Mechanical Durability of ZBLAN and Aluminum Fluoride-Based Optical Fiber

James Colaizzi and M. John Matthewson

***Abstract*—Zero stress aging and static fatigue experiments were performed on fluoride glass fibers of ZBLAN and aluminum fluoride-based compositions to examine the mechanical durability in aqueous solutions. ZBLAN fiber, which has the higher initial strength, becomes weaker than initially lower strength aluminum fluoride-based fiber in less than one hour in pH 7 buffer solution at 30°C. This is shown to be due to dissolution of the glass and precipitation of crystals at the glass/coating interface. In 1N NaOH the solubility is higher, resulting in less precipitation and hence less strength degradation. Although ZBLAN fiber degrades more quickly when a high strain is applied, at low applied strain the residual strength is higher than is observed when no strain is applied. These results indicate that future work on fluoride glass fibers for use in aqueous environments should focus on optimization of the as-drawn strength of durable glass, such as aluminum fluoride-based material, rather than on making small strength improvements to already strong but less durable glass, since such improvements will be quickly lost in aggressive environments.**

I. Introduction

THE PRESENT MOTIVATION for the production of fluoride glass optical fiber is for short range applications (a few meters) which take advantage of such fluoride glass characteristics as transmission at longer wavelengths and the ease of doping with rare earth ions. Applications include optical amplification and transmission of laser light, including laser surgery, and sensing in many environments including liquids. In many cases, conditions would necessitate fiber cables being subject to aqueous environments of varied chemistry, temperature and pH while under high stress due to system design or to unexpected environments [1]. Although the service life of these fibers will not be expected to be as long as that of telecommunication fiber, they must still have high reliability during that life. To be used in practical applications, it is vital that the effect of different environments on fiber strength be understood.

A. The Aluminum Fluoride-Based Compositions

Aluminum fluoride-based ("ALF") glasses have a much higher glass transition temperature than the common zirconium fluoride-based composition, ZBLAN. Although they exhibit a higher tendency to devitrify during fabrication than ZBLAN, it is possible to produce fiber with similar optical quality [2], [3]. In addition, the degradation of the optical transmittance of ALF glasses in water is negligible compared to that of ZBLAN glass [2].

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The authors are with the Fiber Optic Materials Research Program, Department of Ceramics, Rutgers University, Piscataway, NJ 08855-0909 USA.

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TABLE I
PHYSICAL PROPERTIES OF BULK SILICA AND FLUORIDE GLASSES [3], [5], [23]

Composition :	Silica	ZBLAN	AlF_3-Based
Young's Modulus, E (GPa)	72.2	52.7	63.8
Knoop Hardness, H (GPa)	7.7	2.2	3.1
E/H	9.4	24	21
Poisson's Ratio	0.17	0.31	0.31
Glass Transition Temp. (°C)	1100-1700	257	392
Melting Temperature (°C)	1721	450	673

B. Fiber Mechanical Properties

Some physical properties of bulk fluoride and silica glass are listed in Table I. Elastic modulus of fibers may be up to 15% lower than bulk glass due to a higher fictive temperature [4]. The maximum theoretical strength, $\sigma_{\rm th}$, of fluoride glass has been calculated to be 3.3 GPa [5], about 6.0% strain. A minimum strain to failure of ~2% is usually required in the handling of telecommunication fiber, and may be lower for short range applications. The theoretical strength has not been achieved because of the presence of stress concentrating flaws in the fiber surface.

C. Environmental Effects, Aging and Static Fatigue

Slow crack growth due to enhanced rates of reaction between the environment (particularly water) and strained bonds at the tip of pre-existing cracks or defects results in many ceramic materials exhibiting delayed failure under a constant applied stress and lower strengths during slow loading since the environment has more time to grow the crack [6]. Although this behavior has been observed for bulk fluoride glass in various environments [7], other factors may be relevant to the fatigue of fibers, which are stronger than bulk glass. For example, high strength silica fiber can experience strength loss due to the formation of surface roughness caused by surface corrosion [8]–[11]. This is in contrast to the subcritical crack growth model in which mechanical failure of glass is assumed to be caused by long, sharp, residual-stress free cracks; this model does not predict strength loss in the absence of an externally applied stress.

Rather than examining the growth of a sharp crack, the model of Hillig and Charles [12] considers crack lengthening and widening (rounding) during corrosion. The former of these

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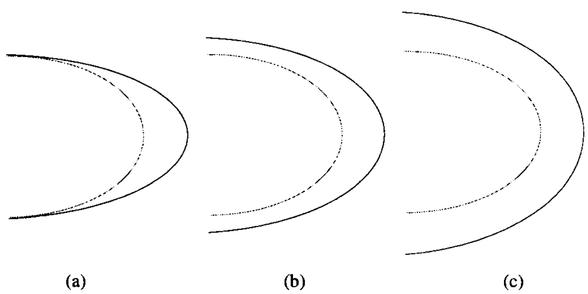


Fig. 1. Flaw growth in a corrosive environment [12]. (a) Flaw sharpening (high applied stress), (b) crack lengthening and rounding balance (fatigue limit) and (c) tip rounding (low applied stress).

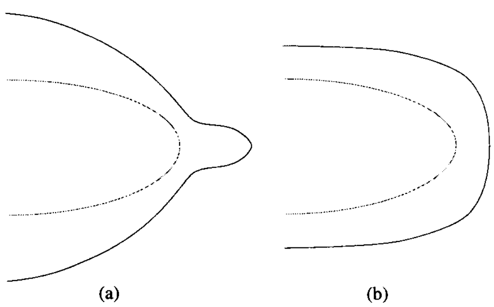


Fig. 2. Crack growth during corrosion [15]. (a) Sharpening with retarded growth (necking) and (b) enhanced blunting near apex.

competing processes weakens while the latter strengthens the material. Fig. 1 shows the three cases for which pits, i.e., cracks which are not atomically sharp, may change shape during corrosion. At high applied stress (Fig. 1(a)) the crack tends to sharpen while at low applied stress (Fig. 1(c)), not only will degradation not be observed, but strengthening may occur [13], [14]. An extension of this model by Chuang and Fuller [15] predicts that there is a range of stress which may result in either enhanced crack sharpening (Fig. 2(a)) or *enhanced crack blunting* (Fig. 2(b)).

The Hillig and Charles model considers that crack blunting can occur due to plastic or viscous deformation as well as corrosion. When under strain, if the stress at a crack tip is not high enough to cause plastic flow, it is possible for the crack to sharpen due to corrosion until the plastic yield stress is reached. Although plastic deformation at flaw tips is very unlikely in silica glass near ambient temperatures since it is covalently bonded and has a high melting point, this may occur in fluoride glasses since the glass transition temperatures are much lower, and the bonding is ionic. Higher values of the ratio of Young's modulus to hardness (*E/H*) indicate a greater tendency to plastic behavior. Table I shows that *E/H* for the fluoride glasses is more than twice that of silica. In bulk glass, relaxation is negligible [16], but it is believed that because fiber is less dense due to fast cooling during drawing, it can plastically deform at temperatures well below the glass transition. ZBLAN fibers under only 79 MPa stress (~0.15% strain) in 100°C air were found to exhibit viscoelastic deformation after two days [17]. Even silicate glass fiber has been seen to deform in bending 365°C below the glass transition [18].

D. Previous Reliability Studies on Fluoride Fibers

Durability has been examined since there is concern for its effect on the optical transmission of bulk fluoride optical components. The dissolution in water is very complicated since many reactions occur. At the surface, the various components of the glass will separate, forming a layer of rosettes, needle-like or blade shaped fluoride crystals whose thickness increases with a time$^{1/2}$ dependence [19], [20]. Although the glass dissolves rapidly, the solubility is very low, so that the dissolved products immediately crystallize on the surface of the remaining glass. This precipitation occurs even with a low surface area to solution ratio because supersaturation occurs locally; only an agitated flow of fresh solution will stop the crystallization [21].

The pH of the solution strongly influences these reactions. The leach rate is lowest in neutral solutions, slightly greater at higher pH, and highest at low pH values [22]. While AlF_3-based glass is generally much more durable than ZrF_4-based glass, the latter is more durable above pH 11 [23]. The pH is most important *after* dissolution since it determines the solubility of the glass, and therefore the extent of precipitation [7]. Many studies have been done, ranging from drawing fiber in helium gas [24] to exposing preforms to an argon-NF_3 plasma [25], in order to raise the initial strength of fluoride fiber by increasingly smaller increments, but few have addressed how the durability affects strength.

When ALF fiber is aged without its polymer coating in pH 7 buffer solution at 80°C, most of its original strength is retained for almost a week, but in pH 10 buffer solution the fiber surface is quickly etched, increasing the strength [26]. During etching, crystals grow on the surface and are pushed radially outward into the surrounding solution. Coated ZBLAN and ALF fibers were directly compared by using fibers of the same initial (relatively low, 0.5% strain to failure) strength [27]. Zero stress aging in buffer solutions ranging from pH 4 to 10 showed that ALF fiber would retain its strength an order of magnitude longer than ZBLAN, and would then degrade much less rapidly. The time to failure of ALF in static fatigue was found to be twenty times greater than that of ZBLAN.

Because many systems which will potentially incorporate fluoride fiber will be expected to be used in aqueous environments, the effect of such environments on strain to failure over time will be examined using fibers of both the common ZBLAN composition and the more durable aluminum fluoride-based composition. The effect of pH and the fundamental causes of strength degradation will also be examined.

II. Experimental Procedure

All fibers were coated with UV-cured polyacrylate. 200 μm diameter ALF fiber of an ABCYSMNZ composition (Table II) was fabricated and drawn in a controlled atmosphere as

TABLE II
COMPOSITION OF ABCYSMNZ GLASS BATCHES (IN MOLE PERCENT)

AlF_3	30.2	SrF_2	13.2
BaF_2	10.6	MgF_2	3.5
CaF_2	20.2	NaF	3.8
YF_3	8.3	ZrF_4	10.2

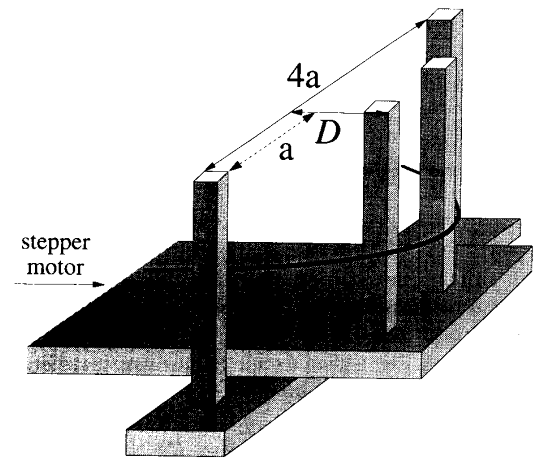


Fig. 3. Four-point bend apparatus. Fiber shown under strain. a = 3530 m.

described in [3]. The ZBLAN fiber studied was a commercially available, 140 μm diameter fiber.[1]

A. Strength Measurement Methods

Although the two-point bend apparatus described in [28] is ideal for strong fiber, it is not always suitable for weak fiber since a finite strain must be applied to load the fiber into the apparatus. Therefore, a deflection based four-point bending technique, shown in Fig. 3, was used in which the fiber can be inserted in the apparatus under zero strain [29]. Although no minimum fiber strength is required for this method, at high deflection a maximum strain is encountered, after which the fiber is pushed through the apparatus and the applied strain decreases. The maximum strain achievable ($\sim$1% with 140 μm diameter fiber and the apparatus used here) depends on fiber diameter and the pin spacing. In both the two- and four-point bend techniques, breaks are detected acoustically with a sensor attached to the container of the liquid test environment. In this study most data points represent measurements of between five and twelve samples. All error bars represent 95% confidence on the mean strain or time to failure.

Since previous studies [30], [5], [31] have not shown a definitive or significant dependence on strain rate for fluoride fiber, a loading rate was selected which was fast enough to complete the experiments quickly, but also slow enough so that no acoustic signals from the breaks would overlap when using the detection system. A speed of 5 μm$\cdot$ s^{-1} was chosen to satisfy these requirements. If the strength of fiber exceeded the maximum strain achievable with the four-point bend apparatus, strain was applied at a comparable rate of 0.5%$\cdot$ min^{-1} with the two-point bend apparatus. On the other hand, very weak fiber (< 0.1% strain to failure) is extremely difficult to handle without breaking, so this sets a lower limit to the measurable strength.

[1] ZBLAN fiber provided by Dr. Danh Tran, Infrared Fiber Systems, Silver Springs, MD.

B. Zero-Stress Aging and Static Fatigue

Fiber was aged in test tubes containing the desired environment, submerged in a constant temperature bath. Static fatigue was performed using the dynamic four-point bend apparatus run in static mode; the fibers were held at a constant position and the time to failure was recorded. A stirring hot plate was needed to keep the environmental temperature constant. Due to safety reasons, the static fatigue experiments in the pH 1 buffer and 1N NaOH environments were performed in two-point bending by bending specimens through 180° and inserting them into precision bore glass tubes, and placing these tubes into beakers with the desired environment [32]. A limited number of sizes of these tubes was available (i.e., a limited number of strains could be applied), so although use of the tubes is more convenient, it was not the preferred experimental setup.

III. RESULTS AND DISCUSSION

Static fatigue and zero stress aging behavior have been studied in order to evaluate the effect of applied stress on the strength degradation. For a fair comparison, the residual strength after aging must be determined in inert conditions since failure occurs in static fatigue when the *inert* strength has fallen to the point where it equals the applied stress. For this reason it is important to determine what constitutes inert conditions. To examine the effects of different environments, the unaged ZBLAN fiber was broken in two-point bending in liquid nitrogen (-196°C), acetone at dry ice temperature (-79°C) and at room temperature in acetone, pH 7 buffer solution, and silicone fluid. The strain to failure in these environments is shown in Fig. 4. Although testing in liquid nitrogen is best performed with stripped fiber to avoid embrittlement of the coating at low temperatures causing premature failure, the stripped fiber would break when attempting to load it in the two-point bend apparatus. However, there was no evidence that coating embrittlement was a problem during these tests.

Apart from liquid nitrogen, the strength of the fibers is substantially independent of the nature of the environment, and in particular, to the availability of water which is low in silicone fluid and cold acetone, but high in pH 7 buffer. Therefore the true inert strength at room temperature will not differ much from the strength in any of these environments. For this reason, and for experimental convenience, post aging strength is measured in pH 7 buffer. While this is an ionically complex environment, it was chosen over pure water for its reproducibility. Any error in assuming these strengths are roughly inert is negligible compared to some of the effects reported here.

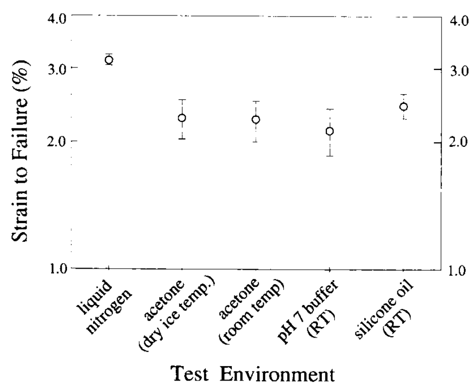


Fig. 4. Strength of ZBLAN fiber tested in various environments.

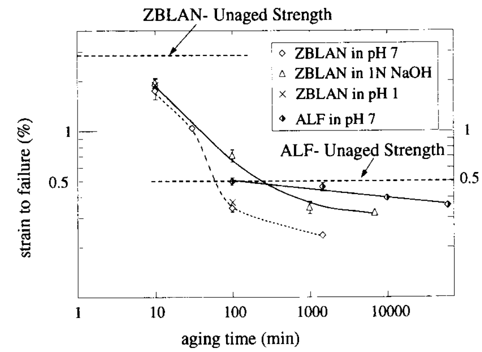


Fig. 5. Zero-stress aging of ZBLAN and ALF fibers in various environments at 30°C.

The reason for the significantly higher strength in liquid nitrogen is not clear. It is not due to the coating supporting more load since in bending curvature is specified by the apparatus rather than a stress. The change in modulus of the glass at low temperature is insufficient to explain the strength increase [33]. Liquid nitrogen was an inconvenient test environment because coated fibers tended to curl because of the thermal expansion mismatch between the fiber and coating and because the fibers were not exactly concentric with the coating.

A. Zero-Stress Aging and Static Fatigue

The aging and static fatigue tests on the ZBLAN fiber were performed at 30°C, since this was controllable and close to room temperature. Fibers were aged in pH 1, 4, 7, and 10 buffer solutions and 1N NaOH solution for times ranging from 10 to 10^4 min. The aluminum fluoride fiber was also aged in pH 7 buffer for comparison at this temperature.

Fig. 5 shows the zero-stress aging behavior. After only a few minutes the strength of the ZBLAN fiber is degraded. In one hour in 30°C pH 7 buffer solution, the strength has dropped to that of the ALF fiber. The degradation was similar in pH 1 buffer. Not until after 100 min does the ALF fiber begin to degrade. The ZBLAN fiber shows much more durability in the 1N NaOH (~pH 14), but the strength still falls below that of the ALF fiber in about five hours. The slope of both aging curves of the ZBLAN glass shown in Fig. 5 decrease at lower strain (about 0.3 to 0.5% strain), and become almost the same as that of the ALF fiber, although the curves are shifted by orders of magnitude of time. This change in slope may be an indication of a change from an intermediate strength to a low strength fracture regime, as indicated by Kurkjian *et al.* [13].

A static fatigue plot shows how the time to failure varies with applied stress. This is identical to, for a given applied stress, how long it takes for the *inert* strength of the specimen to degrade down to the applied stress. By superimposing the zero stress aging data (effectively *inert* strength versus aging time) on the static fatigue plot, it is possible to determine the effect of the applied stress on the degradation. For example, if degradation is independent of applied stress, the aging and fatigue curves would overlay each other. While the aging data are not strictly inert strength, the difference is small. Static fatigue was performed on the ZBLAN fiber for various applied strains ranging from 0.21 to 1.00% in the same buffer and NaOH solutions. Fig. 6 shows static fatigue data together with the zero-stress aging behavior from Fig. 5. At high applied strain (greater than 0.4%), the application of stress reduces the time to failure for both pH 7 and 1N NaOH solutions, as compared to the aging behavior of the ZBLAN fiber. The data for pH 4 buffer shows similar behavior to that of pH 7. The pH 10 buffer causes a slightly shorter time to failure, but there is large scatter in the data.

Interesting behavior is observed in pH 7 buffer at lower applied strain, where some or all of the fibers did not break after 23 h. As the applied strain goes down, the static fatigue curve converges with that of the fiber aged without stress, but then at 0.28% applied strain, the static fatigue experiment results in two types of fiber behavior. Eight of twelve fibers, presumably those which were originally weakest, broke in static fatigue within about 5 h. The other four did not break within 23 h, so at that time the pins of the four-point bend apparatus were advanced to find the residual strength of the remaining fibers, which at this point had essentially undergone an aging experiment under strain. At lower applied strain (0.25%), only two of twelve fibers broke within 2.5 h, the remainder surviving 23 h, at which time they were also broken dynamically. At the lowest applied strain, 0.21%, none of the fibers broke in static fatigue within 23 hours. Fig. 7 shows the residual strength of the ZBLAN fibers aged under various strains. These data are biased because the weakest fibers were not included since they had broken in static fatigue. Therefore, the strain to failure of fibers aged without applied stress were equally biased by using only the corresponding number of strongest fibers, as necessary for each point, for calculation of average residual strength and error bars so that a direct, unbiased comparison can be made. The strength of the fiber aged under strain is much higher than would have been expected without the presence of stress.

Since the residual strength when aging under stress is below the initial fiber strength, normal corrosion must still be occurring [5]. Also, since no strengthening occurred in zero-stress aging, uniform corrosion of pits, which might

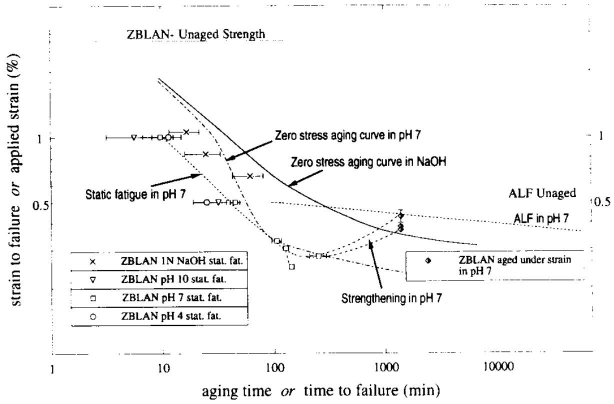


Fig. 6. Aging and static fatigue of ZBLAN and ALF fibers in various environments at 30°C.

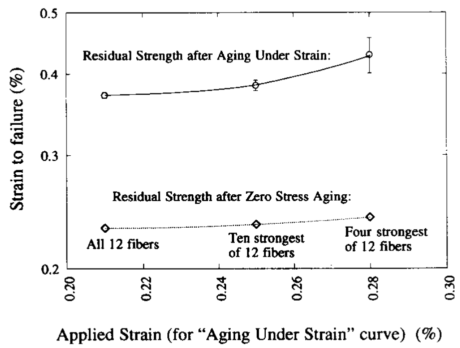


Fig. 7. Strain to failure of ZBLAN fibers after aging in pH 7 buffer under stress for 23 h.

happen in $ZrOCl_2$ solution, cannot be taking place in pH 7 buffer. However, since the residual strength is higher with applied stress during aging, there must be some strengthening mechanism. This mechanism may be plastic deformation at the flaw tip. Although this may seem unlikely in a ceramic material, consider that (a) the glass transition temperature is only about 225 K above room temperature, (b) the bonding is ionic rather than covalent, and (c) the glass is in fiber form rather than bulk, which allows deformation to take place at lower temperatures [18], [17]. It is not unlikely that plastic flow at flaw tips in these fibers could cause stress relaxation to occur over time. The strengthening may also be due to enhanced blunting, as is predicted by the corrosion model of Chuang and Fuller [15].

B. Surface Roughness Analysis

Various fibers from these experiments were examined with an atomic force microscope (AFM) used in contact mode. The silicon AFM tips had curvatures between 30 and 50 nm. Both unaged and aged specimens were examined and were prepared by stripping the coating after aging with methylene chloride. Scans of various sizes were made on each sample, depending on the roughness and features observed on the surface. RMS roughness measurements were made using the equipment's software.

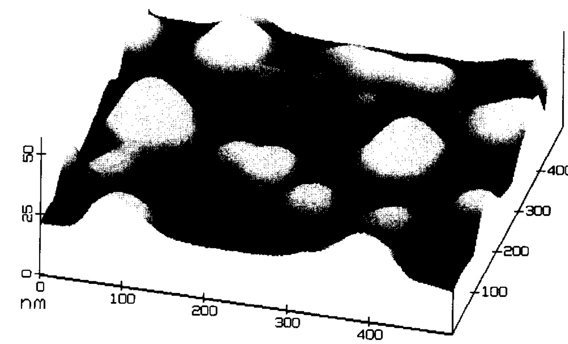


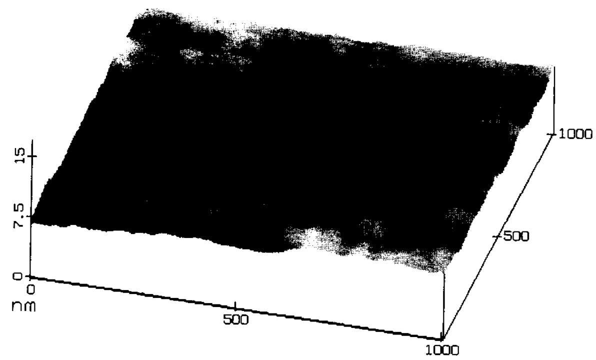
Fig. 8. Atomic force microscopy (AFM) image of unaged ZBLAN fiber surface. RMS roughness = 4.70 nm, z-range = 27.64 nm.

The images produced by the atomic force microscope show both roughness and surface features. The RMS roughness and z-range (difference between highest and lowest points vertically, which is dependent on size of the scan area) are shown in each caption. It should be noted that the vertical scale is exaggerated compared to the horizontal, and therefore the surface is flatter than it appears to be in the images.

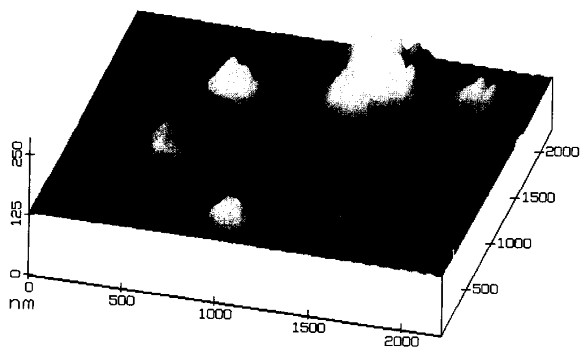
Fig. 8 shows the unaged surface of a ZBLAN fiber. The z-range of the surface is less than 50 nm, and the features are quite smooth. (Silica fiber is even smoother, the z-range being only a few tenths of a nanometer [10], which may be why its theoretical strength has been realized.) Fig. 9 shows that after 10 min in pH 7 buffer solution, while some areas of the fiber appear to be becoming flatter (9(a)), there are also very large features (9(b)) which are precipitated crystals. Because the atomic force microscope cannot resolve features with a radius of curvature smaller than the tip radius, sharp corners and facets of crystals appear rounded, as seen here. In Fig. 10, it is seen that after 100 min the crystals have become large and cover much of the surface. Some crystals seem acicular, as see by [20]. Because they are constrained by the coating material, the crystals cannot grow outward into the solution, and so cause local stress and act as flaws.

The same phenomena occur in pH 1 buffer. However, at a very high pH, the fiber does not appear to be forming crystals on the surface (Fig. 11). Since the glass is more soluble at this pH, there is a smaller tendency to precipitate crystals. This accounts for the less pronounced degradation in NaOH (Fig. 4).

Using the atomic force microscope, the comparison of aluminum fluoride with the ZBLAN fiber demonstrates the importance of durability on strength. Fig. 12 shows that the ALF fiber surface is initially similar to that of the high strength ZBLAN fiber. However, after ten thousand minutes (approximately one week) in pH 7 buffer solution, the surface is relatively unchanged (Fig. 13). Since no crystals were observed on any sample of ALF fiber aged in pH 7 buffer, the surface roughness itself may act as stress concentrators and may be the cause of degradation in this environment. On a larger scale (5000 nm wide scan) it is found that the z-range and roughness increase slightly, which may account for the small decrease in strength of the fiber.



(a)



(b)

Fig. 9. AFM images of ZBLAN fiber aged 10 min in 30°C pH 7 buffer. (a) RMS = 0.66 nm, z-range = 6.27 nm. (b) RMS = 13.1 nm, z-range = 91.3 nm.

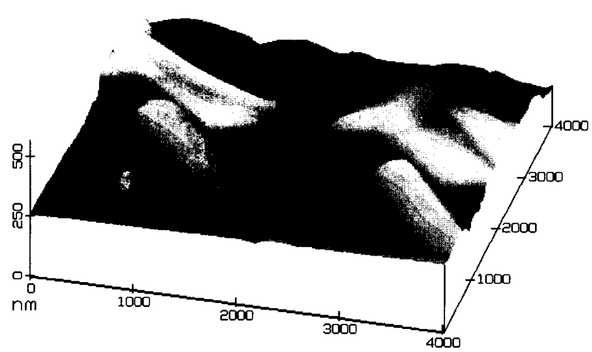


Fig. 10. AFM image of ZBLAN fiber aged 100 min in 30°C pH 7 buffer. RMS = 34.8 nm, z-range = 230 nm.

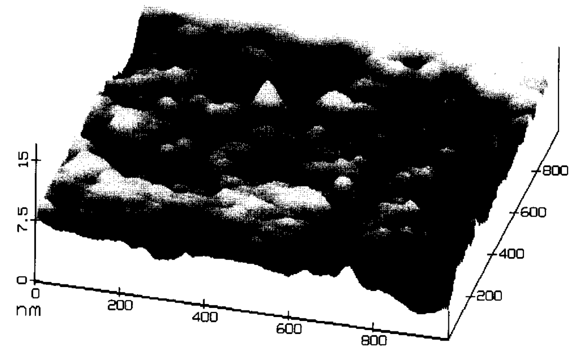


Fig. 11. AFM image of ZBLAN fiber aged 100 min in 30°C 1N NaOH. RMS = 0.71 nm, z-range = 7.12 nm.

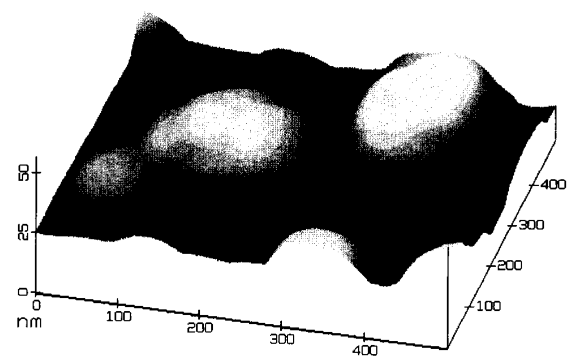


Fig. 12. AFM image of unaged ALF fiber. RMS = 5.04 nm, z-range = 29.4 nm.

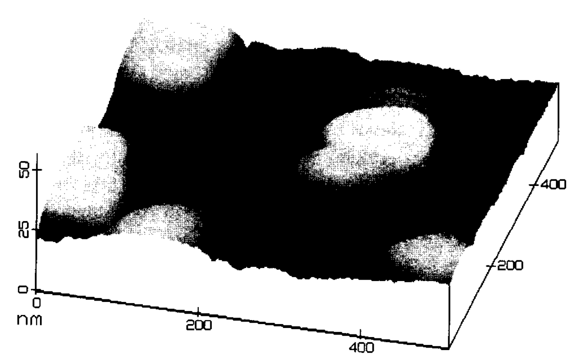


Fig. 13. AFM image of ALF fiber aged 10,000 min in 30°C pH 7 buffer. RMS = 4.90 nm, z-range = 36.8 nm.

Because the degradation of ALF takes place at such a slow rate, as observed by either the residual strength after zero-stress aging, or by roughening measured with the atomic force microscope, the aluminum fluoride-based fiber is clearly superior in aqueous solutions for all except the shortest required lifetimes. If this fiber were manufactured with high initial strengths, it could be used for months or possibly years before it becomes unacceptably weak. It is conceivable that high strength ALF fiber behaves differently than the weaker material so it could possibly experience rapid initial degradation like the ZBLAN; it may not be possible to simply shift the aging curve to a higher strength. However, the difference in the durability of the two types of fiber when compared directly to each other (i.e., weak compared to weak) makes this possibility unlikely [27].

IV. Conclusion

In relatively harsh environmental conditions (pH 7 buffer solution at 30°C) perhaps similar to that of some practical applications, it was found that although the starting strength of commercially available ZBLAN fiber is several times higher, in less than one hour it becomes weaker than aluminum fluoride-based fiber. This was attributed to the formation of crystals on the surface of the ZBLAN fiber as the glass dissolves, which results in localized stress since the crystals are constrained by the coating material. In 1N NaOH solution, strength degradation is not as great, presumably because the higher solubility of the glass at high pH values reduces the amount of precipitation.

In static fatigue, the high strength ZBLAN fiber degrades more quickly than in zero stress aging except at very low stress, in which case the strength becomes higher than would be expected under zero stress, indicating a stress assisted strengthening mechanism. This is believed to be due either to plastic deformation or stress-enhanced blunting at the flaw tips, resulting in a lower stress concentration.

Currently, relatively strong ZBLAN fiber can be made. However, the time which has been spent to further improve the already strong initial strength of ZBLAN fiber by small increments may have been futile for applications in aqueous environments, of which there are many, since it is extremely non-durable. The ALF fiber, which could be thought of as inferior due to its low initial strength, has actually proved to be stronger in the not so long term. Strength degradation occurs only at long times, and is not severe. Since crystals are not observed on the surface of this fiber, the degradation may be due to roughening of the surface, as it is for fused silica. Future work on production of fluoride glass fiber which is to be used in aqueous environments should focus on optimizing the starting strength of more durable compositions, rather than making small improvements to the strength of already comparably strong non-durable compositions since this strength will be lost in a matter of minutes. It is likely that high strength fibers made from the ALF composition would provide months or years of service. Since the use of an aluminum fluoride-based composition does not severely compromise the optical qualities compared to ZBLAN, it should be a good candidate for future applications of fluoride fiber.

Acknowledgment

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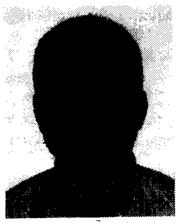

James Colaizzi received the B.S. degree in ceramic engineering in 1990 at Rutgers University, Piscataway, NJ, and the M.S. degree in 1993 at the Fiber Optic Materials Research Program at Rutgers for work on strength and reliability of optical fiber. He is currently working towards the Ph.D. degree at the Center for Ceramic Research at Rutgers.

His current research is in the area of ceramic to metal bonding.

M. John Matthewson received the B.A. degree in theoretical physics from Cambridge University, U.K. in 1975. He received the M.A. and Ph.D. degrees in 1978, also from Cambridge University, for his work at the Cavendish Laboratory on contact mechanics and impact erosion.

He continued his work in this area as concurrently the Goldsmiths' Junior Research Fellow at Churchill College, Cambridge, U.K. and as a Science Research Council Postdoctoral Fellow. He spent two years at AT&T Bell Laboratories as a Postdoctoral Member of Technical Staff before moving to IBM Almaden Research Center, San Jose, CA, in 1986. He has been at Rutgers University, Piscataway, NJ, since 1989, where he is now an Associate Professor in the Fiber Optic Materials Research Program. His research group is concerned with the strength and fatigue of optical materials.