

Environmentally Enhanced Fracture of Glass: A Historical Perspective

Stephen W. Freiman, Sheldon M. Wiederhorn,[†] and John J. Mecholsky, Jr.[‡]

Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-8520

In this paper, we review the phenomenon of delayed failure, a life-limiting process for glasses that are subjected to tensile stresses. With the development of crack-weakening theories (Ingles and Griffith) and the observation that surface damage enhances delayed failure, the scientific community recognized that delayed failure in glass is caused by the growth of cracks that are subjected to tensile stresses. Fracture mechanics techniques were used to quantify crack growth rates in terms of applied stress, temperature, and the chemical environments that cause subcritical crack growth. We review the theories that have been developed to rationalize subcritical crack growth data, including theories based on plastic deformation at the crack tip, chemical adsorption of the reacting species, and direct chemical reaction of the environment with the strained bonds at the crack tip. The latter theory seems to be most consistent with the finding that water reacts directly with the strained Si–O bond because of the ability of water to donate both electrons and protons to the strained bond. Other chemicals having this characteristic also cause subcritical crack growth. Finally, we review the quantum mechanical calculations that have been used to quantify the chemical reactions involved in subcritical crack growth.

I. Introduction

THIS paper focuses on the resistance of inorganic glasses to crack extension in the presence of chemical environments, primarily water. In applications where glass parts or components such as windows, fiber optic cables, or glass containers are subjected to far-field tensile stresses, failure usually occurs by the extension of a crack from the surface of the glass. The crack grows slowly until it reaches a critical size, at which point unstable crack growth ensues; the part fails almost instantaneously once the critical size is reached. Because subcritical crack growth is involved in the failure process, a time delay is often observed between the time of first exposure to stress and the time of failure. Hence, scientists and engineers interested in the mechanical behavior of glass called this phenomenon delayed failure.[§]

D. J. Green—contributing editor

Manuscript No. 25650. Received December 16, 2008; approved March 11, 2009.

[†]Author to whom the correspondence should be addressed. e-mail: sheldon.wiederhorn@nist.gov

[‡]While on sabbatical from the Materials Science and Engineering Department at the University of Florida.

[§]Other terms for this phenomenon include static fatigue and stress corrosion cracking.

Delayed failure is illustrated in Fig. 1. A characteristic of delayed failure is the dependence of component lifetime on the level of the stress. When glass is subjected to a high applied stress, failure occurs in a short time; however, if the load is reduced, the time to failure increases. The shape of the curve is concave-up and, as such, gives the appearance that for very low loads, a failure limit or threshold exists such that below this limit, the glass will never fail. This failure threshold corresponds to a crack growth threshold in glasses, as will be demonstrated during the course of our discussion.

We now know that delayed failure is due to the combined effects of stress and water in the environment, causing surface cracks in the glass to grow slowly with time. From a practical point of view, delayed failure significantly affects the design and use of glass structures when survival over long periods of time is critical. As delayed failure also occurs for other ceramic materials, such as porcelain and aluminum oxide, what has been learned about delayed failure in glass is also applicable to these other brittle materials.

II. Early Experiments

The first significant study of delayed failure was carried out by Grenet,² who observed that the flexural strength of glass depended on the testing rate. Grenet fractured glass plates in three-point flexure, applying the load by hanging a bucket from their center-line and gradually filling the bucket with water at varying rates (Fig. 2). He observed that by decreasing the loading rate from 0.25 kg/min to 0.25 kg/h, a 50% decrease in breaking stress was achieved. Grenet also observed that specimens left under a constant load failed in times as long as 5 days. He was unsuccessful in determining whether this “delay in

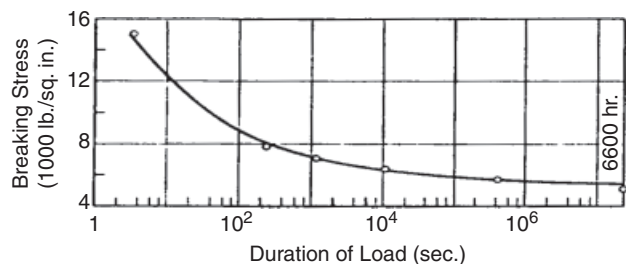


Fig. 1. Stress-time characteristics of glass, from bending tests on 1/4 in. diameter soda-lime-silicate rods. Taken from Shand.¹

Feature

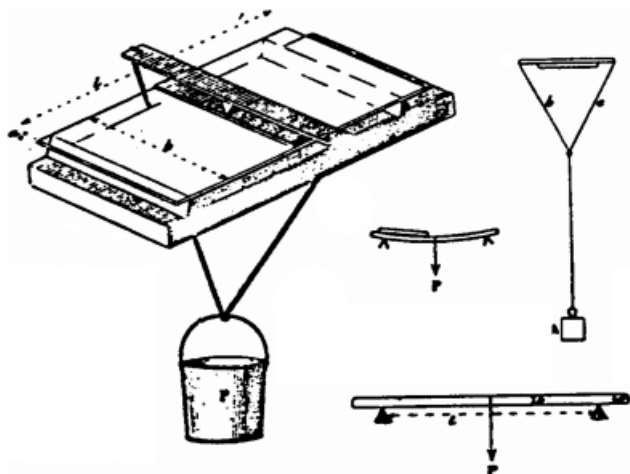


Fig. 2. Experimental setup used by Grenet to study delayed failure.

fracture" was accompanied by any permanent deformation of the glass (to our knowledge, no evidence for permanent deformation in glass has ever been found in specimens loaded in flexure, or tension). Permanent deformation is, however, observed under hardness indentations.³

III. Inglis and Griffith

During the 20 years following Grenet's publication, no direct references to studies of glass strength appear in the scientific literature. However, there was a significant development in mechanics that had a significant impact on our understanding of brittle fracture. In 1913, Inglis⁴ published a paper discussing the role of elliptical holes and notches in concentrating the applied stress. He derived expressions relating the maximum stress at the major axis of an elliptical hole to the length of the ellipse and the radius of the ellipse at its major axis. He assumed that a crack could be approximated by an elliptical hole, with a length $2c$ (length of the major axis of the ellipse), and a height $2h$ (length of the minor axis). The stress at the end of the hole, σ_{\max} , is given by:

$$\sigma_{\max} = \sigma \left[1 + 2\sqrt{\frac{c}{\rho}} \right] \quad (1)$$

where $\rho = h^2/c$ is the radius of curvature of the tip of the ellipse. Inglis' work represents an important step toward our understanding of the importance of cracks in controlling the strength of brittle materials. For long, sharp cracks in brittle materials, $2\sqrt{\frac{c}{\rho}} \gg 1$; hence, the stress is determined almost entirely by the size of the crack.¹ The radius of curvature of the crack tip, ρ , will be of atomic dimensions in brittle materials such as glass, < 1 nm, if indeed one can consider cracks in glass to have a radius of curvature. More likely, what passes for a radius of curvature will be masked by the atomic structure of the glass.

In 1920, a complementary approach to the fracture of glass was developed by A. A. Griffith,⁵ who was the first to point out that glass fails from small surface cracks, and that the density and size of such cracks determines the distribution in strength values. Griffith established a relationship between fracture strength and the energy needed to form the fracture surfaces. He considered a thru-crack of length $2c$ in a plate that was subjected to a constant stress normal to the plane of the crack, and asserted that the crack would begin to grow when the energy supplied by the external elastic stress field equals the energy required to form two new fracture surfaces. At the point of equilibrium, the following relation was found to hold between the

critical stress, σ_{cr} , surface energy, γ , Young's modulus, E , and the crack length, c :

$$\sigma_{cr} = \sqrt{\frac{2E\gamma}{\pi c}} \quad (2)$$

The Griffith equation is fundamental to our understanding of the strength of materials and forms the basis of linear elastic fracture mechanics. The fact that the strength of glass varies inversely with the square root of the crack length is consistent with the Inglis treatment of strength. Also, the idea that small cracks in the surface of glass determine the strength of glass is common to both theories.

IV. Delayed Failure Studies

Recognition of the connection between delayed failure and the condition of the surface of the glass required a long series of experiments: first to show that surfaces of glass contain cracks, then to show that failure originates from these surface cracks, and finally, to quantify the motion of surface cracks so that lifetime could be predicted.

In 1921, F.W. Preston took the first step in this series in a study in which he characterized the structure of glass surfaces that had been abraded.⁶ He described the kind of cracks that formed due to contact with spheres and polished glass surfaces. From his results, he concluded that ground surfaces in glass are filled with fissures and cracks. He later noted that these surface cracks were the sources of fracture in glass.⁷ Preston was one of the first glass scientists to reference and accept Griffith's hypothesis regarding the nature of the flaws that lead to failure.⁷ Preston worked at the forefront of glass fracture research for the next 40 years and made many significant contributions to our understanding of the phenomenon of delayed failure.

In the 1920s we began to see more and more studies on the delayed failure of glasses. Milligan, in 1929,⁸ recognized that both water and water vapor play a key role in controlling the strength of glass. He observed that the strength of glass in dry environments was greater than in water, or in environments containing water vapor. In 1935, Preston studied the effects of load and time on the strength of glass.⁹ He confirmed the findings of Grenet that the lifetime of glass subjected to an applied load will increase as the applied load is decreased. He also speculated on the existence of a stress threshold, below which failure will not occur regardless of how long the glass is subjected to the load. This idea of a stress threshold became a frequent theme in discussions of delayed failure in glasses. Black¹⁰ confirmed the findings of Grenet that the strength of glass depended on the loading rate, strength increasing as the rate of loading increased. He also conducted some constant load tests measuring the strength of specimens that had not failed during the hold period. He found that the strength of these specimens did not differ from the other specimens tested. Because of the very strong exponential dependence of crack growth rate on applied stress, only the largest crack grows. The next largest crack hardly changes size during the constant-stress hold period. A discussion of this problem can be found in reference.¹¹

Tests to characterize the delayed failure of glasses continued from the 1930s to the early 1950s. Glass specimens were tested for both shorter and longer periods of time to determine the functional dependence between applied load and failure time.¹²⁻¹⁴ Holland and Turner¹² were the first to plot time-to-failure data in logarithmic form for which the data appeared to fit a straight line. Other authors preferred a semilog plot of stress vs. log of the time to failure, t , even though the data do not fit a straight line on this type of plot.¹⁵⁻¹⁸

In 1942, Preston¹⁵ made the important observation that the rate of strength decrease during static fatigue is temperature dependent, being small at temperatures less than 0°C, maximizing at $\approx 200^\circ\text{C}$, and then decreasing at temperatures of $\approx 300^\circ\text{C}$ and higher. Preston interpreted these data in terms of the thickness and chemical activity of the water layer absorbed on the

⁴Here, we equate the length of a crack with that of the major axis of the elliptical notch.

glass surface. At low temperatures, the water layer is thick, but chemically inactive; at a high temperature, the water is chemically active but is very thin. At intermediate temperatures, the water layer is both thick and chemically active; in the temperature range of 0° to 300°C, glass is most susceptible to static fatigue. Preston's results were supported by the work of Mould,^{19,20} who studied the time and temperature dependence of the strength of soda lime silicate glass microscope slides. The results of these and other studies suggested that a multiplicity of physical processes controlled the strength of glass: adsorption, chemical reactions, and transport to and from the crack tip. These processes were quantified once the idea of the motion of surface cracks was explored.

V. Direct Crack Growth Studies

The development of fracture mechanics as a scientific discipline and its application to glasses and ceramic materials permitted investigators to gather crack growth data that could be compared directly with the theories used to describe the delayed failure of glass. The use of this discipline marked a turning point in our understanding of crack growth in ceramics and glasses and the relation of crack growth to lifetime and strength. Before the development of fracture mechanics, experimental studies on glasses were limited primarily to flexural strength measurements under a variety of environmental conditions; the role of environment, temperature, glass composition, etc. in crack growth had to be inferred from these measurements. The complexity of the crack growth process could not be understood from such speculations. Once fracture mechanics methods had been developed, these variables were studied quantitatively and were used to predict the lifetime of glasses and ceramics.

Fracture mechanics techniques are characterized by the use of test specimens with large cracks. The stress near the crack tip is dependent on the inverse square root of distance from the crack tip, $1/\sqrt{r}$, a constant, K_I , known as the stress intensity factor and a function of the angle, θ , that depends on the stress being calculated, and on the type of loading (whether the load is normal to the crack plane or contains a shear component).^{21,11} For the stress intensity factor, K_I , all loads and stresses on the test specimen are perpendicular to the crack plane. This mode of loading is the most important mode when considering the strength of glass. Other modes exist, in which shear loads and stresses are applied to the specimen. In glass, these modes control the direction of crack growth.

$$\sigma_{ij} = \left(K_I / \sqrt{2\pi r} \right) f_{ij}(\theta) \quad (3)$$

For a given specimen geometry, the stress intensity factor K_I depends on the geometry, the crack length, and the force or stresses applied to the specimen. By expressing crack growth results in terms of stress intensity factors, universal curves for slow crack growth could be obtained that were applicable to any geometry.

(1) Crack Growth in Nitrogen Gas

The first systematic studies of crack growth in glasses were carried out by Wiederhorn²² and by Irwin.²³ Wiederhorn used double cantilever beam (DCB) specimens similar to those used by Gilman²⁴ to study the cleavage of single crystals. Crack extension was measured as a function of applied force, using an optical microscope to follow the crack motion. The principal result from this study²² is shown in Fig. 3, where crack velocity is plotted as a function of the applied stress intensity factor^{††} for atmospheres in which the relative humidity (RH) varied from 0.017% RH to 100% RH.

[†]For a vector from the crack tip, θ is the polar angle between the crack plane and the point at which the stress is determined.

^{††}As crack lengths and specimen geometry were known, the force data from Wiederhorn²² were converted into stress intensity factors, which are more appropriate to use for stresses near crack tips.

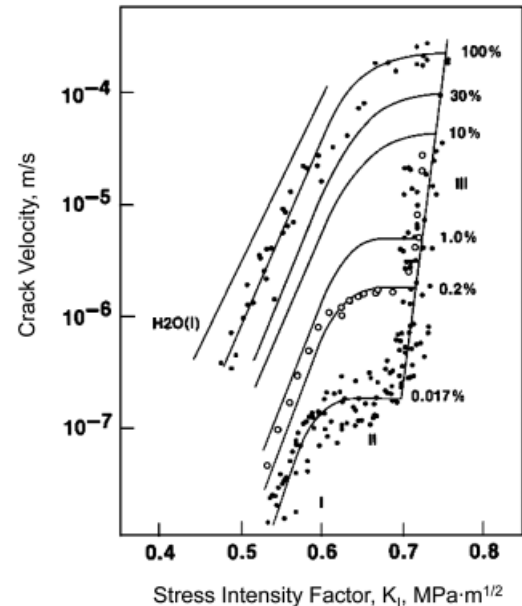


Fig. 3. Crack growth data in soda-lime-silica glass. After Wiederhorn.²²

The data in Fig. 3 are the first to show that crack growth in glass is a complex process, yielding three distinct regions of behavior. In Region I, where the crack growth rate depends on both the applied stress intensity factor and the relative humidity, the rate of growth is proposed to be reaction rate controlled, i.e., dependent on the rate of reaction between water vapor and the strained Si-O bonds at the crack tip. The type of curves shown in Fig. 3 is also observed for other media and glasses: silicate glasses in alcohols^{25,26} and alkanes²⁷; phosphate glasses in air.²⁸⁻³⁰ In all of these, the rate of crack growth in Region I is governed by a stress-enhanced chemical reaction between water and the Si-O bonds at the crack tip.

As the crack velocity increases, the crack starts to outrun the water migrating to the crack tip and a plateau develops in the v - K_I curve. This is Region II crack growth, where the crack growth rate is transport rate limited. Several models have been suggested to describe transport rate-limited crack growth in glass. These all have in common an insensitivity of the crack growth rate to the applied stress intensity factor, and for this reason, the crack growth rate shows up as a plateau on the $\log(v)$ - K_I plot (Fig. 3).

One model that captures the essential features of Region II crack growth assumes free molecular flow of the water molecules to the crack tip,³¹ and is applicable in gases such as air or nitrogen when the crack wall opening is less than the molecular free path water molecules in the gas, < 100 nm. Then the water molecules reach the crack tip by bouncing unhindered from wall to wall. Recent data on silica glass tested in nitrogen gas support this mechanism of crack growth.³² However, if the water sticks to the walls of the crack, the mechanism of crack growth can change from free molecular flow to surface diffusion, or to an adsorption-limited flow process, in which case, the crack growth will have an Arrhenius dependence on temperature. In metaphosphate glasses tested in nitrogen gas, an Arrhenius dependence was observed, and the Region II crack growth was attributed to surface diffusion.²⁸

In liquid solutions, bulk diffusion²² is expected to be the dominant model of crack growth because the molecular free path of the liquids is usually much less than the spacing between the walls of the crack, such as would be expected for water dissolved in a host liquid. Then, the viscosity of the host liquid will be an important parameter in controlling the position of the Region II plateau. The position of the plateau should be inversely proportional to the viscosity of the host liquid, as has been demonstrated in a series of nonaqueous liquids containing small amounts of dissolved water.²⁶ The description of crack

growth in Region II can be further complicated by the condensation of aqueous environments at crack tips during the growth, as has been observed recently by a number of authors.^{33,34}

Once the crack outruns the water in the nitrogen gas, Region III, it will propagate as if it were in a completely dry environment. In Region III, the crack growth curve has a much greater dependence on applied stress intensity factor than in Regions I or II. In Fig. 3, all of the curves, regardless of the relative humidity, join up to form a single curve in Region III. Region III, however, is not the same for all glasses, or environments, but depends on the structure of the glass and the dielectric constant of the fluid at the crack tip, as will be discussed below.

(2) Crack Growth in Aqueous Solutions

In water or aqueous solutions, the crack growth behavior of glasses is somewhat different than that in air. Over most of the crack growth range, only Region I crack growth is observed. The crack growth behavior does, however, depend on the composition of the glass as demonstrated by Wiederhorn and Bolz,³⁵ (Fig. 4). On a plot of the logarithm of the velocity versus the applied stress intensity factor, some glasses plotted as straight lines, whereas others appeared to exhibit a crack growth threshold: soda lime silicate glass shows a threshold, whereas silica glass plots as a straight line. Gehrke *et al.*³⁶ clarified this behavior by showing that glasses containing mobile cations (Na^+ , K^+ , and Li^+) exhibit thresholds on the crack growth curves, whereas glasses containing no mobile ions form straight lines. This behavior is thought to be due to shielding stresses resulting from ion exchange close to the crack tip, as described by Michalske and Bunker.³⁷ In more recent work, data on both silica glass and soda lime silicate glass were obtained at crack velocities as low as 10^{-13} m/s.^{38,39} The newer sets of data are consistent with the data shown in Fig. 4: silica gives no indication of a fatigue limit, whereas soda lime silicate glass continues to decrease at an increasing rate as the stress intensity decreases.

Michalske⁴⁰ and Gehrke *et al.*³⁶ gave definitive evidence of a fatigue limit in glasses containing mobile ions by showing that a

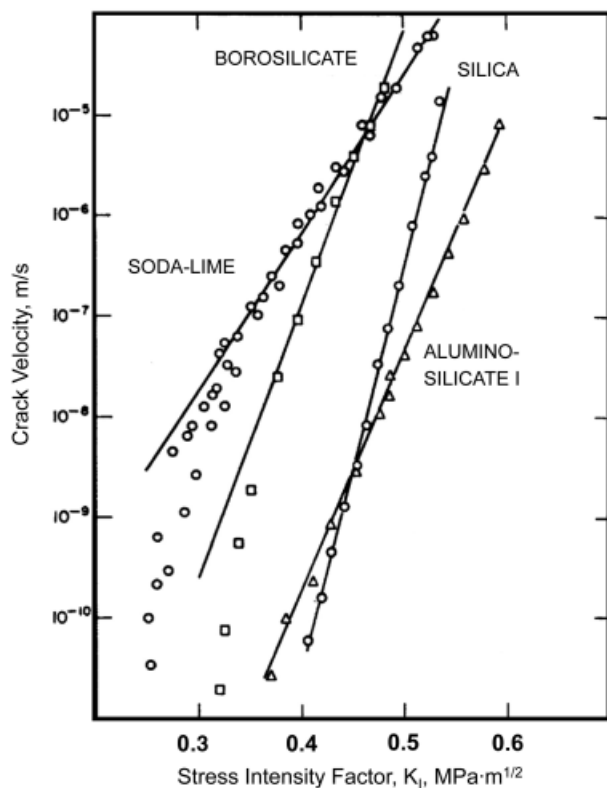


Fig. 4. Glass tested in water. Note the two different kinds of behavior—glasses containing alkali ions exhibit apparent fatigue limits; glasses with no alkali ions form straight lines on this kind of plot.

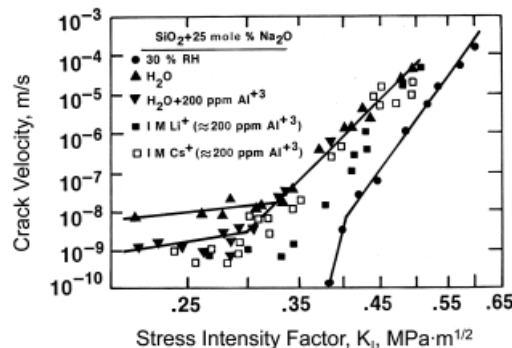


Fig. 5. Crack propagation of a silicate glass containing 25 mol% Na_2O in water, air, or solutions containing Li^+ or Cs^+ . Tests carried out in aqueous environments showed a plateau at stress intensity factors less than approximately $0.3 \text{ MPa} \cdot \text{m}^{1/2}$.

crack loaded at the fatigue limit required additional time to repropagate when the load was increased beyond the fatigue limit. Depending on the time held at load, the time to repropagate can be many hours,⁴¹ or even days.⁴² The delay to failure decreased rapidly when the crack was loaded much higher or much lower than the fatigue limit. These results may be taken as evidence that the crack had really stopped propagating.

Data obtained on some binary alkali-silicate glasses gave results that were entirely unexpected. Depending on the composition, not only were fatigue limits observed, but low-level plateaus were also observed in which crack growth seemed to be independent of the applied stress intensity factor (Fig. 5). Simmons and Freiman⁴³ first observed this effect in a binary silicate glass containing 25 mol% Na_2O , the remainder being SiO_2 (Fig. 5). Similar observations were made by Michalske and Bunker,³⁷ and by Gehrke *et al.*³⁶ Different opinions have been given for these low-level plateaus. Simmons and Freiman suggest that the crack has become blunted by the corrosive environment at the crack tip and that the crack velocity is now determined by the corrosion rate of the glass. Michalske and Bunker argue that ion exchange of Na^+ for H^+ in solution causes a tensile stress around the crack tip, which is now the principal driving force for crack growth. Apparently, the cause of the low-level plateau is still a question of some discussion.

In addition to the observation of plateaus and fatigue limits in glasses immersed in electrolyte solutions, changing the pH of the solutions causes a change in the slope of the crack growth curves of commercial silicate glasses.⁴⁴ In general, the slope of the crack growth curve, Region I, in acids was about twice that measured in basic solutions. Gehrke *et al.*³⁶ also studied effects of acidic and basic solutions on crack propagation in binary and ternary alkali silicate glasses. The change in slope observed by these authors in Region I was not as large as that observed by Wiederhorn and Johnson.⁴⁴ Gehrke *et al.* were more interested in studying the effect of environment and composition on the crack growth fatigue limit. The dependencies of the slopes of the crack growth curves are still to be explained theoretically.

(3) Effect of Temperature on Crack Growth

Studies in water,³⁵ air,⁴⁵ and vacuum⁴⁶ have shown that crack growth depends on temperature. The behavior of soda lime silicate glass in water is shown in Fig. 6. As the temperature is increased, the crack moves faster, as would be expected for an Arrhenius behavior so typical of chemical reactions. Also, the crack growth threshold seems to fall off more sharply with increasing temperature. However, Fig. 6 gives no indication of whether the threshold itself depends on temperature.

In vacuum,⁴⁶ the curves are steep and data are difficult to gather because of the strong dependence of crack velocity on the applied stress intensity factor. Nevertheless, crack growth data have been obtained on several commercial glasses including soda lime silicate glass. The shifts in curve position as a func-

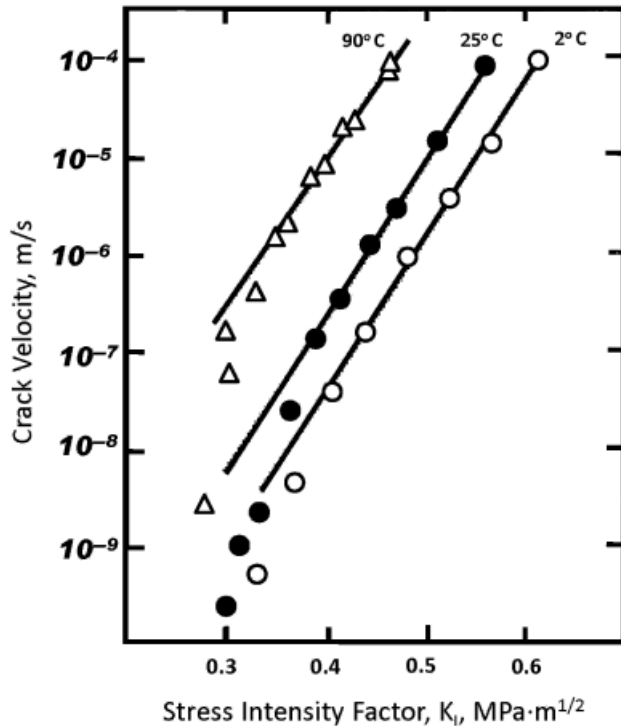


Fig. 6. Soda-lime-silicate glass tested in water as a function of temperature. The apparent fatigue limit seems to be affected by temperature.³⁵

tion of temperature allow the activation energy in vacuum to be calculated. Crack velocity curves on silica glass are so steep that they cannot be collected using the DCB technique; fracture appears to occur instantaneously. A stable fracture mechanics configuration such as the Double Cleavage Drilled Compression (DCDC) specimen^{47,48} has to be used for this purpose. Because K_I decreases as the crack becomes longer, the crack cannot become unstable and it should be possible to estimate the crack growth behavior of silica glass in such an experimental situation.

The effect of temperature on crack growth in nitrogen gas with a controlled concentration of water vapor was studied on silica glass by Suratwala and Steele⁴⁵ and by Hibino *et al.*⁴⁹ The crack growth curves obtained in these two studies resembled the curves shown in Fig. 6. In contrast to theoretical predictions, to be discussed below, Suratwala and Steele observed that in Region I the crack growth rate decreased with increasing temperature. This finding is supported by the work of Fisk and Michalske,⁵⁰ but not by Hibino *et al.*^{49,††} The crack growth behavior of silica glass is anomalous with regard to other glasses, which show a behavior that is more consistent with reaction rate theory. Suratwala and Steele attributed this behavior to a change in the resistance of the glass to crack growth as the temperature is increased. They view this mechanism as competitive to the normal stress-corrosion reaction occurring at the crack tip. Fisk and Michalske, by contrast, argue that the results would be expected if water adsorption on the glass surface near the reactive bond was a necessary prelude to the bond-breaking chemical reaction. If this were the explanation for the anomalous behavior in silica glass, one would have to explain why adsorption is also not important to other “normal” glasses.

(4) Crack Growth in Nonaqueous Liquids

As in air or water, the principal cause of crack growth is water dissolved in the liquid. Crack growth curves are very similar in appearance to those shown in Fig. 3, as illustrated by crack growth

^{††}Hibino *et al.*⁴⁹ obtained a conflicting result as the crack velocity increased with increase in temperature. Hibino *et al.* did not appear to have used a constant concentration of water for all temperatures as in Suratwala and Steele⁴⁵ and Hibino *et al.*⁴⁹ As the relative humidity was defined at each temperature by Hibino *et al.*, the water concentration actually increased in their study.

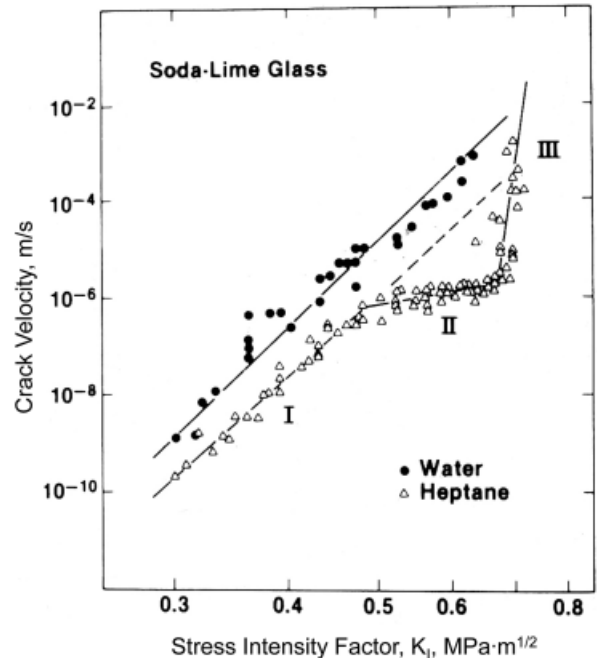


Fig. 7. The data for heptane were taken for a relative humidity of 50%. By comparing these curves with the curves in Fig. 5, one can show that the position of the curve for heptane is located at about 50% RH for air. Data taken from Freiman²⁷

data taken in heptane (Fig. 7).²⁷ Similar results are obtained in other organic liquids.^{25,26} Typically, three regions of crack growth are observed, Regions I and II representing the effects of dissolved water on the crack growth rate. Region I is reaction rate-limited crack growth; Region II is transport rate-limited growth. In contrast to the results obtained in air or inert gases, Region III represents reactions between the liquid and the glass.²⁶

Freiman^{25,27} showed that crack growth in organic liquids such as alcohols or alkanes depended on the partial pressure of water in the liquid. Consequently, no organic liquid can be considered to be completely dry because the partial pressure of water in the liquid will be in equilibrium with water in the air. Water saturated heptane, for example, contains about 20 to 50 ppm of water at normal temperature and pressure,⁵¹ at 50% RH, heptane would contain approximately one-half this amount of water in solution. The net effect of this low concentration of water is to suppress Region II crack growth behavior to about 10^{-6} m/s but to leave the curve for Region I virtually identical to that measured in air at 50% RH (Fig. 7). These results suggest that in Region I the partial pressure rather than the absolute quantity of dissolved water governs the rate of crack growth. By contrast, Region II seems to be sensitive to the concentration of water, as it should be for transport-limited crack growth. This observation also suggests that one must be cautious in ascribing crack-suppressing properties to a “dry” liquid, as the behavior of the liquid will depend on its relative humidity.

Crack growth in Region III is normally thought to be independent of the environment, but in nonaqueous liquids Region III crack growth depends both on the glass composition and on the dielectric constant of the particular liquid at the crack tip.²⁶ As currently envisioned, the fracture process (discussed in the section on molecular models) involves the direct molecular attack of water molecules on strained silicon–oxygen bonds, which in turn involves a separation of charges at the crack tip. The charges created during the bond breaking event will react electrostatically with the crack-tip fluid, the strength of the reaction depending on the dielectric constant of the fluid. Thus, in Region III, there is an electrostatic contribution to the crack growth process. Hence, the slopes of the curves in Region III depend both on the glass composition and on the dielectric constant of the environment.

In addition to the above studies, there is a rich profusion of other crack growth data in glass, and new observations are still being made using fracture mechanics techniques. Discoveries include the observation that ion exchange around the tip gives rise to crack tip stresses that account for both the fatigue limit in glass and low-level plateaus depending on the sign of the stress.^{37,40,42} In porous glasses such as silica-aerogels, or nanoporous glasses, compressive stresses due to water condensation near the crack tip retard crack growth.^{52,53} Thus, increasing the water vapor pressure decreases the crack velocity of nanoporous glasses or aerogels. This result has been explained by a buildup of pressure around the crack tip through capillary action of condensed water near the crack tip.⁵³ Studies on nanoporous thin film glasses have also demonstrated an anomalously high susceptibility to subcritical crack growth in sodium peroxide.⁵⁴ These results are important because of the industrial use of peroxide solutions in the processing of electronic components.

The ability to collect detailed information on crack motion as a function of glass composition, glass structure, environment, and applied load allows us to study the basics of crack growth and to use this understanding to predict lifetime under a variety of conditions. Finally, it is important to note that glasses other than those based on the silicate structure also exhibit similar kinds of crack growth behavior to those described above. Thus, studies carried out on phosphate glasses^{28–30} show the same kinds of trimodal curves in water containing environments as are observed in silicate glasses. Therefore, it is probable that the kinds of physical phenomena we have been discussing with respect to silicate glasses are also applicable to glasses based on other chemistries.

VI. Theories of Crack Growth and Fracture

Commencing in the 1940s researchers attributed delayed failure to the movement of cracks as a consequence of glass composition, stresses applied to the glass, and water in the environment. Before 1960, most of the expressions for delayed failure were empirical and made little contribution to our fundamental understanding of the fracture process. By 1960, the need for a theoretical basis for delayed failure became clearly apparent and several theories were developed to explain the fatigue of glass.

The early theories of glass fracture could be divided into three broad categories, depending on how they explained the water-induced weakening of glass. Theories are based either on crack-tip plasticity, chemical reactions at crack tips or a decrease in surface energy due to water adsorption on the glass near the crack tip. Theories based on a decrease in the surface energy of glass argue that the main role of the water is to reduce the value of the surface energy term in the Griffith equation. The kinetics of crack motion then depends on the kinetics of penetration of water to the crack tip and the rate of adsorption of water onto the crack tip bond or the fracture surface.

Theories of crack growth that depend on chemical reactions argue that at a crack tip, water reacts with strained bonds, causing them to break. The kinetics of crack motion then depend on the kinetics of the individual chemical reactions, particularly on the stress sensitivity of the reactions, and how the water finds its way to the crack tip.

Not all of these theories have been equally investigated or supported in the literature. The chemical reaction-rate theories are most accepted and have been most highly investigated, followed by the surface energy theories. One can argue that these two approaches to delayed failure represent a difference in emphasis rather than a real difference in mechanism because they both deal with the same kinds of surface chemistry. Theories of plastic flow are essentially different from the other two. In this section, we discuss theories that have been important historically to the development of an understanding of delayed failure in glasses.

(1) Plastic Flow

While we now know that it is the growth of small cracks that governs failure, other theories attempting to explain glass frac-

ture were suggested. These include the suggestion by Murgatroyd^{55,56} that glass contains quasiviscous pockets. As the stresses in these pockets relaxed, the load in the glass transferred from the quasiviscous pockets to the more brittle parts of the glass structure. Fracture would occur, from holes in the structure that act as stress concentrators. The time elapsing before fracture is related to the time required for the stress in the quasiviscous material to relax. The model is not now considered to be a viable explanation for delayed failure.

In the paper of Weidmann and Holloway,⁵⁷ the authors used a viscoelastic model to explain crack growth in glasses. They assumed that a plastic zone surrounded the crack tip and that the expansion of this plastic zone to a critical size was essential to the propagation of cracks in glasses. Beyond this critical size, bonds break and the crack propagates with a critical-size plastic zone surrounding the crack tip. Environment affects the growth of cracks by modifying the viscoelastic properties of the plastic zone, and the critical size required for crack advancement. Weidmann and Holloway expressed the logarithm of the crack velocity as a linear function of $1/K_I$, i.e., the inverse of the applied stress intensity factor. Crack growth data on glass, obtained by standard fracture mechanics techniques, fit their data very well. They also showed that the crack growth data could be correlated with hardness data,³ which depended on both the time and the amount of water in the environment. This model has not been widely tested and is not accepted currently.

More recently, models of cavity nucleation and coalescence have become popular in the condensed-matter physics community and the idea has been suggested that cracks in glasses propagate by the nucleation, growth, and coalescence of cavities, as they do in metals.^{58,59} The principal experimental support for this point of view was obtained by observing moving crack tips with the atomic force microscope.⁵⁸ The authors^{58,59} report the observation of “cavities” in a plastic zone extending in front of the main crack. These “cavities” show up as localized depressions within a larger linear depression reported as lying in front of the main crack. With time, the “cavities” are believed to grow and link up as the crack increases in size.

To test the model of cavity formation, Guin and Wiederhorn^{60,61} examined the opposing surfaces of a crack that had been propagated subcritically. If cavities are forming at the crack tip, it should be possible to observe them on the crack surfaces once the specimen has broken in two. The growth and coalescence of cavities along the crack front should leave marks on the fracture surfaces similar to those appearing in metals, or metallic glasses^{62,63} for which crack growth occurs by the nucleation and growth of cavities. Guin and Wiederhorn^{60,61} imaged identical areas on the two opposing fracture surfaces and compared them (Fig. 8). No evidence in the form of residual damage or cavity fragments was found on the fracture surfaces. As far as could be determined, the two surfaces were exact mirror images of each other, casting doubt on a cavitation mechanism of crack growth for glass. A summary of the arguments against a cavitation mechanism of crack growth in glass is presented in.⁶⁴

(2) Surface Adhesion

Orowan's contribution to our understanding of delayed failure rests on his suggestion that the fracture surface energy proposed by Griffith (Eq. (2)) is a function of the environment in which it is measured.⁶⁵ Using experimental data on the cleavage of mica both in vacuum and in air,^{65,66} Orowan found that the fracture surface energy in vacuum is about 16 times greater than it is in air and from this suggested that the strength of glass tested in vacuum should be ≈ 3.5 – 4.5 times greater than that obtained in moist air. He also suggested that the decrease of strength with time was due to crack growth, the rate of growth being governed by the diffusion rate of the adsorbed water to the crack tip. Orowan's paper is important because it predicts an effect of environment on crack growth and suggests that surface chemistry is important in controlling the growth rate.

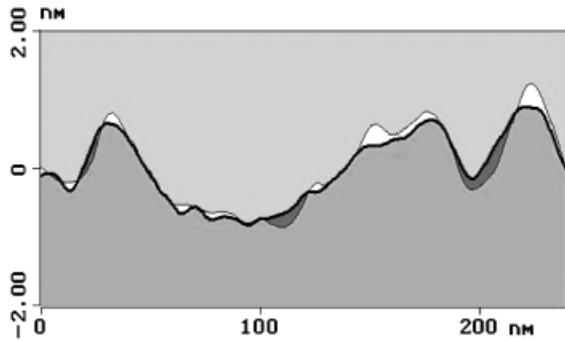


Fig. 8. Profile generated from two opposing fracture surfaces. The profiles of each surface are shown by the dark curve and the light curve. The vertical difference between the two profiles is less than 0.3 nm. This figure suggests that no cavities form during crack growth, within the error of experimental measurement (≈ 0.3 nm vertical; ≈ 5 nm lateral). The images are from soda lime silicate glass tested in air at a velocity of about 1×10^{-2} ms $^{-1}$. From Guin and Wiederhorn.⁶⁰

The ideas proposed by Orowan were later quantified by Lawn *et al.*,^{67,68} who used reaction rate theory⁶⁹ to develop kinetic equations that described the motion of cracks as a function of applied load, temperature, and water content in the environment. Lawn suggests that crack growth occurs by the adsorption of an active chemical species at the tip of the crack. The activation energy for adsorption at equilibrium, δF^* , is modified by the applied force over and above that required for equilibrium, i.e. $G^* - R_E > 0$, where $R_E = 2\gamma$. The parameter, G^* , is the strain energy release rate and γ is the surface free energy of the fracture surface. As suggested by Orowan, the surface energy, γ , and, hence, R_E will depend on the environment. Following normal procedures for developing a kinetic equation from reaction rate theory, Lawn obtains the following equation for the crack growth rate, v :

$$v = v_o \exp(\alpha G^*/kT) \quad (4)$$

where the preexponential term has the following form:

$$v_o = 2v_o a_o \exp(-\Delta F^*/kT) \exp(-\alpha R_E/kT) \quad (5)$$

where v_o is a characteristic frequency, a_o is a characteristic atom spacing of the solid, k is Boltzman's constant, and T the temperature.⁸⁸ The activation area, α , represents an area of molecular size along the crack front, which becomes unstable and separates during the fracture process. The cumulative fracture and linkage of these small areas in front of the crack front are the main cause of crack advancement. In a vacuum, the activation area, α , for silica glass is about 0.14 nm 2 , i.e., approximately 3.5 Si-O-Si bonds. For cracks propagating in water, the activation area is about one-tenth this size.⁶⁷

From the above discussion, the kinetic model based on chemisorption species at the crack tip can be shown to fit the experimental crack growth data.⁶⁷ If the data in Figs. 3–7 were plotted as a function of the strain energy release rate, G , instead of the stress intensity factor, K_I , the data would form the same pattern of straight lines as those observed for Region I when the stress intensity factor was used as a plotting parameter. The slopes of these curves would provide an estimate of the activation area, α . Because of the Arrhenius dependence on temperature, Eq. (4) would also fit the temperature data. Finally, the environmental dependence of the crack propagation rate is given by $\exp(-\alpha R_E/kT)$, where R_E is environmentally dependent. If surface adsorption can be explained by a Langmuir isotherm,⁷⁰ then $\exp(-\alpha R_E/kT)$ is roughly proportional to p_o^η , where p_o is the partial pressure of the water vapor and η is the fractional

surface coverage. Thus, the shift of the crack growth data in Fig. 6 could be related to the partial pressure of the water in the environment, as is actually observed.

(3) Chemical Processes

In 1947, Gurney presented thermodynamic concepts of moisture-enhanced fracture of glass.⁷¹ He suggested that “Due to concentration of strain energy, the material at the end of the crack has a much higher free energy than normal unstressed glass, and is therefore much more chemically active. Atmospheric attack will result in the formation of a complex of glass and atmospheric constituents. The crack will extend continually if the strength of this complex, during or after its formation, is less than the load imposed on it.” Gurney's concepts predated a number of the modern theories used to describe crack growth in glass.

Chemical reaction rate theory was applied to crack growth in glass by Gibbs and Cutler in 1951,⁷² and two years later by Stuart and Anderson.⁷³ These authors assumed that crack motion in glass was due to the sequential rupture of bonds at crack tips. Chemical reaction rate theory was applied to the bond rupture process, assuming that the Gibbs free energy for the rupture process was enhanced by the stress at the crack tip. As the load on the component increased, the stress at the crack tip also increased, resulting in an increased rate of rupture of the crack tip bonds. Consequently, the crack velocity increased as the crack tip stress increased. Stuart and Anderson used the equations for crack velocity as a function of applied stress to calculate the time-to-failure expected experimentally; their theory was consistent with the delayed failure results of Baker and Preston⁷⁴ and Vonnegut and Glathart.⁷⁵ Gibbs and Cutler⁷² used their theory to obtain a better understanding of flaw distributions in the surface of glass. Equations of the type derived by Gibbs and Cutler and Stuart and Anderson would be applied directly to crack growth data, once experimental techniques of fracture mechanics were developed.

Following the work discussed above, Wiederhorn *et al.*^{76,77} applied reaction rate theory to the strained bonds at the crack tip. As the subject of fracture mechanics had now been developed and applied to the study of crack growth in glass, the reaction rate equations could be expressed in terms of fracture mechanics parameters. Wiederhorn assumed that the crack velocity was proportional to the rate of reaction of the bonds at the crack tip. The equation derived to describe crack growth is given below:

$$v = v_o a_{H_2O} \exp(\Delta G^*/RT) \quad (6)$$

where a_{H_2O} is the chemical activity of water at the crack tip and ΔG^* is the activation free energy for the chemical reaction at the crack tip. Modeling the crack tip as a two-dimensional parabolic slit, ΔG^* takes on the following form:

$$\Delta G^* = -T\Delta S^* + \Delta E^* + P\Delta V^* - (\gamma^*V^* - \gamma V)/\rho \quad (7)$$

where ρ is the radius of the crack tip, γ the surface tension of the glass, γ^* the surface tension of the glass in the activated state, V the molar volume of the glass, and V^* the molar volume of the glass in the activated state. The other terms have their usual meaning: T is the absolute temperature, P the pressure at the crack tip, ΔS^* the activation entropy, ΔE^* the activation energy; and ΔV^* the activation volume. Because the reaction is occurring at the crack tip that is subjected to a remote stress, the pressure, P , is set equal to the crack tip stress in the direction of the reaction coordinate, i.e., normal to the crack plane. Hence, $P = -2K_I/(\pi\rho)^{1/2}$, where K_I is the applied stress intensity factor.

On comparing Eqs. (6)–(7) with Eqs. (4)–(5), we observe many of the same features in both sets of equations. The Arrhenius form of the equation accounts for the temperature dependence of the data. The environmental dependence is accounted for by the activity of the water in the environment. The dependence of the crack growth curves on applied load is accounted for by the term containing the stress intensity factor,

⁸⁸Equations (4) and (5) are applicable in the limit where the reverse reaction (healing) is slow relative to the forward reaction (crack advancement) and can be ignored. Lawn's treatment was more general than Eqs. (4) and (5); he also considered crack healing and crack equilibrium.⁶⁷

K_I . Eqs. (6)–(7) fit the experimental data quite well, as can be seen from Figs. 3–7. Because the logarithm of the crack velocity plots linearly versus K_I , the activation volume is a constant and can be determined from the slope, b , of the crack growth curves:

$$\Delta V^* = (b/2)(\pi\rho)^{1/2} \quad (8)$$

Equation (8) has been used to estimate the degree of bond stretching that occurs before rupture. For soda-lime-silicate glass and silica glass tested in water, the estimated activation volumes are $\approx 2.3 \text{ cm}^3/\text{mol}$ and $\approx 4.3 \text{ cm}^3/\text{mol}$, respectively. Using an equation suggested by Hamann⁷⁸ to calculate bond elongation, δl , as the bond passes through the activated state:

$$\Delta V^* = N_A \pi (r_{Si}^2 + r_O^2) \delta l / 2 \quad (9)$$

where N_A is Avogadro's number; the values of δl for soda lime silicate glass and silica glass are $\approx 0.1 \text{ nm}$ and $\approx 0.2 \text{ nm}$, respectively. With the Si–O bond being about 0.16 nm , the degree of strain is 0.63 for the soda lime silicate glass and 1.25 for the silica glass. This degree of stretching is the same as for organic molecules undergoing free radical or molecular dissociations.⁷⁸

(4) Comparison of the Adsorption and Chemical Reaction Approaches

Phenomenologically, there is not much difference between the adsorption and chemical reaction theories. Both fit the available experimental crack growth data. Both theories are derived from a general reaction rate theory and, as such, both predict crack healing, a natural fatigue limit, and an exponential crack growth behavior at large driving forces. The primary difference between the two approaches is that the chemical reaction theory focuses on the rate of reaction of the individual bonds when subjected to stress and a reactive environment, whereas the adsorption theory considers the reduction of surface energy at adsorption sites that lie along the crack front. The stress on the bonds at the crack tip and their strain to failure are the important parameters for the chemical reaction theory. Such considerations lead naturally to activation volumes and applied stress intensity factors as the driving force for fracture. Activation volumes obtained from fracture studies can be compared directly with the theoretical and experimental values of these parameters obtained in the field of high-pressure chemistry, in which results are similarly expressed.⁷⁸ By contrast, adsorption theory deals with adsorption sites, adsorption energies, and areas of these sites, which leads naturally to the use of strain energy release rates and areas of activation as the natural parameters for describing crack growth.

(5) The Fatigue Limit

A mathematical treatment of the static fatigue limit was first presented by Charles and Hillig.^{79,80} Their analysis led to a natural fatigue limit as the stress driving the crack growth decreased. Above the fatigue limit, the crack would sharpen and the crack would grow subcritically (Fig. 9(a)). Below the fatigue limit, the crack would become blunt and the crack would stop growing (to be more exact, slow down to the natural corrosion rate of the glass (Fig. 9(c))).

At the fatigue limit, the radius of curvature of the crack would remain constant as the crack grew (Fig. 9(b)). Thus, the fatigue limit was the stress at which the crack propagated in a self-similar way. Although not discussed by Charles and Hillig, crack sharpness is limited by the molecular structure of the glass. Once the crack tip radius reached the dimensions of the glass network and could no longer sharpen, crack growth would occur without a further change in the crack tip radius. The Charles and Hillig theory was useful as it focused our attention on the crack tip, its structure, and its relation to the fatigue limit. The fatigue limit discussed by Charles and Hillig is kinetic in nature, and not related to the natural thermodynamic limit discussed by Lawn.^{67,68} Since its original publication, there have been other publications further expanding on the original theory.^{81,82}

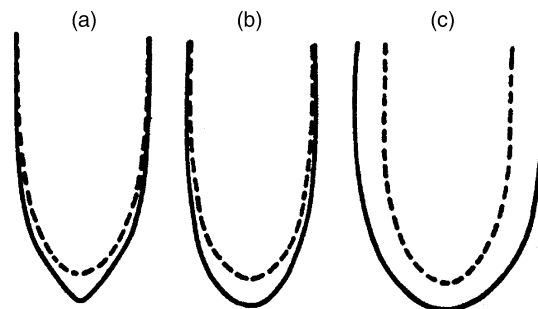


Fig. 9. Change in crack tip geometry due to corrosion: (a) Flaw sharpening for stresses greater than the fatigue limit; (b) Constant flaw sharpness for stresses equal to the fatigue stress; (c) Flaw blunting for stresses below the fatigue limit. From Charles and Hillig.^{79,80}

Whether or not the fatigue limit is caused by crack blunting has been a subject of some recent controversy. An alternate theory assumes that stresses can be set up around the crack tip as a result of ion exchange between the fluid at the crack tip and ions in the glass.³⁷ For soda-lime-silicate glass, hydronium ions in the water can exchange with mobile sodium ions in the glass. The larger radius of the hydronium ion would result in a compressive stress around the crack tip that should retard crack motion. That the ion exchange process at the glass surface actually results in stresses at the surface has been demonstrated by Michalske and Bunker³⁷ and by Fett *et al.*⁸³ In both investigations, curvature developed when one side of a flat plate or disc was exposed to water, indicating the development of bending stresses as a consequence of an ion exchange between the glass and the water.

If ion exchange stresses are the main cause of the fatigue limit in soda-lime-silicate glass, then the crack tip does not have to be blunt to explain the fatigue limit. The shape of a crack tip that has been subjected to an applied load at the fatigue limit is shown in Fig. 10.⁸⁴ On comparing the AFM profiles of the fracture surfaces taken from opposite surfaces of the crack, one can see that the surfaces that formed the open crack were corroded during the hold period and, hence, displaced from one another. The crack tip, however, has not been blunted by the corrosion process. Because the magnifications of the two axes in Fig. 10(a) are not the same, the true shape of the crack tip cannot be discerned in Fig. 10(a). Plotting both axes at the same magnification (Fig. 10(b)), we see that the crack tip is ogee shaped; it comes to a sharp point within the uncertainty of the measurement, $\approx 1 \text{ nm}$. The sharpness of the crack tip is explained by the fact that the crack tip closes as a consequence of glass expansion during the ion exchange.⁸⁴ The closed crack tip prevents the corroding medium from reaching the crack tip, which therefore remains sharp.⁸⁴ In Fig. 10, we see no evidence of crack-tip blunting of the type suggested by the Charles Hillig theory.

VII. Molecular Models for Crack Growth

(1) Protons and Electrons

While it is well recognized that water is primarily responsible for crack growth in glass, the route of attack of water on silica glass was not understood until the experiments of Michalske and Freiman,^{85,86} who described a molecular mechanism by which water, as well as some nonaqueous environments, reacted with strained crack-tip bonds in glass, resulting in their rupture. The model is shown schematically in Fig. 11, which depicts a strained crack tip bond in a silicate glass. Of particular importance is the fact that a water molecule can donate a hydrogen ion and two lone-pair electrons from the unbonded atomic orbitals on the oxygen atom. The three steps in the bond rupture process are:

(1) A water molecule attaches to a bridging Si–O–Si bond at the crack tip. The water molecule is aligned by hydrogen bonding with the $O_{(\text{bridging})}$ ($O_{(\text{br})}$) and interaction of the lone-pair orbitals from $O_{(\text{water})}$ ($O_{(\text{w})}$) with Si.

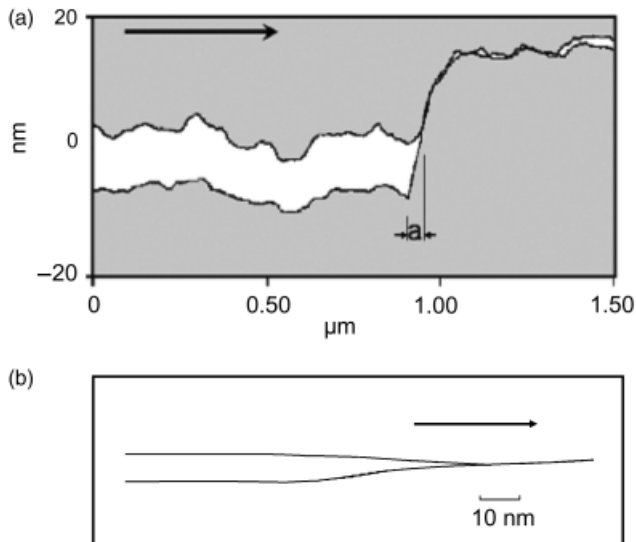


Fig. 10. Atomic force microscopic profile of a crack after being held at the fatigue limit in water for 50 h. The open portions of the crack are a consequence of corrosion by the high pH liquid at the crack tip (pH = 12). (a) The crack profile as taken from the atomic force microscope; the axis normal to the crack plane is magnified 37.5 times that of the axis parallel to the crack plane and (b) the magnification of these two axes are the same and one can see that the crack tip is not blunt, but sharp. The arrow gives the direction of crack growth. Taken from Guin *et al.*⁸⁴

(2) A simultaneous reaction occurs in which a proton transfers to the $O_{(br)}$ and an electron transfers from the $O_{(w)}$ to the Si. During this step of the reaction, the original bridging bond between $O_{(br)}$ and Si is destroyed.

(3) Rupture of the hydrogen bond between $O_{(w)}$ and transferred hydrogen occurs to yield Si–O–H groups on each fracture surface.

This model has some interesting implications. First, there is no requirement for prior dissociation of the water molecule, nor must any reaction products be formed. Second, the model suggests that environmental species other than water can also enhance crack growth if the species possess structural and bonding features similar to water, i.e., proton donor sites at one end and lone-pair orbitals at the other. As observed by Michalske and Bunker⁸⁷, the size of the reactive molecule cannot be too large, or it will be sterically hindered by the walls of the crack and will not reach the crack tip.

By performing controlled crack growth experiments on vitreous silica, Michalske and Freiman^{85,86} demonstrated that molecules such as ammonia, hydrazine, and formamide also cause subcritical crack growth in glass (Fig. 12). All possess proton donor sites and lone-pair orbitals in juxtaposition; these enhance the crack growth rates by coupling across the silicon–oxygen bond to form an activated complex. The test for the effectiveness of these compounds was the absence of a Region II plateau

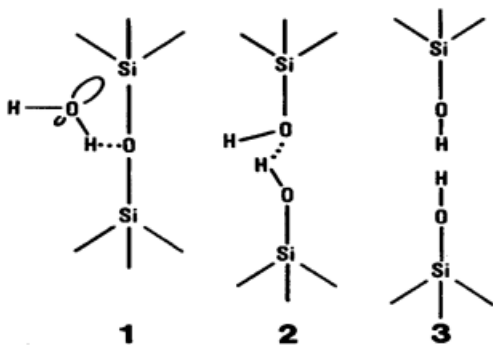


Fig. 11. Schematic of the proposed stress-enhanced reaction between water and a strained crack-tip bond in silica, after Michalske and Freiman.^{85,86}

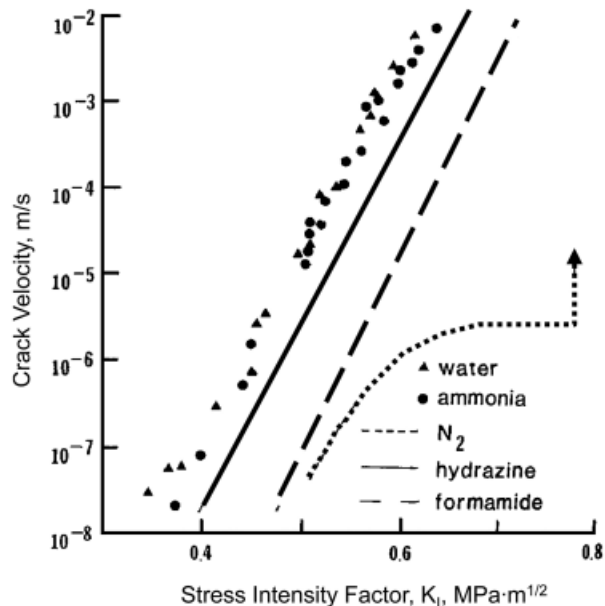


Fig. 12. v – K_I diagram for vitreous silica at room temperature, showing that water, ammonia, hydrazine, and formamide increase the rate of slow crack growth in glass. Taken from Michalske and Freiman.⁸⁵

(Fig. 12), which would have indicated that dissolved water, rather than the liquid itself, was causing crack growth, as discussed earlier in this review. Using this criterion, Michalske and Freiman showed that molecules such as carbon monoxide and acetonitrile, which do not have lone-pair orbitals opposite proton donor sites, do not enhance crack growth in glass. Modifier ions, such as sodium or calcium, do not change the fundamental mechanism of crack growth in soda-lime silica glass⁸⁸ or in binary alkali silicate glasses.⁸⁹ Although there are interesting and unexplained changes in the shape of some portions of the v – K_I curve, the same environments were responsible for crack growth in these glasses as in vitreous silica.

(2) Quantum Mechanical Modeling of Crack Growth

The model presented by Michalske and Freiman is based on the empirical observation that subcritical crack growth occurs when small molecules are able to donate both protons and electrons to the strained Si–O bonds at the crack tip. Whereas experimental evidence of the model is compelling, the theoretical background for such a detailed crack growth mechanism is sparse. Ideally, an *ab initio* quantum mechanical calculation could be used to determine the rate of bond breaking at the tip of a crack into which water has penetrated. Such crack-tip calculations have not yet been accomplished because of the complexity of the problem and the large demands such calculations would place on modern computers. Several approximations have, however, been carried out to capture aspects of the bond breakage with regard to activation energies and activation strains needed for the Si–O bond to break when attacked by a water molecule. In this section, we briefly outline some of these calculations and summarize their results.

In one such study,⁹⁰ *ab initio*, molecular orbital calculations were used to identify the effect of stress and environment on the electron distribution in a pyrosilic acid ($H_6Si_2O_7$) molecule using a Hartree-Fock calculation. It was assumed that this molecule represented the primary structure active at a crack tip. In the first portion of the study, the effects of both bond stretching and bond angle distortion on the charge redistribution in the molecule were analyzed in the absence of an external environment. It was observed that the density of bonding electrons associated with the bridging Si and O atoms decreased with increasing strain up to 20%. It was also found that the density of partitioned electrons associated with oxygen increased, indicating a buildup of charge and a polarization of the Si–O group

as a consequence of applied strain. Clearly, more electrons will be available to interact with an external molecule.

In a second part of the study,⁹⁰ similar strains were placed on the $\text{H}_6\text{Si}_2\text{O}_7$ molecule in the presence of molecules of water, ammonia, formamide, argon, and nitrogen. On approaching the silica molecule, interaction energies were lower for those environments that enhanced crack growth, and the interaction energy decreased with increasing strain. These results suggest that the effectiveness of a substance in enhancing crack growth in silica is controlled, in part, by the magnitude of reaction between that substance and the Si–O bond. The increase in electrostatic charges due to strain, as mentioned above, could aid in attracting an environmental molecule to the reaction site.

A more recent *ab initio* quantum chemical investigation was carried out by Del Bene *et al.*⁹¹ using second-order perturbation theory and included electron correlation effects. They also used a larger basis set than was used by Lindsay *et al.*⁹⁰ The bond length and the angle variations were considered key indicators of the fracture process. More specifically, the authors examined “the dependence of the fracture process on the nature of the interacting water species (monomer, dimer, trimer), the lengthening of the Si–O bond and the bending of the Si–O–Si angle.” The principal finding of the study was that the strongest bonding occurred when water reacted as a dimer (H_2O)₂ with the Si–O bond rather than as a single molecule. Hence, the authors conclude that water reacts with glass as a dimer rather than as the single molecule assumed by Michalske and Freiman.^{85,86} It should be emphasized that both of the molecular studies^{90,91} were carried out on model systems (molecules rather than solid silica located at a crack tip). The applicability of these models to more realistic crack tip situations remains to be seen.

Another approach to subcritical crack growth was adopted by West and Hench,⁹² who used a semiempirical quantum-mechanics-based Austin method AM1⁹³ to quantify the ring contraction method of straining Si–O bonds. They considered the interaction of three-, four-, five-, and sixfold silica rings with a water molecule, and found it to be energetically conservative for these rings to degenerate one step at a time before final rupture of the Si–O bond. Although not mentioned by the authors, if such a process occurs at the tips of cracks in silica glass, glass failure should be very similar to that occurring in polymers for which a craze zone precedes the crack tip.^{94,95} Although such a craze zone has never been observed in glasses, no one has ever looked for them; if they are present, the mechanism proposed by West and Hench would really challenge our current ideas of the structure of crack tips in glass. One possible way to test the presence of a craze zone at a crack tip in silica glass is to estimate the size of the zone using the strip yield model proposed by Dugdale.⁹⁵ An estimate for the length of the plastic zone for silica glass is 0.64 nm, for a critical stress intensity factor of $K_{Ic} = 0.811 \text{ MPa} \cdot \text{m}^{1/2}$ and a yield stress of 10 GPa.⁹⁶ Thus, the size of the plastic zone, 0.64 nm, is about the size of one of the silica rings and would not allow the development of a craze zone.

More recently, the stress corrosion of silica in the presence of water molecules was explored by calculating the stress-dependent, potential energy surface for the reaction of water with a silica nanorod.⁹⁷ Quantum mechanics was used at the level of molecular orbital theory. The calculation involved the reaction of a single water molecule with a nanorod of silica consisting of 36 SiO_2 units arranged in six layers of six SiO_2 units each. All of the Si^{4+} are attached to four O^{2-} , and all of the O^{2-} are attached to two Si^{4+} as would be expected for silica glass. This approach to the stress corrosion problem has an advantage over the cluster calculations discussed above in that the structure allows meaningful calculations of stress and strain. Furthermore, the atoms of the structure are rigidly tied together as they would be in a real physical structure of glass, and the strains and angle changes calculated would be constrained and more characteristic of those actually occurring in a silica glass.

Three reaction pathways were considered and the minimum energy path for each reaction pathway was calculated. The pathways were characterized by three different initiation processes: (I) water dissociation, (II) water molecular chemisorption, and (III) direct siloxane bond breaking. The pathway that had the lowest energy for the widest range of applied stresses was the water molecular chemisorption pathway, which was similar to the mechanism proposed originally by Michalske and Freiman.^{85,86} In addition to determining the lowest energy pathway, the stress dependence of the crack driving force and the reaction pathway was determined. Unlike in classical analysis of energy release rates, a linear stress dependence of the driving force was found. This term was found to be related to a relaxation displacement associated with surface creation and is especially important in nanosize systems when “foreign species are inserted into the fracture process.” The activation barrier is also found to be dependent on the applied stress, and its stress dependence is used to establish the reaction path when competing barriers are present.

Summarizing this section, the earlier modeling of the stress-corrosion processes, which were essentially cluster calculations, had too many degrees of freedom to obtain realistic values for changes in bond angle or bond length. The more recent calculation using nanorods seems to have the kinds of constraints needed to obtain realistic values for these parameters. The calculation seems to provide a realistic description of the reaction of silica nanorods under stress with water. The model should also be tested against other molecules identified by Michalske and Freiman as causing crack growth in glass.

VIII. Summary

Delayed failure is due to the slow growth of cracks that are subjected to a tensile stress. Crack velocity is found, experimentally, to be a strong function of the applied stress intensity factor, K_I , which means that the crack velocity increases rapidly as the crack becomes longer. Failure is assumed to occur at a critical value of the stress intensity factor, at which point the crack is moving fast enough (about 1 m/s) such that failure will appear to occur instantaneously. Delayed failure occurs because of the time required for a crack to grow from a subcritical to a critical size. Water in the environment is the most prevalent cause of subcritical crack growth, decreasing the time to failure as its partial pressure is increased. Finally, the temperature dependence of the failure time is the temperature dependence of the crack growth rate. In an aqueous environment, the time to failure decreases as the temperature is increased. Some anomalous behavior is observed, particularly in highly porous glasses where osmotic forces can lead to compressive stresses around the crack tip that retard crack growth. Fatigue, or crack growth limits are also observed in glasses that contain mobile alkali ions, which can exchange with hydronium ions that cause compressive stresses to build up around the crack tip.

Based on reaction rate theory, models of crack growth have been developed to quantify crack motion as a function of applied force and temperature. Three types of models have been developed: one based on the assumption that plastic deformation occurs at crack tips; the second based on the assumption that crack growth is a consequence of a decrease of environmental adsorption at crack tips; and the third based on the assumption of a direct chemical attack of the environment on the crack tip. Of the three models, the third appears to have the strongest experimental support, primarily because of the experiments of Michalske and Freiman,^{85,86} who demonstrated a molecular route to crack growth that was consistent with a direct molecular attack of the water molecule on the strained bonds at the crack tip. The molecular mechanism of crack growth is one in which the stress-enhanced reaction of the environmental species, e.g. H_2O , reacts with the highly strained Si–O bonds at the crack tip, causing the crack to extend. The mechanism is assumed to be due to the ability of water to donate both electrons and protons to the strained Si–O bonds. Environments other

⁹⁴Craze zones in polymers form at the crack tip normal to the maximum principal tensile stress. In the craze zone, voids form between fibrils, which are bundles of aligned molecular chains. The zone grows by drawing additional material into the fibrils.⁹⁴

than water, e.g. ammonia, and hydrazine, can also donate electrons and protons to the Si–O bond, and therefore, also enhance the crack growth rates in glass.

References

- ¹E. B. Shand, "Experimental Study of Fracture of Glass: I, The Fracture Process," *J. Am. Ceram. Soc.*, **37**, 52–6 (1954); original figure from C.J. Phillips, "Mechanical Strength of Glass," report, Research Laboratory, Corning Glass Works, 1937.
- ²L. Grenet, *Bull. Soc. Encour. Ind. Nat. [Ser. 5]*, **4**, 838 (1899). For translations of the paper see: F.W. Preston, "The Time Factor in the Testing of Glassware," *J. Am. Ceram. Soc.* **18** 220–224 (1935), and *Glass Ind.*, **15** [1] 277–80 (1934).
- ³D. M. Marsh, "Plastic Flow and Fracture of Glass," *Proc. Roy. Soc. (Lond.)*, **282A** [1388] 33–43 (1964).
- ⁴C. E. Ingles, "Stresses in a Plate Due to the Presence of Cracks and Sharp Corners," *Trans. Inst. Nav. Archit.*, **55**, 219–30 (1913).
- ⁵A. A. Griffith, "The Phenomena of Rupture and Flow in Solids," *Philos. Trans. R. Soc. Lond.*, **A221**, 163–98 (1920).
- ⁶F. W. Preston, "The Structure of Abraded Glass Surfaces," *Trans. Optical Soc.*, **23**, 141–64 (1921).
- ⁷F. W. Preston, "A Study of the Rupture of Glass," *J. Soc. Glass. Tech.*, **10**, 234–69 (1926).
- ⁸L. H. Milligan, "The Strength of Glass Containing Cracks," *J. Soc. Glass Technol.*, **13**, 351–60 (1929).
- ⁹F. W. Preston, "The Time Factor in Testing Glass-ware," *J. Am. Ceram. Soc.*, **18**, 220–4 (1935).
- ¹⁰L. V. Black, "Effect of the Rate of Loading on the Breaking Strength of Glass," *Bull. Am. Ceram. Soc.*, **15**, 274–5 (1936).
- ¹¹E. R. Jr. Fuller, S. M. Wiederhorn, J. E. Jr. Ritter, and P. B. Oates, "Proof Testing of Ceramics, Part 2 Theory," *J. Mater. Sci.*, **15**, 2282–95 (1980).
- ¹²A. J. Holland and W. E. S. Turner, "The Effect of Sustained Loading on the Breaking Strength of Sheet Glass," *J. Soc. Glass Tech.*, **24**, 46–57 (1940).
- ¹³T. C. Baker and F. W. Preston, "Fatigue of Glass under Static Loads," *J. Appl. Phys.*, **17**, 170–8 (1946).
- ¹⁴J. L. Glatthart and F. W. Preston, "The Fatigue Modulus of Glass," *J. Appl. Phys.*, **17**, 189–95 (1946).
- ¹⁵F. W. Preston, "The Mechanical Properties of Glass," *J. Appl. Phys.*, **13**, 623–34 (1942).
- ¹⁶C. Gurney and S. Pearson, "The Effect of the Surrounding Atmosphere on the Delayed Fracture of Glass," *Proc. Phys. Soc. B*, **62**, 469–76 (1949).
- ¹⁷R. E. Mould and R. D. Southwick, "Strength and Static Fatigue of Abraded Glass under Controlled Ambient Conditions: II, Effect of Various Abrasions and the Universal Fatigue Curve," *J. Am. Ceram. Soc.*, **42**, 582–92 (1959).
- ¹⁸B. A. Proctor, I. Whitney, and J. W. Johnson, "The Strength of Fused Silica," *Proc. Roy. Soc. A*, **297** [1451] 534–57 (1967).
- ¹⁹R. E. Mould, "The Strength of Inorganic Glasses"; pp. 119–49 in *Fundamental Phenomena in the Materials Sciences, Vol. 4: Fracture of Metals Polymers and Glasses*, Edited by L. J. Bonis, J. J. Duga, and J. J. Gilman. Plenum Press, New York, 1967.
- ²⁰R. E. Mould, "The Strength and Static Fatigue of Glass," *Glastechn. Ber.*, **32K**, III 18–III 28 (1959).
- ²¹H. L. Ewalds and R. J. H. Wanhill, *Fracture Mechanics*. Edward Arnold Ltd, Baltimore, 1984.
- ²²S. M. Wiederhorn, "Influence of Water Vapor on Crack Propagation in Soda-Lime Glass," *J. Am. Ceram. Soc.*, **50** [8] 407–14 (1967).
- ²³G. Irwin, "Moisture Assisted Slow Crack Extension in Glass Plates," A Report of Studies conducted at the Ernst Mach Institute, Freiburg, W. Germany, 6 May–3 August 1965, NRL Memorandum Report, January 28, 1966
- ²⁴J. J. Gilman, "Direct Measurements of Surface Energies of Crystals," *J. Appl. Phys.*, **31** [12] 2208–18 (1960).
- ²⁵S. W. Freiman, "Effect of Alcohols on Crack Propagation in Glass," *J. Am. Ceram. Soc.*, **57** [8] 350–3 (1974).
- ²⁶S. M. Wiederhorn, S. W. Freiman, E. R. Jr. Fuller, and C. J. Simmons, "Effect of Water and Other Dielectrics on Crack Growth," *J. Mater. Sci.*, **17**, 3460–78 (1982).
- ²⁷S. W. Freiman, "Effect of Straight-Chain Alkanes on Crack Propagation in Glass," *J. Am. Ceram. Soc.*, **58** [7–8] 339–41 (1975).
- ²⁸S. N. Crichton, M. Tomozawa, J. S. Hayden, T. I. Suratwala, and J. H. Campbell, "Subcritical Crack Growth in a Phosphate Laser Glass," *J. Am. Ceram. Soc.*, **82** [11] 3097–104 (1999).
- ²⁹T. Suratwala, R. A. Steele, G. D. Wilke, J. H. Campbell, and K. Takeuchi, "Effects of OH Content, Water Vapor Pressure, and Temperature on Sub-Critical Crack Growth in Phosphate Glass," *J. Non-Cryst. Sol.*, **263**, 213–27 (2000).
- ³⁰F. Etter, S. Despetis, and P. Etienne, "Sub-Critical Crack Growth in Some Phosphate Glasses," *J. Non-Cryst. Sol.*, **354**, 580–86 (2008).
- ³¹B. R. Lawn, "Diffusion-Controlled Subcritical Crack Growth in the Presence of a Dilute Gas Environment," *Mat. Sci. Eng.*, **13**, 277–83 (1974).
- ³²T. I. Suratwala and R. A. Steele, "Anomalous Temperature Dependence of Sub-Critical Crack Growth in Silica Glass," *J. Non-Cryst. Sol.*, **316**, 174–82 (2003).
- ³³L. Wondraczek, A. Dittmar, C. Oelgardt, F. Celarie, M. Ciccotti, and C. Marliere, "Real-Time Observation of a Non-Equilibrium Liquid Condensate Confined at Tensile Crack Tips in Oxide Glasses," *J. Am. Ceram. Soc.*, **89** [2] 746–49 (2006).
- ³⁴M. Ciccotti, M. George, V. Ranieri, L. Wondraczek, and C. Marliere, "Dynamic Condensation of Water at Crack Tips in Fused Silica Glass," *J. Non-Cryst. Sol.*, **354** [2–9] 564–68 (2008).
- ³⁵S. M. Wiederhorn and L. H. Bolz, "Stress Corrosion and Static Fatigue of Glass," *J. Am. Ceram. Soc.*, **53** [10] 543–48 (1970).
- ³⁶E. Gehrke, Ch. Ullner, and M. Hähner, "Fatigue Limit and Crack Arrest in Alkali-Containing Silicate Glasses," *J. Mater. Sci.*, **26**, 5445–55 (1991).
- ³⁷T. A. Michalske and B. C. Bunker, "Effect of Surface Stress on Stress Corrosion of Silicate Glass"; pp. 3869–701 in *Advances in Fracture Research, Vol. 6*, Edited by K. Salama, K. Ravi-Chandler, D. M. R. Tablin, and P. Ramao Rao. Pergamon Press, New York, 1989.
- ³⁸M. Muraoka and H. Abe, "Subcritical Crack Growth in silica Optical Fibers in a Wide Range of Crack Velocities," *J. Am. Ceram. Soc.*, **79** [1] 51–57 (1996).
- ³⁹C. Kocer and R. E. Collins, "Measurement of Very Slow Crack Growth in Glass," *J. Am. Ceram. Soc.*, **84** [11] 2585–93 (2001).
- ⁴⁰T. A. Michalske, "The Stress Corrosion Limit: Its Measurement and Implications"; pp. 277–89 in *Fracture Mechanics of Ceramics, Vol. 5, Surface Flaws, Statistics, and Microcracking, R.C.*, Edited by A. G. E. Bradt, D. P. H. Hasselman, and F. F. Lange. Plenum Press, New York, 1977.
- ⁴¹J.-P. Guin and S. M. Wiederhorn, "Crack Growth Threshold in Soda Lime Silicate glass: Role of Hold Time," *J. Non-Cryst. Sol.*, **316**, 12–20 (2003).
- ⁴²J.-P. Guin, S. M. Wiederhorn, and T. Fett, "Crack-Tip Structure in Soda-Lime-Silicate Glass," *J. Am. Ceram. Soc.*, **88** [3] 652–9 (2005).
- ⁴³C. J. Simmons and S. W. Freiman, "Effect of Corrosion Processes on Subcritical Crack-Growth in Glass," *J. Am. Ceram. Soc.*, **64** [11] 683–6 (1981).
- ⁴⁴S. M. Wiederhorn and H. Johnson, "Effect of Electrolyte pH on Crack Propagation in Glass," *J. Am. Ceram. Soc.*, **56** [4] 192–7 (1973).
- ⁴⁵T. I. Suratwala and R. A. Steele, "Anomalous Temperature Dependence of Sub-Critical Crack Growth in Silica Glass," *J. Non-Cryst. Sol.*, **316**, 174–82 (2003).
- ⁴⁶S. M. Wiederhorn, H. Johnson, A. M. Diness, and A. H. Heuer, "Fracture of Glass in Vacuum," *J. Am. Ceram. Soc.*, **57** [8] 336–41 (1974).
- ⁴⁷Ch. Janssen, "Specimen for Fracture Mechanics Studies on Glass"; pp. 23–30 in *Proceedings of the 10th International Congress on Glass*, Vol. 10, Edited by M. Kunigi, M. Tashiro, and N. Soga. Ceramic Society of Japan, Tokyo, Japan, 1974.
- ⁴⁸M. Y. He, M. R. Turner, and A. G. Evans, "Analysis of the Double Cleavage Drilled Compression Specimen for Interface Fracture Energy Measurements over a Range of Mode Mixities," *Acta Mater.*, **43**, 3453–8 (1995).
- ⁴⁹Y. Hibino, S. Sakaguchi, and Y. Tajima, "Crack Growth in Silica Glass under Dynamic Loading," *J. Am. Ceram. Soc.*, **67** [1] 64–68 (1984).
- ⁵⁰G. A. Fisk and T. A. Michalske, "Laser-Based and Thermal Studies of Stress Corrosion in Vitreous Silica," *J. Appl. Phys.*, **58** [7] 2736–41 (1985).
- ⁵¹S. H. Yalkowsky and Y. He, *Handbook of Aqueous Solubility Data*. CRC Press, Boca Raton, 2003.
- ⁵²F. Despetis, P. Etienne, and S. Etienne-Calas, "Subcritical Crack Growth in Silica Aerogel," *J. Non-Cryst. Solids*, **344**, 22–25 (2004).
- ⁵³E. P. Guyer, M. Patz, and R. H. Dauskardt, "Fracture of Nanoporous Methyl Silsesquioxane Thin-Film Glasses," *J. Mater. Res.*, **21** [4] 882–94 (2006).
- ⁵⁴E. P. Guyer and R. H. Dauskardt, "Fracture of Nanoporous Thin-Film Glasses," *Nature Mat.*, **3**, 53–57 (2004).
- ⁵⁵J. B. Murgatroyd, "The Mechanism of Brittle Rupture in Glass," *Soc. Glass. Tech.*, **28**, 406–31 (1944).
- ⁵⁶J. B. Murgatroyd, "Mechanism of Brittle Rupture," *Nature*, **154**, 51–52 (1944).
- ⁵⁷G. W. Weidmann and D. G. Holloway, "Plastic Flow-Slow Crack Propagation and Static Fatigue in Glass," *Phys. Chem. Glasses*, **15**, 68–75 (1974).
- ⁵⁸F. Célarie, S. Prades, D. Bonamy, L. Ferrero, E. Bouchaud, C. Guillot, and C. Marliere, "Glass Breaks Like Metals, but at the Nanometer Scale," *Phys. Rev. Lett.*, **90** [7] 07550 (2003).
- ⁵⁹S. Prades, D. Bonamy, D. Dalmas, E. Bouchaud, and C. Guillot, "Nano-Ductile Crack Propagation in Glasses Under Stress Corrosion: Spatiotemporal Evolution of Damage in the Vicinity of the Crack Tip," *Int. J. Solid. Struct.*, **42** [2] 637–45 (2005).
- ⁶⁰J.-P. Guin and S. M. Wiederhorn, "Fracture of Silicate Glasses: Ductile or Brittle?," *Phys. Rev. Lett.*, **92** [21] 215502 (2004).
- ⁶¹J.-P. Guin and S. M. Wiederhorn, "Surfaces Formed by Subcritical Crack Growth in Silicate Glasses," *Int. J. Frac.*, **140**, 15–26 (2006).
- ⁶²D. Hull, *Fractography*. Cambridge University Press, Cambridge, UK, 1999, Ch. 8.
- ⁶³X. K. Xi, D. Q. Zhao, M. X. Pan, W. H. Wang, Y. Wu, and J. J. Lewandowski, "Fracture of Brittle Metallic Glasses: Brittleness or Plasticity," *Phys. Rev. Lett.*, **94**, 125510 (2005).
- ⁶⁴J. M. López-Cepero, S. M. Wiederhorn, T. Fett, and J.-P. Guin, "Do Plastic Zones form at Crack Tips in Silicate Glasses," *Int. J. Mat. Res.*, **98**, 1170–6 (2007).
- ⁶⁵E. Orowan, "The Fatigue of Glass under Stress," *Nature*, **154**, 341–3 (1944).
- ⁶⁶J. W. Breidmoff, *Proc. Roy. Soc. A*, **127**, 290–7 (1930).
- ⁶⁷B. R. Lawn, *Fracture of Brittle Solids*, 2nd edition, Cambridge University Press, Cambridge, 1993.
- ⁶⁸B. R. Lawn, "Physics of Fracture," *J. Am. Ceram. Soc.*, **66** [2] 83–91 (1983).
- ⁶⁹S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*. McGraw-Hill Book Co. Inc., New York, 1941.
- ⁷⁰I. Langmuir, "The Constitution and Fundamental Properties of Solids and Liquids: Part I. Solids," *J. Am. Chem. Soc.*, **38**, 2221–95 (1916).
- ⁷¹C. Gurney, "Delayed Fracture in Glass," *Proc. Phys. Soc. (Lond.)*, **59**, 169–85 (1947).
- ⁷²P. Gibbs and I. B. Cutler, "On the Fracture of Glass which is Subjected to Slowly Increasing Stress," *J. Am. Ceram. Soc.*, **34** [7] 200–6 (1951).
- ⁷³D. A. Stuart and O. L. Anderson, "Dependence of Ultimate Strength of Glass under Constant Load on Temperature Ambient Atmosphere, and Time," *J. Am. Ceram. Soc.*, **36** [12] 416–24 (1953).
- ⁷⁴T. C. Baker and F. W. Preston, "Effect of Water on Strength of Glass," *J. Appl. Phys.*, **17**, 179–88 (1946).

⁷⁵B. Vonnegut and J. L. Glathart, "Effect of Temperature on Strength and Fatigue of Glass Rods," *J. Appl. Phys.*, **17**, 1982–85 (1946).

⁷⁶S. M. Wiederhorn, E. R. Jr. Fuller, and R. Thomson, "Micromechanisms of Crack Growth in Ceramics and Glasses in Corrosive Environments," *Metal Sci.*, **14**, 450–8 (1980).

⁷⁷S. M. Wiederhorn, S. W. Freiman, E. R. Jr. Fuller, and C. J. Simmons, "Effect of Water and Other Dielectrics on Crack Growth," *J. Mater. Sci.*, **17**, 3460–78 (1982).

⁷⁸S. D. Hamann, "Chemical Kinetics" pp. 163–207 in *High Pressure Physics and Chemistry*, Edited by R. S. Bradley. Academic Press, London, 1963.

⁷⁹R. J. Charles and W. B. Hillig: pp. 511–27 in *Symposium on Mechanical Strength of Glass and Ways of Improving It*. Florence, Italy, September 25–29, 1961. Union Scientifique Continentale du Verre, Charleroi, Belgium, 1962.

⁸⁰W. B. Hillig and R. J. Charles, "Surfaces, Stress-Dependent Surface Reactions, and Strength," pp. 682–705 in *High-Strength Materials*, Edited by V. F. Zackay. John Wiley and Sons Inc., New York, 1965.

⁸¹T.-J. Chuang and E. R. Jr. Fuller, "Extended Charles-Hillig Theory for Stress Corrosion Cracking of Glass," *J. Am. Ceram. Soc.*, **75** [3] 540–5 (1992).

⁸²W. B. Hillig, "Model of Effect of Environmental Attack on Flaw Growth Kinetics of Glass," *Int. J. Fract.*, **143**, 219–30 (2007).

⁸³T. Fett, J. P. Guin, and S. M. Wiederhorn, "Estimation of Ion Exchange Layers for Soda-Lime-Silicate Glass from Curvature Measurements," *J. Mater. Sci. Lett.*, **41**, 5006–10 (2006).

⁸⁴J. P. Guin, S. M. Wiederhorn, and T. Fett, "Crack-Tip Structure in Soda-Lime-Silicate Glass," *J. Am. Ceram. Soc.*, **88** [3] 652–9 (2005).

⁸⁵T. A. Michalske and S. W. Freiman, "A Molecular Mechanism for Stress Corrosion in Vitreous Silica," *J. Am. Ceram. Soc.*, **66** [4] 284–8 (1983).

⁸⁶T. A. Michalske and S. W. Freiman, "A Molecular Interpretation of Stress-Corrosion in Silica," *Nature*, **295** [5849] 511–2 (1982).

⁸⁷T. A. Michalske and B. C. Bunker, "Steric Effects in Stress Corrosion Fracture of Glass," *J. Am. Ceram. Soc.*, **70** [10] 780–4 (1987).

⁸⁸S. W. Freiman, G. S. White, and E. R. Jr. Fuller, "Environmentally Enhanced Crack Growth in Soda-Lime Glass," *J. Am. Ceram. Soc.*, **68** [3] 108–12 (1985).

⁸⁹G. S. White, D. C. Greenspan, and S. W. Freiman, "Corrosion and Crack Growth in 33% Na₂O–67% SiO₂ and 33% Li₂O–67% SiO₂ Glasses," *J. Am. Ceram. Soc.*, **69** [1] 38–44 (1986).

⁹⁰C. G. Lindsay, G. S. White, and S. W. Freiman, "Molecular-Orbital Study of an Environmentally Enhanced Crack-Growth Process in Silica," *J. Am. Ceram. Soc.*, **77** [8] 2179–87 (1994).

⁹¹J. E. Del Bene, K. Runge, and R. J. Bartlett, "A Quantum Chemical Mechanism for the Water-Initiated Decomposition of Silica," *Comput. Mater. Sci.*, **27**, 102–8 (2003).

⁹²J. K. West and L. L. Hench, "The Effect of Environment on Silica Fracture: Vacuum, Carbon Monoxide, Water and Nitrogen," *Philos. Mag. A*, **Volume: 77** [1] 85–113 (1998).

⁹³M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. P. Stewart, "The Development and Use of Quantum-Mechanical Molecular-Models .76. AM1 - A New General-Purpose Quantum-Mechanical Molecular-Model," *J. Am. Chem. Soc.*, **107**, 3902–9 (1985).

⁹⁴T. L. Anderson, *Fracture Mechanics and Applications*, 2nd edition, Chapter 6, 324pp. CRC Press, 1995.

⁹⁵D. S. Dugdale, "Yielding of Steel Sheets Containing Slits," *J. Mech. Phys. Solids*, **8**, 100–4 (1960).

⁹⁶S. M. Wiederhorn, "Fracture Surface Energy of Glass," *J. Am. Ceram. Soc.*, **52** [2] 99–105 (1969).

⁹⁷T. Zhu, J. Li, X. Lin, and S. Yip, "Stress-dependent Molecular Pathways of Silica–Water Reaction," *J. Mech. Phys. Solids*, **53**, 1597–623 (2005). □



Dr. Stephen Freiman graduated from the Georgia Institute of Technology with a B.Ch.E. and an M.S. in Metallurgy. After receiving a Ph.D. in Materials Science and Engineering from the University of Florida in 1968, Dr. Freiman worked at the IIT Research Institute and the Naval Research Laboratory. He joined NIST (then NBS) in 1978. From 1992 to 2002 Dr. Freiman served as Chief of the

Ceramics Division at NIST. Before his leaving NIST in 2006 to start a consulting business (Freiman Consulting Inc.), Dr. Stephen Freiman served for 4 years as Deputy Director of the Materials Science and Engineering.

Dr. Freiman has published over 150 papers focussing on the mechanical properties of brittle materials. He was the first Chairman of the ASTM Subcommittee addressing brittle fracture and a past Chair of the VAMAS steering committee. In the American Ceramic Society, he served as Chair of the Glass and Optical Materials Division, Chair of the Program and Meetings Committee, Treasurer, and President of the Society. He is a Fellow and Distinguished Life Member of the American Ceramic Society.



Sheldon M. Wiederhorn received his B.S. Degree in Chemical Engineering from Columbia University in 1956 and his M.S. (1958) and Ph.D. (1960) in Chemical Engineering from the University of Illinois. His first job was with E. I. Du Pont De Nemours & Co. where his research interests turned toward the study of the mechanical behavior of ceramic materials. After 3 years, he was hired by the National

Bureau of Standards to carry out an independent research program on the mechanical behavior of glasses and ceramic materials.

Dr. Wiederhorn is best known for the experiments that he developed to characterize subcritical crack growth in glasses. The results of these studies illustrate the complexity of subcritical crack growth, which consisted of a stress-enhanced chemical reactions between water and stressed bonds at the

tips of small cracks in glass. A natural conclusion of his study was that the failure of glass was caused by the slow growth of cracks to a critical size that determined the time-to-failure. Based on this work, theories of reliability were developed to assure the lifetime of glass and ceramics subjected to tensile stresses.

At the National Institute of Standards and Technology, Dr. Wiederhorn is now a Senior Fellow Emeritus and continues to carry out a research program on the mechanical properties of ceramic materials. His current interests are to use the Atomic Force Microscope to investigate the atomistics of crack growth in glasses and ceramic materials with the objective of learning more about the crack growth process and its relation to the microstructure of glass. Dr. Wiederhorn is now a Distinguished Lifetime Member of the American Ceramic Society (1998) and has been elected a member of the National Academy of Engineering (1991).



Dr. John J. (Jack) Mecholsky, Jr., Ph.D, is a Professor and Associate Chair at the University of Florida in the Materials Science and Engineering Department. He also serves as Faculty Senate Chair for 2009–2010. He received his B.C.E. in Civil Engineering (1966), Master's Degree in Structural Engineering (1968), and Ph.D. in Materials Science (1973) from the Catholic University of America in Washington, DC.

He received the University of Florida Engineering College's Teaching Award in 2003. Mecholsky received the Schwartzwalder-PACE award in 1984. He is a Fellow of the American Ceramic Society and served as Vice Chair of the New Mexico Chapter, Chair of the Central Pennsylvania Chapter, and Chair of the Florida Chapter. He was a member of the American Society of Testing and Materials, serving as Chair of the Subcommittee on Fracture Testing of Brittle Materials [E24.07], a member of the Materials Research Society, American Society of Engineering Education, International Association for Dental Research, Sigma Xi, National Institute of Ceramic Engineers and Keramos. Mecholsky has over 200 technical publications and over 50 technical reports and holds patents for the development of a laser-hardened composite material and a bioactive tapecast multilayer ceramic/metal composite.