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Evaluation of aluminosilicate glass sintering during differential scanning calorimetry

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Abstract

The aim of this work is to investigate a difference in heat flow observed in the differential scanning calorimetry curves when aluminosilicate glasses are analyzed. Glasses with nominal composition 56.21 SiO_2 18.65 Al_2O_3 25.14 MgO (wt%) were produced by the conventional melting process. Glass frits were milled and sieved in the range of 45–63 μm. The material was analyzed by X-ray fluorescence spectrometry, X-ray diffraction, differential scanning calorimetry (DSC), and differential thermal analyses (DTA). The particle size distribution was determined by laser diffraction technique. The microstructures of the samples were observed by scanning electron microscopy after removing them from the DSC sample holder. The density was determined by He picnometry. The difference in heat flow in the DSC curves is assigned to the sintering process occurring during the heating cycle, which was confirmed by the neck formation in the particle interface, DSC signal variation in isothermal measurements, no change in the heat flow when monolith specimen are analyzed, and in subsequent DSC analysis after cooling. The concurrent crystallization was also determined.

Keywords: A. Sintering; D. Glass; Differential scanning calorimetry

1. Introduction

In a previous work [1], a difference in the heat flow was observed in a DSC curve when an aluminosilicate glass was investigated. At that time, no reasonable explanation was given to justify such event since on a typical DSC curve for a glass, an endothermic event assigned to the glass transition followed by an exothermic peak related to the crystallization process is generally observed [2–4]. Concerning the unexpected change in the baseline, scanning electron microscopy images showed the neck formation in the interface of particles indicating that the sintering process is occurring during the heating cycle [1,5].

The simplest case of single-phase sintering occurs when an aggregate of glass particles is heated [6]. This process is known as viscous sintering. At an initial state the material shrinks, the density increases, and the amount of pores decreases depending on the particle size distribution, surface energy, and the viscosity of the glass phase. As the particles begin to coalesce, a viscous flow of the material towards the interparticle region originates a neck shape [6].

The most conventional techniques to study the sintering process are related to the determination of the material shrinkage. The microstructural features can also provide information about the sintering process. The initial shrinkage of the viscous flow sintering process is predicted by the Frenkel model, and for higher densities, when the pores are isolated in the matrix, the Mackenzie–Shuttleworth model is usually adopted. Both models show that the density variation depends on the temperature-dependent shear viscosity, the glass–vapor surface energy, and the time [7].

Sintering processes are studied with DSC technique when particles are nanometric and the energy release is measured, generating an exothermic peak in the DSC analyses [8].

In the current work, it is shown that the unexpected difference in the heat flow observed in DSC curves during the heating of aluminosilicate glass powders is related to the sintering process.

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2. Material and methods

2.1. Glass powder synthesis

The nominal composition of the glasses was established based on previously reported data [1]: 56.21 SiO_2, 18.65 Al_2O_3 and 25.14 MgO (wt%). Glasses were obtained by mixing and homogenizing Al_2O_3, SiO_2, and MgO (analytical grade). The mixture was heated at 10 °C/min to 1550 °C and melted in an alumina crucible [1]. The liquid was kept at this temperature for 30 min and then poured into distilled water to obtain frits or in a stainless steel mold to obtain a glass piece.

The frits were crushed in a stainless steel device, milled in a planetary mill (Fritsch, model pulverizette) for 10 min, and sieved in the range of 45–63 μm for 1 h.

2.2. Powder characterization

The glass powder was analyzed by energy dispersion X-ray fluorescence spectrometry (Shimadzu, model EDX-720) to determine the final composition. Laser diffraction (Cilas, model 1600) was used to determine the particle size distribution, and X-ray diffraction (Cu*K*α radiation1.54 Å, step: 2 °/min) (Rigaku, model Miniflex) to verify the presence of crystalline phases.

2.3. Differential scanning calorimetry analyses

The glass was analyzed by differential scanning calorimetry (Netzsch, model Pegasus 404) using a dynamic synthetic air atmosphere, heated at the rate of 10 °C/min, in an alumina sample holder, up to 1300 °C. Glass powder and a monolith piece (a piece of glass that was poured in the stainless steel mold small enough to fit the DSC sample holder) were analyzed to evaluate the calorimetric events. In each DSC analysis about 20 mg of glass powder was used. The analyses were also performed in a platinum sample holder to check the possible effects. Different atmospheres were used, and isothermal measurements were performed to check the behavior of the DSC curve.

Differential thermal analyses (DTA) were performed to help the evaluation of the difference in the heat flow. The same equipment was used, changing the assemblage from DSC to DTA.

Thermogravimetry and mass spectrometry analyses were also performed to check the mass variation and gas release during the heating (Netzsch, model STA 402-E).

2.4. Sample examination after the DSC analyses

After the differential scanning calorimetry analyses, the samples were removed form the sample holder and they presented a pellet shape with dimensions in the order of 4 mm in diameter. The pellets did not adhere to the sample holder and could be pulled out easily. For further studies some pellets were also produced using a vertical external tubular furnace simulating the conditions of the thermal analyses. The pellets were analyzed by X-ray diffraction, scanning electron microscopy (Hitachi, model TM3000), and He pycnometry (Micromeretrics, model AccuPyc 1130).

3. Results and discussion

3.1. Powder characterization

The final composition was determined by energy dispersion X-ray fluorescence spectrometry (EDX) as 57.39 ± 0.06 SiO_2 22.27 ± 0.06 Al_2O_3 19.91 ± 0.10 MgO wt%. The values of the final composition are close to the nominal ones; the difference can be attributed to the increase of the alumina content because an alumina crucible was used to melt the raw material and a decrease in the amount of MgO is due to its volatilization during heating. The following contaminants were detected at relatively low concentrations (< 1 wt%): Ca, Fe, Cu, Zr, and S.

From the particle size distribution, the average diameter was determined to be 68 μm, and the presence of particles with size in the range of 1 to 10 μm is evident, although the selection of the particles was done by sieving in the range of 45 to 63 μm. This result can be explained considering that the particles are not perfectly spherical and have an aspect ratio greater than one.

The X-ray diffraction (XRD) pattern does not show any peaks that could be related to the presence of crystalline phases; the diffraction pattern only revealed a halo which is characteristic of amorphous materials.

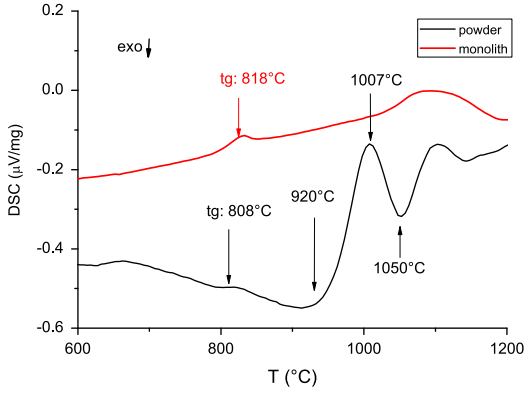

Fig. 1. DSC curves of glass samples as powder and glass monolith. The glass transition temperatures (T_g) were determined in the range of 808–820 °C. Analyzes were performed on a dynamic synthetic air atmosphere with a heating rate of 10 °C/min in an alumina sample holder.

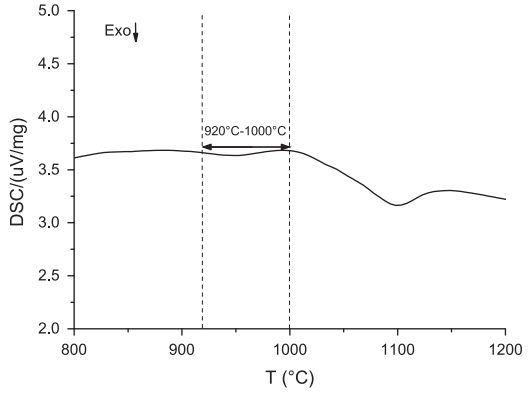

Fig. 2. DSC curve of a glass sample as powder in a platinum sample holder. The analysis was performed on a dynamic synthetic air atmosphere with a heating rate of 10 °C/min.