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Viscous flow flash sintering of porous silica glass

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ABSTRACT

For the first-time compacts of porous glass particles (95 wt% SiO_2, 2.3% Na_2O, 1.6% Al_2O_3) exhibiting macro-, meso- and micro-pores were densified by flash sintering, using DC electric field in the range 1000–3000 V cm^{-1}. The results point out the applicability of this sintering technology to glasses characterized by viscous flow sintering mechanisms. Excluding the anodic region, the specimens resulted well densified using a current limit of 2 mA mm^{-2} and a dwelling time of 30 s. The obtained microstructure at the anode and at the cathode side is asymmetric, the former being characterized by the formation of Na-enriched region, the latter by the local formation of large pores (hundreds of microns). The mechanism, which triggers the flash event, appears to be associated to dielectric breakdown.

1. Introduction

Flash Sintering (FS) is an innovative, electric field-assisted sintering technique which allows a consistent reduction of consolidation time and temperature for crystalline ceramics [1–11]. Indeed, the densification takes place in few seconds at an onset furnace temperature, strictly related to the applied field [12,13], much lower than that needed in the conventional processes.

In a typical flash sintering experiment, a constant electrical field is applied to a green ceramic specimen subjected to isothermal or constant heating rate treatment. Since ceramic materials are characterized by negative temperature coefficient for electrical resistivity, the current flowing through the material gradually increases during the flash sintering experiments. Once an opportune combination of field and temperature is reached, an abrupt drop of the electrical resistivity is observed [1,2,14,15] and a rapid densification takes place, accompanied by some unusual effects like a very strong photoemission [16–18]. The combination of these phenomena is at the base of the so-called flash event. The current flowing through the material is usually limited to avoid damages by setting a current limit in the power source. Once the flash event occurs, the power supply reaches such current limit and then the electric current is kept constant for a certain time.

In 2015, McLaren et al. have shown that also amorphous materials can reproduce a sort of flash event. This has been detected in alkali-containing silicate glass samples [19] where a viscosity reduction was observed at given combination of electric field and furnace temperature, the phenomenon being therefore named as Electric Field-Induced Softening (EFIS).

Recently, flash sintering was applied to an intermediate system containing both crystalline (alumina) and amorphous phase (magnesia-silicate glass) [20]. The current flow was shown to allow rapid densification via liquid phase sintering mechanisms at unusually low temperatures. Conversely, when silica glass-containing alumina system was considered, flash event could not be reproduced [20]. As a matter of fact, according to previous findings [21], very resistive materials cannot be flash sintered, the high electrical resistivity of pure silica inhibiting the runaway for the flash event.

The idea arose to apply the flash sintering process to amorphous materials where the viscous flow activation observed by McLaren et al. on bulk glass specimens could trigger the densification phenomena in glass powder compact. The aim of the present work is therefore to show whether electric field-induced softening could be used for reducing the consolidation time and temperature of amorphous materials, namely nearly-pure porous silica glass.

2. Materials, methods and calculations

2.1. Glass preparation and characterization

Sodium borosilicate glass with composition (wt%) 65.6 SiO_2 – 27.8

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B_2O_3 – 6.0 Na_2O - 0.6 Al_2O_3, was produced in the present work by using the following reagents: silicon dioxide - SiO_2 (Fluka Analytical, 99.87%), sodium tetraborate - $B_4Na_2O_7{\cdot}10\ H_2O$ (Sigma-Aldrich, 99.5%), boron trioxide - B_2O_3 (Riedel-De Haën, 99.94%) and Aluminum oxide - Al_2O_3 (Sigma-Aldrich, 99.7%). After drying the reagents at 115 °C, they were mixed and left to homogenize under mechanical stirring for 20 h. Then, the powder mixture was put into a high purity platinum crucible and heated up to 1600 °C for 2 h in a Deltech DT-31 furnace. The molten material was poured onto a thick steel plate and rapidly pressed with another steel plate: this technique, known as splat-cooling, allows high cooling rates of around 200 °C/s. The obtained glass was then treated at 660 °C for 12 h to promote spinodal liquid phase separation. The glass was manually ground in an agate mortar and the powder was treated in distilled water at 90 °C for 24 h to leach away the Na-B rich phase. After two consecutive washing with distilled water and drying at 90 °C micrometric and nanometric porosity was produced.

The particle size distribution was measured using a Malvern Mastersizer particle size analyzer. Moreover, the produced glass was characterized by energy dispersive spectroscopy X-Ray Fluorescence (XRF), using a S8 Tiger(4 kW) spectrometer from Bruker, and by Differential Thermal Analysis (DTA), using a Q600 analyzer from TA Instruments at 10 °C min^{-1}, in order to determine the final chemical composition and the glass transition temperature, respectively.

2.2. Flash sintering and sample characterization

Cylindrical pellets (diameter ≈ 6 mm, thickness ≈ 4 mm) were produced by uniaxial pressing at 150 MPa using distilled water as binder. The samples were then introduced into a specifically modified dilatometer (Linseis L75), where flash sintering experiments were carried out. The samples were placed between two platinum discs (diameter = 9 mm) used as electrodes. These were electrically connected to a DC power supply (Glassman EW series 5 kV–120 mA) and to a multimeter (Keithley 2100). The electrical parameters, as well as sample shrinkage and furnace temperature, were recorded at 1 Hz. The dilatometer piston was set to apply a load of 500 mN (≈ 17.7 kPa) to ensure good contact between electrodes and glass specimen. The experiments were carried out in static air, using constant heating rate of 10 °C min^{-1}. Different electric fields were used from 0 to 3000 V cm^{-1}. The current limit was fixed at 60 mA (2.0 mA mm^{-2}) for most of the experiments. Other current values (5, 15, 100 mA) were also used for comparison during isothermal treatments at 690 °C. In all cases, the current was let to flow for < 2 min after that the current limit was reached; then, the power supply and the furnace were turned off.

The flash sintered specimen density was determined by the Archimedes' method; the possible presence of crystalline phases was checked by X-Ray Diffraction (XRD, Italstrutture CPS) working with Cu-Kα radiation (8.08 keV) at 40 kV and 30 mA in 2θ range of 10–100°. The samples microstructure was analyzed by observing polished surfaces (by using SiC 1200 paper) under SEM (Jeol JSM 5500). EDS analysis (JEOL IXRF SYSTEMS 500, software Iridium Ultra) were carried out at 20 kV on the anodic and cathodic regions and on the starting glass powder.

2.3. Sample temperature calculation

During the flash sintering experiment, the actual sample temperature (T_S) is likewise higher than the measured furnace temperature (T_F) owing to the current flow along the sample. In order to estimate the real sample temperature, one can consider that the sample temperature derivative with respect to time, dT_S/dt (t = time) is proportional to the difference between power input W_{in} and output W_{out}:

$$mC_p\frac{dT_S}{dt} = W_{in} - W_{out} \tag{1}$$

m and C_p (equal to 1.2 J g^{-1} K^{-1}) being the mass and the specific heat.

Eq. (1) is valid under the following assumptions:

i. The sample is heated as a whole: macroscopic (i.e. between the center and the surface or between the two electrodes) and microstructural (i.e. between the particles surface and core) temperature differences are neglected;
ii. No phase transition occurs.

On such bases, Eq. (1) provides an estimation of the average thermal evolution of the system during the flash process and does not pretend to provide the calculation of the exact sample temperature, also considering that strong temperature gradients may be generated during the flash [22–26].

The power input is the energy dissipated by Joule heating (W_{in} = V I); the power output can be identified with the radiation losses through the lateral surface of the sample. Therefore,

$$mC_p\frac{dT_s}{dt} = VI - \sigma\varepsilon S_{lat}(T_s^4 - T_f^4) \tag{2}$$

where σ is the Stefan-Boltzmann constant, ε the sample emissivity (assumed equal to 1) and S_{lat} the lateral surface of the specimen.

For two consecutive times (t_1 and t_2), the sample temperature changes according to:

$$T_{s2} = T_{s1} + \frac{t_2 - t_1}{mC_P}[V_1I_1 - \sigma\varepsilon S_{lat1}(T_{s1}^4 - T_{f1}^4)] \tag{3}$$

Such equation can therefore be used for estimating the sample temperature evolution.

3. Results and discussion

The chemical composition of the glass powder is reported in Table 1. The analysis confirms the efficiency of the production route, the material being essentially constituted by pure silica (95 wt%), alumina (1.6 wt%) and a residual amount of Na_2O, around 2.3 wt%.

The glass transition temperature, Tg, determined from the diagram in Fig. 1(a) is equal to 888 °C. Fig. 1(b) shows the particle size distribution of the silica glass constituted by powders with a size for the 50% accumulated volume D(v,0.5) of 55.7 ± 0.1 μm.

3.1. Flash sintering experiments

Fig. 2 reports the dilatometric curves of the green glass samples measured at constant heating rate (10 °C min^{-1}) varying the applied E-field. Starting from the conventional treatment (0 V cm^{-1}), the glass powder begins to shrink around 600 °C, then the shrinkage proceeds with a moderate rate at higher temperature.

Conversely, if E ≥ 1000 V cm^{-1}, the flash event occurs with an abrupt and instantaneous increase of the sintering rate, consistent with previous findings on crystalline ceramics; as expected, also the onset temperature for the flash event decreases with the applied electric field (inset in Fig. 2) [2,12,14]. It is interesting to observe that under 3000 V cm^{-1} the material is flash sintered at about 600 °C, temperature at which only very preliminary densification mechanisms are activated in conventional processes. We can also observe that the dilatometric plots of the samples treated with or without field are exactly overlapped until the flash event takes place this being particularly evident if samples treated with 0 and 1000 V cm^{-1} are compared. Therefore, the E-

Table 1
Chemical composition (wt%) of the glass powder.

SiO_2	Na_2O	Al_2O_3	P_2O_5	CaO	K_2O	TiO_2	Fe_2O_3	Y_2O_3
95	2.3	1.6	0.60	0.12	0.090	0.032	0.023	0.007