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Mechanical Properties of Aluminum Fluoride Glass Fibers

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ABSTRACT

The effect of high temperature aqueous solutions of various pH values on the mechanical properties of polymer coated optical fibers of an aluminum fluoride-based composition are examined. It was found that such fibers retain much more strength when aged in these aqueous environments than fibers of the more common zirconium fluoride-based composition. The aging is not affected by pH unless the fiber is under stress, in which case a low pH solution decreases the time to failure of the fiber. In static fatigue, the time to failure of the aluminum fluoride-based fibers is twenty times greater than that of the zirconium fluoride-based fibers.

1. INTRODUCTION

Although the optical properties of fluoride glass optical fibers have been engineered such that they may be used for practical applications, their mechanical properties are still significantly worse than silica fibers. In particular, they exhibit poor chemical durability that leads to significant strength degradation on prolonged exposure to aqueous environments. In an attempt to improve the properties of the common zirconium fluoride based composition, ZBLAN, we are studying an aluminum fluoride-based composition.[1,2] Although this composition has a greater tendency to devitrify during fabrication, it has a higher glass transition temperature, a rate of dissolution in water about 50 times less than ZBLAN, a higher elastic modulus, a higher hardness, and has almost no optical loss induced by water, as occurs with ZBLAN at 3500 and 1700 cm^{-1}.

For such fibers to be used in practical applications, it is necessary not only to understand the mechanical properties of the fibers as drawn, but also when affected by the environment. It is useful to test fibers which have been treated in different ways after drawing. Specifically, "bare", "coated", and "stripped" fiber will be discussed. That is, fiber which has not been coated after drawing, fiber coated with a UV-cured polyacrylate, and fiber which is stripped of coating just prior to testing. The comparison of stripped and coated fiber shows the effects of the coating, while the examination of bare fiber reveals the effects of ambient conditions on the exposed surface.

A recent study examined the effects of the environment on aluminum fluoride fiber.[3] It was found that both "bare" and "stripped" fiber aged under zero stress in pH 10 buffer solution at 80°C becomes stronger. For one set of fibers, strain to failure increased from a value of about 0.4% in the standard test environment (pH 7 buffer solution at room temperature) to about 0.8% after 10 minutes of aging. This is due to the surface of the fiber being etched by the buffer solution which removes surface defects that act as stress concentrators. Etching is accompanied by reprecipitation of the dissolved glass on the now scratch-free surface of the fiber, which leaves a layer of crystals as described by Carter[4] and by Moynihan and Loehr.[5]

The stripped fiber also becomes stronger when pH 4 buffer solution is used for zero stress aging. Acidic solutions are, in fact, commonly used to remove flaws from fluoride glass preforms before drawing into fiber[4,6,7] and are more effective than basic solutions. However, it was found that the bare fiber becomes much weaker in the pH 4 buffer. Optical microscopy revealed that the fiber surface was covered with a crazed pattern of crystals about two to three microns thick. This layer, which appears to be part of the surface, unlike reprecipitated crystals, not only acts as a barrier to etching, but is also a source of flaws, and therefore

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weakens the fiber. This surface structure has been seen by Carter[4] and by Sakaguchi *et al.*.[8] It may be caused by the reaction of a fluoride component in the fiber surface, such as

$$ZrF_4 + 2H_2O \rightarrow ZrO_2 + 4HF. \tag{1}$$

This reaction may occur in the bare fiber surface if it has been hydrated by atmospheric water vapor. While it is known that humid air cannot degrade fiber strength directly, it has been shown that it can cause surface hydration over time.[8]

It was concluded that it is necessary to protect the fiber from the atmosphere by the application of a coating, perhaps a polymer. However, since polymers are not hermetic, it is not known how effective such a coating would be against attack by aqueous solutions. This paper will examine the effects of polyacrylate coating on aluminum fluoride glass fibers and also compare them to fibers drawn from a composition of ZBLAN glass. Both compositions were drawn on the same apparatus and using similar procedures. While the ZBLAN fiber is not as strong as has been achieved,[9,10] it does provide a direct comparison for the aluminum fluoride-based composition and may be used to examine changes in strength under different environmental conditions. Also, the weak fiber models the strength of long lengths of stronger fibers.

2. EXPERIMENTAL PROCEDURE

A rod was fabricated from the composition shown in Table I. The rod was prepared and drawn into 250 μm diameter fiber in a tower with a controlled atmosphere, as described by Shahriari *et al.*.[2] A rod of ZBLAN was also drawn into 250 μm diameter fiber under similar conditions. Both sets of fiber were coated with a UV-cured polyacrylate. The aluminum fluoride and zirconium fluoride based fibers will be referred to using the respective batch designations "AL-298" and "ZR-3".

Table I. Composition of Aluminum Fluoride-Based ABCYSMNZ Glass for batch "AL-298" (in weight percent)

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

The strength of the fibers was measured in a standard test environment of pH 7 buffer solution at room temperature. The AL-298 fiber strength was also measured in liquid nitrogen. Before testing in liquid nitrogen, the coating must first be removed by soaking the samples in methylene chloride since the coating material becomes brittle at liquid nitrogen temperature.

Samples of both batches were aged under zero stress in various pH buffer solutions at an accelerated rate produced by heating to 80°C. The residual strength was then measured in the standard test environment. Samples were also subjected to static fatigue in various pH buffers at 80°C. Different strains were applied and the times to failure were measured.

Strain was applied using a four-point bend apparatus.[11] This device allows weak fibers to be loaded without strain and permits multiple samples to be immersed in solution. Strain is calculated using the equation

$$\varepsilon = (3Dd/8a^2)\gamma \tag{2}$$

where D and a are the fiber displacement and a dimension of the device, as shown in figure 1; d is the diameter

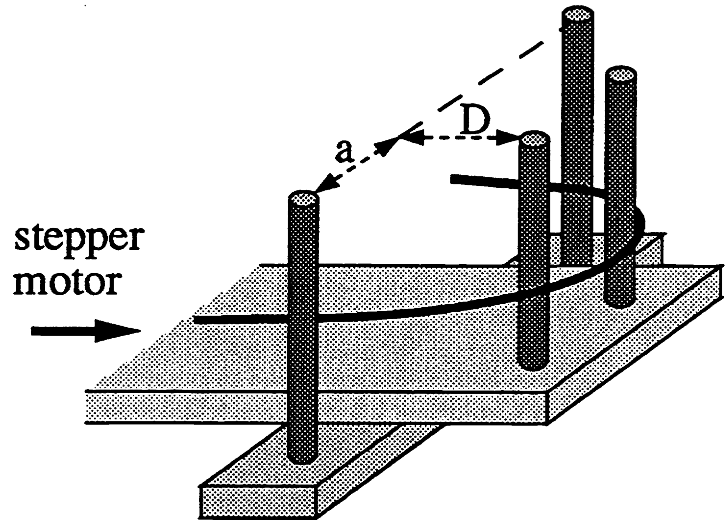

Figure 1. Four-point bend apparatus.

of the fiber, excluding the coating, and γ is a factor of order unity which corrects for finite deflection.[11] Strength was measured by advancing the stepper motor (see figure 1) at a rate of 10 μm per second. The non-aged strength of the AL-298 fibers was also measured at other rates. For time to failure experiments, the stepper motor was advanced to the experimental position at 1000 μm per second before stopping and measuring the time to failure.

SEM micrographs were used to find the mirror constant of several AL-298 fibers. A fracture surface is shown in figure 2. The radius, R, of the flat, semi-circular mirror zone which emanates from the fracture origin and the fracture strength, σ_f, are used to find the mirror constant, A, from the equation[12]

$$A = \sigma_f R^{1/2}. \qquad (3)$$

3. EXPERIMENTAL RESULTS AND DISCUSSION

The strain to failure of the coated aluminum fluoride fibers in the standard test environment is shown in figure 3. At 10 μm per second it is 0.50±0.01%, the error bars representing a 95% confidence on the mean. This is equivalent to a strength of about 280 MPa. These data do not appear to show any dependence of strength on loading rate. If an effect exists, the scatter in the data must be decreased in order to observe it. This would be achieved either by producing fiber with a larger Weibull modulus, or by testing a large number of specimens. Due to limited quantities of such fiber, the latter solution is not practical. The former possibility is also difficult to achieve since the Weibull moduli in these tests are usually less than ten, whereas the value for silica fiber is often well over 100, indicating an extremely small variance in silica fiber's strength. For this reason, all other dynamic tests were conducted at a single speed, 10 μm per second.The

AL-298 fiber has a larger strain to failure in liquid nitrogen, 0.66±0.03%, indicating that the elimination of moisture impedes crack growth, as is the case for many ceramic materials. The strain to failure of the ZR-3 fiber in the standard test environment was slightly less than that of the AL-298, 0.477±0.027%.

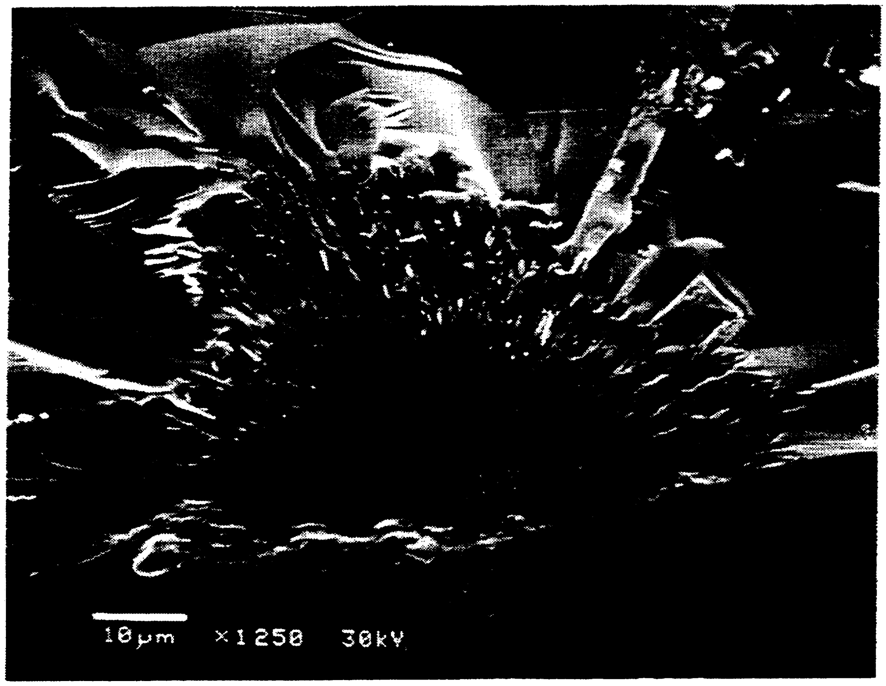

Figure 2. Fracture surface of aluminum fluoride-based glass fiber, showing mirror zone.

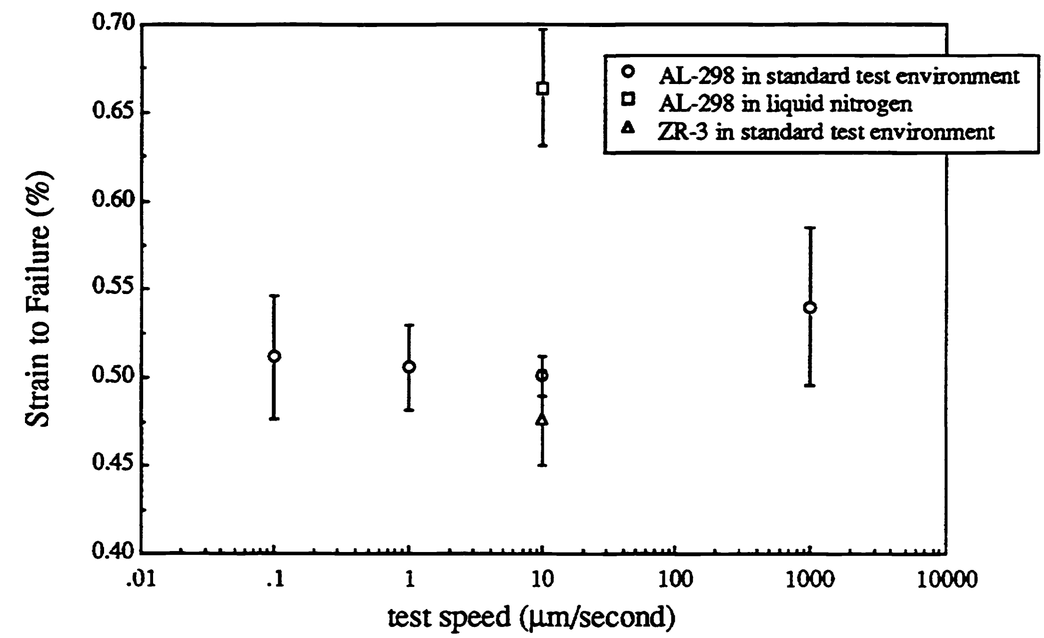

Figure 3. Strain to failure of fluoride fibers.

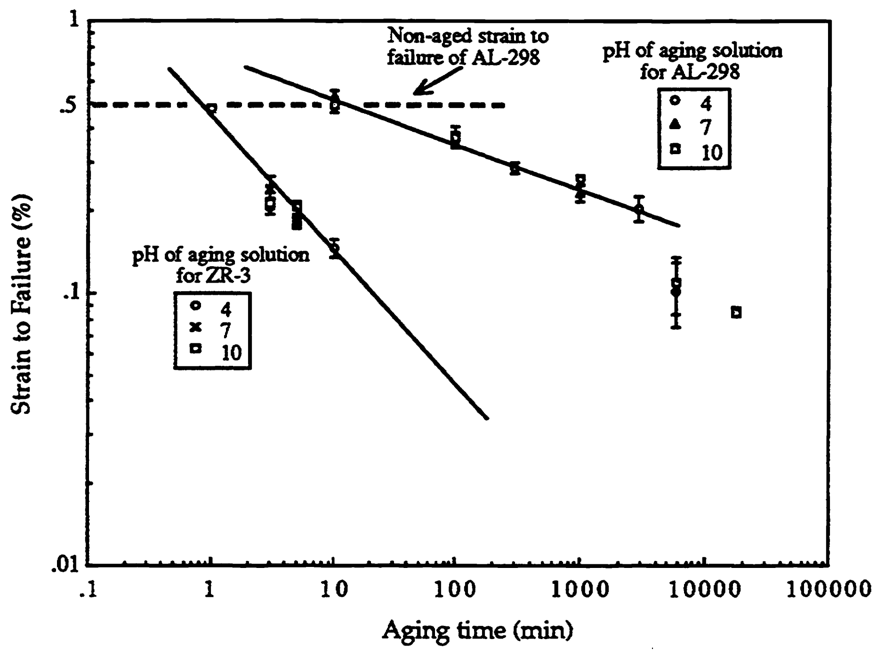

Figure 4. Effect of zero-stress aging of coated fibers on strain to failure at 80°C.

Figure 4 shows the effect of aging the fibers under zero stress on the strength. The residual strength does not appear to be affected by the pH of the buffer solution. The strength of AL-298 fibers starts to degrade after about 10 minutes of aging. At long aging times, the data deviate from the trend. However, fibers with strain to failure of less than 0.1% are extremely difficult to handle without breaking; therefore experiments could not be performed in that region, but at this point they are no longer useful for any application.

The strength of ZR-3 fibers starts to degrade after an aging time of just one minute, and at a faster rate than the AL-298 fibers. After only 100 minutes the fibers could not be handled without breakage, and the surfaces of the fibers aged in pH 4 or 10 buffer solutions appeared to have completely crystallized.

The static fatigue experiments also show a higher rate of strength degradation for the zirconium fluoride-based fibers, as shown in figure 5. The line drawn for the AL-298 fibers is for those aged in pH 4 buffer, and the slope gives the fatigue susceptibility parameter[13] $n = 3.0$. The effect of pH is not obvious, but it should be clear that in any case, the time to failure is much greater than for the ZR-3 fiber. The curves of the two different compositions indicate that the times to failure are separated by a factor of about 20.

By transposing the zero stress aging curves onto the same graph as the static fatigue curves, as is done on figure 6, the effect of the application of strain on aging can be observed. Except for AL-298 fibers aged in pH 4 buffer, the aging and fatigue curves are nearly coincident. This means that the strength degradation is not enhanced by the application of stress which is quite different from the behavior of most other ceramic materials. However for AL-298 in pH 4 buffer, the fatigue specimens fail earlier than the aging behavior would predict, indicating strength degradation is accelerated by stress in this case.

The difference between a fiber lasting 2000 and 100 seconds in static fatigue or degrading in 5000 rather than 10 minutes may not seem important, *i.e.*, the time is too short for practical use in either case. However, at lower temperatures these effects will occur much more slowly. The use of the aluminum fluoride based glass composition may extend the useful life of a fluoride-based glass fiber to the point at which it may be used for practical purposes in extreme environments.

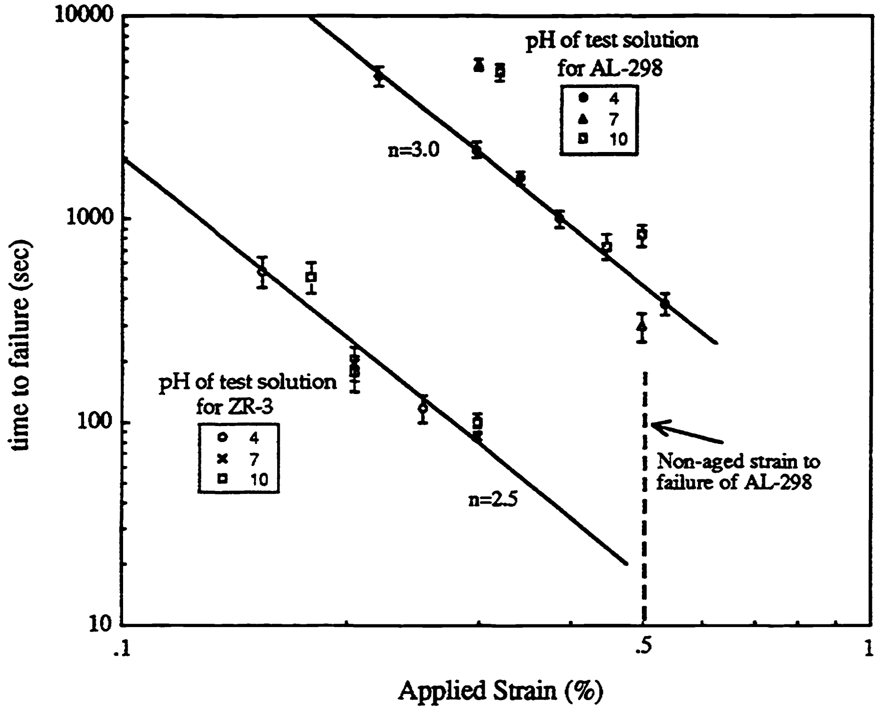

Figure 5. Effect of strain on time to failure at 80°C.

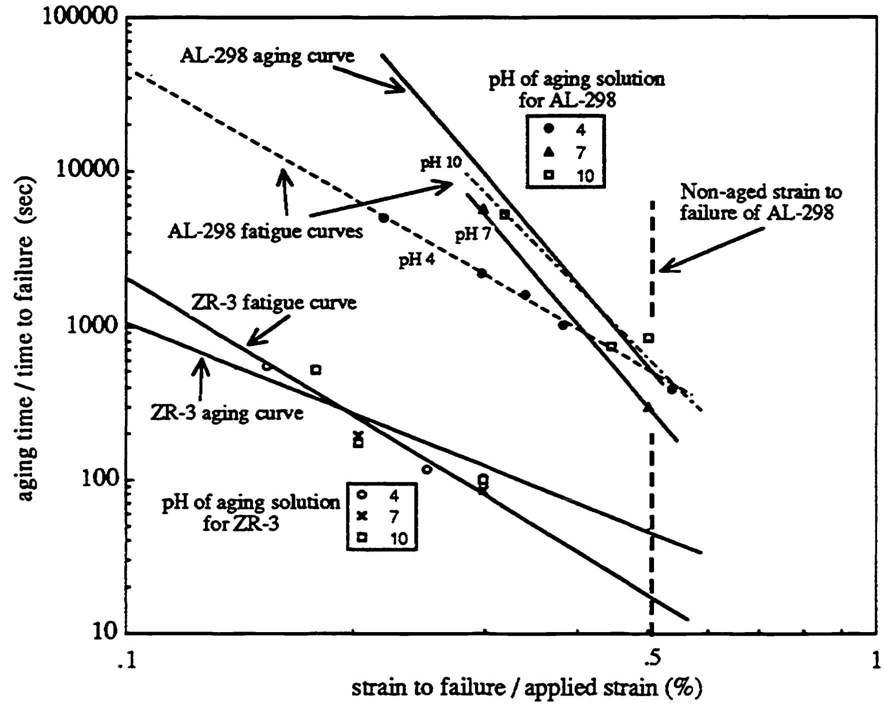

Figure 6. Comparison of static fatigue and zero-stress aging curves.

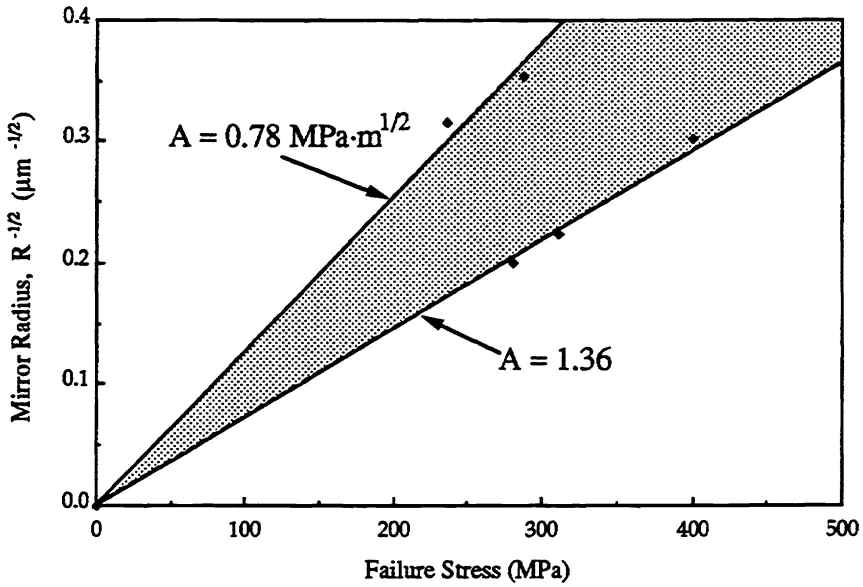

Figure 7. Transformed mirror radius as a function of failure stress.

Figure 7 shows the plot of failure stress vs. mirror radius$^{-1/2}$. While there is considerable scatter in the results, it can be seen that the mirror constant lies between 0.78 and 1.36 MPa·m$^{1/2}$. The mirror constants of other fluoride glasses fall in this range,[14] and it can be concluded that the mirror constant of the aluminum fluoride-based glass is not significantly different from that of ZBLAN glass.

4. SUMMARY

When subject to attack by high temperature aqueous solutions of pH ranging between 4 and 10, polymer-coated fibers drawn from an aluminum fluoride-based composition retain their strength significantly longer than those drawn from a ZBLAN composition. The pH has no effect on the strength degradation of aluminum fluoride fibers aged under zero stress. However, at lower pH values, strength degradation is greater if the fiber is under stress.

The non-hermetic nature of the polymer coatings are quite clear, and research on hermetic coatings for fluoride fibers[15,16] must continue if these types of fibers are to be used for long term applications in aqueous environments.

5. ACKNOWLEDGEMENT

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