Glass matrix composites from solid waste materials

Monica Ferraris [a,*], Milena Salvo [a], Federico Smeacetto [a], Laurent Augier [a], Luisa Barbieri [b], Anna Corradi [b], Isabella Lancellotti [b]

[a]*Materials Science and Chemical Engineering Department, Politecnico di Torino, C.so Duca degli Abruzzi 24, I-10129 Torino, Italy*
[b]*Department of Chemistry, Faculty of Engineering, University of Modena and Reggio Emilia, Via Campi 183, 41100 Modena, Italy*

Abstract

Glass matrix composites have been obtained by mixing and sintering "negative cost" materials coming from municipal solid waste incinerators (MSWIs) and from one aluminium foundry. The bottom ashes from two MSWIs were used to obtain the glass matrix and the solid wastes from an aluminium alloy industry were employed as a second phase. The bottom ashes were vitrified by heating at 1400°C without any additive. The vitrification process reduces the bottom ash initial volume by about 60%. The obtained glass has a Young modulus of 96 GPa and a Vickers hardness of 6 GPa. The composites were prepared in air by a low temperature pressure-less viscous phase sintering process (740–830°C) and were morphologically and mechanically characterised. The composites showed a bending strength up to 50 MPa at room temperature and could be proposed for applications in the field of tiles.
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1. Introduction

The incineration of solid wastes is surely an effective method to reduce the waste volume up to 90%, but it is usually neglected that multiple solid waste incinerators (MSWIs) still produce a large amount of solid wastes: about 750 000 tons/year of bottom ash and 130 000 ton/year of fly ash in Italy.[1] Nowadays, bottom and fly ashes are mostly sent to landfills: this fact can cause leaching and weathering problems, together with the waste of energy necessary to produce bottom ashes (usually obtained by burning wastes at 900–950°C) and the money paid to put the bottom ashes to landfills (about 0.1 Euro/kg). A solution to these problems can be seen in the vitrification of fly and bottom ashes. The vitrification process is well known for the inertisation of radioactive wastes because of the high chemical stability of the glass materials and the considerable volume reduction. Furthermore, in a highly populated country such as Japan, the vitrification of bottom and fly ashes from MSWI, sewage sludge and industrial wastes is widely employed: the vitrification capacity is over 2740 tons/day.[2]

In Europe (Bordeaux, France), an MSWI has been integrated with a vitrification facility by plasma torch that can treat the total fly ash production of the site.[3] It should be taken into account that 1000 kg of solid wastes give only 30 kg of fly ash, but 300 kg of bottom ash:[3] a solution regarding the recycling of bottom ash, as proposed in this paper, seems thus to be of great interest. Further, a larger use of vitrification for bottom and fly ash can be economically justified only if the obtained glass can be recycled to produce added value materials.[4]

Recent papers have reported on the use of bottom and fly ashes in addition to waste cullet glass for the production of glass and glass–ceramics for potential architectural and decorative applications[5–7,9] and glass matrix composites for potential technical applications.[8]

Another side of the waste recycling problem is that many industries (i.e. metallurgy, ore extraction, etc.) produce wastes that are mainly constituted of metal oxides not suitable for vitrification: in most cases, these potential raw materials are sent to landfills.

The aim of this work is to demonstrate the feasibility of a composite material totally made of wastes coming from MSWIs and from a metallurgical industry: bottom ashes from the MSWIs of Bergamo and of Reggio Emilia (Italy) were successfully vitrified without waste

* Corresponding author. Tel.: +49-11-5644687; fax: +49-11-5644699.
E-mail address: ferraris@athena.polito.it (M. Ferraris).

cullet glass addition and the obtained glass was used as matrix for a composite material. Wastes from an aluminium foundry (Teksid S.p.A., Italy) were used as second phase. The composites were prepared in air by a low cost, low temperature pressure-less sintering process and were morphologically and mechanically characterised. The results suggest the possibility of their use as wall tiles,[10] even if much more characterisations have to be done in this direction.

Due to the interesting properties of the glass used as matrix for the composites, above all its high Young modulus, glass fibres were drawn (at Stazione Sperimentale del Vetro, Murano-Italy and characterised at Padova University, Padova-Italy); the fibres show promising mechanical properties and their use could be foreseen in the field of polymer matrix composites.

2. Experimental

Dry bottom ashes from MSWIs of Bergamo (BAS S.p.A, Italy) and Reggio Emilia (Italy) were used to prepare two glass matrices, labelled as BA and S10 respectively. The experimental details and further information regarding the S10 glass are reported in Refs. 7 and 9.

The bottom ashes coming from the MSWI of Bergamo were ball-milled and the powder was submitted to the Atomic Absorption Spectroscopy (AAS-Perkin–Elmer 1100). The vitrification of the bottom ash was performed without any additives at 1400°C for 1 h in air using a chamber furnace (LINN HT 1800) in an alumina crucible. The resulting black–brown glass, (BA) was ground for Atomic Absorption Spectroscopy (AAS-Perkin–Elmer 1100), X-ray diffraction analysis (XRD, Philips PW1710), Differential Thermal Analysis (DTA, Netzsch 4045) and hot stage microscopy (Leitz GmbH AII). The density of BA was determined by a pycnometer. Leaching tests were performed on the BA glass and the bottom ashes according to the present European legislation (UNI 10802).

Glass fibres, obtained from BA glass, were drawn at Stazione Sperimentale del Vetro, Murano, Italy and characterised at Padova University, Padova, Italy. The mechanical properties of the fibres were investigated performing a tensile test using an Instron 1121 UTM with a crosshead speed of 1 mm/min.

Wastes from an aluminium alloy industry (Teksid, Italy) were used as second phase for the preparation of composite materials. The wastes, referred to as AW, were ball-milled and the powder was submitted to the XRD (Philips PW1710) and Atomic Absorption Spectroscopy (AAS-Perkin–Elmer 1100). The density of the AW was measured by a pycnometer.

The composites were prepared by powder technology by sintering greens made of S10 + AW and BA + AW powders. The particle size of the glass powders was chosen between 230 and 140 mesh; the AW particle size was lower than 325 meshes. The glass and AW powders were mechanically mixed in the proportion 3:1 in volume. Some greens bars ($53 \times 10 \times 6.5$ mm^3) were uniaxially pressed (pressure = 15 MPa) at room temperature with the addition of a minimum amount of ethyl alcohol. In order to determine a temperature range for sintering, the greens were submitted to a measure of linear shrinkage versus temperature by heating temperature microscopy (Leitz mod. II A), with a heating rate of 10°C/min. The sintering temperature was varied between 760 and 830°C, the heating rate was 10°C/min and the dwell time was 60 min.

The morphological and structural characterisation of the composites was conducted by Scanning Electron Microscopy (SEM, Philips 525 M) and XRD (Philips PW1710); while the mechanical strength was determined by three-point bending test with 40 mm outer span and a crosshead speed of 0.1 mm/min (SINTEC D/10). The Young modulus of the composites and the BA glass was determined by means of the non-destructive resonance frequency technique (Grindosonic). The apparent density of the composite materials was determined by the Archimedes' technique. The value of the theoretical density was calculated based on the composite composition and on the density of the constituents. The Vickers hardness (HV) was determined for the glasses and composites. The thermal expansion coefficient of the BA glass bulk and the composites was measured by a dilatometer (Netzsch 4045).

3. Results and discussion

The chemical analyses of the wastes used for this work (AW, Bergamo and Reggio-Emilia bottom ashes) are shown in Table 1: the AW waste contains mainly aluminium, silicon and magnesium, in the form of alumina, aluminium, magnesia and traces of silica (quartz), as detected by XRD spectrum (Fig. 1). Due to its composition, AW is not suitable for a direct vitrification, but it can be successfully recycled as a second phase for composite materials. On the contrary, the chemical analysis (Table 1) and the XRD of the two bottom ashes evidenced a relatively high content of SiO_2, and also a glassy phase, which evidenced the possibility of their direct vitrification, as shown below.

The X-ray diffraction pattern (Fig. 2) showed the amorphous nature of the obtained BA glass. A volume reduction by about 60% and a mass loss by about 6% were observed after the vitrification. It must be noted that the solid waste volume, already reduced by 90% by incineration, is further reduced by 60% by vitrification: even if the glass was to be put in a landfill at this stage, a very first result is that the initial solid waste volume would be reduced by about 95% by incineration and

Table 1
Chemical analysis (wt.%) of the aluminium foundry waste (AW) and of the two utilised bottom ashes (Bergamo and Reggio Emilia)

Element (wt.%)	AW	Bergamo bottom ash	Reggio Emilia bottom ash
Si	6.2	19.9	21.1
Al	54.6	9.3	5.1
Fe	0.4	4	2.7
Cu	1.4	0.2	n.d
Mn	0.2	0.1	n.d
Pb	0.1	0.16	0.01
Cr	0.02	0.03	0.03
Ni	0.05	0.02	n.d
Zn	0.4	0.9	0.26
Ca	1.3	11.7	13.4
Mg	5.1	1.4	1.3
Na	3.2	9.6	3.4
K	1.1	1.5	1.1
Ti	0.1	1.5	0.56
Others	Balance	Balance	Balance

vitrification. Moreover, the initial bottom ash leaching results were highly reduced after the vitrification process (leaching test UNI 10802) (see Table 2: each leaching value is lower for the glass than for the bottom ash).

The chemical analyses of the BA and S10 glasses are reported in Table 3, where it is shown that the two glasses have a similar composition. The main constituents of the bottom ashes (Table 1) and consequently of the prepared glasses are silicon, calcium, sodium, aluminium and iron, in the form of their oxides, while traces of chlorine, sulphur and phosphorus were detected by EDS only in the bottom ash. The mass loss (6%) observed after the waste vitrification is probably related

to the formation of gaseous products containing Cl, S and P.

The similarity of the two glasses derived from the vitrification of bottom ashes coming from the two different municipal incinerators seems to guarantee that the properties of the products obtainable by waste vitrification are mostly constant, even if they come from different MWSIs.

Some thermal and mechanical properties of the two glasses are collected in Table 4.

The thermal parameters, falling in the same temperature ranges, point out that the obtained glasses have comparable viscosity, refractoriness and softening temperature. The Vickers Hardness values for the two glasses (BA and S10) are identical (6 GPa) and they are comparable to those of some commercial glasses.

The Young modulus of BA glass (96 GPa) is particularly high compared to those of some commercial glasses: e.g. fused silica ($E = 72$ GPa), soda-lime ($E = 69$ GPa), borosilicate ($E = 62$ GPa) and lead silicate glasses ($E = 52$ GPa). It is more similar to the Young modulus of some alumina–beryllia–magnesia rich silicate glasses (140 GPa).

Preliminary results on the as drawn uncoated fibres show interesting mechanical properties, comparable to those of some commercial glass fibres (Table 5).

The tensile strength (σ_t) of the BA fibres is 0.9±0.3 GPa, while those of some commercial glass fibres range from 1.3 to 4.6 GPa. It must be considered that the tensile strength of the BA glass fibres could be improved by the application of a suitable polymeric coating and some experimental work is going on in this subject. These fibres are in use for the preparation of polymer matrix composites.[11]
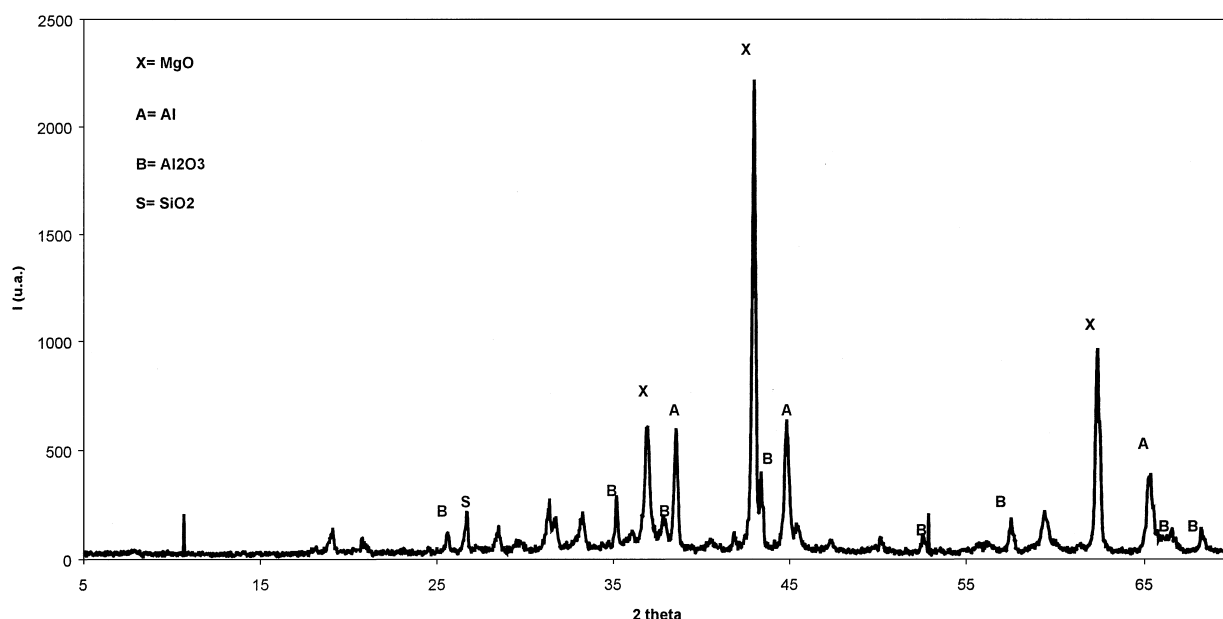

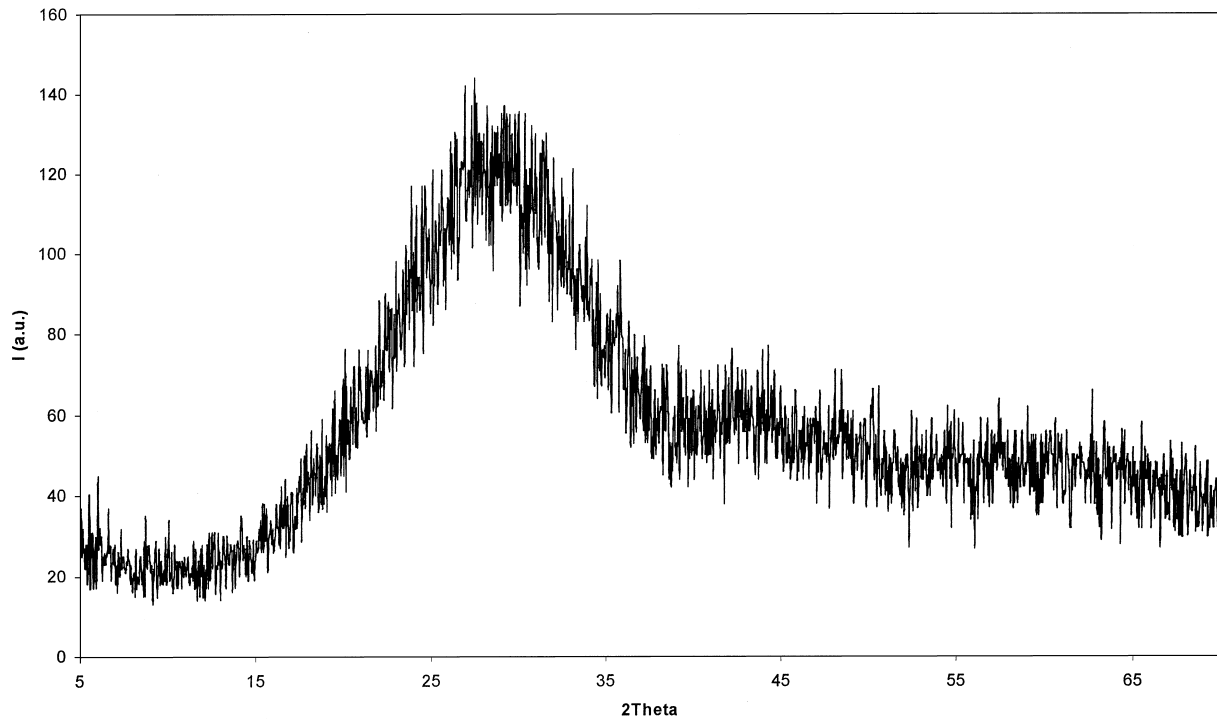Fig. 1. X-ray diffraction pattern of the AW aluminium foundry waste.

Fig. 2. X-ray diffraction pattern of the BA glass showing the amorphous nature of the material obtained by direct vitrification of bottom ashes.

Table 2
Leaching results on MSWI bottom ashes and BA glass (UNI 10802 tests)

	Bergamo bottom ash	BA glass
pH	11.65	8.14
TOC (mg/l)	13	4
Cr (mg/l)	0.16	0.02
Mn (mg/l)	< 0.05	< 0.05
Cu (mg/l)	< 0.1	< 0.1
Ni (mg/l)	< 0.05	< 0.05
Fe (mg/l)	0.1	0 < 0.1
Pb (mg/l)	0.1	0.1
Zn (mg/l)	< 0.05	< 0.05
Cd (mg/l)	< 0.01	< 0.01
Ca (mg/l)	62	10
Na (mg/l)	90.0	8.9
K (mg/l)	51.0	2.4

Table 3
Compositional analysis (oxide contents in wt.%) of the BA and S10 glass

Oxide (wt.%)	BA glass	S10 glass
SiO_2	44.2	52.6
Al_2O_3	17.8	12.4
Fe_2O_3	3.5	4.4
CuO	0.1	0.2
MnO	0.1	0.2
PbO	0.1	0.2
Cr_2O_3	0.1	0.2
NiO	2.10^{-1}	n.d.[a]
ZnO	0.8	0.4
CaO	16.3	19.9
MgO	2.0	2.7
Na_2O	11.6	4.2
K_2O	1.4	1.0
TiO_2	2.0	1.0
Others	Balance	Balance

[a] n.d. = not determined.

The high percentage of aluminium oxide present in BA glass (about 18 wt.%) is likely to be the responsible for the glass durability and leaching behaviour (see Table 2).

The apparent density of the BA and the AW, measured by a pycnometer, are respectively 2.60 and 2.76 g/cm^3. The theoretical densities of the sintered composites BA + AW and S10 + AW, calculated on the basis of their composition are 2.64 and 2.72 g/cm^3, respectively.

In order to choose the composite sintering temperature, the shrinkage of a green of glass plus AW (3:1 volume ratio, glass powder particle size: 230–140 mesh; AW particle size: < 325 mesh) versus temperature was observed by heating stage microscopy. Fig. 3 shows the behaviour of a green obtained by mixing BA glass plus AW (squares) in comparison to the shrinkage of a BA glass green (dots): the maximum shrinkage for the BA plus AW green was recorded between 760 and 810°C. A similar pattern was recorded for a mixture of S10 glass and AW powders with the same volume ratio.

Several sintering processes with a dwell time of 1 h were then performed on BA plus AW and S10 plus AW

Table 4
Thermal and mechanical properties of BA and S10 glass

Properties	BA glass	S10 glass
Glass transition (°C)	630–660	630–650
Softening temperature (°C)	720–730°C	690–700
Crystallisation temperature (peak, °C)	920–925	930–940
Melting temperature (onset °C)	1080–1100	1080
Young modulus (GPa)	96±0.2	n.d[a]
Vickers Hardness (GPa)	6±0.2	6±0.2
Indentation toughness (MPa·m$^{1/2}$)	0.5±0.2	0.8±0.1
Thermal expansion coefficient (10^{-6} K^{-1})	10.7 (100–500°C)	9.0 (100–500°C)

[a] n.d. = not determined.

Table 5
Mechanical properties of BA fibres and other commercial glass fibres

Glass fibre	σ_T (GPa)	Youngs modulus (GPa)
BA	0.9±0.3	96±0.2
Bayer[9]	1.3	98
E-glass	3.4	72
R-glass	4.1	85
S-glass	4.6	86

greens in the range of temperature between 740 and 830°C. In Table 6 some properties are reported of the composite materials sintered at 810°C, the temperature that gave the best results: the maximum value of relative density was obtained for both composites with the sintering temperature at 810°C. For these samples, an open porosity of about 8% and a closed porosity of about 1% were obtained. The composite properties did not

Table 6
Thermal and mechanical properties of BA + AW and S10 + AW composites sintered at 810°C for 1 h

Sintering temperature (°C)	810	
	BA + AW	S10 + AW
Relative density	0.87	0.90
Bending strength (MPa)	36±2	50±3
Young modulus (GPa)	49±0.1	42±0.1
Thermal expansion coefficient (10^{-6} K^{-1})	11.2	–

improve by increasing the sintering time and temperature above 810°C. The relatively low value of the Young modulus could be related to the uncompleted densification due to the pressure-less sintering process and/or to the low elastic modulus of the second phase (AW) which contains not reacted aluminium particles, still present in a small amount in the BA + AW composite, as shown in its XRD spectrum (Fig. 4). Fig. 4 also shows the glass–ceramic nature of the composite material obtained at 810°C; due to the complexity of the XRD spectrum, only some phases were identified: together with an amorphous broad peak, some main crystalline phases were identified as alumina, magnesia, some pyroxenes, gehlenite and traces of aluminium.

The bending strength (three-point bending test) of the composites reached 50 MPa for the S10 matrix composites: for example, this value is comparable with that of the hot-pressed borosilicate DURAN glass[5] and with that of some ceramic materials obtained from recycled waste glass.[12]
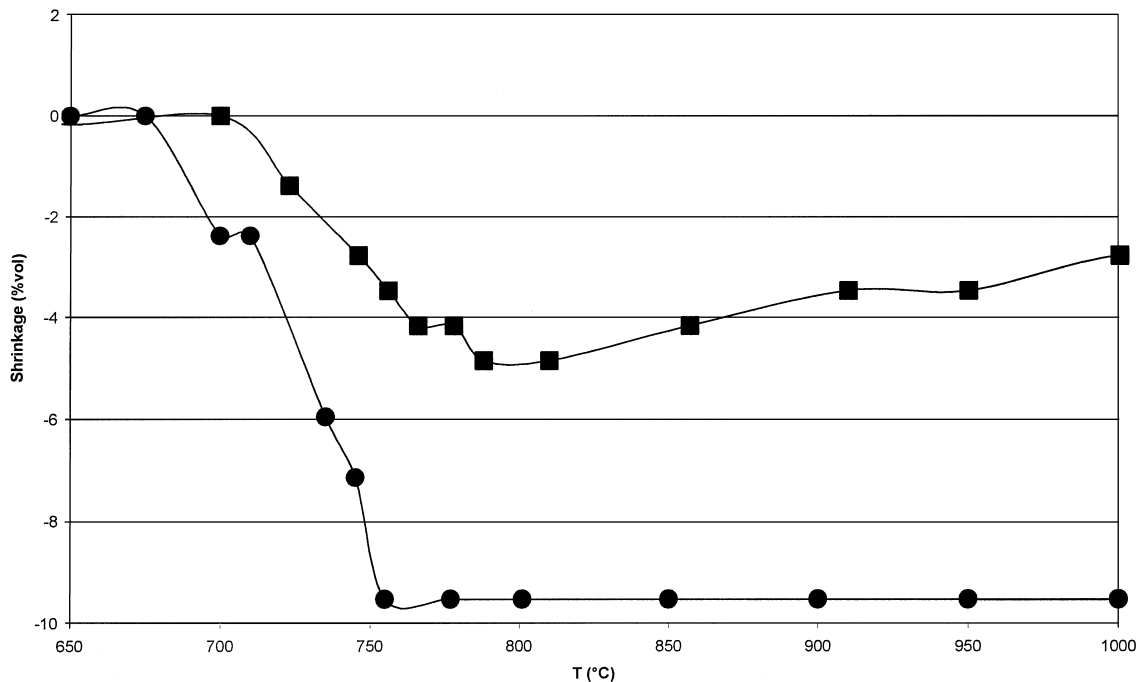

Fig. 3. Shrinkage vs temperature: BA glass and AW (3:1 volume) green (■) and pure BA glass green (●), measured by heating microscopy.

G= Ca2Al(AlSiO7) gehlenite
P= CaMgSi2O6 pyroxene
X= MgO
A= Al
B= Al2O3

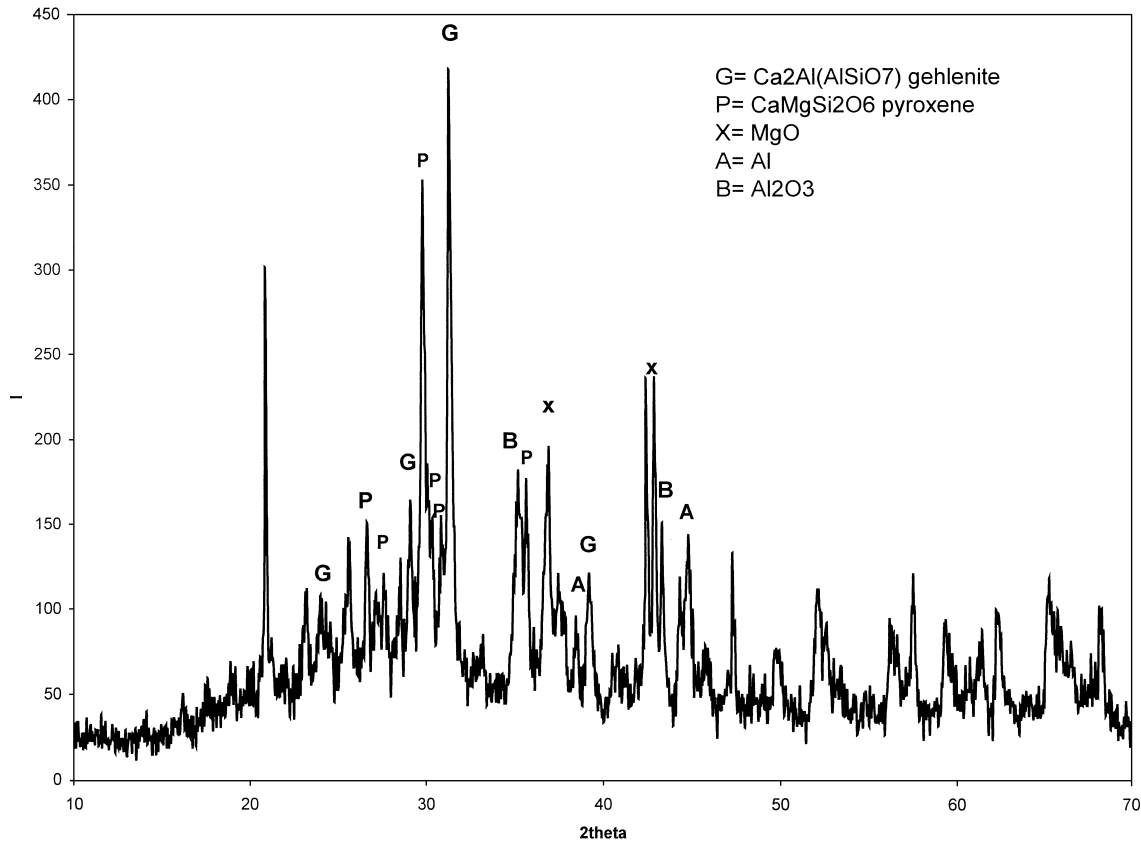Fig. 4. X-ray diffraction pattern of the BA+AW composite sintered at 810°C for 1 h.

The mechanical properties of the two composites (BA+AW and S10+AW) are similar to those requested in Ref. 10 for ceramic wall tiles (i.e. bending strength > 12 MPa). Only the CTE of the BA+AW composite is slightly higher than that requested for ceramic wall tiles (about $9 \cdot 10^{-6}$ K^{-1}). Surely there are many other properties to be tested before proposing these materials as tiles (i.e. dimensional stability during firing, the long-term dimensional stability, etc.), but these preliminary results give encouraging results.

Fig. 5 shows an SEM micrograph of a polished section of a BA+AW composite sintered at 810°C. The composite is homogeneous, but a residual porosity is evident and this could justify the mechanical test results.

Fig. 6 shows the Vickers tip obtained with 50 kg applied on BA+AW composite sintered at 810°C: because of the lack of detectable cracks at the edges of the tip, it was not possible to calculate the composite toughness with this method. Higher loads led to the composite fracture. It is to be underlined that also without obtaining a value for the composite toughness, it should be higher for the composite than for the glass matrix, because the pure glass sintered at the same conditions cracked at only 10 kg, while the composite did not show any crack at 50 kg.

Fig. 7 shows a cross-section of a S10+AW composites sintered at 810°C: also in this case the matrix appears continuous but some residual porosity is present. The
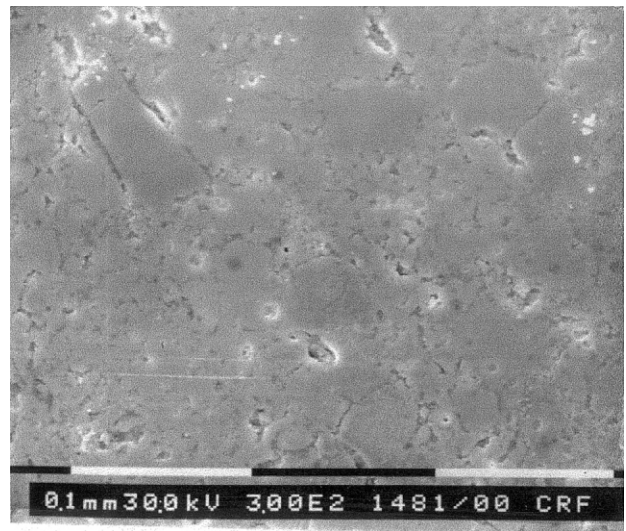

Fig. 5. SEM micrograph of a BA+AW composite sintered at 810°C for 1 h.

Vickers tests on this composite gave the same results shown above for BA+AW and are not reported here.

Fig. 8 shows, finally, the morphology of the different samples obtained by the vitrification of MSWI bottom ashes: BA bulk glass (a), BA+AW composite (b) and S10+AW composite (c). It can be seen that the samples are natural-stone like; this aspect could be important for
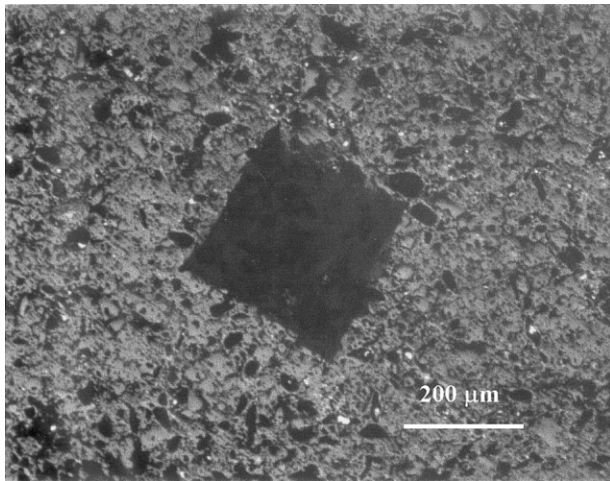
Fig. 6. Optical micrograph of Vickers indentation (50 kg) on a BA + AW composite sintered at 810°C for 1 h.
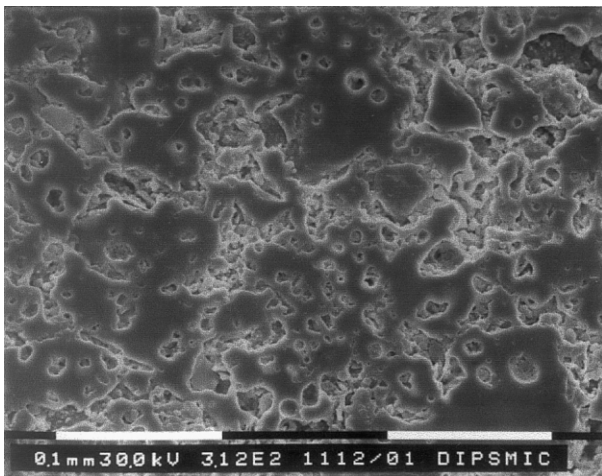

Fig. 7. SEM micrograph of a S10 + AW composites sintered at 810°C for 1 h.
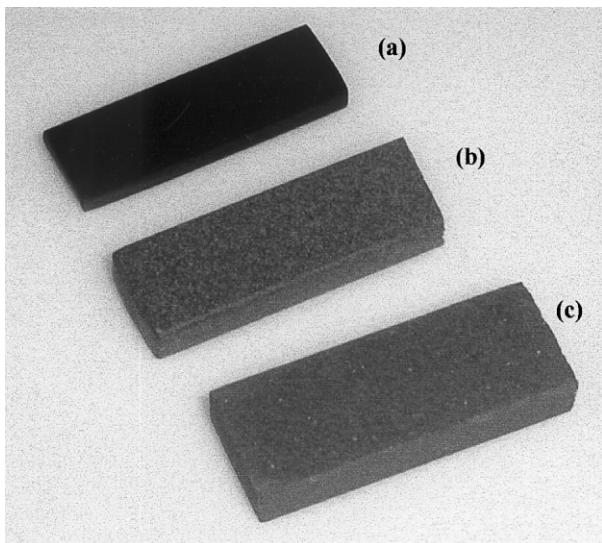

Fig. 8. Photograph of the obtained BA glass, BA + AW and S10 + AW composite.

hypothetical decorative, pavement and wall tile applications.

The future work will be focused on the preparation of a denser and more homogeneous material to be proposed for pavement use. An improvement in the property of these composites could also be obtained utilising a second phase different from AW.

4. Conclusions

The present study was conducted to develop a vitrification process of bottom ashes from two different MSWIs and to utilise the obtained glasses as matrix for glass–ceramic composites. We demonstrated the feasibility of a composite material totally made of wastes coming from MSWIs and from a metallurgical industry: the composites were prepared in air by a low cost, low temperature pressure-less sintering process at temperatures in the range 760–830°C.

Some properties of the obtained composites are compatible with those requested for ceramic wall tiles, even if much more characterisations have to be done in this direction.

Different reinforcing phases will be considered in future works in order to improve the properties and to widen the use of these composites.

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