

Thermal and chemical behaviour of different glasses containing steel fly ash and their transformation into glass-ceramics

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Abstract

Chemically inert and different coloured glasses were prepared by inserting up to 10 wt.% steel plant fly ash into different kinds of inorganic matrices. Three different matrices were tested: municipal incinerator grate ash, glass cullet and a low cost CMAS devitrifiable glass. The experimental techniques used to characterise both the starting and the heat treated (glass-ceramics) glasses were differential thermal analysis, durability and release tests, X-ray diffraction, scanning electron microscopy and colour analysis (CIELab method). The results reached suggest the possibility to recover the steel ash both as a starting material in glass and glass-ceramic formulations and as a colouring agent in place of a pure iron oxide into a colourless base system. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the past, the recovery efforts were impeded by low prices for primary raw materials, sufficient landfill capacities and hence low prices for depositing the wastes, chemical inhomogeneity and reactivity of the solid residuals and negative image of products made from waste materials. On the contrary, in the future the development of recycling technologies will become economically advantageous because refuse disposal is becoming very rare and expensive and legal restrictions for treatment of residuals are getting more and more severe and the amount of products to be recycled will strongly increase. In particular, it has been seen that many kinds of wastes and/or by-products undergo to a vitrification process in order to reduce the waste volume, to destroy the organic components, to immobilise toxic elements and minerals by a structural incorporation in a solid state lattice.^{1–5} The good weather resistance of the glass obtained during vitrification offers the possibility to

immobilise wastes of different origin in a single process thus increasing the homogeneity and the chemical composition reproducibility (necessary requirement for obtaining reliable products for general applications). Hence, vitrification is in line with general effort to recover and reuse valuable raw materials produced from industrial processes or waste treatment technologies. However, this technology, which requires additional process costs mainly due to the melting, can be fully justified if high-quality products can be put into the market.

The most effective way for improving the mechanical and physical properties of the vitrified products is to form glass-ceramics by controlled crystallisation.^{6–8} These materials appear promising, not only because of their outstanding properties, but also because the production process involves conversion of quite common silicate raw materials into substances with superior properties. The characteristics of glass-ceramic materials basically depend on the properties of the finely separated crystalline phase and residual glass which make up the glass-ceramic material. The kind of crystalline phases and thus also the final properties of the glass-ceramic material can be controlled by the initial glass composition and by its heat treatment. In this way an almost unlimited number of types of glass-ceramic

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material can be prepared with various combinations of properties, many of which are useful in practice.

In this work fly ash coming from the filtering operations of an Italian carbon steel plant has been mixed together with other waste raw materials, municipal incinerator grate ash and glass cullet, and then transformed into new amorphous and semicrystalline materials. Furthermore, the effect of the addition of the steel dust on the main properties of a previously studied CMAS (CaO–MgO–Al₂O₃–SiO₂) glass-ceramic system has been investigated.⁹ This kind of metallurgical waste has been chosen because this industrial sector is very important in Italy with a yearly production of about 25·10⁶ tons. The deriving filter powder is produced in an amount of 6.5–21 kg from 1 ton of melted metal.¹⁰

2. Experimental procedure

Original glasses from steel plant fly ash, municipal incinerator grate ash, glass cullet and a low cost CMAS glass-ceramic system (Tables 1 and 2) were obtained by

Table 1
Average chemical composition (wt.%) of the starting materials (ICP analysis)

Oxide	Steel fly ash	Incinerator grate ash	Glass cullet	CMAS glass-ceramic
SiO ₂	3.8	45	70	53
Al ₂ O ₃	1.1	9.7	1.2	9.2
CaO	5.8	19	9.4	25
MgO	3.2	2.2	4.1	13
Na ₂ O	1.4	4.6	13	–
K ₂ O	0.76	1.3	0.33	–
Fe ₂ O ₃	45	3.8	0.27	–
ZnO	25	0.32	0.10	–
TiO ₂	0.080	0.93	–	–
MnO	3.1	–	–	–
Cr ₂ O ₃	0.61	0.040	0.020	–
PbO	2.7	0.010	0.040	–
CdO	0.070	–	–	–
NiO	0.12	–	–	–
CuO	0.49	–	–	–
SnO ₂	0.12	–	–	–
BaO	0.11	0.17	0.060	–
ZrO ₂	–	0.29	–	–

Table 2
Main constituent oxides (wt.%) of the investigated glasses

Composition	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	Fe ₂ O ₃	ZnO
S10	49.7	11.7	18.9	2.61	3.92	4.13	0.36
S9P1 ^a	39.9	11.9	19.9	2.85	2.51	13.4	3.13
V10	70.3	1.16	9.42	4.15	12.7	0.27	0.10
V9P1 ^a	64.0	1.14	10.2	4.24	11.3	4.65	2.63
CMAS10	52.9	9.22	24.5	11.9	–	–	–
CMAS9P1 ^a	49.2	10.6	20.8	10.1	0.21	4.93	2.98

^a Traces of MnO and PbO.

melting them at about 1450 °C in refractory crucibles by heating the starting mixtures in an electrically heated furnace from room to melting temperature. The three matrices (glass cullet = V10, municipal incinerator grate ash = S10 and CMAS = CMAS10) have been compared with the behaviour of three glasses obtained by the addition of 10 wt.% of steel plant fly ash to these systems (V9P1, S9P1, CMAS9P1).

By considering the high iron and zinc oxides content into the steel waste dust and the role played both by iron that provides colour and zinc that can lighten or darken the colours and provide a variety of decorative appearances, 1, 2, 5 and 10 wt.% of this waste has been added to the CMAS glass-ceramic above mentioned.

The following characterisation was performed on the glassy samples. Differential thermal analysis tests, DTA (Netzsch DSC 404), were performed on powders heated at 10 °C/min in air and fired from 20 to 1400 °C. By evaluating the thermal data, interesting information regards the crystallisation mechanism was obtained. Thermomechanical analysis was carried out using a dilatometer Netzsch 402 EP on glassy specimens of 4×0.5×0.5 cm in size heated at 10 °C/min from room temperature to the softening point. Successively, release test in acetic acid¹¹ and in distilled water for 16 days¹² were performed in order to establish the efficiency of the glass matrix in avoiding the leaching of pollutants (heavy metals) and durability tests in water (ISO 719), acid (DIN 12116) and alkali (ISO 695)¹³ to evaluate the chemical resistance of the glass were conducted too. Finally, the chemical analysis of the leach solutions was tested by an Induction Coupled Plasma Varian Liberty 200. Colour measurements were performed using an UV-vis spectrophotometer (Perkin Elmer, Lambda 19) with CIELab method.¹⁴ Mineralogical (Philips XRD PW 3710 in the 5°–60° 2θ range) and microstructural (Philips SEM XL 40) information was collected on bulk heat-treated samples having the dimensions of 1×1×0.5 cm.

3. Results and discussion

The most significant thermal properties are reported in Table 3.

The addition of 10 wt.% of steel fly ash to both the municipal incinerator grate ash and CMAS system causes a decrease in the glass transition (T_g) temperature so rendering the glass less viscous because of the decrease in SiO₂ content (former oxide) and the increase in ZnO content (modifier oxide). The same observations can be drawn for the softening (T_s) point of the CMAS system. A shift of the crystallisation temperature (T_c) toward a lower value can also be observed, this last effect can be attributed to the decrease in silicon oxide and/or the iron oxide nucleating effect. The latter is also responsible

Table 3
Thermal and thermomechanical properties of the studied glasses

Parameter	$T_g(\text{DTA})$ (°C)	$T_c(\text{DTA})$ (°C)	$T_m(\text{DTA})$ (°C)	$T_S(\text{DIL})$ (°C)	$\alpha_{100-500} \cdot 10^6$ (°C ⁻¹)
Composition					
S10	648	937	1091	702	9.0
S9P1	635	871; 990	1093	716	9.2
V10	540	none	980	623	10.9
V9P1	547	807	–	653	10.3
CMAS10	720	932	1250	814	8.0
CMAS9P1	685	889	1221	775	7.9

for a second exothermic peak near 990 °C in the grate ash-containing sample, S9P1, corresponding to the formation of Fe-containing crystalline phases. In the glass cullet-containing samples, the addition of fly ash induces crystallisation since a weak exothermic event is recorded at about 800 °C. Such a peak, absolutely absent in the V10 sample, can again be attributed to the increase in iron content. By considering the melting temperature (T_m) also detected by DTA, the T_g/T_m parameter was obtained. This ratio, according to Zanotto¹⁵ and James et al.¹⁶ helps to predict the crystallisation mechanism: $T_g/T_m > 0.58$ surface crystallisation, $T_g/T_m < 0.58$ bulk crystallisation. The values obtained for the glassy compositions investigated are in the 0.60–0.65 range indicating surface crystallisation.

The linear thermal expansion coefficient, α , determined in the 100–500 °C range decreases passing from the glass-cullet, incinerator grate ash and CMAS series with a strong dependence on the composition. In fact the decrease of alkali, which are modifiers ions breaking up the oxygen bridges, results in a monotonical decrease of the thermal expansion coefficient. At this effect is added the increase of the bivalent cations which are characterised by high field strength responsible for a more connected network.¹⁷ As regards the durability tests, the values obtained divide the glasses into categories where the lower the category number the better the durability. Results listed in Table 4 indicate for the water durability a worsening in the steel added glass (S9P1) with respect to the matrix S10, but an improvement with respect the glass cullet matrix (V10) where the higher Na⁺ content renders the glass more subjected to leaching processes. On the other hand, an acid attack is present in all the investigated glasses probably due to the particularly strong conditions of the test (boiling HCl 6M for 6 h), while all the glasses are very resistant in an alkaline environment. The addition of steel plant fly ash does not affect the chemical resistance of the CMAS system. Furthermore, by considering the particular waste nature of the starting materials, the release tests both in acetic acid for 24 h and in distilled water for 16 days have also been carried out [Table 5(a) and (b)] to simulate the behaviour of the waste incorporated

Table 4
Chemical durability of the glasses investigated

Parameter	Water durability ^a	Alkali durability ^b	Acid durability ^c
Composition			
S10	1	1	4
S9P1	2	1	3
V10	3	1	3
V9P1	2	1	4
CMAS10	1	1	4
CMAS9P1	1	1	4

^a 1 = Very high resistance, 2 = high resistance, 3 = medium resistance.

^b 1 = Low alkaline attack.

^c 3 = Slight acid attack, 4 = high acid attack.

in the glassy matrix when exposed to the leaching both of the rain and of the percolates from organic and inorganic mixed dumps. For all the compositions very low release values for metallic micropollutants were obtained, all in the range allowed by the Italian regulations. Particular importance shows the test in distilled water (the water is renewed at fixed time ranges of 2, 8, 24, 48, 72, 102, 168 and 384 h) because its effectiveness is due to the fact that, providing the change of the liquid phase at different times, it induces the re-establishment of a new equilibrium condition at the interface solute/solvent, which leads to a higher extraction capability of the solution.

Since the addition of steel fly ash, in which iron is the main component, in the glass cullet and CMAS series causes a variation in the colour of the colourless base systems (being S10 composition already dark brown), the colour analysis on the CMAS9P1 and V9P1 samples was performed. It is known that the same Fe₂O₃ percentage introduced in a silicate matrix can confer a different coloration dependent upon the acid-basic character of the glasses.¹⁸ The acidobasicity of a glass depends on the non-bridging oxygens concentration in the glassy network, which is related to the amount of the alkaline oxides that play the role of modifiers cations.¹⁹ Hence, it is possible to foresee a colour variation in glasses, containing the same amount of iron, as a consequence of a change in the alkaline content. For this reason Fig. 1 shows the a^* and b^* parameters as a function of the Na₂O–SiO₂ ratio for V9P1 and CMAS9P1 compositions containing the same steel dust percentage (10 wt.%). Thus, with the increase of Na₂O content (V9P1) it has been noted a slight shift from green to red for a^* parameter (negative and positive values indicate the predominance of the green and red colour, respectively) and a more marked shift from blue to yellow for b^* parameter (negative and positive values indicate the predominance of the blue and yellow colour, respectively).

Table 5

Values of release tests (a) in acetic acid for 24 h and (b) in distilled water for 16 days, compared with the limit values of the Italian regulations (a)

Sample	Al 1 mg/l	Fe 2 mg/l	Mn 2 mg/l	Cu 0.1 mg/l	Zn 0.5 mg/l	Cd 0.02 mg/l	Pb 0.2 mg/l	Ba 20 mg/l	Cr 0.2 mg/l
S10	0.12	0.06	0.01	0.032	0.018	–	0.04	–	–
S9P1	0.02	0.07	–	0.033	0.016	–	0.10	–	–
V10	0.06	0.05	0.01	0.008	–	0.005	0.06	–	–
V9P1	0.03	0.03	0.01	0.011	0.118	–	0.04	–	–
CMAS10	0.09	–	0.01	0.016	–	0.001	–	–	–
CMAS9P1	0.16	0.05	0.01	0.001	0.000	–	0.17	–	–

(b)

Sample	Cu 0.05 mg/l	Pb 0.03 mg/l	Cr _{tot} 0.05 mg/l	Zn 3 mg/l
S10	0.008	0.010	0.04	0.04
S9P1	0.003	0.026	0.037	0.1
V10	0.025	0.015	–	0.02
V9P1	0.005	0.025	0.009	0.07
CMAS10	–	–	–	–
CMAS9P1	0.011	–	0.015	0.03

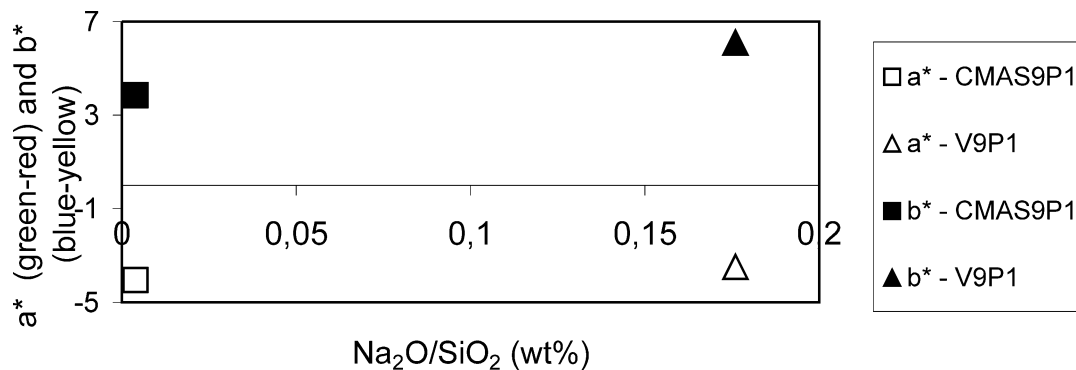


Fig. 1. a^* and b^* parameters as a function of the Na_2O – SiO_2 ratio for the steel added compositions.

As far as the devitrification tendency is concerned, the steel waste dust acts promoting or accelerating the crystallisation process when added to glass cullet and incinerator grate ash, respectively (Fig. 2). In general, the XRD patterns recorded on the above mentioned samples presented a change in the diffraction peaks attributed to the different crystalline phases present depending on the glass-ceramic composition and thermal treatment performed [maghemite Fe_2O_3 , magnetite Fe_3O_4 , anorthite sodian $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$, wollastonite CaSiO_3 and franklinite ZnFe_2O_4]. The pyroxene crystals, augite $\text{Ca}(\text{Fe},\text{Mg})\text{Si}_2\text{O}_6$ and/or diopside $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$, resulted in the thermodynamically most favoured phase, being present in all the studied compositions (except for V10 since it does not crystallise).

These observations are confirmed by SEM analysis. As can be seen in Fig. 3, the crystallisation microstructure of the fresh fractured surface of these glass-ceramics is different depending on the original matrix. In particular, in the V9P1 sample elongated and rhombic shape crystals, embedded in a high fraction of residual glassy phase, are present. As regards grate ash and

CMAS systems, an advanced crystallisation degree is observed with a fine microstructure homogeneously dispersed in the glassy phase in the S9P1 sample.

On the other hand, the addition of the waste in the percentage of 1, 2, 5 and 10 wt.% to the CMAS glass-ceramic does not substantially change the thermal behaviour of the base system except for the lowering of the characteristic temperatures as shown in Fig. 4. This is probably related to the iron and zinc oxides, which playing the role of structure modifiers, lower the glass viscosity and favour the crystallisation kinetics without affecting the mechanism (surface) and the mineralogy (pyroxene) of the material.

As regards the release test in acetic acid, Table 6 shows that also CMAS glasses release amounts of micropollutants in the range allowed by the Italian regulations. In particular the iron ion, present as the main constituent, is completely immobilised into the glassy matrix without interacting with the environment.

Colourless CMAS glass becomes yellow, green or brown depending on fly ash content. Such coloration is due to the presence of the main chromophore element

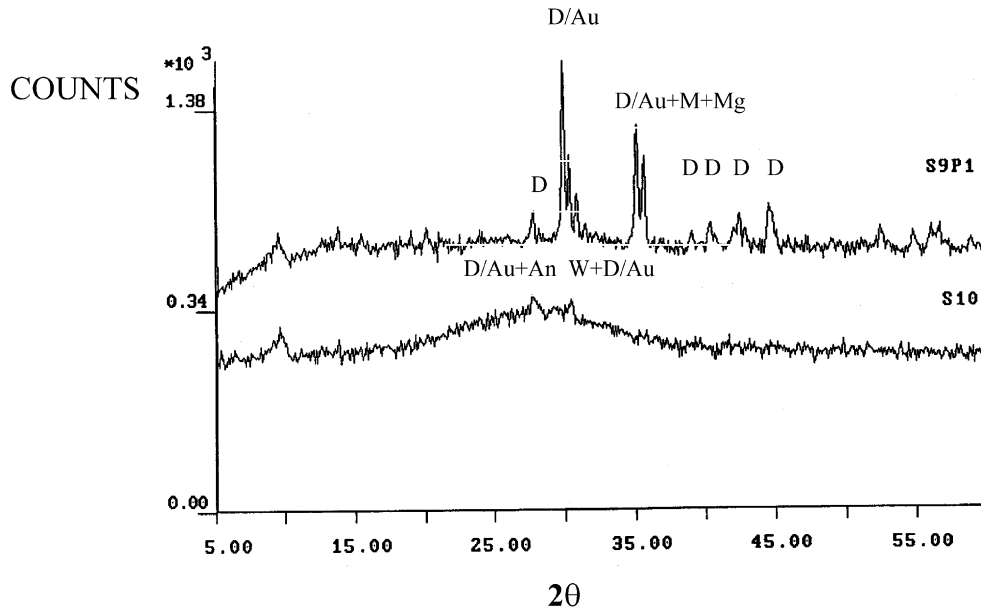


Fig. 2. XRD patterns of the S10 and S9P1 glass-ceramics obtained with a heat treatment at 1000 °C for 1 h on the starting glasses. An = anorthite, W = wollastonite, Au = augite, D = diopside, Mg = maghemite and M = magnetite.

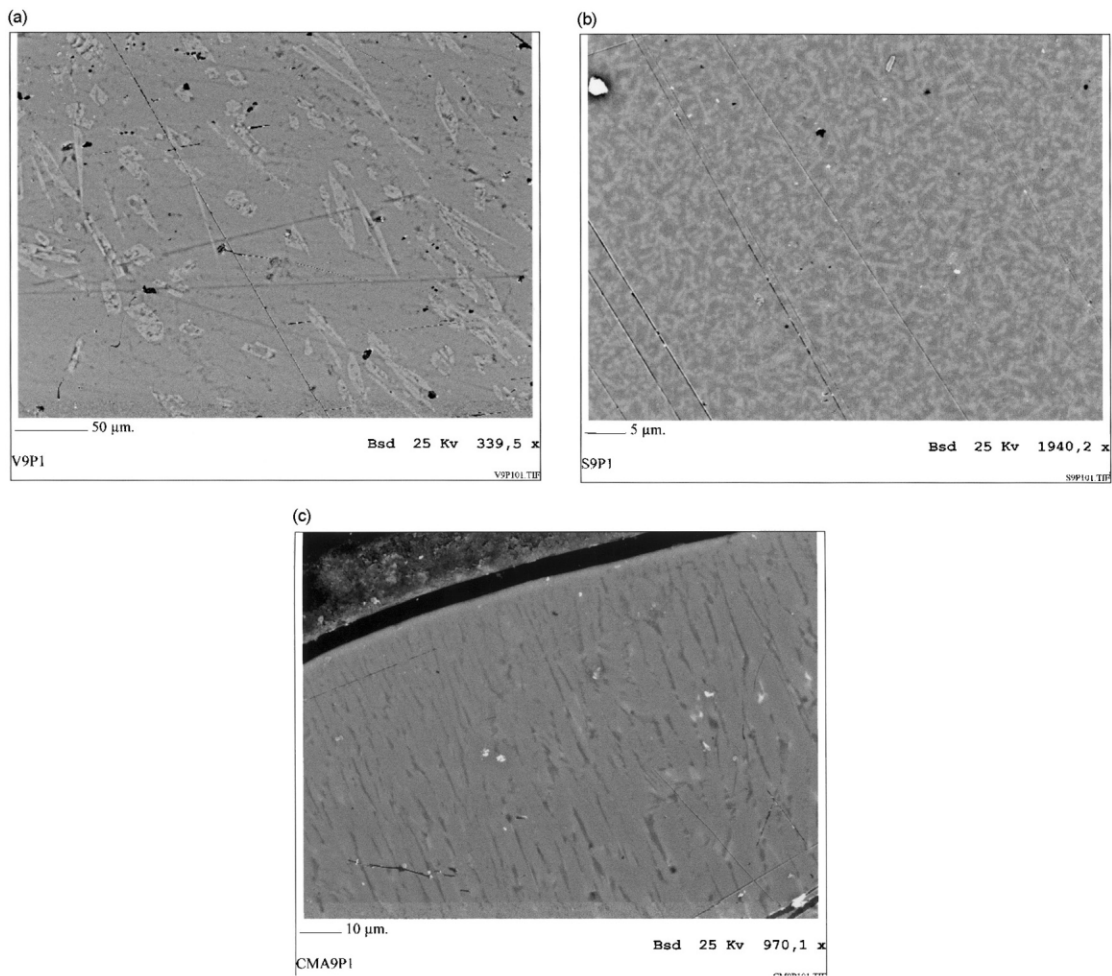


Fig. 3. SEM micrographs of glass-ceramics: (a) V9P1, (b) S9P1 and (c) CMAS9P1.

Table 6

Micropollutants release (mg/l) in acetic acid compared to both the limit values of the Italian regulation and the theoretical release of 2 g of glass when completely leached

Composition	Al (mg/l) 1 mg/l ^a	Fe (mg/l) 2 mg/l ^a	Zn (mg/l) 0.5 mg/l ^a	Mn (mg/l) 2 mg/l ^a	Pb (mg/l) 0.2 mg/l ^a
	Th/Exp	Th/Exp	Th/Exp	Th/Exp	Th/Exp
CMAS	98/0.09	–/0.00	–/0.00	–/0.00	–/0.00
CMAS+SA1	123/0.04	9/0.00	5.2/0.00	–/0.00	0.56/0.05
CMAS+SA2	142/0.02	20/0.00	10/0.00	0.62/0.00	0.93/0.01
CMAS+SA5	119/0.15	34/0.14	23/0.15	3.1/0.01	1.1/0.04
CMAS+SA10	117/0.15	63/0.06	44/0.22	5.7/0.01	2.8/0.05

^a According to Ref. [5].

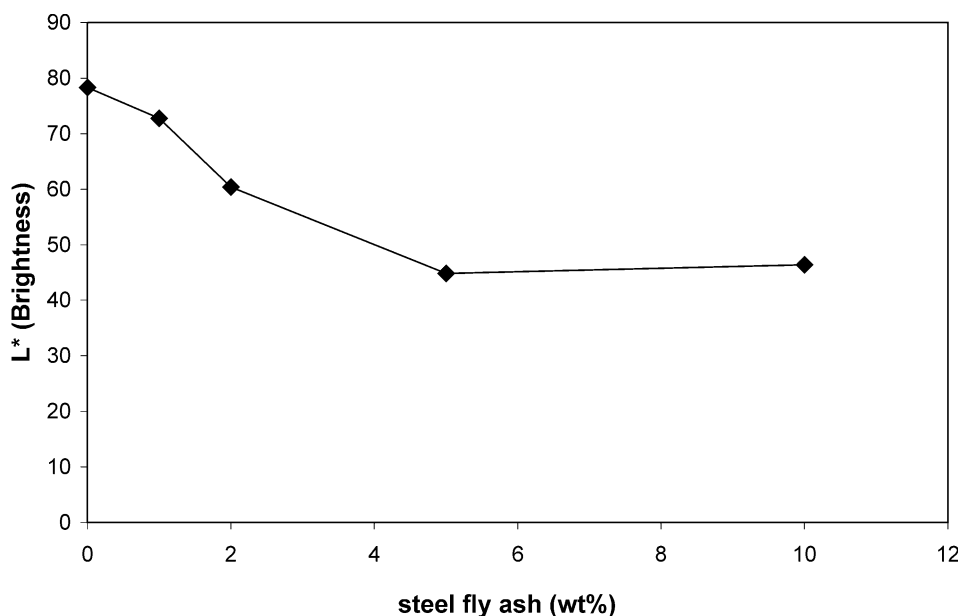


Fig. 5. Variation of the L^* parameter as a function of the composition for the CMAS+SA series.

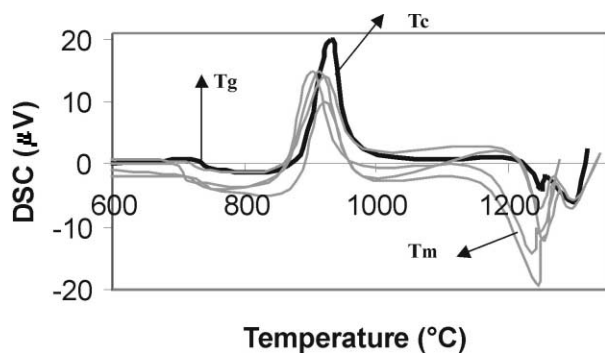


Fig. 4. DTA curves of the compositions CMAS (black), and CMAS added with steel fly ash (grey).

present, i.e. iron. The shift of L^* parameter toward lower values passing from CMAS to CMAS+SA10 composition designates a brightness decrease which is no longer affected by addition of fly ash above 5 wt.% (Fig. 5). Moreover, for all the samples studied, the b^*

parameter values show the predominance of the yellow colour on the blue.

4. Conclusions

The steel fly ash has been successfully mixed together with municipal incinerator grate ash or glass cullet and added to a low cost CMAS glass-ceramic system to produce stable and inert glasses transformed into the corresponding glass-ceramics by controlled heat treatments. All the glasses obtained have a good chemical durability and environmental impact releasing metallic micropollutants in the range allowed by the Italian regulations. All the characteristic thermal parameters decrease by introducing the steel ash in the starting batch because of the Zn modifier and Fe nucleating effect. When the steel dust is added to the CMAS system, because of the iron chromophore high content, its most significant effect is the appearance of a different

coloration (yellow, green or brown) depending on the amount introduced without changing substantially the thermal and mineralogical behaviour. These preliminary laboratory results lead to us foresee the possibility of recovering the steel ash both as a starting material in glass and glass-ceramic formulations and as colouring agent in place of a pure iron oxide into a colourless base system.

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