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High temperature treatment of porous glasses

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The influence of thermal treatment on linear sizes and internal structure of porous glasses has been investigated. A simple connection between porosity and shrinkage has been confirmed to exist, except microporous glasses with silica gel inside the pores, where in the initial stage of annealing the porosity was increasing when the glass shrank. A sponge structure of fracture mirrors of the walls of carcass for glasses heated at about 650 °C is observed.

1. Introduction

The perspectives of wide applications [1] of porous glasses justify interest in their properties. Only few works were dedicated to investigations of their structure and optical characteristics. Description of the observed dependences presented in several papers [2]–[4] is not coherent, because a great variety of porous glasses, which manifests itself in a wide range of such parameters as sizes of pores, total volume of pores and their specific surface, as well as chemical composition of porous glass. In the present work, the influence of temperature and time of annealing at high temperatures on the structure and the linear size of porous glass is investigated.

2. Sample preparation

The porous glass was obtained as a result of chemical treatment of the two-phase sodium borosilicate glass of the following composition (in mol%): SiO_2 – 60.93, B_2O_2 – 31.51, Na_2O – 7.48, Al_2O_3 – 0.08. Two different temperature-time regimes of the thermal treatment were applied to obtain the phase separation in the glass: a) 165 hours at 490 °C, b) 100 hours at 650 °C.

In the glass annealed at the temperature of 490 °C for 165 hours the alkali-borate phase is shaped as a net of small spheres of about 50 nm in diameter, which are connected together. This glass shows faint opalescence. Meanwhile, in the glass annealed for 100 hours at 650 °C a net of channels of different width and length was observed. Diameters of these channels change from 250 to 400 nm. This glass is completely opaque. After separation, rectangular plates of 0.5 mm in thickness and other dimensions from 10 to 40 mm were cut out from a block of glass. The sodium borate phase was being extracted when soaking the samples in 0.5 M HCl solution at 50 °C. Moreover, some of the samples were chemically treated in

0.5 M KOH solution. In this way, four types of porous glasses were obtained, which were marked A, B, C, D (Tab. 1). Finally, the porous glass samples were annealed at different temperatures ranging from 500 to 800 °C.

Table 1. The structural parameters of the samples under investigation.

Glas designation	Thermal treatment	Chemical treatment	Porosity $\Delta m/m$ [%]	Average pore diameter [nm]	Specific surface [m^2/g]	Pore volume [cm^3/g]
A	490 °C, 165 h	HCl	38	26	49.7	0.302
B	490 °C, 165 h	HCl, KOH	54	35	50.6	0.452
C	650 °C, 100 h	HCl	38	274	5.8	0.273
D	650 °C, 100 h	HCl, KOH	48	319	5.9	0.470

3. Experimental details

The electron microscope photographs were used to control the process of phase separation. The porosity of the samples $\Delta m/m$ was determined on the basis of change of the sample mass, which occurred in the process of obtaining the porous glass. The changes of the sizes of glass samples were measured with the accuracy of 0.005 mm using optical microscope equipped with a micrometry ocular. Except the electron microscope, the measurements of the adsorption-desorption of nitrogen at the temperature of liquid nitrogen and additionally the mercury porosimetry [5] were used for investigating the structure of porous glass.

4. Results and discussion

All the samples of the porous glass under investigation shrink as a result of annealing. The relative changes in the lengths of samples as a function of annealing time for different temperatures are shown in Fig. 1. The maximum changes of the linear size of samples $\Delta l/l$ obtained at adequately high temperature and at adequately long annealing time are simply connected with porosity of glasses, as shown in Tab. 2. From Figure 1 it can be seen that the speed of the shrinking of porous glasses A and B is higher than that of glasses C and D. This is in agreement with data given in paper [6], where it is shown that, in the first phase of thermal annealing of porous glass the smallest pores are melted.

Thermal treatment changes the internal structure of the porous glass. The microphotos shown in Fig. 2 and Fig. 3 allow us to observe the changes. They were made for the fresh fracture mirror in the plane perpendicular to the largest

Table 2. The porosity and maximum shrinking of the samples under investigation.

	A	B		C	D
Porosity $\Delta m/m$ [%]	38	54	68	38	48
Shrinkage $\Delta l/l$ [%]	16	25	31	16	20

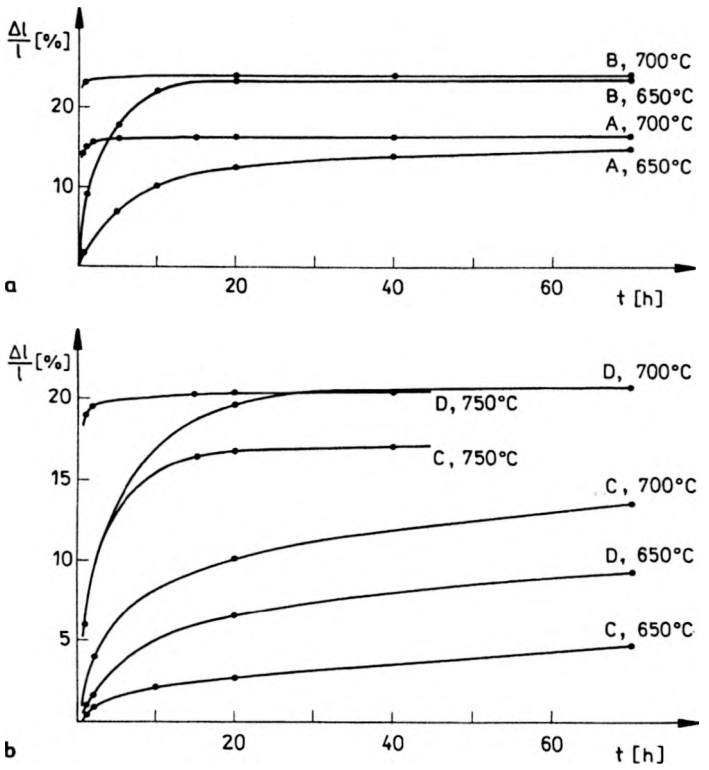

Fig. 1. Relative changes of the lengths of samples as a function of annealing time for different temperatures.

Table 3a. The apparent density ρ_p and total volume V_p of pores at different shrinkage temperatures for the heating time 0.5 h.

	550 °C		650 °C		700 °C		750 °C		800 °C	
	C	D	C	D	C	D	C	D	C	D
ρ_p[g/cm^3]	1.26	1.02	1.26	1.04	1.28	1.13	1.40	1.46	1.78	2.02
V_p [cm^3/g]	0.30	0.46	0.29	0.44	0.28	0.36	0.21	0.25	0.09	0.002
$\Delta m/m$ [%]	38.3	48.2	38.1	48.0	38.0	49.5	38.2	48.6	39.5	48.0

Table 3b. The apparent density ρ_p and total volume V_p of pores at different shrinkage temperatures and heating times.

		650 °C			700 °C		750 °C		
		10 h	20 h	70 h	2 h	70 h	1 h	2 h	15 h
C	ρ_p [g/cm^3]	1.30	1.32	1.38	1.37	1.78	1.39	1.64	2.06
	V_p [cm^3/g]	0.257	0.247	0.213	0.228	0.046	0.196	0.110	0.002
D	ρ_p [g/cm^3]	1.11	1.22	1.34	1.32	2.06	1.80	1.91	2.01
	V_p [cm^3/g]	0.353	0.314	0.260	0.238	0.009	0.027	0.019	0.000

Input parameters: C – $\Delta m/m = 38\%$, $\rho_p = 1.25$ g/cm^3, $V_p = 0.30$ cm^3/g;
D – $\Delta m/m = 48\%$, $\rho_p = 1.04$ g/cm^3, $V_p = 0.46$ cm^3/g;

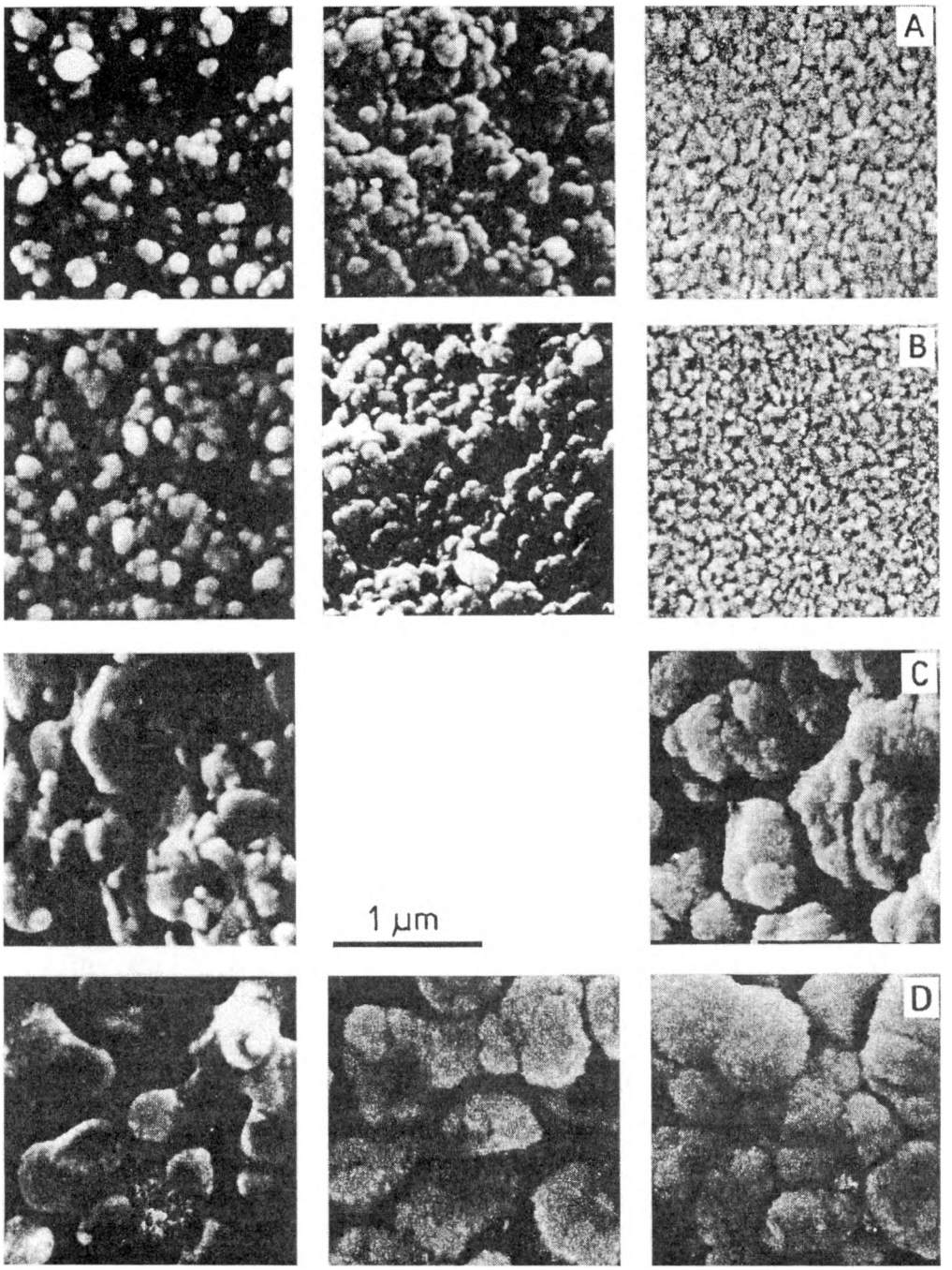

Fig. 2. Electron microphotographs for glasses A, B, C and D not heated (left side) and annealed at 650 °C (middle) and 700 °C (right side) for 0.5 h.

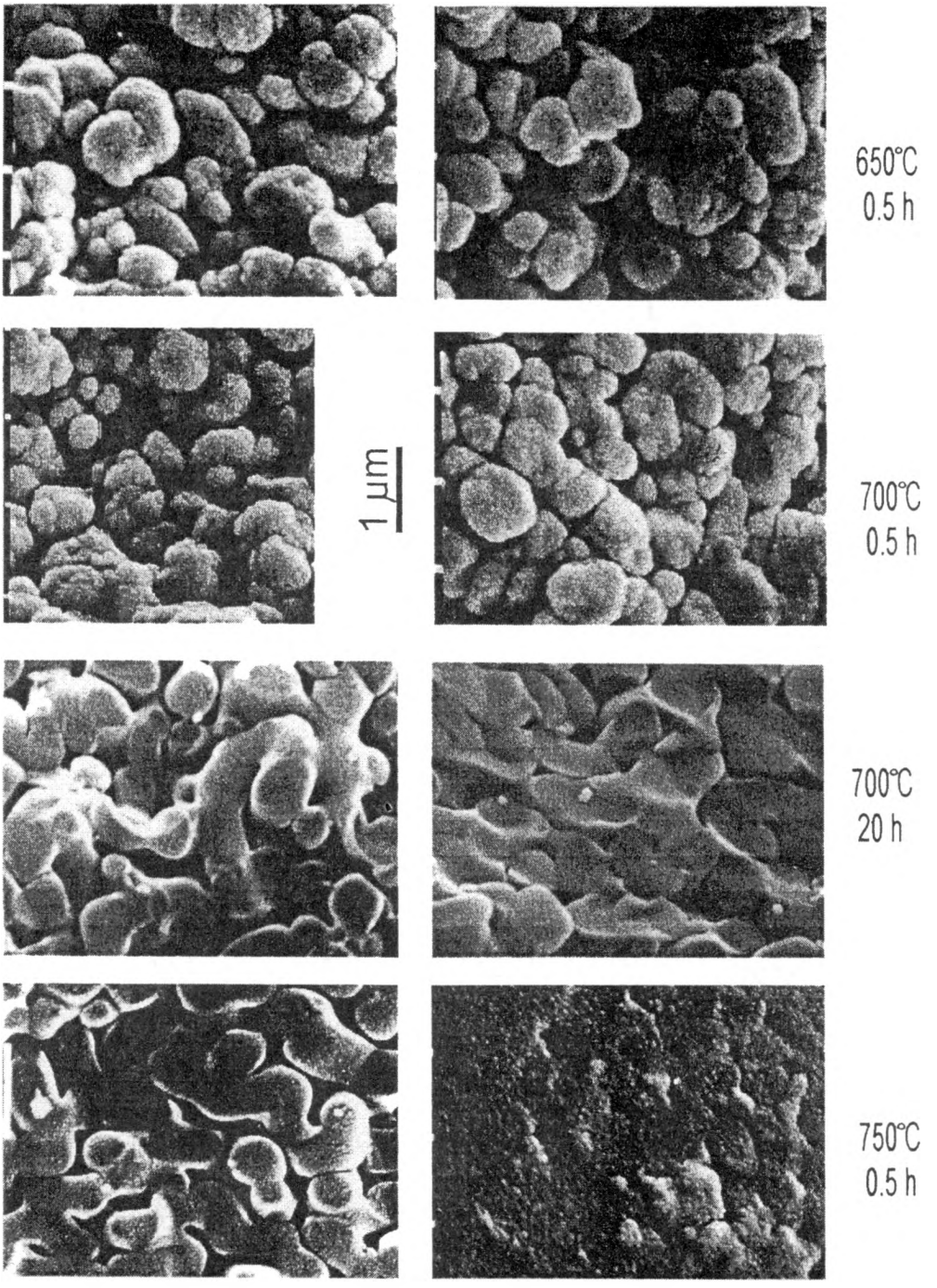

Fig. 3. Electron microphotographs for the thermally treated glasses C (left side) and D (right side).

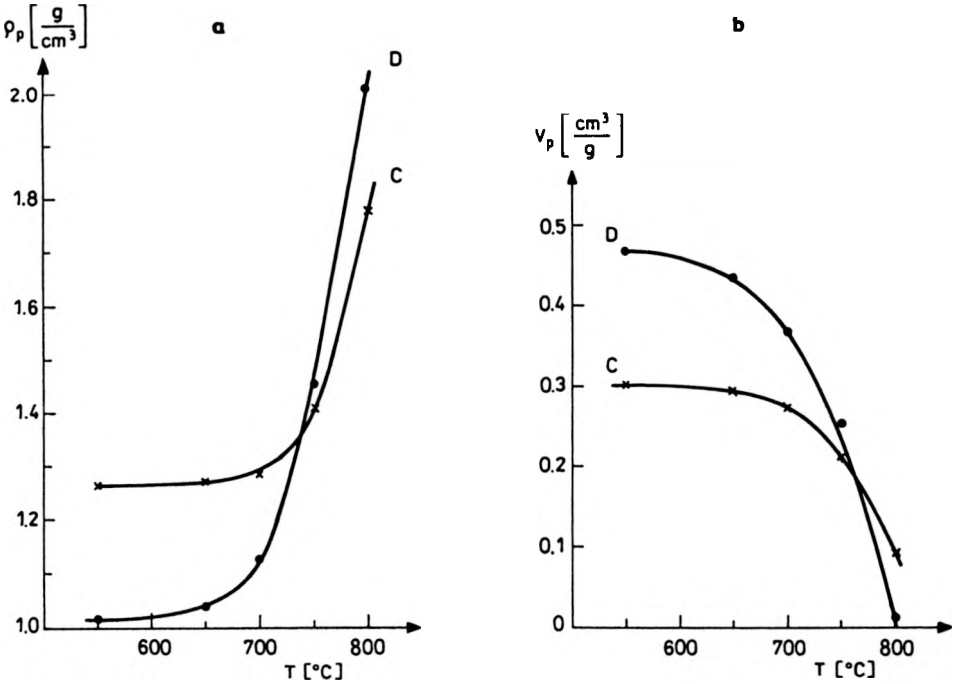

Fig. 4. Dependence of apparent density ρ_p (a) and total volume V_p (b) of pores on the annealing temperature for the heating time 0.5 h.

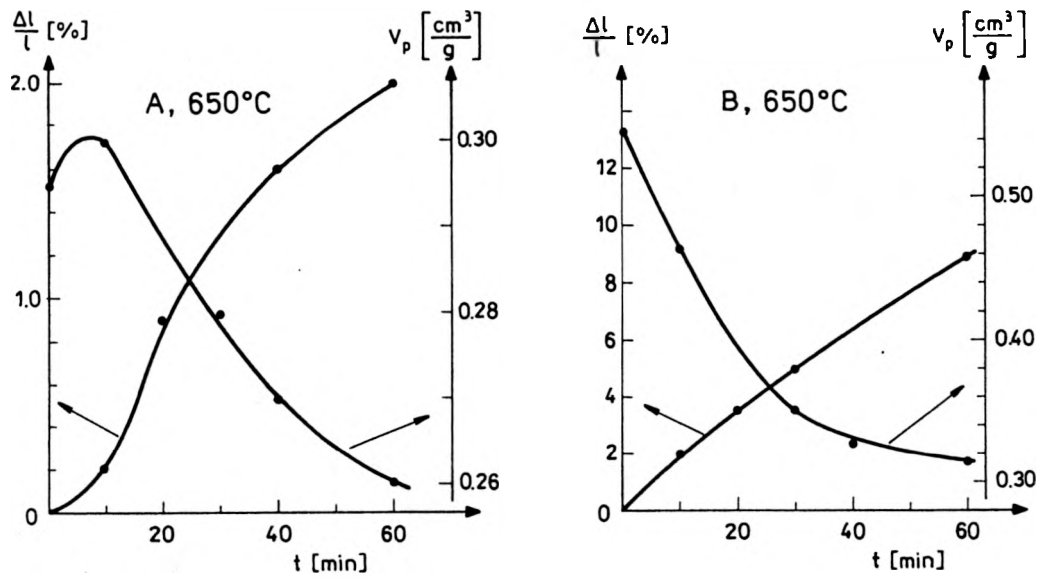

Fig. 5. Percent shrinkage and the total volume of pores for glasses A and B as a function of annealing time.

rectangular surface of the sample. There are three series of pictures of the porous glass shown in Fig. 2, *i.e.*, before thermal treatment, annealed for 0.5 h at 650 °C and annealed for 0.5 h at 700 °C. It can be seen that the processes of consolidation in all the glasses under investigation proceeded in a similar manner. An increase of the annealing temperature causes that granules of silica approach together and compose a carcass of glass that is more tightly packed. The space between granules decreses and apparent density increases (Fig. 4, Tabs. 3a and 3b). The consolidation process is slower in glasses A and C in comparison to their B and D equivalents. The difference perhaps results from the lower content of silica gel inside the pores of glasses A and C in comparison to glasses B and D, where gel was removed during chemical treatment in KOH solution. The presence of silica gel can explain a certain anomaly observed in the case of microporous glass A; namely, in the first few minutes of the annealing of glass A, the total volume of pores in the sample increases, despite that the linear size of the sample decreases (Fig. 5). The silica gel present in the pores of the microporous glas A probably consolidates considerably faster than the carcass of the glass, so there appears more free space inside the pores. The presence of some compounds of other elements in the silica gel, which cause the lowering of the melting temperature may be the reason of that phenomenon. The pores of very small "molecular" sizes in silica gel could give a similar effect. The fracture mirrors of glasses C and D thermally treated at 650 °C and 700 °C for 0.5 h show the spongy structure of carcass. This is seen from the microphotographs (Fig. 3). For samples heated for longer time or at a higher temperature the fracture mirrors of the carcass again are smooth.

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