JOURNAL OF MATERIALS SCIENCE **37** (2002) 2581 – 2585

Production and characterization of glass ceramics from steelwork slag

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Glass and glass ceramics were obtained using steelwork slag as a raw material. Glass was melted at 1500°C and heat treatments were performed at 720°C for nucleation and at 883°C for crystallization. Differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM), with energy dispersive X-ray spectrometer (EDX) were used to investigate glass and glass ceramics. The crystalline phases developed were diopside and augite. The final microstructure was made up of crystals uniformly distributed, with a size of 1 to 3.5 μm.

1. Introduction

Glass ceramic is defined as a polycrystalline material, embedded in vitreous phase and it can be obtained by a process accomplished in two stages: glass melting and posterior controlled crystallization of glass by heat treatment [1]. These materials are interesting due to the possibility of developing of specific microstructures, with different properties and several uses in application that demand hardness, abrasive wear and chemical resistance. Glass ceramics with mechanical properties superior to granites, basalt and natural stones have been developed [2, 3] and they are being used as construction materials to cover large surfaces, wall tiles and also as a substitute for metals [4]. The final properties of glass ceramic depend on several factors: glass composition, heat treatment, nucleating agents, type and characteristics of crystalline phases. At present, the state-of-the-art in glass ceramics allows products with high performance, but the success of the product also depends of its costs. The glass ceramic production by using steelwork slag has been studied by several researchers [2, 4] in order to minimize costs and to recycle solid wastes. The metal mechanical industry has been outstanding in the politics of recycling rejects, mainly for the use of slag, which is being raised to product status.

The goal of this study is the production and the characterization of glass and glass ceramic obtained from steelwork slag generated during steel production. In order to correct the slag chemical composition, others raw materials were added, where it was employed two criteria in the choice of these materials. Firstly, it was to choose raw materials without additional cost, and secondly, to take opportunity of using by-products from different processes. The considered raw materials were: sand, limestone and the residue from bauxite extraction. Sand has been used in the casting process. Limestone is a commercial product used in ceramic industries and the residue from bauxite is a by-product of the aluminum production extractive process.

The metallurgical slag contains elements in the composition, like Fe, that it can act as nucleating agents. In this case, heterogeneous nucleation typically occurs. To promote homogeneous and fine-grained microstructure, TiO_2 can be introduced as a nucleating agent in optimal concentrations of 1 to 10 wt% [5]. In this work the nucleating agent TiO_2 was introduced as ilmenite ($FeTiO_3$).

2. Experimental procedure

The glass composition was made from a mixture of the following raw materials: slag, bauxite, limestone, sand and ilmenite, in an appropriate amount. These raw materials were prepared according to the following stages: grinding, sieving and homogenization. The steelwork slag was milled in an attrition mill, until 60% of the particle distribution size was inferior to 150 mm. The ilmenite was milled until 45 mm. The steelwork slag, ilmenite, residue from bauxite, sand and limestone were homogenized before melting. This mixture, placed in an alumina crucible, was melted at 1500°C for 1 hour in an electric furnace.

The chemical characterization of the raw material (Table I) was done by X-ray fluorescence. X-ray diffraction analysis (XRD) of the powder slag, glass and heat treated glass samples were performed in a Philips Xpert, using Cu K_α radiation in 2θ range 10 to 80°, with a step width of 0.01 and a step time of 2 s.

In order to obtain the vitreous transition temperature (T_g) and glass crystallization temperature (T_c), differential thermal analysis (DTA) was performed in a monolithic glass sample, using a Netzsch STA 409 equipment, with a heating rate of 10°C /min. The values of T_g and T_c were used to determine the temperatures of

TABLE I Composition (wt%) of the raw materials and glass (in oxides)

Oxide	Slag	Limestone	Bauxite	Sand	Glass
SiO_2	7.60	2.70	12.04	99.72	37.3
Al_2O_3	0.85	0.04	44.38	0.11	14.5
Fe_2O_3	36.02	0.07	12.89	0.03	12.4
CaO	38.93	53.87	0.03	<0.01	31.6
MgO	11.6	<0.01	–	–	4.18
MnO	3.32	<0.01	0.36	–	–
P_2O_3	1.18	–	–	–	–
TiO_2	0.50	<0.01	0.90	0.10	2.50
Ignition loss	–	43.19	27.09	0.53	–

nucleation and crystallization events. Different crystallization times were used to evaluate their effect on the crystalline phase [6].

The microstructural characterization was performed in the scanning electron microscope (SEM) in a Phillips XL 30, coupled with energy dispersive X-ray spectrometer (EDX). The glass ceramics samples were etched with HF 0.5% to be analyzed.

3. Results and discussion

3.1. Glass preparation

Table I shows the chemical analysis of the raw materials, in oxides. It can be seen that mainly Fe_2O_3, CaO and MgO constitute the slag. In the residue from bauxite there is Fe_2O_3 and SiO_2, but Al_2O_3 is the principal component. Among industrial wastes, those with less than 17 wt% can be considered low iron systems [7]. The sand and limestone have almost no impurities. The glass composition was based on two ternary diagrams: CaO-Al_2O_3-SiO_2 and CaO-MgO-SiO_2 [8]. The majority elements of each raw material were to consider for valuation. Each raw material added to the slag has a particular function. Sand helps to increase SiO_2 tenors, which stabilize glassy forming [1]. Limestone favors the formation of a CaO rich phase. The residue from bauxite supplies Al_2O_3. Ilmenite introduces TiO_2 as nucleating agent with low costs.

The studied glass composition, in oxides, (Table I) shows a formulation richer in Fe_2O_3 and poor in SiO_2, comparing with traditional compositions from literature where SiO_2 contents are higher than 50 wt% [1]. This composition was formulated in way to take opportunity to use high content of slag without previous treatment.

3.2. Thermal characterization

The DTA characteristic curve of vitreous material can be observed by three events: (i) a change of the slope line, corresponding to the T_g range; (ii) an exothermal peak associated to crystallization and (iii) an endothermic peak associated to fusion of the crystalline phases [9]. In the DTA curve of glass shown in Fig. 1, these three events were observed. In the glass transition range, the beginning of the inflection was chosen as a characteristic temperature, corresponding to $T_g = 700°C$. The temperature at 883°C, corresponding the highest point of the peak, was chosen as the crystallization temperature (T_c) and the melting of the crystalline phase occurred at 1177°C. It is possible to verify that the exothermic peak has a sharp tendency, with a short temperature range. This fact can be correlated with a high crystallization propensity and/or a bulk crystallization mechanism, in spite of the surface mechanism being present [1, 10].

TABLE II Heat treatment conditions

	Nucleation temperature (°C)	Nucleation holding time (min)	Crystallization temperature (°C)	Crystallization holding time (min)
TT1	720	60	883	30
TT2	720	60	883	60

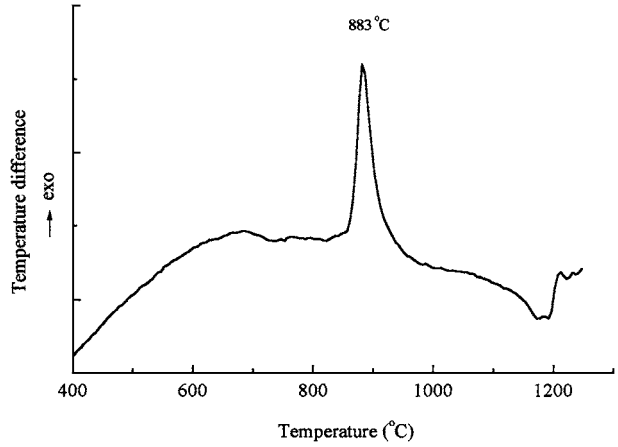

Figure 1 DTA curve of the monolithic glass sample studied.

To obtain glass ceramics with a large number of crystal nuclei with high crystallinity, heat treatments were performed in temperatures near to maximum nucleation and growing rates. The maximum nucleation rate occurs in temperatures slightly above T_g, so 720°C was chosen as the nucleation temperature. As the maximum crystal growth occurs in temperatures near to that of the maximum of the exothermic peak from the DTA curve, 883°C was chosen as second step. Table II specifies the two-step heat treatment conditions, named TT1 and TT2.

3.3. Microstructural characterization

Typical glass behavior, material without long-range structure organization, was confirmed by the X-ray pattern, in Fig. 2a. A subtle elevation of the background in the Bragg angle corresponding to 28–32° is related to vitreous phase. Fig. 2b shows the X-ray pattern of glass powder sample after TT2 (60 min of growing holding time). Well-defined peaks are observed in the X-ray pattern, typical of material with a well-ordered crystalline phase. After the two heat treatments, all samples contained the following phases: (i) diopside, ($CaMgSi_2O_6$) (JCPDS 11-0654) and (ii) augite, ((Ca,Na) (Mg,Fe,Al)(Si,Al)$_2O_6$) (JCDPS 24-0203). Augite and diopside are part of an important solid solution series of the pyroxene group. Diopside is the Mg rich end member, while augite is an intermediate member. In the augite there is Na and Al presence, which occupies the vacancies of the diopside structure [11]. In glass composition, a ratio of CaO : MgO is

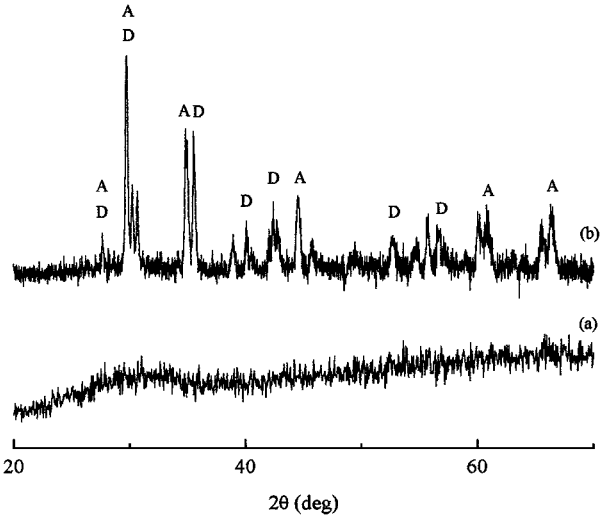

Figure 2 X-ray patterns of (a) glass and (b) glass after heat treatment TT2. The main peaks of crystalline phases are marked: A = augite and D = diopside.

responsible for the crystallization process, since the Mg consumes CaO to form diopside, which has a CaO : MgO of 1 : 1. In this glass study, CaO : MgO is around 7.5, so, the excess of CaO can form augite. Mg may decrease the viscosity of melting, which favors the crystallization process [10]. Diopside is a typical phase developed in Fe rich waste systems and it is an ideal phase for the immobilization of nuclear or toxic elements, thanks to cavities in its structure [7].

The crystallization process was helped by the presence of other minor constituents of raw materials, such as P_2O_5 and MnO. P_2O_5 has been considered an effective nucleating agent in the diopside crystallization process, mainly in low Al_2O_3 content glass [3].

The glass ceramic microstructures developed by heat treatment are composed of crystals involved in a vitreous matrix (Figs 3 to 6). The visual inspection indicates that the fraction of crystalline phase is higher than the residual amorphous phase. It is possible to verify a homogeneous microstructure regarding shape and crystals distribution. The same occurrence was observed in surface regions (Figs 3 and 4). In both cases crystallization starting from the surface is not verified. The obtained glass ceramic samples in the two heat treatments presented homogeneous microstructure from the surface to the center. These facts confirm the tendency observed by DTA analysis, where a bulk crystallization mechanism was predicted as possible.

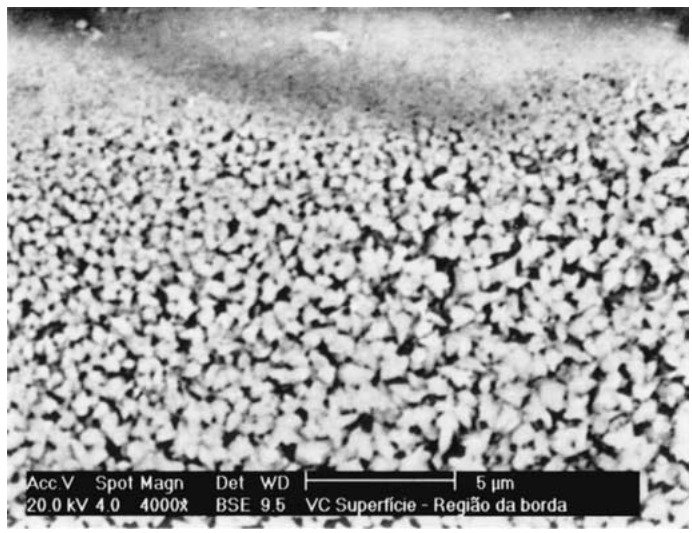

Figure 3 Microstructure of the surface region of the sample treated at 883°C/30 min.

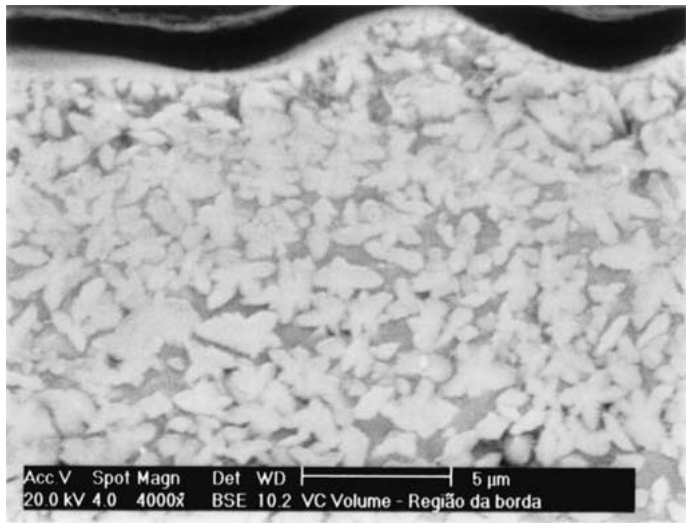

Figure 4 Microstructure of the surface region of the sample treated at 883°C/60 min.

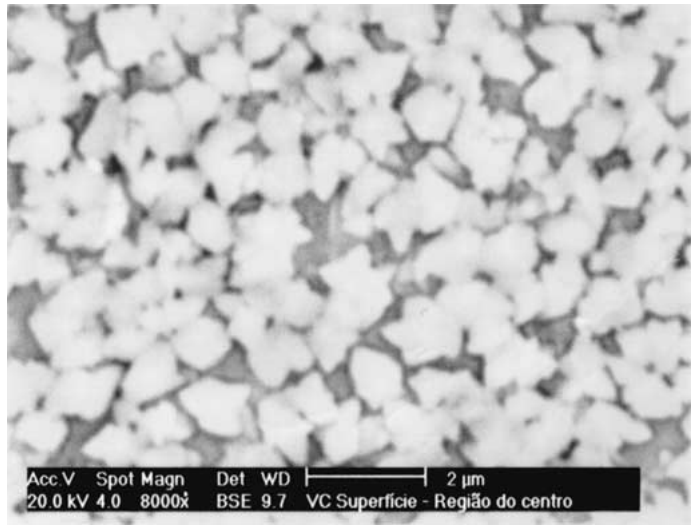

Figure 5 Microstructure of the bulk region of the sample treated at 883°C/30 min.

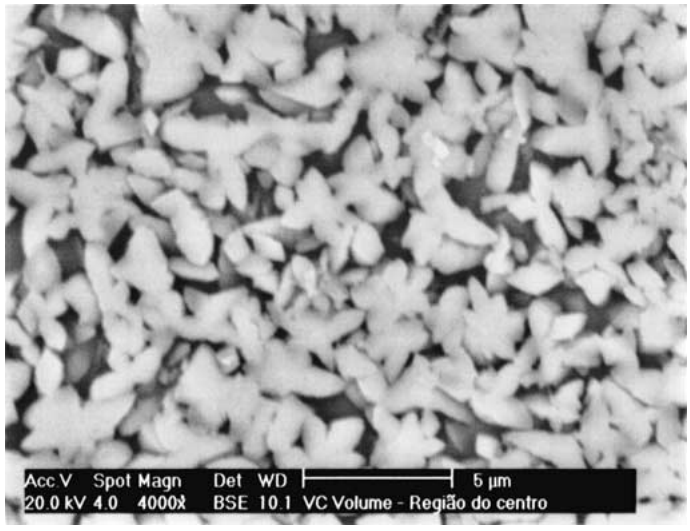

Figure 6 Microstructure of the bulk region of the sample treated at 883°C/60 min.

The influence of crystallization time can be seen in Figs 5 and 6, where for longer time there is an increase in the dimension of the crystals. For shorter time the 1 μm star shaped crystals were verified, while for longer time the crystals reached a size of 3.5 μm with a preferential growth in one direction. In glass compositions with high tendency to crystallization, as slag compositions, it can be easier to control the final glass ceramic microstructure through the variation of the crystallization holding time than of the variation of the crystallization temperature.

EDX analysis showed that chemical elements found in the crystal were the same ones as in the parent glass: Ca, Si, Al, Fe, Mg, Mn and Ti. The chemical elements found by the microanalysis are in agreement with the phases augite and diopside identified by XRD.

4. Conclusions

This study concluded that:

1. The steelwork slag is an appropriate raw material to be used in glass composition and in order to correct the composition other by-products can be added.

2. It was possible to obtain glass ceramics from a composition designed only by raw waste materials, without pre-treatment. This fact makes glass ceramic production economically viable and attractive.

3. The slag is the majority component in the glass composition, which is compatible with high production of this waste.

4. The adequate melting temperature is 1550°C and the heat treatment can be performed in two stages: nucleation at 720°C and crystal growing at 883°C.

5. Diopside and augite phases were developed in the heat treatments, homogeneously distributed in glassy matrix.

6. TiO_2 behavior is in accordance with literature, acting as a nucleating agent in contents less than 3 wt%.

7. The microstructural characteristics, as homogeneous microstructure, high crystallinity and tendency of bulk crystallization mechanism, were attributed to the presence of TiO_2 and the others minority components, that acted as nucleating agents. They favored the decrease of viscosity and the growth of the nuclei.

8. The growing holding time influences the microstructure refining, where for longer holding time the crystals reached a size of 3.5 μm.

Acknowledgements

The authors would like to thank CAPES (C. D. G. Borba) and CNPq (V. Gomes), for financial assistance to the authors.

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Received 6 June 2000
and accepted 11 May 2001