Journal of Non-Crystalline Solids 389 (2014) 50–59

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

# Sinter-crystallization in air and inert atmospheres of a glass from pre-treated municipal solid waste bottom ashes

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ARTICLE INFO

*Article history:*
Received 14 November 2013
Received in revised form 13 February 2014
Available online 2 March 2014

*Keywords:*
Crystallization kinetics;
Sintering;
Glass-ceramics;
Industrial wastes

ABSTRACT

Glass powders, obtained after vitrification and milling of iron-rich Municipal Solid Waste Bottom Ashes (MSWA), were studied towards manufacture of sintered glass-ceramic material. The crystallization kinetics was investigated both in air and argon atmospheres by non-isothermal Differential Thermal Analysis (DTA). The densification behaviors at different temperatures were studied with optical dilatometry. The formed crystal phases were evaluated with X-ray diffraction (XRD) and the microstructure of samples were observed by scanning electron microscopy (SEM).

The investigated composition is characterized with a high crystallization trend and formation of pyroxene solid solutions and melilite solid solutions. Due to additional nucleation process and lower viscosity (because of the lack of $Fe^{2+}$ oxidation) the phase formation in inert atmosphere is accelerated and is carried out at lower temperature.

In the interval 800–900 °C the densification in both atmospheres is inhibited by the intensive phase formation. However, after increasing the sintering temperature up to 1120–1130 °C secondary densification is carried out, resulting in material with zero water absorption, low closed porosity and high crystallinity. Some decreasing of sintering temperature and finer crystal structure are predicted at densification in inert atmosphere.



## 1. Introduction

The sinter-crystallization is an effective method to obtain glass-ceramics from different vitrified industrial or urban wastes. This technique is based on simultaneous densification and phase formation of glass powders or grains, which gives a possibility to produce samples with complicated shapes or large building panels [1–4]. Since milling or grinding of the parent glass frits is necessary, initial glasses with lower degree of refining can be used, which allows significant shortening of the melting time. At the same time, because no nucleation agent and no nucleation heat-treatment are needed, only one step crystallization heat-treatment can be applied. When the initial composition is characterized with a relatively high crystallization trend, this crystallization step is very short and high heating rate can be used [5,6]. These features highlight the idea, that using the sinter-crystallization technique a significant reduction of the cost price is expected.

On the other hand, when the parent glass is characterized by a very high crystallization rate (which is typical for numerous compositions based on huge amount of wastes) the sintering process frequently is inhibited by the intensive crystalline phase formation. This phenomenon might be very useful when glass-ceramic foams are produced [7], but when well sintered monolithic specimens with good mechanical properties can be obtained, the reduced degree of densification is unacceptable. However, it was shown that in some compositions with high crystallization ability, a secondary sintering, near the eutectic temperature, is possible. In this manner well sintered materials with high crystallinity and improved mechanical properties can be obtained. Typical examples are some glasses from iron-rich industrial wastes or basaltic rocks [8,9].

Since many hazardous industrial residues and different radioactive wastes contain high amount of iron oxides numerous iron-rich glasses and glass-ceramics were studied during the last decades [7,10]. In addition, several basalt compositions were investigated for the needs of petrurgy (i.e. re-fused rocks industry) [11–13]. The main part of the results with the iron-rich silicate glasses is related to the nucleation and crystal growth in bulk samples [13–15] and to the fiber production [16–18], while very few studies discuss the sinter-crystallization [4,8,9,19].

In the glass structure iron is presented in both $Fe^{2+}$ and $Fe^{3+}$ forms: FeO acts as a modifying oxide, while $Fe_2O_3$ as an intermediate oxide,

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.02.009
0022-3093/

which partially substitutes $SiO_2$ in the glass network. In addition, the iron oxides have limited solubility in silicate melts, resulting in liquid–liquid immiscibility of the melt at high temperatures (i.e. 1400–1500 °C). This feature provokes spontaneous separation of iron-rich liquid phase during the melt cooling [7,18,20,21], which at a secondary heating leads to fast formation of tiny magnetite spinel crystals ($FeO{\cdot}Fe_2O_3$). In the main part of the studied up to now compositions, the iron oxides vary between 10 and 25 wt.%, $SiO_2$ – between 40 and 60 wt.%, while the amounts of $Al_2O_3$, CaO and MgO are relatively low (i.e. below 10 wt.%). These glasses are located mainly in the large field of pyroxene crystallization [22] and as a result, the initially formed magnetite crystals act as nuclei for epitaxial precipitation of pyroxenes as main crystal phase.

The composition, investigated in this work, differs from the above-mentioned glasses. It contains lower silica percentage and higher amount of CaO and $Al_2O_3$. This glass was produced by post-treated mixed bottom ashes from municipal solid waste incinerators (MSWI). The treatment of these streams is a complex process of selection and physical/mechanical treatment (aging, sieving and washing), which is realized in a plant located in the North of Italy. Then the obtained secondary raw material was separated in two fractions (above 2 mm and below 2 mm); each of them was vitrified as it is (i.e. without additives) and studied as a potential composition for sinter-crystallization.

In the first part of this study [23] the sinter-crystallization ability of these two glasses (labeled *GL* (*large*) and *GF* (*fine*), respectively) was investigated up to 1000 °C. It was demonstrated that *GL* glass (obtained from the coarse fraction, which contains higher $SiO_2$ amount and lower percentages of CaO, $Al_2O_3$ and iron oxides) is suitable for low temperature sinter-crystallization, while the glass, obtained from the fine fraction, shows high crystallization trend which inhibits the sintering process yet in its initial stage. However, *GF* composition shows interesting thermal behavior and curious poly-crystalline structure, which was related to the higher content of iron oxides. These peculiarities provoke the research team to continue the investigations.

In the present part new results with *GF* composition which are mainly related to the kinetics of crystallization and to the possibility to obtain well sintered material after secondary densification at higher temperature are reported. The variations of Avrami parameter and the activation energies of crystal growth in air and argon atmospheres were studied by differential thermal analysis, while the sintering behavior was evaluated by optical no-contact dilatometer up to 1150 °C. The phase compositions and the structure of final material were elucidated with XRD and SEM, respectively.

## 2. Experimental

The melting was carried out in a gas kiln utilizing corundum crucible; 2 kg batch (i.e. fine fraction of the pre-treated mix of MSWA) was heat-treated for 1.5 h at 1400 °C and the obtained melt was quenched in water. The resulting *GF* glass was crushed, milled and sieved below 75 μm. The particle size distribution of the obtained press powder was measured by laser particle sizer (Mastersizer 2000) and the results are reported in the first part of the study [23].

The chemical composition of parent glass powder was determined by inductively coupled plasma (ICP-Varian Liberty 200), while the initial $Fe^{2+}/Fe^{3+}$ ratio of the glass was estimated by Mössbauer spectroscopy (Wissenschaftliche Electronic GMBN). The resulting chemical composition (in molar percentages) is reported in Table 1, together with a hypothetical composition, where whole iron content is presented as $Fe_2O_3$ (labeled as *GF-ox*).

The thermal behavior of *GF* glass powder in the range 50–1400 °C in air was estimated by simultaneous thermal analysis (Netzsch STA 409) at 20 °C/min using a sample of ~30 mg. In addition, the crystallization kinetics in the interval 500–1000 °C was investigated at 5, 10, 15 and 20 °C/min using ~20 mg samples, corundum crucibles and atmospheres of air and argon (at a flux of 200 ml/min) by Perkin Elmer – Diamond TG/DTA. Additional experiments at 20 °C/min with a preliminary nucleation step were also made in both atmospheres.

**Table 1**
Chemical composition (mol%) of parent *GF* glasses and a hypothetical composition with complete iron oxidation *GF-ox*.

| | *GF* | *GF-ox* |
|---|---|---|
| $SiO_2$ | 38.2 | 39.9 |
| $TiO_2$ | 1.4 | 1.5 |
| $Al_2O_3$ | 8.7 | 9.1 |
| $Fe_2O_3$ | 0.8 | 5.4 |
| FeO | 8.8 | – |
| CaO | 30.3 | 31.7 |
| MgO | 6.0 | 6.3 |
| CuO | 0.7 | 0.7 |
| MnO | 0.2 | 0.2 |
| ZnO | 0.4 | 0.4 |
| PbO | 0.1 | 0.1 |
| $Na_2O$ | 2.5 | 2.7 |
| $K_2O$ | 1.0 | 1.1 |
| $P_2O_3$ | 0.9 | 0.9 |

The activation energy of crystallization, $E_{Cr,}$ was evaluated by the Kissinger equation [24]:

$$\ln\left(\phi/T_p^2\right) = -E_{Cr}/RT_p + \text{const} \quad (1)$$

where $T_p$ is the peak temperature of crystallization exotherm and $\phi$ is the heating rate.

The Avrami parameter, $n$, was evaluated by the Ozawa equation [25]:

$$\frac{d[\ln(-\ln(1-\alpha))]}{d(\ln\phi)}|T = -n \quad (2)$$

where the degree of transformation ($\alpha$) is estimated at a fixed temperature, $T$, from exotherms obtained at different $\phi$. The value of degree of transformation is calculated as the ratio of partial area of the crystallization peak at $T$ to its total area. The areas of the crystallization peaks were calculated by using sigmoidal baselines.

The sintering process was studied with horizontal optical dilatometer (Misura – HSML ODLT 1400, Expert System Solutions). The initial green samples (50 mm × 5 mm × 3–4 mm) were obtained by mixing the glass powder with 7% PVA (polyvinyl alcohol) solution and uniaxially pressing at 40 MPa (Nannetti hydraulic press). The addition of PVA increases the green strength and decreases the initial porosity but a preliminary burn-out step at 280 °C was necessary before the sintering experiments.

The crystalline phases, formed during thermal treatments carried out in the DTA furnace, were identified by XRD analysis. X-ray powder diffraction patterns for phase identification were recorded in the angle interval 10 to 80° (2θ) at steps of 0.03° (2θ) and counting time of 3 s/step on a Philips PW 1050 diffractometer, equipped with Cu Kα tube and scintillation detector. Quantitative analysis and cell refinements were carried out by BRASS – Bremen Rietveld Analysis and Structure Suite [26].

Additionally, the formation of crystalline phases at heating and cooling was studied by high-temperature X-ray diffraction (HTXRD) using a conventional Bragg–Brentano powder diffractometer X'Pert PRO, Panalytical with a heating chamber (HTK 16) and rates of 50 °C/min. Parent glass powders were heated on platinum bar from room temperature to different characteristic temperatures (950 and 1120 °C) at which the XRD scanning was performed. In order to elucidate the phase formation at cooling spectra were realized during the cooling at 950 and 25 °C. The X-ray diffraction patterns at each temperature were obtained over a range of diffraction 10–70° 2Θ with time per step equal to 25 s.