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Journal of Non-Crystalline Solids 297 (2002) 91–95

JOURNAL OF  
NON-CRYSTALLINE SOLIDS

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# The fatigue of high-strength fused silica optical fibers in low humidity <sup>☆</sup>

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Received 17 July 2001

## Abstract

The strength and dynamic fatigue of UV-acrylate coated silica optical fibers were measured as a function of relative humidity in the range  $\sim 0.025$ –13% at 25 °C. The degradation kinetics of silica in low humidities was investigated and it was found that the reaction order was approximately first-order with respect to humidity. In our previous work, a second-order reaction was found in the humidity range 20–95% RH at 25 °C and the process for obtaining this reaction order was found to be independent of the mathematical form of the kinetic models used. The change in reaction order observed here verifies some earlier results based on the power law which implied a change in the reaction order from  $\sim 2$  (15–100% RH) to  $\sim 1$  at low humidity ( $< 0.01\%$ ). © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

In previous work [1] three different mathematical forms of a chemical kinetics model were compared and it was found that the model proposed by Wiederhorn and Bolz [2] best described the effect of humidity on the kinetics of subcritical crack growth in high strength optical fibers. This model, which effectively treats the stress at the crack tip as if it were a negative pressure, predicts that the rate of subcritical crack growth is given by

$$\frac{dc}{dt} = A \exp n \left( \frac{K_I}{K_{IC}} \right), \quad (1)$$

where  $A$  and  $n$  are fatigue parameters and  $K_{IC}$  is the critical stress intensity factor.  $K_I$  is normalized by  $K_{IC}$  in order to make  $n$  dimensionless. The influence of humidity on the crack growth rate can be incorporated into this model by assuming a simple chemical kinetics model for fatigue in which the reaction rate between water and silica shows Arrhenius temperature dependence [1]. This gives

$$A = v f(\text{RH}) \exp \left( - \frac{Q_0}{RT} \right) \text{ and } n = \frac{b}{RT}, \quad (2)$$

where  $Q_0$  is the apparent activation energy at zero applied stress,  $v$  is a frequency factor,  $b$  is a constant and the function  $f(\text{RH})$  expresses the dependence of reaction rate on relative humidity.  $f(\text{RH})$  is assumed to be a simple power law

<sup>☆</sup> Supported by Telcordia Technologies, Morristown, NJ.

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$$f(\text{RH}) = \text{RH}^m, \quad (3)$$

where RH is the relative humidity at a particular temperature, and  $m$  is the reaction order. For simple reactions  $m$  can be interpreted as the molecularity of the reaction.

The effect of humidity on slow crack growth in silicate glasses has been evaluated by direct measurement of the crack velocity as a function of stress intensity, temperature, and humidity [3–5]. Wiederhorn [3] found a change in the reaction order with respect to humidity from  $\sim 1$  (10–100% RH) to  $\sim 1/2$  at low humidity (<1% RH) for sub-critical crack growth in soda-lime silicate glasses. This implies that there is a change in the rate controlling mechanism in the silica and water reaction. However, the slow crack growth data are not accurate enough to determine the mathematical form of the kinetics model (e.g. power law or exponential dependence on  $K_I$ ), and the relevance of the data for such large cracks to the behavior of high strength (>1 GPa) silica fiber is not clear.

Duncan et al. [6] and Sakaguchi and Kimura [7] studied the dynamic fatigue of silicone rubber coated fused silica fibers and their results showed a second-order dependence at moderate humidities. The low humidity data (<0.01% RH) of Duncan et al. [6] (see Fig. 1) implies an approximate first-order dependence on humidity, which suggests that the kinetics of the silica and water reaction may be changing for silica fibers also. However, Duncan et al. [6] interpreted their results in terms of a power law, which is defined as follows:

$$\frac{dc}{dt} = A_p K_I^{n_p}, \quad (4)$$

where  $A_p$  and  $n_p$  are fit parameters equivalent to  $A$  and  $n$  in Eq. (1). Duncan et al. [6] estimated the silica and water degradation reaction order by multiplying the slope of the log strain versus log relative humidity (Fig. 1) by  $(1 - n_p)$ . The reasoning behind this can be seen by looking at the relationship between the failure stress ( $\sigma_f$ ) or strain ( $\epsilon_f$ ) and  $A_p$  for two-point bending at a constant faceplate speed, assuming the power law model (Eq. (4)) [8]

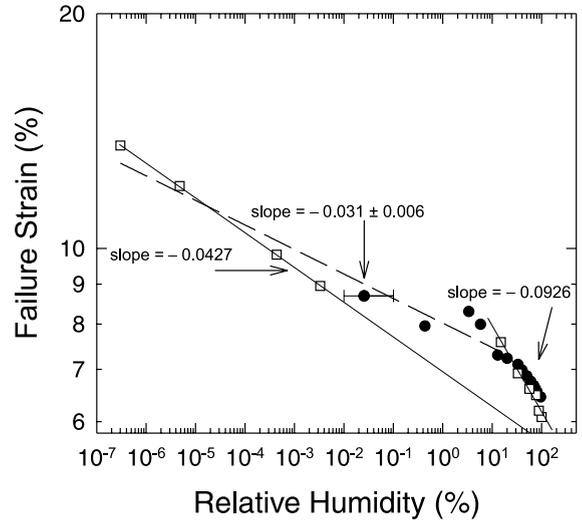


Fig. 1. Strain to failure as a function of relative humidity for (□) silicone coated fiber (Duncan et al. [6]) and (●) dual acrylate coated fiber (present work).

$$\begin{aligned} (E\epsilon_f)^{n_p-1} &= \sigma_f^{n_p-1} \\ &= \frac{(n_p - 1)}{(n_p - 2)A_p E Y^2 (1.198)r} \left( \frac{\sigma_i}{K_{IC}} \right)^{n_p-2} v, \end{aligned} \quad (5)$$

where  $E$  is the elastic modulus,  $Y$  is the crack shape parameter,  $r$  is the radius of the glass fiber, and  $A_p$  is a fit parameter for the power law that can be defined as

$$A_p = v_p \text{RH}^m \exp\left(-\frac{Q}{RT}\right). \quad (6)$$

Eqs. (5) and (6) show that  $\epsilon_f^{n_p-1}$  is proportional to  $1/(\text{RH}^m)$ , so that the slope of the log  $\epsilon_f$  versus log RH is  $m/(1 - n_p)$ . An implicit assumption of Duncan et al. [6] was that the fatigue parameter,  $n_p$ , is a constant and therefore is the same in the high and low humidity regions. They assumed a value of 20 for  $n_p$  suggesting a reaction order of  $\sim 1$  for low humidity and  $\sim 2$  for high humidity, but the calculation of these reaction orders might well be dependent on the use of a power law kinetics model. In addition, the precision of these data can be questioned since, if the data are graphed on a single relative humidity axis, the trends of the low and high humidity data do not intersect at an in-

intermediate humidity. This result does not appear reasonable, but was not obvious since the data were originally graphed with a break and change of scale in the humidity axis [6].

In previous work [1] the kinetics of fatigue of fused silica in humidity in the range 20–95% were studied by measuring the strength and fatigue of high strength fused silica fibers. These results showed that the degradation reaction order was  $\sim 2$  with respect to humidity and also that by use of appropriate calculation methods this reaction order is not dependent on the form of the kinetics model assumed. In this paper, the work has been extended to investigate if a change in the reaction kinetics really occurs at low humidity.

## 2. Experimental procedures

The specimen used in this study was a standard telecommunications grade optical fiber, which consists of 125  $\mu\text{m}$  diameter fused silica fiber coated with dual UV-curable polyurethane–acrylate coatings, giving an overall diameter of 250  $\mu\text{m}$ . The strength of the fiber was measured at five different faceplate velocities (1, 10, 100, 1000, 5000  $\mu\text{m}/\text{s}$ ) using a two-point bend apparatus [9]. The strength was measured in a glove box with the humidity ranging from  $\sim 0.025\%$  to 13% at 25 °C. A DigiSense<sup>2</sup> dewpoint/humidity meter was used to measure the moisture content of the air in the glove box. The sensing range of this meter is  $-50$ – $70$  °C dewpoint temperature, which corresponds to 0.124–100% RH at 25 °C. The glove box environment was controlled by flowing dry nitrogen<sup>3</sup> with an initial moisture content of  $\leq 8$  ppm by volume (which corresponds to  $\leq 0.025\%$  RH at 25 °C) through a water bubbler and then into the box. The moisture content of the nitrogen was controlled by varying the flow rate of the nitrogen gas into the bubbler i.e., slower flow rates resulted in higher moisture content. The driest environment was achieved by steadily flowing dry nitrogen gas into the glove box without using the bubbler. Since

the amount of moisture in the dry nitrogen is specified to be  $\leq 8$  ppm, or  $\leq 0.025\%$  RH, and since this was outside the range of the dewpoint meter it was assumed that this environment corresponds to 0.025% RH. On all of the figures shown in this paper, an error interval has been placed on this data point, which ranges 0.01–0.1% RH, to emphasize the uncertainty in the relative humidity in this particular environment.

Before the fatigue measurements were made on the coated fiber, it was equilibrated in the particular test environment for times ranging from one day ( $>1\%$  RH) to two weeks (0.025% RH). Twenty samples were measured at each speed. The higher humidity strength data were obtained by a similar method [1]. The strength data were fitted to the crack growth kinetics model (Eqs. (1) and (4)) and the fatigue parameters,  $A$ ,  $A_p$ ,  $n$  and  $n_p$ , were determined together with their confidence intervals.

## 3. Results

Fig. 1 shows the results from the work of Duncan et al. [6], which were obtained by measuring the two-point bend strength at a faceplate velocity 37.5  $\mu\text{m}/\text{s}$  in low humidity environments. These environments were obtained by reducing the pressure with a vacuum pump. The humidity was calculated assuming that the mole fraction of moisture did not change with pressure, but these values were not checked by measurement. Also shown in this figure are the results obtained for the dual acrylate coated fiber, which were found by interpolating a linear regression fit to the results of all five faceplate speeds to a speed of 37.5  $\mu\text{m}/\text{s}$  [10]. In Fig. 1, straight solid lines fitted separately to the low ( $<20\%$ ) and high humidity ( $\geq 20\%$ ) data of Duncan et al. [6] intersect beyond 100% relative humidity, which was unexpected, whereas the low humidity (0.025–13% RH) results for the dual acrylate coated fiber intersect the high humidity results (20–95% RH) at around 20%. Drying and absorption studies on silica have found that upon re-adsorption, a monolayer of coverage occurs at 18% RH [11]. This suggests that a change in the degradation reaction might be occurring

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after a monolayer of water is formed on the silica glass surface.

In Fig. 2, the fatigue parameters calculated from Eq. (1) are shown, and  $n$  is roughly constant at  $\sim 50$ . Fig. 3 shows  $\log A$  as a function of humidity. By definition (Eqs. (2) and (3)) the slope of  $\log A$  versus  $\log$  relative humidity is the reaction order,  $m$ . The reaction orders obtained are  $2.08 \pm 0.23$  for the high humidity range and

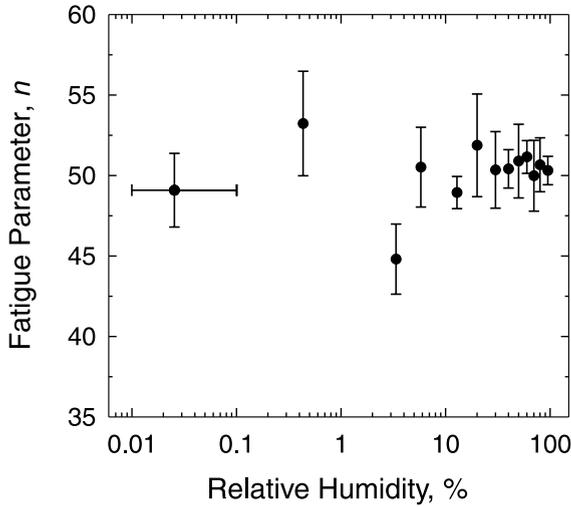


Fig. 2. Fatigue parameter (from Eq. (1)) versus relative humidity.

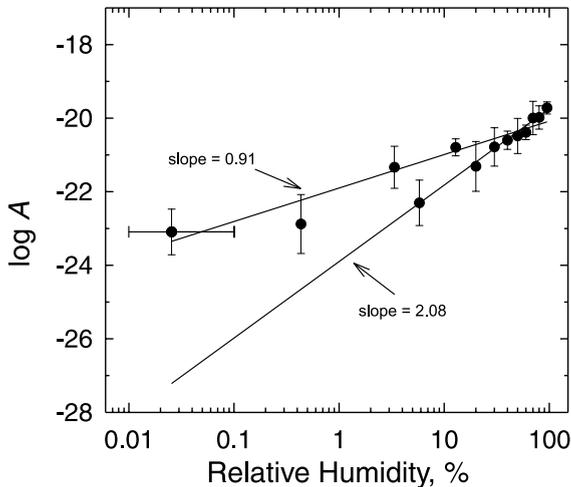


Fig. 3.  $\log A$  (from Eq. (1)) versus relative humidity.

$0.91 \pm 0.54$  for the low humidity range, which are within the range of reaction orders estimated from the power law. Figs. 4 and 5 show results for  $n_p$  and  $\log A_p$  calculated by fitting the power law, Eq. (5). It can be seen that  $n_p$  is not a constant with humidity, whereas  $\log A_p$  is comparatively insensitive to humidity. This result is contrary to the common assumption that  $n_p$  is a constant and the environment dependence is in  $A_p$ . This supports the argument made in earlier work [1] that the effect of humidity is not adequately described by the power law. In this earlier work a consistent and

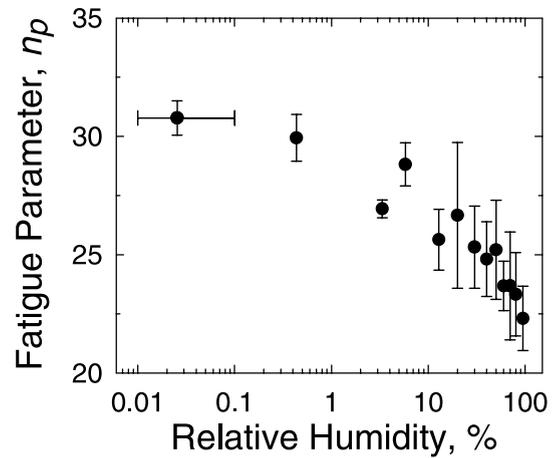


Fig. 4. Fatigue parameter (from Eq. (4)) versus relative humidity.

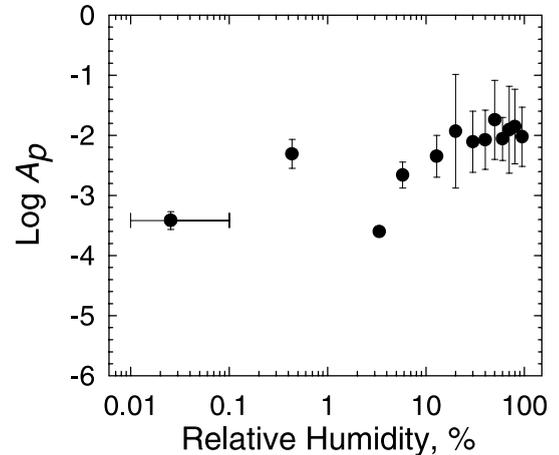


Fig. 5.  $\log A_p$  (from Eq. (4)) versus relative humidity.

reasonable value of the reaction order could only be obtained by assuming  $n_p$  constant with humidity, thus forcing all environmental dependence into  $A_p$ , even though the reverse was observed.

#### 4. Discussion

As stated earlier, the kinetics of the silica and water reaction have been found by Wiederhorn [3] and Duncan et al. [6] to change in the low humidity region. The reaction order obtained from our work shows a change from  $\sim 2$  at high humidity (20–95% RH) [1] to  $\sim 1$  at low humidity ( $\sim 0.025$ –13% RH). These results verify the results from Duncan et al. [6] who found a reaction order of 2 in the high humidity range and a reaction order of 1 in low humidity ( $<0.01\%$ ).

The transition in the reaction order appears to be in the region where a complete monolayer of water is formed on the silica surface ( $\sim 18\%$  RH). In our previous work, [1] it was found that the reaction would appear to be second-order in water if there is a first-order dependence on  $\text{OH}^-$ . Other work in various pH solutions suggests that at around pH 7 the fatigue is dominated by the reaction with  $\text{OH}^-$ , but at low pH, the background reaction with water dominates [12]. Therefore the change in the kinetics of the silica and water reaction may be related to the concentration of  $\text{OH}^-$  that is available at the silica surface. At high humidity  $\text{OH}^-$  must be readily formed by dissociation and must be available to react with the silica glass surface. At low humidity the lack of a monolayer coverage might suppress the formation of free hydroxyl ions so that only reactions with molecular water can occur, which appears to be a first-order reaction.

#### 5. Conclusions

The reaction order for fatigue of high strength fused silica fiber was found to be  $\sim 2$  at high hu-

midity (20–95% RH) and  $\sim 1$  in low humidity (0.025–13% RH). This result confirms an earlier, but non-definitive result [6]. However it also confirms that the reaction orders in this high strength material are approximately double the values obtained from weak silica with macroscopic cracks [3]. The cause of this difference is unclear, but may be related to the different scales of flaw sizes ( $\sim 1 \rightarrow 1$  mm).

The change in the reaction kinetics was also found to occur at about 20% RH. This humidity corresponds to the formation of a monolayer of water on silica. A possible explanation for this change in the reaction kinetics is that at high humidity,  $\text{OH}^-$  and  $\text{H}_2\text{O}$  are reacting with the silica. At low humidity,  $\text{OH}^-$  is not as readily formed, so the silica may just be reacting with a simple water molecule and hence the reaction order is  $\sim 1$ .

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