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Characterization of a wollastonite glass-ceramic material prepared using sugar cane bagasse ash (SCBA) as one of the raw materials

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ABSTRACT

Glass-ceramic material prepared with sugar cane bagasse ash as one of the raw materials was characterized to determine some important properties for its application as a coating material. X-ray diffraction patterns showed that wollastonite-2M ($CaSiO_3$) was the major glass-ceramic phase. The Rietveld method was used to quantify the crystalline (60 wt.%) and vitreous (40 wt.%) phases in the glass-ceramic. The microstructure (determined by scanning electron microscopy) of this material had a marble appearance, showing a microporous network of elongated crystals with some areas with dendritic, feather-like ordering. Microhardness data gave a mean hardness value of 564.4 HV (Vickers-hardness), and light microscopy disclosed a greenish brown colored material with a vitreous luster.

1. Introduction

Glass-ceramic materials with wollastonite as the main crystalline phase are produced from glasses of the SiO_2–Al_2O_3–CaO system by controlled surface crystallization, where conventional nucleating agents such as TiO_2 and ZrO_2, are used in the process. Such glassy materials show special visual effects and other important properties (hardness greater than that of natural stones, zero water absorption, lower density, etc.). They are produced on a large scale and used as coatings (floors and inside and outside walls) in building construction. One of the most important wollastonite glass-ceramic for applications in the construction industry is produced by the Japanese company "Nippon Electric Glass" with the name Neoparis®. A major advantage of this material, in relation to natural stones, is that large flat and curved panels can be produced. Glass crystallization starts at temperatures above 950 °C, forming first wollastonite (triclinic, Tc) by surface crystallization. At 1000 °C, alpha-wollastonite (monoclinic) grows in a needlelike form from the surface of the glass towards the interior of the glass grain, making the material look like granite or marble due to the differences in light diffraction indices between the crystals and glassy matrix. At 1200 °C, beta-wollastonite is produced (monoclinic, pseudo-wollastonite) which shows a granular crystallographic morphology with more opaque crystals [1].

Three different wollastonite (calcium monosilicate) modifications are known: wollastonite (triclinic at ambient temperature), alpha-wollastonite (also 2M, monoclinic or parawollastonite) and beta-wollastonite (also 4A or pseudo- or cyclo-wollastonite), where both monoclinic forms are produced at higher temperatures [2]. Wollastonite appears only in masses of glass cooled slowly from 1120 °C in the form of spheres or large-sized crystalline aggregates. The second one is formed after heating at high temperatures as needles, prisms or ribbons and remains metastable in glassy matrices.

Industrial waste, slag ash, or fly ash is used as raw material in the ceramic industry [3–7] and for glass-ceramic production [1,8–11] in different countries. This process depends on additives and waste composition, which in general, contains numerous secondary components and impurities. The interest in sugar cane bagasse ash (SCBA) is due to its composition, the huge volume that is produced in Brazil (>3 million tons/year) and the prospect of increased production in the coming years to produce alcohol for use as vehicle fuel [12]. Nowadays, the construction industry consumes very large amounts of natural stone (granite and marble) coating. Glass-ceramics have important properties that outweigh those of natural stones, for example, high wear resistance, greater hardness, zero water absorption, easily shaped (curved panels or other forms), among others. Besides their usefulness to the construction industry, the use of glass-ceramics decreases the

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exploitation of natural stone reserves and decreases environmental impacts. The use of SCBA as one of the raw materials to produce glass-ceramic materials is a pioneer project, and there are few data regarding this. Since SCBA was the focus of this study, throughout this paper, the term SCBA glass-ceramic designates the final product obtained from it, mixed with different carbonates.

The kinetics of glass-ceramic formation through crystallization of glass using SCBA was studied in a previous work [8], and in a recent publication [9], we showed the viability of producing glass-ceramic material using SCBA and a widely available material (limestone). In this paper, glass-ceramic material was characterized by using X-ray diffraction and fluorescence, thermal analysis and hardness measuring techniques. The microstructure of the glass-ceramic material was evaluated by scanning electron microscopy (SEM), and the percentages of the crystalline and amorphous phases, which influence the properties of glass-ceramic materials, were determined by the Rietveld method, using a standard with known crystalline and amorphous fractions.

2. Materials and methods

The material studied was bottom ash collected under the boilers in an ethanol/sugar plant in Presidente Prudente County, Brazil. This ash is produced during the burning of bagasse to produce steam and electricity in the boilers of the company [12].

The ash was characterized using X-ray fluorescence (model XRF-1800, Shimadzu Corporation, Kyoto, Japan) and X-ray diffraction (model XRD-6000, Shimadzu) to determine its chemical composition and the main crystalline phases, respectively.

The glass composition was determined using a ternary phase diagram, according to the composition of the ash, the desired final crystalline phase and the calculated melting temperature. The theoretical melting temperature of the composition for production of the silicate glass was calculated using the method proposed by Chengyu and Ying [13]. The ash was mixed with different amounts of MgO and Na_2O. Among the compositions studied, allowing for the fusion at temperatures lower than 1450 °C, the combination of ash (50 wt.%) with calcium (45 wt.%) and sodium (5 wt.%) oxides provided a theoretical melting temperature around 1340 °C. The components of the glass were mixed, homogenized and melted (heated at 20 °C/min) to 1450 °C and held at this temperature for 1 h. The melt was poured into an aluminum container with distilled water to cool quickly (quenching), minimizing the possibility of crystallization (melt-quenching method). This glass is referred to as V1 below.

Glass V1 was ground to 60 μm with a normal particle size distribution and analyzed by XRD to see if there was crystallization during the cooling process and by XRF to determine its chemical composition.

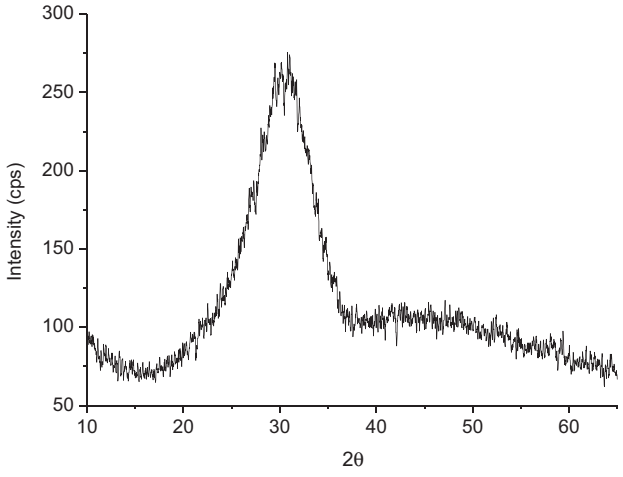

Fig. 1. X-ray diffractogram of the V1 glass (Bragg angle, 2θ).

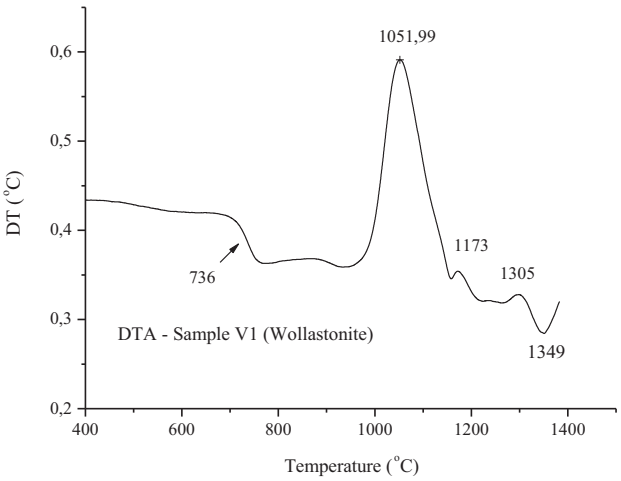

Fig. 2. Differential thermal analysis data (50 °C/min) of the original V1 glass showing the temperatures of: glass transition (arrow), three crystallization peaks and the melting temperature.

Part of the glass powder was heat treated using thermal analysis equipment (model Labsys Thermal Analyzer, Setaram Instrumentation, France) up to 1400 °C at a rate of 50 °C/min to determine glass transition, crystallization and fusion temperatures. Another part of the glass powder was crystallized from poured powder at a heating rate of 50 °C/min and kept as a powder in a crucible for 1 h at the crystallization peak temperature (1050 °C), and afterwards, it was ground and analyzed by XRD to identify the phases formed in the glass-ceramic material. Scanning electron microscopy (SEM model XL 30, Philips, Netherlands) was used to examine the morphology of the crystallized phases on the surface of a sample etched with HF.

To determine sample hardness, a piece of sample was placed in a steel cylinder, glued with Araldite® and polished with sandpapers: P #600 (25.8 μm) to #2400 (9.2 μm). After preparation, samples were placed in the micro-hardness testing machine, and 10 measurements were taken at different positions to obtain an average value. The test was performed with a micro-hardness tester (model HMV 2000, Shimadzu) equipped with a diamond penetrator tip (square pyramid base) for Vickers hardness testing, using a 2.492-N load for 15 s.

To quantify the phases in the glass-ceramic material, a standard sample was prepared using glass powder (the glass-ceramic precursor) and crystalline silicon powder (XRD Shimadzu standard). A known amount of the standard was mixed with the glass-ceramic sample to form a new composite sample, resulting in the following final composition: 6.4 wt.% powdered V1 glass (the glass-ceramic precursor),

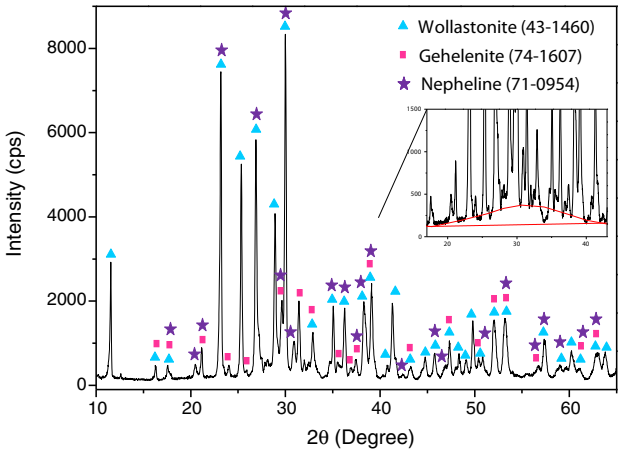

Fig. 3. X-ray pattern of glass-ceramic material V1 shows alpha-wollastonite (2M) as the major phase. Nepheline and gehlenite are the other identified phases.