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Crystallization of blast furnace slag glass melted in SnO_2 crucible

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Abstract

The scope of this work was to study the possibility of obtaining glass–ceramics from Brazilian blast furnace slag. Glass melting on laboratory scale is usually carried out in platinum crucibles, which are normally not attacked by molten silicates and can be easily cleaned and reused. However, the use of platinum-coated furnaces is not economically viable for producing these materials on industrial scale. As an alternative, SnO_2 crucibles were used to melt glasses. Crucible corrosion was observed and thus the effect of SnO_2 on the crystallization behavior of the resulting glass was studied. For this purpose differential scanning calorimetry (DSC), X-ray diffraction, optical microscopy, scanning electron microscopy and micro-Raman spectroscopy were used. Besides merwinite, melilte, larnite and wollastonite, a crystalline phase containing tin was only possible to be determined by Raman spectroscopy, due to the presence of a band at 570 cm^{-1}, attributed to a calcium tin silicate.

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Keywords: Crystallization; Glass ceramics; Slags

1. Introduction

The development of low cost glass ceramics from blast furnace slags is still a major problem in industrial scale. One of the major problems in obtaining these glasses is to find an inert refractory. It is well known that SiC and graphite are successfully used in the blast furnace in reducing atmosphere. However, the atmosphere control study is not the aim of this work since it is intended to obtain a simple process. This is the reason for testing some refractory materials that could be used in oxidizing atmosphere, and SnO_2 [1] was chosen for this purpose. A previous work [2] on a Brazilian blast-furnace slag glass indicated that without addition of nucleating agents, heat-treated glasses showed preferential surface crystallization with faint volume crystallization, and consequently presented low mechanical strength. It was reported that SnO_2 could be used as additive and nucleating agent in silicate glasses [3,4]. A corrosion of the tin oxide crucible from the slag could be an opportunity to study the effect of SnO_2 in the glass crystallization.

2. Experimental

Before melting the slag, the removal of metallic iron from this waste by magnetic separation was carried out. The resulting material was milled for 3 h to ensure slag homogeneity. Batches weighing 30 g were melted, in a homemade tin oxide crucible [5], at 1460 °C for only 30 min since the extension on SnO_2 crucible corrosion was not known. The melts presented appropriate viscosity to pouring it onto a stainless steel plate. Crucible corrosion was observed. Pieces of green glass were obtained and annealed at 640 °C for 5 h to remove thermal residual stress. The slag and glass compositions were determined

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Table 1
Chemical analysis of the slag and glass melted in SnO_2 crucible (wt%)

Constituents	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	TiO_2	MnO	Na_2O	K_2O	SnO_2
Slag	43.5	35.8	11.8	6.2	0.3	0.8	0.7	0.08	0.5	–
Glass	38.4	32.6	9.8	5.1	0.6	0.4	0.5	0.03	0.2	12.0

by inductively coupled plasma-atomic emission spectroscopy (ICP-AES – Thermal Jarrel Ash – model Atomscan 25) and are given in Table 1.

Differential scanning calorimetric (DSC) measurements were performed (Netzsch DSC, model 404), using a 20 °C/min heating rate for determining the glass transition temperature (T_g) and crystallization temperature (T_c). Both fine (<74 μm) and coarse (177–297 μm) powdered glasses were used.

Thermal treatments were performed in an electrical furnace having a thermal stability of ±2 °C under various schedules. Microstructural details were obtained by transmitted light microscopy (Jenapol – Carl Zeiss/Jena) and by scanning electron microscopy (XL-30 FEG – Philips) on previously polished and etched (0.08 vol.% HF + 0.02 vol.% HCl) glass–ceramic samples.

In order to identify the crystalline phases, powder samples were analyzed in an X-ray (Cu K_α) diffractometer (Siemens 5000D) and thermally treated samples were analyzed by Raman spectroscopy. Raman spectra were recorded on a T64000 Jobin-Yvon Raman spectrometer with a microprobe under a 100× objective using the 514.5 nm line of an Ar ion laser. The resolution in the spectra is at about 1 cm^{-1}.

As the resulted glass presented SnO_2 and a large amount of CaO, we decided to prepare $CaSnO_3$ and Ca_2SnO_4 to carry out micro-Raman spectroscopy of these compounds and to compare them with the Raman spectra of the heat treated glasses. $CaSnO_3$ and Ca_2SnO_4 were prepared by combustion reaction technique. The materials used were SnO_2 (99.9% – CESBRA-Brazil), $Ca(NO_3)_2$ (Merck), and urea (NH_2CONH_2 – Synth) reagent grades. The proportions of the initial mixture were calculated based on the pre-established stoichiometric ratio of the metallic ions to form the desired phases. The powders resulting from the combustion reactions were heat treated at 1400 °C for 4 h and characterized by X-ray diffraction and micro-Raman spectroscopy. To the best of our knowledge this method to prepare calcium stannates and Raman spectra of them are here reported by the first time.

3. Results

3.1. DSC analysis

Differential scanning calorimetry investigations were carried out for finely (<74 μm) and coarsely (177–297 μm) powdered glasses in order to determine the crystallization mechanism. Fig. 1 shows the respective DSC curves. It can be observed a reversible endothermic peak at about 760 °C for both samples, indicating that the specific surface area does not affect the glass transition temperature. On the other hand, the maximum crystallization temperature shifts to higher temperatures with increasing particle size, showing a difference of 32 °C for the first crystallization peak and about 25 °C for the second and third peaks. This high difference suggests that the crystallization occurs essentially at the surface [2,6].

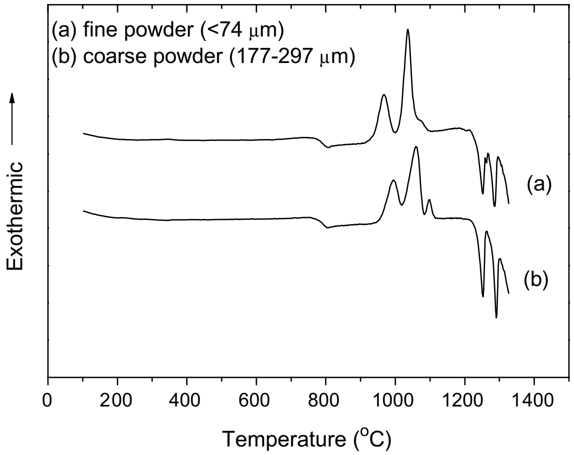

Fig. 1. DSC curves of the powdered glass samples. Heating rate: 20 °C/min.

3.2. Microstructural characterization

Samples of the as-quenched glass were heat treated in the range of 770–810 °C for at most 15 h, followed by heat treatment in the range of 873–1100 °C for different times, for crystal growth. Only surface crystallization was observed. Fig. 2(a) shows an optical micrograph of one glass sample heat treated at 790 °C for 15 h and 873 °C for 3 h, while Fig. 2(b) shows a SEM micrograph of a sample heat treated at 790 °C for 15 h and 1100 °C for 1 h. This result indicates that SnO_2 does not favor the volume crystallization in this glass composition, as being consistent with the by DSC results. Borba et al. [4] reported that tin oxide was efficient in promoting volume crystallization if added with TiO_2. The glass that was obtained in the present study includes a low amount of TiO_2 but is considered not to be efficient to act as nucleating agents in conjunction with SnO_2.

3.3. Crystalline phases

In order to determine the crystalline phases related to the exothermic peaks observed in the DSC curve, finely