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Quartz Crystal Reinforced Silica Glass Obtained by Spark Plasma Sintering

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Abstract
Spark Plasma Sintering (SPS) presents a very low processing time when compared to conventional sintering methods. Such fast processing conditions allow it to control the grain size growth and preserve the powders distribution into the mold during sintering, which makes it possible to obtain graded and nano structured (using nano-powders) materials. High purity powders of vitreous silica and crystalline silica (alpha quartz) were sintered by the SPS process at temperature of 1350°C, which is higher than the annealing temperature of vitreous silica and below the temperature of quartz fusion. Such investigation showed the possibility to obtain high purity SiO_2 material, which is a composite of silica glass matrix reinforced with crystalline alpha-quartz powder at almost any combination of volume fraction of matrix/reinforced structure, with well controlled reinforced grain size. X-ray diffraction and density measurements show the possibility to manufacture a unique glass-ceramic material of controlled crystallinity and density.

Keywords: Spark Plasma Sintering, Glass-ceramic, Vitreous Silica, Quartz Crystal, Quartz Glass

INTRODUCTION

In the sintering process, fine particles of certain material unite themselves creating a unique solid so as to decrease their free energy. In the process, the raw material is heated until it reaches the activation energy of mass transport phenomenon such as surface and grain boundary diffusion [1]. Generally, it is desired to obtain high density materials with little grain size since these features provide important properties to the material for industry applications. However, high temperatures for a long treatment time increases the average grain size once reduces the total energy of grain boundaries [2].

Sintering techniques such as HP (hot pressing) and HIP (hot isostatic pressing), which apply external pressure on the particulate material, result in consolidates with higher density, since the compression induces densification mechanisms such as grain boundary diffusion in polycrystalline materials. In the case of amorphous particles, the mass transport occurs by viscous flow [1].

Spark Plasma Sintering (SPS) is identified by the heat generation from high electric current pulses applied directly on the sample and on the die [3], and also by the uniaxial pressure application on the raw material. This technique shows a great number of benefits in relation to traditional methods of sintering, mainly by the decreasing of time and temperature process, besides the special final properties that the materials acquire [3]. The method is applied in the fabrication of functionally graded materials (FGMs), nano-structured materials, thermoelectric materials, advanced ceramics, bio-materials, in addition to its use for grain growth control, improvement of mechanical properties, and others.

Vitreous Silica

Silica or SiO_2 is a chemical compound easily found in natural soils and it can present a variety of crystalline forms, such as quartz, cristobalite, tridimite, and others [4]. However, it is in the amorphous solidified form that this material is called vitreous silica or fused silica which presents important applications in different sectors of the advanced technological industry as in the production of optical fibers for communication, sensors [5] and amplifiers [6], in the fabrication of crucibles for silicon crystal growth [7], in the confection of special lens [8], beam splitters [9], microlithography applications [10] and other functions such as thermal and electrical insulation. The world market of vitreous silica obtained from natural raw quartz, only for applications for the production of electronics (crucibles for

manufacturing electronic and solar grade silicon) currently handles about 1.1 billion dollars annually [11].

Any crystalline form of silica can be converted into its amorphous phase such as alpha-quartz that becomes liquid at approximately 1400°C [4]. The liquid phase of silica when cooled originates vitreous silica that has the amorphous structure, but characteristics of solid. The passage of the liquid to the vitreous form occurs at the transition temperature "T_g" [12] and both structures are amorphous, they differ only by their viscosities.

Sintering of Silica

Vitreous silica can be obtained by different methods and raw materials [13] which can influence some of the glass properties like viscosity [14]. Sintering is one of the possible processes used for this purpose, starting from crystalline or amorphous silica powders.

Earlier study [15] achieved that the optimum temperature to reach vitreous silica by sintering from pre-compacted bodies of amorphous powder (average particle size of 0,4 μm) was higher than 1400°C in a high vacuum atmosphere (10^{-4} Pa) and with holding time of about 17 minutes. Fused silica was also obtained from crystalline powder (Quartz particles with 70 μm of average diameter) by the SPS technique [16] by using a heating rate of 50°C/min. with final temperatures up to 1600°C, without holding time and a mechanical compression of 20 MPa on the raw material.

Amorphous nanopowder of SiO_2 with particle size lower than 10 nm was consolidated by SPS at the minimal temperature of 1000°C maintained for 5 minutes with the application of 100 MPa of compression at the sample in a vacuum atmosphere [17]. However, the glass obtained presented a transmittance of just 63% at UV-Vis of the light spectrum due to the presence of OH groups in an amount 40 times larger then that of common fused silica.

In another study [18], the mixture of Quartz powders with pyrogenic silica (amorphous nanopowder) was sintered in an electric furnace at 1550°C for an hour using a heating rate of 5°C/min. When processed separately, both resulting samples presented cristobalite as the only crystalline phase, while the sintering of the crystal powder with additions of more than 10% of pyrogenic silica resulted in the presence of cristobalite and quartz crystals in the final compact.

The aim of this study is to investigate the fabrication of glass-ceramic with pure SiO_2, starting from different types of SiO_2 raw materials by the SPS process. Crystalline and amorphous powders of silica and nanopowder of amorphous silica were sintered separately and mixed. The sintered samples were analyzed by X-ray diffractions and density measurements.

METHODS AND PROCEDURES

Spark Plasma Sintering Technique

The Spark Plasma sintering technique has been gaining importance as it allows the achievement of high dense compacts with minor grain growth [1]. The high heating rates, typically between 100 and 600°C/min. bring the sample rapidly to high temperatures assisting densification mechanisms over non-densification mechanisms [19]. The mechanical compression of the sample is another factor that accelerates the material densification in the SPS method [1]. Furthermore, the technique presents lower processing time, lower sintering temperature and higher purity if compared to common sintering methods [3]. Due to these and others features, Spark Plasma sintering became reference in the fabrication of functionally graded materials (FGMs) and nanostructured materials by using nanopowders.

In the SPS process, high electric current pulses are applied directly on the sample through the plungers and on the graphite die. Most of the heating occurs due to Joule effect in the die, plungers, and also between the conductive powder particles when they are in contact and to the sparks generated in the gaps between the particles [1, 3]. The mechanical compression is applied by two vertical electrodes from where the current pulses pass. The mold is set between the electrodes inside the chamber with controlled atmosphere and water cooling system. The SPS is also composed with a unit control and a source of electric power whose scheme is shown in Fig. 1.

The SPS equipment used in this study was the model DR.SINTER® - SPS1050, made by SPS Syntex Inc., Japan, installed at the Department of Mechatronic Engineering, São Paulo University.

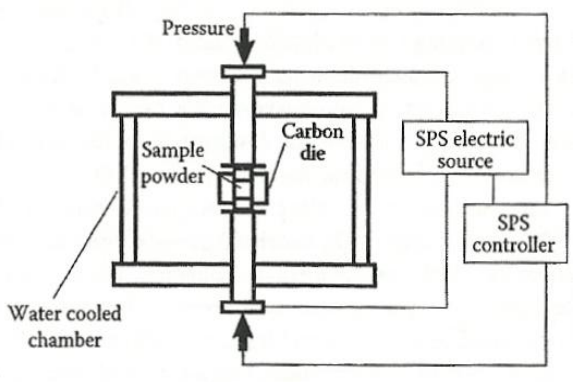

Figure 1. Simplified representation of the SPS system [1].

Mold Preparation and Sintering Conditions
In the preparation of the die, the powders were poured, separated or mixed, in a graphite die of 20 mm of inner diameter that, then, was closed by two plungers of the same material (Fig. 2). After the manual compression of the sample, the die was brought to the chamber of SPS equipment operated at vacuum pressure (from 10 to 15 Pa). The mechanical compression applied during the sintering was fixed as 2 KN for all the experiment and heating rates between 40 and 150°C/min were used.

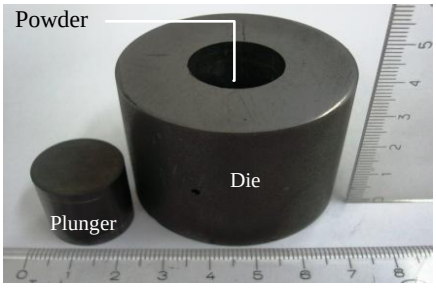

Figure 2. Die and plungers made of high dense graphite.

The temperature was measured by an optical pyrometer at the external surface of the die. The temperature and compression were PID controlled while the axial contraction of the sample - vertical displacement of the plunger during densification - and vacuum pressure of the chamber were monitored during the sintering. All the process parameters can be visualized in real time at the monitor connected to the equipment.

Density measurement
The density measurements of sintered samples were performed using Archimedes principle with the aid of an analytical balance. Weighing dry samples and completely immersed in pure water were carried out.

By knowing the water density at the temperature in which the measurement were done, it was calculate the sample density (d_s) through the Eqn. (1)

$$d_s = m_s.d_w/m_{wd} \quad (1)$$

Where 'm_s' is sample mass, 'd_w' is water density and 'm_{wd}' is the mass of the displaced water. The Archimedes method allows the density measurement of bodies with regular and irregular surfaces.

X-Ray diffraction
The X-ray diffractograms were obtained with the DMax2200 Rigaku X-ray diffractometer with CuKα radiation source, Ni filter, operated at 40 kV and 20 mA. A θ-2θ configuration was used to collect data in the interval of $10° < 2\theta < 65°$, steps of 0.01°. The diffractometer belongs to the Laboratory of Photonic Materials & Devices at the Faculty of Mechanical Engineering, State University of Campinas.

Sintered Raw Materials
The tree types of high purity silicas were used in this experiment. Two amorphous and one crystalline (alpha quartz) silica powders as described in Table 1, were sintered by the SPS process.

Both powders were sintered individually and, for all of them, transparent vitreous silica free from bubbles were obtained. Table 2 shows the typical sintering process parameters of the performed experiments. The density value and the axial contraction can be visualized at this table.

Fixed temperature schedule was used for the sintering of all mixed samples for the sintering of glass-ceramic. Tree different proportions of crystalline and amorphous powders were tested as described in Table 3. The maximum temperature of 1350°C, which is higher than the annealing temperature of vitreous silica and below the fusion temperature of quartz, was used to make glass-ceramics.

Table 1. Characteristics of quartz powders used in the experiments.

Samples	Crystalline structure	Particle size	Obtaining process	Supplier
CR	Alpha-quartz	~ 100 µm	Purified quartz powder from lascas	Kyushu Ceramics
AM	Amorphous	~ 100 µm	Sol-Gel process	State University of Capinas Brazil
AMN	Amorphous	30 to 200 nm	Vapor-phase axial deposition (VAD)	State University of Capinas Brazil

Table 2. Processing parameters for different raw materials of SiO_2 sintered independently by the SPS technique.

Type of powder	Mass (g)	Heating rate (°C/min.)	Final temperature (°C)	Holding time (min.)	Contraction (mm)	Density (g/cm3)
CR	5.7	60 (all process)	1455	2	1.2	2.22
CR	5.7	140 (after 750°C)	1610	0	1.3	2.20
AM	5.7	40 (until 840°C), 100 (after 840°C)	1230	4	3.5	2.20
AMN	2.5	40 (until 840°C), 100 (after 840°C)	1225	4	7.5	2.20

Table 3. Mixture of crystalline/amorphous silica powders used to make glass-ceramics.

Samples	CR (g)	AM (g)	Total mass (g)	Crystalline/Amorphous powder (%)
Mix-1	4.0	1.7	5.7	70/30
Mix-2	2.7	3.0	5.8	47/53
Mix-3	1.7	4.0	5.7	30/70

RESULTS AND DISCUSSIONS

Sintered of Transparent Silicas

The transparent silica obtained from the crystalline powder with greater heating rate, 140°C/min., demanded a higher final temperature up to 1610°C. By using heating rate of 60°C/min. the final temperature of 1455°C was enough to turn the crystalline powder into complete amorphous silica free from bubbles. The production of transparent fused silica starting from the amorphous nanopowder was also possible with the final sintering temperature of 1225°C for the heating rate of 40°C/min. Example of transparent vitreous silica can be observed in Figure 3.

Figure 3. Transparent samples obtained from the sintering of crystalline powder (left) and amorphous powder (right).

All of the transparent vitreous samples presented densities near to 2.20 g/cm^3, same as the value found in the literature for pure and dense vitreous silica.

The X-ray analyses indicated only amorphous structure in these specimens since there were no diffraction peaks which are typical of crystalline formations (see Figure 4).

Sintering of Mixtures of SiO_2 Powders

Raw materials of amorphous and crystalline silica, both with similar average particle size, mixed and sintered as described in Table 3, generated a pure and dense silicas composed of amorphous SiO_2 matrix reinforced with crystalline SiO_2 particles as observed in Fig. 5. The diffractogram of these samples showed intensity peaks according to the peaks of alpha-quartz crystal only.

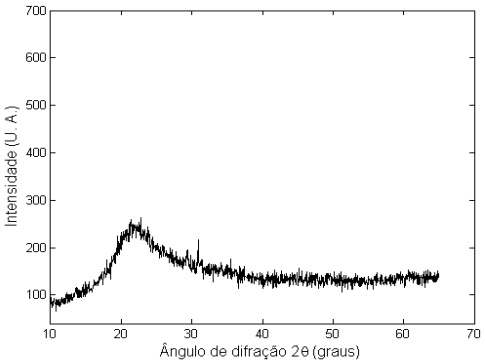

Figure 4. Example of diffractogram of a vitreous sample produced from crystalline powder.

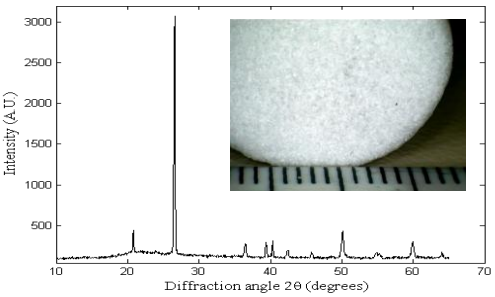

Figure 5. Example of X-ray diffractogram of a glass-ceramics (Mix-2) composed of amorphous silica matrix reinforced with crystalline alpha-quartz particles.

The sintering temperature and axial contraction curves to make the silica glass-ceramics are shown in Fig. 6. As the densification occurs only for the amorphous powder it explains the larger axial contraction for the mixture with higher amount of this powder. It was also observed that larger amount of crystalline phase it demanded higher temperature to initiate the

densification process. Table 4, presents the values of the obtained bulk densities.

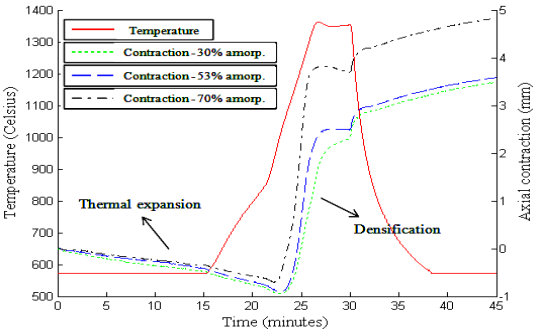

Figure 6. Sintering observed by axial contraction of the samples and temperature as a function of time.

Table 4. Densities of the silica glass-ceramics.

Sample	Density (g/cm^3)
Mix-1	2.19
Mix-2	2.33
Mix-3	2.30

As the density of alpha-quartz is 2.65 g/cm^3, it was expected to observe higher density for the glass-ceramic with higher amount of crystalline phase. This is true for the Mix-2 sample compared with Mix-3. However, the sample Mix-1 that was expected to present the lager density showed lower value for this property. The larger amount of crystalline phase has hampered the penetration of amorphous SiO_2 in the pores between the grains giving no time for the full shrinkage and forming a great amount of closed porosity in the bulk structure, reducing its density.

CONCLUSIONS

Fused silica (vitreous SiO_2) has been produced by Spark Plasma Sintering from different raw materials of pure SiO_2 - powders with amorphous and crystalline structure with dimensions in the order of micrometers and amorphous nanopowders. All of the types of powders separately processed were converted into transparent and bulks of vitreous SiO_2 free from bubbles, while the mixture of crystalline and amorphous powders resulted in a blank material composed of an amorphous silica matrix reinforced with crystalline alpha-quartz grains.

Temperatures around 1450°C were enough to fuse and completely densify the sintered crystalline powder for a heating rate of 60°C/min., while for a rate of 140°C/min. it was demanded a final temperature of close to 1610°C. Silica nanopowder and amorphous powder were full compacted at a temperature of about 1225°C.

The experiments showed the possibility to obtain controlled glass-ceramics of pure vitreous silica reinforced with alpha-quartz particles by using a final sintering temperature of 1350°C which is greater than the sintering temperature of the amorphous powder, but lower than the fusion temperature of the crystalline phase. The holding time at the final temperature will depend of the mixture proportion of crystalline/amorphous for full density glass-ceramic.

The density measurements indicate intermediate values from 2.2 g/cm^3 for 100% vitreous samples increasing its value close to 2.6 g/cm^3 as the crystal phase is increased.

X-ray diffraction confirms the amorphous structure of the fused silica independently of the starting raw silica. And the presence of only alpha-quartz crystals in the sintered glass-ceramics from the mixture of alpha-quartz powder with amorphous powder.

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