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Mechanical properties of metal-particulate lead-silicate glass matrix composites obtained by means of powder technology

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Abstract

The great quantity of waste glasses leads to the need for new applications. The realization of matrices for innovative and cost-effective materials is one possible use. In the present work, lead silicate glasses, recovered from cathode ray tubes (CRTs) are investigated. A low cost powder processing route is proposed for the manufacture of particulate aluminium reinforced glass matrix composites. These composites exhibit an anomalous mechanical behaviour which is thought to be due to a complex metal/glass interaction. In the case of limited metal/glass interaction, good bending strength and fracture toughness are achieved. The obtained K_{IC} level of about 1.20 MPa $m^{0,5}$, together with the observed crack control behaviour, appears promising.

Keywords: Composites; Glass; Mechanical properties; Sintering; Toughness and toughening; Waste materials; Metallic inclusions

1. Introduction

Research activity has been undetaken, since the early 1970s, on the metallic dispersion toughening of ceramics. Significant experience has been obtained not only with crystalline materials, like alumina (Al_2O_3 reinforced with Al), zirconia (ZrO_2 reinforced with Zr), tungsten carbide (WC reinforced with Co) but also with glasses. Glass and glass ceramic matrix composites are undoubtedly easier to fabricate than polycrystalline ceramic composites because of the viscous flow of glass at moderately high temperatures. The first glass matrix composites were reinforced with Ni[1–4] and W[5] particles, prior to extensive work with Al.[6,7] More recent works have demonstrated the feasibility of metallic dispersion toughening with other metals, like Mo,[8,9] V,[9,10] and Cu.[11,12] Some work has been performed with alloys, from the system Fe–Ni–Co.[13,14]

The toughening effect in such metal-particulate glass matrix composites is not as substantial as that in fibre reinforced glasses (C and SiC[15–17] fibres), but metal particles are found to be interesting as they are thought to undergo extensive plastic deformation at the crack tip and thus to modify the stress distribution near the extending crack. Moreover, plastic deformation of the reinforcement is accompanied with particle debonding and pull-out, and crack tilting and twisting around the reinforcement, which, however, lead to a low toughening contribution.

Particular attention must be devoted to the interface conditions. Krstic et al.[6] in the early 1980s, with a 20% by vol. dispersion of Al in M-glass, reached a fracture toughness level of 6.5 MPa $m^{0,5}$; such an extraordinary result was thought to be due to the development of a strong interface between the glass and the preoxidized metal particles and to the low residual stress levels in the matrix brought about by minimizing the thermal expansion mismatch between the phases.

Glass matrix composites, reinforced either with fibres or with metal particles, are usually manufactured by hot-pressing mixtures of glass powders and reinforcement. The viscous flow of the glass matrices is accompanied by a certain mechanical stress, resulting in a high compaction degree, low porosity (especially at the interface) and short process duration. The intended high cost devices allow very refined and high performing parent materials; in the case of SiC fibre (Nicalon® and

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Tyranno®) reinforced glass matrix composites, several products are commercially exploited, mainly in aerospace applications[17].

Since the early 1990s several experiments, mainly in Germany,[18] have been conducted to develop the manufacturing of innovative glass matrix composites for the treatment of silicate wastes. Vitrification, since the 1970s, has been found to be an interesting way to seal and make inert a number of industrial wastes and sludges. The vitrification treatment of Venice lagoon sludge, for example, is at present one of the most significant themes of such research in Italy.[19] The ''waste glasses'' obtained can be easily stored in a landfill, with a very low risk of pollution, as the glass is a material which possesses a high chemical stability. However, the great quantity of waste glass, together with recycled glasses, leads to the need for new applications and for the development of new materials.

A significant example of waste glasses results from dismantled cathode ray tubes (CRTs),[20] whose weight is about two thirds of the total weight of a television or computer monitor. CRTs are made of several glass components, each characterized by a different chemical composition. Closed-loop recycling of CRTs is complicated by the presence of two different types of glass containing lead or barium. These heavy metal additions are essential to absorb the UV and X radiation produced by the electron guns in the CRTs. The front part, usually known as the panel, is made of a barium–strontium glass, free of lead, 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; especially in modern TV and PC monitors, lead in the panel glass is replaced by the more expensive barium, as lead silicate glass has a brown colour. Panels, which need to be colourless, cannot be made with the mixture of lead and barium glass which results when all components are crushed and mixed together.

Only small percentages of mixed CRT glass can be used even in funnel and neck manufacture because the mixture of lead and barium glasses is characterized by inferior mechanical properties. The closed-loop recycling of CRT glass would be profitable only in the case of separation of the two types of glass, which is very difficult as a glass frit joins them in CRTs with a very strong bond. As an alternative to closed-loop recycling also open-loop recycling should be improved; it is well known that the heavy metal content could be an advantage in certain applications, for example in nuclear waste containers or laboratory equipment. However, these applications may absorb only a small quantity of CRT glasses so that they generally end in a landfill, with danger of environmental pollution. The fabrication of matrices for innovative and low-cost composite materials could be a promising way.

The fundamental aim of research on composites starting from waste glasses is to obtain materials exhibiting improved mechanical properties, related to those of the parent glasses, in order to produce a certain economic benefit. If expensive and complex fabrication techniques, like hot-pressing, are employed, the potential economic benefit from the treatment of the wastes is lost. As reported in various works,[18,21–26] glass composites can be fabricated by means of powder technology. Mixtures of matrix and reinforcement are uniaxially pressed at room temperature (cold-pressing) thus forming compacts which are then pressure-less sintered.

Regarding mechanical properties, an improvement in fracture toughness, more than in elastic modulus and strength, is undoubtedly profitable as low fracture toughness is the greatest limit in terms of structural applications for common glass products.

In this paper we describe the metallic reinforcement, by aluminium particles, of lead silicate glasses recovered from TV and PC cathode ray tubes (CRTs), and the feasibility of fabricating glass matrix composites, by using a simple and low cost powder processing route. Particular attention is devoted to the fracture behaviour of the obtained composites.

2. Experimental

2.1. Starting materials

Neck and funnel glasses constitute the part of the CRT hidden inside the TV set as shown in Fig. 1. The neck glass is a lead rich silicate glass enveloping the electron gun. The lead content in the funnel glass, essential for blocking the UV and X radiation escaping laterally from the TV set, is lower than in the neck glass, as shown in Table 1.

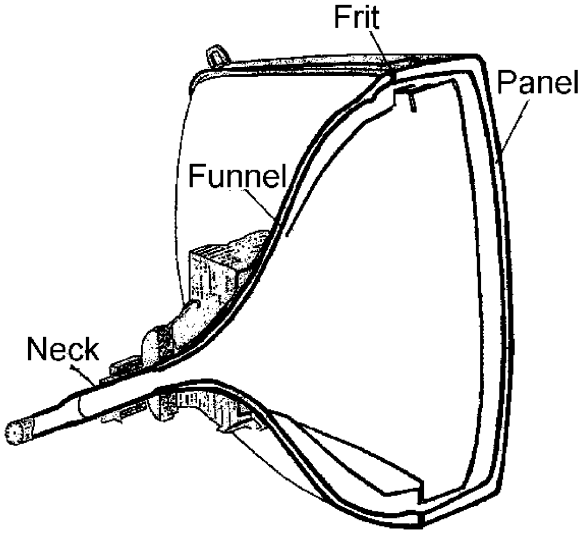

Fig. 1. CRT (cathode ray tube) glasses.

Table 1
Chemical composition and physical properties of investigated lead silicate glasses

Chemical composition in wt.%		
Oxide	Neck glass	Funnel glass
SiO_2	38.153	54.652
Al_2O_3	0.904	1.818
Na_2O	2.008	6.263
K_2O	16.566	8.284
CaO	0.100	3.536
MgO	–	1.515
Fe_2O_3	0.030	0.020
BaO	0.703	0.808
PbO	35.141	22.225
TiO_2	0.020	0.071
Li_2O	–	–
B_2O_3	–	–
SO_3	–	–
Coefficient of thermal expansion		
α $10-^{6}$ °C^{-1}	9.9±0.05	9.9±0.05
Glass transition temperature		
T_g	452.3	481.1
Density		
ρ g/cm^3	3.034	3.050

Neck and funnel glasses were chosen because of their characteristic temperatures. Recent works[27] reported that optimum viscous flow sintering of glass has to be performed between the dilatometric softening temperature, at which the contraction of a sample due to viscous flow is exactly counterbalanced by the thermal expansion, and Littleton's softening temperature, at which gross viscous flow appears. An optimum sintering temperature could be estimated as 50 °C above the dilatometric softening temperature. It must be remembered that viscous flow sintering should not compromise the integrity and the thermal and chemical stability of the reinforcement, so that a sintering temperature lower than the melting temperature of the reinforcement, i.e. aluminium, must be adopted. Both glasses coming from the CRT dismantling were studied with dilatometric analysis, to yield the glass transition temperature T_g for the reported compositions, as illustrated by Fig. 2. Both glasses exhibit dilatometric softening temperature around 550 °C; as a consequence optimum sintering temperature is estimated to be around 600 °C.

A 50% neck–50% funnel powders mixture was studied, in order to eliminate the industrial cost of material selection. A "mixed glass" was created by melting together the neck and funnel glasses in a 50–50% composition. Before melting, the mixture was doped with a low amount (0.1 wt.%) of cobalt oxide. Cobalt oxide is known for its high solubility and for causing a deep blue colouration in glass. It is usually employed as an adhesion promoter: a cobalt-doped glass is often sandwiched between metallic substrates and glass enamels, as cobalt

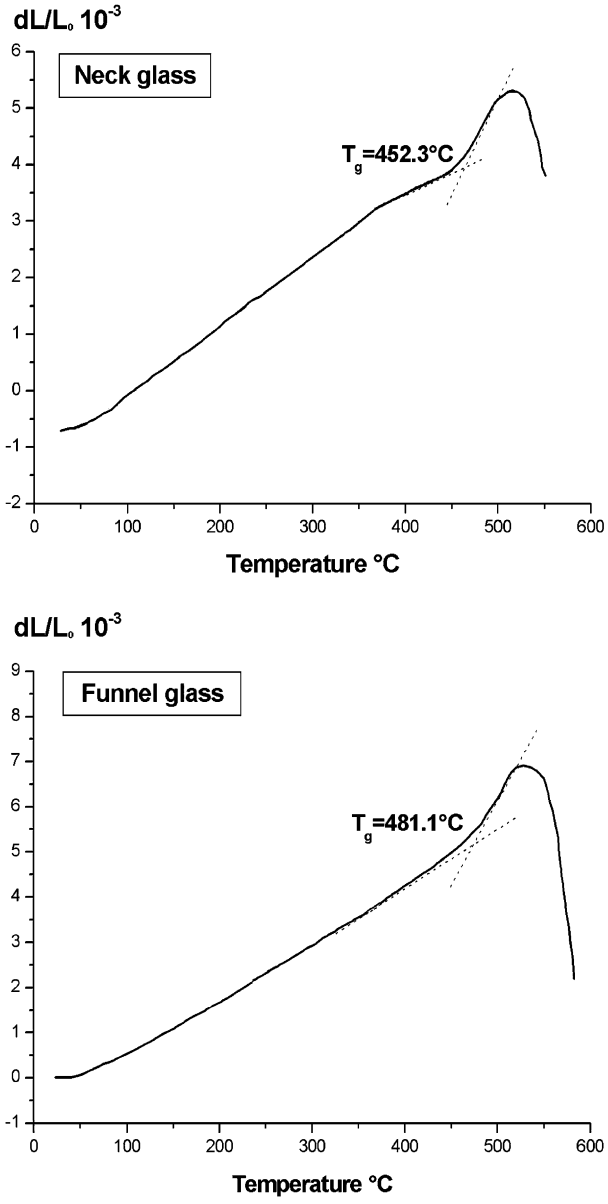

Fig. 2. Dilatometric analysis of neck (a) and funnel (b) glasses, showing characteristic glass transition temperatures.

is thought to lead to a stronger bond.[28,29] The "mixed glass" composition is illustrated in Table 2.

The molten cobalt-doped lead silicate glass was poured into cold water, in order to obtain a glass frit. The obtained coarse glass powder was dry ball milled and sized in order to obtain grains <37 μm. A certain amount of glass powder was ground in a tungsten carbide vibratory mill for 15 min, producing smaller glass particles (about <20 μm).

Aluminium powders were chosen as the reinforcement; they were employed in the as-received state (Sigma-Aldrich Co. Ltd., Gillingham, Dorset, UK). Aluminium has a density of 2.70 g/cm^3, and a coefficient of thermal expansion α equal to 16 10^{-6} °C^{-1}. The particle size of Al powders was <75 μm (200 Mesh).

Table 2
Properties of mixed (50% neck and 50% funnel) cobalt-doped glass

Chemical composition in wt.%	
Oxide	
SiO_2	46.356
Al_2O_3	1.360
Na_2O	4.136
K_2O	12.413
CaO	1.816
MgO	0.757
Fe_2O_3	0.025
BaO	0.755
PbO	28.654
TiO_2	0.045
CoO	0.100
Density	
ρ g/cm^3	3.075

2.2. Composite fabrication: powder technology

Finest cobalt-doped mixed glass powders, those with dimensions <20 μm, were added with Al in a 20 vol.% concentration, then dry mixed in a rotating agate container for 1 h. The mixtures were treated with a small amount of ethyl alcohol and uniaxially pressed in a steel die (rectangular section, 50×34mm) at room temperature, by using an hydraulic press operating at 250 bar (25 MPa). Composite green tiles were then fired at 600 °C for 5 h. A certain porosity remains, as shown in Table 3 (sample A). In order to promote densification, the compaction pressure was enhanced to 350 bar (35 MPa); the firing treatment was unchanged (samples B and C). Some samples were prepared with a firing treatment duration of 10 h (samples D and E). All these latest samples exhibited very low porosity content, as their densities were strictly around the predicted theoretical one. Other samples (sample F, G and H) were produced by pressing at 350 bar, starting from cobalt-doped mixed glass powders of size <37 μm, with a firing treatment duration of 5 h; porosity content is then significant, but not excessive.

Table 3
Sintering behaviour of lead silicate glass and aluminium mixtures

Specimen type	Upper glass particle diameter (μm)	Compaction pressure (bar)	Firing duration Sintering time (h)	Density (g/cm^3)[a]
A	20	250	5	2.8721 [−4.26]
B	20	350	5	2.9327 [−2.24]
C	20	350	5	2.9627 [−1.24]
D	20	350	10	2.9748 [−0.84]
E	20	350	10	2.9563 [−1.46]
F	37	350	5	2.9298 [−2.34]
G	37	350	5	2.9294 [−2.35]
H	37	350	5	2.9334 [−2.22]

[a] Calculated by using Archimedes' principle; deviations from calculated theoretical density ($\rho = \rho_{glass}(1-V) + \rho_{Al}V$, where V is the volume fraction of the Al reinforcement) are given within [] parenthesis.

2.3. Mechanical testing

In every case, composite tiles of about 4×30×43 mm were prepared. Beam samples of about 4×2.5×43 mm, for modulus of rupture and fracture toughness determinations, were cut from these tiles by using a diamond saw. All samples were carefully polished up to a 9 μm finish, by using abrasive papers and diamond paste. A three-point jig with a span of about 38 mm was used for the flexural tests, with a crosshead speed of 0.2 mm/min.

A notch of about 1 mm depth was introduced for fracture toughness determinations on those materials exhibiting higher bending strength, by using a thin diamond saw (0.25 mm thick), and sharpened with razor blades covered with diamond paste of decreasing grain size. K_{IC} tests were performed according to the single edge notched beam (SENB) method, i.e. doing a simple flexural test on notched specimens; the strength data of the notched section were recorded and related to fracture toughness. A four-point jig with 7.5 mm inner span and 18 mm outer span was used for these tests, with a significantly low crosshead speed of 0.05 mm/min. Fracture toughness, with a four-point flexural assembly, as shown in Fig. 3, is given by the equation:[30,31]

$$K_{IC} = \frac{3\sqrt{c}(S_1 - S_2)\xi(\alpha)F_{fail}}{2BW^2} \quad (1)$$

where S_1 and S_2 are the outer and inner span lengths, B and W are the dimensions of the un-notched section and ξ is a compliance function[31] depending on the crack length/specimen thickness α ($\alpha = c/W$) ratio:

$$\xi = \xi(\alpha)$$

$$= 1.99 - 2.47\alpha + 12.97\alpha^2 - 23.17\alpha^3 + 24.8\alpha^4 \quad (1bis)$$

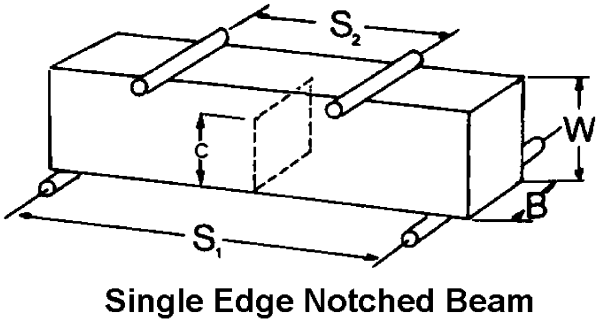

Fig. 3. Four-point bending configuration for SENB (single edge notched beam) fracture toughness determination.

3. Results and discussion

3.1. Modulus of rupture (bending strength)

Various three-point flexural tests were performed on the glass matrix composite samples. At least five bars were tested per sample. Samples obtained by using very fine glass powders (about 20 μm), exhibiting a very low porosity content, resulted in anomalous moduli of rupture. Some specimens showed an high bending strength, much higher than that of monolithic matrix, which has been measured to be 65.40±9.32 MPa[32] (which is close to the values reported in literature for a lead-silicate glass[33]); other specimens, apparently similar to the previous ones, exhibited very low strength. The preparation technique, the pressure and temperature treatment and subsequent porosity content were almost the same for high or low-strength composite samples, as illustrated in Table 4.

One explanation for the anomalous strength behaviour could be the presence of crystalline phases coming out from matrix devitrification or some chemical reaction at the interface between the glass matrix and the metallic reinforcement. In order to verify the devitrification of the lead silicate glass, which is thought to be extremely difficult in this specific type of glass, or to exploit the development of chemical reaction within the composites, the high and low-strength materials were characterized by X-ray diffraction.

The low-strength glass matrix composites exhibited the presence of metallic lead. Fig. 4 reveals typical metallic lead diffraction peaks besides aluminium peaks, which are characteristic of the reinforcing phase. No crystalline phase, in addition to aluminium and sometimes lead, can be distinguished. As a consequence, no devitrification process occurs in the thermal treatment by which these glass matrix composites were fabricated. In certain systems, a chemical reaction, probably at the interface between aluminium reinforcing particles and glass matrix occurs. It must be remembered that lead silicate glasses are prepared under severe oxidizing conditions in order to maintain all lead bonded with oxygen, with no metallic lead precipitation. The presence of aluminium inside the lead silicate glasses seems to cause

Table 4
Mechanical properties of glass matrix composites

Specimen type	Firing duration (h)	Modulus of rupture (MPa)[a]
Samples from finest glass powders (<20 μm)		
B	5	55.24±6.14
C	5	75.10±9.07
D	10	51.57±2.83
E	10	77.41±2.25
Samples from coarse glass powders (<37 μm)		
F	5	73.32±4.45
G	5	71.09±3.12

[a] Moduli of rupture are given with their standard deviation values.

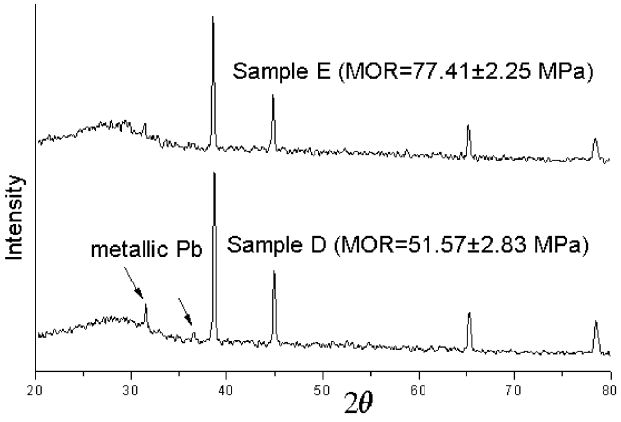

Fig. 4. XRD spectra of aluminium reinforced glasses showing typical metallic aluminium peaks; a certain metallic lead precipitation is found in weakest composite (sample D).

metallic lead precipitation, probably due to the ability of metallic aluminium to act as a reducing component.

A scanning electron microscope (SEM) examination was performed on the fracture surfaces of mechanically tested specimens. Anomalous pore distributions were distinguished in those specimens breaking at low loads. Besides isolated pores in the matrix, coming from the (incomplete) viscous flow densification, which are relatively small, pore clusters can be recognized. The particular cluster shape, which is shown in Fig. 5, suggests that they originate from a different process. It must be noted that the pore clusters are situated near the reinforcing aluminium particles; as a consequence they are thought to be related to the complex chemical and physical interaction at the interface between the glass matrix and the aluminium. The lack of oxidizing conditions may influence also gas solubility within glass. It is well known that lead silicate glasses are mainly produced from Pb_3O_4 (instead of PbO) to ensure oxidizing conditions. A certain amount of oxygen is therefore dissolved within lead silicate glasses; with the lack of

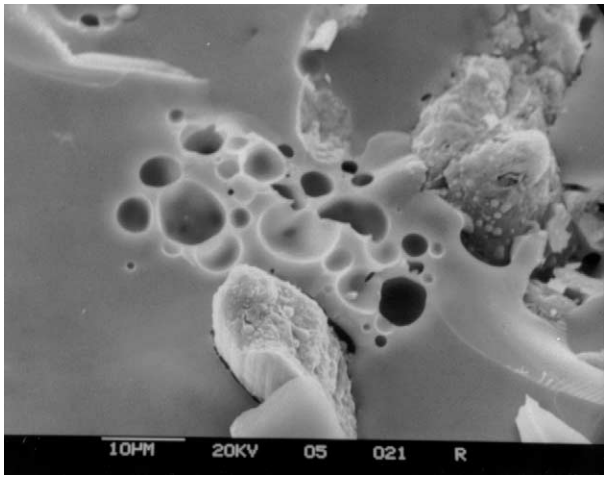

Fig. 5. Pore cluster at the interface aluminium particle/glass matrix in sample D.

oxidizing conditions in the surroundings of aluminium particles, at high temperatures, the lead silicate matrix glass is thought to exhibit a lower gas solubility, so that gas "bubbles" and clusters may develop.

An experimental correlation between metallic lead precipitation and pore cluster evolution is observed. Even if the tendency is general, two samples could be taken as examples. Sample D and E exhibit the most different moduli of rupture and an extremely low data dispersion, which could be seen in the standard deviation in Table 4; at the same time they had been both produced with a firing treatment duration of 10 hours, with subsequent minimum porosity content. Sample D, in spite of a slightly higher compaction degree than sample E, exhibits a drastically lower modulus of rupture; as shown in Fig. 4, a certain metallic lead precipitation is found to be present. Figs. 5 and 6, revealing pore clusters, are related to the same sample. Pore clusters act as a severe discontinuity, so that the stress distribution is locally altered; stress concentration at the pores produces high local stresses at low bending loads, which cause an easy pull-out of the surrounding reinforcing particles, as shown in Fig. 6. Only in the case of small cluster size is the bending strength found to be satisfactory.

The particular mechanical, physical and chemical behaviour illustrated above is not exhibited by composites coming from coarser glass powders (<37 μm). These composites exhibit a regularly high bending strength. Finest glass powders viscous flow sintering is probably faster and probably hinders oxygen diffusion, causing the lack of oxidizing conditions within the lead silicate glass. In composites coming from the coarsest glass powders, oxygen diffusion and oxidation of aluminium particles are thought to be optimised, thus ensuring a strong glass-metal bonding and preventing lead silicate glass from undergoing metallic lead precipitation and "secondary" pore evolution. In this case, fracture behaviour of composites is significantly altered, as illustrated by SEM micrographs, Figs. 7 and 8. Fig. 7 shows a plastically deformed aluminium particle which is still anchored at the glass matrix, after rupture. Besides plastic deformation of the reinforcement, another important toughening mechanism, i.e. secondary crack formation, is observed: the thermal expansion coefficient mismatch between the glass matrix and the inclusions cause circumferential cracking around the particles. The circumferential cracking may be observed above all in Fig. 8, which shows a pull-out cavity; pieces of aluminium particles can be seen around the cavity. The present micrographs are similar to those reported for other studies on aluminium reinforced glasses.[7]

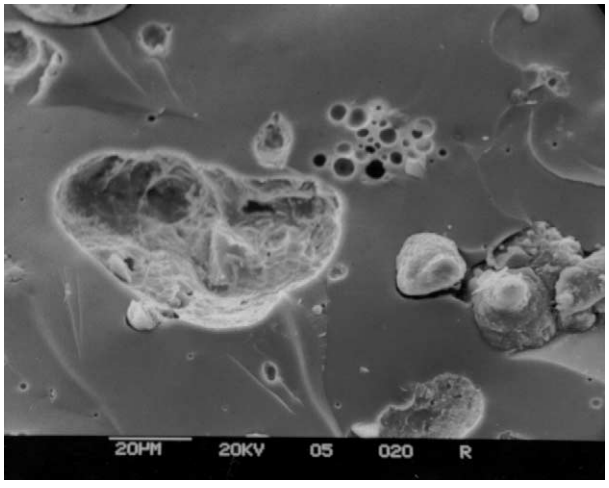

Fig. 6. Particle pull-out in the surroundings of pore clusters.

3.2. Fracture toughness

A fracture toughness determination was performed on the samples coming from the coarser glass powders,

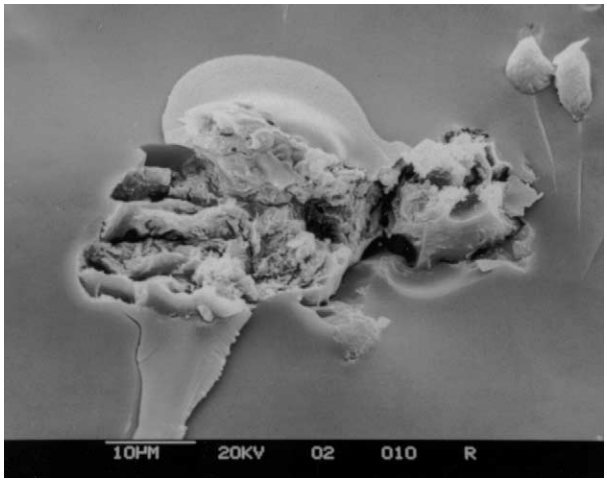

Fig. 7. Broken aluminium particle after a certain plastic deformation, still anchored to glass matrix.

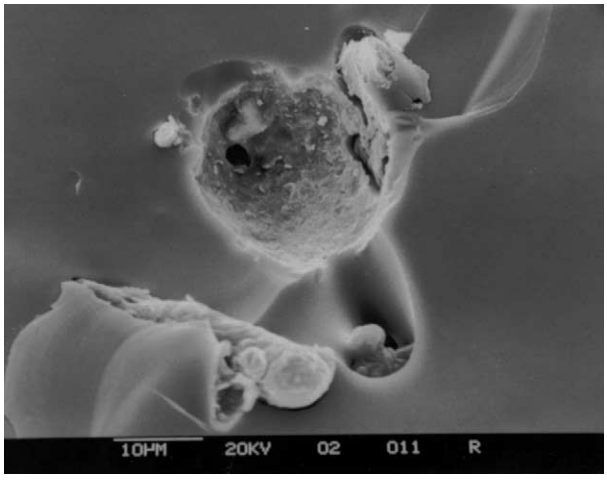

Fig. 8. Particle pull-out with crack deflection evidence; circumferential cracks appear around the pull-out cavity, together with pieces of aluminium particle.

exhibiting a repetitive high bending strength. Besides samples F and G, another sample, H, was prepared for this specific test. As shown in Table 3, sample H exhibits almost the same compaction degree as samples F and G.

As reported above, K_{IC} determination was performed according to the single-edge-notched beam (SENB) method. After notch length measurement by an optical microscope, the flexural strength of notched specimens was analysed. A valid determination is conducted only when the notch on the tensile side of the flexure specimens acts as a real crack, i.e. it is atomically sharp;[30,31] only in this case is the observed flexural strength of the notched section, expressed by the peak load of typical load vs. displacement plots, strictly related to fracture toughness when taken with the previously measured notch length following Eq. (1). For a blunt notch, there is a risk of a significant fracture toughness overestimation.

Aluminium reinforced glass matrix composites exhibited a particular behaviour. Flexural tests on notched specimens were conducted operating at a low crosshead speed of 0.05 mm/min, and load vs. crosshead displacement plots were recorded.

These plots exhibit a significant peak blunting, as illustrated by Fig. 9; before rupture, i.e. the moment of unloading, the load/displacement dependence was modified in the sense of a reduction of flexural rigidity. This behaviour is thought to be related to a subcritical crack growth at the notch tip. As the crack grows the flexural rigidity of the notched section decreases; the curvature effect in load vs. displacement plots is due to the fact that with decreasing flexural rigidity a lower load increment is needed for further displacement. Fracture toughness was calculated from the load peak values and the previously measured notch lengths. The tested composites exhibit a promising fracture toughness of about 1.20 MPa $m^{0,5}$, which is particularly notable when related to the fracture toughness of monolithic matrix, which has been measured to be 0.5938 ± 0.0998 MPa $m^{0,5}$ by means of SENB method[32] (very close to the values reported in literature for lead silicate glass, of about 0.6 MPa $m^{0,5}$ [33,34]). The fracture toughness data are summarized in Table 5. Subcritical crack growth, with peak blunting, gives extremely sharp cracks starting from induced notches, reducing the risk of overestimation of K_{IC}; in addition, the fact that crack length is measured before crack extension reveals that the reported K_{IC} value is probably underestimated. It must be emphasized that notched samples undergo rupture without catastrophic breaking. The specimens during rupture and subsequent unloading phase in the load/displacement plot displayed a certain gradualism. Fracture surfaces appear to be joined by metallic particles, with crack bridging.

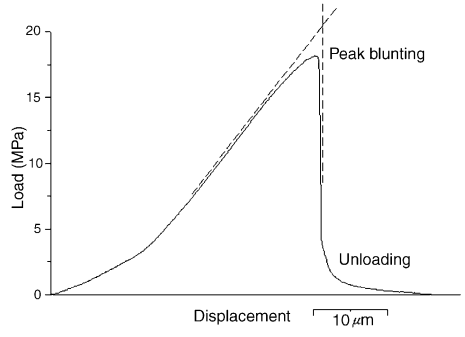

Fig. 9. Peak blunting in a typical load/displacement plot in flexural testing of notched samples, revealing subcritical crack growth at notch tip.

The achieved good fracture toughness value, in spite of the simple and cost-effective powder processing route for composite manufacturing, is thought to be due to the superposition of different toughening effects. As reported above, SEM micrographs demonstrated the feasibility of local plastic deformation of the metallic reinforcement; in addition, a significant crack tilting mechanism is observed, according to thermal expansion mismatch. The advancing crack is therefore influenced by residual thermoelastic stresses: as the thermal expansion coefficient of Al is higher than that of the matrix, a circumferential compression stress is developed in the lead silicate glass around reinforcing particles, causing crack to deviate. As a consequence, as shown in Fig. 10, the fracture surfaces are very rough. This behaviour is possible only in the case of a relatively strong interfacial bonding between Al and the lead silicate glass, which was developed only with coarsest glass powders. In other cases, pore evolution from the Al-lead silicate glass interaction reflects on a weak bonding, and a significant pull-out, as shown in Fig. 6, which causes a low toughening contribution in metallic reinforced glasses, as reported in the works relating to nickel reinforcement.[1–4]

The measured K_{IC} value is significant relating to the data available in the literature. All the metal reinforced glass matrix composites previously reported,[2–14] were manufactured by hot pressing mixtures of glass and metal particles. This procedure causes high compaction degree and a good interfacial bonding; the treatment is generally rapid, thus minimising the risk of metal/glass chemical interactions at high temperatures and preventing from devetrification of the glass matrix. Krstic et al.[6] reached a value of 6.5 MPa $m^{0,5}$ with hot-pressed Al particle reinforced glass matrix composites. In other cases, the improvement in fracture toughness of glass with metallic inclusions is not so substantial. Green et al.[2] reported an increase of the critical energy release rate G_{IC} from 4.8 to 10.5 J/m^2 with a 20% by vol. dispersion of Ni particles in S-glass, thus causing an increase in K_{IC} from 0.59 to about 0.8 MPa $m^{0,5}$. Biswas,[4] with a 10% by vol. dispersion of Ni, reported an increase in fracture toughness from 0.7 to 0.9 MPa $m^{0,5}$.

Table 5
Fracture toughness data of aluminium reinforced glass matrix composites starting from coarsest glass powders

	K_{IC} (MPa $m^{0,5}$)								
	Measured values							Average	S.D.
F	1.2384	1.2620	1.2155	1.1407	1.3220	1.1361	1.1903	1.2150	0.067
G	1.1584	1.2899	1.2157	1.2710	1.1087	1.1133	1.1598	1.1881	0.073
H	1.3156	1.2946	1.1433	1.2187	1.1899			1.2324	0.072

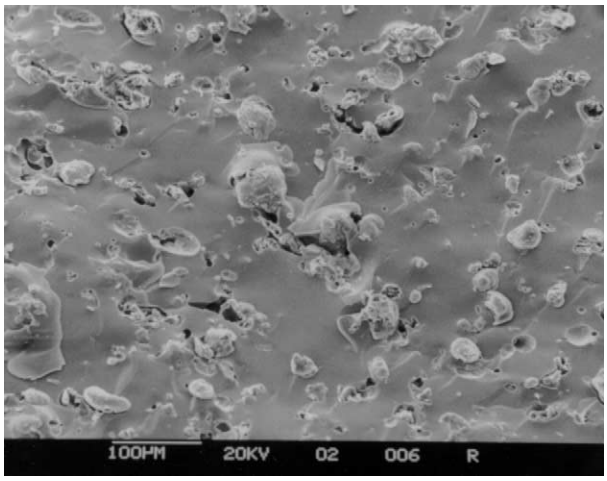

Fig. 10. Rough fracture surface of those aluminium reinforced glasses revealing highest modulus of rupture and fracture toughness.

Dlouhy et al.[9] found a K_{IC} improvement, starting from borosilicate glass, from 0.7 to 1.15 MPa $m^{0,5}$ with Mo inclusions in a 30% by vol. concentration. Dlouhy and Boccaccini[10] showed an analogous improvement, from 0.7 to 1.17 MPa $m^{0,5}$ with V inclusions. Waku et al.[8] reached an excellent K_{IC} value of about 5.5 MPa $m^{0,5}$, with Mo inclusions in M.A.S. glass; in this case, however, the authors' opinion is that the fracture toughness depends strongly on the "flaky" nature of the reinforcement. Banuprakash et al.[11] reported a K_{IC} increase from 0.75 to 3.1 MPa $m^{0,5}$ with a 40 vol.% dispersion of Cu in borosilicate glass; with lower content, 10%, K_{IC} was equal to 1.3 MPa $m^{0,5}$. The obtained K_{IC} improvement (about 100%) in the composites illustrated in the present work is thought to be satisfactory, especially relating to the residual porosity. An improvement of the compaction degree of these composites, without chemical interactions between Al and lead silicate glass, is probably needed in order to maximise the toughening effect of the metallic inclusions.

4. Conclusions

Glass matrix composites from a low cost powder processing route, i.e. cold pressing and firing, were developed. The matrix was a lead silicate recovered from CRTs and the reinforcement was metallic aluminium. An anomalous mechanical behaviour was observed with very fine starting glass powders, which is thought to be due to a complex glass-aluminium interfacial reaction, so that the bending strength is lower than that of the glass matrix alone. This behaviour is not exhibited by samples coming from coarser glass powders, which were characterised by a bending strength higher than that of the glass matrix, in spite of the lower compaction degree. A fracture toughness determination was performed on these composites, which revealed a fracture toughness value of about 1.20 MPa $m^{0,5}$ (with about 100% increase relating to the fracture toughness of the unreinforced glass matrix). A crack growth effect prior to rupture was observed in notched specimens, thus preventing from any K_{IC} overestimation in SENB method. The K_{IC} level obtained in this work appears to be promising, especially considering the simple and cost-effective processing for composite manufacturing, as the toughness is similar to those reported with other metal glass systems prepared by using more expensive techniques.[9,10] The controlled crack propagation, which causes a stable crack growth prior to rupture and crack bridging on unloading, needs further investigation.

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