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# Review
# Static fatigue in glass

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Experimental developments and theoretical treatments of static fatigue in glass are reviewed. Areas requiring further research are highlighted.

## 1. Introduction

After many years of intensive study, the strength of glass is still not completely understood, particularly in relation to surface condition and local environment. The low effective strength, compared with the theoretical strength calculated, for example, from interatomic binding potentials, has very real consequences in the design of glass components which are to be used under sustained or dynamic conditions of loading. Equally, the design and construction of glass containers has to take into account the effect of possible chance abrasions within the component lifetime.

The presence of submicroscopic flaws or so-called Griffith cracks has been a subject of controversy during the last few decades, and particularly with regard to their nature and production in pristine surfaces, prior to extensive surface damage. Many of the theories proposed to account for the strength of glass differ fundamentally in approach and may be identified with the uncertainty which still surrounds the nature and physical properties of glass. In particular, the concept of glass as an ideally brittle material is still attracting much debate; the possibility of limited plastic deformation has influenced several theories for strength and related phenomena. The "non-Hookeian" view of glass and its consequences on the concepts of free surface energy and fracture surface energy has also resulted in discussion concerning the validity of parameters descriptive of the solid and liquid states. Thus the use of terms such as "surface tension of glass" and the possibility of dislocations associated with fracture properties are still being argued by some authors.

Specific difficulties which have arisen include that of establishing a quantitative understanding of the mechanisms responsible for static fatigue behaviour in glass. Static fatigue results in a time dependent deterioration in strength under conditions of sustained loading. As a consequence the design strength of a glass component is reduced still further from values based on experimental determinations of instantaneous strength. Further it has been demonstrated that the study of static fatigue susceptibility involves a knowledge of factors including the composition, the extent of surface damage and local atmospheric conditions.

In spite of the recent development of several theories for static fatigue and a considerable increase in the amount of published experimental data, a complete quantitative explanation which takes into account all the observed phenomena is yet to be produced. This review is an attempt to consolidate the present situation with regard to the development of theories and techniques and to the wealth of experimental data. Particular emphasis is placed upon the need to establish a meaningful correlation between atomistic descriptions of brittle fracture and macroscopic formalisms. It is also considered that any theory which accounts for static fatigue behaviour must necessarily embrace the now well established factors such as environmental sensitivity and composition to allow the required relationships with instantaneous strength measurements to be realized. These prerequisites are based on the belief that the complexity associated with strength and fatigue behaviour should not be underestimated and it is only under ideal conditions that the two phenomena are separable.

## 2. Early studies of static fatigue

### 2.1. Experimental observations

Several early workers presented experimental results which indicated the importance of relationships between loading time and breaking stress for glass specimens under various atmospheric conditions [1–4]. This work demonstrates the sensitivity of fracture stress to load duration and atmospheric water content, an increase in relative humidity being identified with more pronounced fatigue dependent reductions in strength. In contrast an absence of static fatigue was demonstrated for baked out specimens tested under conditions of high vacuum, and for measurements obtained at the temperature of liquid nitrogen. A strong dependence between time to failure and temperature within the range −190 to 520° C was also established; the lowest instantaneous strength measurements were obtained at 200° C in the presence of water vapour.

Some of the better known work on static fatigue is due to Charles [5] who studied delayed failure in soda-lime glass with a view to clarifying the relationship between the extent of strength reduction and atmospheric condition. Using a four-point bending apparatus, 3000 glass rods were tested under controlled conditions of temperature and relative humidity. Static fatigue was found to be highly temperature dependent, time independent failure occurring at −170° C. Delayed failure in soda-lime specimens was most apparent in saturated water vapour and at a temperature of around 150° C. This study was extended [6] to include dynamic loading by applying four different loading rates to 1000 soda-lime silica rods at temperatures of 25 and −195° C under otherwise similar atmospheric conditions. The failure stress was observed to decrease markedly with decreasing loading rate, low temperature failure again proving to be time independent.

Perhaps the most exhaustive study of fatigue effects in glass was carried out by Mould and Southwick [7–10] who investigated delayed failure in soda-lime silica specimens using load durations within the range $10^{-3}$ to $10^3$ sec. In their introductory paper [7] the authors emphasized their view that a complete understanding of the nature of static fatigue necessarily requires a systematic control of the physical and chemical environment before and during the test. The difficulties associated with the study of pristine surfaces were also discussed in relation to surface sensitivity and it was on this basis that samples which had been subjected to controlled degrees of abrasion were considered to be most appropriate for study.

Results for abraded samples [8] tested in water indicated a clear strength reduction with increasing load duration, the effect of different abrasions being apparent in the displacement of curves describing strength as a function of load duration. At the temperature of liquid nitrogen no static fatigue effects were observed. In the analysis of results the reduced parameters, $\sigma_c/\sigma_N$ and log $(t_f/t_{0.5})$ were introduced, where $\sigma_N$ is the strength at the temperature of liquid nitrogen and $t_{0.5}$ (the characteristic duration) is the time associated with the condition $\sigma_c/\sigma_N = \frac{1}{2}$. Measurements obtained for all surface abrasions were found to be consistent with a single function, such that,

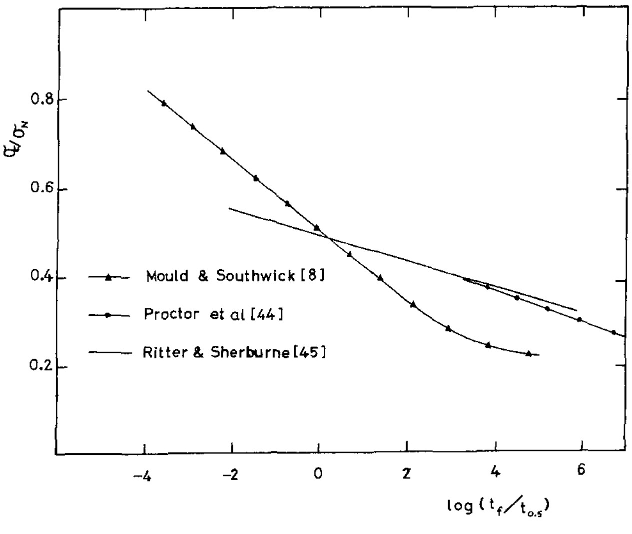

*Figure 1* Universal fatigue curves for abraded [8] and acid etched [45] soda-lime silica glass and for fused silica fibres [44].

$$\frac{\sigma_c}{\sigma_N} = f(t_f/t_{0.5}). \qquad (1)$$

Presentation of static fatigue data in this manner resulted in what has been termed the "universal fatigue curve" (see Fig. 1). This suggested that a particular surface condition is closely related to the characteristic duration, $t_{0.5}$. Further, by plotting $1/\sigma_N^2$ as a function of $t_{0.5}$ it was possible to distinguish between linear flaws (those orientated perpendicular to the direction of stress) and point flaws (those orientated parallel to the direction of stress); samples containing linear flaws appeared to fatigue more rapidly than those containing point flaws.

In a later paper [9], Mould considered the effect of ageing on static fatigue. The variation of reduced strength with load duration for specimens which had been aged in water or vacuum baked, indicated that in "ordinary conditions" the observed increase in effective strength associated with ageing is dependent upon a change in instantaneous strength rather than upon static fatigue behaviour.

In the final paper of the series [10], the influence of the surrounding medium on static fatigue was investigated. For intermediate load durations (greater than $10^{-3}$ sec and less than 1 h) a strong correlation was shown to exist between humidity and strength, an increased relative humidity or immersion in water leading to considerable strength reductions. However, for very short (less than $10^{-3}$ sec) and very long (greater than 1 h) durations the influence of water content was less apparent. The characteristic durations, $t_{0.5}$, for specimens stored in water for 24 h and tested in water and in atmospheres of 43% and 5% r.h. were found to be 8200 and 3500 sec respectively. By considering the possibility of constructing a universal fatigue curve for different environmental conditions, the influence of humidity for intermediate load durations appeared to be related to a change in the rate of static fatigue rather than in intrinsic strength.

Tests carried out in mixtures of distilled water and methyl and isopropyl alcohol indicated a considerable correlation between water contant and short duration strength measurements. The results of tests carried out in pure alcohols were in contrast to earlier results [11], specimens immersed in isopropyl alcohol being stronger than those tested in methyl alcohol for short load durations. Strength was also shown to be invarient to pH in the range pH 1 to 13 although considerable changes were apparent for very basic and very acid solutions (see Fig. 2).

Thus by the early sixties although the mechanisms responsible for static fatigue were unknown, the major factors affecting fatigue sensitivity had become established. These included the effects of local atmospheric constituents and humidity, the extent of ageing prior to loading, the degree of surface abrasion and temperature. This work provided a sound basis for further study and in

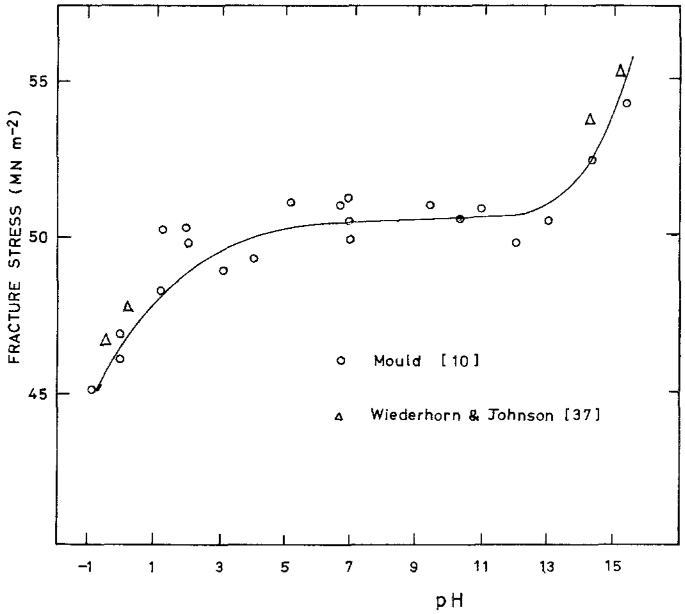

*Figure 2* Influence of environmental pH on the fracture properties of soda-lime silica glass. Fracture stress determinations of Wiederhorn and Johnson were based on crack velocity data.

particular for the investigation of the precise relationships between external constraints and possible mechanisms proposed for delayed failure.

## 2.2. Semi-empirical approaches

Explanations for static fatigue phenomena include those which were based on the fit of experimental data to empirical expressions relating breaking stress and load duration. One of the earliest of these expressions was due to Holland and Turner [12] who suggested the use of the equation,

$$\log t_f = a + b \log \sigma_c \tag{2}$$

where $t_f$ is the time to fracture and $\sigma_c$ is the critical macroscopic breaking stress. In contrast, Glathart and Preston [13] proposed the equation,

$$\log t_f = a + b \frac{1}{\sigma_c} \tag{3}$$

which resulted in good agreement with published experimental data [1]. More physical approaches included that of Orowan [14, 15] who considered that static fatigue is due to a reduction in surface energy owing to the presence of water; this lowers the critical stress required for crack propagation. Using values of surface energy obtained for mica, he suggested that the corresponding reduction in strength with time was consistent with the observations of Baker and Preston for glass [1].

Stuart and Anderson [16] pointed out possible inadequacies of the theories of Murgatroyd and Sykes [17] and Hodgson *et al.* [18] which assume a departure from perfect elasticity, and the statistical rate theory of Taylor [19]. They proposed an alternative statistical rate theory which was based on the assumption that the structure of glass may be considered in terms of two semi-independent structures. One such structure allows the formation of new surfaces through the breakage and reorientation of bonds and thus, eventual crack propagation. The other was considered to permit the reformation of bonds in a manner consistent with the maintenance of strength. This approach which leads to an expression of the form

$$\log t_f = a + \frac{b}{\sigma_c} + \log \sigma_c \tag{4}$$

was claimed to account for the sensitivity of static fatigue effects in relation to changes in activation energy.

## 2.3. Stress corrosion mechanisms

The inability of earlier theories to account completely for all the observed phenomena led Charles [5, 6, 20] and Charles and Hillig [21, 22] to investigate the relationship between slow crack growth prior to catastrophic failure and changes in crack geometry brought about by stress activated corrosion. Adopting a chemical approach [20], Charles showed that the presence of water is consistent with the breaking of Si–O bonds, involving an initial reaction of water with a network modifying alkali ion which results in a free hydroxyl ion and the dissociation of an $H_2O$ molecule. The free hydroxyl ion was considered to interact with the silica network such that

$$\text{Si–O–Si} + \text{OH}^- \rightarrow \text{SiOH} + \text{SiO}^-,$$

leading to the formation of a silanol group, the remaining terminal Si–O$^-$ being capable of further $H_2O$ dissociation. It was also pointed out that initial reactions may also lead to a change in pH due to the excess number of hydroxyl ions, thus having an autocatalytic effect and allowing glass dissolution to be accelerated.

Extending the analysis to include the structural implications of stress corrosion [5], Charles introduced the Inglis expression [23] for the stress at a crack tip (see Fig. 3),

$$\sigma_m/\sigma_a = 2\left(\frac{L}{\rho}\right)^{1/2} \tag{5}$$

where $L$ is the flaw depth, $\rho$ the radius of curvature of the tip, $\sigma_m$, the crack tip stress and $\sigma_a$, the applied stress. Thus, for a crack with critical depth, $L_c$, the equation may be rewritten,

$$\sigma_t/\sigma_c = 2\left(\frac{L_c}{\rho}\right)^{1/2}, \tag{6}$$

where $\sigma_t$ is the theoretical rupture stress and $\sigma_c$ is the critical macroscopic stress.

Charles postulated that crack propagation involves a stress and temperature dependent chemical reaction at the crack tip, and that the radius of curvature of the crack tip is effectively constant such that stress activated corrosion is maintained and proceeds at a faster rate than ordinary corrosion. An expression for crack velocity, $V$ was introduced having the form

$$V|_T = f(\sigma_m) + K \tag{7}$$

where $f(\sigma_m)$ is an unknown function describing crack tip stress concentration, $K$ is the corrosion rate at zero stress and $T$ is the temperature. Clearly for large $\sigma_m$ then $f(\sigma_m) \gg K$ such that $V$ increases rapidly until a crack of critical dimension $L_c$ results in spontaneous fracture. Introducing an empirical form for the function $f(\sigma_m)$ such that $f(\sigma_m) = K'(\sigma_m)^n$ and the Inglis relationship for large stress concentrations, then Equation 7 may be written,

$$V|_T = B\left[K''\left(\frac{L}{L_c}\right)^{n/2} + K\right] e^{-A/RT}, \quad (8)$$

where $R$ is the gas constant and $A$ is an activation energy for both stress activated and non-stress activated corrosion.

Neglecting the term identified with ordinary corrosion and integrating Equation 8 from an initial flaw size $L_o$ to the critical size $L_c$, Charles obtained the expression,

$$\log t_f = n \log \frac{1}{\sigma_c} + b, \quad (9)$$

if $L_c/L_o \ggg 1$. The condition $L_c/L_o = 1$ describes spontaneous fracture.

The experimental results of Charles are in reasonable agreement with Equation 9 for temperatures less than 150° C, resulting in an estimated activation energy of 79 kJ mol$^{-1}$. Considerable departures from the theory were observed for samples tested at 200 and 240° C. Charles attributed this to a completely different mechanism governing high temperature static fatigue although a precise interpretation was not possible.

The effect of different loading rates was also considered by Charles [6] using a similar formalism. By introducing a constant increase in stress such that $\sigma_a = \beta t$ and $\sigma_c = \beta t_f$ then the critical macroscopic stress for failure was shown to have the form

$$\sigma_c = K\beta^{1/(n+1)} \quad (10)$$

where $K$ is a constant. Using the value of $n$ determined from static fatigue data ($n = 16$) experimental results obtained for dynamic fatigue were found to be in accordance with Equation 10.

Perhaps the most widely known theory for static fatigue is due to Charles and Hillig [21, 22], this being an extension of the work of Charles [5, 6, 20]. By considering glass to be perfectly elastic and isotropic a thermally activated and stress dependent corrosion process was proposed. This process, influenced by local stresses and any excess of surface energy, was thought to result in reaction products incapable of withstanding the applied stress. The velocity associated with such a corrosion process may be written in the form

$$V = K \exp -(A^*(0) + \gamma V_m \rho - \sigma_t V^*)/RT \quad (11)$$

where $A^*(0)$ is the stress free activation energy, $\sigma_t$ is the critical stress at the crack tip, $\gamma$ is the surface energy associated with the interface between the glass and reaction products, $V^*$, is an activation volume, $V_m$ is the molar volume and $\rho$ is the radius of curvature at the crack tip. The term, $\gamma V_m/\rho$ may be identified with the molar free energy contribution associated with the curvature of the surface.

Having established a formulation for the stress corrosion process Charles and Hillig went on to consider a time dependent relationship with flaw geometry by using the Inglis expression [23] for the effective stress concentration at a crack tip. Introducing reduced parameters for time and crack length, an expression for the effective change in crack length, $\partial U/\partial \tau$ was deduced in terms of the reduced crack length, $2(L/\rho)^{1/2}$, reduced time, $\tau$, and applied macroscopic stress. Using this formalism it is possible to discriminate between the physical situations associated with different crack tip geometries (see Fig. 3). First, if $\partial U/\partial \tau$ is negative, a rounding of the crack tip occurs (the

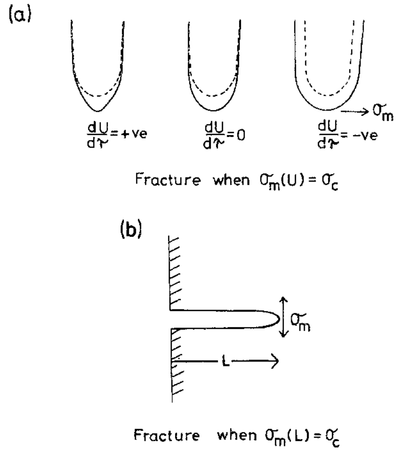

*Figure 3* Crack tip geometry associated with the stress corrosion theories of, (a) Charles and Hillig [21], and (b) Charles [5].

Joffé effect), and therefore the reduced stress concentration ensures that there is no crack propagation. Second, if $\partial U/\partial \tau$ is positive, then crack propagation becomes increasingly likely, owing to the sharpening of the crack tip. Finally, the case of $\partial U/\partial \tau = 0.0$ is consistent with a static fatigue limit, corresponding to constant stress concentration with time and the indefinite support of a particular load.

Further, by integrating over a limited range corresponding to the case of high stress application, Charles and Hillig calculated the time to failure for a particular stress, comparing their results with those of Mould and Southwick [7–10]. From this they concluded that the activation volume was comparable with that associated with alkali ion diffusion in soda-lime glass, and that a predicted fatigue limit, $\sigma/\sigma_N = 0.15$ was consistent with experimental results.

The stress corrosion theory of Charles and Hillig is in accordance with experiment in several respects although the authors were aware of several departures from completeness.

The most important of these is the apparent failure to account for the sensitivity of experimental data to the failure time at half the instantaneous stress. Furthermore both theories of stress corrosion rely on expressions for crack velocity which do not have a firm physical basis, the former being of an empirical nature and the latter being dependent on an analogy with another physical system. It is also important to emphasize that the two theories differ with respect to time dependent variations in crack geometry; the theory of Charles involves an assumption of constant stress concentration, $\Delta\rho = 0$, while that of Charles and Hillig is based on changes in crack tip geometry (see Fig. 3).

## 3. Measurement of slow crack growth

In recent years, as the complexity of fatigue effects in glass has become established, the importance of experimental technique has been emphasized. This has led to the reassessment of many existing techniques for strength measurement [24, 25] and the development of new methods for the study of slow crack growth. The interest in crack growth observation has emerged in recognition of the widely held view that the precise relationship between flaw growth and the local environment must be investigated using fracture mechanics if fatigue effects in glass are to be understood (see review by Wiederhorn [49]).

### 3.1. Double cantilever beam and double torsion techniques

The double cantilever beam technique (Fig. 4) is now becoming established as a means of studying slow crack growth optically [26, 27]. The crack is constrained to the midplane of the specimen, initiation being achieved by cutting a wedge-shaped notch into the edge of the glass. The load is applied in a direction perpendicular to that of crack growth. A solution for the double cantilever geometry leads to expressions for the stress intensity factor, $K_I$, and the displacement of loading points, $y$, in terms of the applied load [28]:

$$K_I = (PL/w^{1/2}b^{1/2}d^{3/2})(3.467 + 2.315d/L) \tag{12}$$

$$y = 4PL^3/Ewd^3 + 7.92\,PL^2/Ewd^2 + 2.65\,PL/G'wd. \tag{13}$$

$P$ is the applied load, $L$ is the crack length and $E$ and $G'$ are Young's modulus and the shear modulus, respectively (see Fig. 4 for the definition of the parameters, $w$, $b$, $d$).

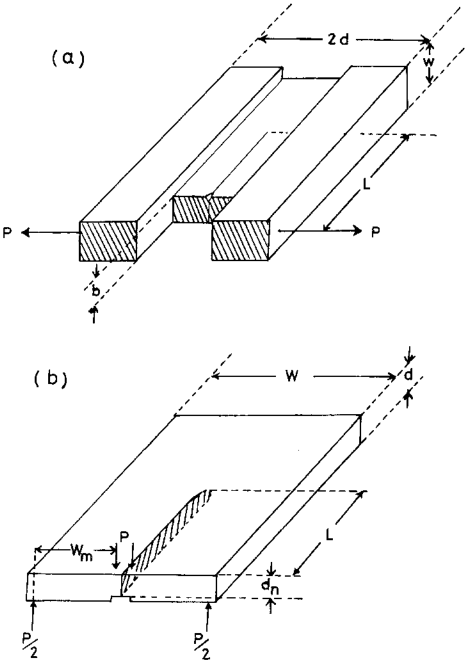

*Figure 4* Experimental methods for the study of slow crack growth in glass: (a) double cantilever beam technique, (b) double torsion technique. (After [27].)

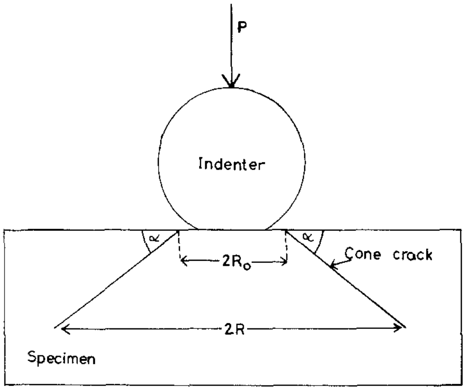

*Figure 5* Microprobe technique for the measurement of cone crack growth in brittle solids. (After [30].)

In the double torsion technique [27] the tensile loading is replaced by torsional loading applied by means of three of four point bending (Fig. 4). A solution for this geometry [29] indicates that the displacement of loading points is directly proportional to crack length under constant torsional loading such that

$$y = P(BL + c) \quad (B \text{ and } c \text{ constants}), \quad (14)$$

$$K_\mathrm{I} = PW_\mathrm{m}\left[\frac{3(1+v)}{Wa^3 d_n}\right] \quad (15)$$

Thus, the stress intensity factor is seen to be dependent on applied load but independent of crack length, resulting in a constant $K_\mathrm{I}$ evaluation of crack velocity. A similar condition may be introduced into the double cantilever beam technique by a modification of the geometry such that a constant applied load may be replaced by a constant moment [27].

## 3.2. Microprobe technique

Swain and Lawn [30] have reported the use of a new technique for measuring slow crack growth in brittle solids based on the Hertzian fracture test [31]. The configuration illustrated in Fig. 5 consists of a machined tungsten carbide ball which is pressed into the flat specimen surface until a cone crack is initiated. The crack tip is followed photographically as it extends into the bulk material for a given increase in applied load. Crack velocities may be obtained from the expression

$$V = (\Delta R/\cos\alpha)/\Delta t \quad (16)$$

where $\Delta R$ and $\Delta t$ are determined from successive frames on the film. Initial tests using an environmental chamber suggest that this technique will be of considerable value.

# 4. Recent experimental studies

## 4.1. Humidity

The influence of water vapour on static fatigue phenomena has been studied by Wiederham [32] who used the double cantilever technique on soda-lime specimens to demonstrate a clear dependence between the humidity of the sample environment and the observed crack velocity. By plotting crack velocity against applied force, Wiederhorn distinguished between three regions describing crack propagation. Crack motion in region I was considered to be limited by the rate of reaction of water at the crack tip while in region II it was suggested that the transport of water to the crack tip is the principle limiting factor. Region III which may be identified with the onset of very rapid crack growth was found to be more difficult to interpret. Rate equations based on the theory of Charles and Hillig [21, 22] accounted for the shape of the curves shown in Fig. 6 but were unable to predict the dependence on water vapour concentration.

Weidmann and Holloway [33] have published results for crack velocity as a function of strain energy release rate for float and sheet glass. A double torsion configuration was used with

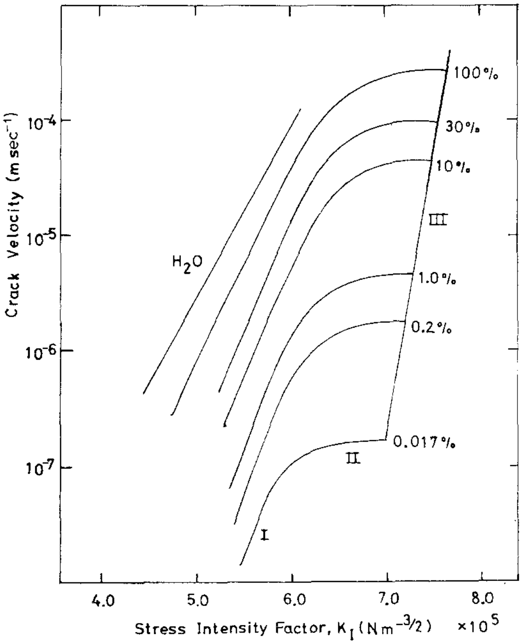

*Figure 6* Influence of humidity on crack propagation in soda-lime silica glass. (After [32].)

four-point bending load application. For tests carried out in air (50% r.h.) and $H_2O$ good agreement was obtained with the results of Wiederham [32] and Schönert *et al.* [34].

## 4.2. Alcohol environments

The influence of alcohols on glass strength has attracted much attention, particularly in view of the work of Westwood and co-workers who indicated that a chain length of seven results in a considerable increase in indentation hardness and has a pronounced effect on diamond bit drilling rates [35]. This effect is difficult to explain and has been attributed to changes in effective surface potential, although the singularity observed using heptanol ($N = 7$) is still subject to much debate. In contrast, Freiman [36] has published results on the effects of alcohols on crack propagation in glass, and has found no confirmatory evidence for the results of Westwood. Crack velocities at high stress intensities appeared to be independent of water content and increased monatonically with alcohol chain length.

## 4.3. Changes in pH

Extending the work of Mould [10], Wiederhorn and Johnson [37] investigated the effect of pH on strength using crack velocity data for a range of compositions (silica, soda-lime silica and borosilicate glasses). Their results confirming those of Mould, and Langitan and Lawn [38] indicated that the strength of glass increases for pH values greater than 13 and decreases for a pH less than 2 (Fig. 2).

For silica glass a linear relationship between crack velocity and stress intensity factor was observed, together with a clear dependence of slope on environmental pH (Fig. 7). Results for the other glasses were more difficult to interpret, departures from linearity being apparent in some cases. It is interesting, however, that experiments on borosilicate glass in acid solutions suggest the existence of a fatigue limit; crack arrest was observed in 1 N HCl for a stress intensity factor of $\sim 4 \times 10^5$ N m$^{-3/2}$. Universal fatigue curve data calculated from these results (see Section 4.4) are shown in Table I. A further study [39] of a high silica glass in 1 N HCl and 1 N NaOH environments suggested that for an alkaline environment it is possible to discriminate between low velocity and high velocity processes, while for an acidic environment no differences arise (Fig. 7). These effects were interpreted in terms of changes in crack tip environment (see Section 5).

Ritter and La Porte [40] have recently used a dynamic loading technique to explore the relationship between stress corrosion susceptibility and test environments of 6 N NaOH, $H_2O$ and 6 N HCl. Abraded and acid etched borosilicate and soda-lime silica glasses were studied; good agreement with crack velocity data for 6 N NaOH and $H_2O$ environments [37] was obtained. Tests

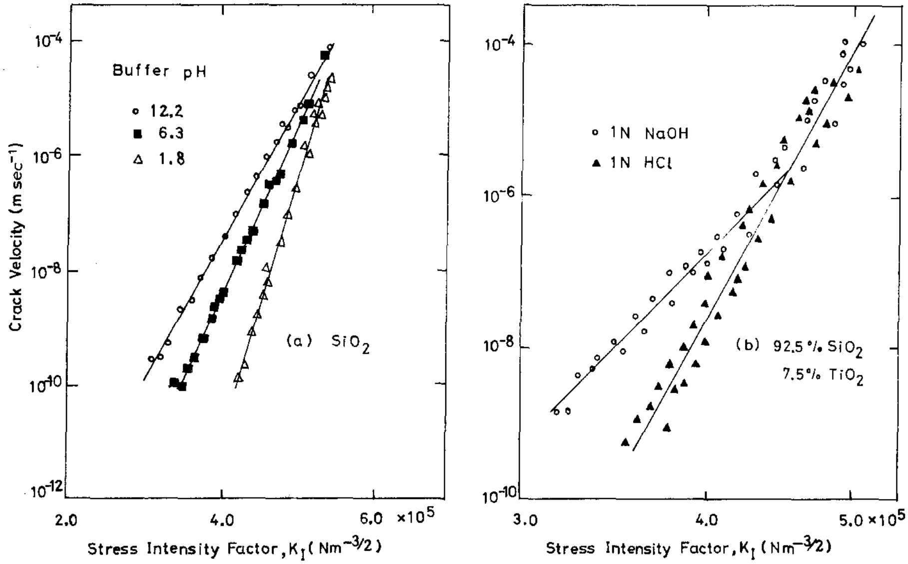

*Figure 7* Influence of pH on crack growth in glass: (a) silica glass (after [37]), (b) 92.5 wt% $SiO_2$, 7.5 wt% $TiO_2$ (after [39]).

carried out in 6 N HCl did not result in correspondence between crack velocity and dynamic loading data.

### 4.4. Composition

The composition of glass is now recognised as being an important factor associated with instantaneous strength measurements and the role of network modifying oxides has been well investigated [41–43].

The need to discriminate between changes in instantaneous strength (measured at low temperature and relative humidity) and different rates of subcritical crack growth has led to a number of interesting experiments concerning the possible relationships between crack growth and static fatigue susceptibility.

Wiederhorn and Bolz [26] extended the analysis of Wiederhorn [32] to include different compositions (silica, alumino-silicate, borosilicate, lead alkali and soda-lime silica glasses). For soda-lime silica and borosilicate glasses an exponential variation of crack velocity with stress intensity factor was apparent for velocities greater than $10^{-8}$ m sec$^{-1}$. At lower velocities a variation greater than the exponential rate was observed, this being suggestive of a fatigue limit. The alumino-silicate and silica glasses showed an exponential dependence throughout the range of crack velocities ($10^{-5}$ to $10^{-11}$ m sec$^{-1}$). The influence of increasing the temperature was also apparent leading to a systematic displacement of curves (crack velocity versus stress intensity factor) for soda-lime glass. There was also an indication of departure from the exponential rate at high crack velocities as the temperature was increased.

Using a method of least squares Wiederhorn and Bolz fitted their experimental data to an expression of the form,

$$V = V_o \exp -(A + bK_I)/RT \qquad (17)$$

yielding activation energies, $A$, within the range 105.3 to 138.3 kJ mol$^{-1}$ (cf. Charles and Hillig [21, 22]). In order that meaningful comparisons might be made with the results of Mould and Southwick [7–10] the form of a universal fatigue curve was predicted by integrating equation 17 between the limits, $K_1$, the initial stress intensity factor and $K_c$ the stress intensity factor at failure. This resulted in equations of the form

$$\begin{aligned} t &= [(2L/K_1^2) V_o \mathrm{e}^{-A/RT}] \int_{K_1}^{K_c} K_I \mathrm{e}^{-K_I/RT} \mathrm{d}K_I \\ &= \frac{2RTL}{K_1 b V_1} \end{aligned} \qquad (18)$$

from which they deduced that

$$\frac{K_I}{K_c} = \frac{\sigma_a}{\sigma_N} = \tfrac{1}{2} - (2.3RT/bK_c) \log(t_f/t_{0.5}) \qquad (19)$$

assuming the relationship, $K_1 = \sigma_a(\pi L)^{1/2}$ where $\sigma_a$ is the applied stress and $L$ is the crack length. It was emphasized by the authors that Equation 19 is not applicable to short failure times and does not predict a fatigue limit. Universal fatigue curves were also calculated by numerical integration using crack velocity data, there being good agreement between results obtained from the two methods. On this basis it was suggested that the necessary correspondence between strength, fatigue and crack velocity data had been established.

Universal fatigue curve slopes (Table I) appeared to confirm a sensitivity to composition indicated from the results of Mould and Southwick [8] and Procter *et al.* [44]. Further, by replotting the fatigue curves in the form of applied load vs. failure time, it appeared that silica and alumino-silicate glasses, having low sodium content, are more resistent to static fatigue, soda-lime silica and lead alkali being the least resistent. Finally, Wiederhorn and Bolz pointed out their overall agreement with the predictions of the stress corrosion theories, thus supporting the view that static fatigue is controlled by a stress activated reaction between glass and water.

Ritter and Sherburne [45] have investigated the dependence of delayed failure on composition using both static and dynamic methods of testing. Annealed and abraded borosilicate glass and fused quartz rods were tested using the dynamic loading approach and good quantitative agreement was obtained with the crack velocity data of Wiederhorn and Bolz [26]. Static fatigue data obtained from HF etched soda-lime silica rods at various relative humidities resulted in a single universal fatigue curve. This curve was not in agreement with that calculated by Mould and Southwick for abraded specimens (see Fig. 1). However, agreement with earlier results for pristine "E" glass [46] and fused silica fibres was apparent [44] (see Table I). This observed sensi-

TABLE I Static fatigue data obtained for various glass compositions and surface conditions

| Glass | Surface treatment | Test condition | UFC slope | $t_{0.5}$ (sec) | Reference and comments |
|---|---|---|---|---|---|
| Borosilicate | Abraded | 100% r.h. | 0.074 | 54.0 | [47] |
| | Acid polished | 100% r.h. | 0.040 | $1.8 \times 10^{-2}$ | [47] |
| | Untreated | 1 N NaOH | 0.050 | 0.63 | [37] Crack growth data |
| | Untreated | 1 N HCl | 0.024 | $\infty$ | [37] |
| | Untreated | Water | 0.034 | 2.14 | [37] |
| Soda-lime silica | Abraded | Water | 0.078 | $4.32 \times 10^{-3}$ | [8] |
| | Acid polished | 100% r.h. | 0.031 | $5.34 \times 10^{-2}$ | [45] |
| | Untreated | 1 N NaOH | 0.065 | 2.04 | [37] Crack growth data |
| | Untreated | 1 N HCl | 0.042 | 0.27 | [37] |
| | Untreated | Water | 0.068 | 0.57 | [37] |
| Silica | Flame drawn fibre | 100% r.h. | 0.034 | $6.6 \times 10^{-4}$ | [44] |
| | Untreated | 1 N NaOH | 0.056 | 2.2 | [37] Crack growth data |
| | Untreated | 1 N HCl | 0.029 | 666.0 | [37] |
| | Untreated | Water | 0.032 | 73.0 | [37] |

tivity to surface condition and apparent insensitivity to composition, was discussed by Ritter and Sherburne who pointed out such phenomena are difficult to explain in terms of a stress corrosion mechanism alone.

Ritter and Manthuruthil [47] extended the analysis of Ritter and Sherburne to include abraded and acid polished borosilicate glass. Their results add further support to the view that the slope of a universal fatigue curve depends primarily on surface condition rather than composition. (Slopes of universal fatigue curves obtained from specimens of different surface condition and composition are summarized in Table I). It was further argued that the wide range of values for universal fatigue curve slope casts considerable doubts upon the suggested relationship between slow crack growth and static fatigue data [26].

Wiederhorn *et al.* [48] have conducted tests on a series of glasses under vacuum conditions, which shed considerable light on the relationship between composition and slow crack growth. Although subcritical crack growth was readily apparent in alumino-silicate, borosilicate crown, 61% lead and soda-lime silica glass, catastrophic failure was only observed for borosilicate glass and fused silica. These results led to interesting speculations concerning the dependence of fracture on macroscopic structural properties. In particular, glasses which exhibit slow crack growth have high thermal expansion coefficients, a negative dependence of bulk modulus on temperature and a positive dependence on pressure. Glasses which fractured catastrophically have opposite elastic and thermal properties. In the cases where slow crack growth was apparent, a strong dependence of stress intensity factor on temperature was apparent, higher temperatures (~ 400° C) corresponding to a decreased value for $K_I$. These changes also appeared to be dependent upon composition.

## 5. Theoretical descriptions of static fatigue

### 5.1. Mechanisms based on slow crack growth

The emergence of stress corrosion theories and recent studies of macroscopic crack propagation have resulted in the acceptance, by many workers, of a static fatigue mechanism based on the slow growth of microscopic surface flaws. This has led to considerable interest in the physical nature of the processes involved.

The importance of crack tip environment as a major factor controlling crack growth has been emphasized by Wiederhorn [49] who suggested that during fracture, alkali ion exchange between the glass and the solution near the surface leads to localised regions of high pH at the crack tip. The crack tip pH may also be affected by other interactions, including the ionization of surface silanol groups and reactions with network formers and modifiers. Wiederhorn stresses that owing to the relativity small volume of crack tip solution compared with the crack fracture surface very large variations in pH may be achieved. Following Charles [20], bond rupture may be viewed in terms of the adsorption of $OH^-$ ions. It is important to emphasize the competitive nature of crack tip processes, this resulting in different crack velocity behaviour at high and low stress intensities [32]. In particular, it has been suggested that for slow crack velocities reactions with the glass composition are the major controlling factor while at high velocities control is maintained by the external environment.

In the light of recent evidence, any viable theory must take into account the apparent importance of composition on crack growth phenomena [45, 47, 48]. Wiederhorn has suggested that crack tip reactions are dominated by ion exchange mechanisms for high alkali glasses, while for a low alkali glass, surface silanol groups take precedence. On this basis, Wiederhorn and co-workers have suggested that the slope of a universal fatigue curve is dependent primarily on surface pH, other factors such as composition and surface condition having indirect influence.

The crack velocity data of Wiederhorn have been analysed by Evans and Johnson [50], enabling the fracture strength to be predicted from slow crack growth observations. Their formalism, based on the presence of three distinct propagation regions (see [32]) relies upon the characterization of each region by an expression of the form

$$V = \frac{\mathrm{d}L}{\mathrm{d}t} = AK^n \tag{20}$$

where $L$ is the crack length and $A$ and $n$ are constants. Relationships between stress rate, $\mathrm{d}\sigma/\mathrm{d}t$ and fracture stress $\sigma_c$ may be obtained from the variation of crack velocity and stress intensity factor. Comparisons made between bending strength measurements and crack velocity data for a soda-lime silica glass in 1% r.h. suggested that the propagation mechanisms associated with pre-existing flaws and macroscopic cracks are similar.

## 5.2. The interpretation of vaccuum measurements

The view that static fatigue may be identified with an activated process dependent primarily on water content and pH leads to problems in the interpretation of slow crack growth data, obtained under vacuum conditions. Wiederhorn and co-workers [48] have considered possible mechanisms for crack propagation in the absence of water and other atmospheric constituents, calculations based on their experiments resulting in values for activation energy in the range 250 to 736 kJ mol$^{-1}$. The possibility of alkali ion diffusion resulting in localized sources of weakness and slow crack growth was rejected on the basis of incompatibility of activation energies and inconsistency associated with experimental results obtained from glasses of different alkali content. Wiederhorn *et al.* did concede, however, that alkali ion diffusion may play a minor role by influencing the activation energy required for a rate controlled reaction.

Mechanisms based on viscous flow and thermally activated processes were also considered. The former possibility was rejected on the basis of inconsistency of relaxation times with slow crack growth at low temperatures. However, a calculated value for the temperature associated with the transition from brittle to ductile fracture was consistent with the cessation of crack growth.

The influence of thermal fluctuations in causing the required deviations of atoms from energetically stable sites to cause localized weakness and flaw propagation has been considered in the past [16, 51, 52]. Wiederhorn *et al.* described slow crack growth in terms of reaction rate theory such that

$$V = V_0 \mathrm{e}^{-\Delta A/RT} \tag{21}$$

where $\Delta A$ is the change in free energy of a bond between initial and rupture states.

Further,

$$\Delta A = \Delta H + P\Delta V - T\Delta S \tag{22}$$

where $\Delta H$ is the activation enthalpy, $\Delta S$, the activation entropy and $\Delta V$ is an activation volume. This type of formalism, which results in a crack velocity equation similar in form to that of Charles and Hillig accounts for slow crack phenomena in some glasses although it is inconsistent with the catastrophic failure observed for fused silica and low alkali borosilicate glass. In conclusion, it was suggested by Wiederhorn *et al.* that a lattice trapping theory similar to that developed by Thomson *et al.* [53] and Hsieh and Thomson [54] might satisfactorily account for their observations.

## 5.3. Lattice trapping theory of fracture

Lawn [55], commenting on the theory of Thomson *et al.* has pointed out the need for an atomistic model for crack growth which allows the required correspondence to be made with energy balance concepts of brittle fracture [56]. Such a model, it was suggested, should include a description of ideal brittle fracture in the following terms.

(1) The Griffith energy equation should apply such that the work done by the applied forces in increasing the fracture surface area is balanced by a corresponding increase in surface energy.

(2) The propagation of a crack through a brittle solid may be described in terms of a succession of bond ruptures, the energy barrier associated with each rupture resulting in effective "lattice trapping" of the advancing crack.

(3) The advancing crack may be represented as a lateral displacement of crack front "kinks" which provide active sites for bond rupture.

(4) The kink displacements may be thermally enhanced.

These ideas were applied to a hypothetical crystalline system of point masses which allowed distinction between linear effects (stretching and bending of bonds) and non-linear behaviour at the crack front. The linear zone, corresponding to the surrounding lattice structure was associated with the mechanical energy of the applied forces while the non-linear zone was considered to contain the surface energy characterization of crack movement; the variation of surface energy with atomic position was approximated using a simple harmonic function. The development of this model for crack growth allowed the explicit characterization of crack velocity and the introduction of external constraints by a suitable modification of the total energy function.

These concepts have recently been applied to a glass [57] by modifying the expression for the periodic variation of total surface energy, $U_s$, (see [55]). This was achieved by replacing the lattice spacing parameter by an area, $a$, associated with rupture of individual bonds at the crack front. In this case,

$$U_s = 2\gamma A - \frac{\gamma_t a}{\pi} \sin\left(\frac{2\pi A}{a}\right) \qquad (23)$$

where $\gamma_t$ is a trapping term, $\gamma$ is the reversible surface energy and $A$ is the area of fresh fracture surface accompanying crack growth. The fracture surface energy may, therefore, be expressed,

$$2\Gamma = \frac{dU_s}{dA} = 2\gamma - \gamma_t \cos\left(\frac{2\pi A}{a}\right) \qquad (24)$$

and a lattice trapping range may be defined as

$$2\Gamma_- < G < 2\Gamma_+ \quad \text{where} \quad \Gamma_\pm = \gamma \pm \gamma_t,$$

and $G$ is the mechanical energy release rate. Thus, defining an activation energy, $\Delta G_f$ such that

$$\Delta G_f = \Delta G_o(1 - G/G_t), \qquad (25)$$

then the crack velocity may be expressed

$$V = V_o \exp(-\Delta G_f/RT), \qquad (26)$$

and hence

$$\ln\left(\frac{V}{V_o}\right) = -\Delta G_o\left(1 - \frac{K_I^2}{K_t^2}\right)\Big/RT, \qquad (27)$$

where $K_I$ is the stress intensity factor, $K_t$ corresponds to the stress intensity when $\Delta G_f = 0$, and $\Delta G_o$, $G_t$ and $V_o$ are constants. Using this formulation, and the experimental data of Wiederhorn *et al.* [48] determinations of parameters in Equation 27 were obtained. It is interesting to note that the essential difference between this analysis and that used by Wiederhorn is the dependence of ln $V$ upon $K_I^2$ rather than upon $K_I$.

## 5.4. Alternative theories

### *5.4.1. Plastic flow*

Weidmann and Holloway [58] have proposed that a mechanism based on limited plastic deformation is responsible for static fatigue in glass. They suggested that the concept of plastic flow is necessary in order to account for the large difference between energy dissipation associated with crack propagation and surface free energy. It was proposed that a zone of plastically deformed material exists around the tip of a propagating crack and that the work done in forming such a zone is the dominant energy absorbing process associated with the advancing crack. Further, it was suggested that for growth to occur plastic deformation must be limited, this limit providing the necessary criterion for bond rupture. Characterizing the size of the deformed zone by $R$, a relationship was established with the corresponding flow stress, $\sigma_f$, and stress intensity factor $K_I$:

$$R = \frac{1}{2\pi}\left(\frac{K_I^2}{\sigma_f^2}\right). \qquad (28)$$

Slow crack propagation was characterized by the expression,

$$V = \left.\frac{\mathrm{d}R}{\mathrm{d}t}\right|_{R_c} = \frac{K_I^2}{\pi\sigma_f}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{\sigma_f}\right). \quad (29)$$

Further, using a relationship between flow stress and time of the form

$$1/\sigma_f = A \ln(Bt), \quad (30)$$

where $A$ and $B$ are constants, conditions for plastic zone stability were obtained, resulting in an expression for slow crack growth,

$$V = \frac{K_I A B}{\pi}(2\pi R_c)^{\frac{1}{2}} \exp - \left(\frac{2\pi R_c}{K_I A}\right)^{\frac{1}{2}}, \quad (31)$$

where $R_c$ is the critical zone dimension.

This analysis allowed a quantitative description of fatigue life-time, by assuming that the flow stress decreases with lapse of time to the level of the applied stress. It was possible to discriminate between pristine and precracked samples, and reasonable agreement was obtained between theoretical predictions and experimental results [8, 45]. However, further comparisons using a wider range of experimental data are required before the validity of this theory may be established.

### 5.3.2. *Ion mobility*

Cox [59] has proposed a mechanism for failure in glass which involves a thermally activated process. He was particularly critical of existing flaw theories of fracture and suggested an alternative mechanism which replaces the "static" view of Griffith flaws by a "dynamic" approach involving the movement of ions within a silica network. This would lead to localized regions of weakness resulting in a self generated flaw. His theory is based on the belief that simultaneous local rupturing of bonds can occur resulting in a new fracture surface, the probability of a particular bond being in an "abortive state" being given by the Boltzmann expression. The occurrence of fracture thus assumes that the probability of simultaneous rupture within a three-dimensional silica network does not decrease indefinitely as the number of bonds under consideration is increased. Mobile alkali ions were regarded by Cox as carrying with them a certain amount of dissociation energy as they migrate from site to site, finally recombining and releasing energy required for the bond rupturing process.

The theory of Cox has been tested by Ritter and Manthuruthil [47] using their experimental results, good agreement being obtained for acid polished soda-lime silica and borosilicate glass. However, values of activation energy for ion mobility obtained using the Cox theory for borosilicate, soda-lime silicate and fused silica glasses were not in accordance with those obtained for the diffusion of sodium ions in these compositions. Furthermore, results for soda-lime silica glass obtained at different humidities were not in agreement with the theoretical predictions.

### 5.3.3. *Ion exchange*

Concluding their paper, Ritter and Manthuruthil [47] considered an alternative theory proposed by Metcalf *et al.* [60] who attributed cracking in "E" glass fibres to a weakening effect associated with the ion exchange of alkali ions and hydrogen ions from adsorbed moisture. The influence of this process on static fatigue properties was discussed in a later paper [61] in which the results of tests on E glass fibres carried out in different environments were interpreted according to the mechanism,

$$\mathrm{SiONa} + \mathrm{H}^+ \rightarrow \mathrm{SiOH} + \mathrm{Na}^+. \quad (32)$$

They suggested that high tensile stresses are generated within the glass surface by volume change during hydrolysis, the stresses reaching a maximum value at the surface with time and then decreasing with continuing hydrolysis. They concluded that their proposed mechanism is consistent with a fatigue limit and accounts for an observed "incubation period" prior to strength loss.

## 6. Conclusions

From the present review it is possible to draw a number of conclusions concerning theories of static fatigue and their degree of success in accounting for experimental observations, as follows:

(1) Although observations of delayed fracture and slow crack growth are now very well documented, only limited success has been achieved in developing quantitative relationships between macroscopic and microscopic crack growth processes. It seems likely that improved progress would result from more intensive studies of the basic phenomena governing static fatigue. This is particularly important because several of the existing theories are based on quite different chemical or physical processes.

(2) While progress has been achieved in the development of theories of an empirical nature, it is becoming clear from recent contributions to the literature that this approach has severe shortcomings and that a more fundamental treatment is required.

(3) At present, no single theory allows a complete description of all static fatigue phenomena incorporating the required dependence on environmental and surface conditions. Thus discrimination between various theories on the basis of their success in predicting experimental observations is rendered difficult.

(4) A number of equations have been proposed to characterize crack velocity which all give some measure of agreement with experimental data. These equations have the form

$$V = V_0 K^n \tag{33}$$

or

$$V = V_0 e^{f(K)}. \tag{34}$$

Uncertainty remains concerning the value to be assigned to $f(K)$, the stress intensity function, since the dependence has been variously given as on $K$ [26], $K^2$ [57] or $1/K$ [58].

(5) The recent experimental observation of slow crack growth under vacuum conditions adds an important factor that must be taken into account in static fatigue theories. This implies that processes intrinsic to the glass are important in addition to external factors and suggests that present stress corrosion theories alone provide an insufficient description of static fatigue phenomena. The lattice trapping concept [55] and the suggestions of relaxation processes based on limited plastic deformation [58] may form the basis for the development of more generally applicable theories.

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