Radiation-Resistant Low OH Content Silica Core Fibers

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Abstract—The radiation-induced attenuation of pure silica core fibers measured at 0.85 μm has been reduced by treating the soot preforms in various oxidizing atmospheres; the most effective of the treatments used in this study was SOCl₂. Fibers treated in SOCl₂ or Cl₂ also have low OH contents. The radiation-induced loss of the treated fibers has been found to follow the square root of the drawing-induced absorption band height at 0.63 μm.

I. INTRODUCTION

EARLY STUDIES of the radiation sensitivity of pure silica core fibers found that the induced attenuation depended strongly on the OH content of the silica [1], [2]. The damage in fibers with high OH concentrations (~1200 ppm) in the core was over an order-of-magnitude less than that measured in similar fibers of low OH content (3–50 ppm). An example is shown in Table I: the loss induced at 0.85 μm in an induction furnace-drawn Fluosil SW fiber with a low OH content Suprasil W core (1.6-ppm OH) is 257 dB/km 10 s after an irradiation of 37 Gy (1 Gy = 100 rad), whereas the induced loss in a similar Fluosil SS fiber with a Suprasil core (~1200-ppm OH) is only 14 dB/km. In contrast to these results, Schneider [3] reported recently that the damage in a Fluosil SW fiber pulled by Heraeus Quarzschmelze was actually less than that in a Fluosil SS fiber during steady-state irradiation. Likewise, Tanaka, et al. [4] observed that the radiation sensitivities of wet and dry pure silica (Diasil) core fibers were similar, provided the preform of the dry fiber had been processed to reduce the 0.63-μm drawing-induced absorption usually evident in fibers with low OH content pure silica cores [5].

Levin and Pinnow [6] recently described the reduction of this drawing-induced absorption by treatment of the pure silica soot preforms in various oxidizing atmospheres. This paper reports results of a study undertaken to more carefully explore the connection between OH and radiation sensitivity of pure silica core fibers and to determine the relationship between their radiation response at 0.85 μm and the presence of the 0.63-μm drawing-induced absorption band.

II. EXPERIMENTAL

A number of pure silica core multimode fibers were measured. In addition to those pulled from preforms prepared in this work, we report data from the following fibers: Heraeus Quarzschmelze Fluosil SW fibers, pulled from the same preform with a torch by Heraeus or with a resistance or induction furnace at Times Fiber Communications (TFC), and Dainichi-Nippon Cables. The two Dainichi fibers were from two different preforms; the SM-100 S fiber had only a primary coating, whereas the SM-100 SY(B) fiber had an additional extruded jacket.

The preparation procedure of fibers for this study was described in [6]. In summary, porous soot preforms were deposited by reaction of SiCl₄ with O₂ in a natural gas-oxygen flame. Reduction of the 0.63-μm drawing-induced absorption band was achieved through oxidation of the silica either by deposition in an excess oxygen flame or by treating the soot preform with Cl₂, H₂O, or SOCl₂ at high temperature (900–1300°C) following deposition. The preforms were sintered to solid glass, pulled into fibers in an induction furnace, and clad with either a polymer or B-doped silica.

The absorption spectra of the fibers were measured by the cutback technique with an 0.005-μm wavelength increment prior to irradiation. The height of the 0.63-μm absorption band was calculated from the height of a baseline under the band, and the OH content was calculated from the band height.

TABLE I

<table>
<thead>
<tr>
<th>Fiber</th>
<th>OH( ppm)</th>
<th>Cladding</th>
<th>10</th>
<th>100</th>
<th>1000</th>
</tr>
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<tbody>
<tr>
<td>0.85 μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raychem RSC 2004</td>
<td></td>
<td>Polymer</td>
<td>9.5</td>
<td>3.4</td>
<td>0.5</td>
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<tr>
<td>Dainichi Nippon SM-100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>S fiber</td>
<td>3.0</td>
<td>F-B-doped</td>
<td>9.8</td>
<td>3.8</td>
<td>1.6</td>
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<td>Heraeus Fluosil SS</td>
<td>1200</td>
<td>F-B-doped</td>
<td>9.2</td>
<td>9.1</td>
<td>5.4</td>
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<td>Dainichi Nippon SP-100</td>
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<td></td>
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<td>SY(B) fiber</td>
<td>7.9</td>
<td>F-B-doped</td>
<td>10.3</td>
<td>7.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Times Fiber SS-100</td>
<td>1200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heraeus Fluosil SW</td>
<td>15.5</td>
<td>F-B-doped</td>
<td>16.3</td>
<td>15.9</td>
<td>11.7</td>
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<td>Hughes Research Lab HAC-100</td>
<td>4.1</td>
<td>F-B-doped</td>
<td>38.3</td>
<td>6.3</td>
<td>0.9</td>
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<td>SOCl₂ Treatment</td>
<td>3.4</td>
<td>Silicone</td>
<td>68.0</td>
<td>2.3</td>
<td>0.1</td>
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<tr>
<td>ITT T-223</td>
<td>1200</td>
<td>Silicone</td>
<td>68.6</td>
<td>43.6</td>
<td>10.7</td>
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<tr>
<td>Heraeus Fluosil SW (Res. F.)</td>
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<td>F-B-doped</td>
<td>120.0</td>
<td>65.9</td>
<td>15.0</td>
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<td>Cl₂ Treatment</td>
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<td>Silicone</td>
<td>184.7</td>
<td>122.7</td>
<td>101.7</td>
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<tr>
<td>Cl₂ Treatment</td>
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<td>94.7</td>
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<tr>
<td>Heraeus Fluosil SM (Ind. F.)</td>
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<td>F-B-doped</td>
<td>256.7</td>
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<td>Controlled Flame</td>
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<td>Silicone</td>
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<td>As-Deposited</td>
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<td>Silicone</td>
<td>895.0</td>
<td>414.6</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Time after Irradiation (sec)
of the 0.95-μm Si-OH overtone band [7]. The growth of the radiation-induced attenuation at 0.83 μm was measured in situ during 60Co irradiation at room temperature at 90 Gy/min dose rate, and the recovery was measured for 10^8 s following an irradiation of 37 Gy. The light intensity in the fiber was <300 nW to minimize photobleaching [8]. A more detailed description of the radiation experiment has been published [8, 9, 10].

III. RESULTS AND DISCUSSION

In general, it was observed that the radiation-induced loss in the pure silica core fibers of this study did not decrease with increasing OH content, in contrast to previous studies [1], [2], [11]. A clear example is shown in Fig. 1 where the OH content of the 3 fibers with drawing-induced absorptions of ~4 dB/km decreases from 128 to 4.2 ppm with a corresponding decrease in radiation-induced attenuation. As shown in Fig. 1 and Table I, the fibers divide into three groups with OH concentrations of ~3, ~60, and ~1200 ppm. The radiation resistance of the best of the fibers with the lowest OH content is virtually the same as that of the best of the high OH content fibers (e.g., Dainichi Nippon SM-100 S versus Raychem RSC-200A). It is thus apparent that OH content does not determine the radiation sensitivity of pure silica core fibers. Rather, it is evident in Fig. 1 that a significant relationship exists between the radiation-induced attenuation of the fibers at 0.85 μm and the drawing-induced absorption at 0.63 μm. The B-doped clad fiber does not follow this relationship due to the radiation sensitivity of the cladding (vide infra), nor do the Heraeus Fluosil SW fibers, presumably because their preforms were prepared by plasma deposition rather than flame hydrolysis [12]. Nevertheless, the relationship between the drawing-induced and radiation-induced absorptions is valid for the fibers prepared in this study, together with the Dainichi Nippon and Hughes waveguides.

Oxidation of the silica by post-deposition treatment of the soot preform in an H2O atmosphere is seen in Fig. 1 to increase the OH content to 128 ppm and to reduce the height of the drawing-induced band, without significantly affecting the radiation-induced loss at 0.85 μm. In contrast, control of the flame during deposition or post-deposition treatments in Cl2 or SOCl2 are substantially more effective in reducing these absorptions. The chemical treatments also decrease the OH content in the fibers to the 3-4-ppm level. As shown in Fig. 1 and Table I, the fibers of this study with OH contents of 3-4 ppm were all treated in either Cl2 or SOCl2. However, it should be noted from Fig. 2 that there are significant disadvantages in using Cl2 to oxidize the silica. Not only are the radiation-induced losses in the Cl2-treated fibers higher than that in the fiber treated in SOCl2, but the recovery of the damage at long times following irradiation is inhibited. In fact, as shown in Fig. 2, there is virtually no additional recovery of the Cl2-treated fibers between 10^3 and 10^5 s after irradiation. Thus Cl2-treated fibers would not be appropriate for deployment in radiation environments where good recovery is required.

Attempts were made to fit the recovery data of several of the fibers from 0.25 to 10^5 s to a series of exponential decays. The data for t ≥ 7000 s was well described by a single exponential with a time constant of 2.8 × 10^5 s, but as many as five additional exponential terms were required to fit the data at shorter times. Hence, the recovery processes at t ≤ 7000 s are relatively complex, perhaps involving a distribution in trap depths, whereas at longer times the recovery appears to be due to an activated process.

Of the preforms prepared in this study, Fig. 1 shows that the lowest drawing-induced and radiation-induced absorptions were obtained with SOCl2 treatment. Although the drawing-induced loss of this fiber is less than that of the Hughes Research Laboratory and Dainichi-Nippon SM-100 SY(B) fibers, the radiation-induced attenuation is greater. It seems plausible to attribute the additional radiation sensitivity of this fiber to the silicate optical cladding since the latter two fibers had glass claddings. Note from Table I that the high OH content fibers also follow this trend: except for the Raychem fiber, which has a proprietary polymer cladding, all these fibers have essentially identical core materials.

![Fig. 1. Radiation-induced attenuation at 0.85 μm measured 0.25 s after a 60Co exposure of 37 Gy at 23°C versus the band height of the 0.63-μm drawing-induced absorption in pure silica core fibers. The numbers near the data points are the OH concentrations in ppm. The line represents a fit of the data to a square-root dependence.](image1)

![Fig. 2. Recovery of the radiation-induced attenuation of selected low OH content silica core fibers at 0.85 after a 60Co exposure of 37 Gy, T = 23°C. The Hughes and Dainichi Nippon (DNC) fibers had glass claddings; the other fibers were polymer clad.](image2)
The radiation sensitivity of the high OH content silica core fibers clad with B-doped silica (Times Fiber SI-100) is only slightly higher than similar fibers clad with F-doped silica, as shown in Table I. However, Fig. 1 and Table I show that the damage in the low OH content fibers with a B-doped silica clad is ~2.5 times greater than in similar C12-treated fibers with polymer claddings. Thus B-doped silica clad fibers with wet cores are potential candidates for deployment in radiation environments (except where high neutron fluxes will be encountered, since \( \text{B}^0 \) has a large cross section for neutron capture [3]). Similar fibers with dry cores have a comparatively larger radiation response and, therefore, may not be as attractive for these applications.

The correlation between the radiation-induced attenuation at 0.85 \( \mu \)m and the 0.63-\( \mu \)m drawing-induced band height shown in Fig. 1 implies that an equilibrium exists in the glass between the precursors to the drawing-induced and radiation-induced defect centers. Although there is considerable scatter in the data, omitting the B-doped silica clad and Fluosil SW fibers, they seem to follow a square-root dependence. This may be taken as evidence that the annihilation of one of the former by control of the deposition flame or by the oxidation treatments in Cl\(_2\) or SOCl\(_2\) results in the removal of two of the latter.

The Heraeus Fluosil SW fibers behave quite differently from the other fibers of this study—significant variations in the radiation response are accompanied by only slight changes in the drawing-induced absorption intensity. Since these fibers were pulled from preforms prepared by plasma deposition [12], rather than by flame hydrolysis, it seems reasonable to assume that the former process creates precursors of the radiation-induced defect centers that are unrelated to the precursors of the drawing-induced defects. The difference between the behavior of the three fibers drawn with the torch, resistance, and induction furnaces shown in Fig. 1 and Table I could arise either from the difference in hot zone geometry or from the different redox conditions during draw. Since the hot zones of the two furnaces would be similar and much broader than that of the torch, we suggest that it is the redox conditions during fiber drawing that strongly influence the radiation sensitivity of Fluosil SW.

It should be noted that the data of the torch-drawn Fluosil SW fiber shown in Fig. 1 and Table I are in agreement with the report by Schneider [3] that Fluosil SS and SW fibers pulled at Heraeus Quarzschmelze (presumably by a torch) had comparable attenuations induced by exposure to \( \gamma \) rays from a reactor. (However in a later paper [11], Schneider concluded that increased OH content leads to decreased radiation sensitivity. Although the data of the Fluosil SW fibers of [3] and [11] are in agreement, those for the Fluosil SS fibers are not. Possible explanations are a somewhat greater light intensity in the latter case, leading to enhanced photobleaching, or fiber-to-fiber variations in impurity content.) In the present study, the induced damage in the torch-drawn SW fiber is slightly higher than in [3] (52 versus 30 dB/km), and the loss in the SS fiber is ~2 \( \times \) less than that in the SW fiber, whereas the opposite was reported by Schneider [3]. Possible differences may be explained by the much lower dose rate in Schneider's study (1.39 versus 90 Gy/min), the different energy spectra of the reactor versus \( \text{Co}^{60} \) radiation, and fiber-to-fiber variations in radiation sensitivity. In any case, our results agree with those of Schneider, as reported in [3].

The nature of the defect center giving rise to the drawing-induced absorption of 0.63 \( \mu \)m has been previously studied by electron spin resonance (ESR) spectroscopy [13]. Although the ESR spectrum of the peroxy radical \( \text{O}_2^\cdot \) was observed in as-drawn Suprasil W fibers, there was no correlation between the radiation-induced defect centers in the low OH content silica core fibers with high OH contents were substantially less in those with low OH content might be due to the absence of the drawing-induced defect centers in the wet fibers [5], [13]. Certainly, the dry fibers that have been processed to minimize the drawing-induced absorption are quite attractive: their low OH content permits them to be used at long wavelengths, and the low radiation sensitivity at 0.85 \( \mu \)m makes them viable candidates for use in radiation environments. Preliminary recovery data of several fibers at 1.3 \( \mu \)m shown in Table I indicate that they are extremely attractive at this wavelength as well. In fact, the induced losses of the Dainichi Nippon SM-100 S fiber are the lowest ever measured at 1.3 \( \mu \)m at this laboratory. The temperature dependence of the radiation damage of this fiber has been reported [4].

IV. Conclusions

The present study has shown that the radiation-induced attenuation at 0.85 \( \mu \)m in pure silica core fibers can be reduced by processing the soot preforms deposited by flame hydrolysis in oxidizing atmospheres; the induced loss of these fibers follows the square root of the 0.63-\( \mu \)m drawing-induced absorption band height. It has been determined that low OH content (3-ppm) silica core fibers can be made whose radiation sensitivity at 0.85 \( \mu \)m is equivalent to the best of the high OH content (1200-ppm) fibers, provided that the drawing-induced defect centers in silica core fibers with high OH contents were substantially less than in those with low OH content might be due to the absence of the drawing-induced defect centers in the wet fibers [5], [13]. Certainly, the dry fibers that have been processed to minimize the drawing-induced absorption are quite attractive: their low OH content permits them to be used at long wavelengths, and the low radiation sensitivity at 0.85 \( \mu \)m makes them viable candidates for use in radiation environments. Preliminary recovery data of several fibers at 1.3 \( \mu \)m shown in Table I indicate that they are extremely attractive at this wavelength as well. In fact, the induced losses of the Dainichi Nippon SM-100 S fiber are the lowest ever measured at 1.3 \( \mu \)m at this laboratory. The temperature dependence of the radiation damage of this fiber has been reported [4]. Measurements of the temperature and dose rate dependence in other silica core fibers are in progress and will be reported in a later paper.

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REFERENCES


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