

Environmental effects on fatigue and lifetime predictions for silica optical fibers

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ABSTRACT

This paper reviews the dependence of strength and fatigue of fused silica optical fiber on the environmental parameters temperature, humidity and pH. 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 kinetics lead to different interpretations of experimental results. Since lifetime 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.

Keywords: Optical fiber, strength, fatigue, stress corrosion, environmental effects.

1. INTRODUCTION

The mechanical reliability of optical fibers is usually assessed using the subcritical 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).¹ It is also known to depend on any solutes in liquid water.²⁻⁴ 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 distribution.⁵ 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.^{6,7} 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) (*e.g.* Refs. 8-11) 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.¹⁰ But, the service environment may well be more aggressive. This is somewhat compensated for by assuming values of the fatigue parameters that are conservative¹¹ 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

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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.¹² 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*.

This paper reviews recent work which attempts to determine this overall governing kinetics model. We describe experimental results and the mathematical methods used to describe those results. The experimental results described here are mostly concerned with the behavior of “pristine” fiber, *i.e.* inert strength ≥ 12 GPa. For long-length applications one is normally interested in much weaker defects, ≤ 1 GPa, that just survive proof testing. While fatigue of these defects is often similar to pristine fiber, there is evidence that the kinetics of fatigue is different in some respects (*e.g.* the reaction order with respect to humidity). However, the work described here is still useful for at least providing a framework for interpreting fatigue data for weak defects.

2. CHEMICAL KINETICS MODELS FOR FATIGUE

The subcritical crack growth model which is used to describe fatigue is itself composed of two independent submodels.¹³ The first submodel describes how a defect causes a local stress concentration:

$$K_I = \sigma Y c^{1/2}, \quad (1)$$

where K_I is the stress intensity factor, σ 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 K_I reaches the critical value, K_{IC} , also known as the toughness. In the absence of a corrosive environmental species, the crack length will not change until $K_I = K_{IC}$. 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 submodel which describes how the crack growth rate, \dot{c} , is a monotonically increasing function of K_I (or κ after normalization to K_{IC}), which for convenience we will put in an exponential form:

$$\dot{c} = \exp\{f(\kappa)\}, \text{ where} \quad (2)$$

$$\kappa = \frac{K_I}{K_{IC}}. \quad (3)$$

Eqs. 1 and 2 can be combined into a first order nonlinear differential equation that can be integrated for any particular loading scheme, $\sigma = \sigma(t)$, (such as static fatigue with $\sigma = \text{constant}$, or dynamic fatigue with $\dot{\sigma} = \text{constant}$). The kinetics submodel is very much more sensitive to the stress so that the final fatigue equation is dominated by the form of the kinetics submodel and is insensitive to the form of the micromechanics submodel. 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 submodel is not predicated on the validity of the other, *i.e.* if the micromechanics submodel 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 submodel. 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".¹⁴ 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.¹⁵ Other mechanisms have also been suggested, such as stress assisted diffusion of moisture into the glass structure ahead of the crack tip,¹⁶ 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 we will consider, Model 1, is a power law form which is widely used:¹⁷

$$\dot{c} = A_1 \kappa^{n_1}. \tag{4}$$

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, Model 2, was suggested when it was first recognized that fatigue was a stress corrosion phenomenon:¹⁸

$$\dot{c} = A_2 \exp(n_2 \kappa). \tag{5}$$

While this form is based on a chemical kinetics model for fatigue¹⁹ 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:²⁰

$$\dot{c} = A_3 \sinh(n_3 \{G - 2\gamma\}), \tag{6}$$

where G is the energy release rate and γ is the fracture surface energy. This form predicts the presence of a fatigue limit, *i.e.* no crack growth occurs until $G > 2\gamma$. 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 (see the paper by Kurkjian in this volume for a discussion of this topic) and that the reverse (healing) chemical reaction is negligible, Eq. 6 becomes Model 3:^{21,22}

$$\dot{c} = A_3 \exp(n_3 \kappa^2). \tag{7}$$

Matthewson²² shows that these three forms can be expressed as special cases of a more general exponential form:

$$\dot{c} = A_i \exp\{n_i f_i(\kappa)\}, \quad i = 1..3, \tag{8}$$

where A_i is a measure of the reaction rate and n_i is a measure of the sensitivity of that rate to the applied stress. For the three models:

$$\left. \begin{aligned} f_1(\kappa) &= \ln \kappa && \text{model 1,} && \text{(i)} \\ f_2(\kappa) &= \kappa && \text{model 2,} && \text{(ii)} \\ f_3(\kappa) &= \kappa^2 && \text{model 3.} && \text{(iii)} \end{aligned} \right\} \tag{9}$$

Temperature is usually incorporated by assuming A_i has Arrhenius behavior:

$$\dot{c} = A'_i \exp\left(-\frac{\Delta H_a}{RT}\right) \exp\{n_i f_i(\kappa)\}, \tag{10}$$

where ΔH_a is the apparent activation energy.

Matthewson²² 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 κ , Eq. 3. An important extension²³ to the usual models²⁴ is that it is assumed that the stress changes the barrier height both through entropic as well as enthalpic terms:

$$\Delta H^* = \Delta H_0^* - f_H(\kappa), \text{ and} \quad (11)$$

$$\Delta S^* = \Delta S_0^* + f_S(\kappa), \quad (12)$$

where ΔH^* and ΔS^* are the activation enthalpy and entropy and ΔH_0^* and ΔS_0^* are the values of these parameters in the limit of zero applied stress. The functions f_H and f_S describe the influence of stress – the signs in Eqs. 11 and 12 are chosen so that a positive value for these functions means that a tensile stress reduces the overall activation barrier height. Assuming for simplicity that f_H and f_S have the same functional form, $f(\kappa)$, gives:

$$\Delta H^* = \Delta H_0^* - n_H f(\kappa), \text{ and} \quad (13)$$

$$\Delta S^* = \Delta S_0^* + n_S f(\kappa), \quad (14)$$

where n_H and n_S are a measure of the sensitivity to the stress intensity of the enthalpy and entropy contributions to the activation barrier.

Matthewson²² points out that 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 ΔG^\bullet (*e.g.* ΔG of vaporization for water vapor or a function of ΔG of dissociation of liquid water if the reaction is with hydroxyl) then:

$$C = C_0 \exp\left(-\frac{\Delta G^\bullet}{RT}\right), \quad (15)$$

where C_0 is a constant. If the chemical reaction is assumed m^{th} order in the reacting environmental species, the overall fatigue rate is given by:²²

$$\frac{dc}{dt} = \nu a C_0^m \frac{k_B T}{h} \exp\left(\frac{\Delta S_0^* + m\Delta S^\bullet}{R}\right) \exp\left(-\frac{\Delta H_0^* + m\Delta H^\bullet}{RT}\right) \exp\left[f(\kappa)\left(\frac{n_H}{RT} + \frac{n_S}{R}\right)\right] \quad (16)$$

Where ν 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. 10 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 $f(\kappa)$ clearly corresponds to the kinetic form $f_i(\kappa)$ of Eq. 8. Ignoring the linear term in T in Eq. 16 (which has little effect on the overall behavior²⁵) and equating the Arrhenius temperature dependence gives:

$$\left. \begin{aligned} \Delta H_a &= \Delta H_0^* + m\Delta H^\bullet - n_H f(\kappa) \\ \Delta S_a &= \Delta S_0^* + m\Delta S^\bullet + n_S f(\kappa) \end{aligned} \right\} \quad (17)$$

or in the limit of zero applied stress:

$$\left. \begin{aligned} \Delta H_{a0} &= \Delta H_0^* + m\Delta H^\bullet \\ \Delta S_{a0} &= \Delta S_0^* + m\Delta S^\bullet \end{aligned} \right\} \quad (18)$$

while equating the stress intensity (κ) dependence yields:

$$n_i = \frac{n_H}{RT} + \frac{n_S}{R}. \quad (19)$$

This last result has been derived by Scanlan²³ assuming 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. 8.

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. 17-19:

1. The apparent activation energy (enthalpy), ΔH_a , and the activation entropy depend on the environment via the terms in ΔH^\bullet and ΔS^\bullet . 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 submodel.
2. In contrast, the fatigue parameter n_i 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 submodel.

These ideas provide tests for the validity of any form of the kinetics submodel. 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. 8, 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, although the data of Muraoka and Abé²⁶ for small indentation cracks is better described by model 2, as are the data of Helfinstine for large cracks over a broad range in growth rate.²⁷ 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, Eq. 9, model 1.²⁹ For example, Fig. 1 shows dynamic fatigue results spanning more than 5 decades in loading rate.²⁸ The figure shows fits to the data using each of the three kinetic forms discussed here. The fitting methods used²⁸ give detailed information on the confidence intervals for the fatigue parameters and a prediction interval. The solid lines represent a 95% prediction interval. Clearly, the power law, model 1, gives a significantly better fit to the data, while some of the data lie outside the 95% prediction interval for model 3, which therefore is not consistent with these data. 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

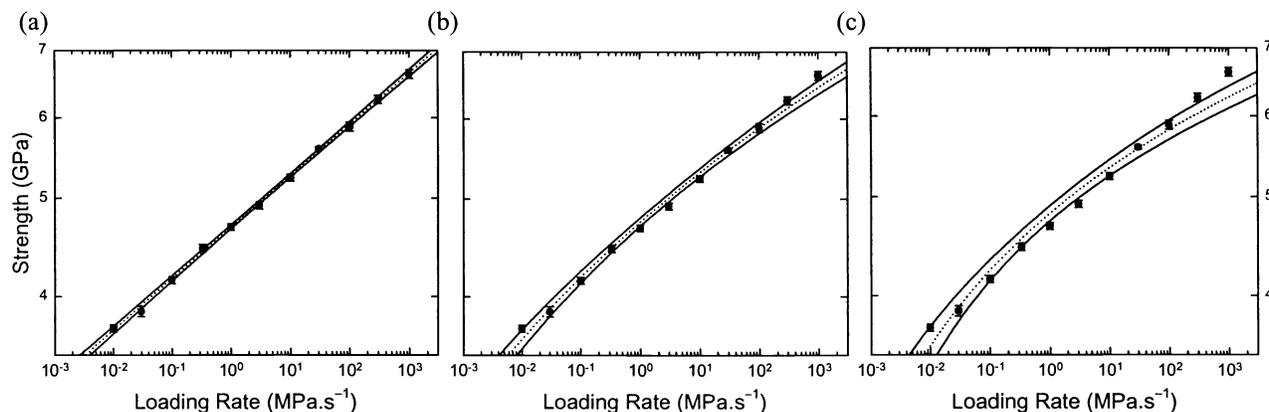


Figure 1. Fits of the three kinetics models of Eqs. 9 to the same dynamic fatigue data measured in two-point bending in 25 C pH 7 buffer solution. (a) Model 1, (b) Model 2, (c) Model 3.²⁸

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,^{26,27} the situation might be different for fiber with lower strengths.

Direct comparison between dynamic and static fatigue provides a check on the validity of the micromechanics submodel since this comparison does not depend on the kinetics submodel. Fig. 2 shows results for static fatigue behavior together with the static fatigue behavior predicted by fitting to the dynamic fatigue data of Fig. 1 taken under identical experimental conditions.³⁰ The predictions and the data lie close together but do not quite overlap (the prediction results are only shown for the power law for clarity, but the other models yield the same conclusion). This implies that the micromechanics submodel, which assumes sharp well-defined cracks that are free of residual stress, does a reasonable, but not fully accurate job of describing the behavior of pristine fiber which contains, presumably, no sharp cracks.

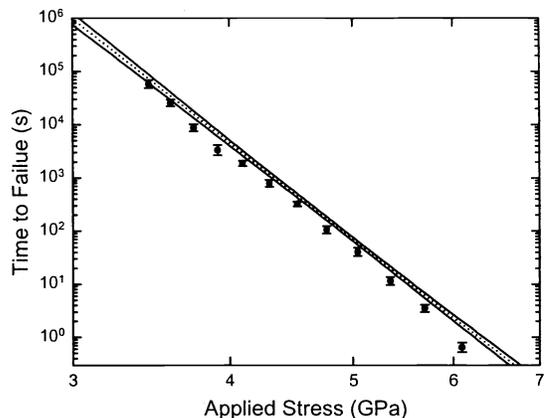


Figure 2. Comparison between static fatigue data, taken under identical experimental conditions as the data of Fig. 1, and the prediction of static fatigue behavior found by fitting model 1 to the dynamic fatigue data of Fig. 1.³⁰

When fitting to fatigue data, such as those in Figs. 1 and 2, it is found that the fatigue parameters, A_i and n_i , are strongly correlated to each other. Fig. 3 shows the 95% confidence ellipse for the fatigue parameters for model 1 and the data of Fig. 1. The ellipse is narrow and tilted. This means that while each parameter can vary over a reasonable range (n can range between ~ 19.6 and 20.8) the values can not access this range *independently*. If n takes a worst case value of 19.6 , A must take a low value too, but low A is actually best case! The parameters can not take their worst case values *at the same time*. This might provide the reason why optical fibers have proved reliable even though the power law has been used to develop design criteria. Typically, worst-case values for A (or equivalently the B parameter) and n are used, e.g. for making calculations associated with proof testing,¹¹ but the worst case values would never be observed at the same time. Therefore, in essence, the industry uses an overly optimistic model but applies it in an overly conservative way to produce design criteria that apparently work!

Another way of 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, n_i , should not depend on the environment – all the environmental dependence should be in the apparent activation parameters and the preexponential 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. This issue will be addressed in subsequent sections.

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 can not be assumed that the same holds true for weak fiber with larger, better defined defects.

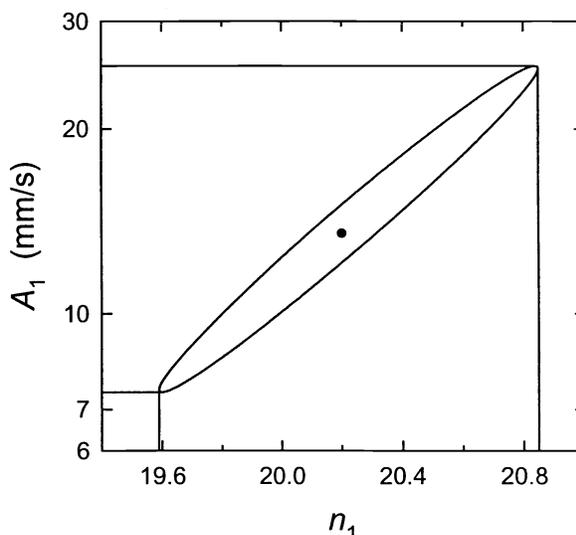


Figure 3. 95% confidence ellipse for the fatigue parameters found by fitting the power law, model 1, to the dynamic fatigue data in Fig. 1(a).

4. EFFECT OF HUMIDITY ON STRENGTH AND FATIGUE

Duncan *et al.*¹ present strength measurements (*i.e.* effectively dynamic fatigue results but at a single loading rate) as a function of humidity. They 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 ($\geq 15\%$). The standard dynamic fatigue equation, assuming power law kinetics, shows that A_1 is proportional to σ^{-n_1} . Combining this with the results of Duncan *et al.*¹ suggests that the intrinsic rate of the fatigue process, quantified by A_1 , is proportional to the humidity raised to the power of $-an_1$.¹² Assuming $n_1 \approx 20$, this further suggests that A_1 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 n_1 , 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 n_1 is not a constant but itself varies with humidity,¹² so simply multiplying a but $n \approx 20$ is not valid for all humidities. 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.

Armstrong *et al.*¹² extend the earlier work of Duncan *et al.*¹ by measuring the strength at several loading rates as 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; A_1 (or equivalently the B parameter) is effectively constant with humidity but that the humidity dependence of strength results from the dependence of n_1 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. 17 to 19. Of the three models discussed here, Armstrong *et al.*¹² 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 n_i 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 1 predicts small or even negative reaction orders. In other work, Mrotek *et al.*³¹ confirm that fatigue is approximately first order in humidity at low humidity $\leq 15\%$, again independently of the assumed kinetics form.

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 n_i are constrained to be constant. Values of approximately two are shown bold. After Armstrong *et al.*¹²

Coating type	Fit constraints	Model 1	Model 2	Model 3
urethane acrylate	unconstrained	0.40 ± 0.28	1.98 ± 0.40	0.75 ± 0.29
	constrained	2.16 ± 0.12	2.31 ± 0.14	2.12 ± 0.22
bare	unconstrained	-1.17 ± 0.87	3.68 ± 0.27	1.51 ± 0.17
	constrained	2.48 ± 0.15	2.18 ± 0.26	2.29 ± 0.34
polyimide	unconstrained	-0.51 ± 0.47	3.41 ± 0.73	1.53 ± 0.52
	constrained	2.19 ± 0.26	2.10 ± 0.16	2.02 ± 0.19
silicone	unconstrained	-0.13 ± 0.84	2.63 ± 1.83	1.18 ± 0.82
	constrained	2.25 ± 0.27	2.42 ± 0.34	2.45 ± 0.27

In addition to the strength measured as a function of humidity at room temperature, Duncan *et al.*¹ also report 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. More detailed measurements by Armstrong *et al.*³² indeed show that, 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. Armstrong *et al.*¹² propose that an apparent second order reaction with humidity can arise if the actual reaction is first order in the hydroxyl ion concentration within the layer of physisorbed water on the fiber surface. 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 order in humidity.

Taylor and Matthewson³³ have measured the strength and fatigue of high strength fibers over a wide range of pH. The polymer coating on a fiber is impermeable to large ions on the time scale of at least weeks at room temperature³⁴ so the glass surface of coated fiber does not see the surrounding pH. For this reason, bare fiber was used throughout the work. Taylor *et al.* found that the variation of strength with pH is complex, showing sigmoidal behavior (Fig. 4). Fits of the three kinetics models demonstrated that the fatigue parameters, A_i and n_i , also showed sigmoidal behavior. In particular, n_i 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. Taylor and Matthewson³³ propose a model to explain the observed behavior. They assume that fatigue occurs by reaction with both molecular water and hydroxyl ions and the overall reaction rate is a sum of the individual rates:

$$R = R_{\text{H}_2\text{O}} + R_{\text{OH}^-} = k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]^y + k_{\text{OH}^-}[\text{OH}^-]^x, \quad (20)$$

where x and y are reaction orders. Since $[\text{H}_2\text{O}]$ is constant (negligible amounts are consumed during fatigue) this may be simplified to:

$$R = k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-]^x. \quad (21)$$

At low pH there are insufficient hydroxyl ions to influence the fatigue so the first term in Eq. 21 dominates and the kinetics are independent of pH:

$$R \approx k_{\text{H}_2\text{O}}, \quad (22)$$

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

$$R \approx k_{\text{OH}^-}[\text{OH}^-]^x. \quad (23)$$

Taylor and Matthewson³³ estimated a hydroxyl 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

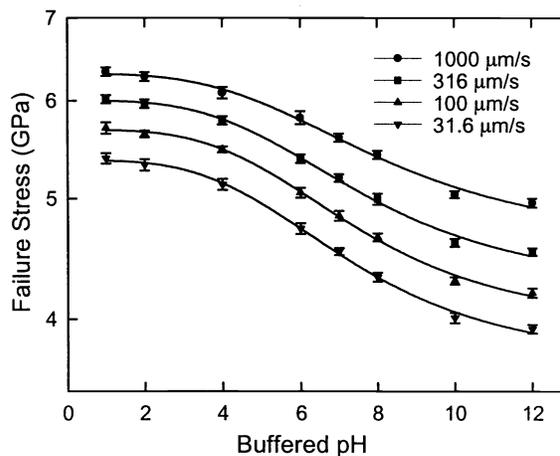


Figure 4. Strength as a function of pH at four different faceplate speeds for measurements made in two-point bending (from Ref. 33).

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.³⁵ Such reactions become rate limiting when the catalyst is in excess, thus explaining the insensitivity of fatigue to pH at $\text{pH} \gtrsim 8$.

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 how 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 coating.³⁶ 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. 10. Inniss *et al.*³⁷ have summarized many of these results. They 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.

Shiue and Matthewson^{25,38} have used the absolute rate theory described here to carefully analyze a variety of temperature data in fundamental terms, and without assuming any particular form for the kinetics model. In extensive measurements of fatigue at different temperatures,²⁵ 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. Table 2 shows the results for the apparent activation enthalpy and entropy in the limit of zero stress, as defined in Eqs. 17 and 18, measured for coated fiber in both distilled water and pH 7 buffer. (The results for the different environments are not greatly different because the coating is a barrier to the diffusion of buffering ions.) Values that are significantly different from zero compared to the confidence intervals are shown bold. It is clear from these results that the nature of the activation barrier deduced from the data depends on which kinetics model is used to interpret those results. If the power law, model 1, is used, the activation barrier is essentially enthalpic while if one of the more physically reasonable exponential forms is used the barrier is essentially entropic. This illustrates how interpretation of data can be dependent on which kinetics model is used. Clearly, to get a full understanding of these parameters a range of kinetics models must be considered.

Table 2. Enthalpic and entropic contributions to the activation barrier in the limit of zero applied stress for dynamic fatigue of polymer coated fiber in distilled water and pH 7 buffer solution.²⁵ Parameters that are non-zero within the 95% confidence interval are shown bold.

Environment	Parameter	Model 1	Model 2	Model 3
distilled water	ΔH_{a0} (kJ/mol)	48 ± 8	-2 ± 14	-4 ± 9
	ΔS_{a0} (kJ/mol.K)	0.05 ± 0.03	-0.46 ± 0.04	-0.38 ± 0.03
pH 7 buffer	ΔH_{a0} (kJ/mol)	44 ± 8	5 ± 16	-12 ± 9
	ΔS_{a0} (kJ/mol.K)	0.03 ± 0.02	-0.43 ± 0.05	-0.40 ± 0.03

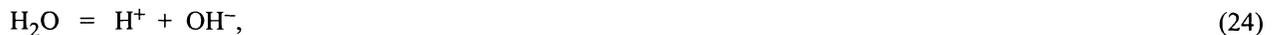
Table 3. Influence of stress intensity on the enthalpic and entropic activation barriers for dynamic fatigue of polymer coated fiber in distilled water and pH 7 buffer solution.²⁵ Parameters that are zero within experimental error are shown in italics while parameters that are of opposite sign to what is expected are shown in bold.

Environment	Parameter	Model 1	Model 2	Model 3
distilled water	$n_H \times 10^{-4}$ (J/mol)	<i>0.7 ± 9.9</i>	-13 ± 3	-35 ± 6
	$n_S \times 10^{-2}$ (J/mol.K)	1.8 ± 0.3	8.7 ± 1.1	17 ± 2
pH 7 buffer	$n_H \times 10^{-4}$ (J/mol)	<i>5.5 ± 9.1</i>	-11 ± 4	-37 ± 6
	$n_S \times 10^{-2}$ (J/mol.K)	1.6 ± 0.3	7.7 ± 1.2	17 ± 2

Shiue and Matthewson²⁵ also use the experimental data to determine how the applied stress intensity changes the activation enthalpy and entropy as given by the parameters n_H and n_S , Eq. 19. The results, shown in Table 3, again show that interpretation of the results depends on which kinetics model is used to analyze the data. For model 1, n_H is essentially zero so that, counter to the common assumption, if the power law is to be used one can conclude that the applied stress does *not* cause fatigue by lowering the activation energy (enthalpy), but rather fatigue is caused by increasing the entropy barrier. In contrast, if either of the exponential forms is assumed, n_H is negative and one can conclude that the applied stress *increases* the activation enthalpy. However, the entropy contribution dominates so that the overall activation barrier height is reduced by stress.

In summary, 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, Shiue and Matthewson³⁸ measured the static fatigue of both coated and bare fibers in both water and pH 7 buffer solution at various temperatures. The apparent activation energy, ΔH_a , was calculated as a function of applied stress and the environment in order to determine the kinetics model by fitting to Eq. 17. 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.³⁹ 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. 17 shows that the apparent activation energy for fatigue is expected to depend on the environment through the parameter ΔH^\bullet . 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:



but the dissociation constant, K_w , varies with temperature. K_w is defined by:

$$K_w = [\text{H}^+][\text{OH}^-], \text{ and hence } \text{pH} + \text{pOH} = -\log K_w. \tag{25}$$

In pure neutral water, pH = pOH while in pH 7 buffer the pH remains roughly 7 giving:

$$\text{pOH} = -\log K_w / 2 \quad \text{pure water}, \tag{26}$$

$$\text{pOH} = -\log K_w - 7 \quad \text{pH 7 buffer}. \tag{27}$$

Since K_w 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.⁴⁰ 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. However, Shiue and Matthewson³⁸ did indeed observe the expected higher apparent

activation energy in the buffer, thus illustrating the usefulness of the chemical kinetics model presented here as a predictive and interpretive tool.

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 silica and water vapor is approximately first order in humidity at low humidity ($\lesssim 15\%$) 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.

In this paper, only the so-called “Region I” 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.¹⁵ In this “Region II” the growth rate is less sensitive to stress. Glaesemann⁴¹ found experimental evidence for Region II during high

speed testing of deliberately weakened fiber. Hanson and Glaesemann⁷ showed that 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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