

Effect of a Reactive Environment on the Hertzian Strength of Brittle Solids

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Hertzian fracture theory, previously developed for ideal brittle solids fractured under essentially environment-free conditions, is here modified to allow for an interaction between the growing cone crack and a reactive environment. Two alternative models, both of which account for the observed detrimental effect of an environment on the Hertzian strength but which predict slight differences in the growth of the cone crack, are offered. The first is based on a surface-energy-lowering concept and the second on a subcritical-crack-growth concept. The theoretical implications of these two models are examined in the light of Hertzian fracture experiments on abraded glass slabs in different test environments. Observations of the growth of the cone crack in fatigue experiments favor the second model for glass. The advantages of the Hertzian test as a tool for the study of environmental effects on the fracture strength of brittle solids in general are discussed in relation to more conventional fracture tests.

I. INTRODUCTION

In recent years increasing attention has centered on the measurement of the fracture strength of brittle solids. One reason for this is that fracture tests may be designed to give a measure of the fracture energy, i.e., the work required to separate two cleavage surfaces. This parameter has importance in that it may, for an ideally brittle material, be identified with the reversible surface energy of the new cleavage faces. In real solids irreversible processes accompany fracture, and the fracture energy will always exceed the inherent surface energy. Nevertheless, certain classes of solid, e.g., diamond-structure crystals, certain glasses, etc., are sufficiently brittle at room temperatures that fracture tests may be expected to provide a reasonable measure of the inherent surface energy. A second reason for the interest in fracture strength is concerned with the important influence of an *environmental medium* on the mechanical properties of a solid. This generally introduces the element of time into the problem since most environmental effects appear to be rate dependent. Inorganic glasses, for instance, show substantial reductions in strength as the duration of testing is prolonged.

The tests most commonly used to investigate the fracture strength of brittle solids may be conveniently classified into two categories:

(i) Those tests in which a specimen is stressed until a catastrophic fracture initiates spontaneously from a surface flaw. Such is the case when suitable specimens are stressed either in uniform tension or in cross bending. Tests of this nature require a detailed knowledge of the size, geometry, and orientation of the nucleating flaw if the analysis is to be made at all quantitative. Since these tests are destructive, only one result may be obtained from each specimen.

(ii) Those tests in which the growth of a crack along a cantilever-shaped specimen is followed optically as the crack mouth is opened. With this type of test a great deal of attention has to be paid to precise details of specimen geometry in order to obtain a meaningful result. Again, the test is destructive in the sense that

only a limited amount of information may be obtained from each specimen.

A third, less common fracture geometry that has been adapted for testing purposes is that of the Hertzian cone fracture. In this test a hard indenting sphere is loaded normally on a flat, brittle test specimen until the elastic limit of the specimen is exceeded. At this point a cone-shaped fracture suddenly initiates beneath the indenter. Since its discovery by Hertz in 1881-1882¹ the cone fracture has, until recently, been regarded as little more than a curiosity in fracture mechanics. A revival of interest during the past two decades, prompted mainly in an attempt to reconcile an apparent anomaly in the fracture behavior with currently accepted fracture criteria, has revealed this test to be potentially useful as a means for measuring fracture strength. Thus, Roesler² and Culf³ show that the fracture energies of glass in the presence of different environments may be estimated by this method. Their measurements involve following the progress of the fully developed cone crack as the applied indenter load is increased. In this sense the experimental procedure closely parallels that of the cantilever arrangement.

In this paper an alternative approach is proposed. A detailed analysis of the growth of the cone fracture (Sec. II.B) indicates that the critical indenter load bears a simple relation to the fracture energy. This establishes the Hertzian test as a potential candidate for determining strength characteristics of brittle solids. Since the surface trace of the cone crack lies just outside the contact circle, any environment has access to the crack mouth. As a means for examining possible effects of environment on strength the Hertzian test has certain unique advantages over the more conventional techniques; these we will summarize in the discussion. We choose glass as a test material for a pilot study not only because of its availability but also because its fracture behavior is highly sensitive to the conditions of testing. This very complication in behavior requires the problem to be stated with some generality, so that the treatment presented here should

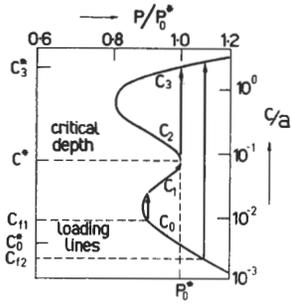


FIG. 1. Plot of c/a as function of P/P_0^* for downward-extending cone crack. Equilibrium curve shown for environment-insensitive conditions. Loading lines shown for two flaw sizes. Heavy arrowed lines indicate stages of crack propagation.

be readily applicable to most other highly brittle solids. The test results on glass suggest that in favorable circumstances some limited conclusions may be drawn as to the mechanism of interaction between a propagating crack and the test environment.

II. MECHANICS OF THE HERTZIAN TEST

In our application of the Hertzian fracture experiment to environmental testing, measurements are made of the critical indenter load P_c required to initiate a cone fracture in the specimen solid. The parameter P_c is then taken as a measure of the "fracture strength" of the solid. Measurements are also made of the duration of testing t_c from first contact to critical loading. This parameter characterizes the rate of interaction of the environment with the propagating crack. In the present instance we will aim to account for any changes in the Hertzian fracture strength that may occur as the environmental conditions of testing are varied.

In setting up a basis for a theoretical approach to the mechanics of Hertzian fracture one begins with the Hertzian elastic contact equations.¹ Of these equations the following are directly relevant to the treatment presented later. The radius a of the mutual-contact circle between indenting sphere and flat specimen surface is given by

$$a^3 = \frac{4}{3}(k/E)Pr, \quad (1)$$

where P is the normal load exerted by the indenter on the specimen, E is the Young's modulus of the specimen material, r is the indenter radius, and k is a dimensionless constant.^{4,5} Again, the distance of mutual approach Z of indenter and specimen from contact is

$$Z = (\frac{4}{3}k/E)^{2/3} P^{2/3} r^{-1/3}. \quad (2)$$

In a test in which the indenter is pressed slowly onto the specimen surface ("static" or "pressure" test) both P_c and t_c are usually recorded directly. However, in a test in which the indenter is allowed to fall freely onto the (horizontal) specimen surface ("impact" test) these two parameters are usually computed in terms of the critical height of fall, h_c : thus, insofar as the quasistatically determined Hertzian stress field is a good approximation in the impact case, we may write^{1,6}

$$P_c = [\frac{1}{3}(10\pi\rho g)^3(E/4k)^2]^{1/5} r^2 h_c^{3/5}, \quad (3)$$

$$t_c = 1.47[(8/g)(10\pi\rho k/9E)^4]^{1/10} r h_c^{-1/10}, \quad (4)$$

where ρ is the density of the indenter material and g is the gravitational acceleration.

A. Environment-Insensitive Conditions

Under certain test conditions the fracture strength of a brittle solid remains unaffected by its surroundings. Such is the case, generally, when tests are performed *in vacuo*, in an inert atmosphere, or in liquid nitrogen. Under these conditions we may apply the theory of Hertzian fracture as developed elsewhere for ideal brittle solids.⁴⁻⁶ We outline here only those essential features of this theory required later for a discussion of the possible influences of a reactive environment (Sec. II.B).

The quantitative analysis of all useful brittle-fracture tests uses as its basis the energy-balance criterion of Griffith.⁷ This criterion, essentially a statement of the first law of thermodynamics, directly relates the decrease in potential energy of the crack system as the crack front extends to the specific surface energy of the solid and implies reversibility in the crack growth. For the cone crack the Griffith condition is applied to the crack at each incremental stage in its growth through the strongly inhomogeneous stress field beneath the spherical indenter. The fracture process is assumed to begin from a particularly favorable surface flaw located at the circle of contact, the crack first forming into a surface ring circumscribing the contact circle and then propagating into a truncated cone (see Fig. 3).

The downward propagating stage is represented in Fig. 1.⁴⁻⁶ The plot is made universal by expressing the length c of the cone crack measured along the downward propagating direction in terms of a and measuring the load P in terms of P_0^* corresponding to the hump in the curve. (Hereinafter, the asterisk denotes values of variables evaluated at $P = P_0^*$, and the subscript zero will indicate environment-free values.) The curve in Fig. 1 is simply a statement of Griffith's condition in its equilibrium form, expressed in terms of the parameters of the Hertzian test. The cone crack will extend if the indenter load is such that the point (P, c) falls to the right of the curve.

The fully developed cone crack corresponds to the c_3 branch in Fig. 1, and the critical load P_c is the load necessary to cause the nucleating flaw to propagate to this branch. We describe the behavior of the flaws during the initial elastic-loading stage in the Hertzian test by means of the broken "loading" lines in Fig. 1. As P is increased the point (P, c_f) migrates along such a loading line until the equilibrium curve is intersected.⁸ At intersection the Griffith condition becomes satisfied, and a further incremental increase in load is sufficient to cause crack extension. Extension will then occur at $P = \text{constant}$ until the point (P, c) once more falls to the left of the curve.

To demonstrate the manner in which the size of the nucleating flaw may influence the value of P_c we show the mechanics of the cone-fracture process for two

flaw sizes in Fig. 1. If c_f lies outside the special size range $c^* \geq c_f \geq c_0^*$, the cone crack will nucleate spontaneously from either the c_0 or c_2 branch. This is shown for the flaw c_{f2} in Fig. 1. In this case P_c is a complicated function of c_{f2} , surface energy, and elastic constants. On the other hand, if c_f lies within this special size range the flaw will first form into a stable ring crack, and this will increase in length with load along the c_1 branch until $P = P_0^*$, at which stage the crack becomes critical. This is shown for the flaw c_{f1} in Fig. 1. In this case the critical load is clearly independent of the original flaw size c_{f1} . We have⁴⁻⁶

$$P_c = P_0^* = K(E)r\gamma_0, \quad (5)$$

where $K(E)$ contains only elastic constants and γ_0 is the specific surface energy of the specimen solid. The proportionality between P_c and r rigorously confirms Auerbach's law, first established empirically in 1891.⁹

By virtue of its simplicity Eq. (5) presents itself as an attractive means for calculating surface energies of brittle solids. In applying Eq. (5), however, it is important to appreciate the limits of its validity. First, it assumes that Griffith's condition is ideally satisfied and that environment plays no part in the crack growth. Second, as stated above, it holds only if the initial flaw size falls within a certain range, and it also assumes that crack growth commences from the contact circle. This second condition can be ensured by abrading the test surface of the specimen in a controlled manner, thus introducing a uniform layer of surface flaws of appropriate size.⁵ Finally, in deriving the curve in Fig. 1, certain approximations have to be made in the theoretical treatment.⁴ While this does not affect the form of Eq. (5), it places some uncertainty on the value of $K(E)$. This precludes any accurate evaluation of absolute values of γ_0 from Hertzian strength measurements.

B. Environmental-Sensitive Conditions

The above theoretical treatment may be modified to take into account the effects of an environmental medium on the fracture strength. We will assume, in accordance with most observations, that the environmental reaction is detrimental to strength. Many theories have been offered in an attempt to explain this weakening effect. In all the theories it is implicitly assumed that elastic constants remain relatively unaffected by the ambient surroundings, thereby ruling out variations in $K(E)$ [Eq. (5)] as a significant factor in environmental weakening (we shall experimentally confirm this assumption for the Hertzian test in Sec. III.A). For our present purposes it thereby becomes convenient to broadly classify the theories into the following two categories:

(i) Those theories which postulate a reduction in the surface energy of the crack surfaces by adsorption of the environmental species. This mechanism requires

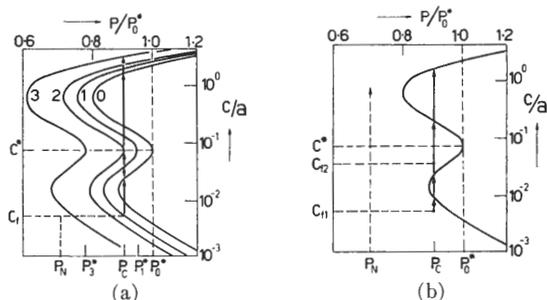


FIG. 2. Equilibrium curves for environment-sensitive conditions: (a) Surface energy lowering model. Note shift in equilibrium curve. Crack propagates to c_3 branch when $c = c^*$. (b) Subcritical growth model. Propagation to c_3 branch occurs when $c = c_2$. Propagation shown for two flaw sizes.

that the environment have access to the crack-tip region, where the adsorbed layer may interact with the extended cohesive bonds so as to reduce the crack-tip stresses necessary to rupture the material.¹⁰

(ii) Those theories which propose a subcritical crack growth. There are numerous mechanisms which pertain to this concept (Refs. 11-16, etc.). The most widely accepted mechanism in this category appears to be that of stress-enhanced corrosion, in which the environmental agent preferentially dissolves material at the highly stressed crack tip without lowering the surface energy.¹⁵

We represent the first of the two above categories in Fig. 2(a). For simplicity in description we consider first that the specimen surface contains flaws within the size range corresponding to the range of validity of (5) and that the surface is loaded to a value $P < P_0^*$ in a time short compared with the reaction time of the environment with the crack. (The load P is shown in Fig. 2(a) as P_c , the ultimate critical load for cone fracture.) The environment is then admitted to the crack tip and the surface energy thereby lowered. The effect of reducing the γ term below γ_0 is to correspondingly reduce P^* below P_0^* [Eq. (5)]. However, the quantity P/P^* is a function only of c/a^{4-6} so that both the shape and vertical location of the equilibrium curve in Fig. 2(a) will remain unaffected by any such changes in γ . The introduction of the environment may therefore be considered to simply shift the equilibrium curve to the left in Fig. 2(a). This is indicated in the figure by means of the continuous transition 0 \rightarrow 1 \rightarrow 2 \rightarrow 3 (curve 0 representing the environment-free curve). If the reduction in γ is sufficiently large, the equilibrium curve will ultimately intersect the point (P, c_f) (curve 1). At this stage the flaw may, if originally on the c_0 branch as shown, propagate to the point (P, c_1) on curve 1. If, however, the environment cannot keep up with the propagating crack tip, the flaw may propagate only to the c_1 branch of curve 0 (i.e., the propagation may be governed by the true surface energy). Regardless of this detail the crack becomes stable again on the c_1 branch, at which stage the environmental agent may

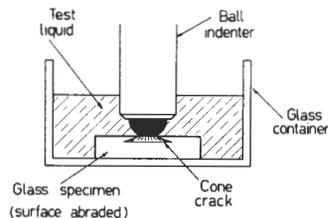


FIG. 3. Arrangement for tests in liquid environment. The incidence of cone fracture may be observed through the side walls of the test specimen or through a microscope located beneath the glass container.

once again penetrate to the crack tip and cause a continuing lowering of γ . This will cause the crack to grow stably to the point (P, c_1) on successive curves. Eventually, when c reaches the critical depth c^* (curve 2), the crack is free to propagate to the c_3 branch. Further reductions in γ will thereafter cause further stable growth at c_3 , as noted in Roesler's experiment.² We see that, as before, the critical load $P_c = P_c^*$ is independent of the original value of c_f . The test value of P_c will then have measured the reduced surface energy at the point of fracture, and the time to fracture after loading will have given an indication of the rate-dependent processes involved (rate of transport of material to the crack tip, rate of adsorption, etc.).

We represent the second theoretical category in Fig. 2(b). In this case γ_0 is assumed to remain unchanged so that no shift in the equilibrium curve occurs. We again load the specimen rapidly to $P < P_0^*$ and then allow the environment to interact with the nucleating flaw. The flaw thereby begins to grow subcritically. For the flaw labelled c_{f1} in Fig. 2(b) this initial growth will proceed from (P, c_{f1}) to (P, c_0) . At this stage unstable propagation will occur. At (P, c_1) further subcritical crack growth will occur until the c_2 branch is reached. At this intersection the cone crack develops. Again the original flaw size is not significant in determining the critical conditions: Fig. 2(b) shows that the subcritical growth for a randomly selected second flaw size c_{f2} ultimately follows the same subcritical growth to (P_c, c_3) as for c_{f1} . In contrast to the mechanism in Fig. 2(a) the subcritical-growth model in Fig. 2(b) provides no information concerning the fracture energy. Rather, the critical load and time to fracture reflect the degree and rate of the corrosion process.

Both models outlined above make similar predictions concerning the critical conditions for cone-crack formation in an environmental medium. There are, nevertheless, certain slight differences in the predicted behavior, which we will take up in the discussion. At this point it is of interest to consider the effect of the loading program on the significance of the critical conditions. In the preceding discussion we assumed, for simplicity, the indenter load to be rapidly raised to its maximum and the environmental effects to operate thereafter at this maximum load. In many experimental arrangements it is more convenient to increase the indenter load monotonically with time until the cone fracture suddenly appears. In this latter case the arrowed lines denoting the various stages of crack growth in Fig. 2 would have

a finite slope, this slope reflecting both the rates of loading and environmental reaction. A little consideration shows that the interpretation of the physical significance of the critical conditions is the same as above. In comparing environmental-strength data it is, however, desirable that a consistent loading program be adopted for all tests.

III. HERTZIAN TESTS ON GLASS

A. Experimental Procedure

Most of our Hertzian tests were made on plates of soda-lime glass measuring $2 \times 2 \times \frac{1}{2}$ in. The specimen surfaces were first abraded with No. 400 SiC abrasive powder mixed into a liquid slurry. A $\frac{1}{2}$ -in.-diam steel ball was used as indenter. [Under these conditions the results fall well within the range of validity of Eq. (5)].⁶ The indenter was mounted in the underside of an Instron testing machine, and the specimen was located in a container of test liquid seated on a compression load cell (Fig. 3). The cross head was lowered onto the surface of the specimen, and the incidence of the resulting fracture was viewed optically.

In most of the experiments the cross head was lowered at a constant speed and the indenter load recorded as a function of time on a chart recorder. Assuming the cross head and indenter mount to be sufficiently rigid that the cross head displacement may be equated to the mutual indenter-specimen displacement Z [Eq. (2)] during contact, we may thus write the cross-head speed $\dot{Z} = dZ/dt = \text{constant}$; thus, substituting $Z = \dot{Z}t$ into (2), we obtain

$$P = \left[\frac{3}{4} (E/k) r^{1/2} \dot{Z}^{3/2} \right] t^{3/2}. \quad (6)$$

From (6) it is clear that the load rate could be adjusted by changing \dot{Z} without altering the functional form of the load-time pulse. Three such load-time curves are shown in Fig. 4. These three curves were almost exactly reproduced in the presence of three test environments—air, water, and toluene. This independence of (6) with respect to environment justifies the earlier statement (Sec. II.B) that elastic constants are relatively insensitive to the surrounding medium.

Also shown in Fig. 4 are the points along the load-time curves at which cone fractures are produced in the three environments. Each point represents a run of at least 10 fractures, and the error bars represent the standard deviations about the mean values of P_c .

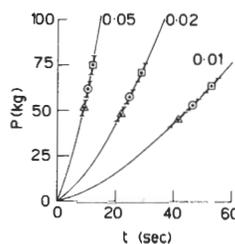


FIG. 4. Indenter load-time curves for tests on glass. Curves represent Instron cross-head speeds 0.05, 0.02, 0.01 cm min⁻¹. Mean values of P_c shown for tests in toluene (squares), air (circles), and water (triangles). Bars denote standard deviations in P_c . All data taken from single specimen.

It is clear that the environment largely influences the fracture strength and that the duration of testing represents an important parameter to be considered in the environment-sensitive fracture of brittle solids.

We now describe some particular experiments on glass. In selecting these experiments we have been guided by the extensive study made by Mould *et al.*¹⁷⁻²⁰ on the strength of glass in cross bending. An intercomparison between such parallel studies permits some useful conclusions to be made. In some special cases it was found desirable to depart from the loading procedure described above; this will be indicated where appropriate.

B. Effects of Specimen History

One of the difficulties in preparing suitable specimens for fracture testing is that the fracture strength may depend on the history of the specimen surface. For example, abraded glass slides subjected to cross bending can show substantial increases in strength as the time between abrasion and testing is delayed.¹⁹ Such aging effects make it difficult to attain reproducibility, an essential requirement if useful comparisons are to be made for different conditions of testing. Again, vacuum baking also increases the cross bending strength of freshly abraded specimens.¹⁹

Now, in any test where fracture initiates spontaneously from a surface flaw, the above effects of specimen history may be attributed either to a change in the effective flaw size (e.g., by rounding of the sharp crack tip, or by flaw healing, etc.) or to a localized change in the fracture energy (e.g., by diffusive penetration of the environmental species into the crack, thereby displacing occluded air at the tip, or by modification of the glass network near the crack tip on heating). In the Hertzian test, however, P_c is independent of any variation in flaw geometry [Eq. (5)] but should reflect any changes in γ . A comparison of results from the two tests should allow a distinction to be made between the two possibilities.

Figure 5 shows some aging results obtained for three different environments. In each case the cross-head speed was fixed at $\dot{Z}=0.02$ cm min⁻¹. For the tests in laboratory air the specimens were abraded in a water slurry and any excess moisture then removed from the test surface by a stream of hot air. For the tests in water the specimens were washed immediately after abrasion and thereafter kept immersed in the test container. A similar procedure was carried out for toluene,

FIG. 5. Aging tests on glass for three test media. Room-temperature data. Cross-head speed 0.02 cm min⁻¹. Duration of each test run (10 tests per run) about 15 min. Each symbol represents a different specimen.

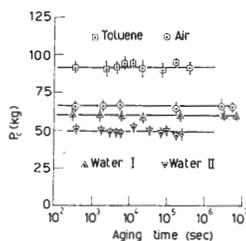
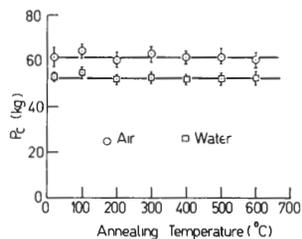


FIG. 6. Annealing tests on glass. Tests made in air and water at room temperature after successively higher anneals. Cross-head speed 0.02 cm min⁻¹. All data taken from single specimen.



with toluene (from a freshly opened bottle) itself providing the liquid base for the abrasive slurry. Toluene was chosen because it absorbs very little water from the atmosphere. At various intervals after completion of the abrasion process test runs were made on each specimen. In Fig. 5 each symbol designates a different specimen, each specimen being taken at random from a different batch of glass. No aging effect is evident in any of the environments.

Another set of experiments was performed in an attempt to determine whether the strength of a solid might reflect the presence of any previous environment. In this case the specimens were all selected from a single batch. After abrasion the specimens were dried, tested first in air, tested a second time while immersed in a test liquid, and finally, after removing and drying the specimens, tested once again in air. The results of tests in a number of liquids are summarized in Table I. It is clear that the specimen surfaces retain no "memory" of their previous environmental history.

A further series of tests was made to test the effect of specimen annealing on P_c . These results, shown in Fig. 6, were all taken from one abraded specimen. The specimen was first tested in air and then in water, at room temperature. The indented specimen was then annealed in air for about 24 h at 100°C and retested in the same way as before. This procedure was repeated for each of successively higher annealing temperatures. It is evident that the annealing process has no significant effect on the results.

The results shown in Figs. 5 and 6 and in Table I indicate that specimen history has no significant effect on the Hertzian fracture strength. This is in contrast to the observed behavior in cross bending, where increases in strength of up to 60% may occur under similar test conditions. The present data demonstrate that we can rule out any influence of specimen history on the fracture energy γ so that the positive effect observed in cross bending would appear to arise solely from the effects of the environment on flaw severity.

From the standpoint of reproducibility of the test results it is evident that, while specimen history does not enter as a parameter, it is necessary to pay some attention to the selection of samples. Specimens selected from a single batch of glass plate from the commercial supplier gave consistent strength values (e.g., those in Table I). Specimens selected from different batches, however, often showed a wide disparity in strength values (e.g., the two specimens tested in water in Fig.

TABLE I. Values of $P_c(kg)$ for Hertzian tests on glass in different environments, using an Instron cross-head speed of 0.02 cm min^{-1} .

Air (before)	Liquid environment	Air (after)
69.8 ± 2.2	water	62.6 ± 2.3
66.7 ± 2.7	benzene	67.0 ± 2.7
68.5 ± 2.9	ether	71.3 ± 2.6
69.0 ± 2.9	methanol	67.4 ± 2.2
63.8 ± 2.6	acetone	64.6 ± 2.6

5). Consequently, to make comparisons viable in all tests described hereinafter a standard strength value $P_c = 45 \text{ kg}$, for a control test in water at room temperature with a cross-head speed 0.02 cm min^{-1} , was arbitrarily selected; all specimens not conforming to this standard strength (within limits of experimental error) were rejected as unsuitable test specimens.

C. Static Fatigue Curves

A series of tests was carried out to determine the effects of varying the load rate on the fracture strength. This was done simply by measuring P_c as a function of t_c , as in Fig. 4, for a wide range of cross-head speeds. The range of speeds available on the Instron model used by us was $0.0005\text{--}5 \text{ cm min}^{-1}$. However, some experimental difficulty was experienced at both ends of this speed range.

For high load rates, in particular for cross-head speeds exceeding 1 cm min^{-1} , the incidence of fracture could not be followed sufficiently quickly by eye to permit a reasonably accurate assessment of P_c and t_c . The data were therefore extended into the short-time range by using impact tests. These tests were performed with $\frac{1}{2}$ -in. steel balls dropped onto 1-in.-thick abraded plate glass; the static strength of the 1-in. plate matched that of the $\frac{1}{2}$ -in. plate. Inserting the test values $h_c = 17.0 \text{ cm}$, $r = 0.635 \text{ cm}$, $E = 7 \times 10^{11} \text{ dyn cm}^{-2}$ (glass), $k = \frac{2}{3}$ (steel on glass), $\rho = 7.8 \text{ gm cm}^{-3}$ (steel), and $g = 980 \text{ cm sec}^{-2}$ into (3) and (4) gives $P_c = 120 \text{ kg}$ and $t_c = 2 \times 10^{-5} \text{ sec}$. In our tests the duration of testing appeared to be sufficiently short that environmental interaction could be neglected; for instance, specimens with both wet and dry surfaces gave indistinguishable critical heights of fall.

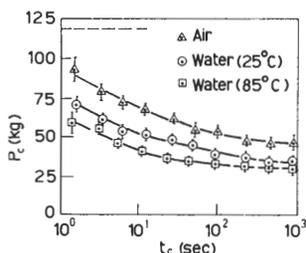


FIG. 7. Fatigue curves for glass tested in air and water (two temperatures.) Horizontal broken line indicates impact strength.

At the other end of the load-rate scale the visibility of the critical stage of cone-crack formation deteriorated. This was particularly so for tests carried out in liquids whose refractive index approached that of glass. Part of the reason for the reduced visibility was that the cone cracks became smaller as the load rate was reduced. More importantly, however, the unstable growth to the c_3 branch of the equilibrium curve simultaneously became less pronounced. This feature in the growth was particularly evident in extended long-time tests. These particular tests, in which specimens were subjected to constant loads (~ 0.2 short-time strength) for prolonged durations (\sim one day), often showed the gradual appearance of a small ring crack without any stage of unstable propagation at all. We interpret this behavior more fully in the discussion.

Some results are shown in Figs. 7–9. In each figure the short-time strength, as computed from (3), is shown as the horizontal broken line. The Instron data points appear to approach this line at high load rates. The full

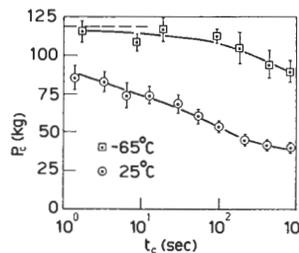


FIG. 8. Fatigue curves for glass tested in toluene (two temperatures). Broken line indicates impact strength.

line through the data points indicates the range of testing times in which an unstable stage in cone-crack growth was observed at critical loading. The transition from full line to broken line (seen only in Fig. 7) indicates the point at which an unstable stage of growth no longer could be detected. The points in the broken-line region represent loads at which a ring crack could just be detected; clearly, this region of the fatigue curve is less meaningful than the other (see Sec. IV).

In Fig. 7 the detrimental effect of water on the strength of glass is demonstrated. The two upper curves, one for tests in laboratory air and one for tests in distilled water, were compiled from room-temperature test data. The lowest curve was compiled from data taken from tests in which a heating coil was immersed in the water; in this case the water was heated for several hours before testing, to allow the system to achieve equilibrium. It is evident that a rise in temperature enhances fatigue. These results are in accord with previous knowledge from other tests.²⁰

In Fig. 8 fatigue curves are shown for toluene as the test medium. The results were taken at room temperature and at about -65°C , the latter temperature obtained by adding dry ice to the toluene bath. The room-temperature tests give strengths higher than those measured in air. The results at the lower temperature

show very little fatigue, even for relatively long testing times.

Results are shown in Fig. 9 for a silicone oil at room temperature. The intention in this instance was to investigate any possible effect arising from an increased viscosity of the test medium. The test results for silicone oil show the least evidence for fatigue of all the liquids used at room temperature. This suggests that the oil may have difficulty in moving with the propagating crack.

Other test environments show behavior similar to that depicted in Figs. 7-9. Tests in mercury gave results closely parallel to those in air. Presumably, the mercury, since it does not wet the glass, has little tendency to displace occluded gases in the abraded specimen surface and to thereby enter the crack mouth. Other tests in organic liquids, e.g., alcohol, benzene, acetone, etc., showed trends similar to those in Fig. 8; in all of these media the fatigue was less than in air, showing a trend similar to that of toluene.¹³ Water was the only test liquid to produce a greatly enhanced fatigue as compared to air. These results all conform with a currently held hypothesis that water may be the dominant agent causing fatigue in glass, the major role of other test media being to regulate the transport of traces of water to the crack tip and to thereby control the time to fracture. Similarly, the role of temperature may be to adjust the rates of interaction between the water and glass, rather than to change the nature of the interaction processes. According to this interpretation the main effect of changing the environmental conditions in a fracture test is to displace the fatigue curves horizontally in Figs. 7-9. This suggests that by suitably normalizing the coordinates the fatigue data might well be fitted onto an empirical universal-fatigue curve, in a manner similar to that described by Mould and Southwick for cross-bending test data.¹⁸

D. Effects of Acidic-Basic Solutions

It is well known that the chemical attack at a fresh glass surface immersed in an aqueous solution is dependent on the pH of the solution. With this in mind Mould²⁰ performed cross bending tests in a number of aqueous solutions, and demonstrated that acidic solutions are more prone to enhance fracture than are basic ones. We have repeated this experiment, recording the Hertzian strength as a function of pH (Fig. 10) for a

FIG. 9. Fatigue curve for glass tested in a silicone oil (two specimens). Broken line indicates impact strength.

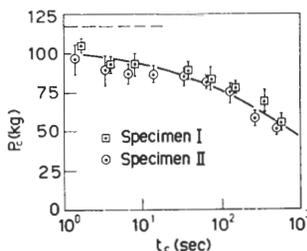
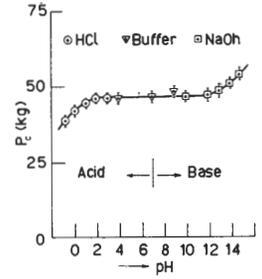


FIG. 10. Hertzian strength of glass as function of pH of aqueous solution. Cross-head speed 0.02 cm min^{-1} .



cross-head speed of 0.02 cm min^{-1} . The pronounced weakening and strengthening at the low and high ends of the pH scale, respectively, in Fig. 10 are in accord with the data of Mould.

IV. DISCUSSION

A. Mechanism of Environmental Interaction

In Sec. II.B we outlined in general terms two models that might permit a description of the weakening effect of an environment on glass. It is not easy to distinguish between the relative merits of these two models in the light of the evidence presented in Sec. III. For instance, both models predict the observed reduction in the size of the cone crack at lower load rates in the fatigue experiments; as P_c becomes smaller the corresponding value of a_c , which determines the scale of the cone crack, decreases according to Eq. (1). Again, assuming a rate-dependent interaction process, both models are capable of accounting for most of the essential features of the fatigue curve. At the short-time end of the fatigue curve, in particular, the tendency for the strength to approach environment-free values ("instantaneous" strength, which we approximate by the impact strength) is a common prediction of all fatigue theories.

It is at the long-time end of the fatigue curve that slight differences appear in the predictions of the two models. In this regard the observation made in Sec. III.C concerning the apparent disappearance of the unstable stage of cone-crack growth to the c_3 branch in Fig. 2 would seem to be consistent only with the second model [Fig. 2(b)]. For the first model the predicted behavior is as follows. The lower limit to the strength ("endurance" limit) is governed by the ultimate equilibrium value of γ resulting from an indefinite exposure of the crack tip to the reactive components (e.g., water) of the environment.¹⁰ This limit being represented by Curve 3 in Fig. 2(a), we note that no unstable propagation to c_3 may occur for loads $< P_3^*$ [e.g., P_N in Fig. 2(a)]. Between the short-time and long-time limits of strength the model depicted in Fig. 2(a) predicts, contrary to observation, an equally pronounced final stage of unstable growth for all tests, notwithstanding the change in the scale of the crack. For the second model the lower limit to the strength is somewhat less definable. According to Fig. 2(b) the

unstable stage from the c_2 to the c_3 branch will become less prominent as the critical load is made progressively smaller, until at the point where c_2 and c_3 merge, no unstable stage should occur at all. At even smaller loads [e.g., P_N in Fig. 2(b)] subcritical growth may continue uninterrupted at a rate determined by the nature of the environmental reaction. Thus, only the second model is capable of explaining the transition in crack-growth behavior mentioned in Sec. III.C. As pointed out in Sec. II the calculation of the equilibrium curve in Figs. 1 and 2 is subject to approximations, which precludes a quantitative estimate of the transition point.

Thus the present evidence leans toward an explanation of fatigue in terms of the subcritical-growth model. It should be pointed out, however, that other fracture techniques may be better equipped to elucidate certain aspects of the crack growth mechanism. In the Hertzian test, as in those tests in which fracture initiates spontaneously from a flaw, little or no observation can be made of the potentially informative stages of initial submicroscopic crack growth prior to critical loading. In this sense the double-cantilever test^{21,22} has a distinct advantage since the crack can be followed clearly at all stages of its growth. A cantilever specimen may be "displacement loaded," as by inserting a wedge at its mouth, or "force loaded," as by loading the ends of the cantilever beams with dead weights. In the first case the crack growth is always stable, with or without environmental interaction, and is therefore not particularly suited as a means for distinguishing between different possible fatigue mechanisms. In the second case, for a test under environment-free conditions, the cantilever crack is observed to propagate spontaneously at a critical load, in much the same way as a crack in a tensile specimen nucleates from a surface flaw: for the same test in a reactive environment a stage of stable growth is observed to precede the critical point. Thus, Wiederhorn²³ interprets this subcritical-growth stage as strong direct evidence for a corrosion mechanism of fatigue in glass. Linger and Holloway²⁴ propose an alternative mechanism based on plastic-zone growth at the crack tip. It may not be possible to unambiguously establish the validity of either of these two mechanisms, or indeed of any other subcritical-growth mechanism, on the basis of macroscopic observations of crack growth alone. Moreover, Orowan¹⁰ points out that, if the transport of environmental matter to the crack tip be diffusion-controlled, even the surface energy lowering concept may account for an apparent subcritical growth. Thus, although the cantilever test presents a clear visual picture of the stages of crack growth, an analysis in terms of crack-stability considerations alone may not be capable of distinguishing with absolute certainty between even broad classifications of environmental mechanisms.

The discussion above indicates that observations of

the mechanics of crack growth in the Hertzian test, and in fact in all currently used fracture tests, provide a very limited insight into the physical or chemical processes responsible for the environmental effects on fracture. Further elucidation in this direction may well require detailed observations of events at the very tip of the crack on an atomic scale.

B. Advantages of the Hertzian Test

In view of the limitation just stated it may not be a straightforward matter to relate the parameters of the Hertzian test to any particular property of the specimen material and its environment. Nevertheless, the critical-fracture load in this test serves as an excellent indicator of strength and permits a study of such phenomena as fatigue, etc. Bearing in mind the requirements of the more conventional fracture-testing arrangements, we summarize below the advantages of the Hertzian test; some of these advantages are unique. The overall economy of the Hertzian test should facilitate the accumulation of a wide range of information concerning the effects of the test environment on brittle strength.

The advantages are as follows:

(i) Experimental simplicity. The test is easy to set up on a standard testing machine. A commercially produced steel ball (ball-bearing type) is usually adequate as an indenter. Specimens require only to be flat-sided, with no stringent conditions of preparation (Sec. III.A). Tests can be performed rapidly, with only a few seconds lost between successive tests.

(ii) Critical-load independence of flaw size. It was pointed out in Sec. II.A that, within the range of validity of Auerbach's law (5), the critical load to cone fracture is independent of the size of the flaw from which the crack ultimately propagates. Thus, an analysis of the strength measurements does not require knowledge of the flaw geometry (which is always difficult to establish), nor does it require a measure of the crack length at any stage of its growth. The test simply involves a measure of the load at which the cone crack suddenly appears (assuming that the conditions are such that this sudden event does occur). In transparent solids the observation of the incidence of cone fracture is straightforward; in opaque solids however, the indented specimen surface has to be examined for evidence of fracture *after* testing, this somewhat lengthening the test procedure.

(iii) Reproducibility of results. About 100 tests can be made on one specimen surface 1 in. square without neighboring cracks mutually interacting to affect the critical load. Thus, it is possible to perform tests on the one specimen surface under a variety of test conditions. In this sense the Hertzian test is nondestructive. Further, since the Hertzian strength does not appear to depend on specimen history (Sec. III.B), reproducibility is not affected by long delays between tests. With a

run of 10 tests on a suitably prepared specimen (Sec. III.1) the critical load can be reproduced to within 10% (standard deviation).

C. Further Studies

Although we have shown that the Hertzian parameter P_c is capable of indicating the effects of an environmental reaction on the fracture strength of a brittle solid, the data presented here must be considered to be preliminary in nature. For instance, we have made no attempt, other than using chemical reagents from freshly opened bottles, to perform experiments with carefully dried liquids. In view of the hypothesis that even small traces of water can play a dominant role in environmental weakening, this point warrants further attention. Experiments in specially constructed environment chambers, within which the ambient conditions can be accurately controlled, appear to be called for. Further, the observation of the initial stages of cone-crack growth deserves a more detailed study than we have been able to provide to date. Such observations have an important bearing on the interpretation of the type of environmental reaction operating at the crack tip. Finally, it is suggested that experiments might be aimed at investigating in a more direct manner the precise mechanism of this crack-tip interaction: macroscopic observations of the progress of a growing crack may provide only limited insight into such environmental effects.

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