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THE MICROSTRUCTURE AND OPTICAL TRANSMITTANCE THERMAL ANALYSIS OF SODIUM BOROSILICATE BIO-GLASSES

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Abstract

The conditions to fabricate the bulk porous specimens have been studied on account of sodium borosilicate (NBS) glasses. Glass composition, heat treatment at phase separation and TiO_2 addition have been considered in this study. Original glass samples of composition in mol%: sample A: 9.19 Na_2O – 23.58 B_2O_3 – 67.23 SiO_2, sample B: 9.29 Na_2O – 3.17 TiO_2 – 23.82 B_2O_3 – 63.72 SiO_2 were prepared by melting reagent grade chemicals (Na_2CO_3, HBO_3, SiO_2 and $AgNO_3$) in platinum crucibles at 1480°C for 1 h in air. The melts were poured onto stainless steel plates and were annealed at 500°C for 0.5 h after cooling. Thus, obtained samples were phase separated at 700°C for 2, 15, 25 and 50 h to study their microstructure by scanning electron microscope (SEM). Besides the direct study of the microstructure by SEM, information on glass structural changes of samples are provided by measuring in situ changes by the optical transmittance thermal analysis. The isothermal measurements were carried out at 700, 720 and 740°C. The temperature of phase separation, the leaching and nucleator addition (TiO_2), significantly influence the microstructure of the resulting leached product. TiO_2 additive seems to suppress crystallization of cristobalite: especially at the extended above heat treatment phase separation runs. The phase-separated domains of glasses containing above 80 moles of SiO_2 are so small that it is very hard to observe them by SEM. The glass composition in our case was selected in a way to have relatively large phase separated areas easily observed by SEM at magnification 20 000·. The influence of TiO_2 is not too pronounced. It seems to suppress the cristobalite crystallization, especially of longer heating runs. The image analysis of leached glasses shows the prevailing content of the skeletal phase in a comparison to pores. The TiO_2 content diminishes the content of the skeletal phase.

Keywords: microstructure, optical microscopy, optical transmittance thermal analysis, SEM, sodium borosilicate bio-glasses

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Introduction

Porous glasses, such as sodium borosilicate glasses are very important from biological point of view due to their utilization in medicine as a soft porous filter as well as a protector from corrosion. Phase separation, in a spinoidal separation region (Figs 1 and 2), is used in a well-known process for making special porous and non-porous glasses [1–3]. In this process, a sodium borosilicate glass melt cooled below its liquidus temperature separates into two intertwined phases: a phase soluble in acid solutions, and insoluble phase. Leaching of phase-separated glass in acid solution removes the acid-soluble phase leaving behind a porous glass consisting of the insoluble phase. The pore size of the remaining phase depends on the composition of the original glass and on the subsequent heat treatment (Figs 1, 2 and 3). The porous glasses have industrial utilization as a nanofiltration membrane [4]. VYCOR porous glass is mechanically hard and strong, nondusting, nonflaking, and chemically inert. These properties permit it to be employed as a noncontaminating getter since it rapidly absorbs water and organic contaminants. VYCOR porous glass (fy Corning) is often used for filtration and separation of compounds. The open-cell network allows permeability on a selective basis. The species must be smaller than the microscopic pores to pass through the porous glass. (The homogeneous pore diameters can be controlled to average between 4 and 20 nm). Advantages of VYCOR porous glass for filtration include rigidity, chemical inertness, high temperature capability (up to 600°C), superior thermal shock resistance (up to 600°C when dry), and controlled microporosity. These advantages allow higher processing temperatures, back flushing or burnout cleansing and processing of most corrosive products. Many authors have investigated biomaterials including porous glasses and also examined their structural, thermal, electrical and biological properties [5–7]. The aim of this study is to synthesize new bio-glasses, and study the influence of TiO_2 addition, the leaching with HCl and HF, microstructure, the temperature of phase separation as well as the presence of communicative pores with an assessment of their size by optical microscopy.

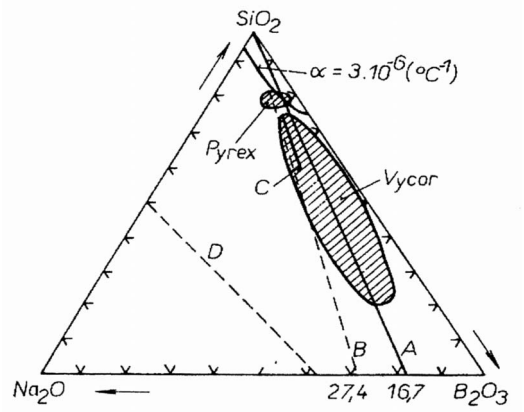

Fig. 1 Phase diagram of the system Na_2O-B_2O_3-SiO_2 [1]

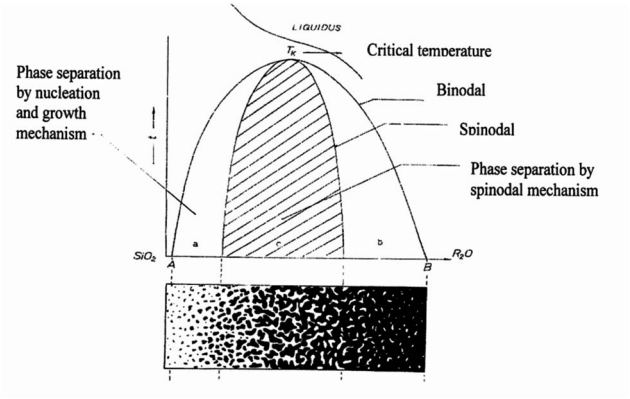

Fig. 2 The nature of the phase separated areas in relationship to mechanism of phase separation [2]

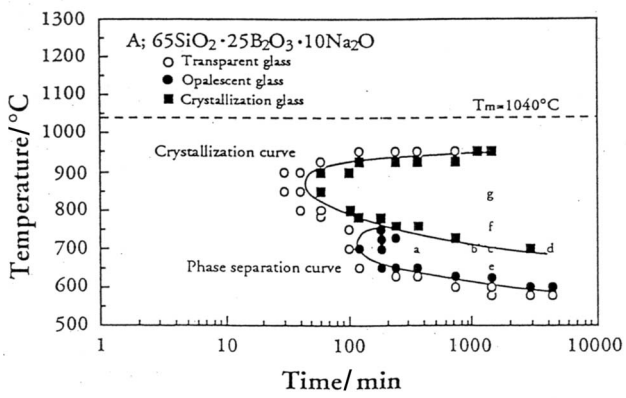

Fig. 3 TTT diagram (time – temperature – transformation) for the composition A

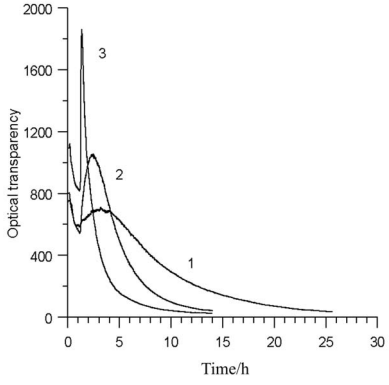

Fig. 4 In situ changes in the optical transmittance thermal curves of samples, treated isothermally 700 (1), 720 (2) and 740 (3)°C

Experimental

Glass preparation

Original glass samples A and B (Table 1) were prepared by melting reagent grade chemicals (Na_2CO_3, H_3BO_3, SiO_2, TiO_2) in platinum crucibles at 1480°C for 1 h in air. The melts were poured onto stainless steel plates and after cooling they were annealed at 500°C for 0.5 h. No phase separation was observed after glass annealing (SEM on etched samples). Thus obtained glasses were cut to square slabs (10·10·2 mm) and heat treated at 700°C for 2, 15, 25, 50 h. Glass composition was checked after the preparation using flame photometry (Na_2O), classical volumetry (B_2O_3) and gravimetry (SiO_2) methods and ICP method (TiO_2). The variation between experimental and theoretical values was < 0.1% in case of all oxides.

Table 1 Composition in mol% glass samples A and B

Oxides	A	B
Na_2O	9.19	9.29
B_2O_3	23.58	23.82
SiO_2	67.23	63.72
TiO_2	0.00	3.17

Measurements

Optical microscopy was also used to identify the presence of communicative pores with an assessment of their size. For the optical microscopic analysis, the glass pieces were leached in 3M HCl aqueous solutions, at room temperature for 168 h, and afterwards immersed in respective 10% iodine in ethanol and methylorange in water solutions. NBS glass samples after 50 h phase separation at 700°C, immersed in ethanol iodine solution (Figs 5a, b) and in water methylorange solution (Figs 5c, d) behave differently. Iodine was used because of its size could enter the pores of leached glass, coloring the glass fragments to brown. Larger molecules of methyl orange do not enter the pores. They remain on the fragments surface. Sucked water expulses air in the form of bubbles.

The phase separated glass pieces (plates) were 'hammer' broken to smaller 2–3 mm pieces. Thus prepared fracture surfaces of the glass samples were further leached in 2% HF aqueous solutions at room temperature for 30, 60, 90 s and cleansed by the ultrasound. Samples of the glasses for SEM examination were prepared in form of fragments. After coating of fracture surfaces by sputter coating with gold in a Balzers SCD 050 the samples were examined in SEM Tesla BS-300 with digital unit Tescan. In all cases we compared the microstructure of non-etched fracture surfaces of samples with samples of glasses after etching with 2% HF, alike in the works of Moisescu and Yue [8, 9]. The samples were etched at a laboratory temperature during

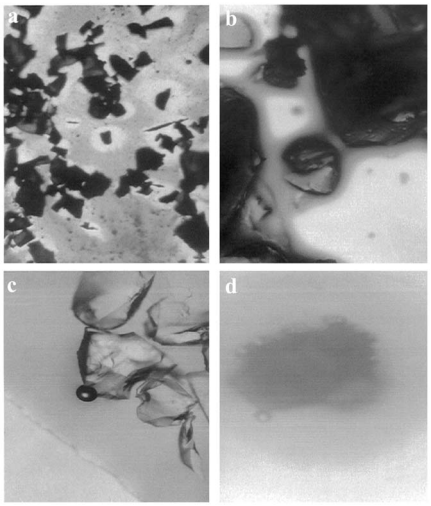

Fig. 5 Optical microscopy of the NBS glass samples after 50 h phase separation at 700°C, immersed in ethanol iodine solution: a – 50x and b – 200x (samples A and B, respectively) and in water methylorange solution: c and d – 100x (samples A and B, respectively)

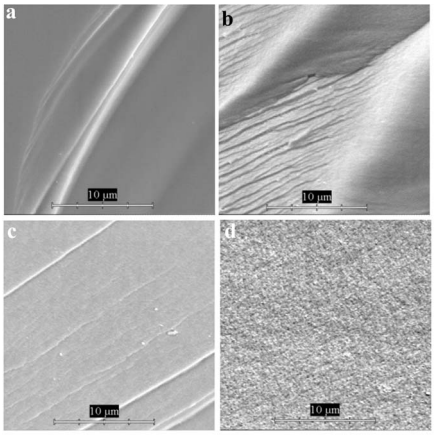

Fig. 6 The microstructure of the glass samples without (a, b) and with (c, d) TiO_2 after phase separation at 700°C: a) 2h, b) 15h, (without etching)

10, 20 and 30 s. Etching with HF is based on a fact that the amorphous phase is etched faster and therefore the crystal phase is emphasized. This principle was explained elsewhere [10]. The inner structure of glass is uncovered.

Optical transmittance measurements were accomplished using an instrument described elsewhere [11–13]. The 'white' light emitting diode (LED) was used as a light source. The light illuminates the sample plate perpendicularly. The transmitted light intensity is evaluated by Si-photodiode. Electric furnace temperature control and data pro-

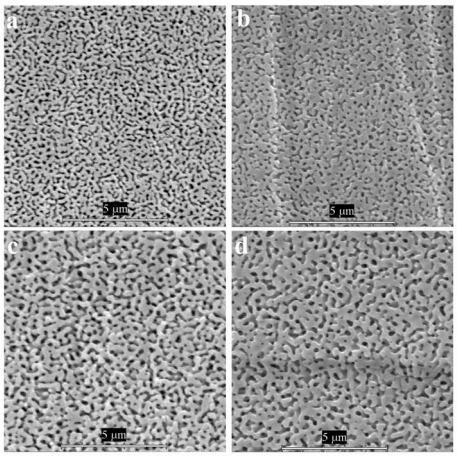

Fig. 7 Comparison of microstructures of the NBS glasses after the phase separation at 700°C: a – 25 h, c – 50 h without TiO_2; b – 25 h , d – 50 h with TiO_2. All samples were etched with 2% HF

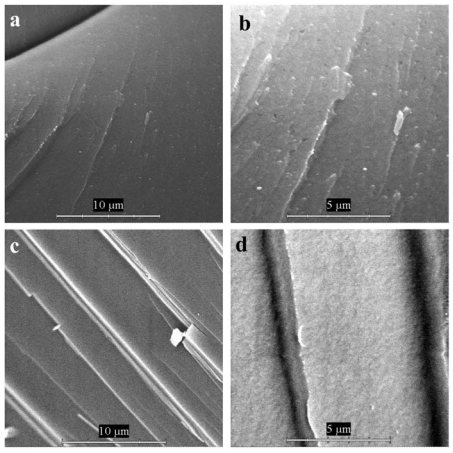

Fig. 8 The microstructure of NBS glass samples without (a, b) and with (c, d) TiO_2 after phase separation at 700°C/50 h (inner structure)

cessing are accomplished by a program, written using Genie (Advantech Development Environment) Software, running under Windows Operation System on PC.

Results and discussion

During the spinoidal separation two mutually penetrating phases with vermicular microstructure are being created, as seen in Fig. 7. The spinoidal separation at particular temperature starts when originally transparent glass matrix becomes opalescent

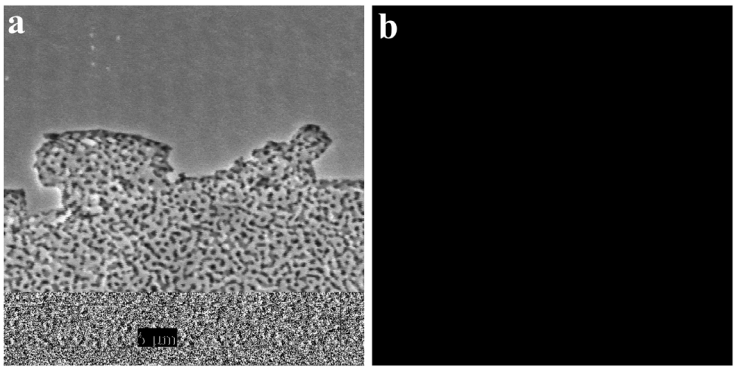

Fig. 9 The microstructure of the surface of the glass samples after the phase separation at 700°C: a – 15 h and b – 50 h. All samples were etched with 2%HF

(Fig. 3) because of the diffusive light (scattering) reflexion on phase boundaries. The preliminary experiments to this respect were made using optical transmittance measurements [11–13] during isothermal glass sample treatment at temperatures 700, 720 and 740°C. Here in Fig 4, the ordinate axis means the transmitted light intensity expressed in arbitrary units. Because of the difference in our glass composition with respect to the glass in Fig. 3 [3] no direct comparison of the onsets of phase separations can be made. Lesser amounts of the Na_2O and B_2O_3 in our glass means that the phase separation, either spinoidal, or by the crystallization, will be shifted to longer times. From this reason one would tend to accept the local maxima on curves in Fig. 4 as starts of the phase separation. The decrease of the optical transmittance in the heating up period (heating rate 10°C min^{-1}) followed by an increase to the local maxima are being unexplained yet.

Optical microscopy was also used to study the structure of the glasses. Optical microscopical studies of the NBS glass samples after 50 h phase separation at 700°C, immersed in ethanol iodine solution (Figs 5a, b) and in water methylorange solution (Figs 5c, d) exhibit significant differences in their structure.

The temperature of phase separation, the leaching and nucleator additive (TiO_2), significantly influence the microstructure of the resulting leached product. TiO_2 additive seems to suppress crystallization of cristobalite: especially at the extended above heat treatment phase separation runs (Figs 6–9). The results of leaching is a formation of a continuous porous network, as is visible on the SEM figures (Fig. 7). The phase separated domains of glasses containing above 80 mol% of SiO_2 are so small that can be hardly observed by electron microscope [14].

The glass composition in all cases was selected to have relatively large phase separated areas easily observed by SEM at magnification approximately 20 000·. The image analysis of leached glasses shows the prevailing content of the skeletal phase in comparison to pores (Table 2). The TiO_2 content diminishes slightly the content of the skeletal phase.

Table 2 Mathematic evaluation os SiO_2 phase and pores in samples of the etched glasses

Sample/time of separation [h]	Matrix -SiO_2/%	Pores/%
NBS/15	62.2	35.5
NBSTi/15	57.8	36.7
NBS/25	62.7	33.5
NBSTi/25	57.4	34.0
NBS/50	63.3	33.9
NBSTi/50	58.6	39.8

The results of mathematic evaluation of the presence of SiO_2 and pores in etched glasses, gained from SEM scans show the apparent influence of the length of separation and TiO_2 addition on three-dimensional set-up of silicate matrix. According to the references, the presence of TiO_2 suppresses the superficial crystallization of cristobalit caused by volatility of Na_2O and B_2O_3 from the glass surface.

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