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# The effect of the environment on the tensile strength of fluorozirconate glass fibres

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Fluorozirconate glass fibres were drawn from rod preforms without a protective polymer coating and under a nitrogen atmosphere. Fibres which had been subsequently stored and tested under an inert atmosphere had strengths ranging between 0.12 and 0.32 GPa. However, the strengths of fibres exposed to the atmosphere and under a relative humidity of 80% deteriorated to a limiting strength of about 0.09 GPa after 4 days.

## 1. Introduction

The chance discovery of a fluorozirconate glass in 1974 [1] has generated a great deal of interest over the years and much work has been published in the literature [2–4]. The main thrust behind the research into $ZrF_4$-based glasses and other fluoride glasses such as the more recent $AlF_3$-based [5] and $InF_3$-based [6] glasses lies in their unique optical properties. They possess a wide transmission range ($\sim 0.25$–$7\,\mu$m) and an extremely low theoretical attenuation ($\sim 10^{-3}$ dB km$^{-1}$) compared with silica ($\sim 0.2$–$3.5\,\mu$m and 0.15 dB km$^{-1}$, respectively) [7]. Obviously, there are numerous practical applications which can take advantage of these optical properties. For instance, high quality optical fibres are required for transcontinental and transoceanic communication systems.

If fluoride glass fibres are to compete successfully with silica fibres, then from a practical viewpoint, they should possess sufficient strength to reduce the likelihood of damage during handling. It is possible to estimate the theoretical strength by using the relationship that the strength is approximately equivalent to one-tenth the elastic modulus [8]. The elastic moduli of fluorozirconate glasses are generally in the range of 55–60 GPa [4], in contrast to silica whose values are quoted at 74 GPa [9]. The particular fluoride glass chosen in this study has an elastic modulus of 56 GPa [10]. This gives an estimated strength of approximately 5.6 GPa which compares favourably with the values routinely obtained for silica fibres [11]. Therefore in theory, these fluorozirconate glasses possess strengths comparable to silica and the fibres should therefore be expected to perform well.

However, an important factor affecting the performance of halide glass fibres under potentially hostile environments is their chemical durability. Although much work has been done to ascertain the effect of water on the properties of bulk fluorozirconate glasses [12–15] very little work has been done to investigate the effect of moisture on the tensile properties of fibres. This is extremely important from both a technical and commercial viewpoint. To the authors knowledge, there have been no studies performed comparing the tensile strengths of bare fibres which have been prepared and tested under an inert environment and identical fibres of the same composition which have been subsequently exposed to the ambient environment for successive periods of time.

## 2. Experimental procedure

High purity starting materials and the absence of moisture are a prerequisite for drawing high quality fibres. To this extent, the entire experimental procedure from initially weighing out the starting materials to melting the glass, drawing the fibres and subsequently measuring their tensile strengths was performed within five interconnected dry boxes. The nitrogen atmosphere inside the dry boxes was maintained so that less than 10 p.p.m. oxygen and less than 5 p.p.m. moisture were present. The materials, preforms and fibres could be easily transferred from one box to another via antechambers located between the boxes. In this way, both the preforms and the fibres would not come into contact with the ambient environment of the laboratory.

The high purity starting materials were weighed out in the appropriate amounts to make up 10 g batches of the ZBLA (ZrBa LaAl fluoride) glass composition shown in Table 1. In addition, several grams of ammonium bifluoride were added to the components prior to melting. On heating, this effectively converted traces of oxide impurities into fluorides.

The components were placed in platinum crucibles with tightly fitting lids and heated in an electric furnace. Typically, the temperature was raised to 600° C where it was held constant for 30 min. This was followed by increasing the temperature up to 900° C and holding for 5 min. The viscosities of fluorozirconate glasses at this temperature are relatively low ($\sim 1$ Poise) [16] and the melt is extremely fluid so that mixing and homogeneity are not considered to be a problem. The melts were subsequently cast into rods by pouring into aluminium moulds preheated to 300° C. The ZBLA glass preforms were then annealed from 25° C below $T_g$($T_g = 313$° C) and allowed to cool slowly to room temperature in the furnace overnight.

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TABLE I The composition of ZBLA glass

| Components, purity and source | | Mol % |
|---|---|---|
| $ZrF_4$ | 99.5% pure, distilled from Cerac Co. | 66.25 |
| $BaF_2$ | Ultrapure grade, Alfa Chemical Co. | 25.0 |
| $LaF_3$ | 99.9% pure, Alfa Chemical Co. | 5.0 |
| $AlF_3$ | 99.5% pure, Cerac Co. | 3.75 |

The glass preforms were polished with 1200 grit silicon carbide paper and then with 1 μm diamond paste. The preforms were then wiped clean and transferred through an antechamber into a dry box containing horizontal fibre drawing equipment [17]. A preform was placed within a set of grips which allowed it to rotate at 15 rev/min around its axis and a circular furnace moved towards the preform at $1.2\,\text{cm}\,\text{min}^{-1}$. Once the tip of the glass rod had sufficiently softened, the fibre was pulled across and attached to a take-up wheel which facilitated continuous drawing of the fibres. The temperature at which the fibres were drawn was 340°C ($T_x = 420°\text{C}$) and corresponded to a viscosity of $10^5$ Poise [18]. The fibres were drawn at approximately $15\,\text{cm}\,\text{sec}^{-1}$ and up to 30 m in length obtained with diameters ranging from 100 up to 360 μm.

At this point the fibres were separated into two groups. One set of fibres were removed from the dry box and placed in the laboratory environment for 4, 8 and 14 days. The other group of fibres were kept within the inert atmosphere of the dry box and therefore represent the unexposed fibres. Both groups of fibres were stored within identical containers and no external stress was applied. The average temperature in the laboratory was approximately 18 ± 5° C and the relative humidity 80 ± 5%. After the appropriate period of time the exposed fibres were then transferred back to the glove box for mechanical testing.

The tensile strengths of the fibres were measured using an Instron (Model No. 1122) under a constant strain rate of $0.25\,\text{cm}\,\text{min}^{-1}$ with fibre test lengths of 25 mm. Gripping of the fibres is a problem most frequently encountered in this type of measurement. Typically, fibres either slip out of the grips or break because of the local applied stress. However, it was found that sealing the fibre ends between two pieces of heavy duty transparent tape and placing these between the pneumatic grips under 75 psi of nitrogen reduced this problem considerably. Even still, some fibres did break near the grips but only those fibres which fractured in between the grips were used in the data analysis. The diameter of every fractured specimen was recorded. Each set of fibres exposed for a set time had a population of 25 fibres. X-ray diffraction and scanning electron microscopy were used to detect the presence of crystalline material and observe the fractured surfaces of the fibres.

## 3. Results and discussion

The statistical analysis of the fracture strength was based on the Weibull method [19]. In this approach, the probability of failure ($\phi$) of a fibre of surface area, $A$, which contains a statistical distribution of non-interacting flaws is given by Equation 1:

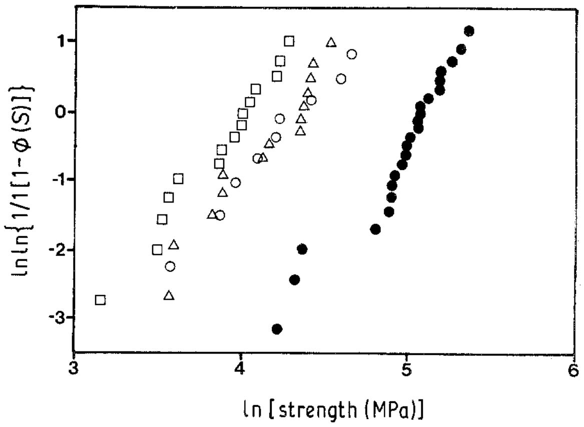

*Figure 1* Weibull plot of strength of ZBLA glass fibres after exposure to a relative humidity of 80% for different times. (●) Unexposed; (□) 4 days; (○) 8 days; (△) 14 days.

$$1 - \phi = \exp\left[\int_A \mathrm{d}A \int_0^S g(S)\mathrm{d}S\right] \qquad (1)$$

where $g(S)\mathrm{d}S$ is the number of flaws per unit area with a strength between $S$ and $S + \mathrm{d}S$. Furthermore, $g(S)$ is assumed to have an asymptotic functional form, such that:

$$\int_0^S g(S)\mathrm{d}S = [S - S_u/S_0]^m \qquad (2)$$

where $S_u$ is the lower limit on strength, $S_0$ is the scale parameter and $m$ is the shape parameter. If $S_u$ is given the value zero, it is possible by simple substitution into Equation 1 and taking logarithms twice, to obtain the following expression:

$$\ln\ln\{1/[1 - \phi(S)]\} = m\ln S - m\ln S_o + \ln A \qquad (3)$$

The values of the distribution parameters, $S_o$ and $m$, can now be easily deduced from strength failure probability data. Figure 1 shows the Weibull plot for the ZBLA glass fibres stored under nitrogen and after exposure to the laboratory environment for up to 14 days. The strengths were determined by dividing the load applied to each individual fibre by the cross-sectional area of that fibre. Although there is some scatter in the data points corresponding to low strength values, the failure of the ZBLA glass fibres under load appears to follow a unimodal behaviour. These low strength values are associated with fibres which break within the pneumatic grips and so for the analysis these data points have been ignored. It is clearly evident that the strength of the fibres is substantially reduced (~ 50%) after 4 days exposure to the atmosphere and thereafter very little change occurs. However, it has been pointed out that the Weibull analysis may not necessarily best characterize the real flaw distribution on the glass fibres [20]. For instance, there is doubt regarding the validity of the assumed functional form of $g(S)$. In a more recent fundamental approach [20], Equation 2 can be manipulated to obtain $g(S)$ in terms of a failure probability without assuming that it has a specific functional form. The fundamental approach assumes that a fibre fails at the maximum stress, $S_m$, and Equation 1 then

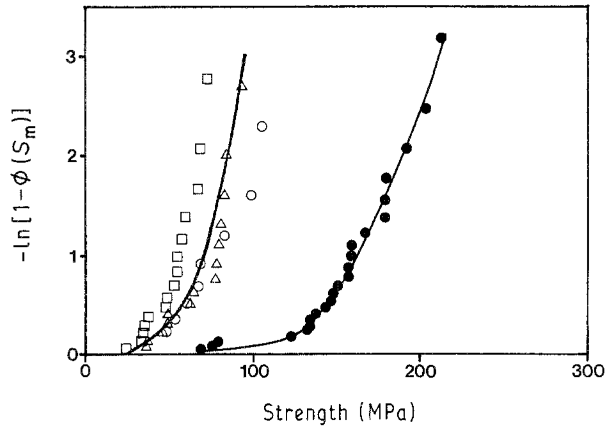

*Figure 2* Plot of $\xi(S_m) = -\ln(1 - \phi(S_m))$ against $S_m$ for ZBLA glass fibres exposed to a relative humidity of 80% for different times: (●) Unexposed; (□) 4 days; (○) 8 days; (△) 14 days.

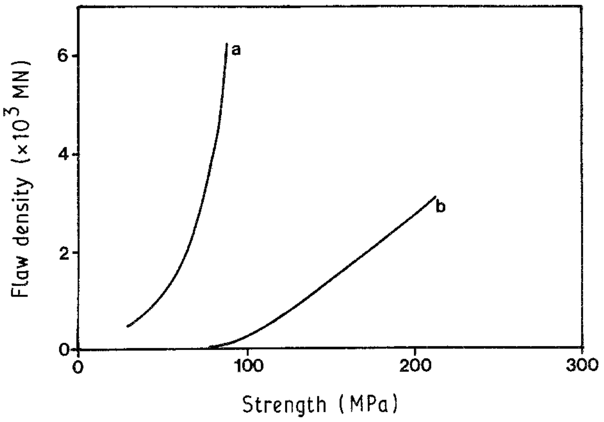

*Figure 3* Plot of the flaw density $g(S_m)$ against $S_m$ for both (a) exposed and (b) unexposed ZBLA glass fibres.

becomes:

$$\xi(S_m) = -\ln[1 - \phi(S_m)] = A \int_0^{S_m} g(S)\mathrm{d}S \qquad (4)$$

where $A$ is the surface area under test and is equal to $2\pi rl$ with $r$ being the fibre radius and $l$ the test length (25 mm). Differentiating Equation 4 with respect to $S_m$ and rearranging gives:

$$g(S_m) = (1/A)\mathrm{d}\xi(S_m)/\mathrm{d}S_m \qquad (5)$$

Hence, the flaw density, $g(S_m)$, at any strength $S_{mi}$, is proportional to the derivative of $\xi(S_m)$ with respect to $S_m$ at $S_{mi}$. Figure 2 shows a plot of $\xi(S_m)$ against $S_m$ for the exposed and unexposed ZBLA glass fibres. A best fit curve is drawn through the data points for the unexposed fibres such that the curve smooths out any local variations. This is because the smoothed data has a significant physical meaning relating to the flaw size distribution while local oscillations are due to statistical variations and merely complicate the form of the derivative $g(S_m)$. It is clearly evident from Fig. 2 that the unexposed fibres have the highest tensile strengths. Although the particular fluorozirconate glass composition in the present study is slightly different, the strength values are comparable to those obtained by Shibata *et al.* [21], Schneider *et al.* [22], Sakaguchi and Mitachi [23] Lau *et al.* [17] and Mimura *et al.* [24]. The strength was effectively reduced by almost 50% after 4 days exposure to the ambient environment of the laboratory. Thereafter, there is very little change. This agrees favourably with the results of Nakata *et al.* [25] who observed that the strength of Teflon FEP-coated ZBLALiPb fibres decreased by approximately 50% of the initial value after 4 days exposure to the ambient environment. However, in sharp contrast, the strength of fibres which had a protective chalcogenide glass coating beneath the Teflon outer jacket did not deteriorate even after one month of exposure to the environment. It should be stressed that the fibres in the present study were not coated with any type of polymer or other protective coating. Figure 3 represents a plot of the flaw density, $g(S_m)$, against strength, $S_m$, for both exposed and unexposed fibres. The curve representing the unexposed fibres was obtained by differentiating the appropriate curve in Fig. 2 and dividing by the average surface area of the fibres, based on an average diameter of 215 $\mu$m. The curve for the exposed fibres is based upon a best fit through the data points for all the exposed fibres in Fig. 2, irrespective of the duration of exposure. It is clearly evident that the exposed fibres are two to three times stronger than the corresponding exposed fibres of the same composition. This can be considered positive proof that atmospheric moisture with degrade the tensile strength of heavy metal fluoride glass fibres. All degradation ceased after 4 days exposure, although at this time, it is not known just how quickly moisture attacks these glass fibres. It may well follow a similar trend to that observed by Nakata *et al.* [25] where the strength of their fibres deteriorated to 85% after 1 day, 65% after 2 days and 50% after 4 days. The rate of attack by moisture will be the subject of a future paper.

The flaw distribution of the unexposed fibres increases continuously up to the maximum observed strength of about 212 MPa (although only 23 points are shown, representing 23 fibres, the 24th fibre will have an ordinate value of infinity and so is not shown. The strength of the 24th fibre was 320 MPa) and is considered to be caused by imperfect preform surface polishing and by fibre handling. This includes removal of the fibres from the take-up wheel, transfer into containers for storage and exposure, separation into correct test lengths and mounting on the instron for strength measurements.

It is possible to estimate the flaw size corresponding to the high strength distribution near the maximum observed strength of 212 MPa from knowledge of the critical stress intensity factor, $K_{Ic}$, by using the following Equation [8]:

$$S_F = K_{Ic}(\pi L)^{-1/2} \qquad (6)$$

where $S_F$ is the failure stress and $L$ the crack depth. Typical values of $K_{Ic}$ for bulk fluorozirconate glasses and fibres lie around 0.3 and 0.5 MPa m$^{1/2}$, respectively, compared with 0.6–0.9 MPa m$^{1/2}$ found in oxide glasses [26]. Therefore, taking a value for $K_{Ic}$ of 0.5 MPa m$^{1//2}$ for the ZBLA fibres gives an estimated crack depth of approximately 0.8–1.8 $\mu$m. This flaw size may well be a direct consequence of the final 1 $\mu$m polish given to the preforms prior to drawing the fibres. The actual

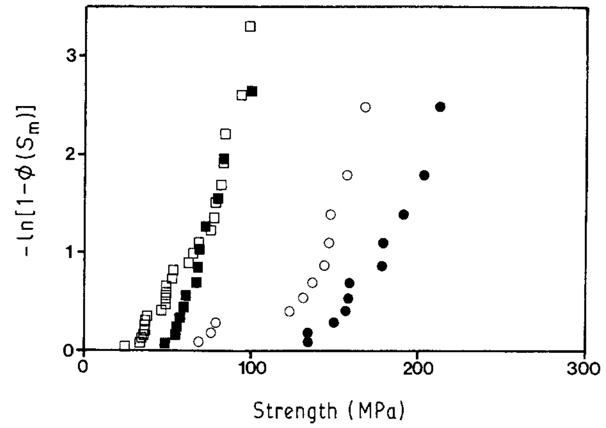

*Figure 4* Plot of $\xi(S_m) = -\ln[1 - \phi(S_m)]$ against $S_m$ for ZBLA glass fibres exposed to a relative humidity of 80% for different times. The fibres have been separated into two groups: (a) Fibre diameter less than 215 $\mu$m: (●) unexposed fibres; (■) exposed fibres. (b) Fibre diameter greater than 215 $\mu$m: (○) unexposed fibres; (□) exposed fibres.

flaw-size range for the unexposed fibres is approximately 0.8–8 $\mu$m. The $x$-axis in Fig. 3 is indirectly related to the flaw size, in so much as, an increasing strength can be considered equivalent to a decreasing flaw size (Equation 6). So, after exposure to moisture the flaw distributions shift to lower strengths and increase continuously up to the maximum observed values. The change in the shape of the curve represents growth of the initial flaws and also the possible formation of new flaws. It was difficult to distinguish between the two types of fibres because the sample length in the scanning electron microscope is relatively small (~ 1 cm) compared with the flaw density. One could also argue that due to the statistical nature of these measurements the flaw density is approximately the same and is highly dependent on the best fit curve through the data for the exposed fibres in Fig. 2. The maximum strengths obtained for the exposed fibres were approximately 0.09 GPa.

Figure 4 shows a plot of the failure probability against strength for the ZBLA exposed and unexposed fibres but split into two groups; namely, those with diameters less than 215 $\mu$m and those greater than 215 $\mu$m. This value was chosen since it represented a mean diameter of all the fibres investigated. It is quite evident that the unexposed fibres with the smaller diameters had the lower probability of failure. This simply relates to the correspondingly lower surface area, and with it, the reduced probability of finding a critical sized flaw. However, after exposure the surface area no longer controlled the strength and within experimental error both sets of fibres have the same limiting strength values.

It was not possible using scanning electron microscopy to distinguish between the exposed and unexposed fibres. However, it can be concluded that the fibres were presumably attacked by moisture thus lowering their strengths. One can rule out the possibility that the strengths deteriorated due to the action of, for example, dust particles from the air scratching and therefore damaging the fibre surfaces. Firstly, the fibres were stored in a contained environment and secondly, one would expect that the fibres exposed for 14 days would be considerably weaker than those exposed for 4 and 8 days. In reality, there was very little difference in strength between any of the exposed fibres, irrespective of the time of exposure. Unfortunately, the mechanism for this degradation is not clearly understood, as of yet, but it could possibly be due to a weakening of the metal–fluorine bonds at the crack tip by water (dissociative chemisorption). This "stress-corrosion" mechanism of weakening has been previously proposed in oxide glass fibres [27] and is considered to be caused by a chemical reaction between water which has been physically adsorbed on the glass surface and the strained chemical bonds found at the tip of a surface flaw. In this model, no new flaws are necessarily expected to be created by the action of moisture but only growth of existing flaws. In addition, mechanical tests conducted on bulk fluorozirconate glasses reveal that the fracture toughness, $K_{Ic}$, is greater in air than in water [28] which further supports the argument that moisture plays a detrimental role on the strength of fluorozirconate glass fibres exposed to the environment.

## 4. Summary

Uncoated ZBLA glass fibres were drawn from rod preforms in a moisture-free nitrogen atmosphere. Fibres stored and tested under nitrogen had tensile strengths ranging between 0.12–0.32 GPa and a flaw size distribution of 0.8–8 $\mu$m. This was presumably associated with the final 1 $\mu$m polish given to the preforms and the subsequent fibre handling. However, the strengths of the fibres decreased after exposure to the atmosphere. The maximum strength observed for the exposed fibres was approximately 0.09 GPa and there was very little change after 4 days. This is positive proof that the atmosphere degrades the tensile strength of fluoride glass fibres and it is clearly evident that fluoride glass fibres need to be protected from the environment. The mechanism of degradation is not clearly understood as of yet.

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