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STUDY OF GLASSY MICROPOROUS FILTERS IN THE SODIUM BOROSILICATE GLASSES WITH APPROPRIATE CARRIERS

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The aim of this work is to prepare a porous filter composed of two porous layers: macro-porous carrier and micro-porous sodium borosilicate (NBS) glass with TiO_2 additive (NBST glass), a Vycor-type glass. In the present work we prepared the macroporous support from the same material (NBST glass) as the upper microporous layer and then by sintering both parts to produce the required composite. This work introduces the results of experiments in the preparation of micro-porous filter on NBST glass base, laid on macro-porous carrier. After sintering of scrap NBST glass, porous samples were prepared to be used as carriers for micro-porous samples of phase-separated NBST glass. In other cases, the following carrier materials were used: a) frita SIMAX, b) Al_2O_3. The properties of the NBST glass and the changes in the glass structure with temperature were studied in order to determine the optimal sintering temperature of the prepared glasses. For the development of the sintered glasses, valuable information was obtained from heating microscopy (HM) and scanning electron microscopy (SEM) studies. The combination of the HM and SEM results with the measurements of the micro-hardness and density directed to the further study of the phase separated NBST glasses.

Keywords: *heating microscopy, micro-hardness, SEM, sodium borosilicate glass, temperature dependency*

Introduction

Present work follows the issue of phase-separated glasses with a possibility of application in microelectronics, such as absorbents, and/or a possibility of bio-applications in the form of membranes. The systems such as sodium-borosilicate (Na_2O–B_2O_3–SiO_2) bio-glasses, in which the phase separation occurs by longer heating in the higher temperatures than the cooling interval, are used for the production of VYCOR type glass and micro-porous glasses [1, 2]. These glasses are used as sorbates and micro-filters. They are developed from phase-separated glasses, which have the inner coupled and vermicular structure [3–6]. This structure is formed during the continual spinoidal separation, when the two penetrating phases are formed in the original glass. The changes in microstructure, optical properties [3, 4] and viscosity [5–7] are connected with the phase separation of the glasses. During the production of glasses, the process of the pretreatment of the glasses with 'powder techniques' is usually used. The principle of this manufacturing process is the disintegration of the glass to powder, which forms the requisite form of the material 'in cold process' and reinforced with thermal treating. The term 'sintering glass' refers to the glass product, created by forming the glass powder of definite granularity within specified range and then reinforced with suitable thermal treating. The compact glassy materials, which were characterized by thermal treating, can be formed with specific porosity. The products, synthesized by the sintering technique of glasses have very different properties and applications. The production of the porous glasses with open pores requires lower sintering temperatures and shorter holding time compared to the production of the sintered glasses with closed pores. It is very important to maintain the following sequence of temperature changes during the sintering of glasses [8]: *i*) heating to the sintering temperature and holding at temperatures, which correspond to the baked binder temperature, *ii*) the holding at the sintering temperature for the hardening and concretion of the product and *iii*) the cooling of the product to the transformation interval temperature for the applied glasses. The products with porous sintered glasses are used as laboratory filters for analytical and preparative works and as bacterial filters for sterile filtration.

The method for the preparation of glass-alumina composites for the possible utilization as membrane carriers is presented in [9]. During the preparation, the α-Al_2O_3 tubes were dip-coated into the suspension of sodium borosilicate glass particles (9.1%

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Na_2O – 29.7% B_2O_3 – 61.2% SiO_2). Sintering converts the particle layer into a nonporous layer of phase-separated glasses. The glass was leached with a strong acid to remove the soluble phase and to obtain the final porous layer of about 10 μm thickness. The glass layers had pore size 1–4 nm after leaching. Many authors have investigated biomaterials including porous glasses and also examined their thermal, structural, biological and electrical properties [10–13]. The aim of this work is to prepare a porous filter composed of two porous layers: macro-porous carrier and micro-porous sodium borosilicate (NBS) glass with TiO_2 additive (NBST glass), and to characterize the prepared materials by SEM, HM, microhardness and density.

Experimental

The preparation of NBS and NBST glasses and applied methods

Original glass samples A and B 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, as is presented in [1, 4]. The compositions of the glasses are given in Table 1. The variation between the experimental data and theoretical expectation is <1%. The powder glass was made for the preparation of the macro-porous carrier from the non phase separated NBST glass by grinding in agate mill FRITSCH. Two fractions: A) 0.160–0.250 mm and B) 0.045–0.063 mm were acquired.

Heating microscopy

We have used a LEITZWETZLAR (Germany) heating microscope consisting of the optical settee, lighting device, electric tube furnace and microscope for the heating microscopic measurement. The spotted sample was located on the base over the weld of the thermocouple in the furnace plug with ceramic tube. This tube was located in the holder of the engaging apparatus. The measured temperature is displayed in the viewing field simultaneously with the shade form of the samples [14].

Table 1 Composition in mol% of 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

Scanning electron microscopy

The SEM studies of the NBST glasses were performed using a scanning electron microscope TESLA BS 300 with digital unit TESCAN. The samples were prepared in powder form (crushed material) and grain (fragment), to observe the surfaces, fracture surfaces (breakages) with and without etching in 2% HF water solution, the polishing surface and the surface after the measurement of the micro-hardness. After ultrasonic cleaning in ethanol, the samples were sputtered with Au using a sputter coater BALZERS SCD 050. SEM images of the samples were obtained at accelerating voltage 15 kV and magnification 50–20 000x.

Micro-hardness and density of glasses

The measurement of the micro-hardness of the phase separated NBS and NBST glasses at 700°C/50 h are carried out using a VICKERS MICRO-HARDNESS TESTER FV-1, by Future-tech. Corp., Japan.

Sintering of the glasses

Preparation of the porous carriers

We have cleaned the prepared powder glasses with triple decantation in ethanol. We determined the temperature, by which it begins to meltdown and sintering of the grains ($t_{1/2Kz}$=752°C) using heating microscope. The temperature holding time was chosen to be 1.5 h.

Preparation of the micro-porous filters on the selected carriers

The macro-porous carrier from NBST glass and the compact NBST glass layer were prepared by sintering at temperature 900°C. The samples were very brittle and do not have adequate operating stability for other mechanical treatments. For this reason, it was not successful to prepare the final product according to scheduled experiments. Therefore, in the next section of our experiments, we prepared the samples in combination with the macro-porous carrier (commercial material) with compact NBST glass as described in [1]. With macro-porous frit SIMAX (article by Sázavan Kavalír), sintering temperature =900°C/1 h and phase separation temperature =700°C/25 h were used. With macro-porous alumina carrier, sintering temperature =1000°C/0.5 h and phase separation temperature =700°C/25 h were used. The preparation technique was exchanged in the deposition process for the layered NBST glasses. The glasses were deposited as the compact layer and not in the suspension form as like as the glazer.

Table 2 The particle sizes /μm of fractions A and B

Particle No.	1	2	3	4	5	6	7	8	9	10
Fraction A	344	422	512	265	249	306	305	361	591	197
Fraction B	122.0	83.7	115.0	110.0	87.4	60.6	135.0	47.5	132.0	99.0

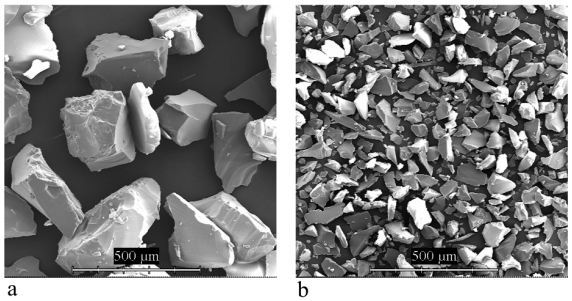
Average value of the particle size fractions A and B are 355.2 and 99.2 μm, respectively

Results and discussion

It was necessary to prepare the glasses of specific size for the preparation of the porous glasses. The exact characteristic of the powder glasses was determined by the fine mesh screen analysis and by the SEM measurements. The experimental data of the particles in both fractions are presented in Table 2. Since the sintering temperature 900°C is higher than the region of the phase separation [7], the sintered samples were kept once again at 700°C for the phase separation.

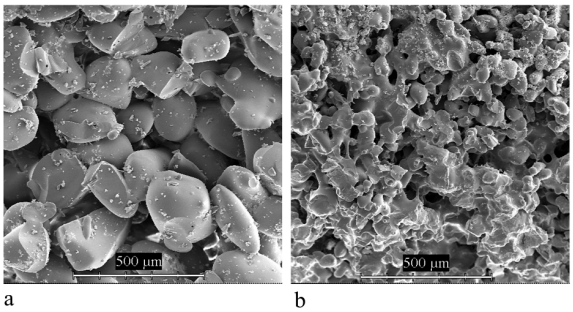
SEM analysis

To examine the preparation of the porous glass composite materials, the microstructures of the NBST glasses (Fig. 1) and sintered fractions of NBST glasses (Fig. 2) were monitored by SEM. Microstructures of NBST + Frit glass 'SIMAX' and NBST + Corundum (α-alumina) glasses are documented in Fig. 3. The two possibilities are the selection of the optimal sintering temperature and the temperature holding time. According to the SEM measurement, it is appropriate to modify the value of either a) the sintering temperature: for the fraction A (0.160–0.250 mm) to increase the sintering temperature at the same holding time (1.5 h) from 750 to 800°C and for the fraction B (0.045–0.063 mm) to decrease the sintering temperature at the same holding time (1.5 h) from 750 to 740°C or b) the holding time: for the fraction A to elongate the holding time at the same temperature (750°C) from 1.5 to 2.0 h and for the fraction B to shorten the holding time at the same temperature (750°C) from 1.5 to 0.5 h.



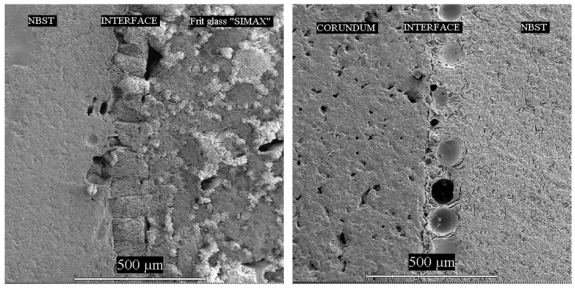
a b

Fig. 1 SEM images of NBST glasses: a) fraction A (0.160 – 0.250 mm); b) fraction B (0.045 – 0.063 mm), magnification 200x



a b

Fig. 2 Microstructure of the sintered NBST glasses at 750°C and 1.5 h: a) fraction A (0.160–0.250 mm); b) fraction B (0.045 – 0.063 mm)



a b

Fig. 3 Microstructure of the prepared glass composites: a – NBST + Frit glass 'SIMAX', b – NBST + Corundum(α-alumina)

Heating microscopy

We have evaluated the changes of the form of the selected NBST glass samples on temperature by the heating microscopy:

- Grain of NBST glass cca 4 mm cubic. The changes of the form of the glass samples by heating are presented in the Figs 4 and 5. The temperature scales with the indicator of their actual value were presented in the bottom of the figures. The outset and the consecutive melting down of the edges of the NBST glass grains are visible in Fig. 4 (a, b, c, d). The first change of the glass form was observed at 740°C.
- In the second case, we observed the NBST glass samples, prepared as follows: The sample was crushed and smeared in agate dish to powder with an average size of particles 0.063 mm. The powder was wetted with distilled water, and was com-

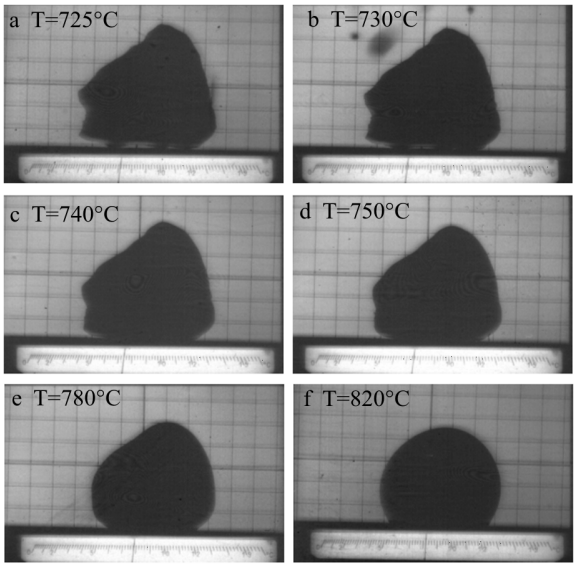


Fig. 4 Changes of the NBST glass grain, which was formed from heating microscopy

pressed with manual press (1 MPa) to form a roller of with 3 mm diameter. The changes of the form of the prepared samples are presented in the Fig. 5. By evaluating the temperature dependency of linear shrinkage (Figs 5 and 6), we obtained the following value of t_D, t_H and $t_{1/2Kz}$: t_D=680°C, t_H=800°C, $t_{1/2Kz}$=752°C, where t_D is the temperature by which a sample begins to contract, t_H is the temperature by which a sample finishes the linear shrinkage and $t_{1/2Kz}$ is the temperature by which the value of the linear shrinkage is at half intensity of the final shrinkage.

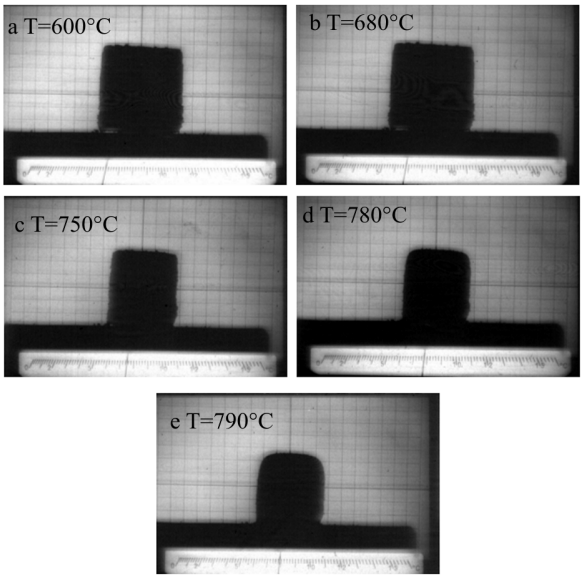


Fig. 5 Temperature dependency of linear shrinkage, which was received by heating microscopy

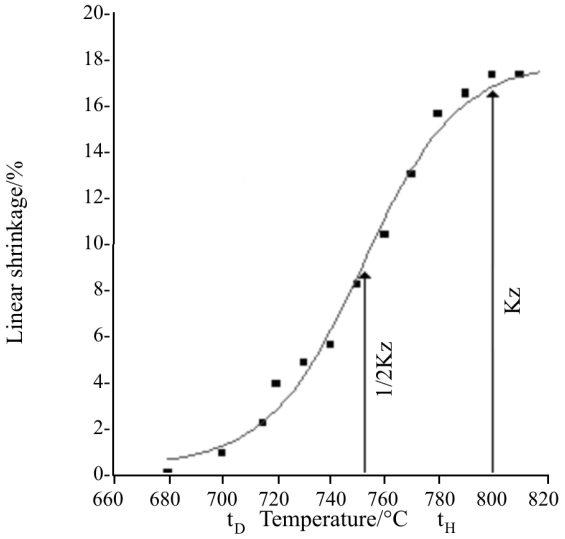


Fig. 6 Temperature dependency of linear shrinkage of NBST glass

The ability of a specified liquid to wet a specified solid is characterized by the contact angle θ for a drop of that liquid resting on a horizontal flat surface of that solid (as measured through the liquid.). We evaluated the temperature dependency of the NBST glass samples by the contact angle θ (Fig. 7. a, b, c, d) and determined the temperatures by which the contact angle θ achieves the values 60 and 90°, Fig. 8.

Micro-hardness

The testing of micro-hardness applies the methods, which are used at present as a part of the normalized testing procedure for the technical control of materials. These methods are used more frequently for the study of the solid material properties such as surface layers, oxidation, anisotropy, brittleness, plastic deformation, rigidity, structural properties and others. In general, the surface of a rigid material has the possibility to resist local defiance (break) by an alien entity.

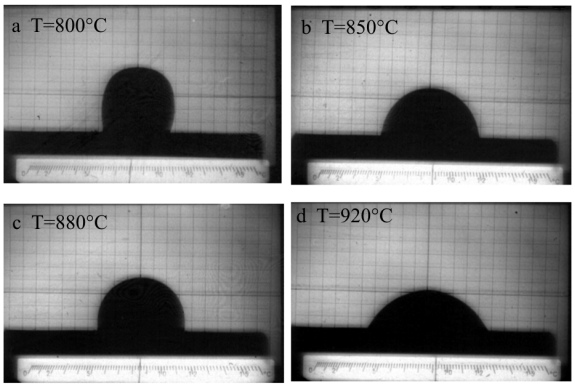


Fig. 7 Records from the heating microscopy for the sample grain of NBST glass

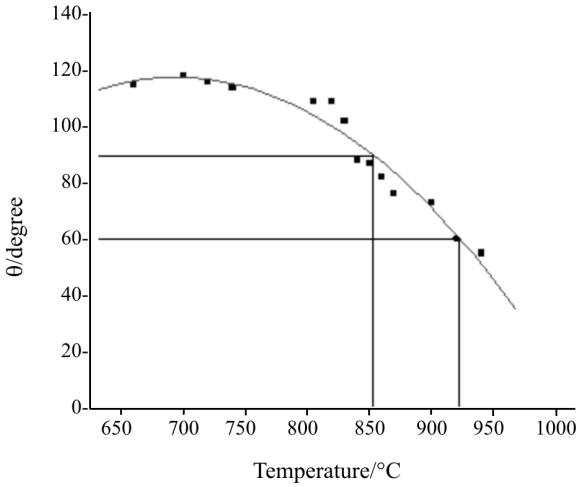


Fig. 8 Temperature dependency of the contact angle θ of the NBST glass

The most common technique to measure micro-hardness of materials is the indentation test. In this indentation test, the indentor is impressed into the plain (polished) surface of the studied materials. The hardness is calculated from the measurable dimensions of the stabs. There are several kinds of indentation tests, which differ in the form and the material of the indentor, loading conditions and type of the evaluation. The most common application has the Brinell and the Vickers micro-indentation technique [15, 16]. The results of the micro-hardness measurement of the phase separated NBS and NBST are studied. The average value of the experimental results for NBS glass is 5.38 GPa. The standard deviation of the measurement is 0.13 GPa. The minimum and maximum values of micro-hardness are 5.12 and 5.43 GPa, respectively. The average value for NBST glass is 5.29 GPa and the standard deviation of the measurement is 0.10 GPa. The minimum and maximum values of micro-hardness are 5.20 and 5.64 GPa, respectively.

Density

Density of the studied glasses was determined by hydrostatic mass. The density of NBS and NBST (with and without phase separation) glasses are 2240, 2253 and 2250 kg m^{-3}, respectively.

Conclusions

The results of the micro-hardness measurements can be used as a supporting fact of the positive effect of TiO_2 on the micro-hardness and the microstructure of NBST glasses. It is known from theory that the TiO_2 additive supports the three-dimensional ordering of the SiO_2 tetrahedrons [17, 18]. The results of the microstructure in the indentation space by the measurements of the micro-hardness and the comparison of the dissipation of the measured values for the NBS and NBST glasses also support this fact. The SEM study of the glass samples after the micro-hardness measurements confirmed the phase separation and the spinoidal separation corresponds to the literature data [7, 8]. The vermicular microstructure, which was induced by the spinoidal separation, was also observed by SEM study in NBS and NBST glass samples. Another parameter, which characterizes the quality of the materials, is density. The density of the NBS, and NBST (with and without phase separation) glasses are 2240, 2253 and 2250 kg m^{-3}, respectively, which is in good agreement with the literature data. The density of this type glass is 2000–2500 kg m^{-3} [19].

Acknowledegments

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References

1 J. Chocholoušek, Preparation of glass-ceramics materials by the controlled nucleation and crystallization methods, Ph.D. Thesis, FCFT STU Bratislava, Slovakia, 2003.
2 J. Pavláková, The micro-structural study of the glass-ceramics systems, M. Sc. Thesis, FCFT STU Bratislava, Slovakia, 2000.
3 J. Kozánková, J. Pavláková, J. Chocholoušek and J. Majling, The micro-structural and optical transmittance study of the glass-ceramics systems (Na_2O–B_2O_3–SiO_2), Proc. 15th Conf. of Thermal Analysis and Calorimetry, High Tatras, Stará Lesná, Sptember 11–13, 2000, p. 155.
4 S. C. Mojumdar, J. Kozánková, J. Chocholoušek, J. Majling and V. Nemecek, J. Therm. Anal. Cal., 78 (2004) 145.
5 M. B. Volf, Technical glasses and their properties, SNTL, Prague, Czech Republic 1987, p. 214.
6 L. Šašek, Special technology of glasses, SNTL, Prague, Czech Republic 1985, p. 107.
7 K. Nakashima, K. Noda and K. Mori, J. Am. Ceram. Soc., 80 (1997) 1101.
8 Z. Petru, The application of the heat microscopy in glass research, Informative review, SVUS, Hradec Králové, Czech Republic, XXIV., 2 (1981) 3.
9 H. Wang and G. R. Gavalas, J. Membr. Sci., 176 (2000) 75.
10 N. Koga, Z. Strand, J. Šesták and J. Strand, J. Therm. Anal. Cal., 71 (2003) 927.
11 J. Majling, P. Šimon and V. Khunova, J. Therm. Anal. Cal., 67 (2002) 201.
12 S. C. Mojumdar, J. Kozánková, J. Chocholoušek, J. Majling and D. Fábryová, J. Therm. Anal. Cal., 78 (2004) 73.
13 G. E. Romanos, V. Kasselouri, K. Beltsios and N. K. Kanellopoulos, J. Therm. Anal. Cal., 73 (2003) 183.
14 Z. Petru, Sintered glasses, Informative review, SVUS, Hradec Králové, Czech Republic, VI., 2 (1963) 7.

15 J. Dvorak, Microhardness of glasses, Informative review, SVUS, Hradec Králové, Czech Republic, XVI., 2 (1973) 4.
16 Ch. Ullner, J. Beckmann and R. Morrell, J. Eur. Ceram. Soc., 22 (2002) 1183.
17 W. Vogel, Structure and crystalization of glasses, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1965, p. 62.
18 M. B. Volf, Technical Glasses, SNTL, Prague, Czech Republik, (1978) p. 239.
19 J. Hlaváč, Fundamentals of Silicate Technology, SNTL, Prague 1988**,** p. 158.

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