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A Fracture Mechanics Study of Subcritical Tensile Cracking of Quartz in Wet Environments

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Abstract – Load relaxation and cross-head displacement rate-change experiments have been used to establish $\log_{10}$ stress intensity factor (K) versus $\log_{10}$ crack velocity (v) diagrams for double torsion specimens of synthetic quartz cracked on the a plane in liquid water and moist air.

For crack propagation normal to z and normal to r at 20°C, K_{Ic} (the critical stress intensity factor) was found to be 0.852 ± 0.045 MN·m$^{-3/2}$ and 1.002 ± 0.048 MN·m$^{-3/2}$, respectively.

Subcritical crack growth at velocities from 10^{-3} m·s^{-1} to 10^{-9} m·s^{-1} at temperatures from 20°C to 80°C is believed to be facilitated by chemical reaction between the siloxane bonds of the quartz and the water or water vapour of the environment (stress corrosion). The slopes of isotherms in the K–v diagrams are dependent upon crystallographic orientation. The isotherms have a slope of 12 ± 0.6 for cracking normal to r and 19.9 ± 1.7 for cracking normal to z. The activation enthalpy for crack propagation in the former orientation in liquid water at temperatures from 20°C to 80°C is 52.5 ± 3.8 kJ·mole^{-1}.

A discussion is presented of the characteristics of the K–v diagrams for quartz.

Key words: Quartz; Fracture mechanics; Stress corrosion.

1. Introduction

Subcritical or slow stable tensile cracking is known to precede the catastrophic brittle fracture of quartz (Scholz, 1972; Martin and Durham, 1975) and this leads to a time-dependence of fracture strength. When it is influenced by the presence of a chemically active species, such as liquid water or water vapour, subcritical crack propagation is known as stress corrosion cracking. In order to understand and ultimately to predict fracture development in the wet rocks that are common in crustal environments it is essential that this phenomenon be well studied.

An idea of the potential importance of stress corrosion cracking can be gauged from the fact that it has been suggested as a key factor in some time-dependent earthquake phenomena (Scholz 1972; Martin, 1972; Bonafede *et al.*, 1976), in the propagation of magma-filled cracks upward through the lithosphere (Anderson and Grew, 1976), in the creep of silicate rocks at temperatures favouring brittle deformation (Scholz, 1968), in the stable sliding of faulted sandstone (Rutter and Mainprice, 1978), and in limiting the potential output of geothermal reservoirs in hot, initially dry rock (Demarest, 1976).

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Linear Elastic Fracture Mechanics (LANGE, 1974) has been shown to be a powerful theoretical tool for the study of crack propagation in ceramics, particularly tensile (mode I) fracture (EVANS and LANGDON, 1976), and it is now being employed to provide new insights into the fracture of rocks and minerals (see, for example, ATKINSON, 1978). Fracture mechanics is of considerable value in the study of subcritical cracking because the crack tip stresses that cause crack growth are directly proportional to the stress intensity factor, K_I (PARIS and SIH, 1965) which is generally found to be uniquely related to the crack growth rate, v, for a given set of environmental conditions (WIEDERHORN, 1974). The stress intensity factor is given by

$$K_I = \sigma_a Y \sqrt{a} \tag{1}$$

(BROWN and STRAWLEY, 1967), where σ_a is the remote applied stress, Y is a constant that depends upon the geometry of loading, crack configuration, etc., and a is half the crack length.

Diagrams that depict the relationship between stress intensity factor and crack velocity (shown schematically in Fig. 1) are therefore of fundamental significance in the study of subcritical cracking. They can be used (1) to predict time-dependent failure properties (EVANS, 1972; WIEDERHORN, 1974) and (2) in the analysis of slow crack growth mechanisms (WIEDERHORN, 1974, 1978; EVANS and LANGDON, 1976).

In this paper I present the results of double torsion experiments designed to establish for quartz in wet environments the stress intensity factor–crack velocity (K–v) relationships at temperatures up to 80°C. This is followed by a discussion of these results: (i) In terms of the mechanisms of crack propagation, (ii) in comparison with the results of others who have worked on quartz and on glasses.

2. *Theoretical aspects of subcritical cracking*

A number of theoretical approaches have been made to the problem of subcritical cracking, mainly to explain the results of slow crack propagation experiments on glasses and ceramics. At the present time experimental data relating to region 1 of the schematic K–v diagram (Fig. 1) are discussed in terms of one of two equations.

The first of these is based upon an equation derived by CHARLES and HILLIG (1962) but which has been reformulated in terms of the Fracture Mechanics parameter K_I by WIEDERHORN and BOLZ (1970). In the Wiederhorn and Bolz equation the crack velocity is given by

$$v = v_0 \exp\left[-\Delta H + 2V^* K_I/(\pi\rho)^{1/2}\right]/RT \tag{2}$$

where v_0 is a pre-exponential kinetic factor, ΔH is the activation enthalpy, V^* is an 'activation volume', ρ is the radius of curvature of the crack tip, R is the gas constant,

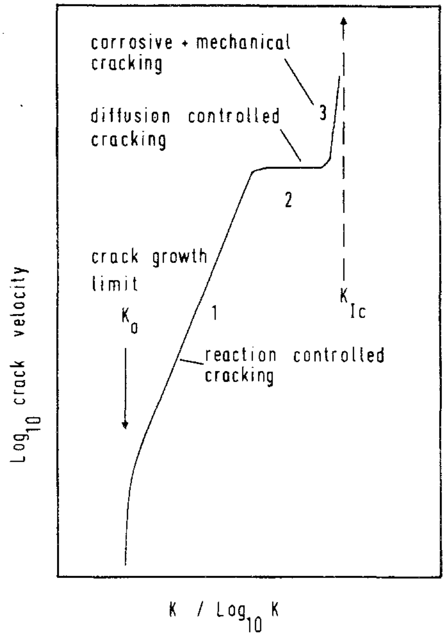

Figure 1
Schematic stress intensity factor–crack velocity diagram representing a summary of data on tensile (mode I) fracture of glasses and ceramics in chemically active environments. According to the most widely accepted interpretation, crack propagation in region 1 is controlled by the rate of reaction between the environment and the crack tip bonds, in region 2 it is controlled by the rate of transport of reactive species to the crack tip, and in region 3 it is controlled by some mixture of mechanical fracture and fracture facilitated by the corrosive action of the environment.

and T is the absolute temperature. Empirical data on stress corrosion of glasses was found by WIEDERHORN and BOLZ (1970) to fit an equation of the form

$$v = v_0 \exp(-\Delta H + bK_{\mathrm{I}})/RT \tag{3}$$

where b is an experimentally determined constant. Equation (3) is identical with equation (2) when $V^* = (b/2)(\pi\rho)^{1/2}$.

Previous workers who have studied slow stable cracking of quartz (SCHOLZ, 1972; MARTIN, 1972; MARTIN and DURHAM, 1975) have also used equations to describe their experimental results that are based on, or are similar to CHARLES and HILLIG's (1962) equation, but these equations were not formulated in terms of Fracture Mechanics Parameters, such as K_{I}.

The second widely used description of slow crack growth is an equation based upon CHARLES' (1958) power law to describe dynamic and static fatigue of glass but which has also been reformulated in terms of the parameter K_{I}. In this formulation the crack velocity is given by

$$v = v_0' \exp(-\Delta H/RT)K_{\mathrm{I}}^{n} \tag{4}$$

(Evans, 1972; Wiederhorn, 1974), where v_0' and n are experimentally determined constants (n is sometimes known as the stress corrosion index).

Of the other theories of slow crack propagation I will mention only those of Stuart and Anderson (1953) and Lawn (Lawn, 1975; Lawn and Wilshaw, 1975).

The rather complicated expression obtained by Stuart and Anderson (1953) from reaction rate theory is open to the criticism that as time-to-failure becomes indefinitely short the stress supported increases indefinitely (Mould and Southwick, 1959) which is at variance with experimental observations.

Lawn (1975) and Lawn and Wilshaw (1975) have modelled chemically enhanced subcritical cracking at the atomic level and related these processes to macroscopic parameters of fracture, such as K_I or the crack extension force, G. They considered a two-stage model of stress corrosion in which reactive species must first be transported to the crack tip before reactions can occur there to facilitate subcritical crack extension. The slowest of the two steps, reaction and transport, will control the rate of the overall process. For a solid/vapour reaction-limited crack velocity (v_r) Lawn (1975) obtains

$$v_r = V(T)\left[\frac{p_a^0}{p_a^s}\right]^{\eta/2} \exp\left(-U_0^*/kT\right) \exp\left(G/2N_a kT\right) \tag{5}$$

where $V(T)$ is a slowly varying temperature-dependent term, p_a^0 is the vapour pressure at the crack mouth, p_a^s is the vapour pressure in some reference state, η is the number of molecules of environmental species reacting with one bond in the solid to produce a weakened state, U_0^* is a collection of various uncertainty energy constants, k is Boltzmann's constant, and N_a is the surface density of crack plane bonds. For a transport limited crack velocity (V_t) Lawn (1975) obtains

$$V_t = \kappa a p_a^0/\eta N_a (2\pi m k T)^{1/2} \tag{6}$$

where κ is an attenuation factor associated with the increasing incidence of retarding, diffuse molecule wall collisions as the gas approaches the crack tip, a is the lattice spacing representing the reaction cross section per unit width of crack front presented to the impinging gas molecules by the crack tip bonds, m is the molecular mass of the gaseous species.

In a review of stress corrosion crack propagation studies Anderson and Grew (1977) conclude that the theoretical aspects are still in an active stage of development. Although for several materials crack propagation in region 1 of the schematic K–v diagram (Fig. 1) can often be described by equations such as that due to Wiederhorn and Bolz (1970) (equation 2) these equations cannot be applied to crack propagation in region 2. Equations such as (6) are needed to explain the plateau in the K–v curves. Furthermore, Anderson and Grew (1977) point out that even atomistic theories such as Lawn (1975) and Lawn and Wilshaw (1975) are still largely empirical, because little is really known about the processes that occur in the crack tip region.

In view of this uncertainty I have followed the practice of EVANS (1972), WIEDERHORN (1974) and a large number of other recent studies of subcritical cracking of glasses and ceramics in using equation (4) to describe my experimental results. This equation has the following advantages. (a) It can be used to describe most experimental data on slow, stable cracking in region 1 at least as well as equation (3) (EVANS, 1972). In preliminary studies it was found that no clear distinction could be drawn between the quality of fit of equations (3) and (4) to the present data set. (b) Equations of the form of (4) can be used with appropriate changes in the constants v_0', n, and ΔH to describe all three regions of the schematic K–v curve (Fig. 1) (EVANS 1972). (c) The relatively simple form of equation (4) facilitates the use of K–v data in theoretical approaches to the prediction of time-dependent failure properties of materials (EVANS 1972; EVANS and JOHNSON, 1975).

3. *Theoretical aspects of the testing method*

The use of the double torsion testing method in studies of slow, stable cracking of glasses and ceramics has been popularised in a number of papers by EVANS and colleagues (EVANS, 1972; WILLIAMS and EVANS, 1973; EVANS *et al.*, 1975). A schematic drawing of a double torsion specimen is shown in Fig. 2.

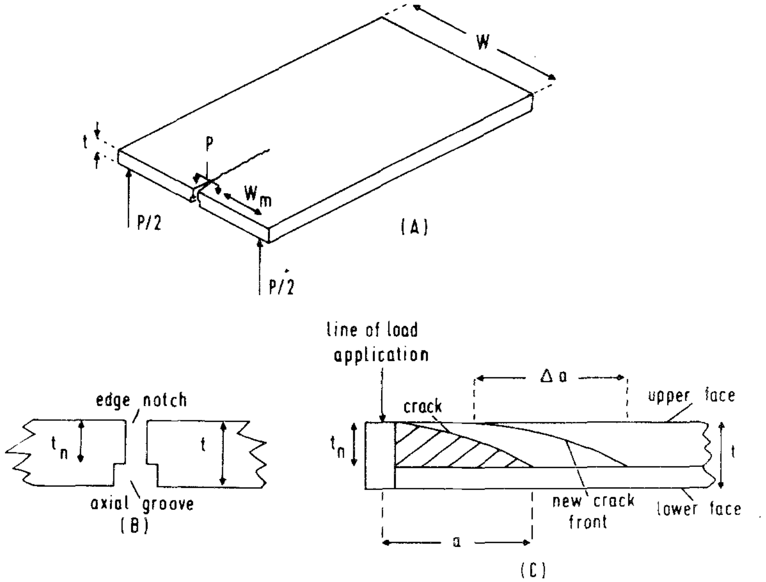

Figure 2
A schematic drawing of a double torsion specimen. (A) General view. (B) Axial cross section. (C) Longitudinal cross section.

Stress intensity factors for the double torsion specimens are independent of crack length and are given by WILLIAMS and EVANS (1973).

$$K_I = PW_m[3(1 + \nu)/Wt^3t_n]^{1/2} \tag{7}$$

where P is the load on the specimen, ν is Poisson's ratio and the other variables are as shown in Fig. 2. This equation gives reproducible results provided that the $W:t$ ratio is greater than approximately 12:1 (ATKINSON, 1978).

Provided that the initial crack length is relatively large the crack velocity can be obtained from load relaxation data using the equation

$$v = -\phi a_{i,f}P_{i,f}(1/P^2)(dP/dt) \tag{8}$$

(WILLIAMS and EVANS, 1973), where a is the crack length and t is the time, and i and f denote measurements made at the beginning and at the end of a test, respectively. ϕ is given by $t_n/\sqrt{(\Delta a^2 + t_n^2)}$ where Δa and t_n are as shown in Fig. 2. For quartz it was found that $\Delta a \simeq 5t_n$.

As an aid to the construction of K–v diagrams, incremental changes in the displacement rate of the cross-head of the deformation machine can be made. The changes that result in the load required to propagate the crack at constant temperature can be used to obtain an accurate value for n, the slope of the $\log_{10} K_I - \log_{10} v$ curve. Provided that equation (4) describes the experimental data, then

$$n = [\log_{10}(\dot{y}_1/\dot{y}_2)/\log_{10}(P_1/P_2)] - 1 \tag{9}$$

where $\dot{y}$ is the displacement rate (EVANS, 1972).

The activation enthalpy for crack propagation in equation (4) is given by

$$\Delta H = [RT_2T_1/(T_2 - T_1)](n + 1)\ln(P_1/P_2) \tag{10}$$

(EVANS, 1972), at constant stress intensity factor.

The major advantages of the double torsion specimen for studies of slow cracking are that: (i) Specimen preparation is relatively simple, (ii) at most, only one measure of crack length is required to obtain crack velocity data, and (iii) when used in the load relaxation mode a complete K–v curve can be obtained from just one specimen, thus reducing errors due to specimen variability. See also ATKINSON (1978) for further advantages of the double torsion specimen, especially with reference to the determination of K_I.

4. *Experimental details*

Experiments were performed using an Instron Corporation universal testing machine. Deformation of the specimens took place inside an environmental chamber in the form of a transparent acrylic box. The loading piston gains access to the interior of the box through a small hole in its top surface. Various environments can be introduced into this chamber through special conduits. The temperature is controlled by water circulating in a copper heat-exchanging coil which surrounds the specimen when it is placed inside the environmental chamber. The heat-exchanger is connected to a 5-litre water reservoir, the temperature of which can be held to within ±0.1°C by a thermistor-controlled heating element. A bead thermistor measures the temperature of the specimen in the vicinity of the crack tip, whilst the temperature elsewhere in the testing chamber is monitored with mercury-in-glass thermometers. The temperature near the crack tip is not allowed to vary by more than 0.5°C. The apparatus reaches thermal equilibrium in about 2 hours.

Load relaxation experiments were performed on pre-cracked specimens (for details of pre-cracking see Atkinson, 1978) from a load close to that for catastrophic crack propagation. A rapid cross-head speed was used to reach the desired load, at which point the cross-head motion was arrested and the load allowed to relax as a result of slow, stable crack extension. Displacement rate-change experiments were also

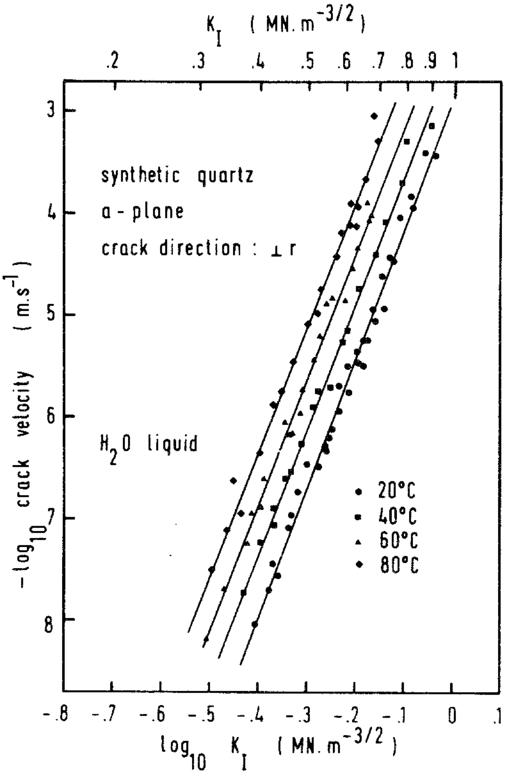

Figure 3
Stress intensity factor (K_I)–crack velocity diagram for synthetic quartz cracked on the *a* plane in a direction normal to *r* at temperatures from 20°C to 80°C.

performed on pre-cracked specimens by deforming them at the slowest cross-head speed available on the testing machine (0.0001 cm min^{-1}) until the crack just started to propagate at constant load. The cross-head speed was then suddenly increased to establish a second, higher load for crack propagation. This procedure was repeated until the crack ran through the specimen.

The test specimens measured 11 cm × 4.5 cm × 0.15 cm and were cut from single crystals of synthetic quartz. They were oriented so that crack propagation occurs on the *a* plane, $\{11\bar{2}0\}$. The structure-bound water content of the quartz was determined by infrared spectroscopy to be approximately 200 $\text{H}/10^6$ Si.

5. *Results*

Experimental results are shown in Figs. 3 and 4. Regression analysis of the data displayed in these figures yields the following values for the stress corrosion index, *n*.

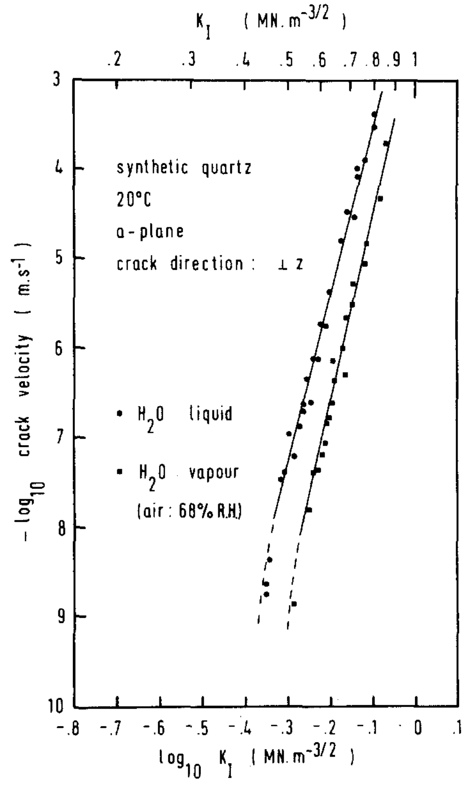

Figure 4

Stress intensity factor (K_I)–crack velocity diagram for synthetic quartz cracked on the *a* plane in a direction normal to *z* at 20°C.

For cracking on the *a* plane in a direction normal to *r*; $n = 12 \pm 0.6$. For cracking on the *a* plane in a direction normal to *z*; $n = 19.9 \pm 1.7$. Values of *n* obtained from displacement-rate change experiments (using equation (9)) were within the spread of results for *n* obtained by regression analysis.

The activation enthalpy of crack propagation was calculated from the data of Fig. 3 using equation (10). This yielded a value for ΔH of 52.5 ± 3.8 kJ mole^{-1}.

The fracture toughness (K_{Ic}) of the two quartz orientations at 20°C, i.e. the stress intensity factor for catastrophic crack propagation, was determined in separate double torsion experiments following the methods described by ATKINSON (1978). The values obtained for a crack on the *a* plane were 1.002 ± 0.048 MN m$^{-3/2}$ for a crack propagating in a direction normal to *r*, and 0.852 ± 0.045 MN m$^{-3/2}$ for a crack propagating normal to *z*.

6. *Discussion*

Mechanisms of subcritical crack propagation in glass can be divided into three broad categories: plastic flow, diffusion processes, and chemical reactions (WIEDERHORN, 1978). It is convenient to consider the present results on quartz under these same categories.

In their transmission electron microscope study of subcritical cracking in single crystals of quartz, MARTIN and DURHAM (1975) found no evidence of dislocation structures that would indicate plastic flow in the vicinity of the crack tips. This mechanism can therefore be ruled out.

It is important to distinguish between two types of diffusion processes in subcritical cracking: (i) those which relate to the motion of vacancies and atoms near the crack tip, and (ii) those which relate to the transport of reactive species through a liquid or vapour along the crack interface to the crack tip.

The latter processes are strictly part of chemical reaction-controlled crack propagation and will be mentioned again elsewhere. Crack propagation by diffusion through the elimination of atoms in the projected crack plane is generally considered to be of importance only at high homologous temperatures, although there have been suggestions that it could also occur in glass at room temperature (see WIEDERHORN, 1978). In quartz there could occur stress-enhanced diffusion of structurally-bound OH^- ions to crack tips where hydrolysis of the strong siloxane bonds to the weaker, hydrogen-bonded Si–OH–HO–Si group could facilitate subcritical cracking. There is some evidence to suggest that intrinsic water in quartz can affect fracture behaviour even at room temperature (HARTLEY and WILSHAW, 1973).

A guide to whether diffusion processes may control crack propagation in the present experiments can be obtained by comparing the activation enthalpy for crack propagation with that for diffusion of various species in quartz (see Table 1). Unfortunately, we do not know in detail how impurities and surfaces will influence diffusion rates. However, some inferences can be drawn from the available data.

Table 1

Activation enthalpies for diffusion of species in quartz compared with activation enthalpies for subcritical cracking

Species	Diffusion ($kJ \cdot mole^{-1}$)	Crack propagation ($kJ \cdot mole^{-1}$)	Reference
O^{18}	230		Haul and Dümbgen (1962)
Proton	84		Kats (1962)
OH^-	63		White (1971)
Na^+	105		Frischat (1970)
		46–100	Scholz (1972)
		63 ± 16	Martin and Durham (1975)
		52.5 ± 3.8	This study

With the exception of OH^- diffusion, the activation enthalpy for crack propagation is too low to be explained by a diffusion mechanism. Although under certain conditions this diffusion mechanism may be important in promoting crack propagation, I think that it is unlikely to have been important in the present experiments for the following reasons: (i) The quartz used in this study was relatively dry. (ii) Crack propagation studies in a similar quartz at room temperature under high vacuum ($< 10^{-3}$ $N \cdot m^{-2}$) failed to reveal any evidence of crack growth (Atkinson and Rees, 1978; unpublished results). (iii) A far greater source of OH^- ions in these experiments lies in the water or water vapour of the test environment.

Thus, a simpler and more plausible mechanism for subcritical cracking in these experiments lies in the possible reaction between the environment and the quartz. Scholz (1972), Martin (1972), Swain *et al.* (1973), and Martin and Durham (1975) all consider that chemical reaction with environmental water best explains the results of their experiments on crack propagation in quartz, some of which were conducted under the same conditions as the present experiments. The chemical reaction they propose is the same as that between structural water and quartz proposed above.

All the data of Figs. 3 and 4 pertain to region 1 of the schematic *K–v* diagram (Fig. 1). At what crack velocities might region 2 behaviour be expected? If the two-stage model of crack propagation proposed by Lawn (1975) and Lawn and Wilshaw (1975) is accepted (see Section 2) then the following points may be made.

Firstly, a plateau region in the *K–v* curve would not be expected for crack propagation in liquid water because the close mutual contact of neighbouring molecules ensures that they have relatively direct access to the crack tip. Capillary flow along the crack is then limited only by viscous forces and these seem to have little influence on subcritical crack velocities in the system SiO_2–H_2O (liquid) (Swain *et al.*, 1973). A plateau region is sometimes found for ceramic-liquid water systems, e.g. porcelain-liquid water (Evans and Linzer, 1973), but this has not yet been satisfactorily explained. In some cases a transport-limited crack velocity could result if a gradient in chemical concentration were to be established along the crack as a result of the inhibition of the diffusion of active species arising from the build up of reaction products in solution near the crack tip (LAWN and WILSHAW, 1975).

Secondly, using equation (6) an estimate of the crack velocity of the plateau region can be calculated for the quartz-water vapour system by considering the propagation of cracks for which the crack-wall separation narrows in the vicinity of the crack tip below the intermolecular mean free path of the vapour. If we consider the siloxane bond-water reaction discussed above then using the data given by LAWN and WILSHAW (1975) plus additional data relevant to the quartz orientation of the present experiments, and provided that an attenuation factor of 0.06 is adopted (LAWN, 1975), it can be shown that a plateau region would be expected at crack velocities of $\simeq 4 \times 10^{-4}$ m·s^{-1} at 20°C. This is just at the limit of the present data.

Severe bending in region 1 of the $K - v$ curve for the soda-lime glass-water system at 25°C has been reported by WIEDERHORN and BOLZ (1970) at crack velocities of ca. 10^{-10} m·s^{-1}, which strongly suggests that a stress corrosion or static fatigue limit is approached at these velocities. This result has been confirmed by EVANS (1972) and WIEDERHORN (1974). Physically this means that there is a stress below which tensile failure will not occur regardless of how long the specimen is subjected to stress. A stress corrosion limit has not been observed in studies of the silica glass-water vapour system or the borosilicate glass-water system at crack velocities down to 10^{-12} m·s^{-1}. This may indicate, however, that the limit is at a lower stress intensity factor than has yet been studied. It can be cautiously inferred from Fig. 4 that there is a bending of region 1 of the K–v curve for quartz cracked normal to the z plane at crack velocities of ca. 10^{-9} m·s^{-1}. Until more results can be obtained at lower K_I values to confirm this inference it must remain highly tentative. In the meantime, however, it is instructive to at least entertain the possibility that a stress corrosion limit is being approached in Fig. 4 at stress intensity factors of approximately 0.45 MN·m$^{-3/2}$. This is approximately 0.52 K_{IC}. No hint of a stress corrosion limit was observed in the room temperature data of Fig. 3, which although they did not go to quite as low velocities as the data of Fig. 4, they were obtained down to a lower fraction of K_{IC}; i.e. 0.39 K_{IC}. The stress corrosion limit in the soda-lime glass-water system at 25°C occurs at approximately 0.25 K_{IC} and that for the porcelain-water system at 25°C occurs at approximately 0.54 K_{IC}. It is of interest to note that in a fine-grained quartz rock (Novaculite)-water system at 20°C a stress corrosion limit was not observed at crack velocities down to $\simeq 10^{-10}$ m·s^{-1}, which corresponds to 0.67 K_{IC} (ATKINSON, 1979).

SCHOLZ (1972) found that crystallographic orientation exerted an influence on the stress dependence of static fatigue of quartz. The data of MARTIN and DURHAM (1975), however, were too scattered to allow such effects to be discerned, although they suggest that some variation in stress dependence should be expected. The present results show a marked influence of crystallographic orientation on stress corrosion index (compare Figs. 3 and 4). The critical stress intensity factor, K_{IC}, is also dependent upon crystallographic orientation (see Section 5). The values obtained for K_{IC} in this study may be compared with the determination of G_{IC} by HARTLEY and WILSHAW

(1973) using bend experiments. They found that at 20°C, in air $G_{IC} = 23\ \mathrm{J{\cdot}m^{-2}}$ ($K_{IC} \simeq 1.74\ \mathrm{MN{\cdot}m^{-3/2}}$) for quartz cracked on $\{10\bar{1}1\}$ planes.

7. *Conclusions*

Slow stable crack growth on the *a* plane of single crystal quartz in the presence of water or water vapour has been observed at crack velocities in the range from ca. $10^{-3}\ \mathrm{m{\cdot}s^{-1}}$ to $10^{-9}\ \mathrm{m{\cdot}s^{-1}}$. Over this range of crack velocities the crack propagation of quartz corresponds to region 1 of the schematic stress intensity factor-crack velocity diagram (Fig. 1). Subcritical crack growth is believed to be facilitated by chemical reaction between the siloxane bonds of the quartz and the water or water vapour of the environment.

For crack propagation normal to *z* and normal to *r* at 20°C, K_{IC} (the critical stress intensity factor) was found to be $0.852 \pm 0.045\ \mathrm{MN \cdot m^{-3/2}}$ and $1.002 \pm 0.048\ \mathrm{MN \cdot m^{-3/2}}$, respectively.

Region 2 of the schematic *K–v* curve (Fig. 1) is calculated to lie at a velocity of about $4 \times 10^{-4}\ \mathrm{m \cdot s^{-1}}$ for crack propagation normal to *z* in water vapour (68% RH) at 20°C. It may tentatively be inferred that there is a bending of *K–v* curves for this orientation at crack velocities of ca. $10^{-9}\ \mathrm{m \cdot s^{-1}}$, corresponding to $0.52\ K_{IC}$, which leads me cautiously to entertain the possibility that the data are approaching a stress corrosion limit. No evidence of such a limit was noted for crack propagation normal to *r*.

The slopes of isotherms in a log stress intensity factor–log crack velocity coordinate frame are dependent upon crystallographic orientation. The isotherms had a slope of 12 ± 0.6 for cracking normal to *r* and 19.9 ± 1.7 for cracking normal to *z*. The activation enthalpy for crack propagation in the former orientation in liquid water at temperatures from 20°C to 80°C was $52.5 \pm 3.8\ \mathrm{kJ\ mole^{-1}}$.

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