The Role of Fluorine-Doped Cladding in Radiation-Induced Absorption of Silica Optical Fibers

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***Abstract*—Radiation-induced absorption spectra and radial distribution of nonbridging oxygen over the fiber core are compared in fibers and preform slices fabricated under different technological regimes with high- and low-hydroxyl silicas in the core. The radiation-induced nonbridging oxygen concentration is found to peak at the core-cladding interface. Fiber perform fabrication and fiber drawing processes are found to have different influence on its value in fibers with low- and high-hydroxyl silicas in the core. The precursors of nonbridging oxygen near the core-cladding interface are argued to arise at the stage of preform fabrication at least in the case of high–hydroxyl fibers. Their concentration decreases with increasing the fluorine concentration in the cladding. In the case of low-hydroxyl silica fibers the increase of the radiation-induced nonbridging oxygen concentration at the core periphery is argued to have a different nature as compared to high-hydroxyl silica fibers.**

***Index Terms*—Nonbridging oxygen, optical fiber, radiation color center, radiation-induced absorption.**

I. Introduction

TWO IMPORTANT applications of optical fibers in the nuclear industry are related to plasma diagnostics in fusion reactors [1] and transmission of image from inaccessible parts of nuclear installations [2]. The relevant doses are above 1 MGy.

Under ionizing radiation point defects—radiation color centers (RCC)—arise in the silica glass network, which results in absorption of the signal transmitted through the fiber. The main RCC in the visible region is nonbridging oxygen hole center (NBOHC). Technological peculiarities of its formation are studied in this paper.

Radiation-induced absorption of pure-silica-core fibers depends, to a certain extent, on the presence of an fluorine (F)-doped silica light-reflecting cladding. With the help of ESR spectroscopy, Nagasawa *et al.* [3] demonstrated that the concentration of NBOHC in fibers with a high-OH (high-hydroxyl) pure-silica core and an F-doped silica cladding, peaks near the core-cladding interface. This experimental observation pointed to the role of the cladding in the NBOHC formation. Based on this evidence, Griscom [4] suggested that the NBOHC precursors—peroxy linkages—are formed in the process of plasma deposition of an F-doped silica cladding on a substrate silica rod via a reaction

$$\equiv \text{Si–OH HO–Si} \equiv +2\text{F} \rightarrow \rightarrow \equiv \text{Si–O–O–Si} \equiv +2\text{HF} \uparrow . \quad (1)$$

Subsequently, under radiation, a peroxy linkage yields two NBOHCs. However, the question still remains how the fluorine effect depends on F concentration in the cladding and on preform and fiber fabrication regimes. Comparing fibers produced under different regimes might provide a deeper insight into the role of fluorine and might allow optimization of the fabrication regimes. Thus, the aim of this work was to compare radiation-induced absorption spectra in fibers fabricated under different regimes of F-doped cladding synthesis with different types of silica in the core and to determine the radial distribution of radiation-induced NBOHC.

II. Experimental

Fiber preforms for this study were fabricated by the plasma outside deposition (POD) process [5] and by the "rod-in-tube" technique, the core material being high-OH low-Cl KU-1 silica or low-OH low-Cl KS-4V silica. KU-1 is a Russian industrial synthetic silica, and KS-4V is an original synthetic silica developed in the Silicate Chemistry Institute of Russian Academy of Sciences [6] (see Table I). In the POD process, an F-doped silica layer (light-reflecting cladding of the future fiber) is deposited on the substrate silica rod (core). F-doped silica is synthesized via chemical reactions occurring in a microwave plasma torch in a gas mixture containing $SiCl_4$, O_2, and freon [5]. In the rod-in-tube technique, an F-doped silica cladding is deposited on the inner wall of a silica substrate tube, thereafter, the silica rod is inserted into the tube and fused with it. The preforms fabricated for this study by the POD-process differed in the amount of fluorine in the cladding (from 2 to 5 atomic%), which was controlled by the deposition temperature (the lower the deposition temperature, the higher the fluorine content in the glass). The fibers drawn from the preforms had an acrylate coating.

The fibers were gamma-irradiated with a cobalt source to 1.00 MGy (4.0 Gy/s, accuracy 5%) at $\sim$40 °C. A detailed description of the irradiation conditions can be found in [6]. Radiation-induced absorption spectra were measured within 1–2 h after the irradiation. Measuring lengths of irradiated fibers varied from 1.5 to 5 m.

To determine the radial distribution of NBOHC in the fiber core, we applied, for the first time, a measuring technique based

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TABLE I
PARAMETERS OF THE FIBERS TESTED

Fiber No.	Preform fabrication technology	Type of silica in the core	OH content, ppm	Cl content, ppm	Core/cladding diameter (μm)	NA
1	POD	KS-4V	0.6	40	100/120	0.16
2	POD	KU-1	800	80	100/120	0.16
3	POD	KS-4V	0.3	40	200/240	0.23
4	POD	KU-1	800	80	200/240	0.25
5	Rod-in-tube	KU-1	800	80	105/250	0.26
6	POD	KU-1	800	80	100/125	0.26

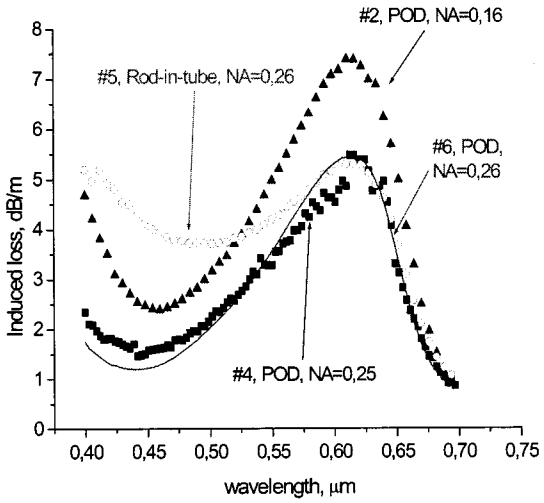

Fig. 1. Induced loss spectra in fibers with KU-1 silica in the core γ irradiated to 1.00 MGy.

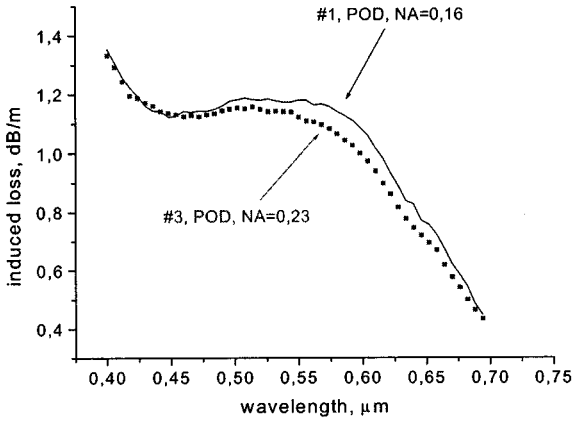

Fig. 2. Induced loss spectra in fibers with KS-4V silica in the core γ irradiated to 1.00 MGy.

on the effect of differential mode attenuation. Near-field light intensity distribution was measured at the fiber output at $\lambda = 630$ nm (near the maximum of the NBOHC absorption band) and at $\lambda = 710$ nm (beyond the band). Then the fiber length was reduced to ~1 m without changing the excitation conditions at the fiber input and the measurements were repeated. The induced absorption at $\lambda = 630$ nm as a function of the radial coordinate in the fiber core was calculated as

$$\alpha(r) = \frac{10}{l} \cdot \log\left(\frac{I_{710,\,\mathrm{long}}(r) \cdot I_{630,\,\mathrm{short}}(r)}{I_{710,\,\mathrm{short}}(r) \cdot I_{630,\,\mathrm{long}}(r)}\right) \qquad (2)$$

where $I_{710}(r)$ and $I_{630}(r)$ with inferior indices "long" and "short" are the light intensities at the two wavelengths measured on "long" and "short" fiber pieces; l is the length difference between the two fiber pieces. Measurements at two wavelengths allowed us to minimize possible influence of the waveguide effects on radial distribution of $\alpha(r)$.

We also measured the induced absorption spectra in different radial positions of transverse preform slices. In this way, the NBOHC radial distribution in fibers and preforms was compared. The measurements of the radial distribution of NBOHC and induced absorption measurements on preform slices were performed two to three weeks after gamma irradiation to 1.00 MGy.

III. RESULTS AND DISCUSSION

Figs. 1 and 2 show the induced loss spectra in the fibers under consideration. We see that the three KU-1 fibers (Fig. 1, fibers #2, 4, and 5) feature different induced absorption. In the two KS-4V fibers (Fig. 2), the difference is not so significant. From comparing the KU-1 fibers fabricated by the POD process (Fig. 1), it may be concluded that the difference in induced absorption is due to different concentrations of NBOHC with absorption bands centered at about 630 and 260 nm. Moreover, the higher fluorine concentration, which is proportional to the numerical aperture (NA), the lower NBOHC concentration. Fibers having approximately the same NA but different core and cladding diameters (fibers #6 and #4) featured the same induced absorption. This fact indirectly confirms the assumption that the formation of the NBOHC precursors occurs at the stage of preform fabrication, not during fiber drawing. The induced loss of fiber #5 fabricated by the rod-in-tube technique is apparently a combination of NBOHC absorption and chlorine-associated absorption monotonically decreasing with wavelength [7]. We believe that chlorine was present in the F-doped cladding synthesized on the substrate tube wall by the low-temperature surface plasma chemical deposition process. Taking into account the chlorine contribution, one may conclude that the NBOHC concentration in fiber #5 is the lowest of the four KU-1 fibers.

It was found that two to three weeks thermal annealing of color centers at room temperature did not distort the induced absorption spectra qualitatively.

The radial distribution of NBOHC in the POD fibers is nonuniform (Fig. 3). For POD fibers with KU-1 silica in the core, the increase of the NBOHC concentration at the core periphery with respect to the core center is greater for the fiber with the smallest fluorine concentration in the cladding. We see

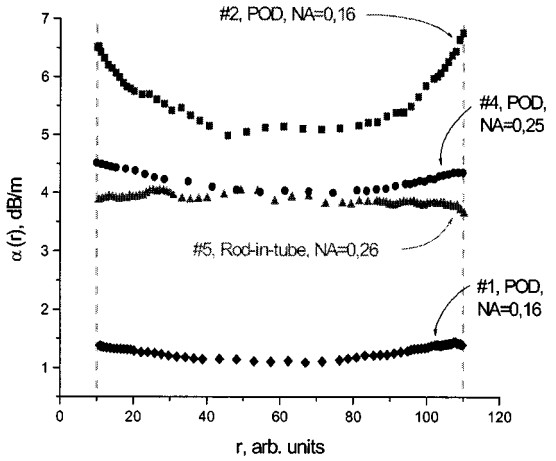

Fig. 3. Radial distribution of NBOHC measured in fibers γ irradiated to 1.00 MGy. The vertical dashed lines show the core boundaries.

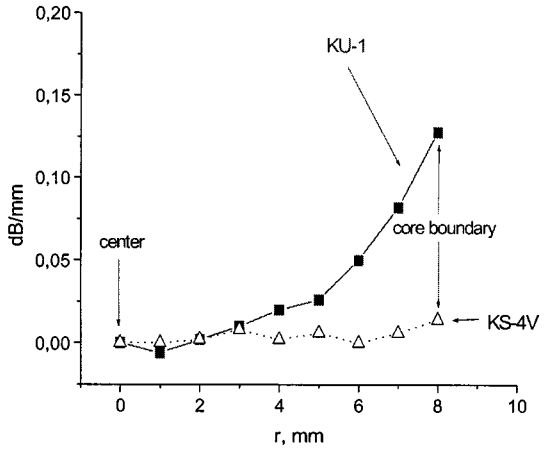

Fig. 4. Radial dependence of radiation-induced absorption at $\lambda = 260$ nm (NBOHC band) in preform slices γ irradiated to 1.00 MGy. For ease of comparison, the values obtained at the preform center were subtracted from the both graphs.

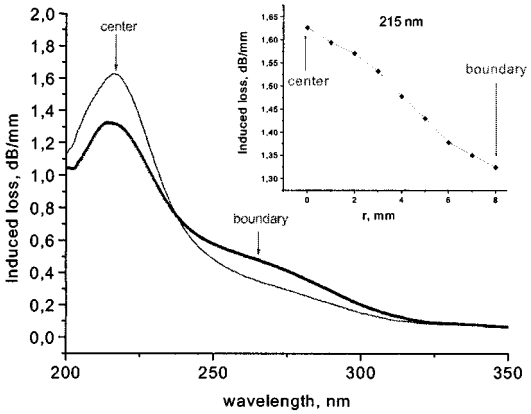

Fig. 5. Induced loss spectra in KU-1 preform slice γ irradiated to 1.00 MGy measured at different radial coordinates. In the inset shown is the induced loss at 215 nm as a function of radial position in the preform slice cross section.

that the radial distribution measurements correlate well with the absorption spectrum measurements (Fig. 1).

A higher NBOHC concentration of the low-aperture KU-1 fiber can be explained in the following way. In the POD-process, the fluorine concentration in the deposited glass is controlled by the process temperature: it increases with decreasing the temperature. Diffusivity and chemical reactivity of fluorine are also lower at a lower temperature; therefore, the formation of NBOHC precursors due to fluorine is less efficient at a lower temperature. It should be noted that this explanation is consistent with the model of NBOHC precursor formation described by (1).

The radial NBOHC distribution of the KU-1 fiber fabricated by the rod-in-tube technique does not feature an increase at the core-cladding interface. This means that the high-temperature fusion of the tube and the rod is not accompanied by significant fluorine diffusion and interaction with hydrogen at the core periphery. From comparing KU-1 fibers fabricated by the two different techniques we may conclude that there exist two mechanisms of NBOHC formation under radiation: one is associated with F-doped silica deposition in the POD process and the other is apparently associated with abstraction of hydrogen from OH groups. The latter mechanism is responsible for uniform radial distribution of NBOHC. Contributions of the both mechanisms to induced absorption at 630 nm are comparable (cf. Fig. 1).

The KS-4V fiber fabricated by the POD process also features an increase of NBOHC concentration at the core periphery (Fig. 3, fiber #1). This increase was approximately the same for the both KS-4V fibers (#1 and #3) and smaller than that in the KU-1 fibers. Because the OH group concentration in KS-4V silica is more than three orders of magnitude less than that in KU-1 silica, the contribution of the mechanism described by (1) to NBOHC formation must be negligibly small.

The radial distribution of NBOHC in an irradiated POD KU-1 preform slice has the same profile as in the corresponding fibers (Fig. 4). It directly indicates that the NBOHC precursors are formed already at the perform fabrication stage. In irradiated POD KS-4V preform slice the radial distribution of NBOHC is more uniform. It should be noted that the loss in the irradiated KS-4V preform slice was an order of magnitude lower than in the KU-1 preform slice. For this reason, a loss increase at the core periphery of the KS-4V perform slice could be overshadowed by the noise background.

Finally, an interesting result was obtained for the radial distribution of the E′-center (the absorption band at 215 nm), which is a complementary defect to NBOHC. In an irradiated KU-1 preform slice (Fig. 5), the E′-center concentration peaks at the core center and slopes down toward the periphery, in contrast to NBOHC. Thus, we may conclude that F-doped cladding influences the formation of NBOHC and E′-center in different ways. Such a behavior of the E′-center radial distribution calls for further study.

IV. Conclusion

The radial distribution of NBOHC in the fiber core was investigated for the first time by the differential mode attenuation technique. This technique is more accurate and informative than the ESR technique previously used for this purpose [3].

F-doped cladding influences the formation of radiation-induced color centers in different ways in “dry” and “wet” silicas. In fibers with high OH silica in the core, there exist at least two mechanisms of NBOHC formation under radiation. One of

them is responsible for uniform NBOHC distribution over the core and is apparently associated with abstraction of hydrogen from OH groups. The second mechanism is responsible for the NBOHC formation at the core periphery. The contributions of the both mechanisms to the induced absorption at 630 nm are comparable. It is important that an NBOHC concentration increase at the core-cladding interface is observed in KU-1 fibers fabricated only by the POD process and is absent from fibers fabricated by the "rod-in-tube" technique. Our experimental results are in agreement with the model of NBOHC precursor formation proposed by Griscom [4]. According to this model, fluorine atoms diffuse into the core region during F-doped silica cladding deposition and make bonds with hydrogen atoms. As a result, peroxy linkages are formed; the NBOHC are precursors. In conformity with this model, we found that the NBOHC precursor concentration at the core periphery increases with increasing the POD-process temperature (that is, it increases with decreasing the fluorine concentration in the cladding). This fact opens up possibilities for optimization of the POD-process regimes. By adjusting the process temperature, it is possible not only to increase the numerical aperture of the fiber, but also to minimize the radiation-induced absorption band at 630 nm.

A different mechanism of radiation-induced NBOHC formation at the core periphery takes place in fibers with low OH/low Cl silica in the core (KS-4V).

In fibers with high OH silica, fiber drawing is found to have no significant influence on radiation-induced NBOHC concentration. It was found that in fibers with high OH silica in the core the formation of radiation-induced E′-center is also affected by the F-doped cladding deposition process, however, the E′-center radial distribution is the reverse of the NBOHC distribution.

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