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Application of electron microscopy methods to the study of porous and quartz-like glasses

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The structure of high-silica porous glasses and quartz-like (Vycor type) glasses has been investigated by transmission and scanning electron microscopy and by electron micro-probe analysis. Porous glasses (PGs) have been manufactured by acid leaching of phase-separated alkali borosilicate glass plates. To obtain the quartz-like glasses the PG samples were sintered at different temperatures up to 900°C. Before sintering a part of PGs was impregnated with salt solutions containing Ag. Features of the structure of quartz-like glass matrix are revealed. The parameters and arrangement of a photosensitive Ag-Hal phase in photochromic quartz-like glasses are determined.

Keywords: porous glass, Vycor type glass, photochromic glass, electron microscopy, electron micro-probe analysis.

1. Introduction

One of the promising examples of using high siliceous porous glasses (PGs) obtained from two-phase alkali borosilicate (ABS) glasses is the manufacture of photochromic quartz-like glasses (PCQGs) [1, 2]. Such glasses contain high concentration of photosensitive Ag-Hal phase surpassing those in usual photochromic glasses, synthesized by stock melting [3]. At the same time the PCQGs have a number valuable properties inherent in quartz glass. The high degree of dimness at small thickness of samples provides high resolution of a material [4]. The high silica content guarantees their increased transparency and photosensitivity in short-wave area of ultra-violet radiation that makes them suitable for use in optical instrument making. Speed of discoloration of PCQGs at room temperature can be close to zero, which allows using them for fixing and storage of the image. PCQGs become colorless upon temperature rising up to 120°C. Depending on conditions of manufacture of PCQGs the criterion of their thermal relaxation can change from 1–2 up to 30–40%. Photochemical properties of PCQGs can be improved due to the variation of such factors as the thickness of PG plates, conditions of preparation of PG samples before impregnation, composition of impregnating solutions, procedure of sintering [3].

Perspectives of practical use of PGs and PCQGs are the reason for studying their structure by electron microscopy methods. Results of the research of the PGs by transmission and scanning electron microscopy (TEM, SEM) depending on conditions of their manufacture are given in [5–8]. Some data on the structure of sintered PG samples (*i.e.*, quartz-like glasses) are presented in [9]. At the same time, no regular research of the structure of PCQGs, including the stage of PG impregnation by photosensitive component, is known. The present work is dedicated to this problem.

2. Technique

The PCs of the present study were derived from 2 mm thick two-phase ABS glass plates by their leaching in HCl solutions. Quartz-like glasses were obtained by sintering PGs in the electric furnace up to pore closing. A part of PGs (so-called photochromic porous glasses – PPGs) was previously impregnated with photosensitive Ag-Hal component. This component was entered into PG plates by two-stage salt solution permeation: by solutions containing ions of silver (1st stage) and halogens (2nd stage). The choice of concrete solutions for PG impregnation is based on results of preliminary research and allows obtaining PCQGs, which possess obvious enough photochromic properties but show low speed of relaxation (*i.e.*, process of discoloration) [3, 4]. We investigated the PPG and PCQG samples, which were preliminarily subjected to irradiation of spherical mercury-quartz lamp DRSh-250.

The structure of the thus made and impregnated with Ag-Hal phase PG samples as well as PCQG's have been investigated by TEM and SEM methods, by X-ray analysis and electron microprobe analysis. TEM-studies were realized via electronic microscope EM-125 at an accelerating voltage of 75 kV. For this purpose a known method of cellulose-carbon replicas was used. The replicas were prepared from the chip surface after its etching in 2% solution HF during 2 s (two-phase glass), or from a fresh chip surface (PG). In the case of quartz-like glasses it was not possible to reveal a relief of the surface of samples by long etching in solution HF because of their high chemical stability. So, a method of thermal etching was used [10] to obtain a carbon replica from the surface of the sample which was heated in a vacuum at 250°C for 30 s.

SEM-studies of sample surface as well an electron micro-probe analysis of glasses were carried out with Camebax microanalyzer. The quantity of photosensitive components (recalculated for Ag^0) was determined in InL_α-radiation by comparison of element radiation intensity I_{rel} in the sample investigated and in the standard. X-ray analysis was carried out using DRON-3 device with monochromatic CuK_α-radiation.

3. Results and discussion

The initial two-phase glass has a structure with interpenetrating phases [8] (Fig. 1**a**). Values of the diameters of the channels occupied with chemically unstable phase (UP) in two-phase glass are 25–45 nm [11]. Parameters of the pore structure of the PG under study, which are caused by destruction UP and by vacation of the channels formed

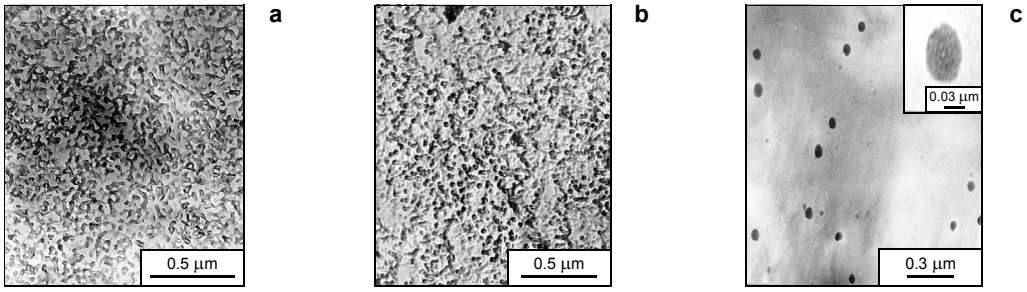

Fig. 1. TEM photographs of an initial two-phase glass 8/70 (**a**); porous glass obtained as a result of its leaching in 3 M HCl solution at 100°C (**b**); quartz-like glass obtained as a result of full sintering of porous glass at T = 870°C (**c**).

by it, correspond to parameters of phase separation structure of an initial two-phase glass (Fig. 1**b**). According to adsorption data the values of pore average radius, volume and specific surface area, the sizes of which are defined by the size of secondary silica particles and density of their packing, are 3.3 nm, 0.27 sm^3/sm^3 and ~100 m^2/g, correspondingly.

Electron micrographs of the chip surface of completely sintering PGs (*i.e.*, quartz-like glasses) show a structure of "micro-liquation" type with the size of inhomogeneities ~6 nm [9] (Fig. 1**c**). The carbon used in preparation of replicas acts also as decorate substance [12]. At the moment of replica formation at carbon dispersion there is a migration of its atoms on the surface of heated glass sample and their primary concentration on the active surface centers which can be sites of micro-crystallization of the boron- and silica-containing products [6]. Dark rounded formations (see Fig. 1**c**) are corresponding with congestion of amorphous carbon. The presence of amorphous carbon was evidenced by typical diffuse halo testified on diffraction patterns, which was obtained by means of selected area electron diffraction (SAED) technique.

According to SEM data, the structure of a thin layer, adjoining the external surface of PG's sample, sharply differs from the basic volume that is caused by regional effects, which take place during two-phase glass leaching [13]. The sintering of PGs results in disappearance of this distinction and in shrinkage of a sample [9, 14].

Figure 2 shows the TEM-photographs of PPG sample. The TEM examination of PPGs shows the samples being non-uniformly filled with an impregnating solution. Denser filling of the pores occurs in peripheral layers of the sample. This is also confirmed by results of electron micro-probe analysis of PPGs (Figs. 3**a**, **c**). The difficulty of timely penetration of an impregnating solution in the process of promotion from the edge to the center of a sample is caused by an increase of diffusion ways and by the presence of secondary silica inside the pores. The packing density of secondary SiO_2 particles in the central layers of PG sample is higher than in peripheral ones, which is proved by an increase in the value of structural resistance coefficient of the central layer of the sample in comparison with the peripheral layer [15]. Besides,

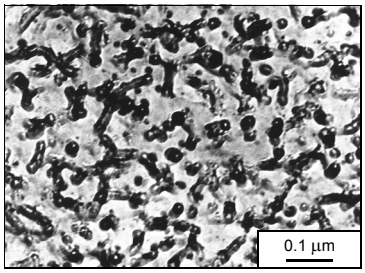

Fig. 2. TEM photograph of a porous glass impregnated with Ag-Hal component.

the central area of the samples of PGs under investigation is less porous and is also filled a boron-containing deposits of the products of UP acid destruction including microcrystalline ones [6, 8].

Higher concentration of photosensitive components in the peripheral layers of PPGs (Figs. 3**a**, **c**) predetermines also its high concentration in peripheral layers (in comparison with the central layer) of the PCQG samples (Fig. 3**d**). At the same time general level of silver in a peripheral layer of PCQG sample is lower, and a little bit higher in a volume in comparison with peripheral layer and volume of PPG sample. One should also note that in order to exclude the artifacts connected with preparation of a sample for shooting, experimental definition of I_{rel} values (Figs. 3**a**, **b**) was made with the some (~50 μm) deviation from the edge of a sample.

Typical TEM photographs of PCQG samples after an irradiation are shown in Figs. 4**a**–**d**. PCQG plates investigated by us externally represented the samples with mixed painting: from the blind-black at the surface to fulvous-yellow towards the center. Based on X-ray analysis data these samples are roentgen amorphous.

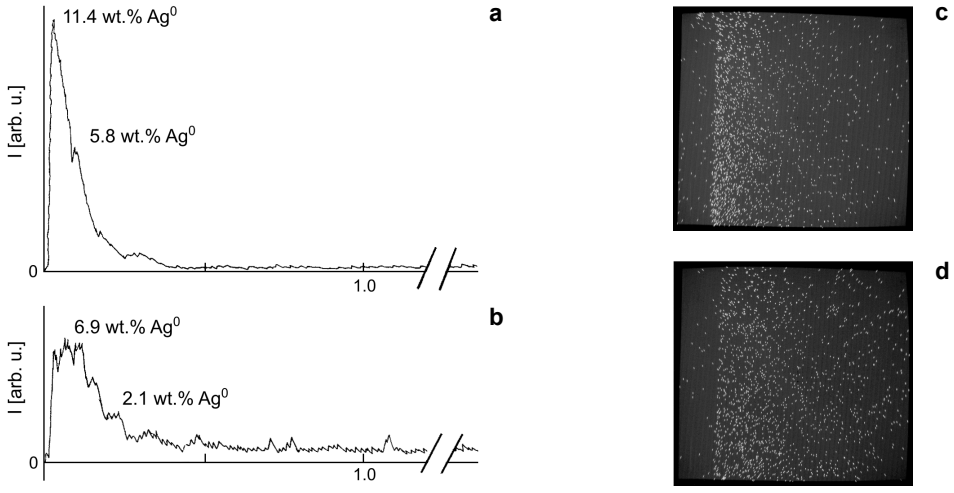

Fig. 3. Qualitative distribution of silver as found with an X-ray microanalyzer over the cross-sections of the samples of photochromic porous glass (**a**) and photochromic quartz-like glass (**b**), and morphology of the surface of these sections (**c** and **d** accordingly) in X-ray radiation AgL_{α}.

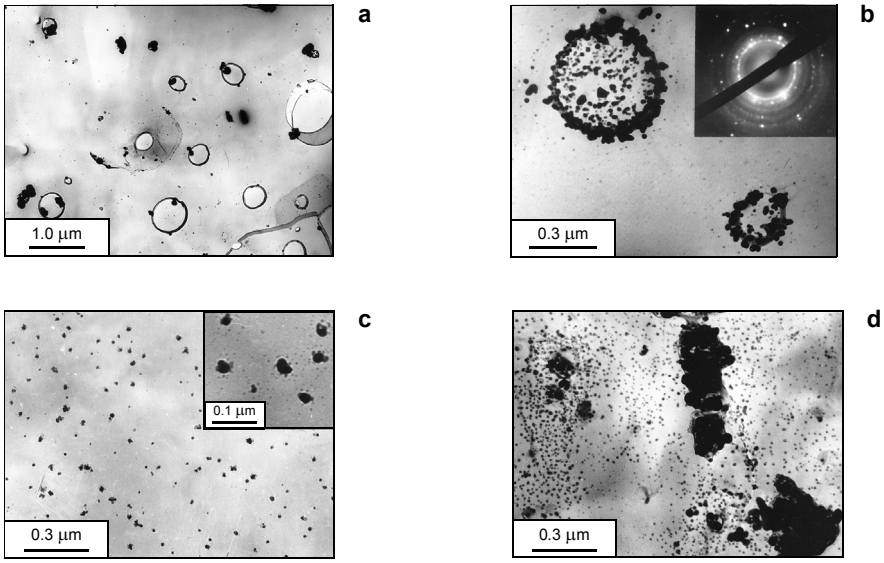

Fig. 4. TEM photographs of the photochromic quartz-like glass: **a** – a general view of a part of the sample located closer to its external surface (edge); **b** – a view of the area occupied with a photosensitive Ag-Hal, and electron diffraction pattern (shown in the inset) of this phase; **c** – a view of the central part of the sample; **d** – a view of the peripheral part of the sample.

Figures 4**a**, **b** show that rounded formations due to a photosensitive phase present in PCQG samples on a background of "microliquation" type structure. The sizes of these domains can reach 1 μm. It is probable that their origin occurs in the active centers which were observed in not impregnated quartz-like glasses (see Fig. 1**c**). The interface of these areas is filled with microcrystalline particles. When identifying these particles by SAED methods a phase of AgCl (a card JCPDS No. 22-1326) was established. In replica preparation this phase was taken from the volume of a sample. It appears unstable in TEM-examination. Namely, its disintegration ("sprinkling") into fine particles caused by an electronic beam is observed. It should be noted, that these domains are located mainly in peripheral layers of a sample, where there is a relatively great volume of a photosensitive phase. The process of Ag^0 formation on reaction $ne^- + nAg^+ \rightarrow nAg^0$ which is complicated with high AgCl concentration is initiated upon irradiation by an electronic beam. Towards the center of the sample a reduction in the size of these domains filled with Ag-Hal phase, up to 8–16 nm is observed (Fig. 4**c**). Around these areas a congestion of particles of the size ≤5 nm is shown. Such sizes of the photosensitive phase areas provide a display of optimum photochromic properties of the given sites of irradiated photochromic glass [16], as against a superficial layer of samples. On the sintering of PCQGs, there is an enrichment of the superficial layer of the sample by Ag-Hal component (Fig. 4**d**) and, thereby, its muffling [3].

4. Conclusions

Using the electron microscopy methods allowed us to reveal a "microliquation" type structure of quartz-like glasses and the presence of active centers on the cross-section surface of these glass samples. There has been observed a non-uniform filling of PG plates with Ag-Hal component from solution with which the gradient of concentration of silver in photochromic quartz-like glasses correlates. It is shown that the optimum sizes of photosensitive phase areas determining photochromic properties of PCQGs, settle down in the central part of a sample. The assumption has been formulated that primary origin of photosensitive areas in PCQGs occurs in the active centers the formation of which is caused by microcrystallization of boron- and silica-containing leaching products in basic PG samples.

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