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Delayed failure in silica glass

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Stable crack-propagation behaviour in silica glass as a raw material for optical fibres is studied under static tensile stress in various environments such as distilled water, NaCl aqueous solution, air and dry nitrogen gas, and the influence of these environments is discussed. The crack-growth rate in distilled water is obtained qualitatively as a function of the stress intensity factor and temperature, and the activation energy of the cracking process is determined as 97.6 kcal mol^{-1}. The growth rate seems to be unaffected by Na$^+$ and Cl$^-$ ions in an NaCl acqueous solution, but is influenced significantly by the humidity in the atmosphere. In a dry atmosphere, the growth rate in Region II cannot be expressed as a single function of the stress intensity factor. A plot of the log of time to failure against the initial stress intensity factor reveals a linear relationship in the environments tested. The critical fracture stress of an optical fibre is evaluated taking account of the crack size on the basis of fracture mechanics concept.

1. Introduction

Optical fibres made of silica glass have many advantages in a communications system, such as low-loss [1], wide bandwidth [2], low weight, and small cross-section. Thus, a great deal of research on optical fibres has been conducted with a view to putting them into practical communications service. Unfortunately, glass is one of the most brittle materials, and its strength is degraded during exposure to various environments. If a fibre contains a flaw, it is easily broken under a small applied stress or strain, and it may even break under a static tensile stress that is less than the fracture stress. Reliable data on the fibre's mechanical performance in various environments is thus needed in order to maintain the high reliability required for communications service.

It is now widely accepted, on the basis of fracture mechanics, that the criteria for brittle fracture is governed by several basic parameters, such as crack size, applied stress, and fracture toughness. The criteria have been applied in studies on failure phenomena of glass and ceramics. In delayed failure or static fatigue of glass, in which spontaneous fracture occurs when subcritical cracks grow to critical dimensions after a long period of time, crack-growth behaviour is characterized by using a stress intensity factor [3, 4]. In the case of silica glass, it has been found that delayed failure is induced by a stress corrosion cracking process in which water plays an essential role [5].

This paper presents the results of a study on crack-growth behaviour in silica glass used as a raw material for optical fibres, in various environments, such as distilled water, NaCl aqueous solution, atmospheric air, and dry nitrogen gas and discusses the effect of these environments, the fracture toughness of the glass, and the critical condition for stress corrosion cracking. The relationship between critical load and crack size was evaluated based on fracture mechanics parameters obtained experimentally.

2. Experimental procedure

2.1. Material and specimen

Fused quartz was used in the delayed failure test. The specimen is a WOL-type compact tension specimen [6], and its configuration is shown in

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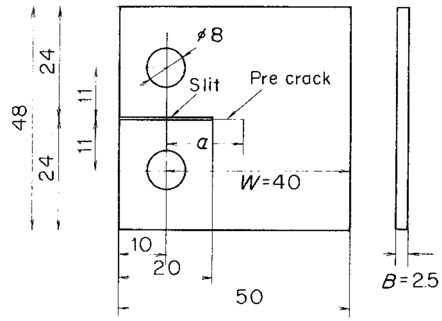

Figure 1 WOL-type CT specimen.

Fig. 1. Pre-cracking of about 5 mm length was carefully introduced at the front of the machine slit by vertically compressing the specimen from the opposite side of the slit.

2.2. Loading equipment

A lever-type tensile apparatus was used to apply a specified static tensile load to the specimen mounted in an environment chamber made of transparent acryc board, 10 litre in volume.

2.3. Environments

2.3.1. Distilled water and NaCl aqueous solution

Distilled water was circulated between the environment chamber and an extra heating bath at a flow rate of 250 ml min^{-1} to keep the environmental conditions constant. The bath contained a heater to warm the distilled water. The temperature in the chamber was measured with a thermo-couple and kept constant to within ± 1° C by a controller.

A 3.5% NaCl aqueous solution was also used.

2.3.2. Humid air

Compressed air of commercial purity was introduced into the chamber through a humidity generator. The humidity in the chamber was measured with a hygrometer and kept constant to within ± 3% r.h. by controlling the flow rate.

2.3.3. Dry air and nitrogen gas

Commercial dry air or nitrogen gas with a relative humidity of 0.08% was released into the chamber from a compressed container through a regulator, a flow meter, and a dehydrator, at a flow rate of 3 litre min^{-1}.

2.4. Crack-length measurement

The specimen mounted in the chamber was kept in the testing environment for an hour prior to the application of the static tensile load. The change in crack length was measured at specified time intervals using a travelling microscope at a magnification of 20 and within an accuracy of 0.01 mm.

The stress intensity factor for the compact tension specimen can be calculated by the following equation [7]:

$$K = \frac{P}{B\sqrt{W}}\ 4.55 - 40.32\left(\frac{a}{W}\right) + 414.7\left(\frac{a}{W}\right)^2 - 1698\left(\frac{a}{W}\right)^3 + 3781\left(\frac{a}{W}\right)^4 - 4287\left(\frac{a}{W}\right)^5 + 2017\left(\frac{a}{W}\right)^6 , \qquad (1)$$

where P is the load, B is the specimen thickness, W is the width from the loading centre, and a is the crack length from the loading centre. Where $0.25 < a/W < 0.75$ the polynomial is accurate to within 0.5% of the experimentally observed K value.

3. Results

3.1. Crack-propagation behaviour

3.1.1. Distilled water

A slow, stable crack-growth behaviour was observed in distilled water at room temperature (24 ± 2° C), 40, and 70° C, and the growth rate, $\mathrm{d}a/\mathrm{d}t$, is determined from crack-growth curves.

Fig. 2 shows plots of crack growth rate $\mathrm{d}a/\mathrm{d}t$ against stress intensity factor K in distilled water at various temperatures. As shown in the figure, the growth rate increases slightly with increased temperature. The broken line refers to the growth rate in atmospheric air at 22 ± 2° C and 50 ± 10% r.h. It was found that the crack-growth rate in distilled water is higher by one order of magnitude than that measured in the air. The growth rate in distilled water at 24° C is about the same as that obtained by using the DCB method [8]. For all cases, the plots of $\log \mathrm{d}a/\mathrm{d}t$ against $\log K$ fall on respective straight lines. Therefore, at a given temperature, the growth rate can be expressed as the following equation:

$$\mathrm{d}a/\mathrm{d}t = AK^n \qquad (2)$$

where, A and n are material and environmental constants dependent on temperature and humidity. The values of A and n are calculated using least square method and are listed in Table I. Values of n range from 38 to 41 in the temperature region involved.

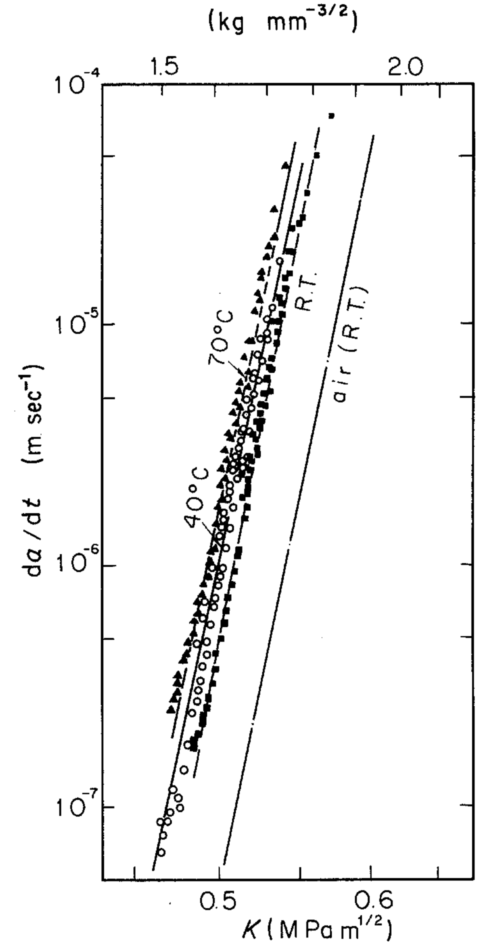

Figure 2 Influence of temperature on crack-growth rate in distilled water.

The crack-growth rate in distilled water increases as temperature increases. The temperature dependence of the crack-growth rate at constant K value is shown in Fig. 3. A linear relationship is obtained between the growth rate and the inverse of the absolute temperature, giving an Arrenius-type temperature dependence. Thus, the crack-growth rate becomes

$$\frac{da}{dt} \propto \exp\frac{-Q}{RT}, \tag{3}$$

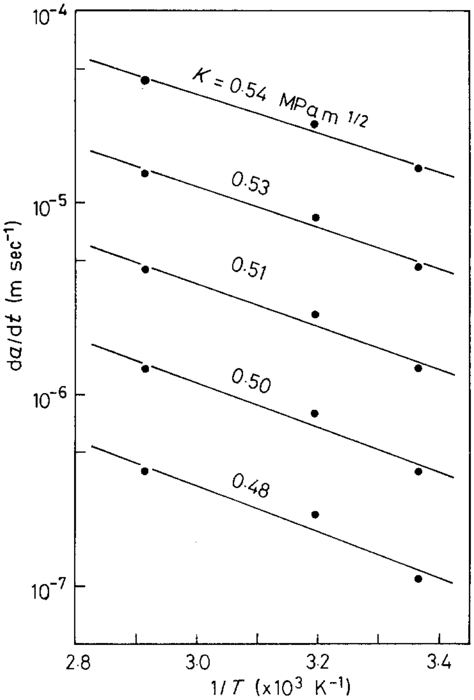

Figure 3 Plots of crack-growth rate against $1/T$ at constant K in distilled water.

where, Q is the activation energy for the crack-growth process, and R is a gas constant. The activation energy, Q, depends on K as shown in Fig. 4, thus, Q can be given as

$$Q = U - b\ln K. \tag{4}$$

From the data in Fig. 4, the value of U and b are calculated as 97.6 kcal mol^{-1} and 7.04×10^3, respectively. This indicates that the crack-growth is due to a stress-dependent rate process.

On the other hand, the crack-growth rate in the stress-dependent rate process can be given as follows [9]:

$$\frac{da}{dt} = BK^{\delta}\exp\left(-\frac{U - b\ln K}{RT}\right), \tag{5}$$

where B and δ are constants dependent on the material and environment. Equations 3 and 4

TABLE I Summary of log A and n (mks units)

	Distilled water			Air at 25° C			
	Temperature (° C)			Relative humidity (%)			
	24	40	70	75	50*	20	0.08
log A	−237	−227	−226	−213	−234	−260	−257
n	40.5	38.8	38.7	36.2	39.8	44.2	43.4

*Open air.

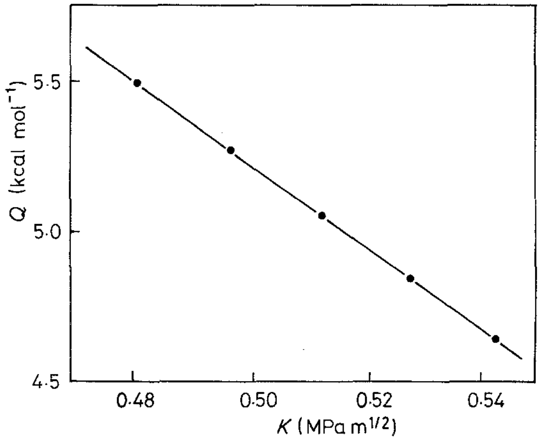

Figure 4 Dependence of stress intensity on activation energy in distilled water.

obtained from the present experiments agree with Equation 5. Comparing with Equations 2 and 5, the parameters n and A are given as

$$n = \delta + \frac{b}{RT} \tag{6}$$

$$A = B \exp\left(-\frac{U}{RT}\right). \tag{7}$$

Fig. 5 shows the plot of n against $1/T$. The open circle presents the data obtained in air. In distilled water, the relationship between n and $1/T$ is about the same tendency presented by Equation 6. Using $b = 7.04 \times 10^3$, δ can be calculated to be 28.1 by least square fit of the data in Fig. 5. Then, Equation 5 becomes

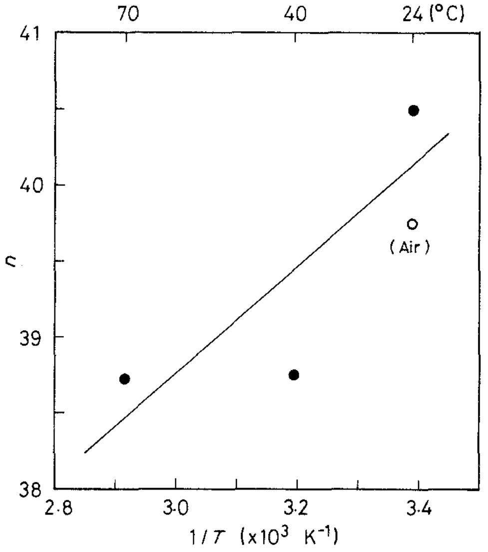

Figure 5 Correlation between n and $1/T$.

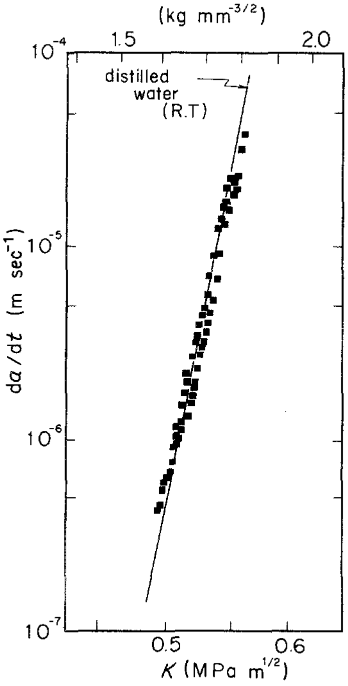

Figure 6 Crack-growth rate in 3.5% aqueous solution.

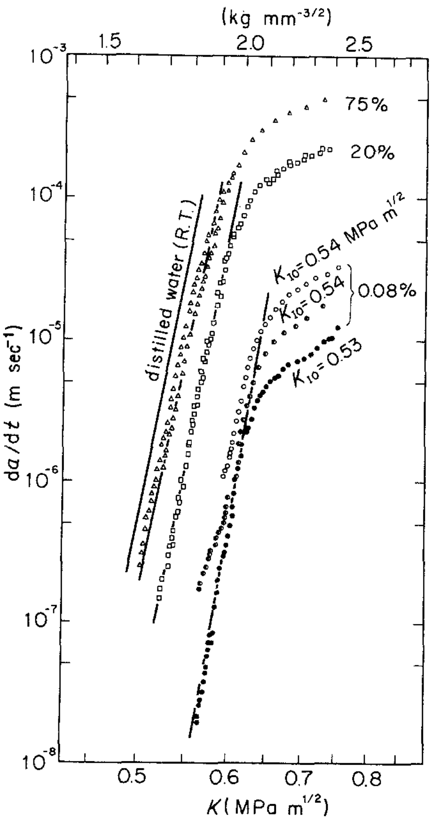

Figure 7 Influence of humidity on crack-growth rate in atmospheric air.

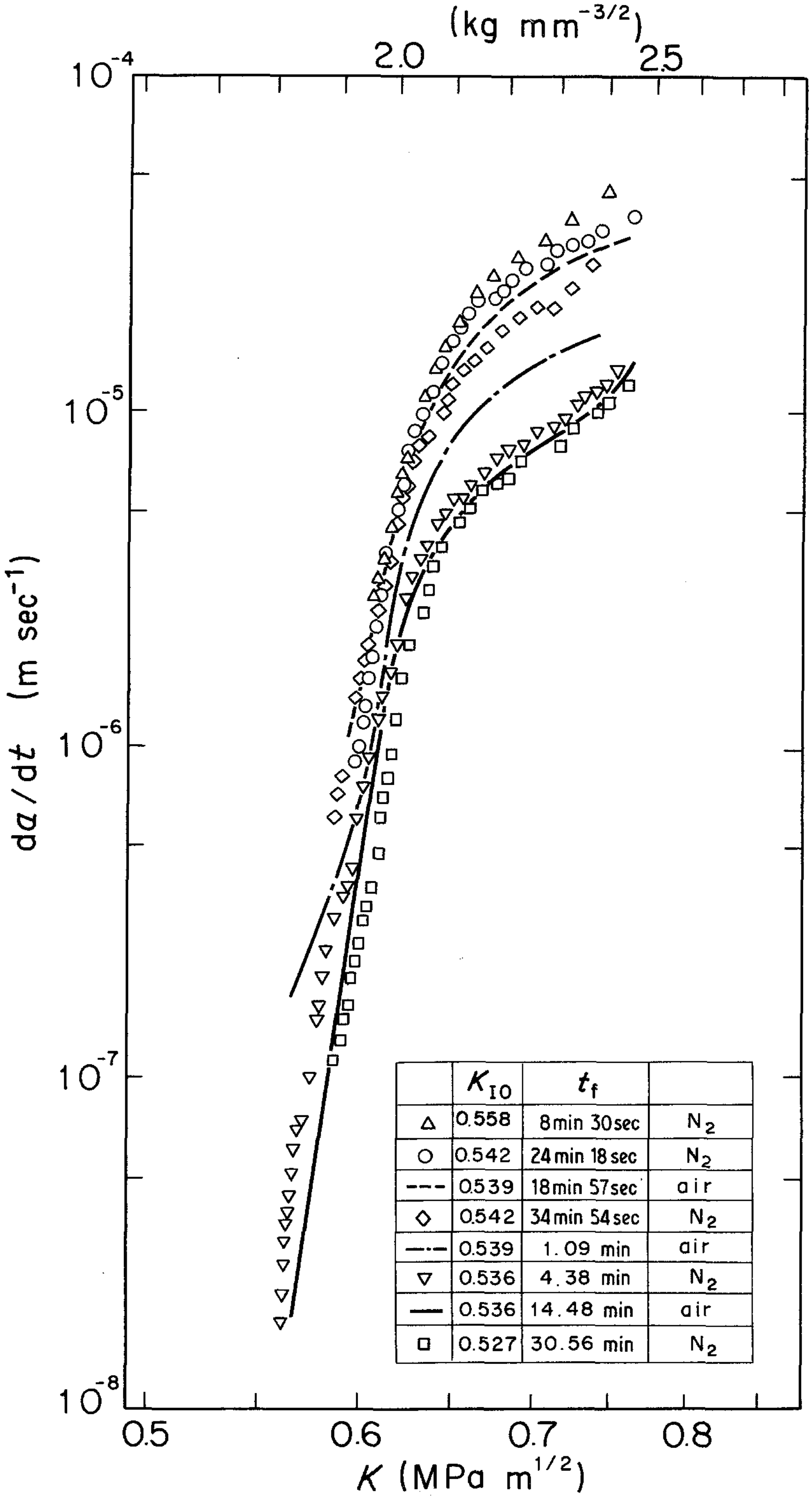

Figure 8 Crack-growth rate in 0.08% r.h. nitrogen gas.

$$\frac{da}{dt} = BK^{28.1} \exp\left(-\frac{97.6 \times 10^3 - 7.04 \times 10^3 \ln K}{RT}\right).$$

Therefore, the activation energy for the fundamental process of crack growth in distilled water is found to be 97.6 kcal mol^{-1} which is of the same order as 33.1 kcal mol^{-1} reported by Wiederhorn and Bolz [8].

3.1.2. 3.5% NaCl aqueous solution

Fig. 6 shows plots of log da/dt against log K in a 3.5% NaCl aqueous solution at 25° C. The same data on crack growth in distilled water at 24° C are presented by the solid line in Fig. 6. The plots of these two environments completely coincide, leading to the conclusion that Na^+ and Cl^- ions do not influence crack-propagation behaviour in silica glass.

3.1.3. Atmospheric air

Crack-growth rates in air at 25° C and relative humidities of 75, 20, and 0.08% are shown in Fig. 7 as a function of the stress intensity factor. The growth rate tends to increase with increased humidity. The growth rate in air at 75% r.h. is close to that in distilled water [10].

The test results shown in Fig. 7 suggest that the crack-growth behaviour can be divided into two regions. In Region I, there is a linear relationship between log da/dt against log K, and the growth rate, da/dt, depends on K to such an extent that a small change in the magnitude of K results in a large change in the growth rate. In Region II, the growth rate depends on K to a more moderate degree. As shown in Fig. 7, the transition from Region I to Region II occurs at magnitudes of K from 0.56 to 0.64 MPa m$^{1/2}$ (1.8 to 2.1 kg mm$^{-3/2}$), tending to occur at smaller value of K in highly humid air. In Region I, the growth rate is given as expressed in Equation 2. The values of A and n fitted to the present experiments are listed in Table I. Values of n are slightly dependent on humidity, and, in highly humid air, are close to values obtained in distilled water (see Table I).

In the case of the data obtained in 0.08% r.h. air, plots of log da/dt against log K in Region II could not be expressed as a single curve. The growth rate seems to change dependent on the initial value of the stress intensity factor, K_{I0}.

3.1.4. Dry nitrogen gas at 0.08% r.h.

A delayed failure test in the dry nitrogen gas at 25° C and 0.08% r.h. was also performed, and plots of log da/dt against log K resulting from this test are shown in Fig. 8. Data obtained in dry N_2, as was the case as in dry air, cannot be expressed as a single curve in Region II and are scattered over a wide range dependent on the initial stress intensity factor K_{I0}. In this figure, the data obtained in dry air are represented by three curves. From both the dry air and nitrogen data, a clear tendency can be seen for crack-growth rate curves to shift to a larger K- and slower da/dt-direction as K_{I0} decreases and time to failure, t_f, increases. This tendency could not be found in the crack-growth behaviour observed in distilled water and humid air, and it may be plausible to assume that this is a singular phenomenon observed only in a very low humid atmosphere.

Generally, the fracture stress σ_f of glass is given as a function of surface energy γ, as $\sigma_f = \sqrt{(2E\gamma/\pi c)}$, where, E is Young's modulus and c is crack length. One explanation of the above tendency may be that the magnitude of γ is affected by humidity in a very dry atmosphere so strongly that the value of σ_f substantially decreases even with small increase in humidity, resulting in a significant decrease in fracture strength. Another reason may be that the growth rate is essentially affected by K_{I0} in such a low humid atmosphere.

3.2. Time to failure

In general, the higher applied stress, the shorter the life time with stress corrosion cracking in silica. However, the time to failure is also dependent on crack configuration. Thus, it may be more reasonable to express the time to failure, t_f, as a function of the initial stress intensity factor, K_{I0}, instead of as a function of initial applied stress.

Fig. 9 shows the relationship between K_{I0} and log t_f obtained in various environments. Data obtained in distilled water do not clearly show the effect of temperature on time to failure in the temperature range involved. However, in detail, there is a barely noticeable tendency for the time to failure to decrease at high temperatures. This tendency is not contradictory to the data on growth rate shown in Fig. 2. The time to failure data in a 3.5% NaCl aqueous solution fall close to this straight line, i.e. Na^+ and Cl^- ions do not appear to have any affect on either the life-time or, as shown in Fig. 6, the crack-growth behaviour.

The open circles in Fig. 9 refer to the time to failure in air. It is found that the life-time in air is appreciably longer than that in distilled water, although the crack-growth rate in air is lower by one order of magnitude compared to that in distilled water at the same levels of stress intensity factor.

The open and closed squares represent the time to failure in 0.08% r.h. nitrogen gas and air, respectively. No difference between them can be

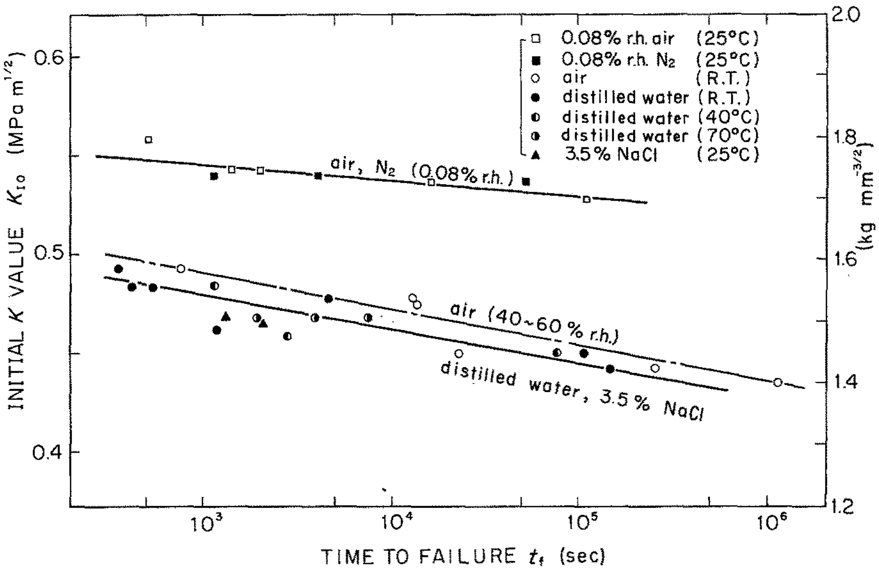

Figure 9 Plots of initial K value against time to failure in various environments.

found. The time to failure in these environments is much longer than the data in humid air and distilled water, suggesting that a dry atmosphere is very favourable for silica glass.

In Fig. 9, assuming that the linear relation of K_{I0} against $\log t_f$ can be extended over a longer period of time, the value of K_{I0} corresponding to a 10-year life-time in distilled water can be estimated at $0.388\,\text{MPa}\,\text{m}^{1/2}$ ($1.25\,\text{kg}\,\text{mm}^{-3/2}$).

It is known that subcritical crack-growth rate decreases with decreased K in Region I and decreases steeply at about $\mathrm{d}a/\mathrm{d}t = 10^{-10}\,\text{m}\,\text{sec}^{-1}$ [3]. This suggests that the stress intensity factor at $\mathrm{d}a/\mathrm{d}t = 10^{-10}\,\text{m}\,\text{sec}^{-1}$ corresponds to the critical value for stress corrosion cracking K_{ISCC}. Assuming that the linear relation of $\log \mathrm{d}a/\mathrm{d}t$ against $\log K$ is kept at the growth rate of 10^{-10} to $10^{-11}\,\text{m}\,\text{sec}^{-1}$ in Fig. 2, extrapolation gives the value of K at $\mathrm{d}a/\mathrm{d}t = 10^{-10}\,\text{m}\,\text{sec}^{-1}$ as $0.394\,\text{MPa}\,\text{m}^{1/2}$ ($1.27\,\text{kg}\,\text{mm}^{-3/2}$) in distilled water at 40° C. This value agrees closely with the estimated value of K_{I0} corresponding to a 10-year life-time. From the above, the value of K_{ISCC} of silica glass in distilled water is $0.37\,\text{MPa}\,\text{m}^{1/2}$ ($1.2\,\text{kg}\,\text{mm}^{-3/2}$).

3.3. Critical stress intensity factor, K_{IX}

The critical stress intensity factor, K_{IX}, at which unstable crack growth just begins as the final stage of stress corrosion cracking, can be calculated from the final crack length measured on the fracture surface of the specimen. The values of K_{IX} obtained in distilled water are plotted against temperature in Fig. 10. No temperature dependence of K_{IX} is apparent in the temperature range of the present experiment, and the average of K_{IX} is $0.89\,\text{MPa}^{1/2}$ ($2.9\,\text{kg}\,\text{mm}^{-3/2}$). The open circle in Fig. 10 represents a K_{IX} in air of $0.87\,\text{MPa}\,\text{m}^{1/2}$ ($2.8\,\text{kg}\,\text{mm}^{-3/2}$). These values compare favourably with the fracture toughness of $0.81\,\text{MPa}\,\text{m}^{1/2}$ ($2.6\,\text{kg}\,\text{m}^{-3/2}$) recently reported by Wiederhorn [11].

4. Discussion

The allowable critical stress for failure of optical fibres can be determined based on fracture mechanics parameters obtained from the delayed failure tests on silica glass conducted during these experiments.

Even if optical fibres are produced with meticu-

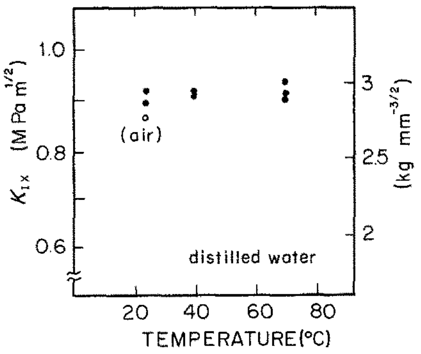

Figure 10 Plots of critical stress intensity factor against temperature.

lous care, it is very difficult to fabricate a defect-free fibre of long length [12]. Assume that a half-penny shaped crack with a radius of c exists on the fibre surface perpendicular to its axis. Since it is reasonable to suppose that the fibre diameter d is sufficiently large compared to c, the stress intensity factor K at the crack tip is approximately described as [13]:

$$K = 1.1 \frac{2}{\pi} \sigma \sqrt{(\pi c)}. \qquad (8)$$

Using Equation 8, fracture stress σ_f and critical stress σ_c needed to initiate stable crack growth in distilled water can be expressed respectively as follows:

$$K_{IX} = \frac{2.2}{\pi} \sigma_f \sqrt{(\pi c)}$$

$$K_{ISCC} = \frac{2.2}{\pi} \sigma_c \sqrt{(\pi c)}.$$

Substituting $0.89\,\mathrm{MPa\,m^{1/2}}$ ($2.9\,\mathrm{kg\,mm^{-3/2}}$) for K_{IX} and $0.37\,\mathrm{MPa\,m^{1/2}}$ ($1.2\,\mathrm{kg\,mm^{-3/2}}$) for K_{ISCC} in the above equations, plots of σ_f and σ_c as a function of crack size can be obtained as shown in Fig. 11. For example, if the fibre contains a half-penny shaped crack with a radius of $c = 1\,\mu\mathrm{m}$ on the surface, the value of static tensile stress needed to initiate slow, stable, crack propagation is estimated at 300 MPa ($30.6\,\mathrm{kg\,mm^{-2}}$). Allowable strain corresponding to this stress is obtained as 0.39% using Young's modulus of silica glass of 76 GPa ($7780\,\mathrm{kg\,mm^{-2}}$). The values of σ_c for crack sizes of 1, 0.1, 0.05, and 0.01 μm are listed in Table II along with corresponding strains.

5. Conclusions

Crack-propagation behaviour in silica glass is studied in various environments in order to evaluate the mechanical performance of optical fibres. The results are as follows:

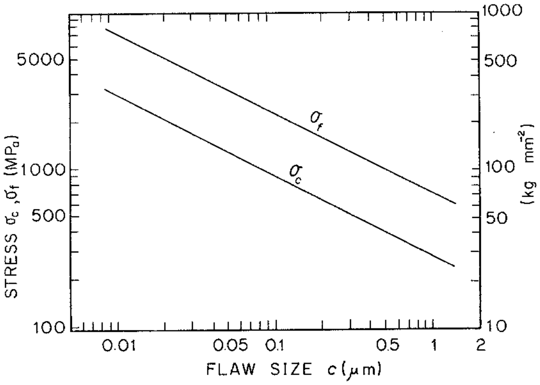

Figure 11 Fracture stress, σ_f, and critical stress for stress corrosion cracking σ_c against flaw size.

TABLE II Allowable stress and strain against crack size

Crack size, c (μm)	Allowable stress, σ_c (MPa m$^{1/2}$, kg mm^{-2})	Allowable strain ϵ (%)
1	300 (30.6)	0.39
0.1	947 (96.6)	1.2
0.05	1340 (136.6)	1.7
0.01	2990 (305.5)	3.9

(1) Crack-growth rate in distilled water is a function of stress intensity factor and temperature, as expressed by the formula

$$\frac{da}{dt} = BK^{28.1} \exp\left(-\frac{97.6 \times 10^3 - 7.04 \times 10^3 \ln K}{RT}\right).$$

The activation energy for the fundamental process of crack growth was found to be 97.6 kcal mol^{-1}.

(2) The stress corrosion crack-growth rate in a 3.5% NaCl aqueous solution agrees closely with the rate in distilled water, and it was found that Na^+ and Cl^- ions do not affect the growth process.

(3) In humid air, the crack-growth rate increases with increasing humidity, and in highly humid air, it approaches the rate in distilled water at the same temperature.

(4) In dry air and nitrogen gas, crack-growth rates cannot be expressed as a single function of K in Region II. The growth rate in this region seems to be affected by initial stress intensity factor K_{I0}, showing a tendency to decrease with a decreasing K_{I0}. This tendency is a specific phenomenon appearing only in a very low humid atmosphere.

(5) A plot of log time to failure against K_{I0} shows a linear relationship in each environment.

(6) Critical stress intensity factor for stress corrosion cracking, K_{ISCC}, is estimated at 0.37 MPa m$^{1/2}$ (1.2 kg mm$^{-3/2}$) for silica glass in distilled water.

(7) Critical stress intensity factor for brittle fracture K_{IX} of silica glass is evaluated at 0.89 MPa m$^{1/2}$ (2.9 kg mm$^{-3/2}$).

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