Super-high-strength metal-coated low-hydroxyl low-chlorine all-silica optical fibers


Abstract.

High-purity KS-4V synthetic silica developed in the Silicate Chemistry Institute of the Russian Academy of Sciences is tested as the core material for radiation hardened optical fibers. Pure-silica-core fluorine-doped-silica-cladding optical fibers with polymer (acrylate) or metal (aluminum) coating are produced as the experimental samples. The light-reflecting fluorine-doped silica cladding is synthesized by the plasma outside deposition process. The aluminum coating technology used provides a very high strength of the fibers, unattainable for polymer coatings, and expands the fiber operating range up to 400 °C. It is established that the metal coating application can result in the annealing of the drawing-induced color centers with an absorption peak at 630 nm. Post-γ-irradiation loss spectra in KS-4V-based fibers measured in 1-2 hours after 2 MGy irradiation at a dose rate of 8.3 Gy/s in the spectral range 350-700 nm are discussed. The 630 nm absorption peak is practically absent from the post-irradiation loss spectra of aluminum-coated KS-4V-based fibers.

I. Introduction

One of the most important current and future applications of radiation-resistant silica optical fibers relates to optical (in particular, visual) diagnostics of the processes occurring in inaccessible, exposed to radiation parts of nuclear and thermonuclear installations [1]. The essential feature required of the fibers to be employed is that they must transmit light over a distance of several tens of meters with minimal loss and minimal spectral distortions in the visible spectral region. It is clear that the radiation-induced loss is the most critical issue. In addition, the requirements on the protection coating become more stringent. In particular, the coating must retain hermeticity, as the latter determines to a large extent the mechanical strength of a fiber.

Radiation-induced absorption in high-purity silica glass is due to optically active point defects that result from the rupture of interatomic bonds. Apart from silicon and oxygen, silica glass may contain admixtures of other atoms, above all hydrogen and chlorine. The presence of chlorine and hydrogen (in the form of OH-groups) stems from the fact that most silica fabrication technologies are based on either vapour-phase plasma pyrolysis or flame hydrolysis of silicon tetrachloride, the latter being the basic raw material. Thus, chlorine becomes a "legal" impurity in the glass (e.g. see [2]). Chlorine-associated color centres are believed to be responsible for a long tail in the induced absorption spectrum, extending from the UV up to near-IR region. Hydroxyl groups are thought to be the precursors of the non-bridging oxygen hole centres (NBOHC), which form an absorption band at 630 nm [3]. Therefore, to fabricate a radiation-resistant fiber, it is necessary to reduce the concentrations of chlorine and hydroxyl simultaneously. In the vapour-phase technologies of glass synthesis, these requirements are contradictory to each other: it is chlorine that is added to the gas mixture as a "drying" component.

The severity of the problem of identifying the chief mechanisms of emergence and decay of radiation-induced color centers is due to the fact that there exist different radiolytic reactions yielding the same color centers. For example, a non-bridging oxygen hole center can result from the rupture of a regular bond (Si-O), disintegration of an OH-group or decay of a peroxy linkage (Si-O-O-Si). The kinetics and temperature dependence are different for the above processes.

The concentration of the radiation-induced NBOHC depends on the initial state of the glass net (i.e. on the concentration of the precursors of these color centers). Obviously, the precursor concentration is dictated by the core glass fabrication technology. Moreover, the preform fabrication and fiber drawing, which are quenching procedures, can also affect the number of the precursors and, consequently, radiation resistance of the fiber. In this connection it is noteworthy that metal coating application is accompanied by heating of the fiber and can produce annealing of the structural defects.

This paper presents tests of all-silica fibers with a core made of low-hydrogen low-chlorine KS-4V silica glass. The tests were performed with the aim to assess the applicability of this glass to radiation resistant image guides and in order to reveal a possible effect of the metal coating application on the optical characteristics of the fibers.

II. Samples and Experiments

In contrast to well-known silica glasses such as Suprasil, Suprasil W, Corning 7440 and their analogues, the KS-4V glass is synthesized without using silicon tetrachloride as the raw material. It is substituted by sol of polysilicon acid with a total concentration of impurities (14 elements) of no more than 10⁻⁴ mass%. The glass synthesis consists in repeated purification and consolidation procedures of the sol. Next, the...
sol is subjected to crystallization in an oxygen atmosphere and to the final purification in atmospheres of active gases at high temperatures. The fabrication process concludes with vacuum fusion followed by compression during half an hour and to the final purification in atmospheres of active gases at 1800°C. The glass sample, about 25 kg in weight, is subjected to crystallization in an oxygen atmosphere.

It should be noted that the first reports devoted to the KS-4V glass appeared nearly 20 years ago [4]. Since then, the technology has been radically improved [5] and is now being brought into Russian industry. At present, the chlorine and OH-group concentrations in the glass are less than 20 ppm and 200 ppb, respectively. As for the most important metal impurities, their concentrations measured in a standard glass sample by means of emission spectroscopy are (in mass%): Al = 2.10^-6; Ca = 4.5.10^-7; Co = 1.5.10^-7; Cr = 1.5.10^-7; Cu = 2.5.10^-7; Fe = 4.10^-7; Mg = 4.5.10^-8; Mn = 4.5.10^-8; Mo = 4.5.10^-7; Ni = 1.5.10^-7; Pb = 1.5.10^-7; Sn = 1.5.10^-7; Ti = 1.10^-6; Zn = 4.5.10^-6; W = 4.5.10^-7.

To produce preforms, rods 20 mm in diameter and 200 mm in length were cut out of the bulk glasses. Fluorine-doped silica was deposited on the surface of the rod by plasmachemical outside deposition (POD). Our technological process differed from the conventional POD in that compact atmospheric-pressure microwave discharge was substituted for radio-frequency discharge [6, 7]. Silicon tetrachloride, freon-113 and oxygen were used as the raw materials.

The final fibers had a core diameter of 100 µm and a light-reflecting cladding diameter of 120 µm. A hermetic aluminum coating was applied onto the fiber during the drawing by the freezing technique [8]. This technique yields silica fibers with a tensile strength of 10 GPa and over [9, 10]. In addition, metal coating application is a thermal treatment which, as will be seen below, leads to annealing of the drawing-induced defects detectable in the visible and UV spectral regions.

Three fiber samples were involved in the investigation. KS-4V-based fibers #1 and #2 were drawn from the same preform with aluminum and acrylate coatings, respectively. Fiber #3, coated with aluminum, had a synthetic silica core material fabricated by flame hydrolysis of silicon tetrachloride, the OH-content in the core being ~ 800 ppm. In the three fibers, optical loss spectra were measured before and after γ-irradiation.

The fibers were irradiated continuously using a 60Co source at a dose rate of 8.3 Gy/s and a temperature of about 40°C to a dose of 2 MGy. The irradiation unit was a cylindrical steel container with an inner diameter of 25 cm and a wall thickness of 4 mm. After lifting up the source from the water pool, the container turned out surrounded with 72 pairs of cobalt rods oriented parallel to the axis of the container. To provide identical irradiation conditions, pieces of the three fibers, up to 20 m in length, were gathered in one bundle, which was bent into a ring, 25 cm in diameter. The ring was fixed on the inner wall of the container in such a way that the ring was strictly coaxial with the container. This arrangement provided uniform irradiation conditions along the fiber lengths.

Optical loss spectra were measured by the widespread cut-back technique [11]. Light from a halogen lamp was mechanically modulated by a chopper, passed through a monochromator and launched into the fiber tested. The fiber length was chosen in a way that the total loss was in the range 1-20 dB. In our case the fiber lengths were in the range 2-500 m depending on the total loss. The output end of the fiber was connected to a Ge-photoreceiver (in measuring loss in the near-IR region) or a photomultiplier tube (in the visible region) by a special adapter. The resultant electric signal was registered by a lock-in nanovoltmeter, to which a reference signal from the chopper was fed. After measuring the spectrum of the light signal I(λ), the fiber was cut, the input fiber end remaining fixed in front of the monochromator slit. Thereafter the light signal spectrum i(λ) was measured on the short fiber piece (~ 60 cm) under the same launching conditions. The optical loss spectra was calculated as

\[ \alpha(\lambda) = (1/L) \cdot \log \left( \frac{I(\lambda)}{i(\lambda)} \right) \]  

where L was the fiber length difference in the two measurements. In measuring loss after irradiation, the input light power of a few nW was launched into the fibers during ~ 10 min, and obviously no tangible photobleaching took place.

### III. Results and Discussion

Fig.1 presents initial loss spectra in the two KS-4V-based fibers that differed from each other only by the coating type. As is seen, a polymer-coated fiber has marked absorption peaks at 630 and 260 nm which degrade the fiber

![Fig. 1. Initial optical loss spectra in two pure-silica-core F-doped-silica-cladding fibres with KS-4V silica glass as the core material. The both fibres were drawn from the same preform and differed in that fibre #1 had an Al coating and fibre #2 had an acrylate coating.](image-url)
Performance in the visible region. The above absorption bands agree well with the computer simulation of the transitions of NBOHC [12]. There are grounds to believe that the major precursor of NBOHC is peroxy linkage Si-O-O-Si [13]. The peroxy linkage concentration may be high in 'dry' silica synthesized in oxidizing conditions [14]. Note also that the calculated formation energy of a cluster containing a Si-O-O-Si defect is close to that of the perfect cluster [12]. Thus, as follows from the polymer-coated fiber spectrum, KS-4V glass may be considered as a glass abundant in oxygen.

Metal coating application drastically improves the loss spectrum in the visible and UV regions (Fig. 1, curve #1): the two NBOHC absorption peaks disappear. Obviously, the NBOHC were annealed, when the fiber was passed through the metallizer (a bath with aluminum melt). It was established previously [15] that practically all the intrinsic defects, including NBOHC, become undetectable by ESR, absorption and luminescence measurements after thermal annealing at 600-650 °C. It is just the temperature range typical of the aluminum coating application.

The metal-coated fiber exhibits a higher grey loss than the polymer-coated fiber. This is due to microbending caused by mechanical stresses. The latter is explained by different thermal expansion coefficients of silica and the metal. The grey loss level depends on the cooling conditions and is strongly reduced, when the fiber is straightened. Cyclic thermal treatment also leads to a reduction of the microbending loss [16]. In any case, an additional loss of several hundredths of decibel per meter is not critical as compared to the radiation-induced loss.

Fig. 2 presents loss spectra measured in the fibers in 1-2 hours after the γ-irradiation described above. We see that the spectrum is rather flat in the visible region for the both KS-4V fibers. The difference in absorption at 630 nm between the Al- and acrylate-coated fibers remains the same as it was before the irradiation. A very pronounced radiation-induced NBOHC absorption peak is demonstrated by fiber #3. Probably, in this case, NBOHC resulted from disintegration of OH-groups. It appears that 'wet' silica is less suitable for fibers intended to operate in radiation environments in the visible region.

The optical loss spectra were also measured in 23 days after the irradiation, the fibers being kept at room temperature. Only a slight decrease of loss, about the same for all the fibers, was observed as compared to the graphs in Fig. 2. So, the residual color centers are rather stable.

Lastly, it was found that the 630 nm absorption peak in aluminum-coated KS-4V-based fiber did not show up in the loss spectrum after fast-electron irradiation either (irradiation to a dose of 10 MGy, dose-rate of 1 kGy/s, electron energy of 8 MeV).

IV. Conclusion

From the standpoint of fabrication technology, KS-4V silica glass ensures low chlorine and hydroxyl contents. This feature is of great importance, if an optical fiber is to be used in radiation environments in the visible spectral region. We have shown that aluminum-coated fibers based on this glass have a flat spectrum in the visible region both before and after γ-irradiation, the post-irradiation induced loss being comparatively low. This property distinguishes KS-4V-based fibers from their analogues that are based on wet silica synthesized by flame hydrolysis of silicon tetrachloride.

An important role in suppressing drawing-induced NBOHC in low-hydroxyl silica glass is played by thermal annealing during the process of metal coating application. Polymer-coated fibers are likely to have a drawing-induced absorption peak at 630 nm. In addition, aluminum-coated fibers have an increased strength and a wide temperature operating range.

The results presented allow us to consider aluminum-coated KS-4V-based fibers as good candidates for applications in optical diagnostics systems intended to work in nuclear and thermonuclear installations.

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Fig. 2. Optical loss spectra measured in different fibers in 1-2 hours after 2 MGy γ-irradiation at a dose rate of 8.3 Gy/s and at 40 °C temperature. Fiber #1: Al-coated KS-4V-based fiber; Fiber #2: acrylate-coated KS-4V-based fiber; Fiber #3: Al-coated fiber with a core material fabricated by flame hydrolysis of silicon tetrachloride (the OH-group content in the core was ≈ 800 ppm). Fibers #1 and #2 were drawn out of the same preform and differed by the coating type only.

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1 While this paper was under consideration for publication, we performed γ-irradiation induced-loss measurements in situ [17]. At doses of ~ 10 MGy a KS-4V-based fiber had pronounced advantage over both a fiber based on 'wet' silica and a fiber based on 'dry' silica with a high chlorine content.
VI. References


