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Investigation of adhesion of chalcogenide glasses to silica glass

V.S. Shiryaev *, S.V. Mishinov, M.F. Churbanov

G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, 49 Tropinin Str., 603950 Nizhny Novgorod, Russia
N.I. Lobachevski Nizhny Novgorod State University, 23 Gagarin av., Nizhny Novgorod 603950, Russia

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ABSTRACT

Adhesion of $As_{40}S_{60}$, $Ge_{10}As_{22}Se_{68}$, $As_{30}Se_{50}Te_{20}$, $As_{40}S_{30}Se_{30}$, $As_{38}Sb_2Se_{30}Te_{30}$, $As_{30}Se_{70}$, $As_{35}Se_{65}$, $As_{37.5}Se_{62.5}$ and $As_{40}Se_{60}$ glasses to silica glass is studied by the steady detachment method in the temperature range of 80–210 °C. The separation tension of the studied chalcogenide glasses from silica-glass substrate increases with temperature exponentially and has the maximum with the value of 2000–2600 kPa at temperatures close to T_g. The value of adhesion is shown to depend on the temperature, the surface roughness of silica glass, the chalcogenide glass composition, and the time of formation of adhesive contact.

1. Introduction

One of the parameters, characterizing the properties of glass optical elements, is the quality of their surface. During production of chalcogenide glass preforms by the melt molding technique the quality of the prepared samples strongly depends on the adhesion of chalcogenide glass melt to the silica glass as a material of apparatus. The data on adhesion value between chalcogenide and silica glasses and its temperature dependence are required in the optimal conditions for manufacturing chalcogenide optical elements with defect-free surface and the lowest contamination by SiO_2 particles. This information is not available in the literature.

During preparation of bulk chalcogenide glass samples the silica-glass ampoules can be broken at the solidification step of the melt, which indicates high adhesion between the formed and constructional materials [1]. The reasons to this high adhesion are likely to be a high surface roughness of silica glass and chemical interactions between the atoms of elements of chalcogenide glass macrocomponents and elementary and complex defects of silica glass, such as non-bridged oxygen atoms, three-fold coordinated silicon atoms, peroxygen bridges≡Si – O – O – Si≡, and oxygen vacancies≡Si – Si [2]. Such interaction can be considered as an analogue to the so-called "polymer graft" known in the chemistry of carbon-chain polymers [3].

High adhesion of chalcogenide glasses to silica glass can be the reason of contamination of surface layers of the prepared samples by particles of container material. Since the coefficient of linear thermal expansion of chalcogenide glasses is much higher than that of silica glass, the sample of chalcogenide glass during its cooling much greatly changes in size than the silica-glass ampoule. It can lead to mechanical separation of particles from the walls of a silica-glass apparatus. The presence of silica-glass layer on the surface of glassy As_2S_3 ingot, described in paper [4], confirms it. The possibility of contamination of chalcogenide glass melt by SiO_2 microparticles with sizes up to 50 μm is indicated in papers [5–7].

From the literature data on the bonding material and the formation of thin films and multilayer structures it is known that the value of adhesion strength is affected by temperature and time conditions of the contact formation, morphology of the contacting surfaces and thickness of the adhesive layer. The type of data dependencies is determined by the nature of the adhesive and the substrate. From the general laws the increase in the overall adhesion strength with increasing temperature of formation of adhesion contact [8–12] can be noted.

The adhesion between chalcogenide and silica glasses has the most negative effect on the quality of tubes of different chalcogenide glasses for manufacturing optical fibers by the "rod-in-tube" technique and microstructured fibers. Therefore, to determine the optimal conditions for manufacturing the perfect substrate chalcogenide tubes, the investigation of temperature dependence of chalcogenide glass adhesion to silica glass is required.

The aim of this work was the investigation of the adhesion between different chalcogenide glasses and silica glass and the determination of factors affecting the adhesive strength. $As_{40}S_{60}$, $Ge_{10}As_{22}Se_{68}$, $As_{30}Se_{50}Te_{20}$, $As_{40}S_{30}Se_{30}$, $As_{38}Sb_2Se_{30}Te_{30}$, $As_{30}Se_{70}$, $As_{35}Se_{65}$, $As_{37.5}Se_{62.5}$ and $As_{40}Se_{60}$ glasses were chosen because of their high prospects for the production of low loss optical core-clad and microstructured fibers [13–15].

* Corresponding author at: G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, 49 Tropinin Str., 603950 Nizhny Novgorod, Russia.
E-mail address: shiryaev@ihps.nnov.ru (V.S. Shiryaev).

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Table 1
Physico-chemical properties of investigated glass.

Glass	T_g, °C *	Density (ρ), g/cm^3 [18]	Young's modulus (E), GPa	Microhardness (H), kg/mm^2 [18]	KTE (α), °C^{-1} [18]
$As_{40}S_{60}$	197	3.2	16.5	134	$24 \cdot 10^{-6}$
$As_{40}Se_{60}$	183	4.55	18.3	150	$20.9 \cdot 10^{-6}$
$As_{38}Sb_2Se_{30}Te_{30}$	134	5.1	18	146	–
$As_{30}Se_{50}Te_{20}$	131	4.9	18	126	–
$As_{40}S_{30}Se_{30}$	190	3.84	–	145	$22.5 \cdot 10^{-6}$
$Ge_{10}As_{22}Se_{68}$	180	4.5	16	154	$24 \cdot 10^{-6}$
SiO_2	1222	2.2	72.1	1200	$2 \cdot 10^{-6}$

* The data on DSC results at the heating rate of 10 K/min.

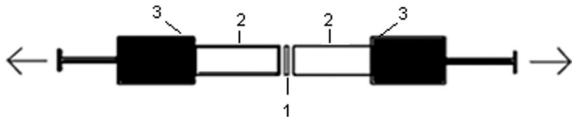

Fig. 1. Scheme for determination of adhesion strength by means of a steady detachment method: 1 — chalcogenide glass, 2 — silica rods, 3 — testing machine cartridges.

2. Experimental

A number of chalcogenide glasses, which are used for the manufacture of preforms of microstructured optical fibers, were prepared to study the adhesion to the silica glass. These glasses were obtained by melting the initial high-purity elements in evacuated silica-glass ampoule and purified additionally by chemical and distillation methods [15–17]. The content of the limiting impurities in the prepared glass samples was determined by laser mass spectrometry and IR spectroscopy as follows: carbon — <2 ppm wt., hydrogen in the form of SH- or SeH-groups <0.1 ppm wt., oxygen — <1 ppm wt., silicon — ≤0.5 ppm wt., metals — ≤ 0.1 ppm wt. The physico-chemical properties of these glasses are given in Table 1.

The investigation of adhesion strength between chalcogenide and silica glasses was carried out by the steady detachment method. This method is used to measure the force required to separate the adhesive from the substrate simultaneously in all areas of contact [19,20]. The magnitude of adhesion is characterized by the force, required to separate the adhesive from the substrate, divided to the surface area of contact. The advantages of this method include the simplicity of implementation and the fact that the apparent adhesion strength in the units of pressure (Pa) is determined immediately after the measurement of separation force and the contact area. In addition, this method allows us to investigate a sufficiently thick layer of adhesives (~300 mkm) used in this work.

To determine the apparent adhesion strength, the samples of chalcogenide glass in the form of plates of 1–2 mm thickness were placed between the ends of two silica rods of 10 mm diameter, 25 mm in length (Fig. 1). The average surface roughness of the silica-glass rods, determined by atomic-force microscopy, was 170 nm. In experiments with $As_{40}S_{60}$ glass, the rods with average roughness of 2.5 nm and 370 nm were used as well. The assembly was heated in the vertical tubular furnace up to the softening temperature of chalcogenide glass, held at this temperature for a certain time, cooled down to a definite temperature, and tested on separation using a dynamometer machine with a limiting force of 200 N. The loading rate was 30 mm/min. Using this technique, the influence of test temperature and time–temperature conditions of contact formation on the value of separation tension of chalcogenide glasses from silica glass surface was investigated.

To determine the temperature dependence of the separation tension of the chalcogenide glass from the surface of silica-glass rods, the assembly was heated for 10 min to the temperature of 400 °C, held at this temperature for 15 min, then cooled down to the definite test temperature and tested for separation.

To determine the dependence of the chalcogenide glass adhesion to the silica glass on the contact temperature, the assembly was heated for 10 min to the definite temperature, held at this temperature for 5 min, then cooled down to the glass transition temperature of the adhesive and tested for separation.

To determine the dependence of adhesion on the exposure time at the maximum heating temperature, the assembly was heated to 380 °C for 5 min and held at this temperature for the definite time. The separation test was carried out at the glass transition temperature of chalcogenide glass.

The separation tension measurements of each glass sample in all experiments were performed 5–10 times, and then the average value and standard deviation of the measured value were determined.

The surface morphology of silica glass was investigated using atomic-force microscope (AFM) Solver Pro M. AFM study was carried out under atmospheric conditions in the non-contact mode using silicon I-shaped cantilevers NT-MDT NSG-01 with a tip radius of curvature <10 nm (according to passport data). Processing of the AFM study results was made by the specialized software for data processing and analysis SPM NT-MDT Nova Image Analysis 2.0 [21].

3. Results

The profilogram of silica glass surface, studied by atomic force microscopy, is shown in Fig. 2. The average roughness of surface R_a determined as the arithmetic average value was equal to 170 nm.

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|Z_i - \overline{Z}|$$

where R_a is the average roughness, Z_i is the height of i-relief; $\overline{Z}$ is the average height of relief, and n is the number of measurements.

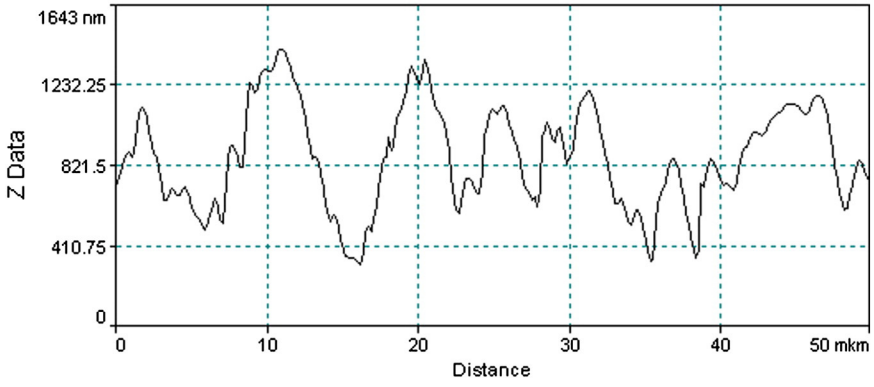

Fig. 2. Profilogram of silica glass surface with an average roughness of 170 nm.