate (5 °C/min) at temperatures between 650 and 750 °C. The bending strength and the relative density were drastically improved for a low sintering temperature, that corresponding to the sintering of the un-reinforced matrix, as shown in Fig. 2b. For the densest sintered products the improvement in bending strength, with increasing platelet content, was substantial, being from 68.5 to 95.3 MPa. The composites sintered at 750 °C, more than those treated at

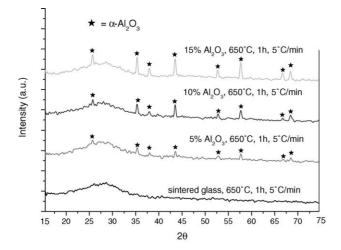


Fig. 3. XRD spectra of selected glass matrix composites and sintered glass matrix (second series) with no evidence of crystalline phases besides α -Al₂O₃.

700 °C, exhibited a slight improvement. The compaction degree of the composites was still found to be independent from the platelet content, even in the case of the densest samples. Such systematic behaviour was consequently attributed to complex chemical and physical interactions.

XRD analyses did not demonstrate any evidence of secondary crystalline phases besides alumina, as shown in Fig. 3. This is consistent with the assumption of alumina as an inert reinforcement of glass. It had been already shown, in the case of metallic reinforcements in lead-silicate glass matrices coming from CRTs, the chemical destabilization of the same glasses due to the reduction of PbO, caused by the oxidation of metal particles, and the precipitation of metallic lead, clearly visible from XRD spectra.¹⁶ In this case, such reaction could not be proposed.

SEM analysis of the fracture surfaces revealed a very particular microstructure, as reported in Fig. 4. A number of "pore clusters" could be recognised in the sintered glass (Fig. 4a) and glass matrix composites (Fig. 4b) of the second series of samples. The deviation from the full densification of the sintered products was attributed to such porosity. The particular pore morphology could be considered detrimental to the mechanical properties, since the clusters may act like stress concentrators.

Composites sintered at higher temperatures (700 and 750 °C), as reported in Fig. 4c and d, showed the formation of large and widespread pores, with no evidence of clusters. The samples of the first series, developed with a heating rate of 10 °C/min, also reported in Fig. 4e and f, exhibited a similar effect.

The fact that the pores did not depend on the reinforcement and the particular "cluster" shape led to the hypothesis of the evolution of gasses from the sintering glass mass. It has been widely reported that lead glasses are characterized by a large amount of gasses dissolved,¹⁶ from the manufacturing process (such glasses are not extensively refined). In particular, with regard to the raw materials, it is well known the usage of minium (Pb_3O_4), instead of PbO (that incorporated in the glass network), in order to introduce some "extra" oxygen, which could be useful for maintaining lead as lead oxide, as follows:

$2Pb_3O_4 \rightarrow 6PbO + O_2(g)$

The gas solubility in the glass mass is thought to become less and less with the increase of the sintering temperature or with the introduction of reducing agents (as reported with the previously mentioned metallic reinforcements¹⁶). The large pores of the composites heated at 700 and 750 °C were attributed to the coalescence of small pores in the clusters; the enhanced effect in the samples heated at 10 °C/min (first series) was likely due to the superposition of the above mentioned effect of differential densification and pore evolution. It must be noted that the employed CRT glasses were particularly critical, since no re-melting process had been performed before sintering and all the glasses contained the same amount of gasses than immediately after formation.

Despite the significant residual porosity and the particular pore morphology observed, the bending strength of the sintered glass and glass-matrix composites of the second series sintered at 650 °C, as above reported, was notable. The Al_2O_3 platelets were found to be suitable for the reinforcement of glass, like in the previous studies²⁷ with a different matrix. The achieved bending strength was attributed to the formation of a relatively strong bond between the glass matrix and the reinforcement, which allowed a certain load transfer between the phases.

The thermal mismatch between the phases was proposed to cause the development of tangential tensile stresses in the matrix around the reinforcement upon cooling from the sintering temperature. A certain crack deflection effect was consequently expected, since cracks were thought to be attracted towards the reinforcement, and propagate further through the rupture of the glass/alumina interface. In the case of a strong interface the fracture propagation in the composites would be consequently more difficult than in the un-reinforced matrix. The crack deflection mechanism was found to be effective, since the roughness of the fracture surfaces of the glass matrix composites was relevant, as illustrated by Fig. 5a and b. In particular, in Fig. 5b it is shown the rupture of the interface, with Al₂O₃ platelets clearly visible on the fracture surface.

The reinforcing ability of alumina and the effectiveness of crack deflection were confirmed by the Vickers' microhardness data and, above all, the indentation fracture energy. The Vickers' microhardness is shown in Fig. 6; an almost linear increase could be observed with increasing platelet content. The achieved hardness enhancement ($H_v > 8$ GPa) by platelets addition made glass matrix composites suitable for applications requiring good wear resistance. The indentation fracture energy also exhibited a notable increase with increasing platelet content, varying from 6.50 J/m² (a typical value for an un-reinforced glass³⁴) up to 26.81 J/m², as shown in Fig. 7. The achieved fracture energy level is comparable

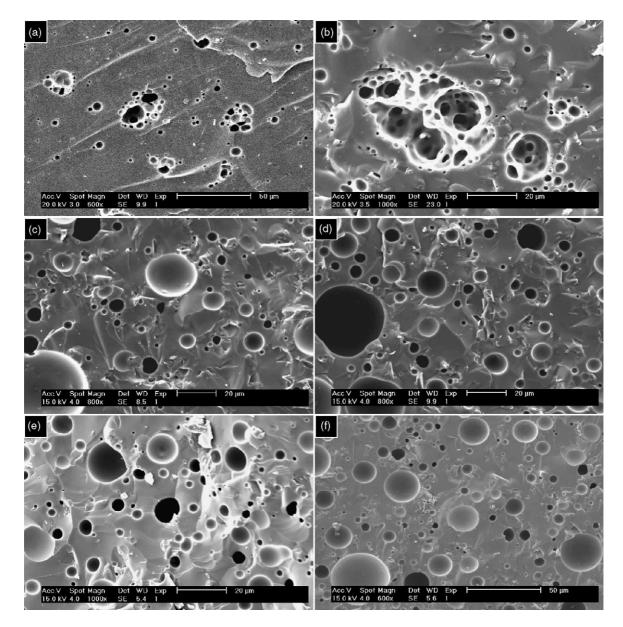


Fig. 4. SEM micrographs (fracture surfaces) with evidence of pores in the glass matrix: (a) sintered glass matrix and (b) glass matrix composite (15 vol.% Al₂O₃) treated at 650 °C for 1 h, with a heating rate of 5 °C/min; glass matrix composites (15 vol.% Al₂O₃) treated at 700 °C (c) and 750 °C (d) for 1 h, with a heating rate of 5 °C/min; glass matrix composites (15 vol.% Al₂O₃) and 750 °C (f, 15 vol.% Al₂O₃) for 1 h, with a heating rate of 10 °C/min.

with the typical values for crystalline ceramics and with the maximum values for glass matrix composites fabricated by hot-pressing.²³ In Fig. 7 it is also shown that the increase was particularly remarkable for low platelet addition, coherently with the findings in the literature³⁵ for the crack deflection effect of various reinforcements. This fact confirmed the original assumption of a relatively low platelet addition (\leq 15 vol.%). The crack deflection effect was confirmed by the observation of the microcrack system developed by the Vickers' indentations, as shown in Fig. 8.

The third series of samples was produced in order to assess the possibility of reducing the porosity due to gas evolution in the sintering mass and improve, above all, the bending strength. In fact, the bending strength determination is more sensitive to the global amount and the morphology of residual pores, than Vickers' hardness and indentation fracture energy, which are measured locally. Un-reinforced glass powders and glass powders with a 15 vol.% Al₂O₃ platelet addition were investigated. The compaction degree of the sintered products was not found to be improved, when compared to the data of the previous series. On the other hand, a dramatic enhancement of the bending strength was achieved, as shown in Fig. 9; the bending strength of the un-reinforced matrix exceeded 84 MPa, while that of the composite exceeded 108 MPa. Such behaviour was thought to be due to the fact that even if the residual porosity was almost the same than in the previous treatment, the pore morphology was different. As demonstrated in Fig. 10, the residual porosity, being

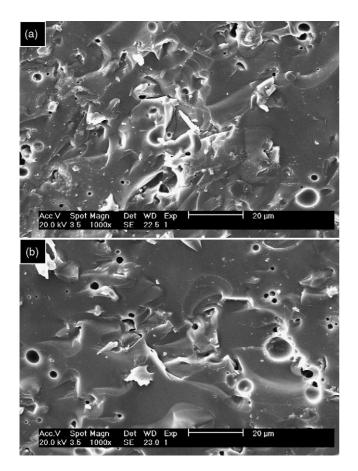


Fig. 5. Rough fracture surfaces of glass matrix composites treated at $650 \,^{\circ}$ C for 1 h (5 °C/min heating rate) with (a) 5 vol.% Al₂O₃ and (b) 15 vol.% Al₂O₃, with evidence of surfacing Al₂O₃ platelets.

constituted by isolated pores, instead of clusters, was due to the sintering process more than the evolution of gasses. The bending strength data of the most significant sintered products, together with density data, are summarized in Table 2.

The last, remarkable, bending strength data, together with the already notable hardness and fracture toughness data of the previous series, contributed to the definition of new sintered materials from the recycling of CRT glasses. It was demonstrated, in practice, that useful products, for technical applications in the field of building industry, could be manufactured from inexpensive raw materials, whose usage is, in addition, environmentally profitable. The mechanical properties were, in fact, comparable to those of glass-ceramics for building applications, which in turn may be developed from

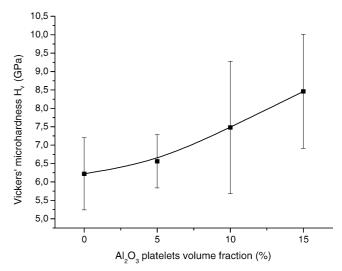


Fig. 6. Vickers' microhardness vs. Al_2O_3 platelets volume fraction plot of the samples sintered at 650 °C for 1 h with a heating rate of 5 °C/min (second series).

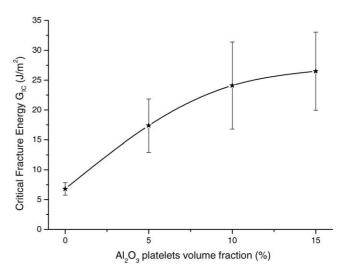


Fig. 7. Critical (indentation) fracture energy G_{IC} vs. Al₂O₃ platelets volume fraction plot of the samples sintered at 650 °C for 1 h with a heating rate of 5 °C/min (second series).

a number of wastes (the well-known Slag-Sitalls)³⁶ but with the need of an energy intensive vitrification process.

The reduction of the processing time, which was found to be mechanically advantageous, could lead to strong

Table 2

Summary of the density and bending strength data of the most significant sintered materials from the treatment of CRT glasses

Al ₂ O ₃ (vol.%)	Theoretical density $(g \text{ cm}^{-3})$	Composites sintered at 650 °C/1 h (second series)		Composites sintered at $650 ^{\circ}\text{C}/15 \text{min}$ (third series)	
		Measured density $(g cm^{-3})$	MOR (MPa)	Measured density $(g cm^{-3})$	MOR (MPa)
0	2.89 ^a	2.74 ± 0.01	68.5 ± 5.1	2.75 ± 0.03	84.4 ± 4.1
5	2.95	2.75 ± 0.03	79.9 ± 3.7	_	_
10	3.00	2.79 ± 0.02	84.1 ± 6.4	_	_
15	3.06	2.88 ± 0.03	95.3 ± 3.4	2.88 ± 0.02	108.7 ± 5.9

^a Data calculated by applying the rule of mixtures to the density data of the individual CRT glasses, reported in Table 1.

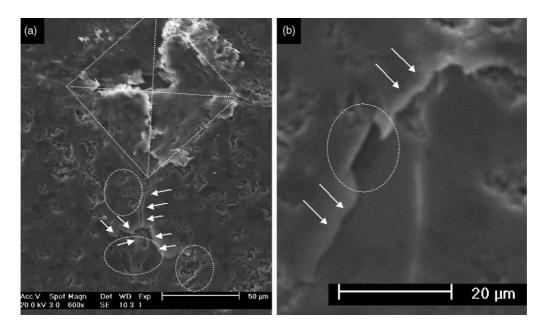


Fig. 8. SEM micrographs of a polished surface of a glass matrix composite sample ($15 \text{ vol.}\% \text{ Al}_2\text{O}_3$): (a) Vickers' indentations with evidence of an induced crack deflected and branched by groups of platelets; (b) detail of a crack induced by Vickers' indentation deflected by the reinforcement.

production economics. In addition, the rapid sintering (15 min) constitutes a rather innovative point in the field of glass matrix composites, since the viscous flow sintering treatments, to the authors' knowledge, are much longer. In the authors' opinion, one likely reason of such unusual result is that three different glasses were employed; the presence of a fraction of glasses with a low softening point might act like a sintering aid of the main glass fraction (corresponding to the Ba-based panel glass). The completion of the manufacture and characterization of glass matrix composites from short-time sintering treatments will be the object of our future experiences.

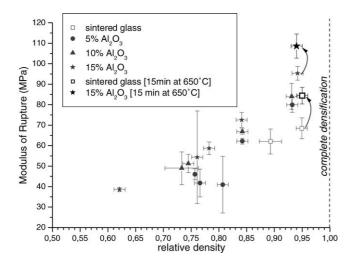


Fig. 9. Bending strength (modulus of rupture) vs. relative density plot for all the obtained sintered glasses and glass matrix composites with pointing out of the data of the third series and the notable increase with regard to the maximum bending strength of the previous series.

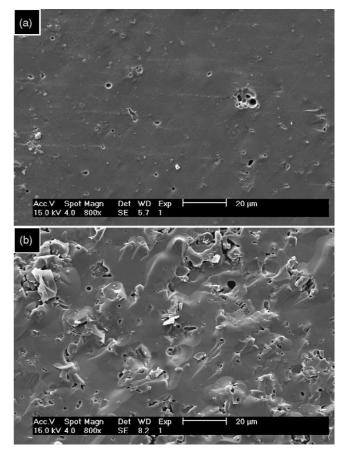


Fig. 10. SEM micrographs (fracture surfaces) of (a) sintered glass and (b) glass matrix composite (15 vol.% Al_2O_3) treated at 650 °C for 15 min, with a heating rate of 15 °C/min, with evidence of isolated pores.

4. Conclusion

Three different glasses coming from dismantled cathode ray tubes (CRTs) were successfully employed in the manufacturing of dense alumina platelet-reinforced glass matrix composites for applications in the building industry. A coldpressing and viscous flow pressure-less sintering treatment had to be suited to several densification anomalies due to the nature of the starting materials. Unlike analogous alumina platelet-reinforced composites the densest composites were not obtained at higher temperatures than that of the unreinforced matrix (650 °C) and the densification degree did not depend on the platelet volume fraction; moreover, an innovative short-time firing treatment (15 min) led to sintered products with higher bending strength than that of composites developed with a longer firing duration. Such anomalies were found to depend on the presence, within the CRT glasses, of dissolved gasses, whose solubility decreases with the increase of the sintering temperature or the firing duration, with the formation of pores detrimental to the bending strength. Since the rapid sintering treatment was successful in controlling the shape of the porosity due to gas evolution, notable bending strength values (>105 MPa) were achieved; such result could be useful in the manufacturing of a number of glass matrix composites from the same CRT glasses.

The particular combination of the glass matrix and the alumina reinforcement was also advantageous in the obtainment of a remarkable microhardness and, above all, a dramatically enhanced fracture resistance (in spite of the relatively low Al_2O_3 platelet addition), due to a crack deflection effect.

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References

- Gutman, R., Thermal technologies to convert solid waste residuals into technical glass products. *Glastech. Ber. Glass Sci. Technol.*, 1996, 69(9), 223.
- Scarinci, G., Brusatin, G., Barbieri, L., Corradi, A., Lancellotti, I., Colombo, P. *et al.*, Vitrification of industrial and natural wastes with production of glass fibers. *J. Eur. Ceram. Soc.*, 2000, **20**, 2485–2490.
- Sarkisov, P. D., The modern state of technology and application of glass-ceramics. In *Glass' 89 Survey Papers of the XVth International Congress on Glass Leningrad*, 1989, pp. 411–441.
- Bayer, G. and Koese, S., Reaction of foaming additives with waste glass powders in the preparation of lightweight materials. *Riv Staz Sper Vetro*, 1979, 5, 310–320.

- Ducman, V. and Kovačević, M., The foaming of waste glass. *Key* Eng. Mater., 1997, 132–136, 2264–2267.
- Boccaccini, A. R., Bücker, M., Bossert, J. and Marszalek, K., Glass matrix composites from coal flyash and waste glass. *Waste Manag.*, 1997, **17**(1), 39–45.
- Trusty, P. A. and Boccaccini, A. R., Alternative uses of waste glasses: issues on the fabrication of metal fibre reinforced glass matrix composites. *Appl. Compos. Mater.*, 1998, 5(4), 207–222.
- Hreglich, S., Falcone, R. and Vallotto, M., The recycling of end of life panel glass from TV sets in glass fibers and ceramic productions. In Proceedings of the International Symposium on "Recycling and Reuse of Glass Cullet", University of Dundee, UK, 19–20 March 2001, pp. 123–134.
- Nordyke, J. S., *Lead in the World of Ceramics*. The American Ceramic Society, Westerville, OH, USA, 1984.
- Hamann, B., Hülsenberg, D. and Leutbecher, T., Glassware manufactured on the basis of cullets containing heavy metal oxides. *Glastech. Ber. Glass Sci. Technol.*, 1995, **68**(2), 183–190.
- Boccaccini, A. R., Bücker, M., Trusty, P. A., Romero, M. and Rincón, J. M., Sintering behaviour of compacts made from television tube glasses. *Glass Technol.*, 1997, **38**(4), 128–133.
- Macauley, M., Palmer, K. and Shih, J. S., Dealing with electronic waste: modeling the costs and environmental benefits of computer monitor disposal. *J. Environ. Manage.*, 2003, 68, 13–22.
- Townsend, T. G., Musson, S., Jang, Y. and Chung, I., *Characterization of Lead Leachability from Cathode Ray Tubes Using the Toxicity Characteristic Leaching Procedure*. Florida Center for Solid and Hazardous Waste Management, State University System of Florida, report no. 99-5.
- Bernardo, E., Scarinci, G. and Hreglich, S., Foam glass as a way of recycling glasses from cathode ray tubes. *Glastech. Ber. Glass Sci. Technol.*, in press.
- Mear, F., Yot, P., Cambon, M. and Liautard, B., Valorization de verres de tubes à rayon cathodique. *Verre*, 2003, 9(2), 72–77.
- Bernardo, E., Scarinci, G. and Hreglich, S., Mechanical properties of metal-particulate lead-silicate glass matrix composites obtained by means of powder technology. *J. Eur. Ceram. Soc.*, 2003, 23, 1819–1827.
- Bernardo, E., Scarinci, G., Maddalena, A. and Hreglich, S., Development and mechanical properties of metal-particulate glass matrix composites from recycled glasses. *Composites Part A*, 2004, 35, 17–22.
- Boccaccini, A. R. and Pearce, D. H., Toughening of glass by a piezoelectric secondary phase. J. Am. Ceram. Soc., 2003, 86(1), 180–182.
- Minay, E. J., Desbois, V. and Boccaccini, A. R., Innovative manufacturing technique for glass matrix composites: extrusion of recycled TV set screen glass reinforced with Al₂O₃ platelets. *J. Mater. Process. Technol.*, 2003, **142**, 471–478.
- Gadkaree, K. P. and Chyung, K., Silicon-carbide-whisker-reinforced glass and glass-ceramic composites. *Am. Ceram. Soc. Bull.*, 1986, 65(2), 370–376.
- Chaim, R. and Talanker, V., Microstructure and mechanical properties of SiC platelet/cordierite glass-ceramic composites. J. Am. Ceram. Soc., 1995, 78(1), 166–172.
- Boccaccini, A. R., Sintering of glass matrix composites containing Al₂O₃ platelet inclusions. J. Mater. Sci., 1994, 29, 4273–4278.
- Boccaccini, A. R. and Trusty, P. A., Toughening and strengthening of glass by Al₂O₃ platelets. J. Mater. Sci. Lett., 1996, 15, 60–63.
- Cherian, I. K., Lehigh, M. D., Nettleship, I. and Kniven, W. M., Stereological observations of platelet-reinforced mullite- and zirconia-matrix composites. *J. Am. Ceram. Soc.*, 1996, **79**(12), 3273–3281.
- Huang, X. and Nicholson, P. S., Mechanical properties and fracture toughness of α-Al₂O₃-platelet-reinforced Y-PSZ composites at room and high temperatures. J. Am. Ceram. Soc., 1993, 76(5), 1294–1301.
- Lee, S. and Kniven, W. M., Toughened oxide composites based on porous alumina-platelet interphases. J. Am. Ceram. Soc., 2001, 84(4), 767–774.

- Bernardo, E. and Scarinci, G., Sintering behaviour and mechanical properties of Al2O3 platelet-reinforced glass matrix composites. *Ceram. Int.*, 2004, **30**, 785–791.
- Monchamp, A., Evans, H., Nardone, J., Wood, S., Proch, E. and Wagner, T., Cathode ray tube manufacturing and recycling: analysis of industry survey. In *Electronic Industries Alliance Spring Conference, Arlington, VA, USA, April 2001.*
- Dorre, E. and Hübner, H., *Alumina*. Springer-Verlag, Berlin, Heidelberg, 1984.
- Collins, J. A., Failure of Materials in Mechanical Design. John Wiley & Sons, New York, 1993.
- 31. Anstis, G. R., Chantikul, P., Lawn, B. R. and Marshall, D. B., A critical evaluation of indentation techniques for measuring fracture

toughness: I. Direct crack measurement. J. Am. Ceram. Soc., 1981, 64(9), 533–538.

- Boccaccini, A. R., On the viscosity of glass composites containing rigid inclusions. *Mater. Lett.*, 1998, 34, 285–289.
- Ray, A. and Tiwari, A. N., Compaction and sintering behaviour of glass-alumina composites. *Mater. Chem. Phys.*, 2001, 67, 220–225.
- Mecholsky, J. J., Quantitative fractographic analysis of fracture origins of glass. In *Fractography of Glass*, ed. R. C. Bradt and R. E. Tressler. Plenum Press, New York, 1994.
- Chawla, K. K., Ceramic Matrix Composites. Chapman & Hall, London, 1993.
- Höland, W. and Beall, G., *Glass-Ceramic Technology*. The American Ceramic Society, Westerville, OH, USA, 2002.