

## Modeling of glass sintering applied for the fabrication of porous glass bodies

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**Abstract** The sintering behavior of borosilicate and soda-lime mono-sized glass beads was investigated with the aim to fabricate transparent porous glass balls and cylinders. As the glasses tend to crystallize, temperatures where the sintering was in advantage compared to crystallization were used. Isothermal studies were undertaken for modeling the evolution of sintering necks as a function of radii of beads, temperature and time. The Frenkel model of viscous flow was applied to predict first and second stage of sintering. As the sintering of the glasses without crystallization was only possible at high temperatures the process is very fast and has to be controlled precisely. The results of this work were applied for the fabrication of porous bodies with specific characteristics: different geometries and sizes, transparency, high porosities to be achieved during first stage sintering of spherical glass beads. The porous parts with these characteristics are used for the investigation of hydrodynamic processes in the pore network of glass parts.

### Introduction

Porous glass bodies can be used in many applications. For investigations of hydrodynamic processes such bodies serve e. g. as model samples for natural or technical filters and sediment deposits. For this purpose the material of the

samples has to be transparent, making possible the optical-laser investigations of flow processes in the pore network. Thus, for this application the crystallization of the glass is an undesirable effect. In order to control both the densification and the degree of crystallinity during sintering, a large experimental effort is often necessary to adjust the suitable sintering conditions. The application of sintering models can then help to establish the sintering program best suited for these requirements [1, 2].

Different models have been developed to describe the mechanisms of sintering. The first stages of sintering can be described by Frenkel's model. It describes the sintering of spherical, monodispersed particles by the mechanism of viscous flow [3]. Frenkel has shown that if sintering of particles occurs by viscous flow, the relationship between the radius of the neck  $x$  and time  $t$  shown in Eq.1 is obeyed.

$$\left(\frac{x}{r}\right)^2 = \frac{3\gamma}{2\eta(T)r}t \quad (1)$$

$\gamma$  is the surface energy of the material which is almost independent on temperature,  $\eta(T)$  is the temperature dependent shear viscosity and  $r$  is the initial particle radius [3–5].

In this work, the microstructural evolution of spherical glass beads in the two first stages of sintering was investigated in a range of temperatures at which densification is in privilege comparing to crystallization. The neck growth was investigated depending on glass, temperature, time and size of beads. With the study it was possible to test the Frenkel's sintering model and predict the time-temperature program to obtain glass bodies of determined geometries and sizes sintered in first stage sintering.

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## Experimental procedure

For this work two kinds of glasses were used: borosilicate spherical glass beads of composition (in wt%) 81% SiO<sub>2</sub>, 13% B<sub>2</sub>O<sub>3</sub>, 4% Na<sub>2</sub>O, 2% Al<sub>2</sub>O<sub>3</sub> and soda-lime spherical glass beads of composition 72.5% SiO<sub>2</sub>, 13.7% Na<sub>2</sub>O, 9.8% CaO, 3.3% MgO, 0.4% Al<sub>2</sub>O<sub>3</sub>, 0.2% FeO/Fe<sub>2</sub>O<sub>3</sub>, 0.1%K<sub>2</sub>O. Both glasses were supplied from Worf Glaskugeln GmbH, Germany. The borosilicate glass beads had a size of 2.5 (±0.05) mm in diameter, while soda-lime beads with diameters of 3 (±0.15), 2 (±0.1), 1.5 (±0.15) and in the range of 0.8–1.2 mm were used. The softening point is 815 °C for borosilicate and 704 °C for the soda-lime glass, respectively. The densities are 2.23 and 2.50 g/cm<sup>3</sup>, respectively.

The study of the sintering behavior of the glasses was taken in isothermal conditions. Additionally, crystallization of the glass should be prevented as the crystallized surfaces of the beads do not flow and inhibit further sintering, and transparency should be achieved. Thus, concerning the tendency of glasses to crystallize, a range of temperatures at which the sintering of the glass is in privilege comparing to crystallization was found in initial investigations [6–9].

The modeling of the evolution of the sintering neck formed between the borosilicate glass beads with time in the first and second stages of sintering was taken at temperatures of 915 °C, 931 °C and 957 °C and times between 5 and 25.5 min. For the soda-lime glass the temperature selected was 842 °C and the evolution of the neck with time for different size beads was studied. The parameters used are shown in Table 1.

Each sintering experiment was taken with samples of glass beads in hexagonal packing disposed in one layer of a cylindrical mold. In all cases the samples were sintered in dry air in an electrical oven with a thermocouple attached to it. The samples were heated directly in the preheated furnace at the isothermal temperature and cooled rapidly afterwards in order to prevent crystallization in the heating and cooling path. The sintered samples were analyzed using Scanning Electron Microscope, SEM (Camscan 24). In each sample, 12 individual necks were chosen in two regions of packing and digital images were taken at magnification of 53000. The size of the necks was measured with the help of an imaging analysis program.

**Table 1** Table of sintering experiments for soda-lime glass (842 °C)

Beads diameter [mm]	Time [min]	
1	2	3
1.5	2	3
2	3.5	5
3	3.5	5

Finally, highly porous glass spheres and cylinders were produced using ceramic molds produced by the freeze gelation process FGP with defined geometric cavities [10]. In the cavities with high dimensional precision, a release agent was introduced to prevent the glass beads from sticking on the mold surface. As the interface between the glass and the release layer was the weakest link of the system the glass parts could be easily removed from the molds after the molds had been broken.

## Results and discussion

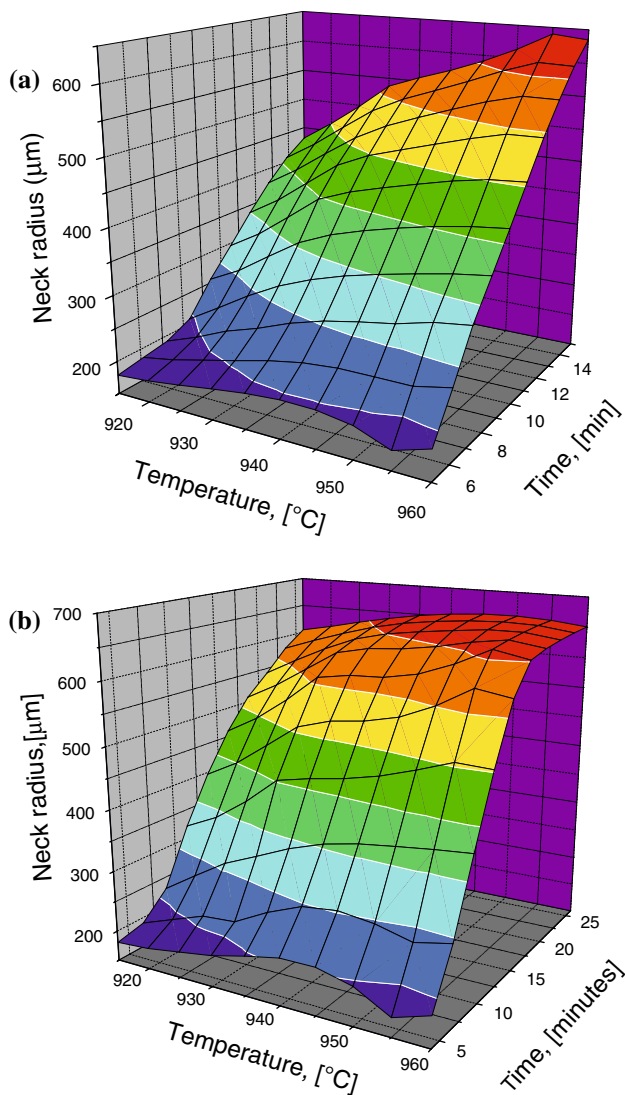
### Modeling of borosilicate glass sintering

Figure 1 shows the size of neck radius  $x$  as a function of time and temperature. In these three-dimensional plots it is visualized that the higher the temperature and the time of thermal treatment, the larger is the size of the neck. With higher temperature sintering becomes faster.

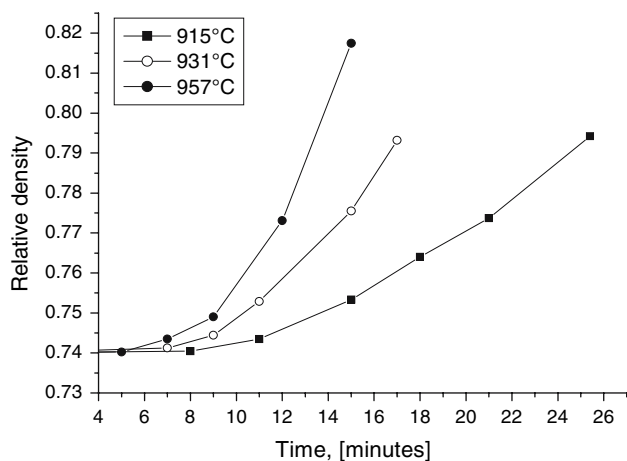
In Fig. 1a the neck size is plotted in the time interval of 5–15 min. The region of 957 °C and 15 min represents the higher relation neck radius/bead radius ( $x/r$ ) of 0.52. It is also easily seen in Fig. 1a that the sintering time in the range of temperatures studied has a strong influence. When sintering for 15 min from 915 °C to 957 °C the neck radius grows for 225 μm. When the sintering is taken from 5 to 15 min at constant temperature of 957 °C, the neck radius grows 495 μm. In Fig. 1b all values are plotted (sintering times from 5 to 25.5 min). It is seen that in the lower temperatures of 915 and 931 °C in 25.5 and 17 min of sintering respectively it is achieved a  $x/r$  relation of 0.48.

The evolution of relative density (Fig. 2) is in accordance with the evolution of the neck radius (Fig. 1). The higher the temperature the faster the neck radius growths and consequently densification increases. For example, when sintering the samples at 957 °C for 15 min a relative density of 0.82 is achieved. If the experiments were taken for longer times at the temperatures of 915 and 931 °C the densities would reach 0.82.

The microstructure resulting from sintering was also studied. Table 2 shows the  $x/r$  ratio in 4 conditions. Figure 3 shows the evolution of neck size as function of the temperatures of 931 and 957 °C, after 7 and 15 min of sintering, respectively. At 931 °C, after 7 min (Fig. 3a) of sintering the spheres are in tangential contact representing the beginning of first stage. When going from the temperature of 931–957 °C (Fig. 3b) the  $x/r$  ratio grows from 0.19 only to 0.24, still representing the first stage of sintering. At 931 °C, after 15 min of sintering (Fig. 3c), the beads adopt forms of hexagons and the pore channels are enclosed in the bead edges, which corresponds to second



**Fig. 1** Neck radius  $x$  as a function of time and temperature: (a) in the region of 5–15 min. (b) in the region of 5–25.5 min



**Fig. 2** Evolution of relative density versus time and temperature

stage of sintering [11]. At this point the  $x/r$  ratio is 0.43. At 957 °C (Fig. 3d). the pores become spherical. This can be defined as the end of second stage. Then the ratio  $x/r$  is 0.52 and the relative density is 0.82. Beyond this point neck measurements are not representative anymore for the study of the sintering evolution and pore size or density measurements should be taken.

Comparing the  $x/r$  ratio (Table 2) and the pictures corresponding to the temperatures of 931 °C and 957 °C in the times of 7 and 15 min (Fig. 3) it can be seen that a variation of temperature from 931 °C to 957 °C brings in average 23.5 % increase of the ratio  $x/r$ , while varying the time from 7 to 15 leads to an increase of the ratio of more than 100 %.

### Modeling of soda-lime glass sintering

The influence of the size beads on sintering was investigated using the soda-lime glass beads. The times of sintering used for each bead diameter are presented in Table 1. The temperature used was 842 °C. In Fig. 4 the calculated relative density is drawn as a function of sintering time and size of the beads. The beads of 1 mm when sintered for 2 min have a relative density of 0.74 which corresponds to tangential contact. After 3 min of sintering the relative density becomes 0.80 and the pores become isolated. In this case the densification is extremely fast. If the diameter of the beads is 1.5 mm, after 3 min of sintering the density is 0.76 and second stage of sintering is reached (Fig. 5a). Beads with diameter of 3 mm sintered for 3.5 min show a density of 0.74 which is just tangential contact (Fig. 5b). So, it is proved that the size of the beads has direct influence in the sintering mechanism. The smaller the diameter the faster the densification will occur.

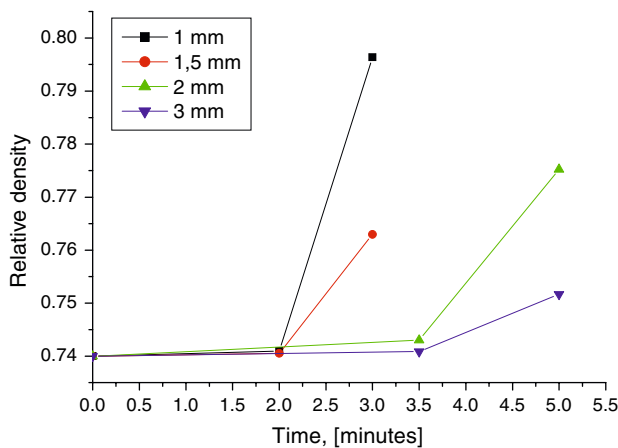
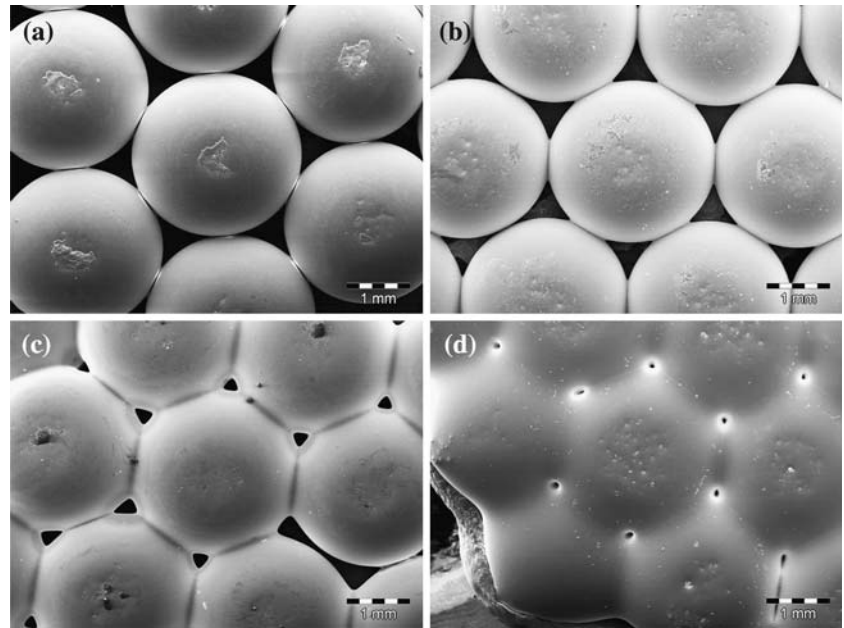
### Application of the Frenkel model

As the experiments are taken at high temperatures, the mechanism of viscous flow is very fast and the samples are sintered in first and second stage in only a few minutes. The samples are heated directly to the isothermal temperatures, but the oven takes some minutes to stabilize again after the sample has been placed. These minutes of stabilization correspond to non-isothermal sintering and play a significant role in the results. For evaluation of isothermal

**Table 2** Influence of temperature and time on the  $x/r$  ratio

	Temperature		Time (min)
	931 °C	957 °C	
$x/r =$	0.19	0.24	7
$x/r =$	0.43	0.52	15

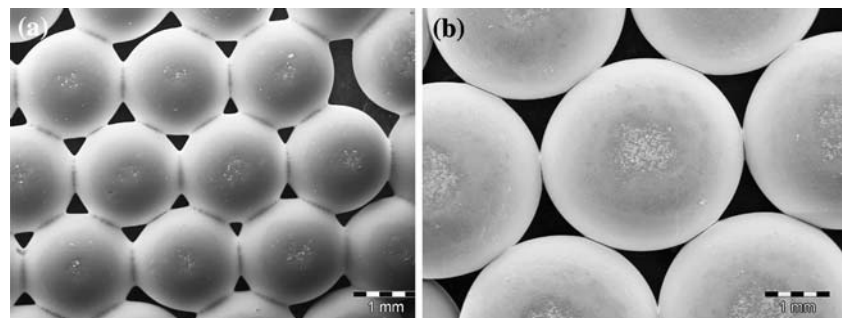
**Fig. 3** Borosilicate glass sintered at: (a) 931 °C-7 min; (b) 957 °C-7 min; (c) 931 °C-15 min; (d); 957 °C-15 min



**Fig. 4** Evolution of density of soda-lime glass as a function of time and size of beads

sintering behavior the influence of the time where the samples are at non-isothermal conditions are discounted. A starting point (time  $t_0$ , neck size  $x_0$ ) was defined which

**Fig. 5** Soda-lime glass beads of: (a) 1.5 mm sintered during 3 min. (b) 3 mm sintered during 3.5 min

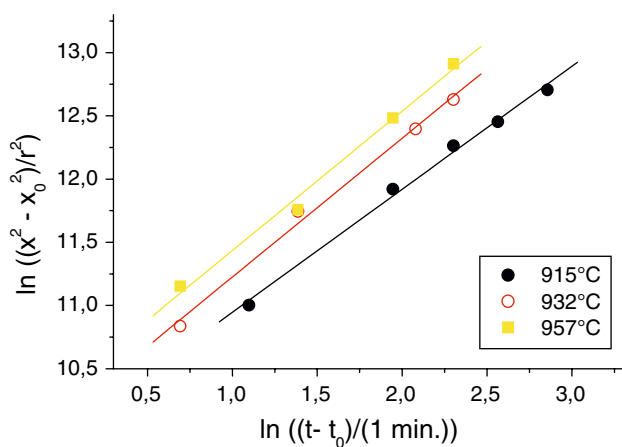


corresponds to the time necessary for thermal stabilisation of the oven. These values were discounted from the further times of sintering  $t$  and measured neck sizes  $x$ . After this treatment, the results were used for testing the viscous flow sintering model from Frenkel (Eq. 1). Changing the equation from Frenkel to logarithm scale and taking the influence of the non isothermal sintering time, the following equation is used:

$$\ln\left(\frac{(x^2 - x_0^2)}{r^2}\right) = \ln\frac{3\gamma}{2\eta(T)r} + \ln(t - t_0) \quad (2)$$

#### Borosilicate glass

Figure 6 shows experimental curves of the evolution of neck radius  $x$  with time for borosilicate glass. To show the relation of  $x$  with time the results were treated as shown in Eq. 2. In each plot the intersection of the y axis corresponds to  $\ln(3\gamma/2\eta r)$  (identified as parameter A) and the slope is the power law relationship between  $x^2$  and time. These



**Fig. 6** Rate of interface growth between borosilicate glass spheres. Where t is in min

**Table 3** Parameters calculated from the plot of  $\ln((x^2 - x_0^2)/r^2)$  vs  $\ln(t - t_0)$

Temperature [°C]	Parameter A: intersection of y axis: $\ln(3\lambda/2\eta r)$	Slope
915	9.97	0.97
931	10.13	1.09
957	10.33	1.10

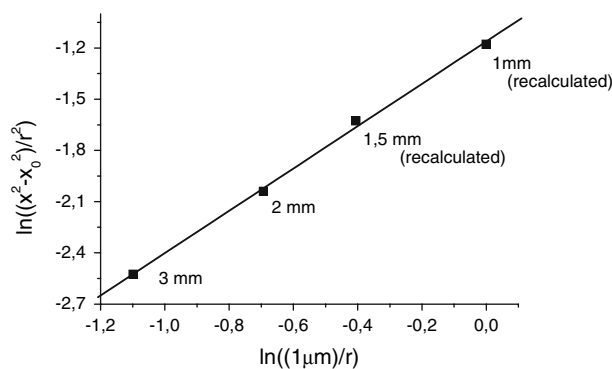
parameters are shown in Table 3. The slope of approximately 1 is in agreement with previous works with glass and indicates that viscous flow is the dominating sintering process as indicated in Frenkel’s equation. The smaller the temperature the smaller is the deviation from 1 in the values of the slopes. In Eq. 2 only viscosity is dependent on temperature. Therefore, the difference in the parameter A between the three sintering curves (Fig. 6) is due to the dependence of viscosity on temperature.

*Soda-lime glass*

The influence of the size of the soda-lime glass beads was evaluated using the first stage sintering viscous flow model. From Eq. 2 plots of  $\ln((x^2 - x_0^2)/r^2)$  versus  $\ln(1/r)$  were determined taking into consideration the time of non-isothermal sintering (Fig. 7). For the beads of diameter of 1 and 1.5 mm  $\Delta t$  was 1 min and for the beads of 2 and 3 mm  $\Delta t$  was 1.5 min. Thus, for the beads of 1 and 1.5 mm of diameters, the neck values at 1.5 min ( $x_{1,5}$ ) were calculated:

$$\ln(\Delta x_{1,5}^2/r^2) = \ln(\Delta x_1^2/r^2) - \ln \Delta t_1 + \ln \Delta t_{1,5} \quad (3)$$

with  $\Delta x = x - x_0$  and  $\Delta t = t - t_0$ . Results are shown in Fig. 7. The slope of 1.2 is in approximation with the model



**Fig. 7** Influence of radius of beads in the evolution of neck between soda-lime glass beads at 1.5 min. Where r is in  $\mu\text{m}$



**Fig. 8** Porous glass spheres made with 1.5 and 0.8–1.2 mm of beads

of viscous flow, although with some higher variation. Some sources of mistakes in this study are the glass bead size variation, the low viscosity of the glass at the temperature of study, and additionally the small times of sintering.

The use of Frenkel’s model results in a reduction of the number of experiments necessary to reach the desired densification.

Porous glass bodies

In the glass sintering study the progress of sintering was investigated as being dependent on temperature, time and glass bead size. These relationships were applied for the sintering of spheres and cylinders of soda-lime glass in first stage sintering without crystallization.

For the achievement of the glass bodies a manufacturing technology for ceramic molds with the defined geometric cavities via freeze gelation was developed. The glass beads were filled in the ceramic molds obtaining an initial random packing of the beads with a relative density of approximately 0.60. Sintering was performed at 842 °C between 3 and 5.9 min depending on the size of the beads and the size of the bodies desired.

**Table 4** Characteristics of the porous bodies

Geometry	Size of the beads [mm]	Sintering time [min]	Average diameter [mm]	Volumetric porosity
Sphere	0.8–1.2	3	8.8 ± 0.4	0.64
Cylinder and sphere	0.8–1.2	5.5	18.9 ± 0.2	0.64
Sphere	1.5	5.9	18.9 ± 0.2	0.62

Table 4 presents the characteristics of the bodies obtained concerning the glass beads size, sintering time, and size, shape and porosity of the final bodies.

Spherical and cylindrical glass bodies could be produced with relative densities between 0.62 and 0.64. The porous components show a very high precision of their dimensions and the variation of the diameter is typically below  $\pm 0.4\%$ . This low variation value could be observed due to the use of freeze gelation derived ceramic molds and sintering taking place in the first stage with relative densities less than 0.65 [12].

Figure 8 shows an example of porous glass spheres of 18.9 mm obtained by sintering of glass beads of 1.5 mm and 0.8–1.2 mm diameters, respectively. The glass beads are transparent and no crystallization occurs. The transparency of the bodies is not evident in the picture because of the difference in the refraction index between the glass and the air in the pores.

## Conclusions

It was possible to model the sintering behavior of borosilicate and soda lime glass in a range of temperatures where crystallization does not occur. Two characteristic relations were found between microstructure and neck evolution. The relation  $x/r$  of 0.52, and relative density of

0.82 were defined as the end of the second stage of sintering, while the relation  $x/r$  of 0.34 represents the borderline between first and second stage of sintering. The evolution of neck radius  $x$  with time  $t$  and with radius of glass beads is in good agreement with the Frenkel model of viscous flow up to a  $x/r$  ratio of 0.52. With the sintering study, porous glass bodies with differently sized beads, shapes and sizes could be produced, reducing the number of experiments to reach an optimum condition.

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