Effect of chemical stripping on the strength and surface morphology of fused silica optical fiber

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ABSTRACT

Examination of the surface profile of silica optical fiber using the atomic force microscope (AFM) has proved a useful technique for understanding strength degradation of the fiber upon aging in aggressive environments in terms of the production of surface roughness. However, before AFM examination it is necessary to remove the polymer protective coating and this is usually achieved by dipping the fiber sample in methylene chloride (MeCl) or hot (~200°C) sulfuric acid. This raises the possibility that the stripping technique modifies the fiber surface. In this work it is shown that hot acid stripping does not affect the fiber strength. It does, however, remove a surface layer from the aged fiber, probably of hydrated silica, which does not contribute to the strength. Therefore, treatment with hot acid is necessary in order to reveal the strength controlling surface profile, even if there is no polymer coating requiring removal. MeCl does not remove the surface layer and does not reveal the strength controlling surface.

1. INTRODUCTION

Pristine silica optical fiber is subject to strength degradation upon zero-stress aging in harsh environments[1] and the mechanism responsible for the strength loss is now well understood to be surface roughening. Direct evidence for this mechanism was first obtained for gold coated fiber by Robinson *et al.*[2] and was later confirmed on bare fiber using atomic force microscopy (AFM) by Yuce *et al.*.[3] These results were later confirmed by several authors using AFM.[4-7] In order to observe the fiber surface with AFM, the polymer coating must be removed and usually this is done by stripping it in hot sulfuric acid;[2,3,5-8] in some cases, the fiber samples for AFM have been stripped in methylene chloride (MeCl).[4]

The hot acid technique for removing the coating of fused silica fiber[1] consists of dipping the portion of fiber to be stripped into sulfuric acid at a temperature in the range of 180-200°C for 15-20 s; the stripped length is then rinsed in acetone and then water to remove residual acid and other materials. By using this method, the coating is removed chemically by the hot acid and the bare surface of the fiber is never in contact with any solid object; this minimizes the possibility of mechanically damaging the fiber surface. This chemically aggressive treatment raises two questions. Firstly, does the acid remove more than just the polymer coating, especially after aging the fiber? Secondly, is the resulting surface therefore characteristic of the stripping technique rather than of the effect of the environmental treatment on the fiber that is being investigated? The work on fiber surface profilometry shows implicitly, and more recent results show explicitly,[9] that the strength of unaged fiber is not significantly degraded by stripping in hot acid; differences in strength between coated and stripped fiber can be explained by the presence of the coating. Also, there is not evidence that the surface morphology of pristine fiber is changed by the acid.

As an alternative to hot acid, methylene chloride (MeCl) can be used to remove the coating. This technique consists of immersing the fiber length to be stripped in MeCl at room temperature for a few seconds. The MeCl softens and swells the polymer coating, which is usually removed mechanically for example by wiping with a soft cloth or by using a wire stripper or by manually pulling. This method is chemically less aggressive than the hot acid; however, it is usually unsuitable for measuring the mechanical properties of the fiber because when it is wiped to remove the softened polymer, the pristine (in the case of unaged fiber) surface of the fiber is usually damaged, thus compromising the significance of the results. Several detailed descriptions and images of fiber surface damage caused by various types of handling and stripping tools are available in literature.[10]

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The purpose of the work presented here is to evaluate different stripping techniques for AFM analysis and to determine their effects on strength and surface morphology after different aging times.

2. EXPERIMENTAL

2.1 Stripping

125 μm diameter fused silica fiber with a commercially available UV-curable acrylate coating was used in this work. The samples were stripped either by dipping them for ~20 s in sulfuric acid at approximately 190±10°C followed by a brief rinse in acetone and deionized water, or by soaking them in MeCl for a few minutes and then removing the coating by gently pulling it from one end of the specimen. To facilitate the pulling operation, the coating was indented with a sharp blade at a position which would not be under examination during mechanical tests or AFM analysis.

2.2 Residual Strength

The strength of bare fiber was measured using a two-point bending technique in which the sample is bent through 180° between two polished faceplates.[11] The specimens were broken at room temperature, immersed in pH 7 phosphate buffer solution and at a constant stress rate of 60 $MPa \cdot s^{-1}$. The measured strengths were corrected for small fluctuations of the ambient lab temperature.[12]

The strength was measured on unaged fiber and also after zero-stress aging for 89 and 336 hours in pH 7 buffer solution at 90°C. Both bare and coated samples were subjected to aging. For fiber aged bare, some samples were tested after aging without any further treatment, others after treatment with hot acid, and others after treatment with MeCl. In the case of fiber aged coated, the samples were preliminarily stripped in hot acid and then either tested immediately or tested after being subjected to a second treatment, either in hot acid or in MeCl. The second treatment in this case was not expected to affect the strength but was performed as a control.

2.3 Atomic Force Microscopy (AFM)

AFM profilometry was used to study the surface morphology after different types of treatment. In addition to samples treated like those for the residual strength measurements, AFM analysis was also performed on samples stripped in MeCl, both unaged and aged coated. Furthermore, after the longest aging time it was possible to remove the coating from the specimens by pulling it off without using any chemical; AFM was used on samples prepared in this way. In the case of samples stripped in MeCl the mechanical damage caused on the fiber surface during the coating removal was not observed in AFM since it is a localized effect.

3. RESULTS

3.1 Residual Strength

A direct comparison of the two stripping methods by measuring the differently stripped fiber strengths was not meaningful because the specimens stripped using MeCl exhibited large scatter in the results due to the surface damage caused by the mechanical removal procedure required by the coating used in this work. For this reason, and also because this work was concerned primarily with the effect of hot acid and MeCl on the fiber surface, all the strength measurements were performed on samples preliminarily stripped in hot acid. The results compare three different treatments performed on samples without the coating: no treatment, immersion in hot sulfuric acid, and immersion in MeCl (after the two latter treatments, the samples were briefly rinsed in acetone and deionized water). Half of the samples were stripped before aging so that the effect on residual strength of the two solvents could be evaluated and compared to the aging effect alone. The remaining samples were stripped after aging; in this case the effect of MeCl on the aged fiber strength was evaluated and compared to the effect of stripping in hot acid alone; the further treatment in hot acid was used as a control.

Fig. 1 shows the residual strength of the fiber after zero-stress aging and the subsequent different types of treatment. Fig. 1*a* refers to the fiber aged bare, while Fig. 1*b* compares the results for the samples aged coated. The aging times were, respectively, 0, 89 and 336 hours. Each data point represents the average of about 20

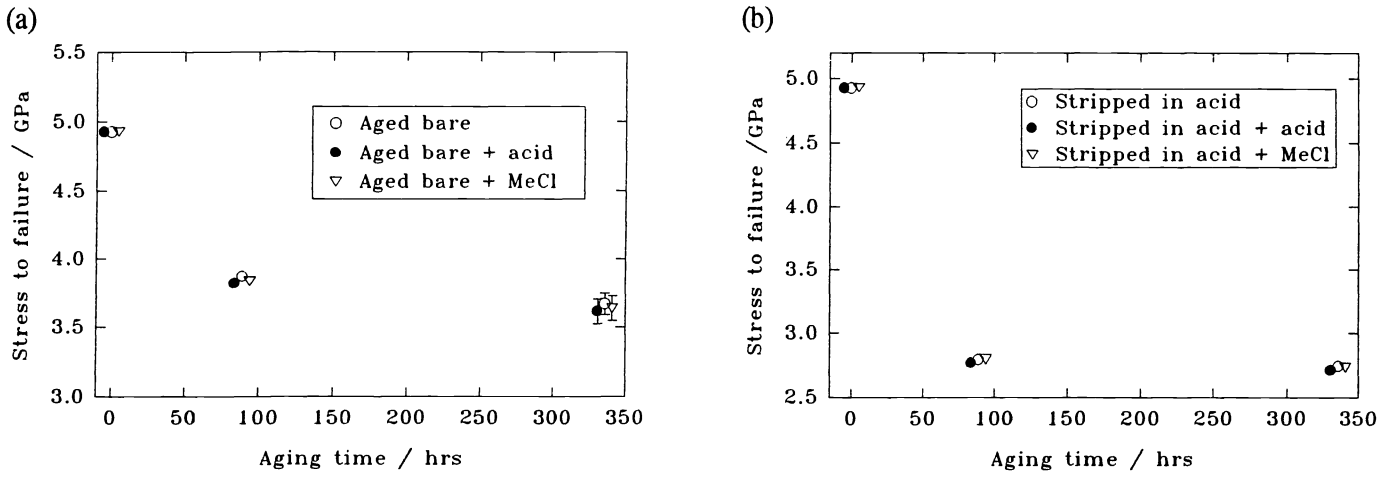

Fig. 1. Residual strength of samples aged in pH 7 at 90°C (a) bare and (b) coated and subsequently broken in two-point bending. Samples aged coated were stripped before testing.

specimens and the error bars correspond to 95% confidence intervals. These figures show that the different post-stripping treatments have no statistically significant effect on the strength of the fiber. This means that the hot acid treatment does not affect the strength of aged fiber when the surfaces are no longer pristine.

3.2 Atomic Force Microscopy

In the case of the AFM measurements, the problem of the localized damage on the fiber surface caused by the mechanical removal process associated with stripping in MeCl is not relevant. Therefore, in addition to the samples used for residual strength measurements (all first stripped in hot acid), the surface profiles of samples aged coated and then stripped in MeCl were also analyzed. This was necessary to evaluate the effect of MeCl on the surface morphology independently of the hot acid effect. In fact, in the case of samples aged coated and then stripped in hot acid, a second treatment either by MeCl or hot acid had no effect on the surface morphology.

Figs. 2 to 4 show the AFM profiles of the fiber subjected to different aging times and surface treatments. Table I summarizes the measured root mean square roughnesses of the different samples. (All roughness values quoted in this paper represent the root mean square. This value is substantially independent of the scan size of the AFM image. This can not be said about the highest peak to deepest valley distance sometimes considered in the literature.)

Table I. Root mean square roughnesses in nm of AFM profiles after different aging times and surface treatments

	Unaged	89 hrs aged bare	336 hrs aged bare	89 hrs aged coated	336 hrs aged coated
Untreated	–	0.65	0.56	5.07	1.03‡
Hot acid	0.55	1.18	8.28	3.91	6.26
MeCl	0.48	0.75	0.85	1.11†	1.06†

†Stripped in MeCl.
‡Coating removed mechanically without using any chemical.

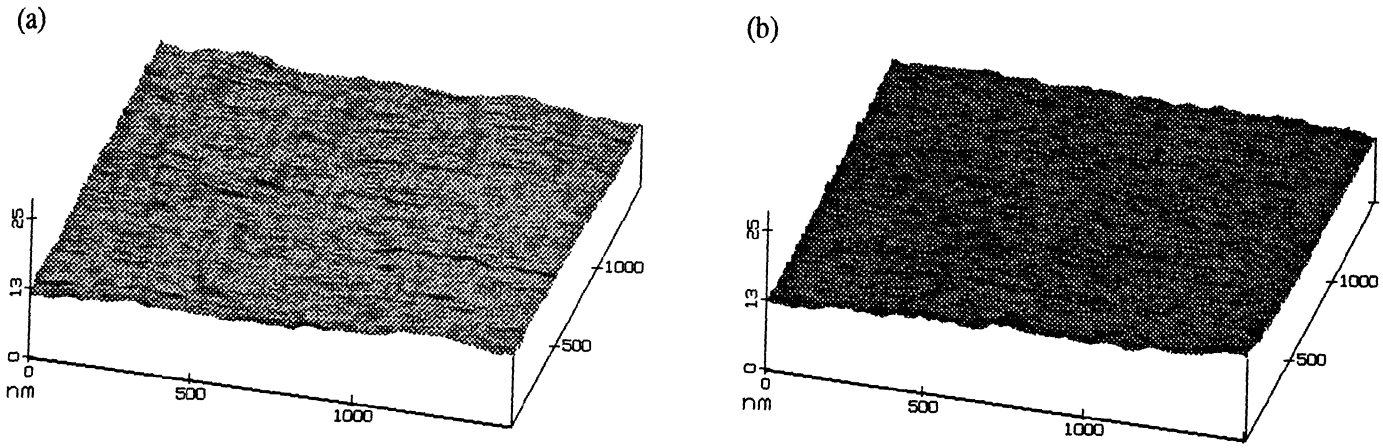

Fig. 2 AFM profiles of the surface of unaged fiber stripped (a) in hot sulfuric acid and (b) in MeCl. The roughnesses were 0.55 and 0.48 nm, respectively.

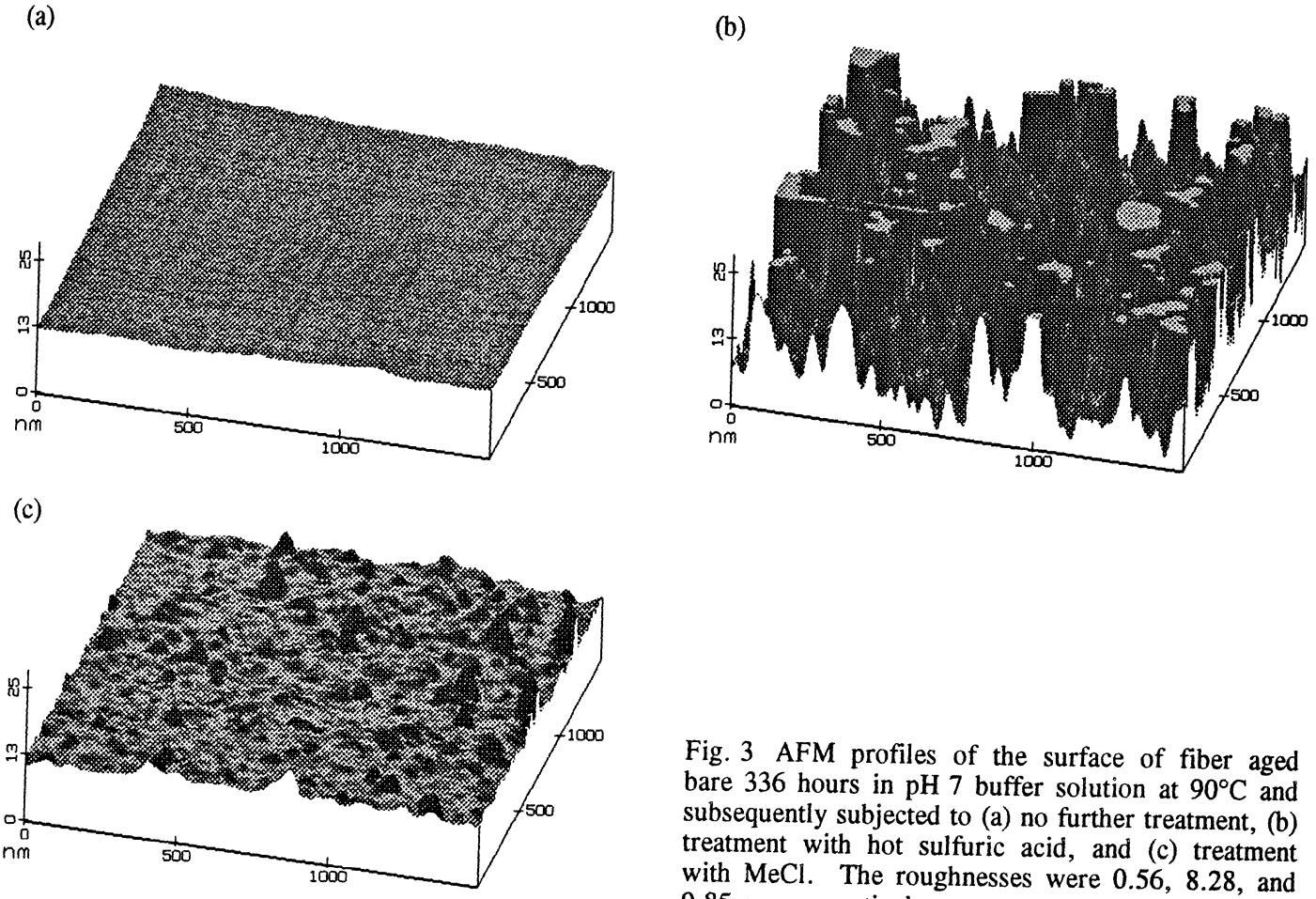

Fig. 3 AFM profiles of the surface of fiber aged bare 336 hours in pH 7 buffer solution at 90°C and subsequently subjected to (a) no further treatment, (b) treatment with hot sulfuric acid, and (c) treatment with MeCl. The roughnesses were 0.56, 8.28, and 0.85 nm, respectively.

Figs. 2*a* and 2*b* show the surface of unaged specimens stripped in acid and in MeCl; no differences are observed. The measured roughnesses were 0.55 and 0.48 nm, respectively.

Fig. 3*a* shows the surface profile of a specimen aged bare for 336 hours and not subjected to any post aging treatment; the surface has a roughness of 0.56 nm and appears like the unaged surface. However, after dipping the aged samples in hot acid (Fig. 3*b*) a profile with a much higher roughness of 8.28 nm becomes evident; a profile rougher than the unaged fiber is expected since the strength has degraded about 26% after 336 hours aging. The treatment with MeCl (Fig. 3*c*) only shows a slightly rougher surface than the unaged fiber with a roughness of 0.85 nm.

Figs. 4*a*, 4*b* and 4*c* show AFM profiles of fiber samples aged coated for 336 hours and show similar trends to the samples aged bare. Fig. 4*a* shows the profile of a sample whose coating was removed simply by pulling it off manually. After this aging time the coating was not adhering to the fiber surface and it was therefore possible to remove it without using any chemical. The roughness of the sample in Fig. 4*a* was 1.03 nm. A much rougher profile (6.26 nm) is evident for the fiber treated in acid shown in Fig. 4*b*. The sample shown in Fig. 4*c*, stripped in MeCl, has a much flatter surface with a roughness of 1.06 nm.

The surface profiles of samples aged coated, stripped in hot acid and subsequently untreated do not differ substantially from the profiles of fiber treated with hot acid or MeCl after stripping in hot acid, because the preliminary removal of the coating in acid determines the surface profile independently of any subsequent treatment.

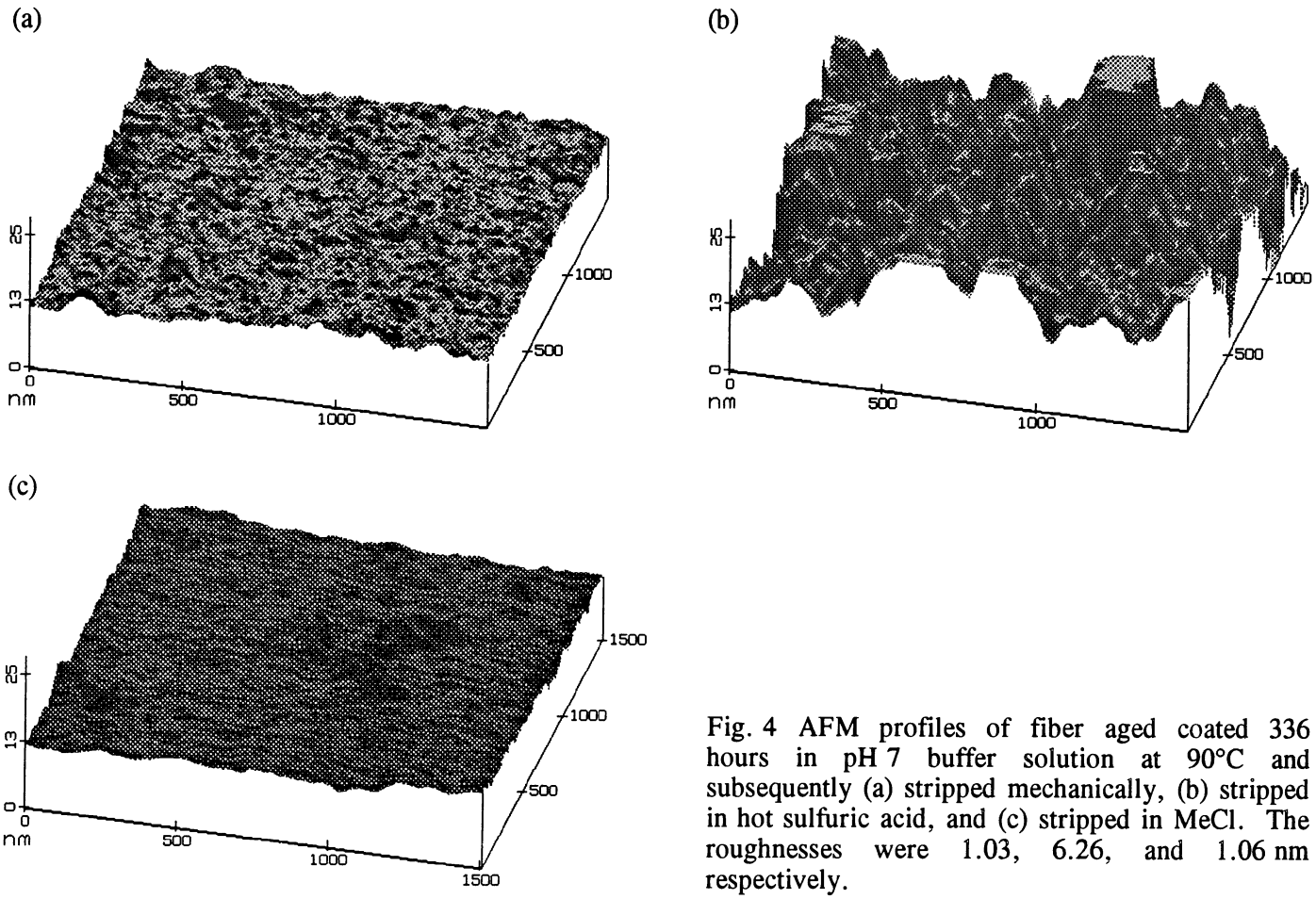

Fig. 4 AFM profiles of fiber aged coated 336 hours in pH 7 buffer solution at 90°C and subsequently (a) stripped mechanically, (b) stripped in hot sulfuric acid, and (c) stripped in MeCl. The roughnesses were 1.03, 6.26, and 1.06 nm respectively.

4. DISCUSSION

The aim of the aging tests was to determine if the acid or the MeCl have any effect on the mechanical behavior or the surface morphology of the fiber. In particular, since it is well known that aging causes progressive roughening of pristine silica surface through dissolution-based mechanisms (and this, in turn, is responsible for the strength degradation),[5,7,8] the surface examination was extended to the case of aged, *i.e.* roughened, surfaces.

The strength measurements show, as has been observed before,[1,13,3] a significant strength decrease with increasing aging time. Interestingly, the strength degradation is higher when the fiber is aged coated rather than bare. This phenomenon has been observed before[13,3] and a mechanism has recently been proposed.[14] The residual strength measurements do not show any statistically significant difference between the samples untreated or treated with either solvent; therefore, whatever the acid and the MeCl do to the surface of the fiber, they do not affect the fiber strength.

The AFM profiles of all aged samples, except those treated with hot acid, appear relatively flat and similar to the unaged surface. They therefore do not reflect the observed strength loss. In contrast, treatment with hot acid reveals a rough surface on aged fiber which closely correlates with the residual strength, as has been observed in previous work on fiber aged coated and stripped in hot acid.[2-8] Clearly, the acid is removing something from the surface of aged fiber, in addition to the coating. This is most likely a surface layer of hydrated silica. The surface revealed after removal of this layer is the strength controlling surface since the roughness then correlates with the residual strength. A key finding of this work is that fiber aged bare must also be treated with hot acid in order to reveal the rough profile. Clearly then, the layer removed by the acid does not contribute to the fiber strength, as would be expected if it were a gelatinous layer of hydrated silica.

While we have not unequivocally proved that the acid treatment reveals the true strength controlling surface, it is shown that the acid treatment produces a substantially better approximation to that surface than the other treatments examined.

5. CONCLUSIONS

The removal of the polymer coating of fused silica optical fiber using hot sulfuric acid does not affect the intrinsic strength of the fiber both in the as-drawn condition and after severe zero-stress aging. The acid removes a surface layer formed during aging in pH 7 buffer solution (possibly a gelatinous layer of hydrated silica) and so reveals the underlying strength controlling surface of the fiber. Direct evidence of such a surface layer was obtained using atomic force microscopy by comparing the surface profiles of fiber aged bare with that of fiber aged bare and subsequently dipped in hot acid, and by comparing the profiles of samples aged coated and then stripped either in hot acid or in methylene chloride (MeCl).

Stripping in MeCl is usually unsuitable for mechanical testing purposes since in most cases it is necessary to remove the coating mechanically and this may cause damage to the fiber surface. The MeCl has little effect on the surface layer formed during aging and therefore does not reveal the strength determining surface.

It is shown that hot acid stripping is an appropriate technique for removal of the polymer coating prior to examination of the surface profile using AFM. More importantly, it is also shown that the fiber should be treated with hot acid *even if it has no polymer coating to be removed.*

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