

NUCLEATION OF NANOPORES IN GLASS OPTICAL FIBERS UNDER INFLUENCE OF TENSILE STRESS: EXPERIMENT

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Abstract. The article reports on observation of nanopores nucleated under a tensile stress in the core of the germanosilicate optical fibers doped with boron. Pores were observed with an atomic-force microscope on the faces of cleaved fiber tips. Under certain experimental conditions, pores form a quasi-periodic structure and their sizes are in a good agreement with predictions of the earlier proposed model based on the theory of phase transitions. The theoretically estimated threshold stress level for effective nucleation of pores corresponds well to the results of experimental observations.

1. Introduction

Optical glass attracts considerable research interest as promising structural material for traditional applications as well as for high-tech applications in optoelectronics, lasers and optical communications. Despite the large amount of research activities performed in glasses and other brittle materials, some aspects of glass fracture and its strength still are not clear in details. The difficulty is in the complicated structure of amorphous materials and very strong influence of technological process parameters on the final properties of glass, even for glass samples with the same chemical composition. In this context, research on mechanical strength, radiation induced damage, and laser processing of glass are actual fields of scientific research in technology and physics.

Oxide-based glass materials, such as fused quartz or silicate glass, are considered as typical brittle materials. Usually, glass fracture occurs without detectable deformation by a rapid crack propagation. When a critical external tensile load is applied to a uniform glass sample, the direction of crack propagation coincides well with the direction perpendicular to the tensile force vector. A commonly accepted mechanism is based on the break of interatomic bonds in the glass structure leading to a very smooth mirror-like rupture surface. However, the real technical strength of the glass is much below than the one estimated using an inter-atom bond strength. The empirical model of crack propagation in brittle solids, developed almost 100 years ago [1], is based on existence of defects (micro-cracks) operating as stress concentrators in a volume of the brittle material or on surface of the material sample.

In recent years, there exists significant and increasing interest to interaction of intense laser radiation with solids. Laser processing of materials is now a rapidly progressing field of technology. In optics, a micron-size local permanent modification of the glass properties is very

cause damage to the optical fiber core made of germanosilicate glass. Studies using elasto-optical polarimetric techniques [15] have shown that even with relatively low power of the recording light (which is necessary to maintain the mechanical strength of the optical fiber) compaction of the glass structure (glass densification) occurs in the fiber core. With increasing of irradiation dose and glass densification, tensile stress in the fiber core is growing up to a certain level. A further increase of exposure results in a slow decrease of axial tensile stress in the fiber core. The beginning of the stress reduction correlates well with appearance of the so-called negative FBG of type IIA in the optical fiber. It was supposed [15] that there is a dilatation of the core material in the irradiated areas of the fiber core, but no physical mechanism of such dilatation of the glass was suggested.

The structure of the silicate glass is a random network of well-defined structural units of SiO_4 tetrahedrons (with a silicon atom at the center and four oxygen atoms in corners) interconnected through bridge oxygen atoms. Each oxygen atom of the tetrahedron is a part of a neighboring tetrahedron combining cell and forming a complex amorphous structure containing different size rings of tetrahedrons. Because of the manufacturing technology of optical glass fibers, the core material has a large number of defects such as wrong bonds, oxygen vacancies, etc. That makes glass structure even more complex. So, there are free space cavities between the tetrahedrons in the network. In glasses, spaces empty of atoms can be considered as voids of spherical shape with a maximum radius of about 3 \AA [2]. Existence of vacancy-type defects (voids) in the material structure makes possible to apply the theory of phase transitions of the first kind to describe the nucleation and development of nanopores (new phase) in brittle materials from gas of vacancies [16]. Later, this approach was extended to glass [17]. Based on fluctuation mechanism of the pore nucleation and its dependence on stress and temperature, a microscopic mechanism for the type IIA FBGs was proposed [17]. The theory of phase transitions being applied to nucleation of pores makes possible to estimate the basic parameters of the emerging new phase (pores), such as the critical radius of a stable pore, rate and time of nucleation, etc.

Following [16, 17], the expression for the critical radius can be written as

$$R_{\text{cr}} = 2\gamma/\sigma. \quad (1)$$

Here $\sigma = I_1(\hat{\sigma})/3$; $I_1(\hat{\sigma}) = \sigma_1 + \sigma_2 + \sigma_3 = \sigma_{rr} + \sigma_{\phi\phi} + \sigma_{zz}$ - the first invariant of the stress tensor; $\sigma_1, \sigma_2, \sigma_3$ - principal stresses; γ - the surface tension coefficient. The nucleation rate for pores has the form

$$I_0 = \frac{2\gamma^{1/2}\beta_0\sqrt{\delta}}{\sqrt{k_B T}} \exp\left(-\frac{16}{3} \frac{\pi\gamma^3\delta}{k_B T \sigma^2}\right), \quad (2)$$

where $k_B = 1.38 \cdot 10^{-23} \text{ J/K}$ is the Boltzmann constant, β_0 is a kinetic coefficient associated with the vacancy diffusion coefficient. The nucleation time can be estimated by using the following equation

$$t_i = \frac{2k_B T \gamma \delta}{\beta_0 \omega^2 \sigma^2}. \quad (3)$$

In the work [17], it was shown that the magnitude of the surface tension in the fiber is approximately equal to $\gamma = 0.2 \text{ J m}^{-2}$, δ is a coefficient taking into account change in energy of pore appearance during the process of pore nucleation on phase interface, defects, etc. As a rule, $\delta = 10^{-1}$. β_0 is a kinetic coefficient, representing the equilibrium flow of vacancies joining and emitted off the pore. It influences significantly the rate of nucleation and depends

The standard telecom single-mode optical fiber has a cladding diameter of 125 microns; the fiber core with diameter of 8 microns (for the operation wavelength of 1550 nm) locates concentrically in the center of the cladding. Normally, the cladding is made of pure silicate glass, and the fiber core is doped with germanium oxide to create the waveguide properties.

To verify the possibility of nucleation of nanopores in the core of an optical fiber, we used a special photosensitive single-mode fiber. In such photosensitive fibers, FBGs of type IIA can be written relatively easily using a pulsed excimer laser (wavelength 248 nm) and straining the fiber during FBG recording. Figure 2 shows the scattering of light by gratings recorded in such a photosensitive fiber. In the photosensitive fibers, a concentration of germanium in the core is several times higher when compared to standard optical fibers. The fibers used in our experiments, the fiber core contained about 10 % GeO₂ and it was additionally doped with B₂O₃ to preserve the core diameter to be matched to the core size of the standard single-mode fiber.

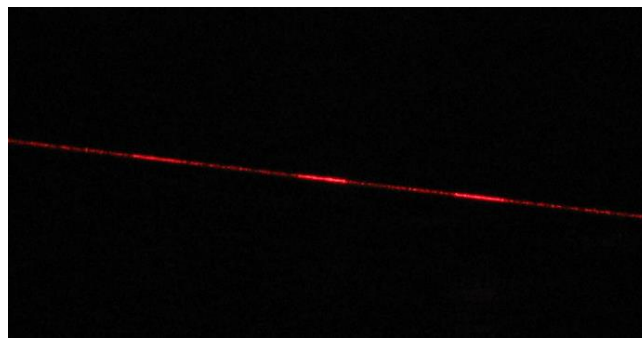


Fig. 2. Rayleigh scattering of red light propagating in an optical fiber containing 3 FBGs of the type IIA separated by unexposed section of the fiber.

An important result of a high doping level is an increased level of the internal tensile stress in the fiber core at room temperature. As it was measured in [15], the intrinsic tensile stress can reach 0.1 GPa in the core of the germanosilicate fiber doped with boron. An additional external tensile loading of such a fiber can result in approaching a threshold stress level in the fiber core while maintaining the cladding stress still much below the stress in the core. Since the size of the core is much smaller than the fiber cladding, the fiber can maintain its integrity with the core stress approaching the threshold for nucleation of nanopores.

As one can see from data presented in Fig. 1, a level of tensile stress is the most important factor affecting the nucleation rate. Our experiments were completed at room temperature with samples of the photosensitive fiber. No irradiation of the fiber was performed. Instead, the optical fiber was subjected to tensile load with a fixed force. The sequence of steps is shown schematically in Fig. 3. The fiber was kept under the load for 30 minutes. Then, the load was removed and the fiber section was cleaved with standard fiber-optic tools. For this purpose, a small scratch was produced on the fiber lateral surface. Then, a strong axial tension was applied to the fiber. A rapid propagation of the surface crack through the cladding cleaves the fiber leaving the fracture surfaces perpendicular to the fiber axis. Then, the surface of the fiber tip was investigated with the atomic force microscope Park Systems XE70.

Figure 4 demonstrates images of 2 complimentary fiber tips. The tips were obtained by a single cleaving of the fiber sample. The fiber sample was not loaded during the first 30-minutes step (no tension was at the first step shown in the Fig. 3).

In images, the fiber core is clearly visible in the central part while the periphery part represents a very smooth surface of the fiber cladding. As can be seen, the core surface is slightly recessed relative to the surface of the cladding. This is due to the free surface deformation under pulling stresses in the inner core of the fiber. A similar deformation is visible in both images of the core.

Then, in the next stage of the experiment, we analyzed the cleaved surface of the loaded fiber sample. Figure 5 shows images obtained for the fiber which has been previously exposed to the tensile force of 2.5 N during 30 minutes at room temperature.

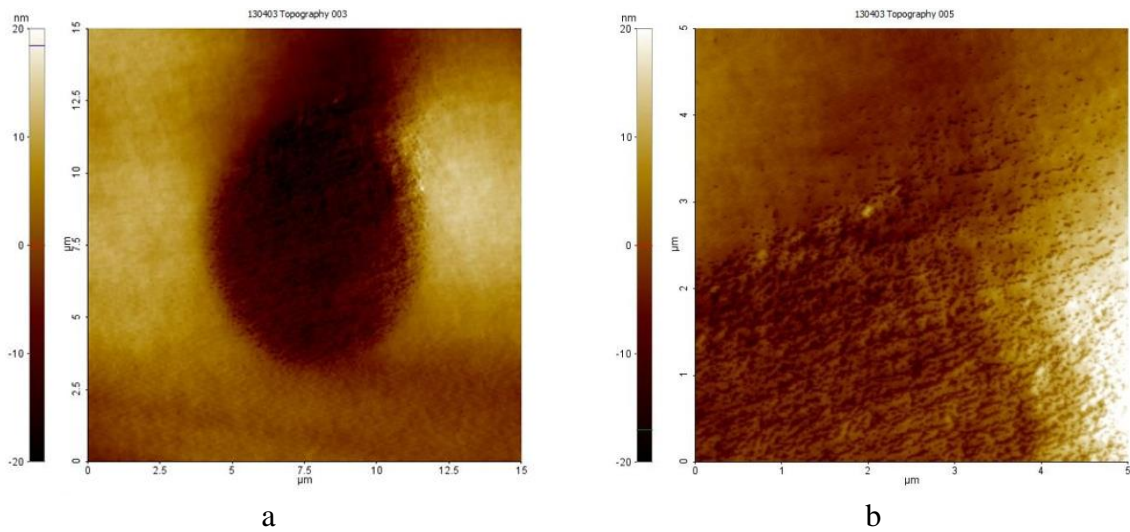


Fig. 5. The image of the central part of the fiber tip surface when the fiber before the cleaving was pre-exposed to externally induced tensile stress of 0.2 GPa. Being combine with existing intrinsic stress in the fiber core, the resulting stress value is close to the calculated threshold for nucleation of nanopores; (a) the core image and the adjacent part of the fiber cladding, (b) the image of the core-cladding interface with the scan area of $5 \times 5 \mu\text{m}^2$.

In two images shown in the Fig. 5, it is clearly visible a pattern of pits with depth of less than 10 nanometers and lateral dimensions of 20-30 nm. We suggest that the observed surface structure corresponds to the presence of nanopores with typical dimensions of 10-20 nm in diameter. At the same image, the cladding region (a few micrometers away from the core-cladding interface) is free from the pits and its surface is close to the plane surface with irregularities beyond the resolution of our atomic force microscope. In the Fig. 5b, some regularity in the pit structure can be observed, where pores are forming a line structure. This property is under theoretical analysis now and results will be presented somewhere.

Given that, the fiber cladding has diameter of 125 micrometers, the external tensile force was of 2.5N, and taking into account the initial internal tensile stress of the fiber core of 0.1 GPa [15], the total stress in the core can approach the level of 0.3 GPa. This value correlates very well with the tensile stress threshold level calculated for the pore nucleation at room temperature.

6. Conclusions

Experimental results on study of cleavage surfaces of the photosensitive optical glass fiber with the core made of germanosilicate glass doped with boron are presented. The fiber samples were subjected to different level of the tensile stress before the cleaving. It was found that the fiber cladding made of silicate glass provides very flat and smooth fracture surface, with irregularities beyond the resolution of the atomic-force microscope of 2 nm in depth. At the core-cladding interface appears specific no homogeneities extended asymmetrically into cladding area in the direction of the crack propagation. At the stress level corresponding to the theoretical threshold for effective nucleation of nanopores, a clearly visible pattern of pits was observed in the core area. Sizes of the pores correspond well to prediction of the theory developed in our previous works.

