Original Paper

Drawing of fluoride glass fibers in NF_3 [1])

Armin Staudt, Achim Schoberth and Hartmut W. Schneider
Siemens AG, Research Laboratories, München (FRG)

Due to their low intrinsic optical loss in the infrared wavelength region, optical fibers drawn from heavy-metal fluoride glasses are currently under development for optical signal processing, technological processing and medical engineering applications. The susceptibility of these glasses to crystallization induced by hydrolysis, however, reduces the strength of the drawn fibers.

A process designed for the fabrication of high-strength fluoride glass fibers is described. The strength of fibers drawn from glasses of the compound systems $ZrF_4 \cdot BaF_2 \cdot LaF_3 \cdot AlF_3$ (ZBLA) and $ZrF_4 \cdot BaF_2 \cdot LaF_3 \cdot AlF_3 \cdot NaF$ (ZBLAN) was measured by a bending method. Glass surface damage was significantly reduced by adding NF_3 to the furnace atmosphere, which increased the strength of ZBLAN fibers by about 40 % and that of ZBLA fibers by even about 75 %. ZBLA fibers drawn in an atmosphere containing fluorine exhibit a mean bending strength in the order of 1400 MPa, which is almost the strength level of smoothly etched fibers. The strength of the fibers that have been etched in a $ZrOCl_2$ solution is shown to be correlated with the light scattering of the preform; it was found to be possible to make fluoride glass fibers with a mean bending strength of at least 1600 MPa.

Ziehen von Fluoridglasfasern in NF_3-Atmosphäre

Optische Fasern aus Schwermetallfluoridgläsern werden wegen ihrer niedrigen intrinsischen Dämpfung im Infraroten für die optische Nachrichtenübertragung sowie für prozeßtechnische und medizinische Anwendungen entwickelt. Oberflächenkristallisation auf Grund der Hydrolyseempfindlichkeit der Gläser beeinträchtigt jedoch die Faserfestigkeit.

Es wird ein Verfahren zur Herstellung von Fluoridglasfasern mit hoher Festigkeit vorgestellt. Die Fasern wurden aus Gläsern der Mehrstoffsysteme $ZrF_4 \cdot BaF_2 \cdot LaF_3 \cdot AlF_3$ (ZBLA) und $ZrF_4 \cdot BaF_2 \cdot LaF_3 \cdot AlF_3 \cdot NaF$ (ZBLAN) gezogen und die Faserfestigkeit mit einer Biegemethode gemessen. Durch Zudotieren von NF_3 zur Ofenatmosphäre wurde die Schädigung der Glasoberfläche beim Faserziehen deutlich vermindert. Dies führte bei ZBLAN-Glasfasern zu einer Festigkeitssteigerung um etwa 40 %, bei ZBLA-Glasfasern sogar um 75 %. Mit mittleren Biegefestigkeiten bis zu 1400 MPa erreichten damit die in fluorhaltiger Atmosphäre gezogenen ZBLA-Glasfasern annähernd das Festigkeitsniveau glatt geätzter Fasern. Es wird außerdem gezeigt, daß die Festigkeit nach dem Ätzen der Fasern in $ZrOCl_2$-Lösung mit der Lichtstreuung der Vorform korrelierbar ist und mittlere Biegefestigkeiten von mindestens 1600 MPa bei Fluoridglasfasern möglich sind.

1. Introduction

Fibers drawn from heavy-metal fluoride (HMF) glasses are under investigation for long-haul communication links due to their potential low loss in the infrared wavelength region. Moreover, a variety of possible short-range applications are currently being explored, e.g., remote infrared spectroscopy, remote temperature measurement, laser power transmission for medical or industrial equipment. Besides optical loss, the mechanical properties of the fibers, e.g., flexibility or load-bearing capability, are critical for practical applications. However, mean tensile strength values previously reported range between 100 and 400 MPa [1 to 3], which is less than 10 % of the standard strength of SiO_2 glass fibers. One reason for the weakness of HMF glass fibers may be seen in the crystallization tendency of the hot glass during the fiber drawing process.

The strength improvement obtained by drawing HMF glass fibers in a fluorinated atmosphere using an NF_3 dopant will be described. An additional increase in strength was obtained by etching the fibers in $ZrOCl_2$ solution after drawing. The strength results for unetched and etched fibers will be compared, clearly demonstrating that surface defects are largely avoided using NF_3 and that the pristine strength of well-drawn fibers mainly resembles the bulk strength measured after etching [4].

2. Experimental techniques

Fibers were drawn from preforms, prepared by a conventional melt-casting method. Starting materials were high-purity fluorides (E. Merck, Darmstadt (FRG)). Single-material glass rods of compositions (in mol%) $57\,ZrF_4 \cdot 34\,BaF_2 \cdot 5\,LaF_3 \cdot 4\,AlF_3$ (ZBLA) or $53\,ZrF_4 \cdot 20\,BaF_2 \cdot 4\,LaF_3 \cdot 3\,AlF_3 \cdot 20\,NaF$ (ZBLAN), 7 or 10 mm in diameter and 150 or 200 mm in length, were prepared by quenching the melt in gold-plated brass molds. To characterize the

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homogeneity, the preforms were illuminated with a HeNe laser beam and the scattered light was recorded with a video camera normal to the beam direction. A relative scattering intensity was obtained by comparison with a reference signal. After etching in a solution of $0.4\,n$ $ZrOCl_2 \cdot 8\,H_2O$ in $1\,n$ HCl to remove the hydrated and partially crystallized surface layer [5], the preforms were drawn into fibers with a diameter of 140 µm using an N_2 or an 1 vol% NF_3-doped N_2 flushed furnace with an r.f.-heated carbon susceptor. Drawing rate was about 5 m/min. During drawing, HF evolution was checked with an HF monitor (Micro Sensor Technologie GmbH, München (FRG)). Fiber strength was measured by a two-point bending method. Fibers (diameter d) were bent into a U configuration between two movable parallel plates which were slowly shifted together. The maximum bending stress σ_b is correlated to the plate distance D at fiber breakage by [6]:

$$\sigma_b = 1.198 \cdot E \cdot d/(D - d)\,. \qquad (1)$$

The Young's modulus E was determined from sound velocity and density measurements (ZBLA: 50.4 ± 0.3 GPa, ZBLAN: 50.4 ± 0.2 GPa) and was assumed to be independent of strain. To characterize the strength of a fiber, 20 short samples were tested by the bending method. Typical plate distances at fiber breakage range between 3 and 15 mm.

3. Surface investigations

When a preform is drawn into a fiber without special precautions residual moisture in the furnace atmosphere or on the preform surface may react with the glass at drawing temperature. Then a thin opaque layer will form on the surface, which tends to tear during stretching in the neck-down region, producing a characteristic pattern (figure 1). Raman microprobe analysis was applied to distinguish between the chemical nature of the clear and the opaque surface regions. While the clear parts yielded a glass spectrum, the turbid surface reflected a characteristic line spectrum (figure 2a). The close correspondence between the peak positions and those of ZrO_2 powder (figure 2b) proves the hydrolysis reaction:

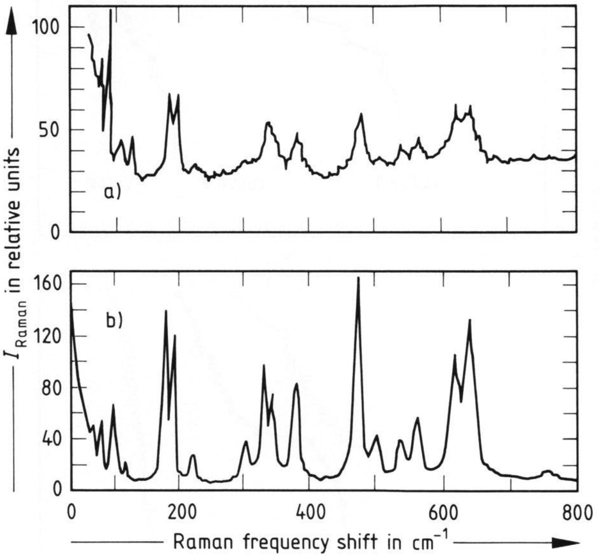
$$ZrF_{4\,(glass)} + 2\,H_2O_{(gas)} \rightleftharpoons ZrO_{2\,(solid)} + 4\,HF_{(gas)}\,. \quad (2)$$

Removal of the water as well as the addition of HF will shift this equilibrium to the left [7]. Both may be realized by adding NF_3, some of which converts to HF, following the equation:

$$H_2O + NF_3 \rightarrow 2\,HF + NOF\,. \qquad (3)$$

To explore the onset of the reaction between NF_3 and H_2O for the special flow conditions in the experi-

Figure 1. Partially crystallized ZBLAN preform surface of neck-down region.



Figures 2a and b. Raman microprobe spectra of a) crystallized neck-down surface, b) ZrO_2 powder.

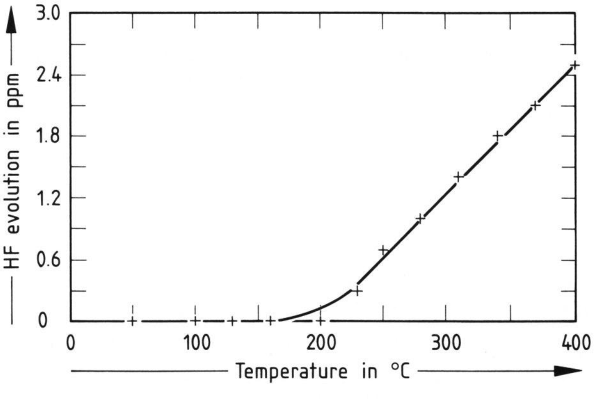


Figure 3. HF evolution of an N_2 gas flow doped with 1 vol% NF_3 and 0.2 vol% H_2O.

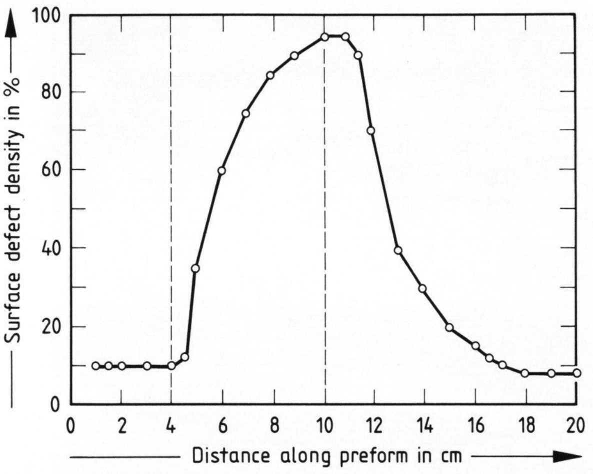
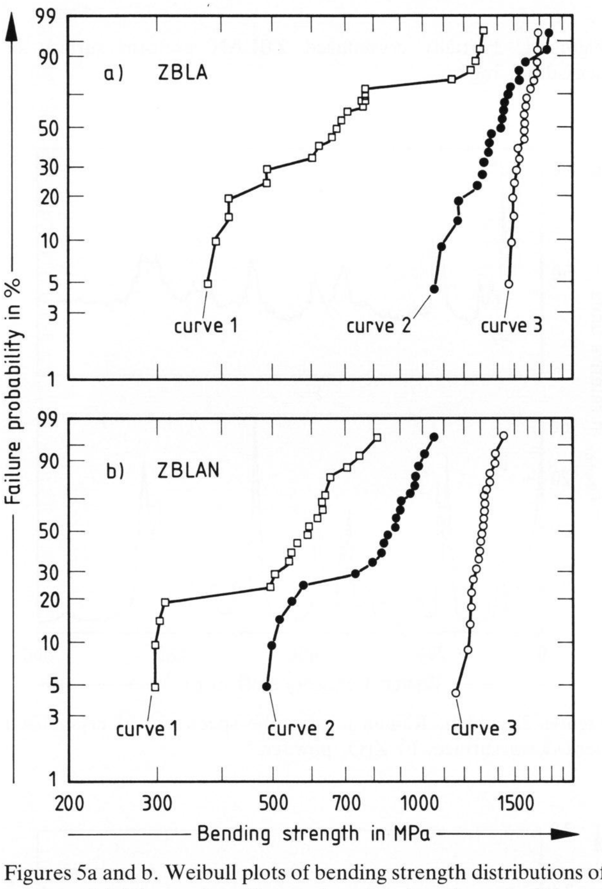


Figure 4. Effect of gas purge during heat treatment on the etch pit density of a ZBLAN preform.



Figures 5a and b. Weibull plots of bending strength distributions of groups of 20 bare glass fibers after drawing through different atmospheres; a) ZBLA, b) ZBLAN. Curve 1 = after drawing in N_2 atmosphere; curve 2 = after drawing in NF_3-doped N_2 atmosphere; curve 3 = after drawing in NF_3-doped N_2 atmosphere and etching for 1 min.

mental setup, the empty drawing furnace was flushed with N_2 doped with 1 vol% NF_3 and 0.2 vol% H_2O (figure 3). The addition of H_2O to the nominal dry N_2 gas flow was necessary to overcome the gas monitor's detection limit for HF. The onset of the reaction was found at a susceptor temperature of about 200 °C; the HF concentration in the exhaust gases increased with rising temperature. To prove that NF_3 also removes water adsorbed on a glass surface as well as chemically bonded water, which may also produce surface crystallization, a ZBLAN preform was moved slowly through the drawing furnace, whose temperature was kept below the softening temperature of the glass. The furnace was flushed with N_2 mixed with 1 vol% NF_3. During this run the NF_3 flow was interrupted for a certain time. For the detection of surface defects the preform was afterwards briefly etched in $ZrOCl_2$ solution. Characteristic etch pits are found in regions where crystallization has taken place, whereas glassy regions are congruently etched, leaving an even surface. The surface defect density is defined here by the ratio of the etch pit area to the total area. Those regions of the glass surface which were flushed with NF_3 during the heating cycle showed a low defect density, whereas the middle region showed a high defect density (figure 4). The characteristic response curve of figure 4 reflects the gas residence time in the system. The experiment clearly shows the crystallization of the glass surface via hydrolysis to occur in a nominally dry atmosphere with the residual moisture even at temperatures below the drawing temperature of the glass. This hydrolysis can be avoided by adding NF_3.

4. Strength results

As may be anticipated from these investigations, fiber strength can be improved by drawing in NF_3 atmosphere. To evaluate the effect of the furnace atmosphere, the strength values of fibers drawn in an N_2 atmosphere doped with 1 vol% NF_3 were compared with those drawn without halogen. Results are shown as Weibull plots for ZBLA (figure 5a) and for ZBLAN (figure 5b) glass fibers. Drawing in an atmosphere containing NF_3 increases the mean bending strength from 800 to 1400 MPa for ZBLA and from 600 to 850 MPa for ZBLAN glass fibers. Similar bending strength values were recently obtained for ZBLAN fibers by treating the etched preform in a plasma-activated NF_3 atmosphere at 20 °C before fiber drawing [8].

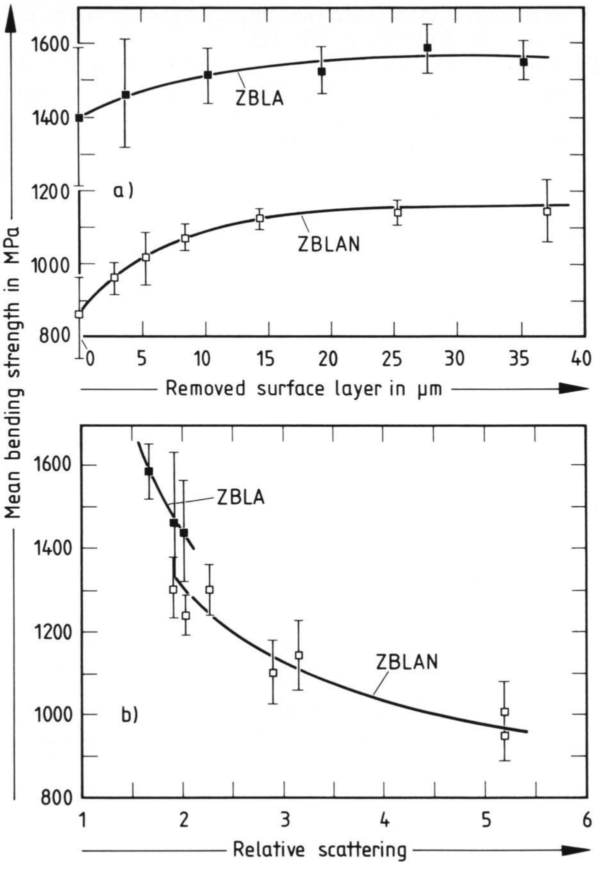
To distinguish between surface and bulk defects some fibers were additionally etched in $ZrOCl_2$ solution directly before bending. It was observed that in general etching the fibers increased the mean bending strength as well as the slope of the distribution. ZBLA fibers drawn in NF_3 show a very steep cumulative failure distribution, but only a small additional mean bending strength improvement up to 1600 MPa, whereas the strength improvement up to 1300 MPa realized by etching ZBLAN glass fibers was slightly larger. This is evidence of the efficient inhibition of surface crystallization of ZBLA glass fibers drawn in NF_3, whereas drawing ZBLAN glass fibers in NF_3 seems to result in lower efficiency because of the lower drawing temperatures. After removal of the degraded surface layer with a $ZrOCl_2$ solution, a fiber strength may be measured that corresponds to that of the bulk material. As seen from the plot of the mean bending strength of NF_3-drawn fibers versus the thickness of the subsequently removed surface layer (figure 6a), the strength of ZBLA and ZBLAN fibers stabilizes once an etch depth of about 10 μm is reached. This fiber strength after prolonged etching does not depend on the furnace atmosphere during drawing and may be regarded as the inherent fiber strength of the specific fiber under test. The mean bending strength of the best ZBLA glass fiber was found to be 1586 ± 64 MPa, corresponding to a bending diameter of nearly 3 mm for the etched fiber with a diameter of 80 μm. Obviously ZBLAN glass fiber seems to be of lower strength, the reasons for this observation will be discussed in section 5.

5. Relation between glass scattering level and fiber strength

Strength values of less than 1600 MPa may be due to defects larger than 50 nm. Inhomogeneities of this magnitude should have a marked influence on the light scattering of the glasses. When a laser beam is launched into an HMF glass preform it is apparent to the naked eye that discrete bright pinpoints are immersed in a homogeneous medium with lower level continuous scattering, which depends mainly on the melting conditions of the glass. The nature of this scattering is difficult to analyze. It has been reported that the scattering intensity is correlated to the concentration of oxygen in the glass [9]. Alternatively reduced glass species, such as ZrF_2, may be regarded as a source of continuous scattering [10]. In any case, scattering greatly determines the transmission loss of the fiber. It has been observed that the continuous scattering level measured on the preform before drawing also correlates to the inherent fiber strength. Only fibers drawn from relatively clear rods exhibit high strength values (figure 6b). Obviously fiber strength as well as fiber attenuation are influenced by the scattering material. Higher glass quality is therefore essential not only for low attenuation but also for high fiber strength.

6. Conclusions

The strength of as-drawn fibers is largely determined by surface degradation during the fiber drawing process. Drawing the fibers in a furnace atmosphere doped with NF_3 inhibits surface hydrolysis, so allowing the production of ZBLA fibers with a mean bending strength of 1400 MPa. After removing the crystallized ZrO_2-containing surface layer with the



Figures 6a and b. Variation of the mean bending strength a) with the thickness of the etched layer, b) of etched fibers with the preform scattering level. Explanation: each error bar represents the standard deviation of the arithmetic mean strength value of 20 measurements.

etching solution, the inherent fiber strength, which is largely determined by preform quality can be measured. For the first time mean bending strength values of almost 1600 MPa were measured for etched ZBLA fibers.

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