

MACROPOROUS GLASS WITH P₂O₅ AND FLUORIDES CONTENT

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Abstract

The addition of P₂O₅ and fluorides to glasses in the Na₂O-B₂O₃-SiO₂ system has enlarged the phase separation region towards a low silica region, decreased the activation energy of volume diffusion during spinodal phase separation, accelerated considerably the phase separation process and influenced the composition of chemically less resistant phase. The chemical composition of high silica phase stayed almost without changes.

About 80 to 90 % of P₂O₅ and fluorides were displacing during the spinodal phase separation in the given system to alkali borate phase and it caused a considerable decrease of SiO₂ content in this phase. The acceleration of alkali borate phase leaching in acids and a significant suppression of secondary precipitation of the high-dispersion SiO₂ in pores, was the consequence of this effect. Therefore, the following leaching of this high-dispersion SiO₂ by alkali solutions during the macroporous glass preparation proceeded very quickly.

From a practical point of view the addition of P₂O₅ and fluorides to the initial glasses of the Na₂O-B₂O₃-SiO₂ system enabled the macroporous glasses preparation with a considerably higher mean pore size \bar{d} and in case of massive samples a greater wall thickness than in the original system without P₂O₅ and fluorides.

Key words: porous glass, pore size, phase separation, spinodal phase separation, activation energy, Na₂O-B₂O₃-SiO₂ system, additive, phosphorus(V) oxide, fluoride

I. INTRODUCTION

Under the term "porous glass" we usually mean materials prepared by leaching of chemically less resistant phase from a two-phase phase separated glass with interconnected phases. These materials can be divided according to pore size to macroporous (mean pore size above 7.5 nm) and microporous (mean pore size up to 7.5 nm). The macroporous glasses can be prepared in a form of crushed glass or massive samples (plates, tubes, rods) and they are used in practice as separator membranes or catalyst and enzyme carriers in biotechnology, medicine and technical chemistry [1].

Porous glasses are, however, very interesting from a scientific point of view as well, since it is possible to obtain by their study a lot of experimental and theoretical knowledge on processes of spinodal phase separation of glasses.

During preparation of macroporous glasses for biotechnology in the Na₂O-B₂O₃-SiO₂ system it was found in agreement with bibliography [1, 2] that in practice reachable maximum values of mean pore size of these glasses are in case of massive samples in a form of tubes approx. 100 nm and in case of crushed glass approx. 300 nm. The mean pore size is dependent, besides the chemical composition of the initial glass, on temperature and time of heat treatment. At high temperatures, however, an intensive surface crystallization occurs and the really usable temperature and time range are limited by it [3].

With the addition of P₂O₅ and fluorides to the initial glass as in the Na₂O-B₂O₃-SiO₂ system it is possible to accelerate the phase separation process considerably and to influence the composition of chemically less resistant phase, as well. The addition of P₂O₅ (without fluorides) in amount of 0.5 - 2 mol.% was used for accelerating the phase separation and leaching of Vycor type glass by Park [4].

II. EXPERIMENTAL PROCEDURES

Initial glasses for macroporous glasses preparation have been melted in PtRh crucible at 1400 °C and casted into blocks. The chemical compositions of these initial glasses are given in Table 1 [5].

Table 1 Chemical compositions of the initial glasses, types E to H (according to the chemical analysis in wt. %)

Component	E	F	G	H
Na ₂ O	8.95	8.65	11.9	10.3
B ₂ O ₃	29.8	33.6	35.5	37.1
SiO ₂	60.4	56.8	50.5	49.8
P ₂ O ₅		0.14	0.35	0.45
F		0.47	2.20	2.75

Heat treatment of the initial glasses has been carried out in an electrical furnace with an accurate temperature control at 577 °C/24 h, 604 °C/24 h and 633 °C/48 h. After the heat treatment a part of blocks was crushed to particle size ranging from 0.09 to 0.315 mm. Leaching of crushed glass was carried out in a solution of HCl, concentration 1 mol.dm⁻³ at a temperature of 62 °C. It was followed by leaching in 2 % solution of NaOH at 20 °C during 2 hours. Plates, wall thickness 2 mm were prepared from the heat treated blocks, as well, which were treated by leaching using a similar method.

In Table 2 the chemical compositions of the previous initial glasses, types A, C and D [6], are given where the kinetics of processes proceeding during the preparation [3], was studied in detail. Glass, type A with its chemical composition is close to the standard initial glass for the preparation of macroporous glasses marked 7/23 (mol. %) [2].

Texture parameters of prepared macroporous glasses were measured in the laboratory of the Mining Research and Safety Institute in Paskov, Czech Republic, using the mercury porosimetry (mean pore sizes \bar{d} , width of the pore size distribution curve H_d, pore volume V_H and V_p) and nitrogen adsorption (specific surface area A_p).

A more detailed description of the methodology of texture parameters determination was published separately [7]. In Table 3 the texture parameters of crushed macroporous glasses, types E to H prepared of the initial glasses after the heat treatment at 633 °C/48 h, are summarized.

The chemical analyses have been carried out in the laboratory of the Glass Institute. The results of chemical analyses of leached macroporous glasses, types A, C and D prepared from the initial glasses after the heat treatment at 600 °C/24 h, 602 °C/24 h and 606 °C/24 h, respectively, are given in Table 2.

Table 2 Chemical composition of the initial and leached glasses (according to the chemical analysis in wt.%), pore volume V_p (in vol.%) and calculated chemical composition of the acid soluble phase after the heat treatment of the initial glass

	A	C	D
Initial glasses			
Na ₂ O	6.55	6.41	6.47
B ₂ O ₃	26.7	25.8	25.3
SiO ₂	66.2	67.0	66.4
P ₂ O ₅		0.22	0.55
F		0.32	1.52
Leached glasses			
Na ₂ O	0.11	0.11	0.17
B ₂ O ₃	7.09	7.00	7.48
SiO ₂	92.8	92.8	92.2
P ₂ O ₅		0.03	0.05
F		0.06	0.25
V_p	54.4	48.5	41.0
Soluble phase			
Na ₂ O	12.0	13.2	15.6
B ₂ O ₃	43.4	46.0	51.2
SiO ₂	44.6	40.1	30.0
P ₂ O ₅		0.4	1.3
F		0.6	3.4
corr. to F content		-0.3	-1.5

Table 3 Texture parameters of crushed macroporous glasses (heat treatment of the initial glasses at 633 °C/48 h)

Parameter	E	F	G	H
\bar{d} [nm]	114.1	181.5	350.3	425.9
H_d [%]	6.1	3.8	4.2	7.9
V_H [cm ³ .g ⁻¹]	0.668	0.522	0.825	0.531
V_p [%]	59.5	53.4	64.5	53.9
A_p [m ² .g ⁻¹]	26.2	12.8	12.4	6.9

III. RESULTS

From the chemical composition of leached glasses, types A, C and D and from the pore volume an approximate chemical composition of the acid soluble phase, was calculated. The calculation results are given in Table 2.

For the description of the mean pore size \bar{d} dependence on temperature and time of heat treatment of the initial glass, an equation (1) for the growth of two-phase phase separated glass texture, corresponding to the process controlled by volume diffusion, was used [8]. The validity of this equation for glasses, types A, C and D was verified experimentally [3].

The form of equation used:

$$\bar{d}^3 = K_d \cdot \tau \cdot \exp(-E_d/RT) \quad (1)$$

where: K_d - proportionality factor [$\text{nm}^3 \cdot \text{h}^{-1}$]

τ - time [h]

E_d - activation energy of diffusion [$\text{J} \cdot \text{mol}^{-1}$]

R - gas constant [$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$]

T - absolute temperature [K]

Using the temperatures and times of heat treatment of the initial glasses and experimental values \bar{d} corresponding to them, determined by mercury porosimetry, the parameters of the equation (1) were calculated. Found values of activation energies E_d of a volume diffusion during phase separation, are given in Table 4.

Table 4 Values of activation energies E_d of a volume diffusion during phase separation (in $\text{kJ} \cdot \text{mol}^{-1}$)

	A	C	D	E	F	G	H
E_d	311.8	289.3	251.2	380.2	335.4	333.8	296.6

validity range: types A, C and D 550 to 660 °C, 24 to 150 h; types E to H 577 to 633 °C, 24 to 48 h.

IV. DISCUSSION

A comparison of the chemical composition of leached glasses, types A, C and D showed that the influence of P_2O_5 and fluorides content in the initial glass on the final composition of high silica phase was minimal and that about 80 to 90 % of P_2O_5 and fluorides were displaced during the spinodal phase separation to the alkali borate acid soluble phase.

The calculation results of the approximate chemical composition of the acid soluble phase in glass, type A (Table 2) gave a little higher value of the SiO_2 content in comparison with the published value, obtained with glass with similar chemical composition (heat treatment at 600 °C/123 h, after recalculation to wt. %: 13.7 Na_2O , 48.1 B_2O_3 , 38.2 SiO_2) [9]. The apparently higher SiO_2 content in the acid soluble phase of glass, type A can be probably explained by a longer effect of the NaOH solution to glass during leaching and, therefore, the dissolution of a certain amount of

high silica phase. A considerable dependence of the SiO₂ content decrease in the acid soluble phase (and the decrease of the total pore volume connected with this) with increasing P₂O₅ and fluorides content in the initial glass, was very interesting, indeed. By plotting the obtained values of both mentioned phases chemical composition into a phase diagram with a course of tie-lines in the Na₂O-B₂O₃-SiO₂ system [9], was observed that a considerable enlarging of the phase separation region to the lower SiO₂ content occurred by P₂O₅ and fluorides addition to the initial glass. The direction of tie-lines was the same.

An acceleration of this phase leaching in acids [3] which corresponds to results published by Antropova [10] was in a direct consequence the of SiO₂ content decrease in alkaliborate phase, as well.

Another effect observed was a considerable decrease of secondary precipitation of high-dispersion SiO₂ in pores during the leaching process in acids. The mechanism of suppression of this effect is not known but it is very probably caused by HF and H₃PO₄ acids released during the decomposition of the alkaliborate phase in the course of acid leaching.

A suppression of secondary high-dispersion SiO₂ precipitation was presented by a very considerable decrease of time necessary to its following dissolution in NaOH solution [3], as well. The preparation of massive samples of macroporous glasses, wall thickness up to several millimeters, is enabled by this process. In the course of macroporous glasses preparation from the initial glasses of the original Na₂O-B₂O₃-SiO₂ system, the velocity ratio of secondary high-dispersion SiO₂ dissolution in pores and a high silica phase in NaOH solution is much more disadvantageous and, therefore, the reachable wall thickness of massive samples is limited.

The activation energy values of volume diffusion E_d during the phase separation (Table 4) show a significant decrease with an increasing P₂O₅ and fluorides content in the initial glasses. The phase separation is proceeding quicker with an increased P₂O₅ and fluorides content and the resulting mean pore size \bar{d} is considerably greater under corresponding conditions of heat treatment.

Using the equation (1) it is possible to determine by interpolation the conditions of heat treatment of the initial glass reliably and to reach the required pore size \bar{d} . By extrapolation (with regard to limiting factors, especially the surface crystallization of glasses at higher temperatures) it is possible to calculate a reachable range of mean pore sizes \bar{d} , as well. The real expectable ranges of mean pore sizes \bar{d} for the used initial glasses, are given in Table 5.

V. CONCLUSIONS

About 80 to 90 % of P₂O₅ and fluorides are displacing during the spinodal phase separation in the Na₂O-B₂O₃-SiO₂-P₂O₅-fluorides system to the alkaliborate phase and a considerable decrease of the SiO₂ content in this phase is thus caused. The chemical composition of the high silica phase, is practically not influenced, indeed. In the phase diagram it results in an enlarged region of phase separation towards the low silica region, the direction of tie-lines is the same.

The P₂O₅ and fluorides content in the initial glass causes a decrease of the activation energy of volume diffusion at spinodal phase separation, a considerable

acceleration of the phase separation process and increasing the linear dimensions of regions formed.

The alkaliborate phase leaching in acids is proceeding quicker with respect for a lower SiO₂ content in this phase and the secondary precipitation of high-dispersion SiO₂ in pores is significantly limited. A mechanism of this effect is not known but a considerable influence of HF and H₃PO₄ released during the decomposition of alkaliborate phase in the course of acid leaching, is supposed. In a consequence of this effect the following leaching of this high-dispersion SiO₂ by alkali solution during the preparation of macroporous glass, is much quicker.

Table 5 Real expectable ranges of mean pore sizes \bar{d} of macroporous glasses reachable for the individual initial glasses (a) and their comparison with experimentally prepared samples (b)

Initial glass		\bar{d} [nm]		
		crushed glass	plates	tubes, rods
A	a	10 - 180	15 - 150	15 - 85
	b	12 - 93	n	16 - 68
C	a	20 - 250	20 - 210	20 - 120
	b	21 - 198	71 - 124	27 - 97
D	a	30 - 350	35 - 300	35 - 170
	b	40 - 278	278	35 - 143
E	a	10 - 230	15 - 170	15 - 75
	b	30 - 114	30 - 114	n
F	a	25 - 350	30 - 270	30 - 120
	b	55 - 183	55 - 183	n
G	a	50 - 670	55 - 500	55 - 230
	b	105 - 350	105 - 170	n
H	a	70 - 800	75 - 600	75 - 300
	b	143 - 427	143 - 220	n

n - not prepared

From a practical point of view the addition of P₂O₅ and fluorides into the initial glasses of the Na₂O-B₂O₃-SiO₂ system enables the preparation of macroporous glasses with a considerably greater mean pore size \bar{d} and in case of massive samples a greater wall thickness than at the original system without P₂O₅ and fluorides. There were prepared experimentally samples of crushed glass, plates and tubes with \bar{d} up to 427 nm, 278 nm and 143 nm, respectively, and a pore volume ranging from 35 to 65 %. After optimization of conditions it is possible to expect reaching of mean pore size \bar{d} up to 800 nm in case of crushed glass, up to 600 nm in case of plates and up to 300 nm in case of tubes, by the given initial glasses in the Na₂O-B₂O₃-SiO₂-P₂O₅-fluorides system.

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