

Activation energy and entropy of dynamic fatigue of pristine silica optical fibers

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ABSTRACT

Subcritical crack growth in fused silica can be modeled as a stress assisted chemical reaction between water and strained bonds at the crack tip. The stress influences the crack growth rate by reducing the free energy of the activated complex. In principal, the stress changes both the activation enthalpy (energy) and entropy; however, the influence of stress on entropy has generally been ignored. The dynamic fatigue behavior of “pristine” optical fiber can be used to determine the fatigue kinetics parameters with unprecedented precision. It is shown that the entropy contribution is at least as significant as the enthalpy and therefore should not be ignored.

Keywords: Optical fiber, strength, fatigue, reliability, activation energy, entropy.

1. INTRODUCTION

1.1 Fatigue models for silica glass

The fatigue model which has been most commonly used for brittle ceramic materials is the well-known subcritical crack growth model.¹ A crack locally amplifies the applied stress, σ_a :

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

where K_I is the stress intensity factor, Y is a parameter which describes the crack shape, and c is the length of the crack. The principal mechanism for subcritical crack growth involves the combined influence of stress and chemical reactions with reactive environmental species. Fatigue (strength degradation under stress) in silica glass is well known to result from the chemical reaction between strained siloxane bonds and ambient moisture.^{2,3,4}

A mathematical form for the kinetics of crack growth is needed to estimate the failure time. Various kinetics models have been proposed in the literature, which describe the relationship between the stress intensity and the resulting slow crack growth velocity, \dot{c} . The first model considered here is the widely used empirical power law:^{5,6}

$$\dot{c} = A_1 (K_I)^{n_1}; \quad \text{model 1} \quad (2)$$

the second model is based on simple chemical kinetics:^{7,8}

$$\dot{c} = A_2 \exp(n_2 K_I); \quad \text{model 2} \quad (3)$$

and the third model is obtained by simplifying a chemical potential model⁹ by ignoring the reverse reaction:^{10,11}

$$\dot{c} = A_3 \exp(n_3 K_I^2). \quad \text{model 3} \quad (4)$$

The A_i are parameters which depend upon the environment and the material, and the n_i are the fatigue parameters which are also known as the stress corrosion susceptibility. It is not known which of these three mathematical form best describes the fatigue of silica glass.^{11,12} Therefore, all three models will be used in this paper to analyze dynamic fatigue data for fused silica optical fiber.

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1.2 Activation enthalpy and entropy for subcritical crack growth

Subcritical crack growth in silica can be treated as a stress assisted chemical reaction between water and silica. Absolute reaction rate theory, which considers a short-lived activated complex that must be formed for the reaction to proceed, can be used to explain the reaction rate of a chemical reaction,¹³ and will be used to discuss the crack growth reaction. The activation free energy is reduced by the applied stress thus increasing the reaction rate. However, it is generally assumed that the stress reduces the activation enthalpy (the “activation energy”) and the influence of stress on that activation entropy is not considered.

The three kinetics models suggest different stress dependencies for the activation energy: model 1 suggests that the activation energy depends logarithmically on stress,¹² model 2 suggests the stress dependence is linear, and model 3 suggests it is quadratic. Published studies of the stress dependence of the apparent activation energy for fatigue of silica optical fibers are inconclusive.^{14,15}

Absolute reaction rate theory states that the rate constant of a chemical reaction, k_r , is:¹³

$$k_r = \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right), \quad (5)$$

where k_B is Boltzmann’s constant, h is Planck’s constant, κ is the transmission coefficient which is usually taken as unity, and ΔG^\ddagger is the free energy of the activated complex relative to the initial state. Since the free energy is composed of both enthalpy and entropy terms, and the reaction dominating the crack growth is stress assisted, it is reasonable to assume that **both** the activation enthalpy and entropy are stress dependent. If the stress dependency is linear, *i.e.*, model 2 is correct, the activation enthalpy $\Delta H^\ddagger(K_I)$ and the activation entropy $\Delta S^\ddagger(K_I)$ can be written as:

$$\Delta H^\ddagger(K_I) = \Delta H_0^\ddagger - b_{H2} K_I, \quad (6)$$

$$\Delta S^\ddagger(K_I) = \Delta S_0^\ddagger + b_{S2} K_I; \quad (7)$$

so that the total free energy of activation is given by:

$$\Delta G^\ddagger = \Delta H^\ddagger(K_I) - T\Delta S^\ddagger(K_I). \quad (8)$$

ΔH_0^\ddagger and ΔS_0^\ddagger are the activation parameters in the limit of zero applied stress. The signs of the terms containing b_{H2} and b_{S2} are chosen such that if these parameters are positive, increasing K_I decreases the barrier height and so increases the crack growth rate.

Combining Eqs. (5) and (8), the crack growth velocity can be expressed as:¹⁶

$$\dot{c} = c_0 \cdot k_r = c_0 \frac{k_B T}{h} \exp\left(\frac{-\Delta H^\ddagger(K_I) + T\Delta S^\ddagger(K_I)}{RT}\right), \quad (9)$$

where c_0 is the increase in crack length per breaking bond. Substitution of Eqs. (6) and (7) give:

$$\dot{c} = c_0 \frac{k_B T}{h} \exp\left(\frac{-\Delta H_0^\ddagger}{RT} + \frac{\Delta S_0^\ddagger}{R}\right) \exp\left[\left(\frac{b_{H2}}{RT} + \frac{b_{S2}}{R}\right) K_I\right]. \quad (10)$$

Comparing Eqs. (10) with (3) enables interpretation of the fatigue parameters in terms of fundamental kinetic parameters:

$$A_2 = c_0 \frac{k_B T}{h} \exp\left(\frac{-\Delta H_0^\ddagger}{RT} + \frac{\Delta S_0^\ddagger}{R}\right), \quad (11-1)$$

$$n_2 = \frac{b_{H2}}{RT} + \frac{b_{S2}}{R}. \quad (11-2)$$

This derivation is based on the assumption that the reaction depends on the stress linearly. However, if the stress dependency is quadratic, *i.e.*, model 3 is correct, we can write $\Delta H^\ddagger(K_I)$ and $\Delta S^\ddagger(K_I)$ as followings:

$$\Delta H^\ddagger(K_I) = \Delta H_0^\ddagger - b_{H3} K_I^2, \quad (12)$$

$$\Delta S^\ddagger(K_I) = \Delta S_0^\ddagger + b_{S3} K_I^2. \quad (13)$$

Following the same approach as for model 2, the fatigue parameters for model 3 are given by:

$$A_3 = c_0 \frac{k_B T}{h} \exp\left(\frac{-\Delta H_0^\ddagger}{RT} + \frac{\Delta S_0^\ddagger}{R}\right), \quad (14-1)$$

$$n_3 = \frac{b_{H3}}{RT} + \frac{b_{S3}}{R}. \quad (14-2)$$

Unlike models 2 and 3, model 1 does not have any special physical meaning, and as is commonly assumed, n_1 is taken as constant at all temperatures, and A_1 is assumed to exhibit Arrhenius temperature dependence, which is stress independent. Matthewson¹² shows that a consistent model can be developed if the activation parameters vary linearly with $\ln K_I$. However, we can still write the fatigue parameters for model 1 as:

$$A_1 = A_0 \exp\left(\frac{-\Delta H_0^\ddagger}{RT} + \frac{\Delta S_0^\ddagger}{R}\right), \quad (15-1)$$

$$n_1 = \frac{b_{H1}}{RT} + \frac{b_{S1}}{R}. \quad (15-2)$$

Clearly, this derivation shows that the stress dependence of the activation entropy could play an important role in fatigue. This is expected because the activated complex will have fewer rotational and translation degrees of freedom than the reactants, so that an entropic contribution to the activation barrier height will exist.

1.3 Background

There has been little published work concerning activation entropy. The activation entropy for fatigue of a porous alumina was found to be stress dependent by Avigdor and Brown.¹⁷ The importance of activation entropy to the crack growth rate in bulk silica was first proposed by Scanlan.¹⁶ He reanalyzed crack growth rate data for bulk silica glass of Wiederhorn and Bolz,⁸ and showed that not only the activation enthalpy depends on stress, the activation entropy is stress dependent as well.¹⁶ Inness *et al.*¹⁸ reanalyzed static fatigue data of Kao¹⁹ for silica optical fiber, and showed that the activation entropy term exists. However, the effect of stress on the entropy was not discussed in their paper. In all these studies, the data were not extensive and detailed enough to accurately assess the entropy effects.

All the earlier studies on activation entropy were on static fatigue data. Such data are convenient to use since the fatigue parameters can be obtained graphically for all three kinetics models.¹⁰ However, static fatigue is experimentally less convenient than dynamic fatigue. Dynamic fatigue experiments can generate fatigue data within a reasonable duration but the fatigue parameters need to be determined by numerical integration.¹⁰

For the work described here, pristine silica optical fiber was used because it exhibits high strength with an extremely narrow strength distribution; this improves the accuracy of the fatigue data obtained, and thus makes the estimates of the fatigue parameters more accurate. In contrast to previous work in which specimens were subjected to tensile stresses, we have measured the strength of the fiber using a two-point bend technique,^{20,21} which can measure the strength of many specimens simultaneously. The work presented in this paper aims to study the activation enthalpy (energy) and entropy by examining the temperature dependence of the fatigue parameters.

2. EXPERIMENTAL PROCEDURES

Dynamic fatigue experiments were performed on a polymer coated fused silica optical fiber using a two-point bend technique with five faceplate speeds: 0.1, 1, 10, 100, and 1000 $\mu\text{m/s}$.²² The fiber used was of standard configuration with a 125 μm glass diameter and a 250 μm diameter UV-curable acrylate coating. The strength of the fiber was measured in distilled water at temperatures ranging from 30°C to 80°C, controlled to $\pm 0.1^\circ\text{C}$. Twenty specimens were measured under

each testing condition. All specimens were pre-equilibrated at room temperature in distilled water over night before performing the dynamic fatigue tests. The fibers were not pre-equilibrated under the testing conditions (*i.e.*, at the high temperatures) to avoid the possible strength degradation caused by zero stress aging. The samples were immersed in the testing environment at the test temperature for 5 minutes before starting the experiments to ensure the fiber reached thermal equilibrium.

The fatigue parameters, A_i and n_i , were determined by fitting the three different kinetics models to the data using a computer program written for this purpose. The values of certain parameters needed to be assumed to determine the fatigue parameters, their values were: the critical stress intensity factor $K_{IC} = 0.75 \text{ MPa}\cdot\text{m}^{1/2}$, $Y = 1.16$, and the initial strength $\sigma_i = 12 \text{ GPa}$. These values do not influence the estimates of the n_i ; they do influence the magnitude of the A_i but the trends in the A_i are not affected. None of the conclusions we will draw from this work depend on these values.

3. RESULTS AND DISCUSSION

3.1 Strength and as-calculated fatigue parameters

Figure 1 shows the mean strength of the fiber with error bars representing a 95% confidence interval²³ at various temperatures as a function of the faceplate speed. The 95% interval is the confidence on the mean, *i.e.* 95% of estimates of the “mean” would lie in this range, not 95% of the data.²³ As expected, the strength exhibits little scatter. The fatigue parameters, n_i and A_i , found by fitting the kinetics models to the dynamic fatigue data in figure 1, are shown as a function of temperature in figures 2 and 3. Comparing figures 2 and 3, A_i shows roughly Arrhenius behavior, while n_i does not change significantly with temperature. In contrast for models 2 and 3, the temperature dependence is predominately in n_i , rather than in A_i . However, the large error bars shown in figures 2 and 3 raise doubts about what the real temperature dependencies are.

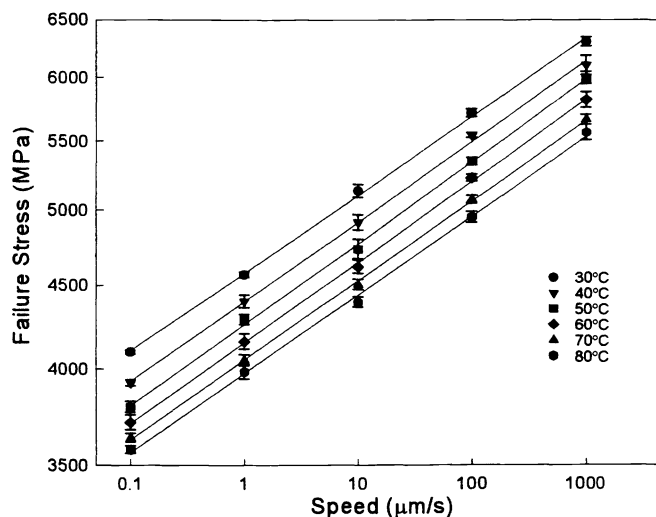


Figure 1. The strength of the fiber measured at various temperatures as a function of faceplate speed .

3.2 Confidence intervals and constrained fatigue parameters

The 95% confidence intervals for A_i and n_i were determined together with their variances and covariances. Figure 4 is a schematic of the 95% confidence ellipse of the $\log A_i$ and n_i . Both parameters can have significant uncertainty in their value even though the overall quality of fit (represented by the area of the ellipse) is small. If one of the parameters can be determined with high precision, the correlation means that the uncertainty in the other parameter is automatically reduced as well. Each kinetics model assumes that the n_i is a constant with temperature. Therefore a better estimate for the n_i can be found by averaging all the estimates for the different temperatures. As shown in figure 4, constraining n_i to be this mean value greatly reduces the error bar in A_i . Reanalyzing the data in this way indeed greatly reduces the error bars of A_i , but the temperature dependence trends are the same as shown in figure 3. This proves the trends with temperature seen in figures 2 and 3 are real, despite the large error bars.

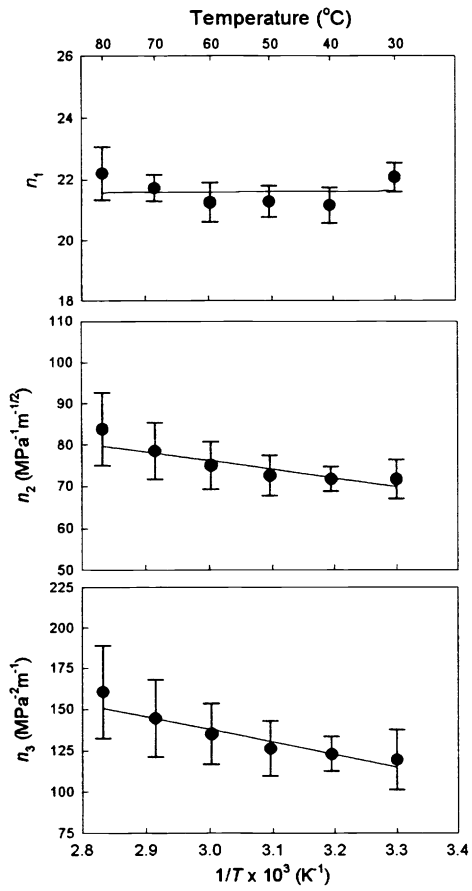


Figure 2. As-calculated n_i for (a) model 1, (b) model 2, and (c) model 3 as a function of temperature.

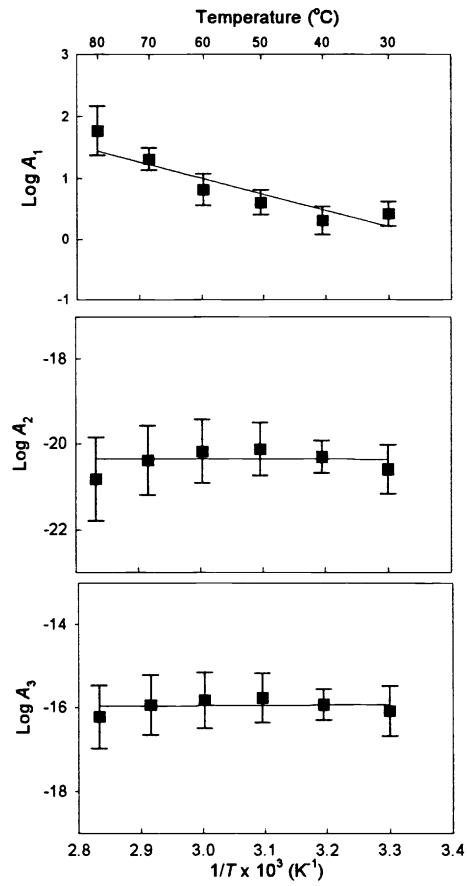


Figure 3. As-calculated $\log A_i$ for (a) model 1, (b) model 2, and (c) model 3 as a function of temperature.

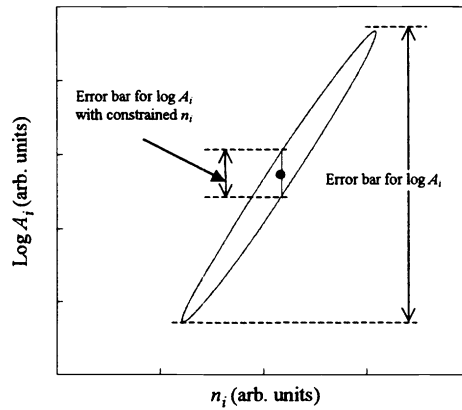


Figure 4. The 95% confidence ellipse relation for A_i and n_i .

3.3 Activation enthalpy and entropy

The activation enthalpy and entropy in the limit of zero stress are given approximately by the slope and intercept of the regression line shown in figure 3. However, from Eqs. (11-1) and (14-1), the activation enthalpy and entropy for models 2 and 3 are more accurately obtained from the slope and the intercept of a plot of $(\ln A_i - \ln T)$ vs. $1/T$. The $\ln T$ term is usually neglected in the literature, since it has little effect on the results. Calculations show that the enthalpy obtained from $\ln A_i$ vs. $1/T$ (*i.e.*, figure 3) and $(\ln A_i - \ln T)$ vs. $1/T$ only differ by ~ 3 kJ/mol, which is less than the 95% confidence interval. However, for accuracy, the $\ln T$ term has been taken into account here.

To obtain the value of the entropy, it is necessary to assume a value for c_0 . For the calculations here, c_0 is assumed to be 2.5 \AA , the same value used by Scanlan.¹⁶ The values of the zero stress activation enthalpy and entropy calculated from figure 3 for the three kinetics models are summarized in table 1.

Table 1. Summary of the zero stress activation enthalpy and entropy for the three kinetics models.

| | Model 1 | Model 2 | Model 3 |
|----------------------------------|-----------------|------------------|------------------|
| ΔH_0^\ddagger (kJ/mol) | 51 ± 8 | -2 ± 14 | -4 ± 9 |
| ΔS_0^\ddagger (kJ/mol·K) | 0.16 ± 0.03 | -0.46 ± 0.04 | -0.38 ± 0.03 |

As shown in table 1, the activation enthalpy calculated using model 1 is in agreement with the previous activation energy results obtained from static fatigue data.¹⁵ (Note that the static fatigue results did not assume a kinetics model). However, the activation enthalpy calculated using models 2 and 3 are negligible. The activation entropy for model 1 is positive, but is negative for models 2 and 3. Since the water molecules react with silica to form an activated complex, it is expected the reactants are more disordered than the activated state, *i.e.*, the activation entropy should be negative.²⁴ The results shown in table 1 therefore indicate two things. Firstly, model 1 exhibits a positive zero-stress entropy which is not expected. Secondly, models 2 and 3 have effectively zero activation enthalpy when there is no applied stress. The reaction then is dominated by the activation entropy, which is negative as expected.

3.4 Stress dependence of the activation enthalpy and entropy

The results in table 1 are the activation parameters extrapolated to zero applied stress. We will now consider how the activation parameters vary with finite stress. Model 1 usually assumes the activation energy is stress independent, and that n_1 is roughly a constant as shown in figure 2(a). However, the activation enthalpy and entropy obtained for models 2 and 3 do show stress dependence. The b_{Hi} and b_{Si} , which represent the stress dependence, can be calculated from the slope and intercept of the linear fits to the data of figure 2. Table 2 summarizes the stress dependence results. It is observed that both b_{Hi} for models 2 and 3 are negative. This means the activation enthalpy would increase with the increasing stress. Although this is an unexpected result, it is in consistent with some apparent activation energy data obtained from the static fatigue experiments.¹⁵ The activation entropy is also found to be stress dependent. All the b_{Si} are positive, meaning the activation entropy increases with the increasing stress. This stress dependence on the activation entropy is consistent with the previous results for slow crack growth in bulk silica glass,¹⁶ and the static fatigue of porous alumina in water.¹⁷

Table 2. Values of the b_i (SI units), representing the stress dependence of the activation enthalpy and entropy.

| | Model 1 | Model 2 | Model 3 |
|-------|--------------------------------|---------------------------------|---------------------------------|
| b_H | $(0.1 \pm 1.3) \times 10^{-1}$ | $(-1.8 \pm 0.5) \times 10^{-1}$ | $(-6.4 \pm 1.1) \times 10^{-7}$ |
| b_S | $(2 \pm 0.4) \times 10^{-3}$ | $(1.2 \pm 0.1) \times 10^{-3}$ | $(3.1 \pm 0.4) \times 10^{-9}$ |

4. CONCLUSIONS

Dynamic fatigue of a polymer coated fused silica optical fiber was performed in distilled water using the two-point bend technique and the results were fitted to three kinetics models. The fatigue parameters, A_i and n_i , were obtained from dynamic

fatigue data taken over a range of test temperatures. It is found that the temperature dependence is mainly shown in the n , for the power law, while it is mostly shown in the A , for the exponential forms.

These results are then used to determine how the activation enthalpy and entropy depend on stress. This is the first time the activation enthalpy and entropy have been measured and discussed together. It is found for all models that the activation entropy is significant. Further, if the data are interpreted in terms of the exponential forms, the calculated activation barrier height and its decrease with stress are dominated by the activation entropy. Clearly, entropy effects must be considered when analyzing the temperature dependence of fatigue.

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