INFLUENCE OF THE STRUCTURAL RELAXATION ON THE INDENTATION BEHAVIOR OF THE SURFACE OF SILICA OPTICAL FIBER

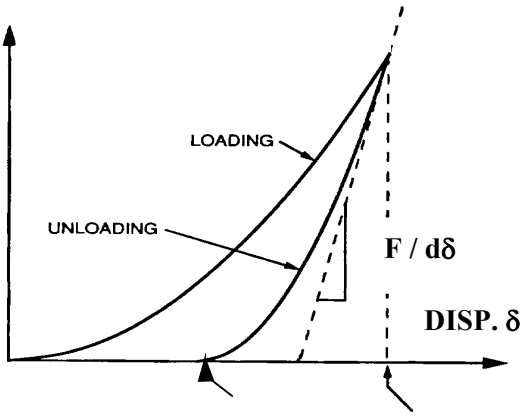
N. Gougeon, R. El Abdi and M. Poulain
Rennes1 University, Rennes, France.

Abstract: Structural relaxation is a major characteristic of liquids and glasses. It relates to the structural transformations induced by temperature changes and its kinetics is governed by viscosity.
Vickers indentations were performed on silica optical fibers subjected to water interaction by a hydrothermal treatment. The observation of the Vickers impression provided direct evidence of a lateral displacement of material of the fiber submitted to the hydrothermal treatment. This indentation behaviour is consistent with a structural relaxation promoted by the water and the glass network interaction. It is suggested that the water could acts as a modifier since the deformation combines the densification and the plastic flow of the material. When the relaxed surface layer is chemically etched, the anomalous behavior of silica under indentation is restored as the deformation is controlled only by densification.
In the present work, we obtained AFM images of Vickers impressions made on several optical silica fibers. It is the purpose of this paper to examine the influence of the structural relaxation on the indentation behaviour of the surface of silica optical fiber.

Introduction: Structural relaxation is a major characteristic of liquids and glasses. It relates to the structural transformations induced by temperature changes and its kinetics is governed by viscosity [1]. The time required for such transformations becomes larger when temperature decreases and glass transition occurs when this time is close to that of the experience or the observation. Below glass transition temperature Tg, relaxation time is so large that vitreous materials appear rigid and consequently behave as solids.
In previous work, we observed a permanent deformation of aged fiber under bending in hot water at 85°C [2]. This is surprising because this temperature is far lower than the silica glass transition, and numerical simulation would lead to the conclusion that the effect of such a relaxation is negligible.

ADDRESS CORRESPONDENCE TO:IUT Rennes-B.P.90422-35704 Rennes-France
Abstract Number : 28
Name : El Abdi Rochdi
Phone : (33) 2 23 23 41 12
Fax : (33) 2 23 23 41 0 1
E-Mail : relabdi@univ-rennes1.fr

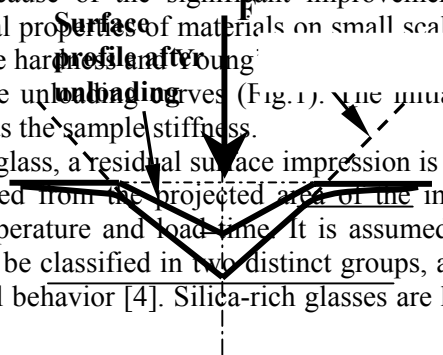
Then one may assume that external stress and water could promote structural relaxation at low temperature. This implies that relaxation time is different at surface and in the bulk. This hypothesis is consistent with the observations of Tomozawa *et al* [3]. Water can exist in glass as hydroxyl attached to the glass as silanol groups (-OH in Si-OH) and molecular water (H_2O). The molecular water can diffuse in the glass and react with the glass network to form hydroxyls by: Si-O-Si + H_2O ↔ 2 Si-OH.
Since the mechanical strength of a glass is controlled by the surface characteristics of the glass, it is useful to ation on the mechanical behavior of the fiber.



nearly one hundred years for measuring the hardness of

pushing an indenter into the sample under precise load lepth and then extracted, giving the loading force over the

lentation because of the significant improvement in the ıe mechanical properties of materials on small scales. From dentation, the hardness and Young xample)
slope of the unloading curves (Fig.1). The initial rate of) is defined as the sample stiffness.



aded onto a glass, a residual surface impression is observed rally estimated from the projected area of the impression d load, temperature and load time. It is assumed that the Glasses can be classified in two distinct groups, according " mechanical behavior [4]. Silica-rich glasses are known to

exhibit anomalous behavior under load since volume densification has been obtained while in normal glasses shear lines due to plastic flow have been observed [5]. Fused silica is known to densify relatively easily during indentation owing to its open three-dimensionally co-ordinated structure [6]. Peter [5], in microscopic observations of the indentation topography, detected a transformation from essentially radial ("sink-in") to lateral ("pile-up") displacement of material about the indenter as the modifiers content in silica glass was increased, suggesting a corresponding transformation from densification to plasticity in the deformation mechanism. The role of modifying ions in the structure is to provide "easy-slip" paths through another rigid, strongly covalent network [7].

Fig.1 : A schematic representation of load versus indenter displacement data for an indentation experiment.

Fig. 2 : A schematic representation. of a section through an indentation.

DISPL. δ

In the present work we obtained AFM images of Vickers impressions made on several optical silica fibers. It is the purpose of this paper to examine the influence of the structural relaxation on the indentation behavior of the surface of silica optical fiber.

Experimental procedure

Samples preparations

The samples were commercial silica optical fibers made by an MCVD method with a diameter of 80 μm with an epoxyacrylate coating corresponding to an overall diameter of 125 μm. The fibers were heat-treated at 150°C during 48 hours under wet atmosphere using an autoclave. Part of the sample was rolled on mandrels with a diameter of 5 mm corresponding to an applied tensile stress and compressive stress of 1160 MPa [8] (Fig.3). Some stress-free fibers were also heat-treated. After the heat-treatment, the rolled samples exhibited a permanent deformation when the bending stress was removed. Then the coating of all samples, heat-treated stress-free, heat-treated curved and as-received, was removed by soaking the fibers in dichloromethane at room temperature. In order to examine the curved samples in the compressive side and the tensile side two holders were specially designed with respectively convex and concave shape.

In order to remove the relaxed surface layer, part of the heat-treated fibers were submitted to a chemical etching using a commercial-grade hydrofluoric acid at 40%. First the bent fibers were immersed in HF acid solution till the fiber straightened again. We assumed that the relaxed layer was completely removed when the fiber became straight. After the reaction took place, the fibers were rinsed immediately with deionised water and acetone. The thickness of the removed layer was determined by microscopic examination and was found to be equal to 4 μm.

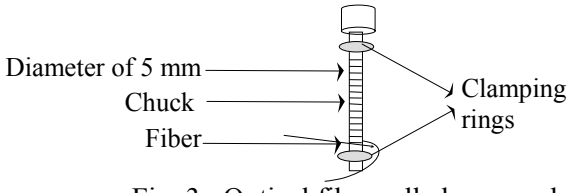


Fig. 3 : Optical fiber rolled on mandrel.

Indentation experiments

Indentations experiments were performed on a Matsuzawa apparatus equipped with a Vickers diamond indenter. Concerning the curved sample, indentations were performed on the compressive side and on the tensile side. A 0.098 N load was applied during 10 s in air at room temperature. Vickers diamond pyramid hardness is determined in practice by measuring the diagonal length of the indentation produced by the penetration of a square-based pyramid having an angle of 136° between opposite pyramid faces. The hardness number H_V is given by the relation:

$$H_V = \frac{2P\sin(0.5\theta)}{d^2} \quad (1)$$

where P is the applied load, d is the average value of the diagonals and θ is 136°. Although the diagonal, d, in relation (1) is obtained by measurement after the removal of the load, it is known that the change in the lengths of the diagonals upon unloading is very small [9] and almost insignificant when compared to the diagonal length itself. Thus, the Vickers hardness number is given by $H_V = 1854.4P/d^2$, in kg/mm^2, where P is in kilograms and d is in millimeters [10].

Indentation observations

An atomic force microscope (Digital Instruments NanoScope III) was used to profile the residual indentation. The observations were performed in tapping mode. The AFM has proven to be a helpful experimental technique for studying the impression topography.

Results

After removing the coating on the curved samples the bent radius was found to be equal to 4.5±0.1 cm.

The Vickers hardness was calculated for each sample using the average residual area of 5 indentations. The average value of the diagonals of the indentation was determined using the AFM cross section profile of both diagonals. Here, we considered that elastic recovery of impression corners is negligible [11] and that the relation between diagonal, d, of square base and corresponding height, h, of Vickers pyramid is d/h=7. Vertical elastic recovery of glass can be defined as $e^v(r) = |h(r) - h_i(r)|$, where r is the distance from impression center h_i is the impression depth and h is the depth of the indenter at maximum load [11].

The results for each sample are summarised in Table 1.

Samples	Average diagonal (μm)	Impression depth. H_i (in nm)	Depth at max. load H_r (nm)	Vertical elastic Recovery (nm)	% of elastic recovery	Vickers hardness (GPa)	Indentation observation
Non-treated	4.88	419	697	278	40	7.78	Sink-in
Heat-treated Internal curvature	4.96	434	708	274	39	7.53	Pill-up
Heat-treated External curvature	4.61	430	658	228	35	8.72	Pill-up
Heat-treated, Stress free	4.78	468	683	215	32	8.10	Pill-up
Non-treated +HF etched	4.38	420	626	206	33	9.65	Sink-in
Heat-treated +HF etched	4.29	398	612	214	35	10.09	Sink-in

Table 1: Summarize of the results obtained for all samples. Uncertainty on Vickers hardness values is ± 0.05 GPa.

Fig. 4 shows an AFM image of a Vickers impression produced on the surface of the glass fiber without any treatment, with a 10 g applied nominal load.

The AFM topographic image and the cross section of the indentation made across the indentation following one of the diagonal of the indentation show that this indent was subjected to sinking-in (Fig. 5).

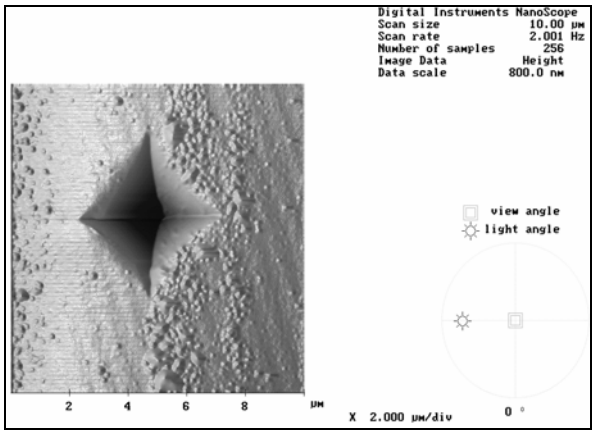


Fig. 4: AFM image of a Vickers impression on as-received silica optical fiber produced with a nominal load P=10 g.

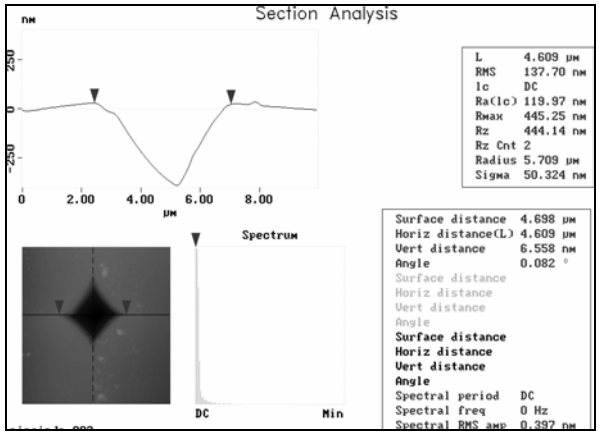


Fig. 5: AFM topographic image and cross section of an indentation on as-received silica optical fiber showing sinking-in of material.

Fig. 6 shows the AFM image of the Vickers impression produced on the surface of the compressive side of the bent heat-treated fiber, which corresponding to the internal side of the curvature.
Fig. 7 shows the AFM topographic and the cross section of this indentation. Here we can point out that this indent is subjected to pilling-up, as we observed a lateral displacement of material around the indentation.

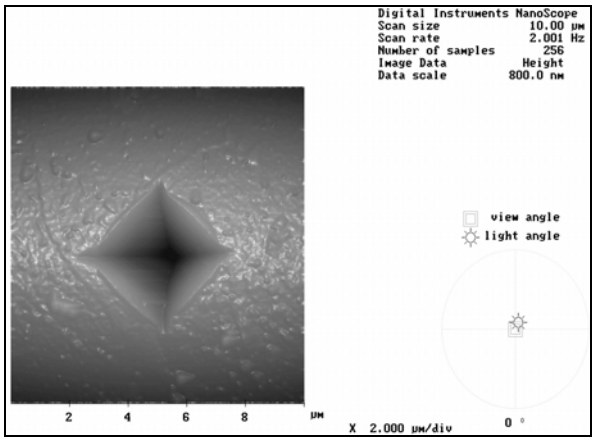


Fig. 6: AFM image of Vickers impression on the internal side of the curvature of the bent fiber after hydrothermal treatment.

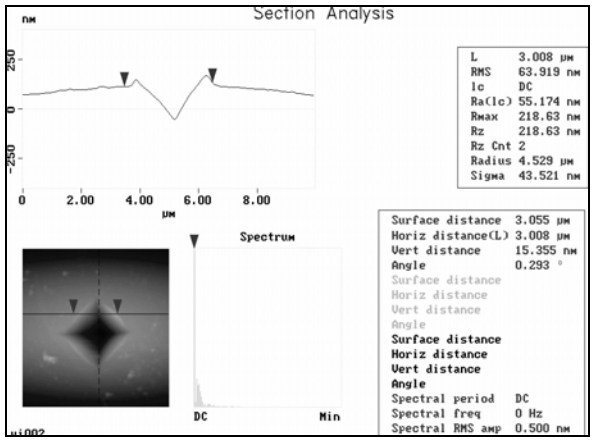


Fig. 7: AFM topographic image and cross section of an indentation on the internal side of the curvature of the bent fiber after hydrothermal treatment showing pilling-up of material around the indentation.

Fig. 8 shows the AFM image of the indentation of the heat-treated sample submitted to HF etching. The AFM topographic and the cross section of this indentation look like those observed for the non-treated fiber (Fig. 9).

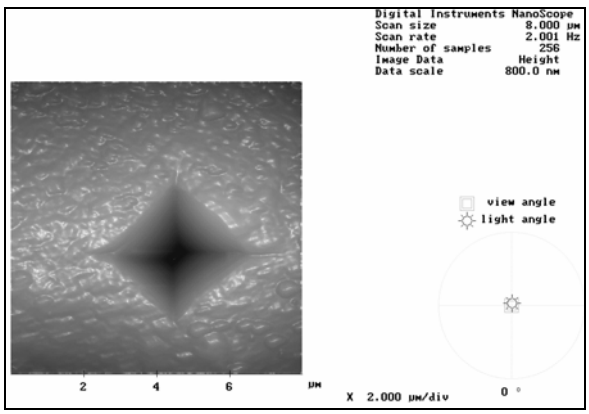


Fig. 8: AFM image of Vickers impression on heat-treated fiber submitted to HF chemical etching.

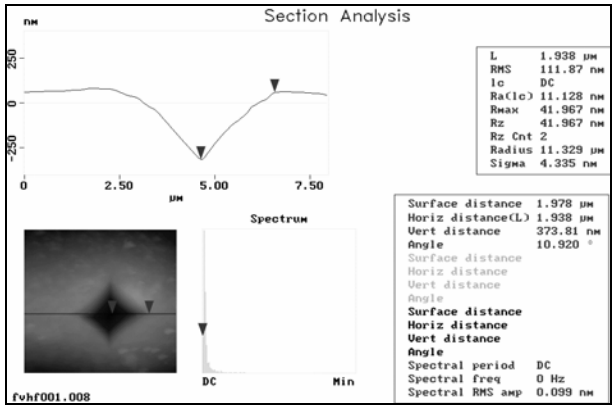


Fig. 9: AFM topographic image and cross section of an indentation on heat-treated fiber submitted to HF chemical etching showing sinkin-in of material.

Discussion: Since a permanent impression is left after indenter removal for all samples, and considering that sample mass remains unchanged, a small volume of the glass should reorganise during indentation process.
It is well established that the structure of silica glass having only bridging oxygens is not compact, but very open, and the strength of the Si-O bonds is large, giving the high glass transition temperature of around 1200°C. For this reason, it is considered that structural units (SiO_4) can be reorganised without bond breaking but by changing the angle of the Si-O-Si bond during loading. Therefore, we observed a densification and a sinking-in of the materiel as shown in Fig.5. The Vickers value (H_v=7.78) and the large elastic recovery of around 40% were found to be in accordance with the literature [4, 5, 11].

On the other hand, the indentation topography of the hydrothermal-treated fiber under stress exhibited a pilling-up of the materiel. This pilling-up phenomenon is usually caused by a lateral displacement of material, hardly imaginable without flow. A difference in deformation mechanism is likely to account for the differences between the non-treated and the heat-treated fibers. It is generally considered that modifying ions located in the interstices of the Si-O network are responsible to such an indentation behavior. Typical modifiers are cations which interact with the bridging oxygens to depolymerise the network. Small molecules - e.g. hydrogen - may diffuse in silica glass as this glass is far from being compact. Water molecules may act in the same way, especially at temperature larger than 100 °C. They fill voids in the network constructed by the SiO_4 tetrahedra. As they are neutral molecules they appear different from modifying cations. However, they are polarized units and may react with the bridging oxygens of the network according to the chemical reaction:

$$\text{Si-O-Si} + H_2O \leftrightarrow 2\ \text{Si-OH}. \qquad (2)$$

These non bridging anions are weak points in the network that enhance plastic flow in the same way as modifiers. Thus, water molecules can also be considered as modifiers. The results concerning the bent fiber exemplify this idea as the elastic recovery of the internal side of the curvature (i.e. the compressive side) was found to be higher than that of the external side. The combined effect of water and tensile stress are supposed to accelerate the surface relaxation while water and compressive stress would decelerate the relaxation [12]. This acceleration of the surface relaxation should lead to the increase of the Si-O-Si angle and therefore should increase water diffusion in glass. Thus the concentration of water diffused in the tension side should be much higher than that in the compressive side. This would lead to a more important contribution of the plastic flow process during indentation and also to a smaller elastic recovery.
The removal of the relaxed surface layer using HF chemical etching inhibits the permanent deformation. When the fiber is removed from the mandrel the curvature radius is larger than the mandrel radius. Thus the relaxed surface layer is submitted to an inverse stress given by the bulk of the fiber in order to restore the straight shape of the as-received fiber. The Vickers hardness value was found to be surprisingly higher for the surface treated under tension than those for the surface under compression. The effect of the stress induced by the bulk fiber on the relaxed surface and the competition between the densification and the plastic flow should be the cause of such a hardness value.
The hydrothermal-treated fiber without stress exhibited also a contribution of the plastic flow process as pilling-up was observed on the rim of the indentation impression.
The indentation behavior of both HF chemical etched fiber (non-treated and heat-treated) are quite similar and exhibit once again the anomalous behavior of the silica glass. This indicates that the relaxation process, as assumed earlier, should principally occur on the surface. The increase of the Vickers hardness value indicates that the chemical etching induces some structural difference on the fiber surface by comparison to the as-received fiber. As the indentation occurred on a freshly etched fiber, the reaction between the surface and the moisture of the atmosphere should be less than for the as-received fiber.

Conclusion: The effects of the surface structural relaxation on the indentation behavior of silica optical fiber were investigated. This surface structural relaxation was promoted by a hydrothermal treatment of the fiber. The glass surface of the as-received fiber exhibited an anomalous behavior under load as sinking-in and densification were observed.
The observation of the Vickers impression provided direct evidence of a lateral displacement of materiel (exemplified by a pilling-up phenomenon) of the fiber submitted to the hydrothermal treatment. It suggested that the water could act as a modifier since the deformation was found to be due to the combination of the

densification and the plastic flow of the materiel. When the relaxed surface layer is chemically etched, the anomalous behavior of silica under indentation is restored as the deformation is controlled by densification.

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