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Strength increase of silica glass fibers by surface stress relaxation: A new mechanical strengthening method

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ABSTRACT

Pristine silica glass fiber is well known to become mechanically weaker when heat-treated in the presence of water vapor. However, the same fiber was found to become stronger if heat-treated while held under a sub-critical tensile stress at a temperature far below the glass transition temperature. The added strength of the stress-treated fiber was nearly equal to the applied tensile stress. This added strength was attributed to the formation of a compressive stress layer on the surface of the glass, created by a surface stress relaxation process that occurred while being held under the tensile stress. The presence of the surface compressive stress was confirmed by observing the bending of the fiber when 1) a tensile-stressed fiber was sliced and 2) a bending-stressed fiber was released from the stress. In the present paper we demonstrate that even though heat-treatment of a silica glass fiber in water vapor weakens the glass, a tensile stress application during the heat-treatment can increase the strength of silica glass fibers. Silica glass fibers with estimated strengths of ~7–8 GPa were produced, exceeding that of other fibers previously reported to have a maximum strength of ~5.5 GPa at room temperature in air. This new glass strengthening method does not require glass to be of a minimum thickness, as in tempering, or a glass containing alkali ions, as in ion-exchange.

1. Introduction

The mechanical strength of pristine glasses is extremely high but the strength of practical glass products is much lower primarily due to surface flaws. However, these glasses can be made mechanically stronger by forming a compressive residual stress on the surface. There are two popular methods to produce a compressive surface stress on the glass surface: One is thermal tempering in which a glass product is heated to near the softening temperature and then rapidly cooled [1]. This produces a temperature gradient with the surface of the product being cooler than the interior, and at room temperature, a residual compressive stress results on the surface. Automotive side and rear windows are made stronger by this method. The second method is ion-exchange or chemical tempering, in which glasses containing smaller alkali ions, e.g. Na^+, are treated in a molten salt containing larger alkali ions, e.g. K^+, at a temperature below the glass transition temperature [2]. This process, sometimes called ion-stuffing, can produce a surface layer with an extremely high compressive stress on the glass and is currently employed to strengthen products such as aircraft windows and scratch resistant touch-screens on electronic devices. Although these processes are extremely effective in making glasses mechanically stronger, there are limitations to both. Tempering requires the product to be of finite thickness, a few mm, in order to achieve the necessary temperature gradient during cooling. Ion-exchange processing requires the presence of alkali ions as a main glass component.

In the present research, silica glass optical fibers were made stronger by an alternative compressive surface residual stress formation method. The method is based upon a surface stress relaxation process while a sub-critical (i.e. a value less than the fracture strength) tensile stress is applied at a temperature, below the glass transition temperature, in the presence of water vapor, where upon release of the tensile stress a surface compressive stress is formed. This mechanism was proposed previously, and the extent of surface residual stress formation was evaluated using a fiber bending method [3]. Unlike alternative strengthening mechanisms, there is no minimum thickness or compositional requirement for its utilization. In the present paper the strengthening data of silica glass fibers treated at various temperatures in low water vapor pressure under various tensile stresses are presented together with the estimated surface residual compressive stress of fibers treated at various temperatures in the same atmosphere.

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2. Experimental

2.1. Silica glass fiber strength measurement by tensile test

Fracture strength measurements were first performed via tensile testing using an Instron machine (Model 4204) with rubber grips. Silica glass fiber (Suprasil II with plastic coating) specimens with a 150 mm gauge length were used. Thick cardboard was used as a tab material to provide extra cushion and prevent undesired breakage of the fiber in the grips. A 5 cm section in the middle of the gauge length was dipped into 96% H_2SO_4 at 200 °C for 5 s to remove the plastic coating and obtain bare fibers with a diameter of 125 μm. Matthewson et al. observed earlier, using silica glass optical fibers with the same plastic coating, that H_2SO_4 treatment at 200 °C for 5, 50, and 500 s produced nearly the same strength without adversely affecting the surface condition [4].

The samples were loaded into the grips and subjected to tensile stresses of 1 GPa, 2 GPa, or 3 GPa at a stressing rate of 100 MPa/s. While held at a constant stress, an approximately 1 cm length of the central portion of the bare fiber was exposed for 60 s to a N_2 gas passed through a heated coil as shown in Fig. 1. The back end of the gun is not sealed, allowing additional air intake, and as a result the gas blown over the glass fiber is a mixture of laboratory air and tank N_2. The humidity of the gas exiting the gun is estimated to be approximately that of lab air, ~6 Torr. The temperature of the exiting gas was controlled at 100 °C, 200 °C, 300 °C, 400 °C, or 500 °C ± 10 °C using a variable AC transformer. After 60 s, the hot gas flow was stopped, and then the fiber was unloaded. About 10% of glass fibers stressed at 3 GPa and 500 °C failed during the 60 s heat-treatment, but fibers did not break under other treatment conditions including 3 GPa stressing at 200 °C.

Without removing the fiber from the grips, the tensile strength of each fiber was tested at room temperature in air (22 °C with 20–30% RH) at a crosshead speed of 150 mm/min, and the failure stress was recorded. For comparison, some fibers which were untreated, and fibers that were heat-treated in the same manner but under zero stress were also measured. Approximately 15 fibers were tested for each treatment condition. Care was taken during every step of the procedure to avoid letting the bare fibers contact any solid object.

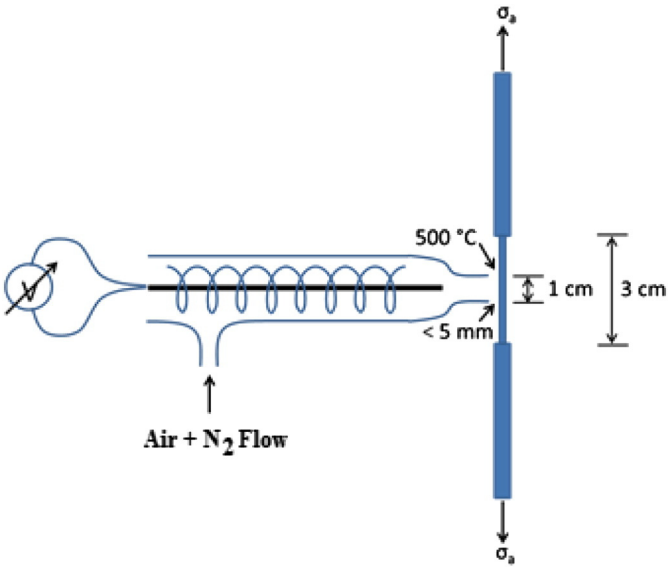

Fig. 1. Schematic drawing of the system used to perform spot heat-treatments on the loaded fiber. The temperature of the exiting gas was controlled by resistively heating a metal coil using a variable AC voltage controller. (Variac).

2.2. Silica glass fiber strength measurement by two-point bend test

In order to probe the strength of only the 1 cm heat-treated portion of the fiber, two-point bend testing was also conducted [5–7]. Failure strain measurements were performed using a two-point bend apparatus (Fiber Sigma, NJ, USA) with grooved faceplates. Fiber specimens for use in the two-point bend testing were first subjected to a tensile stress at various temperatures in low water vapor pressure using an Instron machine by an identical method to that outlined in Section 2.1.

After each thermal and mechanical treatment, the position of the fiber heated with N_2 gas was specified by the distance from the edge of the coating removal with an accuracy of ±2 mm before the 5 cm length of bare fiber was broken out of the tensile specimen using tweezers. The sample was then placed into a two point bending grooved holder which clamps the ends in such a way that the mid-section of the fiber remained free from any contact with solid objects at all times.

The bending strength of each fiber was tested at room temperature in air (22 °C with 20–30% RH) at a constant faceplate velocity of 1000 μm/s, and the failure strain was recorded. It was ensured from prior measurements that the vertex of the bend during testing occurred at the same position as the middle of the heat-treated length. After every 5 fibers the faceplate contact position was zeroed to prevent any zero point drift. For comparison, the failure strains of some fibers which were untreated, and fibers that were heat-treated in the same manner but under zero stress, was also measured. Approximately 15 fibers were tested for each treatment condition.

2.3. Surface stress relaxation and residual stress development measurement by fiber bending for low stress

It was found previously that when glass fibers were heat-treated in a two-point bend configuration in the presence of water vapor at a temperature far below the glass transition temperature, there was retained residual curvature when the bending stress was removed at room temperature [3]. This effect was attributed to surface stress relaxation accelerated by water diffusion, resulting in the formation of residual stress, and a simple method was developed to calculate an effective surface stress relaxation diffusion coefficient [3,8]. Such diffusion coefficients were evaluated experimentally for silica glass treated at various temperatures between 300 °C and 700 °C under various bending stresses in air with water vapor pressures of 355 Torr and 0.6 Torr [3]. In the present work, the effective surface stress relaxation diffusion data were obtained at selected temperatures corresponding to the treatments for mechanical strength testing under various water vapor pressure conditions. Silica glass optical fibers made by Furukawa Electric Co. were used in the present stress relaxation experiments as well as in the earlier stress relaxation measurement [3].

The plastic coating on the fibers was removed by immersing the fiber in 96% H_2SO_4 at 200 °C for 10 s to obtain bare fibers with a diameter of 125 μm. A longer immersion time of 10 s compared with the time of 5 s used for Suprasil II fibers was employed because Furukawa silica glass optical fiber had a thicker coating. This longer immersion time is still short enough to prevent damaging the surface [4]. The glass fibers, after removing the plastic coating, were subjected to a bending stress by placing them in silica glass tubes with an inner diameter of 2.2 cm, in a two-point bending arrangement with the two ends of a fiber being parallel and in full contact with the inner wall of the tube. The bent silica glass fibers were under a maximum tensile stress of 493 MPa, as estimated using the equation derived by Matthewson et al. [5].

Two-point bent fibers were heat-treated at 400 °C, 500 °C, 550 °C, 600 °C, 625 °C, and 700 °C in two different water vapor pressures, room temperature air with ~6 Torr H_2O and a wet atmosphere of 60 Torr H_2O, for various lengths of time. The water vapor pressure of the room temperature air has been estimated from the humidity of the room, that being approximately 23 °C and 30% relative humidity.