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Raman measurements of the rate of OH uptake in silicone-clad pure fused silica optical fibers (530 ppm initial OH), immersed in water at room temperature, were accomplished with and without tensile stress by determining the integrated intensity of the OH-stresses of 1.56 GPa (15.6 kbar), no significant changes in the rate of OH uptake, relative to the uptake rate for an unstressed fiber, were observed. For diffusion through silicone rubber, a 14% increase in the overall Raman OH signal from the fused silica

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RAMAN INVESTIGATION OF THE RATE OF OH UPTAKE IN STRESSED AND UNSTRESSED OPTICAL FIBERS*

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Abstract

Raman measurements of the rate of OH uptake in silicone-clad pure fused silica optical fibers (530 ppm initial OH), immersed in water at room temperature, were accomplished with and without tensile stress by determining the integrated intensity of the OH-stretching contour at ~ 3690 cm^{-1}. Up to tensile stresses of 1.56 GPa (15.6 kbar), no significant changes in the rate of OH uptake, relative to the uptake rate for an unstressed fiber, were observed. For diffusion through silicone rubber, a 14% increase in the overall Raman OH signal from the fused silica occurred in 200 h. This 14% increase means that a large increase in the OH concentration occurred within a few microns from the surface of the 200 μm diameter fiber, because diffusion of water is very slow in fused silica at room temperature.

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Introduction

The effects of tensile stress from 0 to 3.3 GPa (33 kbar) on the Raman spectra from pure fused silica optical fibers were examined in previous work.[1] Subsequently, the effects of irreversible uniaxial compaction (90 kbar),[2] of reversible hydrostatic compression (10 kbar),[3] and of reversible torsion[4] on the Raman spectra from pure fused silica were studied. The present work constitutes a further Raman study in which the rate of OH uptake in silicone-clad pure fused silica optical fibers initially containing 530 ppm OH was examined under tensile stresses from 0 to 1.56 GPa (15.6 kbar).

In this new Raman work, pure fused silica optical fibers, clad with silicone rubber, were submerged in water for long periods of time, and examined with and without the application of the tensile stress. The uptake of OH by the fused silica after diffusion through the silicone rubber cladding (above the amount present before diffusion), was then monitored by measuring the integrated Raman intensity of the OH-stretching peak at 3690 cm^{-1}, relative

to the integrated Raman intensity of the Si-0-Si bending peak from fused silica at 800 cm^{-1}.

The Raman techniques and OH uptake data are now presented and discussed.

Experimental Methods

Two identical optical fiber samples, clad with 100 μm of silicone rubber, and both 20 m in length and 200 μm in core diameter (manufactured by Optelecom, Inc.[5]) were simultaneously immersed in water using appropriate pulleys. A schematic illustration of the experimental arrangement is shown in Fig. 1. Approximately 16 m of one of the fibers was subjected to a tensile stress of 0.69 GPa (6.9 kbar) by applying a load of 2.2 kg to one end. The detailed procedure for applying tensile stress is described in Ref. (1). Excitation was accomplished by illuminating one end of the fiber with 514.5 nm light from an argon ion laser at a power level of 600 mW. The other end of the fiber was inserted into a slitless optical fiber Raman spectrometer, consisting of a 3-prism single monochromator described elsewhere.[6] The intense forward-scattered exciting radiation from the fiber end was attenuated by using a Corning 3-69 optical filter. The 3-69 filter severely weakened spectral features below 500 cm^{-1}, but good quality spectra could be obtained from 500-4000 cm^{-1}.[6,7]

Attempts were also made to increase the stress on the optical fiber by applying stresses above 0.69 GPa, but breakage became a problem as the fiber took up more OH. To overcome this problem, a fiber was stressed to 1.56 GPa and then the OH uptake was measured after the stress was removed.

Experimental Results

Raman data from stressed and unstressed optical fibers immersed in water

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at room temperature ($\sim 20°C$) were obtained from 500 to 4000 cm^{-1}. With slitless optical fiber laser-Raman techniques[6] the signal-to-noise ratio, S/N, at the 3690 cm^{-1} CH-stretching peak can reach 200,[6] and thus accurate integrated intensities can be obtained for the OH peak, as well as for the 800 cm^{-1} peak from pure fused silica, used here as an internal reference standard for intensity. Areas under the Raman peaks at 3690 cm^{-1} were determined by weighing. Baselines were estimated by examining large regions of the Raman spectrum on either side of the 3690 and 800 cm^{-1} peaks.

Raman data showing the rate of OH uptake (the uptake by fused silica is definitely not in the form of H_2O)[8] for silicone-clad pure fused silica optical fibers are shown in Fig. 2 for three different conditions, where the nominal integrated intensity ratio, I_{3700}/I_{800}, is plotted versus time in h. In (A) of Fig. 2 the data refer to an unstressed fiber, in (B) the Raman data were <u>actually obtained</u> while the fiber was under a tensile stress of 0.69 GPa (6.9 kbar), and in (C), the fiber took up OH under a tensile stress of 1.56 GPa (15.6 kbar), but the Raman measurements were made after the stress was removed. Within the small scatter of the data, all three slopes of Fig. 2 are virtually identical, namely $(5.0 \pm 0.4) \times 10^{-4}$ h^{-1}, which corresponds to an increase of approximately 14% in 200 h.

Discussion

In order to discuss all of the present Raman data in detail, it would be necessary to know (in addition to specific features of the optical processes involved) the rates of diffusion, and also the solubilities of the H_2O and OH species in the silicone rubber and in the fused silica, as well as how these quantities change under tensile stress. Such detailed information is not readily accessible, but it is, nevertheless, instructive to consider the

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available data relative to OH uptake without tensile stress.

The highest concentration of water attained in silicone rubber after immersion for 168 h at room temperature is about 0.12% by weight. This corresponds to an H_2O concentration of ~ 1.5×10^{-3} g cm^{-3}.[9] Also, the maximum solubility of water as OH in pure fused silica is about 0.3%.[10] This corresponds to a concentration of OH of about ~ 6.6×10^{-3} g cm^{-3}. However, each molecule of H_2O produces two Si-OH groups when it reacts with fused silica. Hence, twice the maximum H_2O concentration in silicone rubber is not far below (1/2) the maximum OH solubility of fused silica. Further, the diffusion coefficient of H_2O in fused silica at room temperature has recently been estimated to be as large as 3×10^{-16} cm^2 sec^{-1},[11] and the diffusion coefficient for H_2O in silicone rubber is about 10^{-9} cm^2 sec^{-1}.[12] Thus, in terms of solubilities, and of diffusion coefficients, there is little doubt that the rate determining process in OH uptake involves the fused silica and not the silicone rubber. In other words, as far as the rate of OH uptake is concerned, the present experiment is roughly equivalent to immersing a bare fused silica fiber directly in water. However, the details of the multimode excitation of the optical fiber must also be considered to understand the data fully.

In view of the small diffusion coefficient for water in fused silica at room temperature, it is obvious that surface OH groups are formed preferentially. For example, if $D = 3 \times 10^{-16}$ cm^2 sec^{-1}, the diffusion depth in 200 h would be roughly $\sqrt{20 \times 10^{-10}}$ cm^{-2}, or 0.5 μm. The initial OH content of the optical fiber was determined to be about 530 ppm [1] and a 14% increase in the overall Raman OH signal was observed in this work. But it is certain that this 14% cannot refer to the entire fused silica fiber. The laser launching condition employed here was such that high-order multimode excitation occurred,

that is, most or all of the numerical aperture of the 200 μm fiber was filled. The lowest-order LP_{01} mode, of course, would travel directly down the axis of the fiber and would see an OH concentration of 530 ppm. Whereas, modes of higher order would be reflected from the fiber surface, and hence would contribute disproportionately to the Raman OH radiation that would be produced by OH groups on, and just below, the surface. Therefore, the present method yields data applicable to the way in which water attacks the glass fiber at the polymer-glass interface, rather than at greater penetration depths in the fiber itself.

To understand the essential features of the present effect, a simple model is employed which initially assumes that the exciting laser radiation is completely uniform across the fiber radius, i.e., the mode structure of the radiation is completely ignored. Then, the penetration depth having a constant OH concentration near the surface of 3000 ppm (the maximum solubility), can be calculated. This maximum OH concentration near the surface raises the overall Raman signal from that corresponding to the initial value of 530 ppm, to 604.2 ppm, a 14% increase. If P is the penetration depth in μm, that is, the thickness of the surface shell having a uniform OH concentration of 3000 ppm, then for a radius of 100 μm, P is given by

$$3000\ P + 530(100-P) = 604.2 \times 100. \tag{1}$$

From Eq. (1), P = 3 μm, which means that the OH penetration involves only 3% of the fiber radius near the surface.

Consideration of the mode structure of the exciting radiation, however, will change the value of P, but in the present case P will be decreased, because high-order mode excitation was involved, which tends to favor surface

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Raman scattering. This may be seen by Eq. (2),

$$3000 \; E_1 P + 530 \; E_2(100-P) = 60420,\tag{2}$$

where E_1 and E_2 refer to the excitation efficiencies in the penetration shell, and in the remainder of the fiber, respectively. If the total OH Raman scattering arbitrarily corresponds to 60,420 units, Eq. (1), and if (arbitrarily) $E_1 = 1.1$ and $E_2 = 1.0$, then $P = 2.7 \, \mu m$. Alternatively, for P to equal the value of 0.5 μm, calculated from the previous high estimate for the diffusion coefficient, D, $E_1 = 5.1 \; E_2$, which is rather large, and which suggests that even a D of $3 \times 10^{-16} \; cm^2 \; sec^{-1}$ may be too small for thin optical fibers. Nevertheless, it cannot be doubted, at least qualitatively, that a thin surface layer of the fused silica fiber takes up most of the OH that results from diffusion through the silicone rubber cladding.

It should be mentioned that selective mode launching conditions in principle constitute a possible means of assessing the radial distribution of OH in the fiber. For example, in the preceding discussion, it was stated that an LP_{01} mode would see an OH concentration of 530 ppm, whereas selectively higher modes could be generated which would interrogate regions farther from the fiber axis. However, because of the pulley suspension system used here, Fig. 1, and because of the variable tensile stress applied to the fiber, selective mode launching seemed unwarranted, and was not performed. Indeed, one reason for the use of the 800 cm^{-1} band as an internal Raman intensity standard, that is, for measuring the intensity ration I_{3700}/I_{800}, rather than I_{3700} alone, was that the optical transmission of the fiber was found to decrease markedly with increasing tensile stress, further emphasizing the impracticality of carrying out selective mode experiments.

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The present data indicate that the 14% rate of OH uptake in 200 h is also essentially independent of tensile stress to 1.56 GPa. This additional feature of the data may also be related to uptake of OH at, or just below, the fused silica surface.

It is known, for example, that the intensity of a Raman peak from fused silica at 490 cm^{-1} rises with increase of tensile stress.[1] This peak has recently been attributed to a low concentration of ring structures involving Si-O bonds of high energy.[13] Thus, for a fiber under tensile stress, it is not unreasonable to assume that the overall energy of the system would be lowered by the attack of H_2O preferentially at the high energy Si-O sites. However, it is not known whether these ring structures are of overriding importance at the surface or not.

The surface of fused silica almost certainly involves high concentrations of reactive high energy configurations arising from the constraints of network termination on the topology. The range of such reactive configurations would probably not be very sensitive to the modest tensile stresses applied here. Thus, the observed independence of the surface OH uptake rate on tensile stress is not too surprising, and appears to agree with other recent measurements.[14]

Finally, it should be pointed out that the conventional method of determining OH in an optical fiber, namely, by measuring the ~ 1.4 μm infrared overtone band is not applicable in the present case. At 530 ppm OH, the loss at 1.4 μm would be above 5×10^5 dB/km, which is unacceptably high. Further, the present Raman method measures the OH fundamental directly without complications arising from combination tones from the OH and the fused silica, and is capable of providing information over the entire range of OH concentrations, from 100 ppm OH or slightly less, to the maximum solubility of about 3000 ppm.

Summary

Laser-Raman methods involving forward scattering in silicone clad fused silica optical fibers immersed in water have yielded an increase of 14% in the fused silica OH content in 200 h, which is thought to occur primarily at the fused silica-silicone rubber interface. This OH increase was also found to be independent of tensile stress to 1.56 GPa. The new technique appears to provide a general method for assessing polymer coatings on optical fibers with regard to their impermeability to water.

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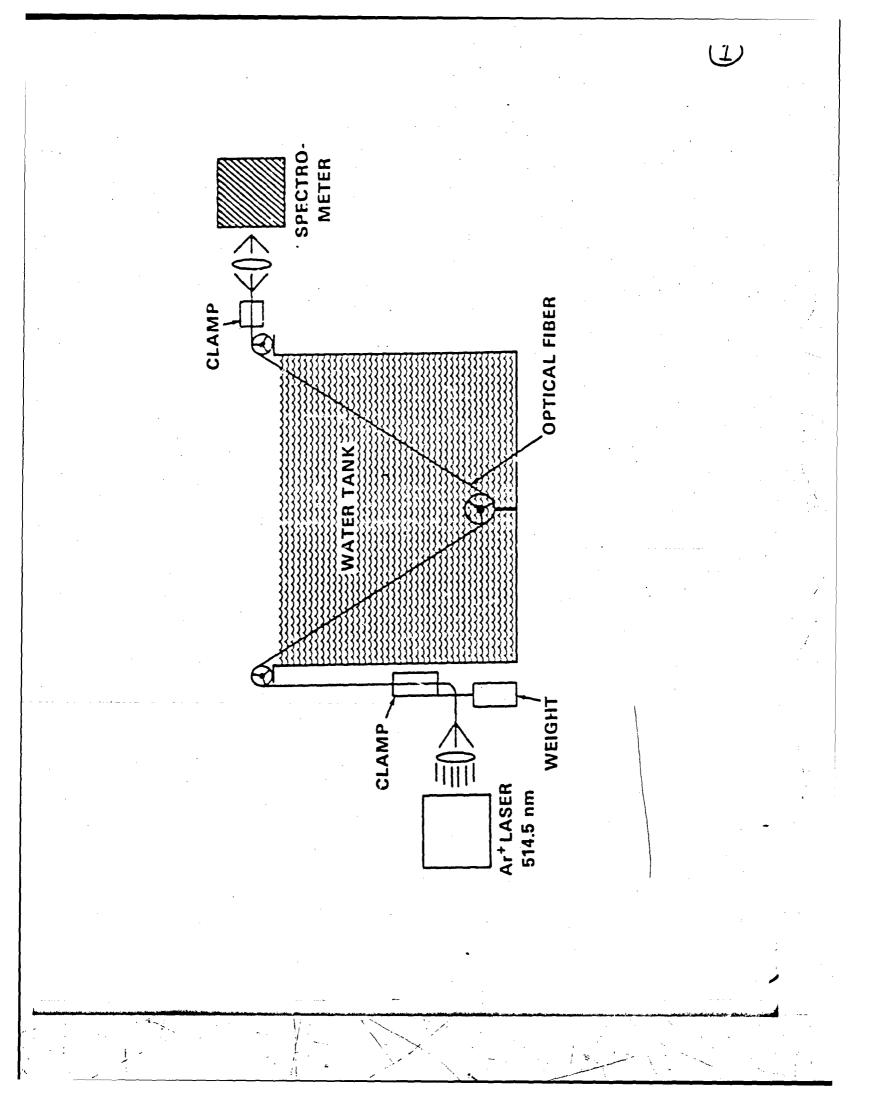
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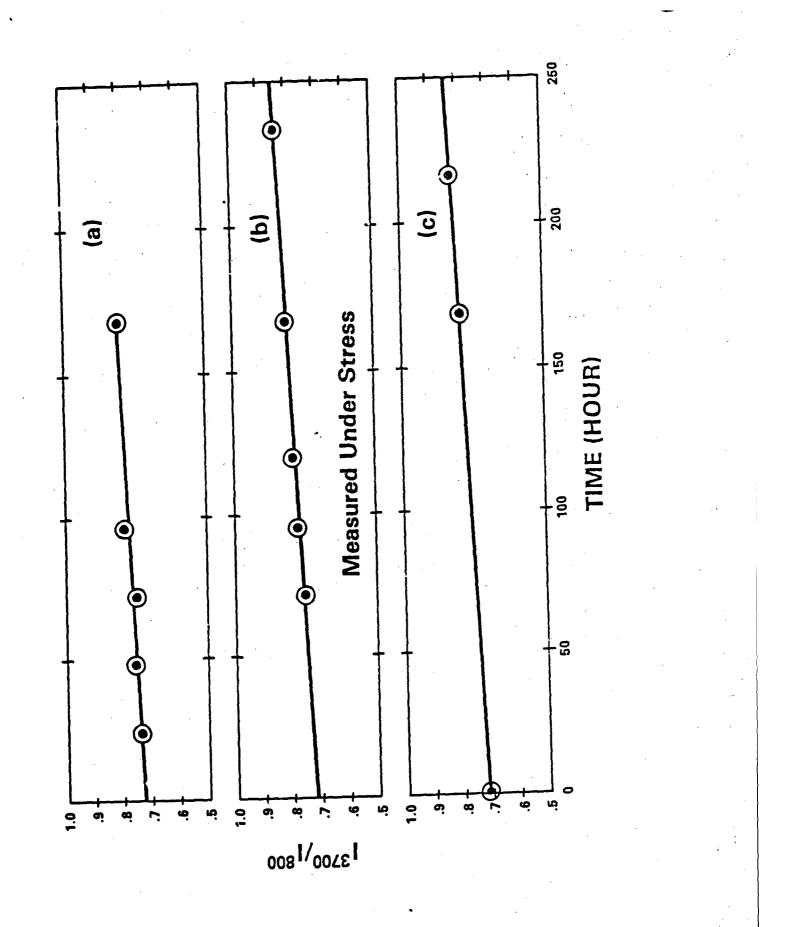
Figure Captions

Figure 1   Schematic illustration of the laser-Raman method for measuring OH uptake rate in silicone-clad fused silica optical fibers.

Figure 2   Integrated Raman intensity ratio, I_{3700}/I_{800} <u>versus</u> time in h. Area at 3700 cm^{-1} refers to a gain 15 times that used at 800 cm^{-1}. (A) -- No tensile stress. (B) -- tensile stress, 0.69 GPa (6.9 kbar). (C) -- Tensile stress, 1.56 GPa (15.6 kbar).

SPECTRO-METER

CLAMP

OPTICAL FIBER

WATER TANK

CLAMP

WEIGHT

Ar⁺ LASER
514.5 nm

Measured Under Stress

TIME (HOUR)

I_{3700}/I_{800}