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Integrated approach to establish the sinter-crystallization ability of glasses from secondary raw material

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ABSTRACT

The sinter-crystallization ability of two glasses obtained by post-treated bottom ash of municipal solid waste incinerator (MSWI) at two particle size (coarse and fine) was investigated. The phase formation was estimated by DTA and XRD, while the sintering process was evaluated by optical dilatometry, linear shrinkage and water absorption. The porosity variations were estimated by density measurements. The microstructure and morphology of the glass-ceramics were observed by scanning electron microscopy. This integrated experimental approach together with theoretical study (by the methods of Ginsberg, Raschin–Tschetveritkov and Lebedeva) permitted to establish a better sinter-crystallization ability for the glass obtained from coarse MSWI ash fraction.

1. Introduction

The generation of municipal solid waste (MSW) in Italy in 2007 was 32.55 million tons and the amount of incinerated waste was around 4.5 million tons [1]. Solid outputs of incineration are represented by fly and bottom ashes that in the case of municipal solid waste incineration (MSWI) ranges from 3–5 to 20–35% by weight of the original quantity of waste for fly and bottom ash, respectively [2,3]. The fly ash constitutes a potential for hazard health because it often contains high concentrations of heavy metals such as lead, cadmium, copper and zinc as well as small amounts of dioxins and furans [4]. The bottom ash seldom contains significant levels of heavy metals. While fly ash is always classified as hazardous waste, bottom ash is generally considered safe for regular landfill, after a certain level of testing defined by the local legislation [5].

Many efforts have been made to improve the environmental quality of residues from waste incineration and to recycle or utilise at least part of specific residue flows. The recovery of waste matrices otherwise destined for disposal allows to save resources, reducing the need for natural raw materials. Considering that recycling has priority over disposal/deposition in landfill sites and the use of secondary raw materials reduces costs and conserves resources, it is a need in the processing of waste materials into utilisable, quality-assured secondary raw materials (SRM). In the last years in Italy some specialized companies in post-treatment technology of bottom ashes were developed. The objective is minimizing waste production by transforming it in secondary raw material. The treatment starts from a complex process of selection and physical/mechanical treatment (ageing, sieving and washing) of incineration ash. The material which originates from the process, although derived from waste-recovery operations, is classified as SRM substituting extracted raw materials mainly for cement. Another interesting opportunity can be represented by other products such as glass and glass-ceramic useful in the ceramic sector.

Vitrification is a known technology for the inertisation of various industrial residues that permits to obtain stable glasses [6–9]. By properly selecting the glass composition and thermal treatment this method gives possibility for re-utilisation of the glass or glass-ceramic as raw material for different industrial applications.

The powder sinter-crystallization technique is considered an alternative for the production of glass-ceramics, which allows the production of specimens with complicated shape and different sizes [10–15]. Further, no nucleation step is required and parent glasses with low purity and degree of homogenization can be used.

During sinter-crystallization, the densification and the crystallization take place in the same temperature interval. As a result, when the crystallization trend is too high, the sintering rate may be considerably reduced, leading to residual porosity and decreasing in the mechanical properties. For this reason glasses with lower crystallization rate are usually used [16,17].

It was also shown that it is difficult to improve the degree of densification by simply increasing the temperature and holding time. However better sintering and properties were reached by applying higher heating rate [18,19].

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Several studies with MSWI ashes were carried out on the chemical durability of the vitrified products [20–22], on the crystallization behaviour of the parent glasses [22–24], on the structure and properties of bulk glass-ceramics [22,25–27] and on the possibility to obtain different sintered glass-ceramics [11,12,27–32].

In the present work a technological integrated approach to establish the sinter-crystallization ability of MSWI glass frit produced by a SRM (post-treatment bottom ash) at two different grain size is discussed.

2. Experimental procedure

In this study as SRM, MSWI post-treated bottom ash, was chosen. Bottom ash coming from different municipal solid waste incinerators mainly located in the North of Italy is transported to the industrial plant in the North Italy. It is then pre-treated to obtain a semi-finished product. The treatment mainly consists of three steps: 3 months ageing of bottom ash as received, during which processes occur such as uptake of CO_2 from the air due to the moisture, draining of excess water and oxidation; grinding in mill to obtain two fractions with particle size of 0–2 mm and 2–8 mm; separation of iron and aluminum by means of magnetic and eddy current systems. The separated metals are about 8% (7% iron and 1% aluminum) of the total bottom ash and they are sent to recycling. About 80 wt.% of the bottom ash is recovered as secondary raw material, it is a silicon-based chemical matrix having chemical–physical characteristics suitable for cement and concrete production as a substitute of gravel and sand. The rest is water evaporated during the ageing treatment (about 10%) and unburnt waste.

Two glasses were prepared by melting of the two fractions SRM mentioned without any additives. The melting was carried out in a gas kiln utilizing corundum crucibles; the batches (2 kg) were heat treated at 1400 °C for 1.5 h and the melts were quenched in water. The glass obtained with the fine fractions (0–2 mm) was labelled GF and what obtained by coarse fraction (2–8 mm) labelled GL. The chemical analysis of the glassy frits was determined by inductively coupled plasma (ICP-Varian Liberty 200) and compared to that of SRM.

The two glasses obtained were crushed and sieved and the fraction passing 75 μm, after a control of the particle size distribution by laser granulometer (Mastersizer 2000), was used in order to prepare the samples.

The theoretical ability to form a glass-ceramic and to crystallize was studied through Ginsberg–Raschin–Tschetveritkov–Lebedeva diagrams.

The crystallization behaviour in the 20–1000 °C range of the GF and GL parent glass powders (<75 μm) was investigated by Thermo-gravimetric-Differential Thermal Analysis (Perkin Elmer — Diamond TG/DTA) using 20 mg samples in air and argon (200 ml/min) atmospheres at a heating rate of 20 °C/min.

Green samples of dimensions 50 mm × 4 mm × 3 mm were obtained by mixing the glass powder with 7% PVA (polyvinyl alcohol) solution and by uniaxially pressing at 100 MPa. The use of PVA is useful for increasing the green strength, but a dewaxing step will be industrially evaluated if necessary. After having dried, the samples were treated in an electric laboratory furnace (Nambertherm) under non-isothermal conditions for 1 h at 950 °C at different heating rates (5 °C/min and 40 °C/min). A preliminary 60 min step at 280 °C (using heating rates of 10 °C/min) was applied to eliminate the PVA binder. In order to elucidate the crystalline phases evolution, additional thermal treatments — under non-isothermal conditions for 1 h at 700, 750, 800 and 850 °C and at the heating rate of 5 °C/min — were also carried out (Lenton laboratory furnace). The crystalline phases induced by the thermal treatments were identified by XRD analysis (X-Pert Phillips, Cu Kα) and the data recorded in the 5–70° 2θ range with step size (°2θ) of 0.020 and time for step of 1.00 s. The identification of crystalline phases was made under comparison with data on the JCPDS files.

The sintering in air was followed by Optical Dilatometer (HSM ODHT 1600/80, Expert System Solutions) at 10 °C/min in the temperature range of 20–1000 °C.

The degree of densification was evaluated by measuring apparent, ρ_a, skeleton, ρ_s, and absolute, ρ_{as}, densities and by estimation of corresponding total, P_T, closed, P_C, and open P_O porosities:

$$P_T = 100 \times \frac{\rho_s - \rho_a}{\rho_{as}} \quad (1)$$

$$P_C = 100 \times \frac{\rho_s - \rho_a}{\rho_{as}} \quad (2)$$

$$P_O = 100 \times \frac{\rho_s - \rho_a}{\rho_{as}} \quad (3)$$

ρ_a was obtained by measuring the weight of the samples and their volumes (by precise micrometer), while ρ_s and ρ_{as} by Argon displacement Pycnometer (AccuPyc 1330). First the skeleton density was measured and then the absolute density one, after crashing and milling the samples below 26 μm. The experimental associated errors to the evaluation of ρ_a, ρ_s, and ρ_{as} were estimated as ±0.01, ±0.003 and ±0.005 g/cm^3 respectively, which correspond to ±0.6 and ±0.3% errors of P_T and P_C respectively.

Measurements of linear shrinkage (LS%) and water absorption (WA%) were also performed according to ISO 10545-3.

The degree of sintering and the structure and morphology of the crystals in the final glass-ceramics were observed by Scanning Electron Microscopy (ESEM, Quanta-200, FEI Co., equipped with an EDS).

3. Results

Table 1 reports the chemical composition of the SRM before (BAGL and BAF, coarse and fine particle size fractions respectively) and after vitrification (GL and GF, coarse and fine particle size fractions respectively). The good agreement between the data related to bottom ash and the corresponding glasses underlines negligible reactivity with the crucibles used. Moreover, it is evident that GF — with respect to GL glass — presents a lower amount of Si and Na oxides, but a higher content of Fe, Al, and Ca oxides.

The particle size distributions of glass powders (fraction below 75 μm) used in this study are very similar. The trend can be considered monomodal, with a medium particle size (D_{50}) around 30 μm, 90% fraction of particles below 80 μm and only 10% below 5 μm. The results for glass GL are shown in Fig. 1.

Table 1
Chemical composition (wt.%) of the bottom ashes (BAGL and BAF) and respective glasses (GL and GF). The associate error evaluated by the instrument is ±0.5 ppm.

Oxide	BAF	GF	BAGL	GL
SiO_2	30.31	35.09	47.40	48.47
Al_2O_3	13.03	13.64	9.95	11.12
Fe_2O_3	10.02	11.53	4.38	4.48
CaO	23.05	26.06	18.80	19.52
MgO	2.83	3.73	2.91	4.00
Na_2O	1.94	2.44	4.53	4.95
K_2O	0.94	1.45	0.98	1.81
TiO_2	1.07	1.71	0.75	1.29
MnO	0.18	0.17	0.11	0.15
ZnO	0.73	0.54	0.34	0.61
PbO	0.36	0.17	0.31	0.12
P_2O_5	1.96	1.90	1.26	1.96
CuO	0.68	0.83	0.47	0.60
Others	1.14	0.50	1.26	0.42
L.O.I	11.7	–	5.58	–
Total	99.94	99.76	99.03	99.50