

CHEMICAL KINETICS MODELS FOR THE FATIGUE BEHAVIOR OF FUSED SILICA OPTICAL FIBER

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ABSTRACT

There have been numerous studies of the fatigue and strength behavior of fused silica optical fibers. However, no coherent model has emerged that self-consistently describes the simultaneous effects of stress, temperature and activity of the corroding species (*e.g.* water). A power law degradation kinetics model (relating the crack growth rate to the applied stress intensity factor, K_I) is widely used although various exponential forms based on chemical rate theory have also been proposed. The dependence of fatigue on parameters such as humidity, pH and temperature, has usually been treated in an empirical manner. Sometimes it is even ignored - for example, the service environment is often assumed to be the same as the proof test environment when making lifetime predictions, thus avoiding the need for understanding the humidity dependence; this assumption is often unjustified. This paper reviews the dependence of fatigue on environmental factors and highlights some of the inconsistencies in published data. It is then attempted to present a coherent kinetics model that simultaneously accounts for stress temperature, humidity, *etc.* Several possible forms of the model are compared to a range of experimental data of several different types. The comparison is made using fitting techniques that account for correlation between fit parameters. It is found that a simple exponential form of the degradation kinetics model gives the best overall description of the temperature, humidity and pH effects on static and dynamic fatigue. It should be noted that the exponential form predicts shorter lifetimes than the ubiquitous power law model. Therefore, under some circumstances, the predictions of "worst case" models based on power law kinetics are unduly optimistic.

INTRODUCTION

The mechanical behavior of fused silica optical fiber exhibits two regimes - one where the time to failure depends sensitively on the applied stress (stress corrosion cracking) and a second in which strength degradation can occur even in the absence of an applied stress. This latter regime, which tends to occur in the most aggressive environments, is not the subject of this paper. Here we are concerned with the first regime, and in particular the functional form for how the degradation depends on the applied stress.

Subcritical Crack Growth Model

The reliability of silica optical fiber under stress is usually described by the subcritical crack growth model. It is assumed that the strength is controlled by defects which are invariably modeled as sharp cracks that locally amplify the remotely applied stress, σ_a , as described by the well-known Griffith equation:

$$K_I = \sigma_a Y \sqrt{c}, \quad (1)$$

where K_I is the stress intensity factor (a measure of the intensity of the stress field near the crack tip), c is the crack length and Y is a crack shape parameter of order unity.

Slow crack growth occurs when environmental moisture attacks the strained bonds at the crack tip and an empirical power law relationship between the growth rate and the local stress (as quantified by K_I) is usually assumed:

$$\frac{dc}{dt} = A K_I^n, \quad (2)$$

where A and n are constants to be found for any particular glass and environment. This form is assumed principally for mathematical simplicity. For any given loading mode (variation of σ_a with time) equations 1 and 2 may be integrated to obtain the time to failure as a function of the loading. The resulting equations can be fitted to experimental data to obtain values for the fatigue parameters, A and n , and then used to make predictions of reliability under service conditions. However, such predictions invariably involve extrapolation from experimental data and so can only be trusted if the correct form of the relevant equations are known. It turns out that because n is typically ~ 20 for fused silica, the fatigue equations are very much more sensitive to the form of the kinetics function, equation 2, than to Griffith's equation, equation 1. As already stated, the power law form is usually chosen for its mathematical convenience but is not based on any physical model. The purpose of this paper is to discuss other possible forms for the kinetics function and to compare these with measurements. Reaction rate theory is applied to slow crack growth, and it is shown that the dependence on stress, equation 2, and the dependence on the environment (which influences A and n) are inextricably linked and should not be treated separately. The intent, therefore, is to construct a chemical kinetics model that simultaneously and self-consistently describes the effects of stress and environment (temperature, humidity, pH, *etc.*).

Kinetics Functions

The power law function of equation 2 is better written in the form:

$$\frac{dc}{dt} = A_1 \left(\frac{K_I}{K_{IC}} \right)^{n_1} = A_1 \kappa^{n_1}, \quad (3)$$

to give the pre-exponent, A_1 , sensible units. For convenience the stress intensity factor is normalized to the critical value; κ is the normalized value. Equation 3 will be designated model 1. Other forms of the kinetics function have been proposed. Many are empirical but some describe the crack growth as a chemical reaction between strained siloxane bonds and water. In the earliest work on fatigue Wiederhorn¹ proposed an exponential form for the kinetics function which can be expressed as:

$$\frac{dc}{dt} = A_2 \exp(n_2 \kappa). \quad (4)$$

Wiederhorn derives this by assuming that the tensile stress at the crack tip, which causes a hydrostatic tension, can be treated like a negative pressure. This pressure then reduces the free energy of activation thus increasing the reaction rate. Wiederhorn also incorporates a free energy term for the excess energy at the crack tip due to its curvature; however, this term becomes unimportant if the curvature remains constant as the crack advances. His model fitted experimental data for slow crack growth quite well, but this is not surprising given the sensitivity to K_I and the scatter in the data.

Wiederhorn's derivation is not rigorous since the stress influences the kinetics through a tensile pressure. Firstly, the stress field at the crack tip is not purely hydrostatic. Secondly, pressure affects free energy through the pdV work term in the first law of thermodynamics - the pressure is the uniform pressure applied at the boundaries of the thermodynamic system, while the tensile pressure associated with the crack is local to the crack tip. A more rigorous approach due to Lawn² considers changes in the stored elastic energy associated with the crack as it extends and effectively substitutes a Gdc work term in the first law where G is the strain energy released rate.

Lawn permits a reverse, crack-healing reaction with the same rate constants. This suggests the existence of a fatigue limit at some finite stress when the forward and reverse reaction rates balance. However, since there is no clear evidence for a fatigue limit in fused silica optical fiber either there is no fatigue limit or, more likely, all data are sufficiently far from that limit. Under these circumstances the crack healing reaction can be ignored and Lawn's model reduces to the form which we shall designate model 3:

$$\frac{dc}{dt} = A_3 \exp(n_3 \kappa^2). \quad (5)$$

Comparing models 2 and 3, the stress effectively reduces the activation energy linearly with K_I in model 2 as an activation volume term. In model 3 the activation energy reduces quadratically with K_I with the elastic strain energy directly reducing the free energy via the chemical potential.²

At this point one can stand back and treat the problem phenomenologically. So far the problem is described in terms of subcritical crack growth. However, as already discussed above, the form of the kinetics function dominates over the Griffith equation. We may therefore treat the trends of the final fatigue equations as describing any stress-assisted reaction between silica and water. For example, Tomozawa³ has suggested that stress assisted diffusion of water into glass may be the underlying mechanism for fatigue. The analysis presented here can therefore be applied equally well to that model. While the results will be interpreted in terms of crack growth, the trends with stress, temperature, humidity *etc.*, are not bound to the crack assumption. This is important because high strength optical fiber does not contain simple sharp cracks, but we can still use the results of such a model to describe trends.

Is the Form of the Kinetics Function Important?

Predicted lifetimes can be sensitive to the form of the kinetics function.^{4,5} It is only important if making reliability predictions involves extrapolation rather than interpolation. In principle, reliability predictions can be made in two ways. The first involves fitting to short-term laboratory data for short lengths of fiber (*i.e.* high strength "pristine" material) and then extrapolating to longer times and lower intrinsic strength. The second involves studying the behavior of deliberately weakened fiber (to simulate flaws just surviving the proof test) and then extrapolating to longer times. This second approach is simple extrapolation from data taken on the time scale of hours to behavior in the lifetime of many years. Clearly, any such prediction will be highly sensitive to the kinetics function.

The first, more commonly used approach involves extrapolation over two variables, namely time and starting strength. Griffioen⁶ suggests that these extrapolations are effectively in opposite directions - the crack velocity is similar for both small cracks on a short time scale and large cracks on a long time scale. Therefore the effects cancel leaving predictions insensitive to the kinetics function. Bubel and Matthewson⁵ verify this trend. However, the cancellation is not complete. For example, the three kinetics functions have been fitted to dynamic fatigue of fiber in pH 7 buffer measured in two-point bending at loading rates of 25, 2.5, 0.25 and 0.025 %/min as specified in a standard test procedure.⁷ Figure 1(a) shows the fits extrapolated to a 25 year lifetime assuming the starting (inert) strength of the fiber is 12 GPa. The permitted service stresses vary by over an order of magnitude for the three models, the power law, model 1, giving the least conservative estimate. Figure 1(b) now makes the same extrapolation (*i.e.* assumes the same fatigue parameters) but for an initial strength of 0.7 GPa, *i.e.* that of a flaw that just passes a 0.7 GPa proof test. Now there is less variability between the models, but there is still a substantial difference between the allowed service stress predictions. Clearly, the double extrapolation does not completely cancel and it is again necessary to know the correct form of the kinetics function.

There is a second reason for needing to know the correct kinetics model that does not involve extrapolation: it is needed to interpret certain kinds of experimental data. For example, Duncan *et al.*⁸ present strength data as a function of relative humidity. For humidity in the range 15 to 100% the log-log graph of strength versus humidity has a slope of -0.0928. If the power law is

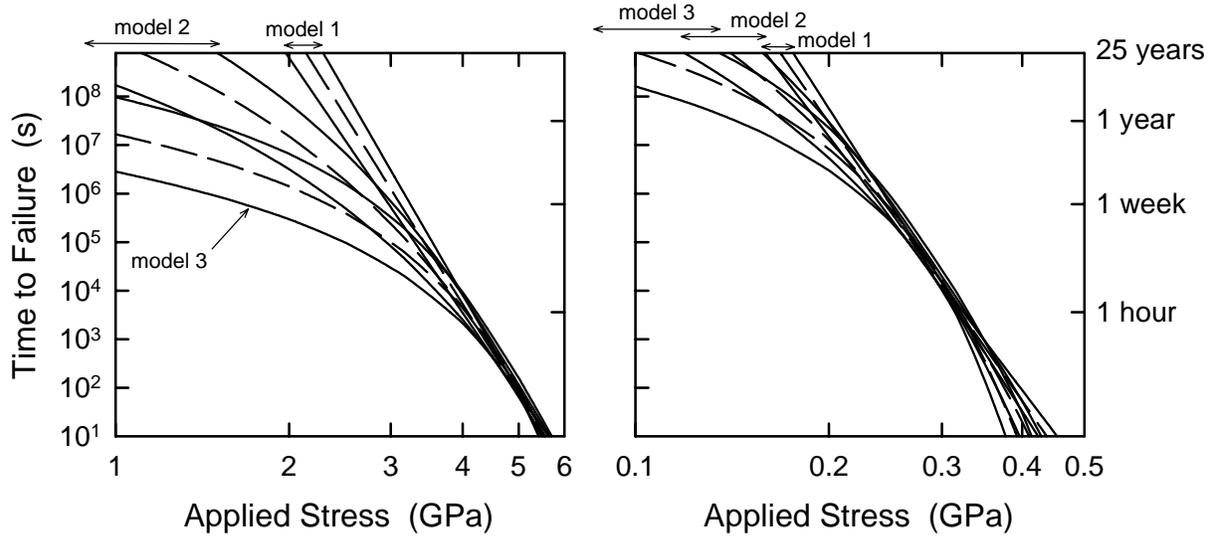


Figure 1. Fit to dynamic fatigue data taken under standard loading rates⁷ extrapolated to long lifetimes under a static stress. Results are calculated assuming (a) a pristine inert strength of 12 GPa and (b) extrapolated to an inert strength of 0.7 GPa. Bands represent a 95% confidence interval.

assumed then this straight line should have a slope of $m/(n - 1)$ where m is the reaction order. Given $n = 23$ for these data, $m = 2.04$ so the reaction appears roughly second order in humidity. An unanswered question is whether this result depends on the assumed form of the kinetics function.

Effect of Coatings

It is reasonable to suppose that the polymer buffer coating applied to the fiber might have a substantial impact on the reaction kinetics. This is certainly the case for the corrosive regime in which the coating can have a dramatic effect on the onset of the zero-stress aging degradation.⁹ In contrast, it appears that many coatings do *not* perturb the crack growth kinetics provided sufficient time is allowed for equilibration with the test environment.¹⁰⁻¹² These results are persuasive because they directly compare coated and bare fiber behavior. Equilibration times vary from hours for a simple humid air environment¹³ to weeks for more complex aqueous environments, such as pH buffers.¹⁴ While coating effects have sometimes been claimed, it is not clear that such systems have been properly equilibrated with the test environment.

CHEMICAL KINETICS THEORY

We will now develop a phenomenological model based on absolute rate theory that can incorporate any of the three kinetics functions described above. The net crack growth rate (or more generically, the degradation rate) can be considered as the difference of both forward (extending) and reverse (healing) reactions that depend on the chemical activity of the reactants and products, respectively:

$$\frac{dc}{dt} = k_+ f(a_{\text{reactants}}) - k_- f(a_{\text{products}}). \quad (6)$$

The activities of the various species will depend on their concentrations. Assuming we are operating far from a fatigue limit, we need only consider the forward reaction with a single rate constant, k :

$$\frac{dc}{dt} = k f([\text{reactants}]). \quad (7)$$

Transition state theory¹⁵ can be adapted to give the form of k :

$$k = \nu a \frac{k_B T}{h} \exp\left(-\frac{\Delta G^*}{RT}\right), \quad (8)$$

where ΔG^* is the free energy of the activated complex, a is the distance the crack advances when one bond is broken and ν is a vibrational frequency. k_B , h and R are the Boltzmann, Planck and gas constants. Splitting ΔG^* into enthalpy and entropy contributions and substitution into 7 gives:

$$\frac{dc}{dt} = \nu a \frac{k_B T}{h} f([\text{reactants}]) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right). \quad (9)$$

Effect of Environment

The environmental dependence of the growth rate, $f([\text{reactants}])$, may itself be thermally activated. For example, the saturated vapor pressure of water and the hydroxyl concentration in aqueous solutions are both thermally activated and roughly follow Arrhenius behavior. If the apparent reaction order for the reactants is m , we may write:

$$f([\text{reactants}]) = [\text{reactants}]^m = \alpha \exp\left(-\frac{m\Delta G^\bullet}{RT}\right), \quad (10)$$

where ΔG^\bullet is the activation free energy of the reactant concentration. Substitution into 9 gives:

$$\frac{dc}{dt} = \nu a \alpha \frac{k_B T}{h} \exp\left(\frac{\Delta S^* + m\Delta S^\bullet}{R}\right) \exp\left(-\frac{\Delta H^* + m\Delta H^\bullet}{RT}\right). \quad (11)$$

Effect of Stress

In the models of Wiederhorn¹ and Lawn² the stress at the crack tip is assumed to reduce the activation energy (enthalpy). In general, therefore, we may write:

$$\Delta H^* = \Delta H_0^* - f_H(\kappa), \quad (12)$$

where ΔH_0^* is the activation energy under zero stress and $f_H(\kappa)$ is some as yet unspecified function.

Scanlan¹⁶ suggests that stress could also change the activation entropy. This is reasonable since the stress might, for example, change the number of vibrational states available to the system. He found that this approach is a better description of data¹⁷ for the temperature dependence of growth velocity of macroscopic cracks. Analogous to equation 12, we may write:

$$\Delta S^* = \Delta S_0^* - f_S(\kappa). \quad (13)$$

Equation 11 now becomes:

$$\frac{dc}{dt} = \nu a \alpha \frac{k_B T}{h} \exp\left(\frac{\Delta S_0^* + m \Delta S^\bullet}{R}\right) \exp\left(-\frac{\Delta H_0^* + m \Delta H^\bullet}{RT}\right) \exp\left(\frac{f_H(\kappa)}{RT} - \frac{f_S(\kappa)}{R}\right). \quad (14)$$

For simplicity we will assume that f_H and f_S take the same functional form though with different constants:

$$f_H(\kappa) = b_H g(\kappa), \quad (15a)$$

$$f_S(\kappa) = b_S g(\kappa), \quad (15b)$$

giving:

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

Recognizing that model 1 may be rewritten as:

$$\frac{dc}{dt} = A_1 \kappa^{n_1} = A_1 \exp(n_1 \ln \kappa), \quad (17)$$

the particular forms of $g(\kappa)$ that correspond to the three kinetics models may be deduced:

Model 1	$g_1(\kappa) = \ln(\kappa),$	
Model 2	$g_2(\kappa) = \kappa,$	(18)
Model 3	$g_3(\kappa) = \kappa^2.$	

If, as is usual, we assume the pre-exponents, A_i ($i = 1 \dots 3$), are Arrhenius with apparent activation energy, E_a :

$$A_i = A_i' \exp\left(-\frac{E_a}{RT}\right), \quad (19)$$

by comparing the models with 17 and 19 we find:

$$A_i' = \nu a \alpha \frac{k_B T}{h} \exp\left(\frac{\Delta S_0^* + m \Delta S^\bullet}{R}\right), \quad (20)$$

$$n_i = \frac{b_H}{RT} - \frac{b_S}{R}, \quad (21)$$

$$E_a = \Delta H_0^* + m \Delta H^\bullet. \quad (22)$$

Examination of equations 20 to 22 yields the following conclusions:

1. Both the pre-exponents, A_i , and the apparent activation energy depend on the environment through m and ΔG^\bullet . They are therefore not universal constants for a given material.
2. The n_i do not depend on the environment but do change linearly with reciprocal temperature. If the entropy is important then n_i vs. $1/T$ should have a finite intercept.

DETERMINATION OF THE KINETICS FUNCTION

The kinetics function describes how the stress affects the rate of strength degradation. The obvious way to determine the correct functional form is to compare theory with experimental data for the stress dependence of strength and fatigue. However, the above analysis shows that environment effects can also be used to deduce the kinetics function. For example, n for any model should be a constant at a constant temperature; if it varies with the environment (e.g. humidity or pH) then that model is inappropriate.

Stress Dependence

The stress dependence can be determined in several ways. Observation of the v - K (dc/dt vs. K_I) behavior for macroscopic cracks is the most direct. Most such data are not sufficiently accurate and reproducible to distinguish between the three models discussed here. However, Helfinstine and Gulati¹⁸ (data shown in reference 19) made particularly extensive and careful measurements and found best agreement with the simple exponential, model 2. Muraoka and Abe²⁰ found similar results for both annealed and unannealed indentation cracks.

Alternatively, the stress dependence can be found indirectly by either static or dynamic fatigue. In this case we need to distinguish between the behavior of weak and “pristine” fiber. Data for deliberately weakened fiber usually exhibit too much scatter to identify the kinetics function. In a particularly extensive study of abraded fiber, Glaesemann²¹ shows high-speed dynamic fatigue data that show upwards curvature on a log-log plot hence showing a closer fit to the power law than the exponential forms.

The situation is clearer for pristine fiber behavior because the small scatter and ease of testing this material can readily provide data with the required precision. A review of the literature shows that most data for pristine fiber give a good fit to the power law, model 1 (provided the corrosive “knee” region is avoided). For example, power law behavior is observed for high speed dynamic fatigue in air²² and for long duration static fatigue in 80°C water²³ provided the fatigue knee is avoided. Particularly careful experiments designed to test the power law gave a best fit to it in both static and dynamic fatigue of both coated and bare fiber in both liquid and vapor.²⁴ This shows that the power law dependence is not a coating artifact since it is observed for bare silica. While model 1 gives the best fit, the simple exponential, model 2, gives a reasonable fit. Model 3 generally gives a poor fit to all data cited above.

Environment Dependence

The derivation above shows that the fatigue parameters should depend on the test environment in a particular way (equations 20 to 22). We have recently conducted careful experiments to measure the fatigue parameters as a function of the test environment in order to test the various kinetics functions. An important aspect of this work is that both coated and bare fiber have been considered in order to explicitly account for any coating effects. In general, coated fiber behaves in the same way as bare provided sufficient time is allowed for equilibration.

Humidity

Armstrong *et al.*¹¹ have measured the fatigue parameters as a function of humidity (20-95%) of fibers both bare and coated with a range of coatings including acrylate, silicone and polyimide. For the power law, it is found that almost all the humidity dependence is in n_1 , and little in A_1 ; *i.e.* the opposite of what is expected. This means that the “ B ” parameter is roughly constant, contrary to common assumptions. In contrast, almost all the humidity dependence is in

A_2 for model 2 and n_2 is roughly constant as the model assumes. For model 3, both n_3 and A_3 show humidity dependence; the agreement with this model is not as good as model 2 but better than model 1.

Armstrong *et al.*¹¹ found an effective reaction order of approximately 2 for humidity, confirming earlier work.⁸ In contrast to the earlier work, they showed this result is also valid for bare fiber and is independent of the kinetics function provided the data are analyzed correctly: the reaction order should be calculated assuming n is a *constant* with humidity, *even though it is not* for models 1 and 3.

pH

Taylor and Matthewson¹⁰ have measured the fatigue parameters in a range of pH buffers. The results are similar to those for humidity: model 2 gives the best fit to the data (*i.e.* n_2 shows the least dependence on pH) while models 1 and 3 show significant dependence of n on pH.

Temperature

Shiue and Matthewson²⁵ have measured the static fatigue parameters as a function of temperature in both distilled water and pH 7 buffer environments. The buffer maintains the pH at roughly 7 in the temperature range 25-90°C, while the pH of pure water decreases with temperature due to the temperature dependence of the dissociation constant of water, K_w ; pH 7 is basic compared to pure water above room temperature. As a result Shiue predicts that the apparent activation energy for static fatigue in water should be higher than in pH 7 buffer and verifies this prediction by experiment. This result explains for the first time the well-known observation that failure occurs faster in pH 7 buffer than in water at elevated temperatures; it can be explained by a simple pH effect rather than invoking some unknown interaction with the ions in the buffer. In other work Shiue²⁶ shows that entropy effects are important.

DISCUSSION

Summarizing these results, we observe that the stress dependence of the fatigue of high strength fiber generally gives a good fit to the unphysical power law kinetics function. In contrast, the environmental results are best described by the exponential form of model 2. Overall, model 2 is the most consistent description of both stress and environment. The most physically meaningful model, model 3, gives overall the worst description of experimental data.

The discrepancy between the stress and environment data will now be discussed. The situation can be understood if the underlying behavior is exponential but some factor perturbs the stress dependence in such a way that the exponential appears as a power law. Several mechanisms can be proposed.

Figure 2 shows a v - K diagram of crack growth velocity, v , as a function of the normalized stress intensity, κ . The diagram shows how the three kinetics functions would appear on a semi-log plot. If the underlying behavior were exponential, then the straight line shown in the diagram would have to have concave downwards curvature in order to appear like a power law. In other words, the crack growth or degradation rate would have to be slower than expected at low applied stress. One can postulate several

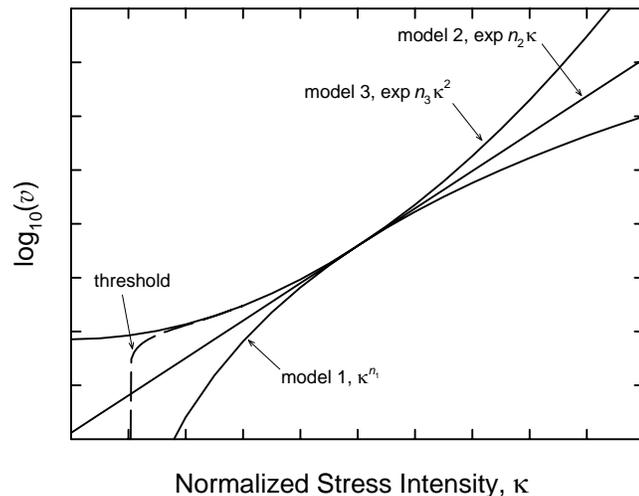


Figure 2. Schematic on a semi-log scale of the expected v - κ behavior for the three kinetics functions.

mechanisms that could have such an effect.

The analysis presented here ignores the effect of the reverse reaction in which silanol groups at the crack tip condense to eliminate water and reform a siloxane bond, thus healing the crack. Healing will be more significant at low applied stress. Lawn's model² does account for a reverse reaction which leads to a threshold K_{I1} . However, because v is so sensitive to K_I (n is so large), the reverse reaction only has any significant effect close to the threshold. The dashed line in figure 2 shows how the reverse reaction influences model 3; it has negligible effect away from the threshold and so can not explain the overall reshaping towards the power law.

Another possibility is that in the high strength material the flaws are of atomic dimension. Growth of the flaws means breaking discrete bonds and perturbations from continuous growth could be large. Scanlan²⁷ presents a bond failure model in which the crack is modeled as a ladder of bonds (figure 3). The effective crack growth rate depends on the bond length, a , and the mean time to failure of the bond, \bar{t} . He assumes \bar{t} is Arrhenius with model 2 stress dependence:

$$\frac{dc}{dt} = \frac{a}{\bar{t}} \propto a \exp(b K_I). \quad (23)$$

Scanlan shows the time it takes to break the first bond is a significant part of the time to failure. This is a bigger effect at short times/high stress to failure, thus providing a systematic perturbation with stress potentially turning the exponential into an apparent power law. Figure 4 shows the results of simulations of static fatigue using Scanlan's approach. The figure shows the results for both the discrete (solid line) and the continuous (circles) growth of the crack using identical fatigue parameters for both. The results coincide except at the very shortest times. Therefore the discrete nature of the bond rupture has negligible effect on the overall failure kinetics and can not explain the power law.

Also shown in figure 4 is the time it takes the first bond to break in the discrete model (dashed line). At short failure times the first bond can account for half of the time to failure and still accounts for 10% at long times. This illustrates a difficulty with our understanding of the behavior of high strength fiber. Scanlan's bond rupture model considers the mean time to failure for each bond but any given bond will have a constant probability of failure per unit time, p (which depends on stress) giving an exponential distribution of failure times:

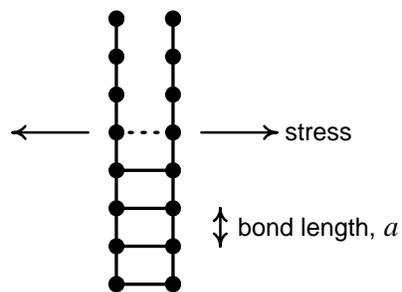


Figure 3. Schematic of the bond failure model due to Scanlan.²⁷

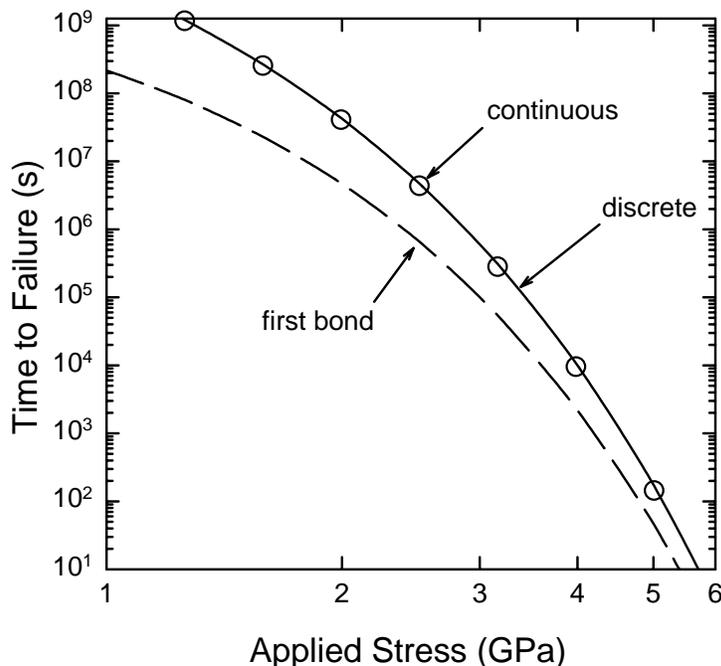


Figure 4. Predicted static fatigue behavior using Scanlan's bond failure model²⁷ (solid line) and the continuous growth function, equation 4 (circles). Also shown is the mean time to failure of the first bond in Scanlan's model (dashed line).

$$F(t) = \frac{1}{p} \exp(-pt). \quad (24)$$

The standard deviation and mean of this distribution have the same value, so that their ratio, the dispersion, is 100%. The dispersion in the total time to failure will be less than this since it involves averaging over several bonds. In other work Scanlan²⁸ shows that the Weibull modulus (an inverse measure of the dispersion) can be related to the number of bonds broken before catastrophic failure ensues. Therefore we expect more scatter in the time to failure in the stronger material since fewer bonds are averaged before catastrophic failure occurs. This is not observed in experiment; the scatter in the strength of pristine fiber is extremely small.²⁹ While the scatter in time to failure is larger, most of it can be understood from the experimental variability in the applied stress.³⁰

Other possibilities that might result in apparent power law kinetics could involve the stochastic nature of the glass structure. For example, a semi-circular surface flaw will have fewer crack tip bonds than a larger flaw. Since the bond strength is statistically scattered, this means the weakest bond at the tip of a small flaw is stronger than the weakest for a large flaw, thus providing a systematic perturbation with stress. However, these and related ideas remain topics for future research.

CONCLUSIONS

In this paper we present a unified chemical kinetics model which can incorporate any of the commonly used crack growth kinetics models as a single kinetics function. We show that the effects of stress and environment are not separable and make specific predictions for how the fatigue parameters should vary with environment. Many of these predictions have been verified by experiment. While the model is derived assuming the presence of sharp stress-free cracks, this assumption is not valid for defects in the strength range of practical interest (from the proof stress, ~0.7 GPa, up to the inert strength, ~12 GPa). However, the results are not sensitive to this assumption and the model is therefore still useful as a phenomenological description of a thermally activated stress-assisted degradation process.

Reliability predictions are sensitive to the assumed form of the kinetics function. Comparisons with experimental data do not provide a unique answer for the form; except for macroscopic crack growth data, the stress dependence is best described by the unphysical power law while environmental dependence is best described by a simple exponential. The exponential provides the best overall description of both effects. It must be noted that the exponential form gives shorter times to failure than the widely used power law form; this has obvious practical implications.

These results can be rationalized if it is assumed that the underlying kinetics function is the exponential, as evidenced by the environmental dependence and the behavior of macroscopic cracks, but that something peculiar to very high strength silica glass perturbs the stress dependence so that it appears to be a power law. While we propose several possible causes of this behavior involving the discreet and random nature of the glass, some are disproved and the rest are merely speculative at this stage.

Most of the data discussed here are for “pristine” silica fibers. In practice one is more interested in weaker flaws with strengths similar to the proof stress. Such flaws are difficult to study, especially because of the large scatter in their behavior. However it would be interesting to accurately determine the kinetics of their behavior though residual stresses can perturb their behavior.³¹

REFERENCES

1. S.M. Wiederhorn, *J. Am. Ceram. Soc.* **55** (2) 81-85 (1972).
2. B.R. Lawn, *J. Mat. Sci.* **10** 469-480 (1975).
3. M. Tomozawa, *Annu. Rev. Mater. Sci.* **26** 43-74 (1996).
4. K. Jakus, J.E. Ritter, Jr. and J.M. Sullivan, *J. Am. Ceram. Soc.* **64** (6) 372-374 (1981).
5. G.M. Bubel and M.J. Matthewson, *Opt. Eng.* **30** (6) 737-745 (1991).

6. W. Griffioen, *Opt. Eng.* **33** 488-497 (1994).
7. Rep. # TIA/EIA-445-76 (TIA, Washington, DC, 1993)
8. W.J. Duncan, P.W. France and S.P. Craig, in Strength of inorganic glass edited by C.R. Kurkjian (Plenum Press, New York, 1985) pp. 309-328.
9. H.H. Yuce, J.P. Varachi, Jr., J.P. Kilmer, C.R. Kurkjian and M.J. Matthewson, OFC'92 Tech. Digest postdeadline paper-PD21 (1992).
10. A.T. Taylor and M.J. Matthewson, *Proc. 47th Int. Wire & Cable Symp.* (in press).
11. J.L. Armstrong, M.J. Matthewson, C.R. Kurkjian and C.Y. Chou, Proc.46th Int.Wire & Cable Symp. (IWCS, Inc. Eatontown, NJ, 1997) pp. 902-909.
12. J.L. Armstrong, M.J. Matthewson and C.R. Kurkjian (in this volume).
13. C.R. Kurkjian, J.L. Armstrong, M.J. Matthewson and I.M. Plitz, *Proc. Nat. Fiber Optic Engineers Conf.* **2** 133-138 (1996).
14. C.Y. Chou, J.L. Armstrong and M.J. Matthewson, abstract in *Am. Ceram. Soc. Bull.* **77** (4) 234 (1998).
15. K. J. Laidler, Chemical kinetics, 3rd ed. (Harper & Row, New York, NY, 1987).
16. I. Scanlan (unpublished work).
17. S.M. Wiederhorn and L.H. Bolz, *J. Am. Ceram. Soc.* **53** (10) 543-549 (1970).
18. J.D. Helfinstine and S.T. Gulati, abstract in *Ceram. Bull.* **71** 470 (1992).
19. S.T. Gulati, *Mat. Res. Soc. Proc.* **144** 67-85 (1992).
20. M. Muraoka and H. Abé, *J. Am. Ceram. Soc.* **79** (1) 51-57 (1996).
21. G.S. Glaesemann, *Proc. Soc. Photo-Opt. Instrum. Eng.* **2611** 38-44 (1996).
22. T. Svensson and A. Hjorth, *Proc. 45th Int. Wire & Cable Symp.* 490-494 (1996).
23. E. Cuellar, M.T. Kennedy and D.R. Roberts, *Proc. Soc. Photo-Opt. Instrum. Eng.* **1791** 7-17 (1992).
24. M.J. Matthewson (unpublished work).
25. Y.S. Shiue and M.J. Matthewson (this volume).
26. Y.S. Shiue, PhD thesis, Rutgers University, 1998.
27. I.F. Scanlan, abstract in *Ceram. Bull.* **68** 741 (1989).
28. I. Scanlan, in Physics of Fiber Optics (Advances in Ceramics V 2) edited by R. Bendow and S.S. Mitra (Am. Ceram. Soc. Columbus, OH, 1981) pp. 166-175.
29. C.R. Kurkjian, J.T. Krause and U.C. Paek, *J. de Phys.* **43** (12) C9-585-586 (1982).
30. M.J. Matthewson and C.R. Kurkjian, *J. Am. Ceram. Soc.* **70** (9) 662-668 (1987).
31. C.R. Kurkjian, M.J. Matthewson and M.M. Chaudhri (in this volume).