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Study of the chemical stage of the phase-separated sodium borosilicate glass leaching process and the porous glass structure*

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The chemical stage of the leaching process of the phase-separated sodium borosilicate (SBS) glasses has been investigated. The main resutls were received at the single-phase SBS glasses the composition of which being identical to that of unstable phase (UP) of the phase-separated SBS glasses. It has been found that the B_2O_3/SiO_2 molar ratio values in those glasses influence the equilibrium concentrations of the glass components. According to X-ray diffractometry the relative amount of crystalline phase in the precipitates produced on leaching of the glasses with acid increases with increasing B_2O_3/SiO_2 molar ratio in the glasses. The correlation between the temperature dependence of the structure resistance coefficient and porous glass (PG) optical characteristics has been found.

1. Introduction

Our model of the phase-separated SBS glasses is schematically shown in Figure 1. This model was considered in detail in paper [1] (see also [2]). It is an elaboration of the ideas whose foundation was laid by Hood and Nordberg, USA, and Grebenshikov and his followers, USSR, (see review in [3]).

Figure 1 schematically shows the section of the boron-rich unstable phase channel of the phase-separated SBS glasses for the case of the single-direction diffusion (a), the equilibrium values of the solubility of both UP components and acid in the reaction zone and in the external solution (b), the pH gradient in porous layer (PL) depending on the concentration of acid which reacts with the glass (c).

In imitation the chemical stage of the leaching process is implied mainly in the process of the dissolution of the UP components in acid, the rate of which is influenced by such factors as the diffusion of both acid and dissolving products of glass dissolution through the PL, and the silicagel formation of the silica forming a part of UP. It is well known that the PG structure parameters are conditioned by the structure of this gell.

Let us consider the case when the leaching process is not limited by the diffusional process inside PL that is when both the dissolution of the UP com-

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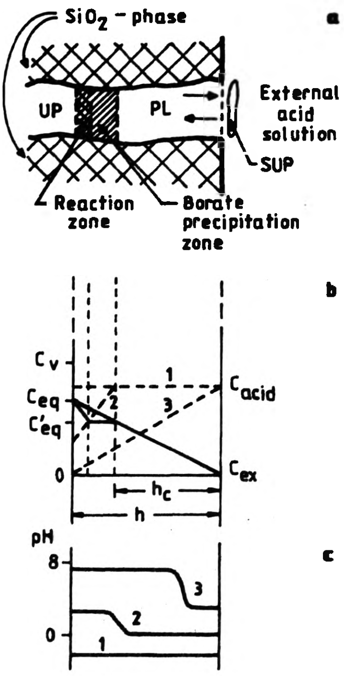


Fig. 1. Scheme of the leaching process of the phase-separated sodium borosilicate glasses. SUP — the sample surface square engaged by unstable phase (for explanation, see text, and [1], [2])

ponetns and the diffusional extraction through PL result from relative rates which are compared with each other.

If the chemical reaction stage relative rate is compared with the diffusional stage relative rate, the concentration gradient of the dissolved UP components in the PL is equal to C_{eq}/h (if $C_{ex} \ll C_{eq}$), the rate line $C_{eq}-C_{ex}$ in Fig. 1b, where C_{eq} — the equilibrium concentration of glass components, C_{ex} — its concentration in the external solution, h — the PL thickness value found by using an optical microscope. In this case, the reaction zone is not supersaturated by sodium and boron containing products. The kinetics of the PL thickness is described by the following equation [1], [2]:

$$h = [2Dt/(C_v/C_{eq}-0.5)]^{1/2} \tag{1}$$

where D — diffusional coefficient, t — time, C_v — volume concentration of the UP components. This equation presents the substance extraction kinetics from the small diameter capillary [2]. In this case, the values of h and h_c are agreed (h_c — PL thickness values calculated accordingly to the quantity of the extracted UP components).

Now let us consider the other case, namely the case when the leaching process is limited by diffusional processes inside PL. In this case, the reaction zone solution is supersaturated with respect to the hard dissoluble boron-containing products including the crystalline ones [4]. These products may precipitate inside PL, for example, near the reaction zone. The delay of the UP components inside PL gives rise to lag of PL thickness value h_c with respect to the h. The formation of the boron-containing precipitates breaks the linear dependence between both the stream of dissolved substances and the gradients of their concentrations through PL (the broken line $C_{eq}-C'_{eq}-C_{ex}$ in Fig. 1**b**, where C'_{eq} – equlibrium concentration of the boron-containing precipitate (crystalline hydrate)).

The possibility of the crystallization of the boron-containing products inside PL was first confirmed thermodynamically and roentgenographically (X-ray) in collaboration with SHAKMATKIN and POLYAKOVA [4] during the investigation of the so-called model glasses. Now, we have the data received from PG samples by electron diffraction method which evidenced such crystallization about which we may judge on the base of the dot reflexes recorded on electronograms (Fig. 2).

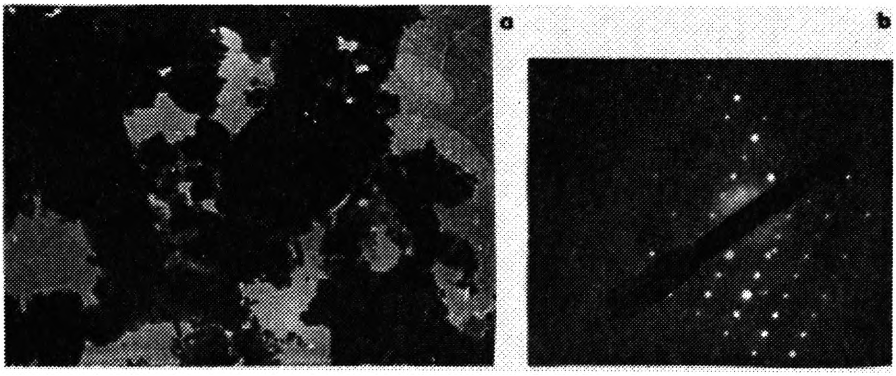


Fig. 2. Electron micrographs of the powder particles from porous glass samples received in 1 M HCl at 100 °C (**a**) and the electron diffractograms of these particles (**b**)

This work having being done in collaboration with DROZDOVA [5] is now in progress. Depending on concentrations of an acid as well as sodium and boron in the reaction zone, certain pH gradient arises in PL (Fig. 1c). In this case, the pH value in the reaction zone can sharply exceed the pH value of the external solution owing to the sodium-boron buffer effect.

2. Experimental part

So-called model glasses are the single-phase SBS glasses being identical in composition with the UP of the phase-separated SBS glasses most often used in practice to produce the PG [3]. The compositions of the model glasses under investigation are listed in the Table and shown in Fig. 3 [6], [7].

It may be assumed that the concentration of the UP components in the solution near the reaction zone is caused by the composition of this phase because of the different stability of its structural elements as regards to hydrolysis and hydration reactions [6]. Figure 4 demonstrates the influence of the B_2O_3/SiO_2 molar ratio in model glasses on the concentration values. It is shown that an increase in this ratio causes a reduction in chemical durability of these glasses, especially if immersed in a more concentrated acid.

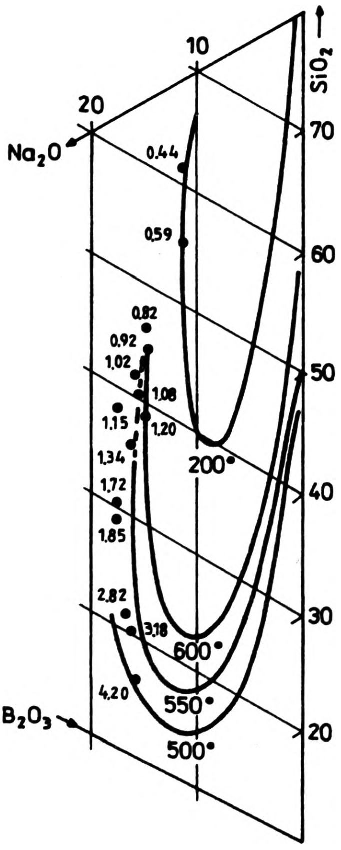


Fig. 3. Part of the immiscibility diagram of the $Na_2O-B_2O_3-SiO_2$ system. Dots represent the compositions of the single-phase SBS glasses under study. Near the dots the B_2O_3/SiO_2 molar ratio values are shown

T a b l e. Composition of single-phase sodium borosilicate glasses

Glass number	Analysed composition [mol %]			Molar ratio	
	Na_2O	B_2O_3	SiO_2	B_2O_3/SiO_2	Na_2O/B_2O_3
1	11.6	27	61.4	0.44	0.43
2	11.84	32.63	55.53	0.59	0.36
3	14.8	38.3	46.9	0.82	0.39
4	14.25	41.02	44.73	0.92	0.34
5	16.01	42.44	41.55	1.02	0.38
6	16.13	43.55	40.32	1.08	0.37
7	17.25	44.26	38.49	1.15	0.39
8	14.45	46.59	38.96	1.2	0.31
9	16.41	47.79	35.8	1.34	0.34
10	18.1	51.84	30.06	1.72	0.35
11	17.92	53.21	28.87	1.85	0.33
12	17.01	61.98	21.78	2.82	0.28
13	16.09	63.86	20.05	3.18	0.25
14	15.09	68.25	16.66	4.2	0.22

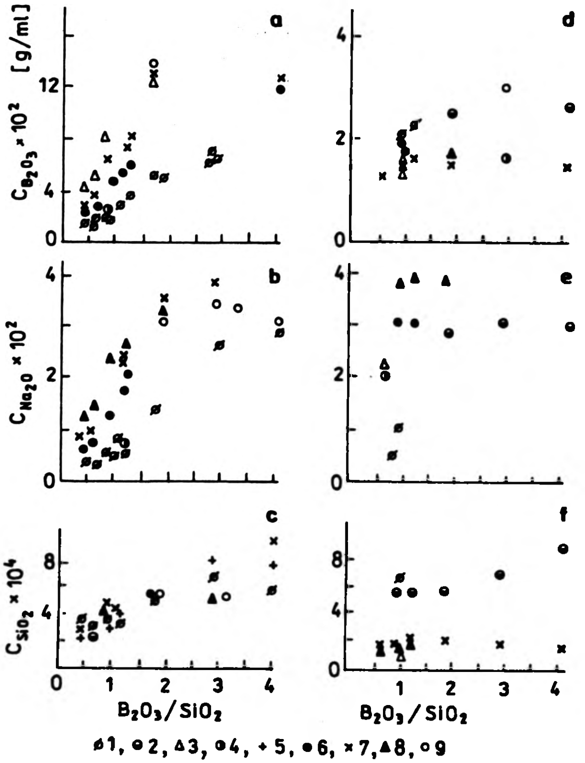


Fig. 4. Values of equilibrium solubility of the components of the single-phase SBS glasses (powder, SA/V = (130–150 cm)$^{-1}$) in acid solutions at 20 °C *vs.* B_2O_3/Si_2O molar ratio in glass. HNO_3 concentration, M: (a–c) — 0.1, (d–f) — 3.0. Time of interaction of the glass with acid in days: 1–1, 2–5, 3–7, 4–9, 5–17, 6–25, 7–55, 8–65, 9–200

According to ZHDANOV *et al.* [8], an increase in the number of boron-oxygen links reduces the stability of the glass immersed in the acid owing to the formation of a less compact silica skeleton. Moreover, the structural elements $[BO_{2/3}]$ and $[BO_{4/2}]^-$ pass into solution at different rates because they are hydrated by different mechanisms. The $[BO_{3/3}]$ elements are hydrated by the energetically more advantageous acceptor-donor mechanism, and the $[BO_{4/2}]^-$ elements are hydrated with the rupture of the more conservative pH^3-hybrid bonds [9].

Figure 5 demonstrates the influence of the B_2O_3/SiO_2 molar ratio on the relative intensities I_{rel} of the characteristic peaks for the crystalline H_3BO_3 phase that is formed in the products when the model SBS glasses are leached in 3 M acid (HCl, HNO_3) solutions at 20 °C and the precipitates are additionally dried at 70 °C for 16 hours (Fig. 5a). (Noteworthy, the crystalline borate phase is present in appreciable amounts in the just-formed ("wet") precipitates, as well [4]). The tendency for the I_{rel} in H_3BO_3 to increase the B_2O_3/SiO_2 molar ratio in the glass correlates, according to TGA, with the concurrent loss of weight by precipitation due to heating (curves 1, 3 in Fig. 5b) and with an increase in corresponding endothermic effects according to DTA (curves 2, 4 in Fig. 5b).

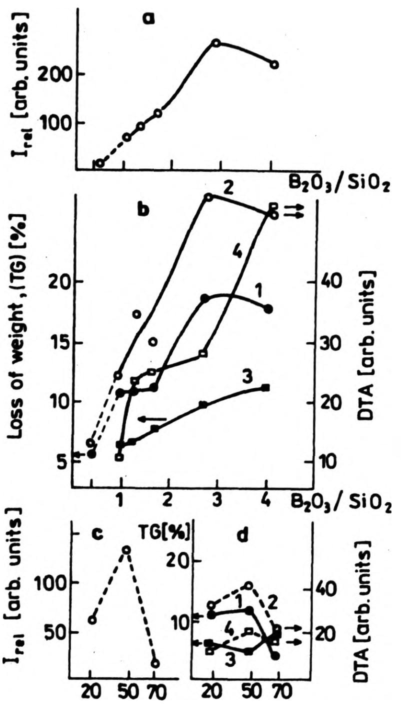


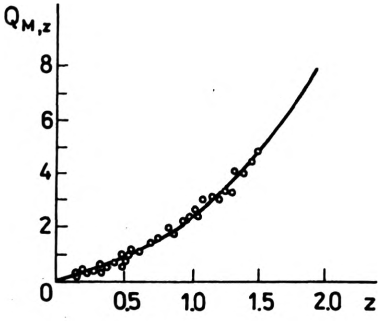
Fig. 5. Amount of crystalline H_3BO_3 observed by X-ray diffractometry (relative intensity I_{rel} in arb. units) in precipitated products of leaching of the model glasses in HNO_3 solutions (a, c), thermogravimetric loss of weight (TGA, %) and the associated endothermic effects (DTA, peak height in arb. units upon heating of the precipitates to 400 °C (b, d), plotted against glass composition at 20 °C (a, b) and temperature of 3 M HNO_3 (c, d). b, d – loss of weight and DTA effects associated with decomposition of H_3BO_3 (1, 2) and dewatering of samples (3, 4); c, d – glass No. 5 ($B_2O_3/SiO_2 = 1.02$). Method: TGA – 1, 3; DTA – 2, 4

When the solution is saturated with glass components, any one or two forms can be in equilibrium with the liquid phase, depending on the glass composition and the condition of leaching in acid. These forms can be either composed of boron-rich gel-like product (a concentrated sol) and a solid residue with crystalline inclusions, which are crystalline hydrates of alkali borates (in the case of a dilute acid) or boric acid (in the case of a concentrated acid) [7].

With a fixed B_2O_3/SiO_2 ratio the temperature dependences of the relative amount of the crystalline phase in the products of the glass leaching formed in the temperature range 20–70 °C pass through maximum at 50 °C (Fig. 5c). It has been observed that the endothermic effects which occur during heating the precipitated products take on maximum values when the glasses are leached at 50 °C and that the loss of weight by these precipitates tends to decrease when the leaching temperature is higher than 50 °C (Fig. 5d).

It may be shown that in a number of the cases the leaching process of the phase-separated SBS glasses proceeds in a mixed diffusional-and-kinetics region [10]. Also it may be shown that the well known concept of interdiffusion facilitated by the hydrolysis of the glass network [11] is applicable to the mechanism of the acid leaching of single-phase SBS glasses that is the leaching of the UP of phase-separated SBS glasses [10]. Figure 6 illustrates such an applicability of the concept mentioned above.

Let us consider the other problem that is the problem of PG structure. The pH gradient and the boron-containing crystalline hydrates precipitation inside PL in



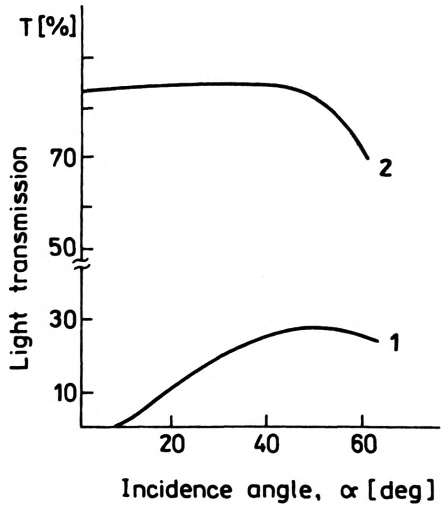


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Fig. 6. Quantity of the $Q_{M,z}$ ($Q_{M,z}$ is the dimensionless yield) sodium and boron extracted from single-phase SBS glasses by acid solution (HNO_3) *vs.* dimensionless time of acid treatment z (calculation is carried out according to procedure described in [11]). Solid line is theoretical curve [11]

Fig. 7. Light transmission (T, %) as a function of the incidences angle α of a laser beam (wavelength 632 nm) on the disks (thickness 2 mm, diameter 20 mm) of porous glasses produced by face-to-face HCl treatment of two-phase SBS glass the composition of which (according to synthesis, mol. %) is: $8N_2O \cdot 22B_2O_3 \cdot 70SiO_2$. HCl concentration, M: **1** – 1.0, **2** – 3.0. Temperature: **1** – 100 °C, **2** – 50 °C

the course of the glass treatment create the special conditions for the PG structure formation owing to expense of the silicagel formation process. Now, it is well known that two main kinds of inhomogeneities in PG are found experimentally (see reviews of the works by Dobychin, Altschuller *et al.* in [3]). These are the so-called strata or flaky sediments of the silicagel in the planes parallel to the faces of the PG sample (from our works see, for example, [12]) and so-called spindle-like silica inhomogeneities arranged perpendicularly to the face of the samples (see, for example, [13]). Both kinds of silica inhomogeneities formation were interpreted according to our model in paper [1]. Here, it should be only mentioned that we connect stratum formation with the pH gradients inside PL, and spindle-like inhomogeneities formation connected with boron-containing products precipitation inside PL.

In collaboration with KRYLOVA [13], it was shown that for spindle-like inhomogeneities acting as optical waveguides to form in the PG, the solution in the reaction zone should have a pH value of about 5–8. For thin glass samples (of 2–3 mm thickness), such conditions can be provided by treating them with 0.1–2 M acid solutions. Figure 7 shows typical dependencies of the light transmission (T, %) *vs.* the incidence angle α of a laser beam on disk of PG for different regimes of PG production.

It should be noted that inside PL (in the central part of samples) dense regions were detected whose structure and orientation with respect to front-junction layer is governed by the conditions under which PG samples have been produced, Fig. 8

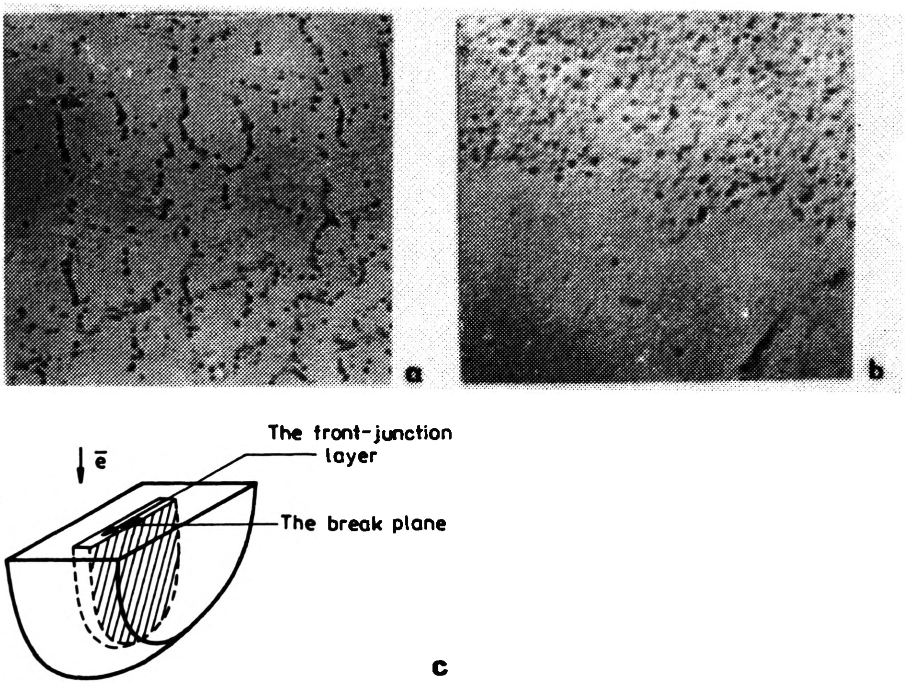

Fig. 8. Electron micrographs of near the central part of the samples produced in 1 M HCl at 100 °C (a) and 3 M HCl at 50 °C (b). The electron beam is incident parallel to the major faces of the samples. The diagram of fracture planes and investigated area in the glass (c)

[5], [14]. In the PG samples possessing waveguide properties these regions are threated by less dense structures (oriented at right angle to the major faces of the samples) of a diameter comparable with that of the phase-separated channels filled by the UP of the two-phased glasses.

The PG structure parameters were investigated not only by electron microscopy methods but also by colloid chemistry methods in collaboration with Sidorova and Ermakova. These parameters were investigated by the study of the structure

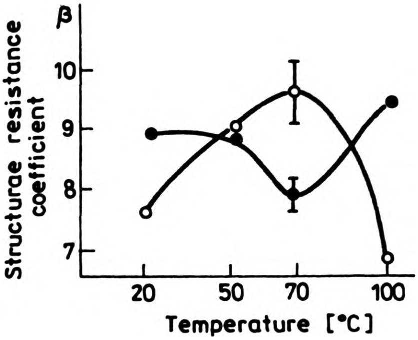

Fig. 9. Resistance coefficient values *vs.* the temperature of the acid solutions in which porous glass samples were produced

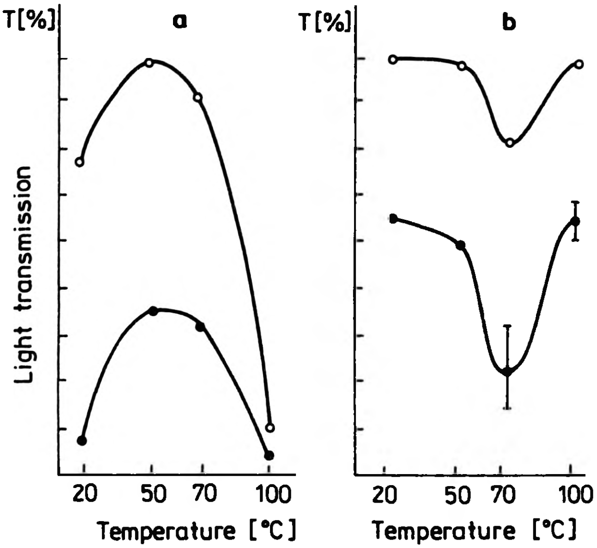

Fig. 10. Light transmission (*T*, %) of porous glass samples as a function of acid solution temperature. HCl concentration, M: **a** — 1.0, **b** — 3.0 (for different wavelengths)

resistances coefficient values by means of electrical conductivity method [15]. Figure 9 demonstrates the structure resistance coefficient dependencies on the temperature of the acid solution which contacts with phase-separated SBS glasses. In Figure 10, light transmission values are adduced in dependence on acid solution temperature, also. It should be noted that there is a correlation between the results in those two figures.

3. Conclusions

The chemical stage of the phase-separated sodium borosilicate glasses subject to acid leaching is investigated using the samples of the single-phase SBS glasses the composition of which being identical to the unstable phase of two-phase glasses.

It was found that the glass composition influenced the equilibrium concentrations of glass components in the solution, as well as the quantity and hydration degree of the crystalline phase in the products of the interaction between SBS glass and acid.

By means of electron microscopy methods it was shown that the dense silica regions exist inside the porous glasses. Part of this silica can crystallize near the front-junction layer mainly.

Structure parameters of porous glass such as its structure resistance coefficient values were investigated by electrical conductivity method. The correlation between the temperature dependencies of the values mentioned above and light transmission values of porous glass has been found.

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