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# Environmental Effect on Fatigue and Lifetime of Silica Optical Fibers

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## Abstract

Fiber optics as a transmission lines using for transmitting the signals and data information at minimum losses. It is using with modem communication which has the high immunity to' electromagnetic interference for transmitting the information, light weight, low cost, no corrosion , safety because the electric nature which eliminates the spark hazard , wide band width (more channel can be transmitted), low signal attenuation than other propagation systems . It is using the light as a carrier for modulation signals information (l013 – 1014 ) HZ comparing to radio frequencies of (l06 – 109) Hz. Light sources as light emitting diodes (LED) & light Amplification by stimulated emission of radiation (LASER),each one using with proper type of fiber which are multi mode (step index), Graded index , single mode. Signal strength loss can occur for several reasons, such as: Attenuation, Rayleigh scattering, fresnel reflection , cracks , connector loss, splice loss…....

For the strength and fatigue of fused silica optical fiber on the environmental parameters temperature, humidity and PH (chemical acid, neutral or alkaline). It is shown that the stress corrosion parameter (n) is not a constant but depends on the nature of the environment. Further, different kinetic forms for the stress corrosion kinetic lead to different interpretations of experimental results? Since life time predictions are very sensitive to the value of (n) and the kinetic form it is important to know which form is correct. It is shown that the empirical power law form that is almost exclusively used by the fiber optics industry provides a good fit to fatigue data for high strength fiber, but an exponential form provides a more self- consistent description of fatigue in different environments . From our research the following results are:

1. Life time of the optical fiber (silica) obviously affected by the environmental climate. The fatigue at the fibers affected by the presence of the chemical materials; (according to that types and concentration) affected directly to the concentration of the fiber starting from the external surfaces to the clad and then to the core which happening the cracks and these cracks increases continuously by the affect of that materials. That obviously by equation research (part 2).
2. the effects of stress or high weight on fiber may be happen the bending or a small bend inside the fiber then dispersion of the light signal will be take place, then the reflection way cannot becomes write, or cracks can be happens.

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3. The effects of continuously humidity on strength of the fiber (according to the belly-band), relative fatigue be occurs, and that affected to the construction of fiber. (Table No.1).
4. Effected of PH (concentration of hydrogen) on the strength and fatigue of the fiber follows to the faster fused silica. As we know the limit of PH generally start from (1-14) as a number (acid, passivity or neutral) the No.7 at the middle neutral concentration of Hydrogen ions will be basic, under to (7) will be acid. The equations and Fig. 1 noted that.
5. The effected of temperature on the strength and construction of the fiber lead to fatigue or fused silica (Eq.9) or increasing of the hardening, then lost the flexibility and then may be broken or cracks appears on it which lost the specification.

## تاثيرات الظروف المحيطة على الاجهاد وفترة الخدمة الالياف الضوئية السيكا

### الخلاصة

الالياف الضوئية عبارة عن خطوط نقل تستخدم لنقل الاشارات وبيانات المعلومات باقل ما يمكن من الخسائر وهي تستعمل في الاتصالات الحديثة حيث انها تحتوي على ممانعة عالية تجاه التداخلات الكهرومغناطيسية عند ارسال المعلومات، خفيفة الوزن، كلفة قليلة، لاتصدأ، امينة تجاه الصدمات الكهربائية، مجال مرور واسع (يمكن ارسال قنوات اكثر) ، اضمحلال الاشارات قليل نسبة الى بقية انظمة الاتصالات. يستخدم الضوء كحامل لتضمين الإشارات ( 1014 – l013) هيرتز مقارنة بالترددات الراديوية الاعتيادية (109 – l06) هيرتز.

المصادر الضوئية ، الثنائي المشع الضوئي والليزر وكل منهم يستخدم مع نوع من الليف المناسب التي هي متعددة الانماط والمتدرج والاحادي النمط. فقدان شدة الاشارة يمكن ان تحصل ولعدة اسباب ، منها الاضمحلال ، استطارة رايلي (التبعثر) ، انعكاس فرينيل ، التشقق ، الفقد عند اللصق (اللحيم).

بالنسبة الى الشدة والإجهاد في الألياف الضوئية (السيليكا) هنالك مؤثرات محيطية كالحرارة والرطوبة والمواد الكيمياوية (حامضية، متعادل او قاعدية) كذلك يتبين خطورة عنصر الاندثار (n) (الاستهلاك) وهو غير ثابت ويعتمد على الظروف المحيطة او الطبيعة. اضافة الى ذلك اختلاف فترة شدة الاندثار او التاكل في الليف والتي تعتمد على متغيرات لنتائج عملية وبذلك طول عمر الليف يكون حساسا ومحسوبا تبعا لقيمة (n). من المهم معرفة أي شكل من الاشكال المؤثرة واسبابها في عمل وفترة خدمة الليف. يظهر ان قانون القدرة التجريبي عموما والذي يستخدم في معامل صنع الالياف الضوئية يحاول تامين ملائمة عالية لنقل وجودة البيانات بالليف. لكن من الواضح اكثر هو معرفة الخصائص الذاتية للاجهاد تحت مختلف الظروف المحيطة. من خلال البحث تم التوصل الى النتائج التالية:

1. عمر او فترة الخدمة للالياف الضوئية (السليكا) تتاثر بشكل واضح بتاثير الظروف المحيطة حيث وجد بان الاجهاد الحاصل بالالياف وبتاثير المواد الكيمياوية وحسب انواعها وتركيزها تؤثر وبشكل كبير على تركيبة مكونات الليف ابتداء من الاغلفة الخارجية وصولا الى القشرة ومن ثم اللب محدثة التشققات والتي تزداد بزيادة تاثير تلك المواد حيث تم توضيح ذلك بالمعادلات المشاؤ اليها في البحث.
2. ان تاثيرات الضغوط او شدة الثقل على الليف محدثة نبرة او انبعاج فيه الى الداخل حيث سيؤدي الى حصول التشتت في مرور الاشارة الضوئية ولن تحصل عملية الانكسار الطبيعي خلال اللب.

3. تاثيرات الرطوبة المستمرة على متانة الليف وحسب نوع الاغلفة المستعملة محدثة اجهاد نسبي واضح على تركيبه (جدول رقم (1)) يوضح ذلك.
4. تاثيرات الـــ PH (تركيز ايون الهيدروجين) على متانة الليف وما يحصل له من اجهاد او انصهار السليكا والمعروف ان حدود الـــ PH عموما من (14-1) حامض ، قاعدي او متعادل والحد الفاصل هو الرقم (7) تركيز متعادل واعلى من ذلك يكون تركيز ايون الهيدروجين قاعدي واقل من (7) يكون حامضي ، تم توضيح ذلك حسب المعادلات المرفقة والشكل رقم (1).
5. التاثير الحراري على قوة وتركيبة الليف والذي يمكن ان يؤدي الى الاجهاد وثم انصهار السليكا (معادلة 9) او زيادة في التصلب الذي يفقد مرونته ومن ثم يتعرض بسهولة للكسر او ظهور اعراض التشققات والتي تفقد من مواصفاته.

## 1. Introduction

The mechanical reliability of optical fibers is usually assessed using the sub critical crack growth model for fatigue in which ambient moisture preferentially attacks the strained bonds around stress-concentrating surface defects (normally assumed to be cracks) to cause the defects to grow at applied stress levels which do not cause immediate failure. Eventually the most severe defect extends until it reaches the critical size for fast fracture and failure ensues. This "fatigue" process is usually thought of as a stress-assisted chemical reaction between water and silica and so depends on the nature of the environment - fatigue occurs faster at higher temperature and at higher water activity (at higher humidity or in liquid water). It is also known to depend on any solutes in liquid water. An optical fiber fatigues throughout

Its life whenever any stress is applied. There are three processes in which fatigue is important. Firstly, almost all fibers are proof tested to remove the worst defects. The stress pulse which is applied during proof testing causes surviving defects to fatigue slightly and hence weakens the fiber, though the average strength of the surviving fiber is increased due to truncation of the low end of the strength distributions. Of key importance is the fatigue which occurs during the unload cycle of proof testing since this controls the strength of the weakest surviving defect, and so controls the ultimate lifetime of the fiber under stress. Secondly, during service, any applied stress causes further weakening and, at least for long length applications, one is normally concerned about the lifetime of the weakest flaw that just survives proof testing. Thirdly, in order to make quantitative predictions of lifetime and reliability an estimate is needed of the key kinetics parameters for the fatigue process (usually the well-known n and B parameters) and, in principle, these are measured during laboratory fatigue testing. Typically, models for fiber lifetime do not explicitly include parameters describing the environment (i.e. temperature and humidity) and so there is an implied assumption that the environments during proof testing and laboratory testing, as well as the service environment, are all the same. This is clearly not the case! If the service environment is less aggressive (colder, lower humidity) than the proof test and laboratory environments, then the lifetime predictions are conservative. But, the service environment may well be more aggressive. This is somewhat compensated for by assuming values of the fatigue parameters that are conservative or "worst case" - this also obviates the need to measure the fatigue parameters for every fiber sample. However, for the most aggressive environments the lifetime predictions might still be overly optimistic. Conversely, for relatively benign environments (such as space which is dry) the lifetime model might be grossly conservative resulting in design criteria (for maximum service stress, minimum bend radius, etc) which are hard to achieve.

Clearly what is needed is a detailed model for how the kinetics of fatigue depends on the environmental factors, such as temperature, humidity, pH, etc., so that design criteria can be determined for any environment of interest. Unfortunately, a strictly empirical approach to the way in which fatigue depends on the environment, while a good first step, suffers from the problem that interpretation of the results can depend upon what mathematical vehicle is used to interpret those results. A semi-empirical approach is preferred in which experimental data are fitted to chemical kinetics models that are based on physical models that have been established. Ideally, the result would be an overall kinetics model for fatigue that self consistently describes the effect of all key parameters simultaneously.

## 2. Chemical Kinetics Models for Fatigue

The sub critical crack growth model which is used to describe fatigue is itself composed of two independent sub models. The first sub model describes how a defect causes a local stress concentration:

$$K_I = dYC^{1/2} \qquad \ldots(1)$$

Where KI is the stress intensity factor, $d$ is the remotely applied stress, Y is the crack shape parameter, and c is the crack length (or the effective crack length if the defect is not a sharp, well-defined crack). Uncontrolled failure will occur when reaches the critical value, KIC, also known as the toughness. In the absence of a corrosive environmental species, the crack length will not change until K1= KIC However, if a corrosive species, most importantly water, is present, it will break the stressed bonds at the crack tip leading to a rate of growth of the crack which is controlled by the kinetics of the chemical reaction which is itself controlled, amongst other things, by the stress in the region of the crack as quantified by the stress intensity factor. This leads to the second sub model which describes how the crack growth rate, $C^{\bullet}$ , is a monotonically increasing function of K1 (or K after normalization to KIC), which for convenience we will put in an exponential form:

$$C^{\bullet} = \exp\{f(k)\} \qquad \ldots(2)$$

Where,

$$K = \frac{K_I}{K_{IC}} \qquad \ldots(3)$$

Eqs. 1 and 2 can be combined into a first order nonlinear differential equation that can be integrated for any particular loading scheme, $s = s(t)$, (such as static fatigue with 6 = constant, or dynamic fatigue with $s^{\bullet}$ = constant). The kinetics sub model is very much more sensitive to the stress so that the final fatigue equation is dominated by the form of the kinetics sub model and is insensitive to the form of the micromechanics sub model. For example, power law kinetics results in power law fatigue equations and exponential kinetics results in fatigue behavior that is close to being an exponential. Further, the validity of each sub model is not predicated on the validity of the other, i.e. if the micromechanics sub model is wrong (e.g. if the defects were not simple sharp cracks) it does not imply that the kinetics model is wrong. Therefore, because of the sensitivity to the kinetics model, fatigue measurements will not be sensitive to the micromechanics sub mode 1. This is both an advantage and a disadvantage: a disadvantage because fatigue data will not readily determine whether the micromechanics model is appropriate, but an advantage because our primary interest here is in kinetics so that all the conclusions drawn here are not predicated on the validity of the micromechanics model. This is fortunate because the validity of Eq. 1 for pristine silica fibers is not clear given that the strength of these fibers is close to the theoretical strength and so they are perhaps "flaw free". Besides the assumption of Eq. 2 that the fatigue process involves a stress assisted chemical reaction between silica and water at the crack tip, it can also be suggested that the process is rate limited by stress assisted diffusion of water along the crack into the crack tip region. Other mechanisms have also been suggested, such as stress assisted diffusion of moisture into the glass structure ahead of the crack tip, but it is reasonable to suppose that Eq. 2 would still be valid for these other mechanisms. Therefore, while the formalism described here assumes a stress assisted chemical reaction, the conclusions would be equally valid even if fatigue is due to some other process.

Several mathematical forms for Eq. 2 have been suggested in the literature. The first is a power law form which is widely used.

$$C^{\bullet} = A_1 K^{n_1} \qquad \ldots(4)$$

model1

This form is mathematically convenient since static and dynamic fatigue equations can be found in analytical closed form and it is mathematically compatible with the weibull distribution commonly used to describe the statistical variability in strength, but is not based on any physical model. An exponential form, was suggested when it was first recognized that fatigue was a stress corrosion phenomenon.

$$C^{\bullet} = A_2 \exp(n_2 k) \qquad \ldots(5)$$

model2

While this form is based on a chemical kinetics model for fatigue it assumes that the crack tip stress affects the chemical kinetics through an activation volume in much the same way that pressure is known to affect chemical kinetics. However, the stress tensor at the crack tip has a substantial deviatoric component and is not accurately modeled by a hydrostatic pressure. A more rigorous treatment yields a form.

$$C^{\bullet} = A_3 \sin\left(n_3 \{G - 2g\}\right) \quad \ldots(6)$$

Where G is the energy release rate and y is the fracture surface energy. This form predicts the presence of a fatigue limit, i.e. no crack growth occurs until G > 2$g$ . However, since there is as yet no convincing evidence for a fatigue limit in fused silica optical fiber, it is prudent to avoid assuming one exists. Thus, assuming that we are operating well away from any fatigue limit and that the reverse (healing) chemical reaction is negligible.

It is shows that these three forms can be expressed as special cases of a more general exponential form:

$$C^{\bullet} = A_i \exp\{n_i f_i(k)\} \text{ i=1…3} \qquad (7)$$

Where Ai is a measure of the reaction rate and n is a measure of the sensitivity of that rate to the applied stress. For the three models:

$$\left.\begin{array}{lll} f_1(k) = \ln k & \text{model 1} & (1) \\ f_2(k) = k & \text{model 2} & (11) \\ f_3(k) = k & \text{model 3} & (111) \end{array}\right\} \ldots(8)$$

Temperature is usually incorporated

$$C^{\bullet} = A_i \exp\left(-\frac{\Delta \mathrm{H_a}}{RT}\right) \exp\{n_i f_i(k)\} ..(9)$$

Where $\Delta H_a$ is the apparent activation energy.

It is developed a general model for the kinetics of fatigue based on absolute reaction rate theory in which it is assumed that there is an activation barrier to fatigue and further assumed that the height of the barrier is affected by the stress intensity at the crack tip, as quantified by k, Eq. 3. An important extension to the usual models is that it is assumed that the stress changes the barrier height both through entropic as well as enthalpic terms:

$$\Delta H^* = \Delta H_o^* - \mathrm{f_H}(k), \text{ and} \qquad (10)$$

$$\Delta S^* = \Delta S_o^* + \mathrm{f_s}(k), \qquad (11)$$

Where $\Delta H$ and $\Delta S^*$ are the activation enthalpy and entropy and $\Delta H_o^*$ and $\Delta S_o^*$ are the values of these parameters in the limit of zero applied stress. The functions fH and fs describe the influence of stress, the signs in Eqs. 10 and 11 are chosen so that a positive value for these functions means that a tensile stress reduces the overall activation barrier height. Assuming for simplicity fH and fS have the same functional form, f(K), gives:

$$\Delta H^* = \Delta H_o^* - \mathrm{n_H} f(k), \qquad ..(12)$$

$$\Delta S^* = \Delta S_o^* + \mathrm{n_s} f(k) \qquad ..(13)$$

Where nH and nS are a measure of the sensitivity to the stress intensity of the enthalpy and entropy contributions activation barrier.[12]

It should be recognized that while changing the temperature changes the reaction rate, it can also change the concentration of reacting species (e.g. both the saturated vapor pressure of water and the pH/pOH of solutions are temperature dependent). If the concentration of the reacting species is C, and the activation free energy for formation of that species is $\Delta$ G* (e.g. $\Delta$ G of vaporization for water vapor or a function of AG of dissociation of liquid water if the reaction is with hydroxyl) then:

$$C = C_o \exp\left( -\frac{\Delta G^*}{RT} \right)$$

Where Co is a constant. If the chemical reaction is assumed m order in the reacting environmental species , the overall fatigue rate is given by :

$$\frac{dc}{dt} = V_a C_o^m \frac{K_B}{h} \exp\left( \frac{\Delta S_o^* + m\Delta S^*}{R} \right) \exp\left( \frac{\Delta H_o^* + m\Delta H^*}{RT} \right) \exp\left[ f(k) \left( \frac{n_H}{RT} + \frac{n_s}{R} \right) \right] \qquad ...(15)$$

Where v is a vibrational frequency, a is the bond length (i.e. the distance the crack extends when one bond is broken), $K_B$ is the Boltzmann constant, h is the Planck constant and R is the gas constant.

Comparing this general form with the semi-empirical form of Eq. (9) term by term yields several predictions if the observed fatigue rate is to be described by a general absolute rate theory model. Firstly, the function f(k) clearly corresponds to the kinetic form fi(k) of Eq. 7. Ignoring the linear term in T in Eq. (15) (which has little effect on the overall behavior), and by the effect of temperature gives :

$$\left.\begin{aligned} \Delta H_a &= \Delta H_o^* + m\Delta H^* - n_H f(k) \\ \Delta S_a &= \Delta S_o^* + m\Delta S^* - n_S f(k) \end{aligned}\right\} \qquad (16)$$

or in the limit of zero applied stress

$$\left.\begin{aligned} \Delta H_{ao} &= \Delta H_o^* + m\Delta H^* \\ \Delta S_{ao} &= \Delta S_o^* + m\Delta S^* \end{aligned}\right\} \qquad ...(17)$$

While equation the stress intensity (k) dependence yields;

$$n_i = \frac{n_H}{RT} + \frac{n_S}{R} \qquad ...(18)$$

This last result which assumed model 2 exponential kinetics. It is shown here that it is a general result true for any kinetics model that can be expressed in the form of Eq. 7.

If we want any kinetics model that will be used to describe fatigue to be consistent with absolute rate theory, which is reasonable, then we can conclude from Eqs. 16-18:

1. The apparent activation energy (enthalpy), $\Delta H_a$ and the activation entropy depend on the environment via the terms in $\Delta H^*$ and $\Delta S^*$ . This means that the apparent activation energy for fatigue in the limit of zero applied stress is not a single constant, but varies from environment to environment. This should be the case independent of the form of the kinetics sub model.
2. In contrast, the fatigue parameter h} should not depend on the test environment but should vary linearly with reciprocal absolute temperature. If the temperature dependence is weak it means that the applied stress causes fatigue principally through its effect on the height of the entropy activation barrier. Again, this conclusion should be the case independent of the form of the kinetics sub model.

These ideas provide tests for the validity of any form of the kinetics sub model. Any kinetics model that violates the above conclusions is not compatible with absolute reaction rate theory and is therefore probably invalid and can not be used to provide The basis of the overall governing kinetics. These ideas will now be applied to experimental data obtained for the dependence of fatigue on a variety of environmental parameters.

## 3. Effect of stress on fatigue

The most direct method for determining the dependence of the kinetics on the stress intensity, as given by Eq. 7, is to directly measure the crack growth rate as a function of applied stress intensity. Such measurements have been made for macroscopic cracks but the data are generally not accurate enough to distinguish between the three models ,and for small indentation cracks is better described by model 2, as are the data for large cracks over a broad range in growth rate. However, the strength of a specimen containing cracks large enough to be found and observed easily is extremely weak and is weaker than fiber with a practically useful strength. Further, the existence of such cracks in the pristine material is doubtful.

An alternative approach is to measure static or dynamic fatigue over a broad range of applied stress or stress rate. Such results for high strength fiber generally favor the power law,Eq8,model 1. The other results that will be described here are also generally consistent with the power law in terms of direct fits to fatigue data. This leaves us with the unfortunate result that the kinetics model with the least physical significance (model 1) gives the best fit to fatigue data while the model with the most physical significance (model 3) gives the worst fit. However, this result has only been found for high strength pristine fiber and, as suggested by the results on larger cracks, the situation might be different for fiber with lower strengths. Also for determining the appropriate form of the kinetics model is to make use of the predictions of the absolute rate theory model. This model suggests that the fatigue parameter, ni should not depend on the environment - all the environmental dependence should be in the apparent activation parameters and the pre exponential factors. Therefore, any kinetics model for which n is found to vary significantly with the nature of the test environment is clearly not consistent with a chemical kinetics model for fatigue and so is less desirable.

Once again it must be emphasized that the data for which the power law give a clear best fit are all for pristine fiber. It cannot be assumed that the same holds true for weak fiber with larger, better defined defects.

## 4. Effect of humidity on strength and fatigue

The strength measurements as a function of humidity. The analyzed their results in terms of a power law and show that the strength is proportional to the humidity raised to the power of a, with a = -0.0427 at low humidity ( $\leq 10^{-3\%}$ ) and -0.0926 at high humidity ($\leq 15\%$). The standard dynamic fatigue equation, assuming power law kinetics, shows that A1 is proportional to $s^{-n}$. The intrinsic rate of the fatigue process, quantified by A1 Eq. (4), is proportional to the humidity raised to the power of –an1. Assuming n1 ≈ 20, this further suggests that A1 depends approximately on the square of the humidity at moderate to high humidity and is proportional to humidity at low humidity, i.e. fatigue is a second order reaction with respect to moisture at high humidity but a first order reaction at low humidity. However, it is clear that this result is intimately bound to the assumption of power law kinetics, through the dependence on the assumed value of n1, and so it is not clear that it is real or simply an artifact of the use of power law. The situation is further complicated by the observation that n1 is not a constant but itself varies with humidity, so simply multiplying a but n $\approx$20 is not valid for all humidifies. Therefore, it is important to know the correct kinetics model in order to correctly interpret experimental data in a fundamental way, as opposed to simply an empirical way.

By measuring the strength at several loading rates which it is a function of humidity, thereby calculating the fatigue parameters, not just the strength, as a function of humidity. In addition, they analyze their results using all three of the kinetics models discussed here to directly determine the effect of assuming different fatigue models. They find that the power law does not give a consistent description of the effect of humidity; A1 (or equivalently the B parameter) is effectively constant with humidity but that the humidity dependence of strength results from the dependence of n1 on humidity. This is inconsistent with a chemical kinetics model for fatigue since it would imply that humidity has no effect on the chemical reaction rate through a concentration term, but changes the sensitivity of the activation energy to stress, in contradiction to Eqs. 16 to 18. Of the three models discussed here, and then found that model 2 gives the overall best description of the data. Their results confirm that the chemical reaction is approximately second order for humidity $\geq$15% , they also find this result for all three kinetics models, provided the data are analyzed assuming that n1 are constant with humidity, even if they are found to vary, as is the case for models 1 and 3. Their results for several fibers are shown in Table 1;

unless n is constrained to be constant, model I predicts small or even negative reaction orders.

Table 1. Reaction order with respect to humidity for fatigue of fiber with four different coatings for the three different forms of the kinetics. 95% confidence intervals are also given for the estimate of the order. Results are shown for unconstrained fits to the data as well as for fits for which the n1 are constrained to be constant. Values of approximately two are shown bold.

In addition to the strength measured as a function of humidity at room temperature, the results of strength measurements at 100% humidity at temperatures between -140 and 100°C, and of strength measurements at 20°C at various pressures with low water content. When both sets of data are plotted simultaneously as strength as a function of dew point temperature, both are found to roughly coincide. It is therefore tempting to suppose that the effects of temperature and humidity on fatigue can be combined into a single variable, namely the dew-point temperature. While an enticing idea, dew point temperature is determined by the equilibrium thermodynamic properties of water in the vapor, liquid and solid phases. It is therefore unreasonable to suppose that dew point temperature determines the kinetics of the reaction between water and silica, while the dew point temperature does partially combine the effects of temperature and humidity (heating air with a given water content reduces the strength because of faster kinetics, but increases it because of a reduction in relative humidity), the strength can by no means be expressed as a function of dew point temperature alone.

## 5. Effect of pH on strength and fatigue

The well-known result that strength is lower and fatigue is faster for fused silica at high pH suggests that the dominant fatigue reaction in liquid aqueous environments is with hydroxyl ions rather than with molecular water. The change of reaction order from about 2 at moderate humidity to 1 at low humidity also lends support to this idea. At low humidity, surface water is primarily .chemisorbed so that dissociation to form hydroxyl is negligible and fatigue is controlled directly by molecular water and so appears first oyder in humidity.

The polymer coating on a fiber is impermeable to large ions on the time scale of at least weeks at room temperature so the glass surface of coated fiber does not see the surrounding pH. For this reason, bare fiber was used throughout the work. The variation of strength with pH is complex, showing sigmoidal behavior (Fig. 1). Fits of the three kinetics models demonstrated that the fatigue parameters. Ai and ni also showed sigmoidal behavior. In particular, n^ varied substantially with pH except for model 2. Therefore, like the humidity data, the pH data support model 2 since we expect n to be independent of pH. The fatigue occurs by reaction with both molecular water and hydroxyl ions and the over all reaction rate is a sum of the individual rates:

$$R = R_{H_2O} + R_{OH^-} = K_{H_2O}[H_2O]^Y + K_{OH^-}[OH]^X \qquad \ldots(19)$$

Where x and y are reaction orders. Since ( $H_2O$ ) is constant (negligible amounts are consumed during fatigue) this may be simplified to:

$$R = K_{H_2O} + K_{OH^-} + K_{OH^-}\left[OH^-\right]^X \qquad \ldots(20)$$

At low pH there are insufficient hydroxyl ions to influence the fatigue so the first term in Eq.2 dominates and the kinetics are independent of PH:

$$R \approx K_{H_2O} \qquad \ldots(21)$$

While at moderate PH the second term dominates and the reaction rate is sensitive to pH or pOH:

$$R \approx K_{OH^-}\left[OH^-\right]^X \qquad \ldots(22)$$

If the estimation of ahydroxyl reaction order of approximately x = 0.3 to 0.4 but the actual value might be higher since they did not have sufficient data in the pH range of 4 to 8 to get a precise estimate: their results are not inconsistent with a first order reaction with OH- .

They note that hydrolysis of siloxane bonds consumes water, not hydroxyl ions, so the hydroxyl is actually a catalyst; this is an example of a "specific base catalyzed" reaction. Such reactions become rate limiting when the catalyst is in excess, thus explaining the insensitivity of fatigue to pH at pH ^ 8.

To summarize this work, the strength and fatigue is sensitive to pH in the intermediate range of pH 4 to 8, but insensitive outside this range. The polymer on coated fiber shields the glass surface from the external pH so that at least some of the difference in strength observed between different fiber specimens can be explained by differences in ho-w the specific coating chemistry influences the local pH at the glass surface. In particular, the strength of a fiber can increase or decrease slightly upon removal of the coaling. This can be simply explained by chemical effects, rather than more complex and unlikely mechanical effects.

## 6. Temperature

The effect of temperature on the strength and fatigue of fused silica optical fiber is often interpreted in terms of an apparent activation energy, as in Eq. 9. It found that the reported values of the activation energy by different investigators show considerable variation. They claim that the activation energy varies linearly with applied stress, though none of the data used to draw this conclusion are extensive enough to distinguish the behavior and hence to favor one kinetic model over another. Detailed interpretation of the available results has

been lacking. For example, to extract an activation energy from temperature data one needs a measure of the fatigue rate. In static fatigue, the measure of rate is usually taken as the reciprocal of the time to failure. However, while the applied stress is constant for static fatigue, the stress intensity at the crack tip is the parameter that controls the kinetics, and that varies during the experiment, so the resulting value of the activation energy is really for an integration over a range of stress intensity. Analysis of the results of dynamic fatigue do not yield directly a rate and some assumption about the kinetics model must be made in order to interpret such data.

In extensive measurements of fatigue at different temperatures, they were able to determine the apparent activation energy and to interpret the variation of this parameter in terms of the influence of the applied stress intensity on the activation barrier enthalpy and entropy.

The importance of the way in which the applied stress affects the activation energy (enthalpy) depends on which kinetics model is assumed. However, independent of which model is assumed, we see that fatigue is driven by entropic effects and that enthalpic effects do not promote fatigue but rather hinder it if exponential models are assumed.

In other work, the measuring static fatigue of both coated and bare fibers in both water and pH 7 buffer solution at various temperatures. The apparent activation energy, Δ Ha, was calculated as a function of applied stress and the environment in order to determine the kinetics model by fitting to Eq. 16. While the results showed too much uncertainty to reach any conclusions in this regard, their results did show that the activation energy in pH 7 buffer is higher than in pure water. It has been observed in the past that when temperature is used to accelerate fatigue, the fatigue is faster in pH 7 buffer than in pure water. While it can be suggested that the complex ionic environment of the buffer might enhance fatigue compared to pure water, the chemical kinetics model discussed here provides a much simpler explanation. Eq. 16 shows that the apparent activation energy for fatigue is expected to depend on the environment through the parameter $\Delta H^*$ . In the previous section it was observed that the fatigue under near-neutral conditions is dominated by the reaction with OH-. However, the hydroxyl ions are formed by the dissociation of water:

$$H_2O = H^+ + OH^- \qquad \ldots(23)$$

But the dissociation constant, Kw varies with temperature Kw is defined by:

$$K_w = [H^+][OH^-] \quad , \quad \text{hence}$$

$$PH + POH = \log K_w \qquad \ldots(24)$$

in pure neutral water, pH=pOH while in pH7 buffer the pH remains roughly7 giving:

$$POH = -\log K_w / 2 \quad \text{pure water} \qquad \ldots(25)$$

$$POH = -\log K_w - 7 \quad \text{PH7 buffer} \qquad \ldots(26)$$

Since Kw increases with temperature, pOH decreases faster with temperature in buffer than in pure water so pH 7 buffer is basic compared to water at elevated temperatures. As a result, the apparent activation energy in pH 7 buffer is expected to differ from that in pure water by one half of the free energy of dissociation for water. The situation is somewhat more complicated because of the temperature dependence of the concentration dissolved carbon dioxide, which is a difficult-to-avoid contaminant of aqueous solutions.[2,6,7]

## 7. Conclusions

Several forms for the stress dependence of fatigue have been proposed in the literature. It is found that lifetime predictions are very sensitive to the form, and that the widely used power law predicts substantially longer lifetimes than the physically more reasonable exponential forms. Published data have not unequivocally suggested what is the correct kinetics form, although the weight of the evidence is in favor of an exponential form. In addition to the practical importance of the validity of lifetime predictions, assumption of one or other form of the kinetics can change the interpretation of the results of fatigue experiments. In order to clarify this issue a generalized chemical kinetics model for fatigue has been developed that is based on absolute reaction rate theory. This model does not assume any particular form for the kinetics, but can be used with any of them. It also permits the applied stress to influence the activation entropy for the fatigue process as well as the enthalpy. The model provides alternative methods for determining which kinetics form might be valid; for example, the fatigue parameter, n, should be independent of the test environment. We note that the power law n is well-known to vary with humidity, and so is not consistent with absolute rate theory.

The kinetics model presented here is used to interpret experimental data for the dependence of fatigue on applied stress, humidity, pH and temperature. While some interpretations of the results are dependent on the particular kinetics form used, several have emerged that do appear to be generally true. For example, the stress corrosion reaction between and water vapor is approximately first order in humidity at low humidity ($\leq$15%) but second order at higher humidity. This may be due to the dominant corrosion reaction at high humidity being with hydroxyl ions rather than with molecular water. In aqueous environments the dependence on pH is complex but does show that under near-neutral conditions the fatigue is sensitive to the hydroxyl ion concentration, but is insensitive to pH in highly acidic or basic environments.

Some aspects of the interpretation of the results of a study of the temperature dependence of fatigue do depend on the assumed kinetics form, but it is clear that the fatigue phenomenon occurs because the application of stress lowers the free energy barrier for the chemical reactions by increasing the entropy barrier. While it is widely assumed that fatigue occurs because of a lowering of the activation energy (enthalpy) by the applied stress, it is clear that this is not the case - stress dependence of the activation enthalpy is either negligible or serves to impede fatigue.

The generalized chemical kinetics model for fatigue which is presented here has proved extremely useful for interpreting a variety of fatigue data. In particular, it successfully describes the effect of more than one environment variable (stress, temperature, humidity, etc.) simultaneously and in a self-consistent manner. It therefore provides the basis for predicting the lifetime of optical fiber that is exposed to various environments that differ from either the proof test environment or the test environment used to determine fatigue parameters. By not building in any unjustified optimistic assumptions, it can provide a tool for making conservative lifetime predictions that are based in the physics of the fatigue, rather than on unsubstantiated unphysical kinetics equations.

Many of these conclusions are drawn from the results of experiments on high strength fiber. There are suggestions in the literature that some aspects of the behavior of weaker fiber might be different. Therefore some of the specific conclusions (such as reaction order with humidity) may not be relevant to the behavior of fiber with lower strength of practical importance. However, the ideas driving the work are just as applicable to weak fiber. In particular, the reliance on power law kinetics is probably unwise. The methods used here for analysis and interpretation of experimental data should also be applied to weaker fiber.

For this we called (Region 1) which crack growth has been considered where the growth is a stress activated process. At higher applied stress/crack velocity, the growth rate is controlled by mass transfer of moisture to the crack tip . For (Region II) the growth rate is less sensitive to stress. During high speed testing of deliberately weakened fiber. Region II growth can be encountered during proof testing and so can influence the distribution of flaws that just service the proof test. While this work has important practical implications, very little is known of the crack growth kinetics in Region II No data have been reported for the dependence of Region II on temperature, humidity etc. for silica fiber, so the impact of the proof test environment on the fiber reliability can not be assessed in detail at the present.

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**Table (1)**

| Coating | Fit | Model l | Model | Model |
|---|---|---|---|---|
| **urethane aerylate** | **unconstr** | **0.40 ±** | **1.98 ±** | **0.75+0.2** |
| | **constrain** | **2.16** | **231** | **2.12** |
| **Bare** | **unconstr** | **-** | **3.68+0.** | **1.51** |
| | **constrain** | **2.48 ±** | **2.18** | **2.29 ±** |
| **Polyimide** | **unconstr** | **-0.51** | **3.41** | **1.53** |
| | **constrain** | **2.19** | **2.10+0.** | **2.02 ±** |
| **Silicone** | **unconstr** | **-** | **2.63 ±** | **1.18** |
| | **constrain** | **2.25 ±** | **2.42 ±** | **2.45 ±** |

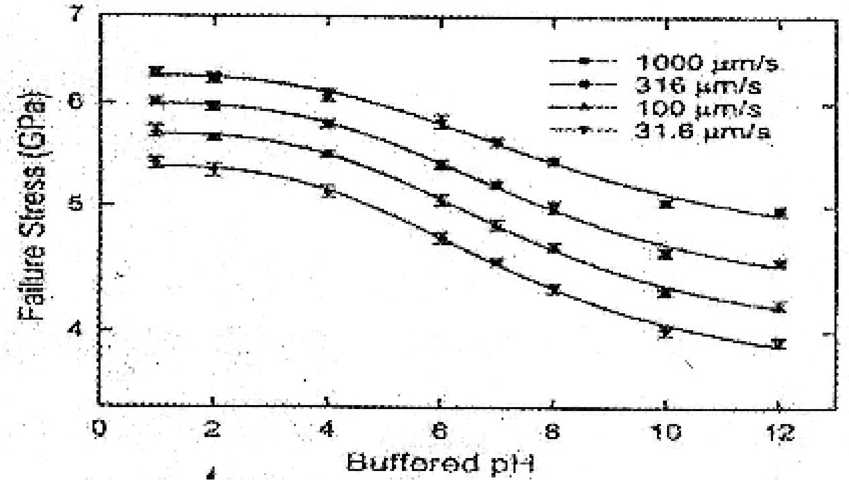

Figure (1) Strength as a function of pH at four different faceplate speeds for measurements made in two-point bending

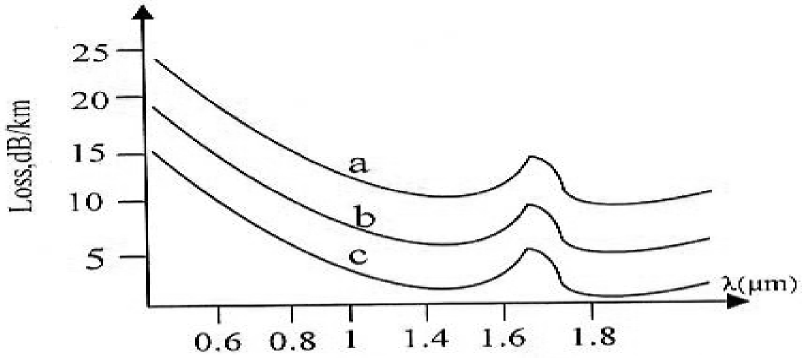

Fig. dependence of loss on fiber drawing temperature (Exp.step-index fiber with $\Delta n_1=0.013$:) (a),(b),(c) different temperature.