Effects of heat treatment and HF etching on the strength of silica lightguides

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ABSTRACT

Often lightguide fiber processing involves steps that may cause degradation of very high strength or flaw-free, perfect fiber. A very obvious type of degradation is the development of abrasion flaws during handling. Also, heating of a fiber to moderate temperatures (~300−600°C), for instance during the soldering of pigtails, has been shown to result in strength degradation of strong fiber. It has been suggested that the use of HF etching may be a reasonable technique for the elimination of many types of strength-lowering defects. In this paper we discuss early results from the literature on the effects of heating and HF etching on the strength of silica glass and present new results on both.

Keywords: Optical fiber, strength, degradation, etching, heating

1. INTRODUCTION

The strength of as-drawn, perfect silica lightguide fibers can only be increased by removing water from the glass surface and/or from the atmosphere. On the other hand, almost anything else that is done to these fibers may lead to a reduction in their very high strength: there are many known mechanisms by which the strength may be reduced.

While the most commonly encountered mechanism for the reduction in fiber strength is mechanical damage, it is known that treating the fiber with water and many solutions can also lead to strength reductions.[1] In such cases, Yuce *et al.*[2] have shown that as a result of inhomogeneous solution of the surface of the fiber, a general surface roughness develops. This roughness acts to concentrate stress, thus reducing the measured strength. Several studies have shown that HF etching can increase the strength of weakened glasses, although no studies have been made to indicate whether HF etching can cause roughening and thus weakening of 'perfect' silica fibers.

Krause and Kurkjian[3-5] have shown that it is possible to produce fusion splices (*i.e.*, heating to temperatures between room temperature and ~2000°C) having essentially original strengths using special torches. However, other workers[6-8] have shown that normal reheating of silica fibers can cause strength reductions by the attachment of solid particles to the fiber surface,[7] as well as by the reaction with water. Wissuchek[9] has shown that the fusion of refractory particles in the glass surface will lead to residual stresses as a result of thermal expansion mismatch between the silica and the particle. It is unclear whether such a mechanism would be operational at temperatures well below the softening point of the glass. Here we attempt to study the strength degradation of high strength fibers due to moderate heating under 'normal' conditions.

Vitman *et al.*[6] found that heating will generally reduce the strength of silica glass, while HF etching can recover the strength of fibers weakened by either heating or abrasion. However it was found that while substantial strength increases were observed after etching, the very high strength of as-drawn fiber was not recovered.[6,10] Both the heating and etching effects are of scientific as well as practical importance. We are thus interested in substantiating these early results and in understanding the processes involved. That is: (1) is the heating effect intrinsic, and (2) can the initial high strength of perfect fiber be entirely recovered by HF etching or alternatively, is the high strength of the original fiber degraded by HF etching? In the past we have argued that surface roughening can account for the strength decreases when fibers are aged in either liquid water or in water vapor at moderate temperatures (*i.e.*, < 100°C). From a scientific point of view it is important to investigate if heating and HF etching of high strength fiber will result in similar strength degradation and

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if the mechanisms involved are the same. From a practical point of view, an understanding of both of these effects is important for their application to post draw processing.

2. EXPERIMENTAL

All strength measurements were made in two-point bending.[11] The tests were performed at a faceplate speed of 1000 μm/sec in distilled water at ~25°C. 125 μm diameter, 250 μm dual acrylate-coated Suprasil silica fibers were used. If bare fibers were to be studied, the coating was removed by soaking in methylene chloride (dichloromethane, CH_2Cl_2) for ~60 s, during which time the coating was observed to delaminate and peel away from the fiber. It has been shown that strengths were not degraded by this procedure. Etching was carried out using a 10wt.% HF, 10wt.% H_2SO_4 solution. Such an etching solution was found by Dabbs and Lawn[12] to remove many of the surface flaws in commercial silica rods.

In addition to the studies of bare fiber, because of possible practical interests, etching studies were also carried out on the dual-coated fibers. In this case, the coated fibers were placed in the etching solution for the desired period of time, after which they were rinsed in DI water. For direct comparison with fibers etched bare, the coating was removed with the process described above prior to strength testing. In order to more completely understand the process in the case of coated fibers, we also studied the possibility of continued etching after removal of the fiber from the etching solution. In this case, the strength of the fibers was measured while coated after removal of the fiber from the HF solution and rinsing in DI water, as a function of time after removal from the HF.

Heating studies were carried out in air (~50%RH) in a box furnace at ~450°C for 15 minutes. Four or five fibers were placed in a silica holder and inserted into the furnace for the desired time. After removal from the furnace they were tested in DI water as described above.

3. RESULTS

3.1. Etching

The results of the etching studies on both bare and coated fibers are shown in Fig. 1. For the bare fibers we find that the initial strength (5.5 GPa) is rapidly reduced to a plateau of ~3.5 GPa. Additional etching continues to reduce the fiber diameter, but does not result in significant further degradation of the fiber strength. For the coated fibers, while the strength reduction occurred much more slowly, the plateau was somewhat less, ~3.0 GPa. These plateaus are in reasonable agreement with the earlier results in which the strength of weak fibers was increased by etching.[6,10] Fig. 2

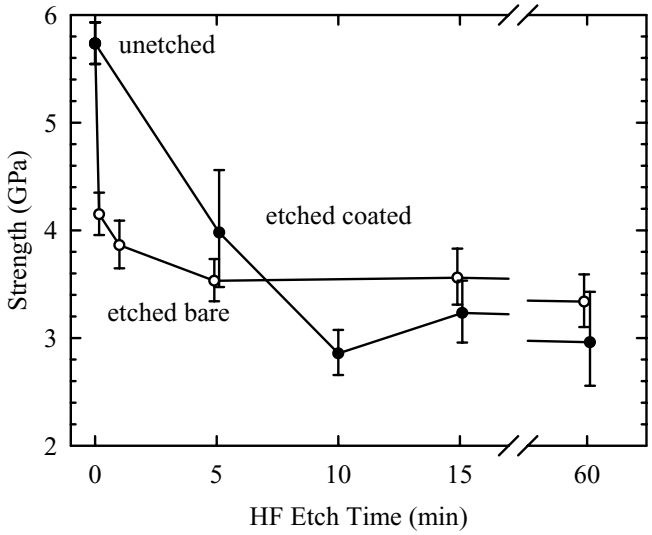

Fig. 1: Strength of bare fiber as a function of HF etching time for fiber that was stripped of its coating before (o, etched bare) and after etching (●, etched coated).

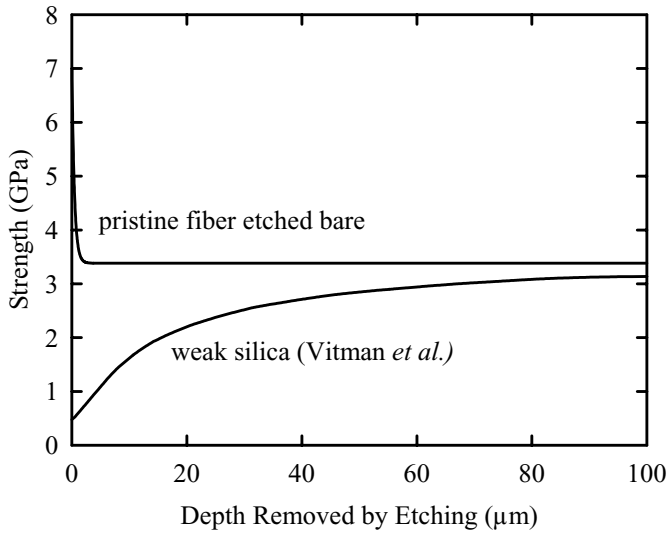

Fig. 2: Strength as a function of etch depth showing trends for the pristine fiber data of Fig. 1 and for data for weak silica from Vitman *et al.*[6]

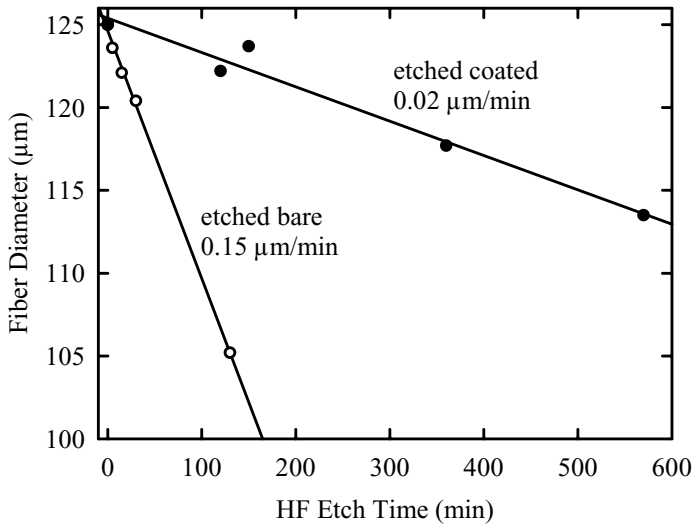

Fig. 3: Fiber diameter as a function of HF etching time for fiber that was etched bare (o) and etched coated (●).

illustrates that the plateau is approximately the same in both cases. The appearance of this plateau is practically important since it means that quite large flaws may be removed without the strength falling to a disastrously low level. While this plateau value would seem to be intrinsic, and we would argue it is due to surface roughening of the perfect fiber surface, it is somewhat disappointing from the point of view of the recovery of fiber strength in practice. Such a strength level is, however, still a useful one considering that mechanical damage can result in strengths significantly lower than 1 GPa. In addition, the results found with the coated fibers are encouraging. Although we have not looked at strengthening, it appears that it is quite feasible to recover the strength of degraded fibers with the coating in place. This will reduce the possibility of developing damage to the uncoated fiber. Fig. 3 compares the etching rate for bare and coated fibers. As expected, bare fibers etch at a substantially faster rate than coated fibers. An important problem is illustrated in Fig. 4. Here we show that strength degradation continues after removal of a coated fiber from the etching solution. It is clear that residual HF inside the coating continues the etching process.

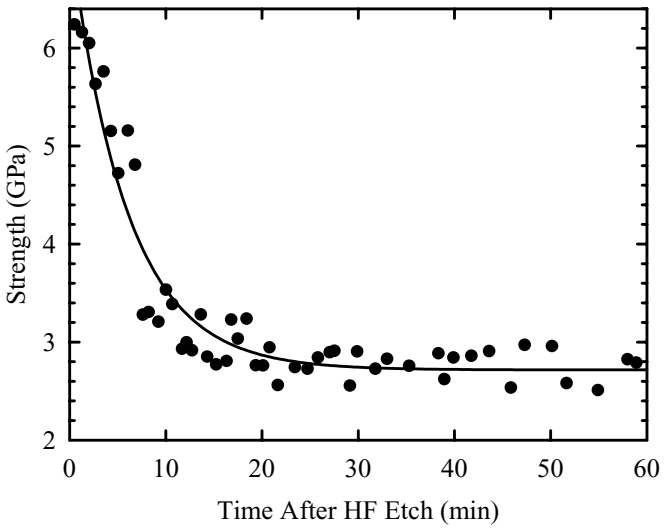

Fig. 4: Strength of coated fiber as a function of time after removal from a 5 minute exposure to HF etchant.

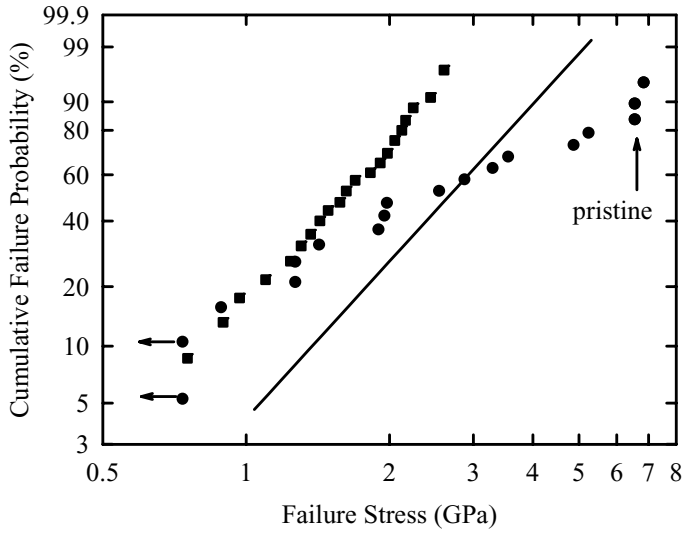

Fig. 5: Weibull plot of post heating strength. ● – current work, strength measured in two-point bending for fiber heated for 15 minutes in laboratory air heated to 450°C; ■ – strength measured in tension of fiber heated for 1 minute in laboratory air heated to 550°C.[13] The line is typical behavior for fusion splices measured in tension.[13]

3.2 Heating

A summary of the results that we described in an SPIE proceedings some time ago[13] on the heating of a hot acid stripped fiber is shown in Fig. 5. In this work, the experiment involved removing the coating from the center 25 mm of a 250 mm length of fiber with hot sulfuric acid. Hot nitrogen gas containing different amounts of water vapor was passed over this section of bare fiber, and the strengths were then measured in tension. While it has been shown that hot acid stripping does not degrade the fibers strength *per se*,[14] it is not clear whether the fiber surface is clean enough to be heated without undergoing 'extrinsic' strength degradation. In addition, when this work was done, occasional breaks occurred outside of the bare, heated section, implying the possibility of effects at the interface between the coated and stripped sections. In the present experiments we used two-point bending so that such interfacial effects were eliminated. However, we were unable to use hot acid stripping, but rather a methylene chloride swelling procedure was used. Our

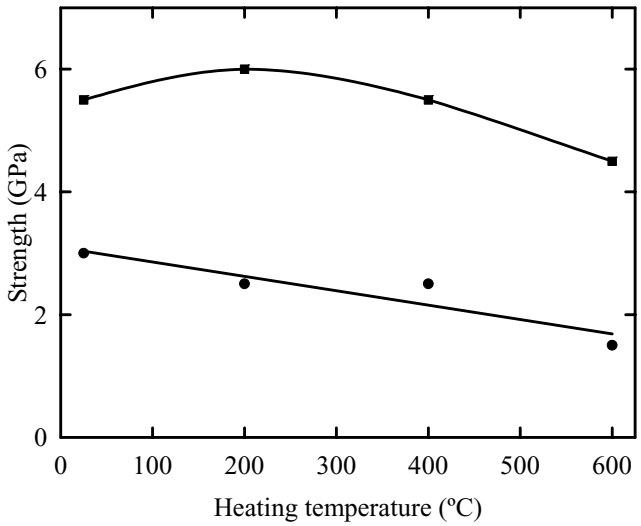

Fig. 6: Strength measured at 20°C after heating for one hour as a function of heating temperature. Measurements were made in three-point bending (■) and tension (●). Data from Ref. 8.

present attempts to study the effects of heating are shown by the circles in Fig. 5. It can be seen that while the present results show a considerably broader distribution, the mean strengths are in reasonable agreement even though the experiments are different in many respects. In particular, the coating removal techniques and the heating procedures differed. Krause and Kurkjian[3-5] have shown that by using specially designed oxygen/chlorine/hydrogen torches, very little strength degradation takes place on heating to temperatures above the softening temperature. They essentially showed that the strength degradation (of hot acid-stripped fibers) depended on the water activity in the gas. It is interesting to note that while these splicing experiments and the earlier work described above both involved flowing gases, the present heating was done in a static environment in a box furnace. Another important difference between these two experiments is the testing techniques: tension in the earlier work *versus* two-point bending in the current work. For an additional comparison, in Fig. 6 we show the results of Piggot & Yokom[8] in both tension and three-point bending on hand drawn fibers similar to those described by Proctor, Whitney and Johnson.[7] While Piggot's results in tension are very similar to those of Proctor *et al*.,[7] the three-point bending results are quite high; substantially higher than the present results in two-point bending. Piggot's fibers were never coated and heating was carried out in the static environment of a box furnace. There may be questions about the calculation used by Piggot for his three-point bending (he used 50 μm diameter fibers and 75 μm separation of supports). On the other hand, whatever the calculation and thus the absolute values of strength, he shows minimal strength degradation after heating.

4. DISCUSSION

4.1 Etching

The results of HF etching seem relatively straight forward. Similar to the effects observed with the aging in liquid water at temperatures below 100°C, in the case of HF etching it would seem that surface roughness acts to concentrate stress. Early studies of the aging degradation in water showed an increase in fiber surface roughness with aging time that correlated with the strength decrease[2].

Studies of the effects of HF etching had shown that strength of as-received silica rods can be improved to ~3 GPa by such etching.[6,10] These studies can be understood by consideration of the work of Roach and Cooper.[15] They studied the etching of indented soda-lime-silica glass rods and found that when the etched depth is greater than five times the original crack depth, the developed etch pits are hemispherical. After that point the pits etch uniformly, *i.e.*, the pit radius and depth remain equal, the pits remain hemispherical and thus the strength does not change. This is qualitatively in agreement with the model of Proctor[10] who assumed that the etching rates of all surfaces are equal. Certain discrepancies have been observed, possibly due to the difficulty of achieving penetration of the acid into narrow crack openings[15]. This information is useful in predicting the etching depth necessary to increase a given low starting strength.

A second interesting result of these etching studies is that it may be possible to study the existence of a fatigue/aging limit using such an etching technique. We are presently studying the behavior of progressively more dilute etching solutions in order to validate this plateau under such conditions, and will then attempt to apply it to the study of a fatigue (and aging) limit as seen by Sglavo and Green.[16]

Tests on the continued weakening of the coated fibers after removal from the acid are important. These results show that etching continues after the fiber is removed from the etching solution; presumably the result of HF trapped inside the coating. A few tests carried by heating to fibers to ~120°C for 10 minutes after removal from the HF suggested that heating can be an effective technique for removing the trapped HF, and thus stopping the etching.

4.2 Heating

With regard to the heating experiments, there are two questions:

1. In those cases where the strength degradation by heating is clearly controlled by water interaction, what are the details of the process? Why is the distribution so broad?
2. In a more 'normal' heating process of stripped fibers, under what conditions is the degradation due to factors other than the activity of water?

We find that the heating results of Proctor *et al.*[7] (fibers in tension), Vitman *et al.*[6] (three-point bending of etched rods) and Piggott and Yokom[8] (fibers in tension) are essentially the same. Heat treatments reduce the strength to less than 2 GPa. Piggot's three-point bending results are substantially higher. Most workers suggest that the reduction is due to the action of water vapor and/or the effects of impurity particles attaching themselves on the glass surface. Thus, the mechanism of strength reduction resulting from heating under 'normal' conditions is still unclear and the present experiments do little to clarify this.

In previous work[13] it was shown that degradation correlated with the water content in the atmosphere when heating high strength fibers in a stream of water-containing nitrogen. In addition, the earlier work on splicing[3-5] showed that under certain controlled conditions, the removal of water from the silica surface and/or from the atmosphere results in no strength degradation. These earlier heating studies were carried out because of our interest in fusion splicing. As a result of these studies, we assumed that, whether or not the degradation was intrinsic, under the conditions of splicing, *i.e.*, hot acid stripping and subsequent heating for the fusion, the water vapor activity was an important variable. While splicing with an oxy-hydrogen torch resulted in similar strength degradation, substitution of Cl_2 for H_2 in the fusion torch showed no degradation. Later studies with a specially designed three section concentric tube torch showed that if a high velocity oxygen flow were used in the outer tube, very little degradation occurred. This was interpreted to mean that the water at the surface of the fiber that would normally cause degradation was swept away by the high velocity oxygen stream. While these were very short time heating experiments, they strongly suggest that at least in this case, the heating degradation is the result only of the reaction with water vapor. This is in agreement with earlier studies.[13] Of course it is always possible for contamination to have an additional effect.

It had earlier been suggested[13] that rather than 'geometrical' pits, what we might call 'chemical pits' could be responsible for the strength decrease in vapor. Tomozawa[17] has pointed out that at normal water activity as used in Fig. 5, the amount of water dissolved would be small and not likely to affect much of a change in the mechanical properties. Tomozawa and Peng[18] suggest a mechanism that involves the increased relaxation rate resulting from the diffusion of water in the fiber surface and the corresponding change in fictive temperature of the surface. In earlier unpublished work[17] no increase in roughening was observed after heating to 400°C for some hours.

Earlier work studying fiber splicing suggested devitrification may give rise to cracks.[19] It was found that crystals approximately 1 μm in size formed after heating for 10 s between 1500 and 1550°C. For any sensible value of the activation energy for crystallization, the time required to form such crystals at 450°C would be many orders of magnitude longer than the 15 minute heating used here. It is therefore highly unlikely that the strength degradation we have seen is caused by devitrification.

5. SUMMARY AND CONLUSIONS

The results presented here for HF etching confirm that the inhomogeneous solution of the silica fiber surface, either by water or acid, can reduce the fiber strength, presumably as the result of surface roughening. While this can occur quite rapidly, it is interesting and important to note that in this case, an 'aging limit' is reached at ~3.5 GPa. The behavior of coated fibers was similar except for the increases in time necessary for the HF to penetrate the coating. Etching was found to continue after removing the coated fiber from the acid.

We have also confirmed what other workers have seen, that heating, even to moderate temperatures (415°C) for relatively short times (~15 minutes) can drastically reduce fiber strength. These times and temperatures would seem to preclude even the partial fusion of impurity particles to the fiber surface. Nor does it seem reasonable that any polymer remnants would cause such strength reduction. Under these conditions, earlier work showed that water was involved in such strength reduction. On the other hand, the formation of actual etch pits seems to be precluded since there is no transport mechanism available in water vapor or air, and the amount of water that will be dissolved under the test conditions seems insufficient to cause any stress-concentrating pits to develop. At the moment we have no good model to either explain or predict the observed fiber weakening under normal heating conditions.

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