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Measurements of OH Diffusion in Optical-Fiber Cores

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A color-center laser was used at 0.95 μm to determine the activation energy for OH diffusion in the cores of current multimode fibers. The temperature range of 600 to 800°C was investigated and the activation energy determined to be 19,700 ± 1600 cal/mole in agreement with previous values reported for bulk silica. Based on this value, some 23,000 years would be necessary at 90°C to produce a 3-percent change in the 0.95-μm OH absorption at the core center. Apparently, OH diffusion over a service life of optical fibers should not be a problem in presently envisioned lightwave applications.

I. INTRODUCTION

The diffusion of water (H_2O) into optical fiber cores can affect both fiber loss[1] and bandwidth.[2] Water contamination of the fiber core could occur during three different periods—preform manufacture, fiber drawing, and long-term environmental exposure. The first two have previously been studied;[3-5] however, environmental data on fused silica require longer exposure times[6] because of slow diffusion rates. It would be ideal to have an activation energy which would allow the calculation of concentration changes as a function of temperature. Thus, the effect of water diffusion in a fiber could be calculated based on the expected operating conditions for that fiber. Reported here is the first measurement of the activation energy for OH diffusion in a fiber core.

In the transmission wavelength region of current interest, 0.8 to 1.5 μm, two major OH absorption bands appear. These bands are at 1.38 and 0.95 μm and are, respectively, the first and second overtone bands of the fundamental stretching vibration at 2.7 μm. Two candidates for system wavelengths are 0.87 and 1.3 μm—very close to the OH absorption bands. A 10-ppm increase of OH would increase the loss by about 12 dB/km at 0.95 μm, 1.0 dB/km at 0.90 μm,[7] and 7 dB/km at 1.3 μm.[8] Thus, knowledge of the OH diffusion rate in optical fiber waveguides

becomes increasingly important as attention shifts to longer wavelengths.

II. THEORY

Water probably does not exist as a molecule of H_2O in glass. On attacking a silica surface, water undergoes the following reaction:

$$H_2O + (\equiv Si—O—Si\equiv)_{glass} \rightleftarrows 2(\equiv Si—OH)_{glass}.$$

This process is interpreted as the conversion of one molecule of water into two OH groups by the addition to an Si—O—Si bridge to form two (Si—OH) groups. This mechanism is supported by data indicating the solubility of water in silica (concentration) to be proportional to the square root of the vapor pressure.[7]

Diffusion is then viewed as the reformation of the Si—O—Si bridge and the transfer of the OH group to an adjacent bridge.

$$(\equiv Si_A—OH) + (\equiv Si_B—O—Si_B\equiv) \rightleftarrows (\equiv Si_B—O—Si_A\equiv) + (\equiv Si_B—OH).$$

This process is unlike ordinary diffusion where preferred sites are involved, and it is probably incorrect to refer to OH in glass as OH ions or OH radicals since charged ions or free radicals are unlikely to exist in the above process. The measured loss attributed to OH is simply that arising from the O—H stretching vibration of the OH functional group.

The diffusion of a line source located at the origin in cylindrical coordinates is given by:

$$C(r, t) = \frac{\alpha}{4\pi Dt} e^{-r^2/4Dt} \tag{1}$$

(see Appendix A for derivation),[9] where

α = concentration per unit length of the line source
C = concentration (mole fraction) at radius r and time t
D = diffusion coefficient
r = distance from the line source.

If r is in cm and t in seconds, then D has dimensions of cm^2/s. The diffusion coefficient is a function of temperature and is given by the following equation:

$$D = D_0 \exp(-E/RT), \tag{2}$$

where

D_0 = a constant
E = the activation energy
R = gas constant in cal $mole^{-1}$ $kelvin^{-1}$
T = temperature in kelvin.

Equations (1) and (2) are used to obtain the activation energy E.

Two problems of interest are the diffusion of water from the cladding into the core of the fiber and from water surrounding the fiber into the cladding and the core. Since light does not propagate with low loss in the cladding, optical loss measurements in the cladding are difficult. Measurement of the diffusion of water out of the core region is easier since optical loss measurements in the fiber core are used for fiber diagnostics. Because of microscopic reversibility, the diffusion coefficient inside the core is the same for diffusion into or out of the core. This approach avoids surface recombination effects observed when H_2O diffuses onto and off a silica substrate.[10] The question we address is, Given that water is already inside the fiber, what is its diffusion rate into or out of the fiber core?

III. EXPERIMENTAL

The experimental setup illustrated in Fig. 1 incorporates a tunable, single-mode, color-center laser.[11] This laser is pumped by a continuous wave krypton-ion laser and is tuned to the OH absorption peak at 0.95 μm. The reel of fiber chosen for test was 1.9 km long and had abnormally high loss at 0.95 μm because of OH absorption. Fifty meters were reeled off and the OH spatial profile determined at the end of that 50-meter section by measuring the absorption component of the loss calorimetrically, while traversing the color-center laser beam across the fiber core. About 100 meters more were reeled off and the OH spatial profile measured again at the end of the 100-meter section. These two spatial profiles agree with each other within the

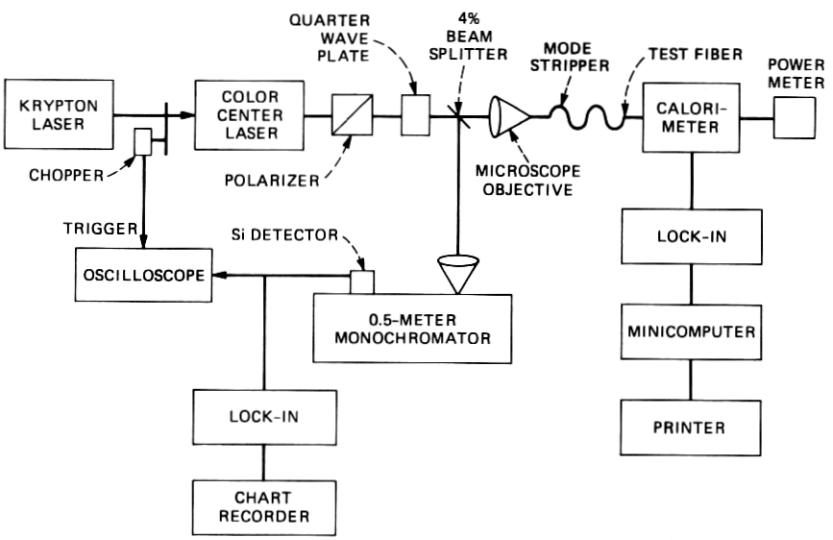

Fig. 1—Experimental setup for OH diffusion measurement.

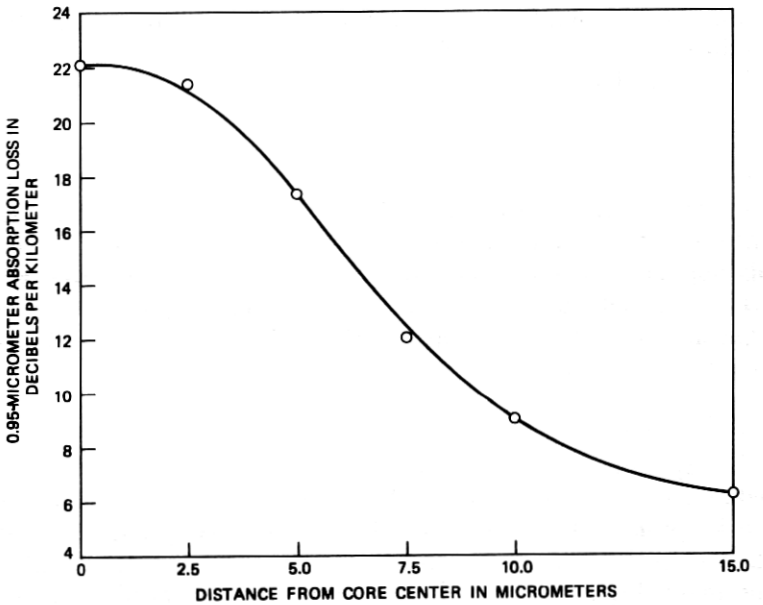

Fig. 2—The 0.95-μm loss because of OH in the control fiber.

error of the calorimeter measurement (±0.2 dB/km). This 100-meter section was used as the fiber for the diffusion experiments. Finally, the spatial profile was measured at the beginning of the 100-meter reel. This represents the control fiber and is illustrated in Fig. 2. It shows the OH absorption profile to be peaked at the fiber core center and decreasing towards the core-cladding boundary. These precautions ensured that the OH distribution was uniform over the length of the test fiber and ensured the same initial conditions for each test. This fiber had a germania-phosphosilicate core, with $\Delta = 1.3$ percent, and 1–2 percent phosphorus added for fining; its core was about 40 μm in diameter.

A number of two-meter samples were cut from the 100-meter fiber length. The coating was stripped from the samples, and each sample was heated in an oven for one day at a fixed temperature. Six temperatures were chosen to give measurable diffusion rates: 600, 655, 680, 700, 750, and 800°C. The oven temperature was monitored with a Chrome-alumel thermocouple and held constant within ±2°C. After removal from the oven, each sample was placed in the calorimeter and the OH spatial profile measured. The spatial resolution is limited by the focused spot size to about 5 μm.

Since this fiber has a core diameter of only 40 μm, the scattering loss due to the core-cladding boundary increased dramatically in the region near 20 μm. In Fig. 3 the spatial profiles for four of the temperatures

and for the unexposed control sample show how the absorption profile changes with increasing temperature. In the region of 15 μm, a rising loss versus radius may indicate in-diffusion from the cladding for the 800°C sample; however, this indication is not evident in the lower temperature samples. The rise is negligible at $r = 10$ μm, even for the 800°C sample; therefore, we neglected in-diffusion effects from the cladding in analyzing the loss measured at $r = 0$.

IV. RESULTS AND DISCUSSION

In evaluating the results, one must consider the following effects:

(*i*) The fiber as produced already contains diffused water as a result of preform manufacture and fiber drawing. Unfortunately, we do not know how long the preform or fiber was exposed to each temperature in this process. As a result, the OH in the starting fiber already has a Gaussian distribution rather than the line source distribution that would simplify the analysis.

(*ii*) In the measurement method used, the laser was focused to a spot on the fiber face and the loss at each radial position determined calorimetrically. Determining the concentration of OH by evaluating the loss at radius r in the fiber core is not straightforward since the exciting beam, localized at $r = r_1$, excites modes which cover a large range of r. To make the analysis tractable, only losses measured for

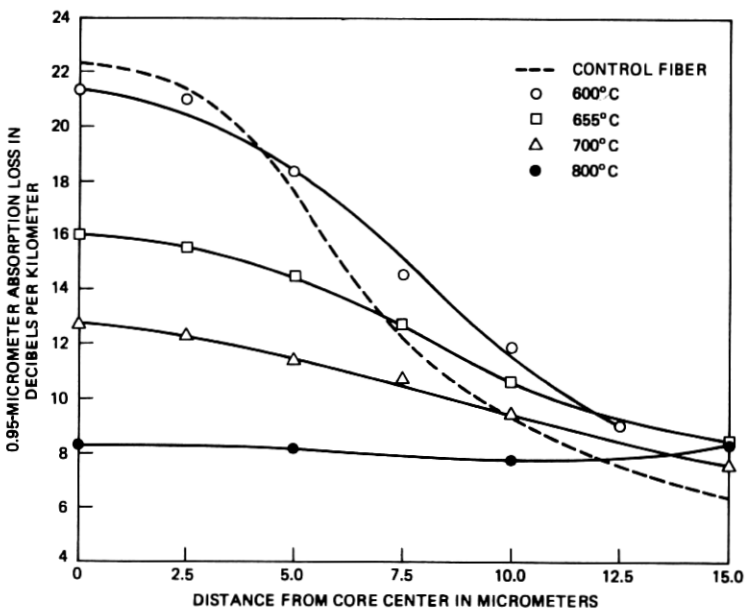

Fig. 3—Diffusion profiles for four of the exposure temperatures.

the $r = 0$ excitation condition will be used in deriving the activation energy.

Despite these complications, Appendix B shows that γ_{in} and $\gamma_{out}(T)$, the 0.95-μm absorption losses at $r = 0$ before and after exposing the fiber for one day at temperature T, are related by:

$$\ln[(\gamma_{in}/\gamma_{out}(T)) - 1] = \text{constant} - \frac{E}{RT}. \tag{3}$$

Figure 3 indicates that the $r = 0$ loss measured for the control fiber and the 600°C exposure are very nearly the same. Because of the uncertainty associated with each measurement, and their similar magnitude, the expression $\ln[(\gamma_{in}/\gamma_{out}(T) - 1]$ has a large uncertainty associated with it. Thus, the 600°C temperature was omitted from the data analysis.

Equation (3), plotted for the five remaining exposure temperatures in Fig. 4, should result in a straight line of slope $(-E/R)$. The value of the activation energy determined from the slope is 19,700 ± 1600 cal/mole or 0.854 ± 0.07 electron volts. While an uncertainty exists in the activation energy from thermodynamic considerations alone, the overall uncertainty in the measured value is the uncertainty in the slope.

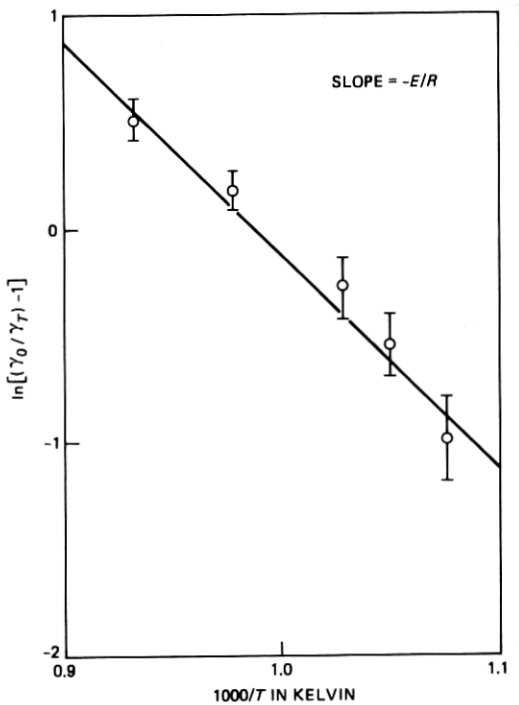

Fig. 4—Plot of eq. 3. The slope gives the activation energy.

It is this calculated uncertainty in the slope which is ±1600 cal/mole. This value for the activation energy compares quite favorably with the values 17,300 ± 2000 cal/mole and 18,300 ± 500 cal/mole determined between 600 and 1200°C in bulk silica by Moulson and Roberts.[10] They determined two different diffusion coefficients—one for absorbing of the OH centers,

$$D = (1.0 \pm 0.2) \times 10^{-6} \exp(-18{,}300 \pm 500)/RT \text{ cm}^2 \text{ s}^{-1}$$

and one for removal,

$$D = (2.7 \pm 1.0) \times 10^{-7} \exp(-17{,}300 \pm 2000)/RT \text{ cm}^2 \text{ s}^{-1}.$$

They point out, however, that the activation energy is the same within their experimental error and our value of 19,700 ± 1600 cal/mole overlaps theirs once the experimental uncertainty is taken into account.

Moulson and Roberts attribute the difference in the pre-exponential factor $(1.0 \pm 0.2) \times 10^{-6}$ for absorbing versus $(2.7 \pm 1.0) \times 10^{-7}$ for removal, to the process

$$H_2O + \text{Si—O—Si} \rightleftarrows 2(\text{Si—OH})$$

being slightly exothermic by 6 kilocalories. Also, the recombination of hydroxyl groups at the glass surface may introduce an appreciable nonzero concentration of water just below the glass surface—an assumption made for their calculations, but unnecessary in this study.

From eq. (18), we can relate the different diffusion times for various temperatures. Suppose one fiber is exposed for time t at a temperature where the diffusion coefficient is D, and a second fiber for time t' at D'. If the fibers are initially identical ($\gamma_{in} = \gamma'_{in}$ in Appendix B) and the exposures are equivalent [$\gamma_{out}(T) = \gamma_{out}(T')$], then eq. (18) gives $Dt = D't'$. From Fig. 3, apparently a temperature of about 600°C is required to produce diffusion in one day that results in a 3-percent change in the absorption at 0.95 μm. Using our measured value of E, the time required for this to occur at the highest acceptable exposure temperature in the field ($T' = 90$°C) is t', where

$$\frac{D_{600°C}}{D_{90°C}} = \frac{\exp(-E/RT)}{\exp(-E/RT')} = \frac{t'}{1 \text{ day}} = \frac{1.169 \times 10^{-5}}{1.375 \times 10^{-12}}$$

$$t' = 23{,}000 \text{ years}$$

which greatly exceeds the projected 40-year service life for an installed cable. Since the OH absorption loss at 1.3 μm is of the same order of magnitude as at 0.95 μm, this confirms that OH diffusion is not likely to be a problem for presently envisioned applications.[6]

We have made many assumptions in analyzing these data. We have assumed the diffusion coefficient to be independent of concentration,

and over the small concentration changes observed here, this is probably a valid assumption. We have assumed the activation energy to be independent of temperature. In addition, the equation used to model the data does not account for changes in viscosity or molal volume of the glass. Work is progressing to extend these measurements to lower temperatures to check for a temperature dependence of the activation energy. At a temperature of 325°C, this extension will require 6.2 months of exposure in the oven if the present calculations are correct.

Data on viscosities and molal volumes for ternary glasses like GeO_2—P_2O_5—SiO_2 are sparse or nonexistent. Moreover, little is known about the prediction of liquid diffusivities, to say nothing of diffusivities of very high viscosity materials such as glass. Refer to Refs. 12 and 13 for excellent texts on the subject of liquid and high-density transport phenomena.

V. SUMMARY

The OH profile and activation energy for diffusion have been measured in a fiber core using a color-center laser and calorimeter. The 600 to 800°C results presented here agree with the bulk silica results of Moulson and Roberts. Thus, the compositional gradients, internal stresses and geometry peculiar to the fiber apparently have no significant effect on the activation energy. This procedure is a novel approach to measuring diffusion and adds confidence that long-term OH diffusion will be no problem in currently proposed lightwave systems. Plans are being made to extend these measurements to even lower temperatures.

VI. ACKNOWLEDGMENTS

I would like to thank H. T. Lamar for conducting some of the loss programs, and I appreciate the many helpful discussions with W. B. Gardner.

APPENDIX A

Derivation of the Diffusion Equation

In 1855, Adolph Fick empirically proposed that diffusion in one dimension was described by:

$$J_x = -D\frac{\partial C}{\partial x}, \tag{4}$$

where

J_x = the flux in the x direction per unit time
C = concentration of the diffusing species
D = diffusion coefficient.

Consider a volume element of material between x and $x + dx$ having

unit cross-sectional area as shown in Fig. 5. The flux into the element minus the flux out equals the rate of accumulation of a species within the element.

$$J_x - J_{x+dx} = \frac{\partial \bar{C}}{\partial t}\, dx, \tag{5}$$

where

$\bar{C}$ = Average concentration in the element
$\bar{C}dx$ = Total amount in the element at time t.

Expand J_{x+dx} about x in a Taylor series

$$J_{x+dx} = J_x + \frac{\partial J_x}{\partial x}\, dx + \frac{\partial^2 J_x}{\partial x^2}\, \frac{(dx)^2}{2} + \cdots. \tag{6}$$

In the limit as $dx \to 0$, eq. (5) has the form

$$-\frac{\partial J_x}{\partial x} = \frac{\partial C}{\partial t}. \tag{7}$$

This is simply a treatment of the conservation of matter. Combining eqs. (7) with (4) yields

$$\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) = \frac{\partial C}{\partial t}. \tag{8}$$

If D does not vary with x, we have

$$D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}. \tag{9}$$

Also, if D does not vary with t, this is a linear partial differential equation known as Fick's Second Equation.

In the case of a fiber with cylindrical geometry, (9) becomes,

$$D\,\tilde{\nabla}^2\, C = \frac{\partial C}{\partial t}. \tag{10}$$

This has the solution

$$C(r, t) = \frac{\alpha}{4\pi Dt} \exp[-(r^2/4Dt)] \qquad r > 0, t > 0, \tag{11}$$

where α is a constant relating to the initial concentration.

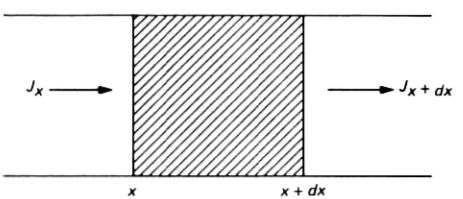

Fig. 5—Diffusion through a unit volume element.

APPENDIX B

Derivation of the Activation Energy

The distribution of power in a fiber core when the beam is focused at $r = 0$ is approximated by:

$$P(r) = P_0 \exp[-(r/r_0)^2]. \tag{12}$$

The OH concentration for diffusion of a line source into a cylinder was derived previously [eq. (11)]:

$$C(r, t) = \frac{\alpha}{4\pi Dt} \exp[-(r^2/4Dt)], \tag{13}$$

when the laser beam is focused at $r = 0$, the parameter that is measured is the 0.95-μm absorption loss $\gamma(t)$:

$$\gamma(t) = K \int_0^a P(r)C(r, t)(2\pi r dr) \tag{14}$$

a = core radius

K = a constant.

Define a new constant:

$$r_1 = \left(\frac{1}{r_0^2} + \frac{1}{4Dt}\right)^{-1/2}. \tag{15}$$

Now substitute (12) and (13) into (14):

$$\gamma(t) = \frac{KMP_0}{2Dt} \int_0^a r \exp[-(r/r_1)]^2 dr$$

$$= \frac{KMP_0 r_0^2}{4Dt + r_0^2} \{1 - \exp[-(a/r_1)^2]\}. \tag{16}$$

If $a \gg r_1$, then $\exp[-(a/r_1)^2] \ll 1$; therefore, (16) becomes

$$\gamma(t) \cong \frac{KMP_0 r_0^2}{4Dt + r_0^2}. \tag{17}$$

The $a \gg r_1$ assumption is equivalent to the common practice of replacing

$$\int_0^a \quad \text{with} \quad \int_0^\infty.$$

If $r_0 < a/2$, then

$$\exp[-(a/r_1)^2] < 0.02$$

(regardless of $a^2/4Dt$), and the assumption is valid.

If γ_{in} is the loss when the fiber enters the oven and γ_{out} is the loss when the fiber is removed from the oven one day later, then eq. (17) gives

$$\gamma_{out}^{1} - \gamma_{in}^{-1} = 4D \times (1 \text{ day})/KMP_0 r_0^2. \tag{18}$$

The diffusion coefficient at the oven temperature T is $D = D_0 \exp(-E/RT)$, where E is the activation energy and R is the molar gas content. Multiplying (18) by γ_{in} and taking the ln then gives

$$\ln[(\gamma_{in}/\gamma_{out}) - 1] = \text{constant} - E/RT. \tag{19}$$

Plotting

$$\ln[(\gamma_{in}/\gamma_{out}) - 1]$$

versus $1/T$ gives a straight line of slope $-E/R$.

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