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SINTERING OF SILICA FUME IN FURNACE ATMOSPHERES WITH CONTROLLED WATER VAPOUR PARTIAL PRESSURE

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Abstract

Sintering process of compacted silica fume samples with respect to various water vapour partial pressures (p_{total} = 101 kPa) within the furnace atmosphere has been characterized by means of dilatometry and bulk density measurements. Dilatometric study shows the strong dependence of sintering process on the water vapour partial pressure. Water vapour intensifies the process and affects relative densities of the final product, as well.

Keywords: furnace atmosphere, silica fume, sintering

Introduction

Condensed silica fume is a potential precursor for preparation of high silica glassy materials at relatively low temperatures. It consists of non-aggregated SiO_2 particles of colloidal size. Particles of this origin do not show any discrete X-ray diffraction maximas. Individual particles are built up by a network of Si–O–Si bonds, with presence of –OH groups, in small amounts in bulk as well as on the particle surfaces. Individual particles are of spherical shape with diameters smaller than 500 nm [1].

Particles of the silica fume are transformed by sintering into glass-ceramics. It is considered that the mechanism of this process is controlled by viscous flow. However, it is a well known phenomenon that viscosity of glass is strongly affected by content of –OH groups [2], thus the process of transformation of xerogel particles into glass and/or glass-ceramics could be controlled by the content of –OH groups. The amount of –OH groups fixed on active centres at the surface of particles and in bulk or in melted glass is in equilibrium to the water vapour partial pressure in a furnace atmosphere [3].

The main purpose of the present paper is to characterize the sintering of condensed silica fume compacts with respect to the water vapour partial pressure in the furnace atmosphere. The mechanism of sintering is discussed and some properties of products are described.

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Experimental

The used condensed silica fume is a by-product in the manufacture of ferrosilicon alloys, e.g. in the metallurgical plant in Mníšek pod Brdy, Czech Republic. The silica fume is a precipitate from a gas phase, what basically defines its properties. The condensed silica fume from this source consists of SiO_2>98% (main impurities are Al_2O_3, K_2O, CaO, MgO and Na_2O).

Powdered silica fume was compacted in a steel die, the size of green bodies was 10 mm in diameter and 10 mm in height. The relative density of green bodies was ca 25% (related to the density of pure silica glass). The sintering of samples was carried out in a tube furnace equipped by a dilatometer apparatus made from mullite-corundum ceramics. The special apparatus enabled precise control of the purge furnace atmospheres. All samples were heated up by the same temperature regime –10°C min^{-1} (Fig. 1). The furnace atmosphere (total pressure of about 101 kPa) with chosen partial pressure of H_2O was preheated to 300°C before inlet into the furnace. Samples were isothermally heated for 40 and 60 min at constant temperature 1030°C (following the heating up period). Density of samples was determined measuring volume and weight of sintered bodies. The linear shrinkage was registered dilatometrically. The presence of crystalline phases was detected by X-ray diffraction method (Dron 2, CuK$_\alpha$ ra-

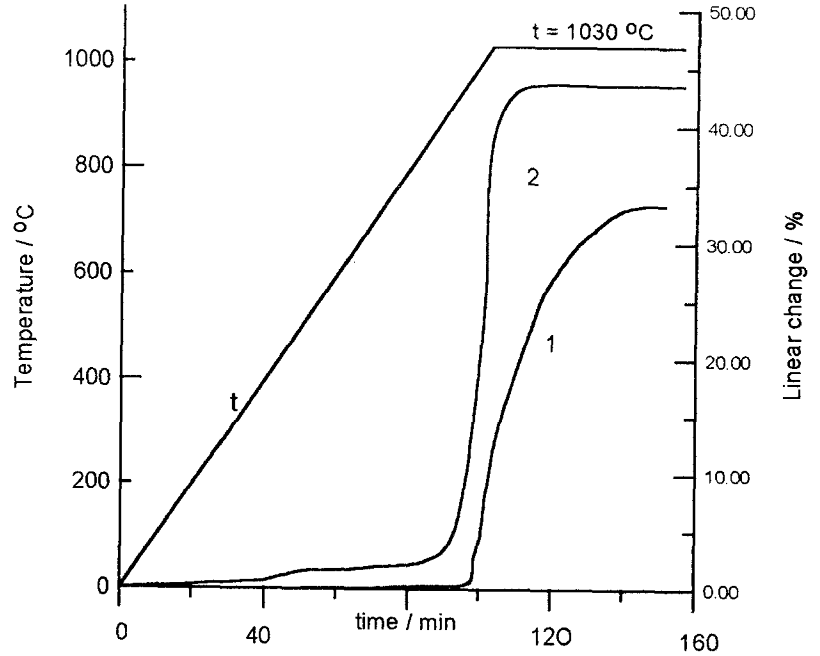

Fig. 1 Dilatometric curves of sintered silica fume: 1 – in dry atmosphere, 2 – in water vapour atmosphere. (Total pressure of 101 kPa)

diation). The total pore volume and pore size distribution of sintered bodies was measured by mercury porosimetry (Carlo Erba 1520).

Results and discussion

Dilatometric measurements show that the sintering is strongly dependent on the water vapour partial pressure in the furnace atmosphere. Figure 1 shows the dependence of relative shrinkage of the sample during sintering *vs.* temperature in both dry and water vapour atmosphere. The presence of water vapour in the furnace atmosphere shifts the beginning of the sintering towards lower temperatures and also speeds up and intensifies this process. The final density at a given temperature is after sintering in water vapour higher than that after sintering in a dry atmosphere. The results are supported by porosimetry measurements of sintered samples. Both samples, sintered in the water vapour atmosphere and also in the dry atmosphere, are totally recrystalized into cristobalite after sintering runs. The dependence of the relative density of sintered samples *vs.* the water vapour partial pressure in the furnace atmosphere is plotted in Fig. 2. Straight line represents regression line of experimental data in coordinates relative density and $(p_{H_2O})^{1/2}$ respectively.

The sintering and transformation process is strongly intensified by the presence of water vapour [2, 3]. Shrinking of samples starts at about 930°C in water vapour atmosphere and ends in narrow time interval, which is of about

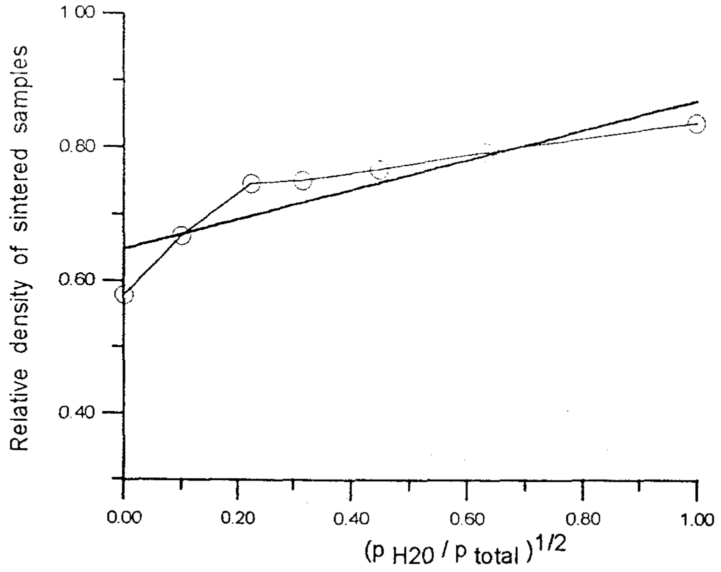

Fig. 2 Relative density of sintered samples *vs.* water vapour partial pressure in furnace atmosphere

one half of that in dry atmosphere. Shrinking of samples in dry environment is shifted to higher temperatures and the final bulk density is about 20% lower, compared with that in steam atmosphere. Main reason for the latter is transformation of amorphous material to cristobalite between 980–1030°C, what suppresses densification by viscous flow. We suppose the following effect of water vapour on mechanism of sintering: Si–O–Si bonds on the surface of particles preferentially may interact with molecules of H_2O from the furnace atmosphere, this interaction reduces the activation energy of viscous flow and the activation energy of recrystallization process. The interaction between particles and water vapour as well as densification of samples are function of the partial pressure of water vapour in ambient furnace atmosphere. This dependence is nearly consistent with linear dependence of the solubility of H_2O in glass melts on $(p_{H_2O})^{1/2}$, described e.g. by Schäffer [3].

Differences in bulk densities of sintered samples due to various furnace atmospheres are responsible for differences in further properties of the sintered material as well [4].

Conclusion

The presence of water vapour in the furnace atmosphere intensifies sintering process and strongly affects the microstructure of the final product as well. Depending on the water vapour partial pressure we can receive products with different characteristics.

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