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PHYSICAL PROCESSES IN ELECTRON DEVICEs

Absorption Loss at High Temperatures in Aluminum- and Copper-Coated Optical Fibers

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Abstract—Thermally induced variations in the optical loss of optical fibers with metal (copper and aluminum) coatings are studied. It is demonstrated that an increase in the loss related to the OH groups depends on the medium in which the annealing takes place (an increase in the loss related to the OH groups in argon is greater than the increase in air) and on the dopant (an increase in the loss in the core doped with GeO_2 + P_2O_5 is greater than the increase in GeO_2).

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INTRODUCTION

Recent interest in the optical fibers that can work at temperatures of greater than 500°C, which are significantly higher than the working temperatures of the conventional communication fibers (85°C) has been driven mainly by the development of the fiber temperature sensors. In this regard, optical fibers with metal (aluminum, copper, tin, and gold) coatings were studied in [1].

Metal coatings of optical fibers allow an increase in the working temperatures to the levels that are determined by the melting points of the coatings. In addition, the impermeability of metal coating makes it possible to reach a strength level of 13 GPa, which corresponds to the theoretical strength of the quartz glass. However, the metal coating causes an increase in the microbending optical loss due to the difference between the coefficients of linear thermal expansion of optical fiber and metal coating. This circumstance leads to a uniform increase in the optical loss of multimode optical fibers [2, 3]. Note also that the optical fibers with metal coatings exhibit an increase in the loss related to the hydroxyl (OH) groups at relatively high temperatures [3].

The OH groups are among the technological impurities that cause additional optical loss at wavelengths of 950, 1240, and 1389 nm, which are related to a principal absorption wavelength of 2720 nm [4].

For the modified chemical vapor deposition (MCVD), which is widely used in the production of blank fibers, the reasons for the contamination with the OH groups are as follows: (i) the diffusion of water vapor from atmosphere to the gas medium in the case of insufficient air tightness, (ii) the diffusion of water vapor and molecular hydrogen from the flame of the oxygen–hydrogen burner to the original quartz tube, (iii) the diffusion of the OH groups contained in the quartz tube to the light-reflecting cladding and core, and (iv) the presence of the hydrogen-containing substances in the halides and oxygen that are delivered to the tube.

In spite of the extensive study of an increase in the loss in optical fibers with metal coatings at high temperatures, the data on the direct comparison of such losses in the fibers with different metal coatings are missing. We demonstrate in [5] that the optical fibers with aluminum coatings exhibit a significantly stronger increase in the optical loss related to the OH groups in comparison with the optical fibers with copper coatings. The comparative analysis shows that the reason for such a difference lies in the saturation of the lightguiding core with molecular hydrogen. Note the lack of detailed data on the optical loss of metal-coated optical fibers related to microbending at high temperatures.

1. EXPERIMENTS

To study the effect of the type of the metal coating on the optical loss of the metal-coated fiber, we perform the following experiment. The lightguiding core is formed in the original KUVI quartz tube (produced at the Dzerzhinskii plant in Gus'-Khrustal'nyi) at a relatively high content of the OH groups (200–400 ppm) using the MCVD method [4]. The external diameter of the preform is increased using the jacketing (pressing) with the aid of another KUVI quartz tube that also contains a relatively large amount of the OH groups. The numerical aperture of the preform is NA = 0.2, and the difference of the refractive indices of the core and cladding is Δn = 0.014. Two multimode gradient fibers are drawn from the preform, and various metal coatings are simultaneously deposited. First, the carbon sublayer with a thickness of 20 nm is deposited using the pyrolysis method. Then, the metal (aluminum or copper) coating is deposited with the aid of frosting. The thickness of coating is 25 μm, the inner diameter of the optical fiber is 200 μm, and the outer diameter is 250 μm. Two 240-m-long optical fibers were drawn, rewound from the coil to a hank, and placed in the electric furnace for annealing. We control the opti-

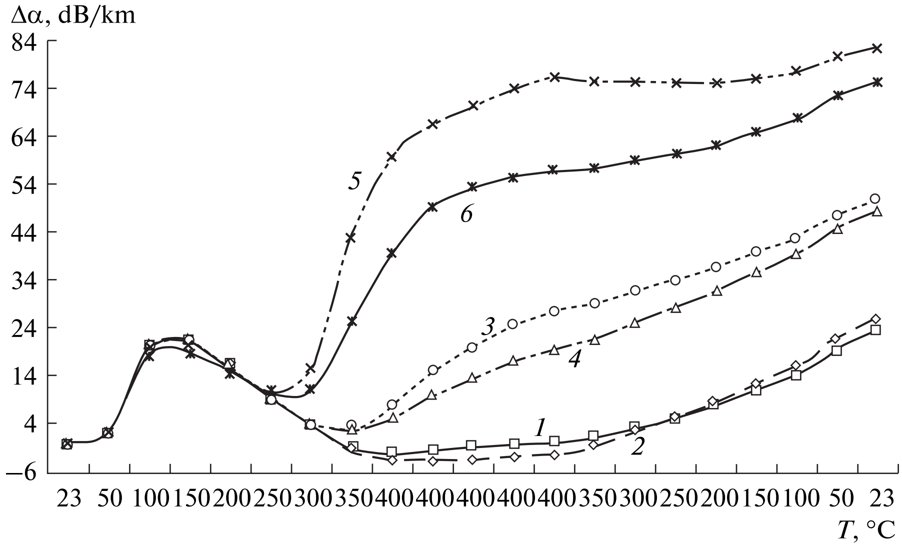

Fig. 1. Increase in the optical loss of the aluminum-coated optical fiber vs. temperature (*X* is the characteristic temperature interval) for the heating–cooling cycle at the wavelengths λ = (*1*) 850, (*2*) 1060, (*3*) 1240, (*4*) 1300, (*5*) 1389, and (*6*) 1550 nm.

cal loss using an YORK S15 spectrum analyzer, which works in the wavelength interval 800–1600 nm. Both fibers are annealed in the temperature range 20–400°C with a heating step of 50°C at a time step of 15 min. The fibers are stored at a temperature of 400°C over 1 h (five time steps). The original loss for the fiber with the copper coating is 2.4 dB/km at a wavelength of 1300 nm. The original loss for the fiber with the aluminum coating is 3.5 dB/km at a wavelength of 1300 nm.

In the next experiment, we study the optical loss in the short-wavelength range and employ the aluminum-coated optical fiber whose core is doped with GeO_2. The optical loss is measured using an Anritsu MW98A reflectometer at a wavelength of 850 nm.

At the next stage, we study the effect of dopant (GeO_2 + P_2O_5 or GeO_2) and the annealing medium (argon) on the optical loss. For this purpose, we fabricate the third fiber and deposit aluminum using the above procedure. The preform is fabricated using the MCVD method from a Suprasil F-300 glass tube in which the concentration of the OH groups is less than 1 ppm [4]. We use the electric furnace instead of the oxygen–hydrogen burner to reduce the amount of the OH groups and hydrogen provided by the burner [6]. The core of the optical fiber is doped with GeO_2 + P_2O_5. The diameter of the optical fiber is 125 μm. The fiber is annealed at a high temperature using the above procedure.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1 and 2 demonstrate relative variations in the spectral loss of optical fibers versus temperature for the samples with aluminum and copper coatings, respectively.

Figure 1 shows that the aluminum-coated optical fiber annealed at a temperature of 300°C exhibits only microbending loss. We prove this statement by the fact that variations in loss in the temperature interval 0–250°C are wavelength independent, which is typical of microbending loss [2, 3]. In the temperature interval 150–250°C (characteristic interval in Fig. 1), we observe a decrease in the optical loss. Such an effect was reported in [3] but a comprehensive interpretation is missing. In accordance with [7], this temperature interval corresponds to the aluminum recrystallization. In our opinion, additional study is needed.

At a temperature of greater than 300°C, the optical loss related to the OH groups (λ = 1389 and 1240 nm) increases to 75 db/km (at 1389 nm). Note that the wing of the of the absorption band peaked at 1389 nm causes an increase in the loss at wavelengths of 1240, 1300, and 1550 nm. To characterize the microbending loss, we use the result obtained at a wavelength of 1060 nm, where the effect of the loss related to the OH groups is insignificant. At the end of the procedure, the sample is cooled to 20°C and the loss related to the microbending increases.

Upon the annealing of the copper-coated optical fiber (Fig. 2), a variation in loss predominantly results from the microbending loss, which is wavelength independent. In addition, in the temperature interval 200–250°C, we observe the minimum microbending loss (characteristic interval in Fig. 2), which corresponds to the copper recrystallization point [7]. Additional study is also needed in this temperature interval.

When the temperature exceeds 300°C, the loss increases owing to the OH groups (1389 nm). At a temperature of 400°C, the loss reaches a level of 18 dB/km with allowance for the microbending loss. We can estimate the microbending loss from variations in the optical loss at wavelengths of 1060, 1300, and 1550 nm.

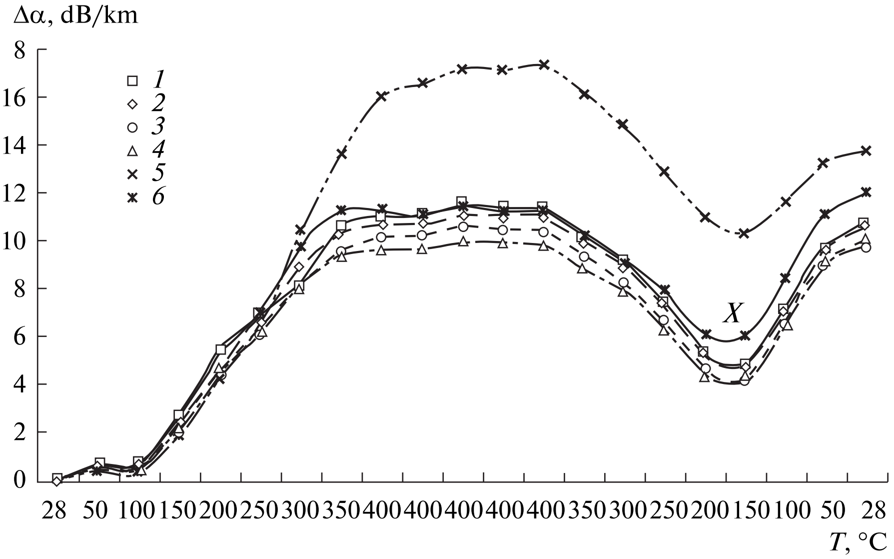

Fig. 2. Variations in the optical loss of the copper-coated optical fiber vs. temperature (*X* is the characteristic temperature interval) for the heating–cooling cycle at the wavelengths λ = (*1*) 850, (*2*) 1060, (*3*) 1240, (*4*) 1300, (*5*) 1389, and (6) 1550 nm.

The comparison of Figs. 1 and 2 shows that, at a wavelength of 1389 nm, an increase in the loss of the aluminum-coated optical fiber related to the OH impurities (more than 70 dB/km) is greater than an increase for the copper-coated optical fiber (about 6 dB/km).

To characterize the behavior of the aluminum-coated optical fiber, we perform the comparative analysis. It is known from [8] that the ratio of the levels of loss at wavelengths of 1389 and 1240 nm due to the absorption of the OH groups is 23 : 1. The absorption band related to the presence of molecular hydrogen is also peaked at λ = 1240 nm. We recalculate the experimental data using the formula

$$\Delta\alpha = \alpha_{1240} - \frac{\alpha_{1389}}{23} \quad (1)$$

where $\Delta\alpha$ is the difference in dB/km and α_{1240} and α_{1389} are optical losses at wavelengths of 1240 and 1389 nm, respectively. For the absorption related only to the OH groups, we obtain $\Delta\alpha \sim 0$. With allowance for hydrogen, we find $\Delta\alpha > 0$. Figure 3 shows the results of the calculations. It is seen, that $\Delta\alpha \sim 0$ for the copper-coated optical fiber and $\Delta\alpha$ increases for the aluminum-coated fiber when the temperature is greater than 350°C. In our opinion, this result proves an increase in the content of molecular hydrogen in the quartz glass.

We can estimate the content of molecular hydrogen using the results from [9–11] on the dependence of the additional loss in the optical fiber saturated with hydrogen on the external hydrogen pressure and the heating temperature of the fiber:

$$\Delta\alpha(H_2) = A(\lambda) \times \exp\left(\frac{8670\,\mathrm{J/mole}}{R * T}\right), \quad (2)$$

Here, $\Delta\alpha(H_2)$ is the additional loss related to molecular hydrogen and $A(\lambda)$ is the spectral dependence of such loss. At the wavelength λ = 1240 nm, the coefficient is $A(1240)$ = 0.27 dB/(km atm). Thus, we obtain $\Delta\alpha$ = 1.27 dB/km at a temperature of 400°C. In the case under study, the additional loss is about 19 dB/km (Fig. 3). Hence, the equivalent external pressure must be about 15 atm and, in accordance with [9], the concentration of molecular hydrogen is about 7.5×10^{18} mole/cm^3 (about 2800 ppm). This result is significantly greater than the bulk concentration of the OH groups in the original tube (200–400 ppm). To reproduce the effect, we perform the annealing for 20 samples (ten samples with copper coating and ten samples with aluminum coating).

The results of the second experiment yield an increase in the optical loss of the aluminum-coated optical fiber in the short-wavelength spectral range and the absence of such an increase for the copper-coated fiber. We assume that such an effect can be due to an increase in the loss related to the Rayleigh scattering. For the verification, we perform an additional experiment in which one part of the aluminum-coated fiber is stored at a temperature of 20°C and another part is heated to 400°C. In such an experiment, a characteristic step on the curve indicates that the loss related to the Rayleigh scattering increases at the interface of the two parts. However, the characteristic step is absent (Fig. 4). Thus, we conclude that the short-wavelength loss is not related to an increase in the Rayleigh scattering and is caused by the saturation of the lightguiding core with molecular hydrogen [10] (and the corresponding short-wavelength absorption of molecular hydrogen).

In our opinion, the reason for such a behavior of the aluminum-coated optical fiber is as follows. It is known

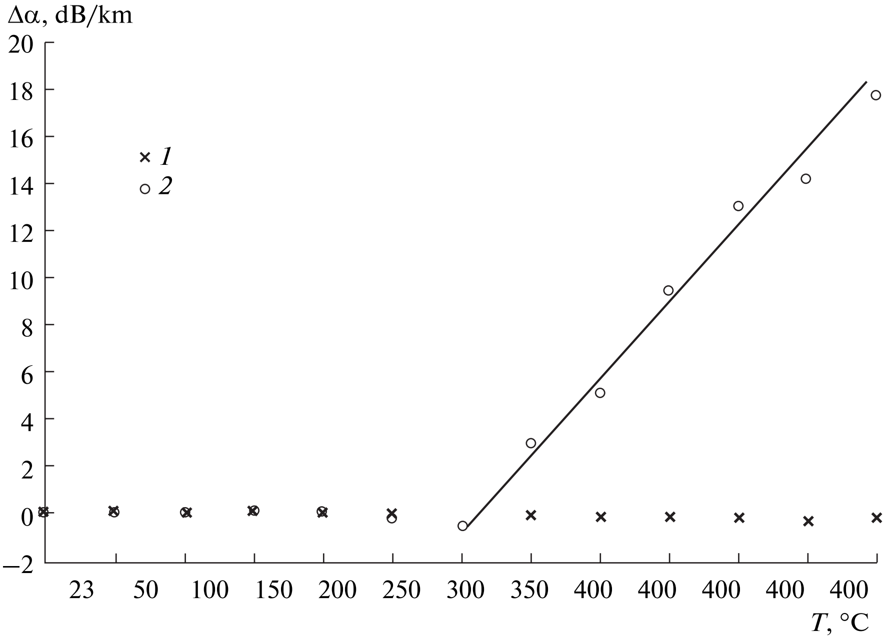

Fig. 3. Plots of the ratio of the optical losses $\Delta\alpha = \alpha_{1240} - (\alpha_{1389}/23)$ for the optical fibers with (*1*) copper and (*2*) aluminum coatings.

that the interaction of water vapor with aluminum coating in accordance with the reaction

$$3Al + 3H_2O \rightarrow Al_2O_3 + 3H_2. \quad (3)$$

causes the generation of molecular hydrogen due to the fact that aluminum is on the left-hand side relative to hydrogen in the electrochemical series, so that aluminum can be involved in the splitting of pairs with the liberation of molecular hydrogen [12].

Note also the growth of the Al_2O_3 oxide film. Molecular hydrogen penetrates through the carbon film, which does not serve as a barrier at relatively high temperatures [11]. Hydrogen reaches the core of the optical fiber, causes an increase in the loss at a wavelength of 1240 nm, and interacts with atomic defects and impurities in the quartz-glass lattice. Molecular hydrogen causes the formation of the OH groups and, hence, additional optical loss at the wavelength $\lambda = 1389$ nm [2, 13]:

$$\equiv Si{-}O{-}O{-}Si\equiv + H_2 \longrightarrow 2\equiv Si{-}OH. \quad (4)$$

The interaction of molecular hydrogen with the GeO_2 defect centers leads to the formation of the Ge–OH bonds, which exhibit an absorption band peaked at the wavelength $\lambda = 1410$ nm [2]:

$$\equiv Si{-}O{-}O{-}Ge\equiv + H_2 \longrightarrow \equiv Si{-}OH + H{-}O{-}Ge\equiv. (5)$$

Figure 5 shows the corresponding results. Figure 6 demonstrates two absorption bands peaked at 1389 and 1410 nm for the optical fiber with the aluminum coating.

Consider the experimental data on the effect of the doping metal in the core of the aluminum-coated optical fiber on the optical loss upon the high-temperature annealing (Fig. 7). The aluminum-coated optical fiber doped with GeO_2 + P_2O_5 exhibits a more significant increase in the optical loss related to the OH groups (950, 1240, and 1390 nm) (curve *1* in Fig. 7) in comparison with the optical fiber doped with GeO_2 (curve *2* in Fig. 7). For comparison, curve *3* in Fig. 7 shows the spectrum of optical loss of the original fiber. The increase in the loss is related to the fact that the presence of GeO_2 + P_2O_5 results in an increase in the rate of the reaction of hydro-

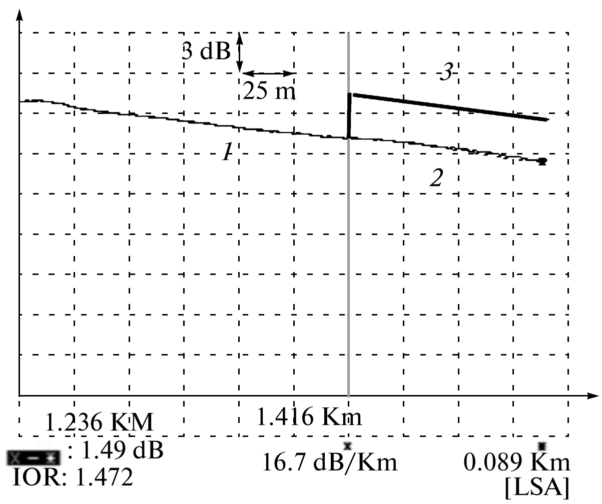

Fig. 4. The reflectograms of the optical loss of the aluminum-coated optical fiber at a wavelength of 850 nm measured at (*1*) room temperature (20°C) and (*2*) 400°C and (*3*) the theoretical curve corresponding to an increase in the Rayleigh scattering.

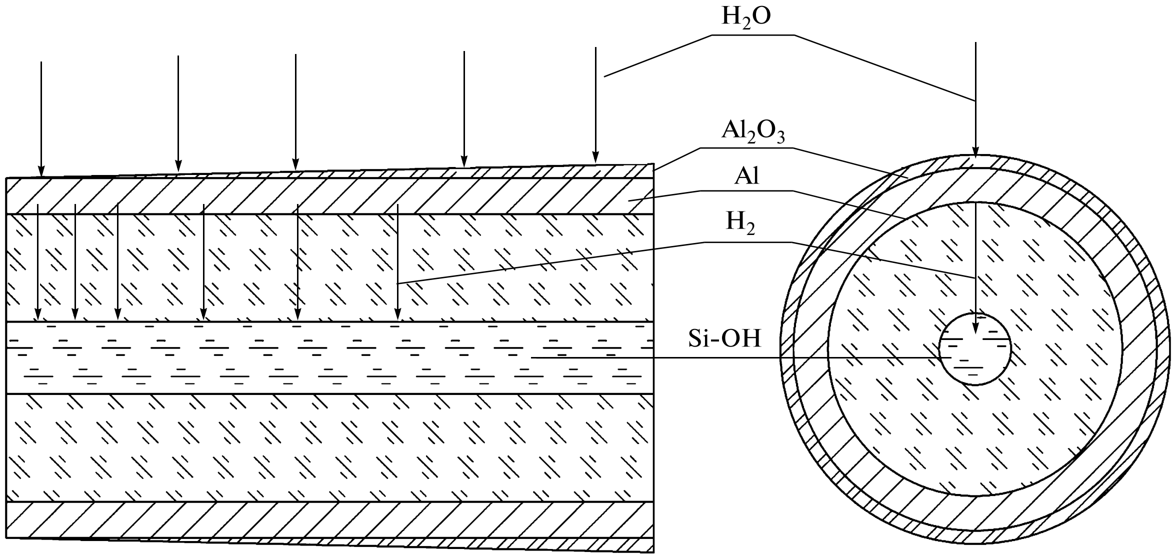

Fig. 5. The splitting of water vapor with the liberation of molecular hydrogen, which saturates the fiber core (the effect of the thickness of the Al_2O_3 layer on the penetration of water vapor and, hence, the resulting amounts of hydrogen and OH groups).

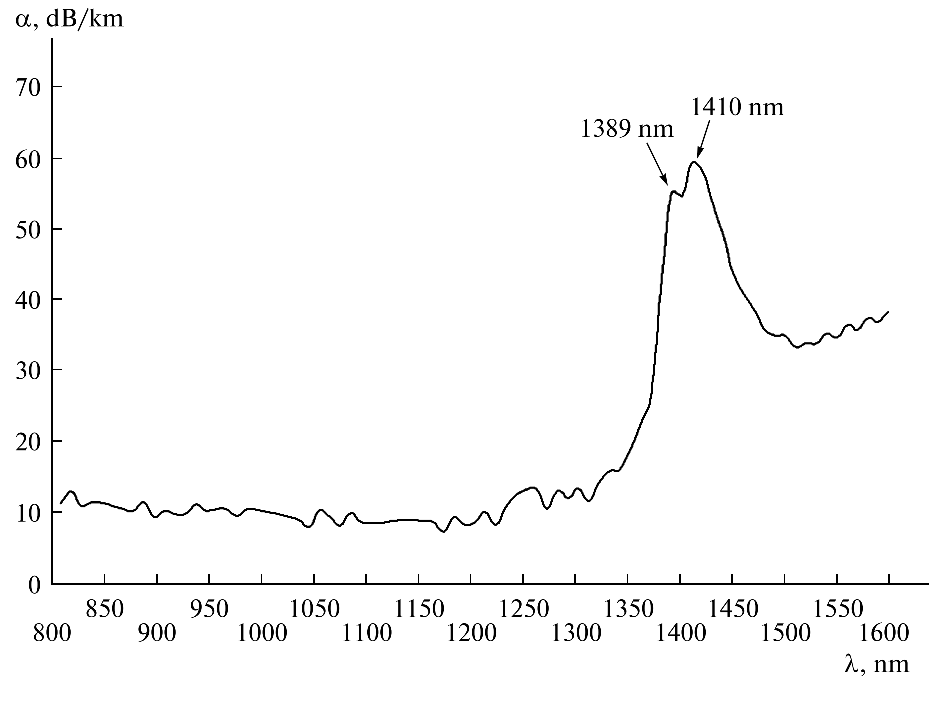

Fig. 6. Optical loss in the aluminum-coated optical fiber at a temperature of 350°C.

gen with quartz glass [2], since the doping with GeO_2 + P_2O_5 provides a stronger damage of the quartz-glass lattice [11]. To characterize the microbending loss, we can use the optical loss at a wavelength of 1060 nm.

The further study is aimed at the analysis of the effect of the annealing medium on the optical loss. We perform the additional annealing of the aluminum-coated optical fiber whose core is doped with GeO_2 + P_2O_5 in the argon medium (Fig. 8).

It is seen that, for the aluminum coated optical fiber, the increase in the optical loss related to the OH groups (950, 1240, and 1390 nm) in the argon medium (curve *1*) is significantly greater than the increase in air (curve *2*). For comparison, curve *3* in Fig. 8 shows the initial (prior to annealing) loss of the aluminum-coated optical fiber

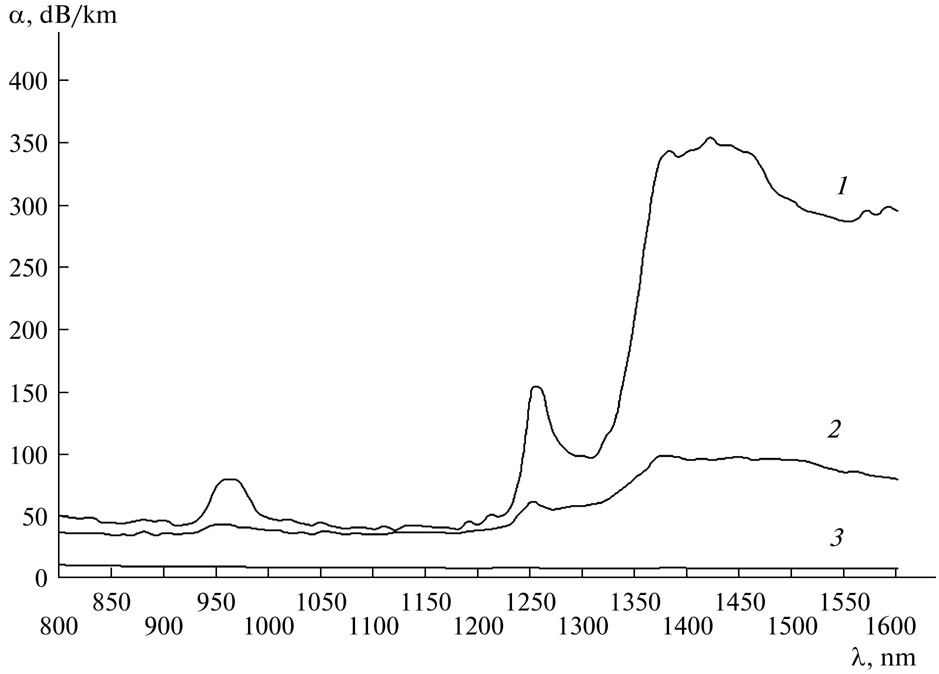

Fig. 7. Post-annealing optical loss of the aluminum-coated optical fibers whose cores are doped with (*1*) $GeO_2 + P_2O_5$ (125 μm) and (*2*) GeO_2 (200 μm) and (*3*) the initial optical loss of the aluminum-coated optical fiber whose core is doped with $GeO_2 + P_2O_5$.

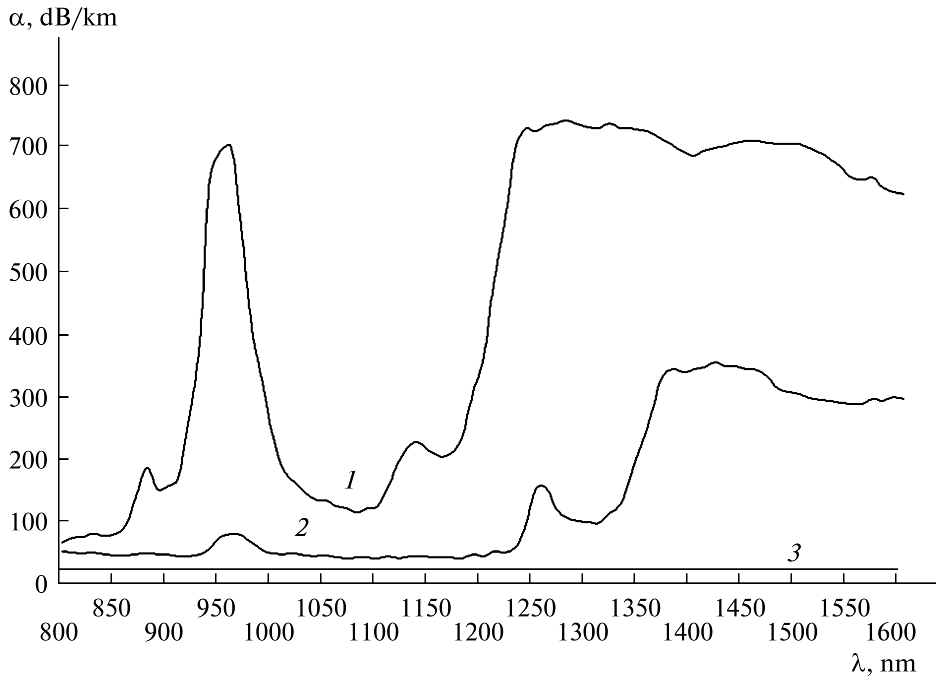

Fig. 8. The optical loss of the aluminum-coated optical fiber doped with $GeO_2 + P_2O_5$ after annealing in (*1*) argon and (*2*) air and (*3*) the initial optical loss.

whose core is doped with $GeO_2 + P_2O_5$. In our opinion, the reason for the experimental results obtained for the annealing in argon is as follows. The access of water vapor to aluminum is terminated when the thickness of the Al_2O_3 film reaches the impermeability level [15]. In an inert medium, the growth of the Al_2O_3 film is terminated due to the absence of oxygen. Water vapor, whose content in argon can be as high as 0.009% [16], interacts with the aluminum coating. This interaction causes the additional formation of molecular hydrogen.

In our opinion, the presence of the Al_2O_3 film results in the additional sealing of the aluminum-coated optical fiber and, hence, a decrease in the loss related to the OH groups.

A chain of chemical reactions impedes the quantitative estimation of an increase in the optical loss related to the OH groups versus the concentration of water vapor in the annealing medium (argon).

CONCLUSIONS

The experimental results indicate variations in the optical loss of the copper-coated optical fibers in the temperature interval 20–400°C due to the microbending of the coating. An increase in the radiation loss related to the OH groups at a temperature of 250°C is insignificant.

Variations of the optical loss of the aluminum-coated optical fibers in the temperature interval 20–250°C are only due to the microbending of the coating. At temperatures of greater than 250°C, the fiber core is saturated with molecular hydrogen. This effect leads to the interaction with the core and an irreversible increase in the optical loss related to the OH groups. The efficiency of such interaction is affected by the dopant: the efficiency for $GeO_2 + P_2O_5$ is higher than the efficiency for GeO_2. In addition, the interaction depends on the annealing medium, so that the increase in the loss in the inert medium (argon) is greater than the increase in air.

It is expedient to employ copper and other metals lying on the right-hand side relative to hydrogen in the electrochemical series for the fabrication of coatings for high-temperature optical fibers.

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