

Fracture Growth (Subcritical) in Brittle Materials

This article gives a survey of mechanisms that govern kinetic crack growth in intrinsically brittle materials—glasses and ceramics—at subcritical loads. After a brief historical summary, the article describes a generic model for the stress dependence of crack velocities in terms of a thermally activated bond-rupture process. Specific atomistic mechanisms for this activation process are then described, with special attention to the important influence of intrusive chemical species from the environment. At higher velocities, the controlling rate process can change from one of thermal activation to one of rate-limited molecular diffusion of environmental molecules. The roles of critical variables, stress intensity, environmental concentration, and temperature are discussed.

1. History

In the mid-twentieth century many studies sought to explain the monotonic decrease in strength of silicate glasses and other brittle materials with time under sustained load. While it was acknowledged that the source of this so-called “static fatigue” was some kind of chemical interaction with water in the environment, the underlying mechanisms remained obscure. An

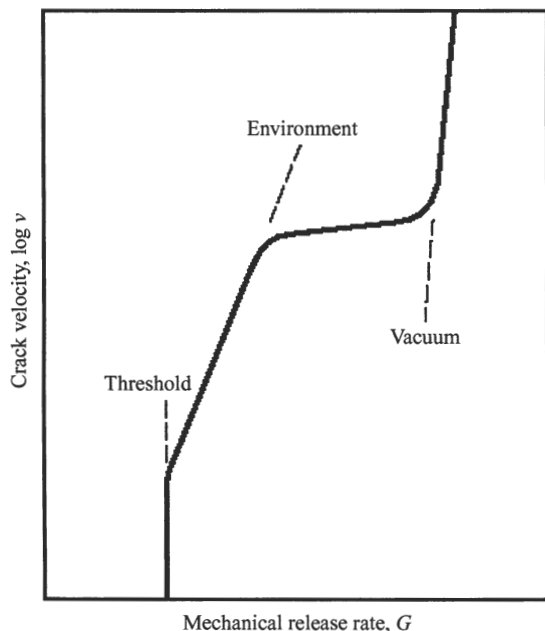
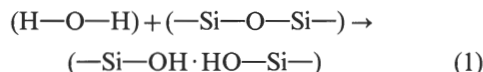


Figure 1
Schematic of crack velocity curve, summarizing different regions observed in experimental data.

early theory by Orowan (1944) proposed that the reduction in strength was due to adsorption of water molecules on the pristine crack walls, and that the rate effect was controlled by the kinetics of diffusion to the crack-tip reaction zone. In the 1960s Charles and Hillig (1962) proposed that the fatigue could be accounted for by a stress-corrosion process involving an activated dissolution of material at rounded flaw tips in glass, leading to extension of cracks at loads below the critical levels required for fast fracture. The notion of subcritical crack growth was born.

Subsequently, classical experiments were performed (Wiederhorn 1967, Wiederhorn and Bolz 1970) to validate the slow crack growth concept. Well-defined cracks were introduced into double-cantilever glass specimens and the velocities of the advancing tips at fixed loads in controlled aqueous environments were measured. In this way crack growth rate data were obtained as a function of mechanical energy release rate, G , or stress intensity factor, K . It was noted that there was an extremely high sensitivity of crack velocity, v , to G or K . Data from these earlier studies, with a focus on silicate glasses, are presented in *Mechanics of Subcritical Crack Growth in Brittle Materials*. A schematic $v(G)$ curve is shown in Fig. 1. Region I is strongly dependent on applied stress, temperature, and environmental chemistry. This region is bounded at its lower end by a threshold, below which the crack may retract and, in favorable cases, heal. Region II is insensitive to applied stress, suggestive of a transport process in which the active environmental species are increasingly unable to keep pace with the crack front as G increases. This intermediate branch “connects” region I to a steep region III, which identifies with an intrinsic bond-rupture response in vacuum.

Most focus in the literature has been on region I of Fig. 1, where the velocity is slowest and lifetime controlling. Wiederhorn attributed the crack velocity in this region to the rate of chemically enhanced bond rupture at the crack tip according to the reaction:



2. Crack Growth as a Thermally Activated Process

It is possible to derive a generic relationship for the crack velocity function in regions I and III by treating crack growth as a thermally activated process, based on the premise that extension is controlled by sequential bond rupture (Lawn 1993). The bond-rupture reaction rate is (Glasstone *et al.* 1941):

$$R = v_0 \left[\exp(-\Delta F_+/kT) - \exp(-\Delta F_-/kT) \right] \quad (2)$$

where ν_0 is a fundamental lattice frequency, kT the Boltzmann thermal energy, and ΔF_+ and ΔF_- molecular free energies of formation of a stress-activated complex from the unbroken and broken bond states, respectively. The crack is in equilibrium at $R = 0$, corresponding to the Griffith energy balance condition $G = 2\gamma$. Expanding about this equilibrium yields:

$$\Delta F_{\pm} = \Delta F' \pm \alpha(G - 2\gamma) + \dots \quad (3)$$

where γ is a solid-environment surface energy, $\Delta F'$ a quiescent activation energy, and $\alpha = -(\partial F/\partial G)$ an activation area. Substituting Eqn. (3) into Eqn. (2) gives crack velocity Ra_0 , with a_0 an interatomic spacing:

$$v = 2\nu_0 a_0 \exp(-\Delta F'/kT) \sinh[\alpha(G - 2\gamma)/kT] \quad (4)$$

At $G > 2\gamma$ the crack extends, at $G < 2\gamma$ it retracts. Apart from providing a simple expression for the stress dependence of velocity, Eqn. (4) allows for a threshold at $G = 2\gamma$, and for healing below that threshold, accounting naturally for a fatigue limit in strength data. This formalism has the advantage of a sound physical basis, rooted in the laws of irreversible thermodynamics and chemical kinetics. Note that it says nothing specific as to the underlying mechanism of thermal activation: $\Delta F'$ is strictly a thermodynamic quantity. As indicated, Eqn. (4) may equally well be applied to regions I and III, with activation energies $\Delta F'_I \ll \Delta F'_{III}$.

Another more commonly used crack velocity function is:

$$v = v_0 (K/K_0)^n \quad (5)$$

where n , v_0 , and K_0 are adjustable parameters. This function, although entirely empirical, fits most region I crack velocity data equally well (apart from the threshold region), and is used most widely in engineering calculations of strength and lifetime characteristics (see *Mechanics of Subcritical Crack Growth in Brittle Materials*).

3. Specific Models

The description in Sect. 2 says nothing about the actual mechanisms that control subcritical crack growth in regions I and III, other than that they are thermally activated. Specific models for chemistry-controlled region I are outlined in Fig. 2. Figure 2(a) assumes that the kinetics are confined to the bonds along a well-defined linear crack front: bonds ahead of this line are unbroken, those behind are broken. Such a model presumes that the interacting species have free access to the crack tip. This may be a reasonable approximation for brittle materials with relatively

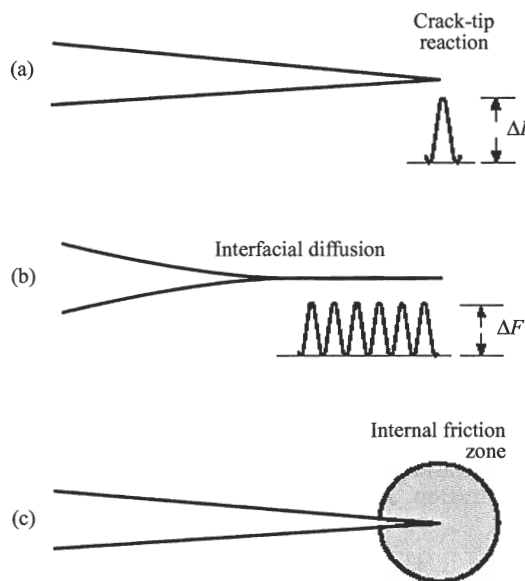


Figure 2

Activation models for region I of crack velocity curve: (a) concentrated chemical reaction at crack front; (b) diffusion of active species within constrained adhesion zone; (c) dissipative internal friction zone around crack front.

“open” molecular structures, like silicate glasses. An elaboration of this model for glasses, based on the reaction in Eqn. (1), is illustrated in Fig. 3 (Michalske and Freiman 1981). Three stages of activated bond strain are envisaged. (a) *Adsorption*. At small bond strain the water molecule attaches itself physically to the bridging Si—O—Si bond. The electron orbitals in the water are tetrahedrally coordinated about the oxygen—two orbitals form bonds with the hydrogen atoms (excess positive charge) and two form lone pairs (excess negative). The bond also has some polar character (silicon excess positive), so the water molecule physically aligns itself in readiness for the next stage. (b) *Reaction*. At higher bond strain the water molecule donates an electron to one of the silicon atoms and a proton to the linking oxygen, forming two new O—H bonds. (c) *Separation*. After electron redistribution the polar terminal bonds mutually repel, completing the bond-rupture process. This model accounts for the observed tendency for polar environmental molecules, not only water but other species such as ammonia, to interact with ionically bonded ceramics.

Figure 2(b) presents an alternative model. It recognizes that opposing crack walls in most low-toughness ionic/covalent brittle solids are highly constrictive in region I of the $v(G)$ curve so that intrusive environmental species do not have unrestricted access to the crack front. It becomes necessary to consider how the

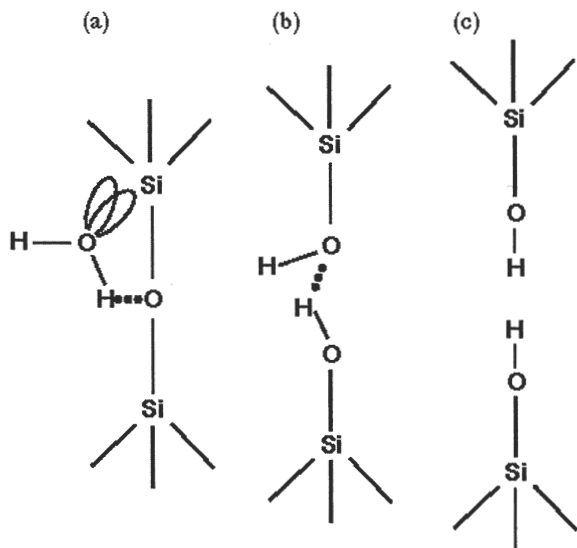


Figure 3

Concerted reaction model for water-induced bond rupture at a crack front in silicate glass: (a) adsorption; (b) reaction; (c) separation.

intrusive molecules are accommodated at the atomically constrained interstices between the narrowing crack walls. Figure 4 shows a calculated crack-wall profile in mica, with atoms in the mica and water molecules represented as hard spheres in accordance with atomic radii (Lawn *et al.* 1987). The water molecules interact with the mica walls along a laterally extended interaction zone. The energy barriers to crack extension now come from interstitial diffusion of the water molecules along the crack interface, in a manner somewhat similar to that envisaged by Orowan (1944). Equilibrium (threshold) arises when the activation barriers for forward and backward diffusion fluctuations are equal, i.e., at $G = 2\gamma$. In this case the force-separation function, $p(u)$, defining the surface energy between separating mica walls in the presence of water

$$2\gamma = \int_0^\infty p(u) d(2u) \quad (6)$$

may be oscillatory, corresponding to metastable states in which integral layers of water molecules are accommodated within the structured crack interface (Israelachvili 1985). These metastable states can lead to occluded water layers in healed cracks.

A third model, a variant of a crack-tip plasticity "process zone" concept widely used to account for the toughness of metals, proposes that the crack front is surrounded by a viscous zone, to which environmental water has access. A continuum model based on this postulate has been described (Maugis 1985). Energy is

assumed to be dissipated by "internal friction" in the material immediately surrounding the crack front (Fig. 2(c)). It is argued that it is the viscous component in the bulk constitutive law, not the adhesion or diffusion kinetics, that determines the velocity function. The viscous process allows for water-facilitated rearrangement of the molecular structure around the crack tip, but does not change the fundamental mode of sequential bond rupture along the crack front implicit in Eqn. (4). Such a model may have an appeal for polymeric materials, and perhaps also for some open-structure glasses. In tougher, polycrystalline ceramics, energy may be dissipated at a coarser, microstructural level, either ahead of the advancing crack front (e.g., in rock salt structures by limited dislocation activity, and in zirconia by phase transformations) or behind the front (e.g., by frictional pullout of "bridging" grains)—the effect of the crack-tip "shielding" in such cases is not so much to control the kinetics as to shift the intrinsic velocity curves along the G or K axis (Lawn 1983).

Which of the above models more correctly applies to any given brittle solid remains a matter of debate. As indicated, the concerted reaction model probably is valid for open structures like silicate glasses. The diffusion barrier model is likely more applicable to ceramic solids with relatively dense atomic packing. The third model is less well accepted, especially in dense, brittle crystals like sapphire, silicon carbide, and silicon where local dissipative processes are conspicuously absent around sharp crack tips (Lawn *et al.* 1980). All models account for the crack velocity dependencies on the critical parameters of applied load, chemical concentration, and temperature. All can also account for a velocity threshold, as a quiescent point where stress-activated forward and backward barriers are equal.

The connecting region II of the curve in Fig. 1 is observed in moisture-containing gaseous environments, or in liquids where the interactive species (water) is in dilute concentrations. In the case of gases, the crack-wall separation inevitably narrows below the mean free path between colliding gas molecules, typically $< 1\mu\text{m}$ (but still wide relative to atomic-scale separations in the near-tip lattice diffusion zone depicted in Fig. 4). The transport of interactive species to the front is then governed by the rate of "free molecular flow" along the crack interface, in which impinging molecules are physically adsorbed onto the crack walls and desorbed at random scattering angles (Knudsen gas). In this region the velocity is:

$$v_{\text{II}} = \frac{\kappa a_0^3 p}{\eta (2\pi m k T)^{1/2}} \quad (7)$$

where p is the partial pressure of interactive molecules, m is the molecular mass, a_0 the adsorption site spacing, η the site occupancy of adsorbate molecules, and κ a Knudsen attenuation coefficient (Lawn 1974). κ is

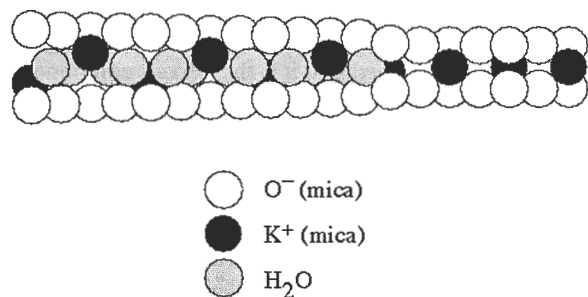


Figure 4
Crack-wall profile in mica, showing intrusion of water molecules. Water lowers surface energy of mica. Crack velocity is determined by interfacial diffusion rate.

only weakly dependent on G or K . Simplistically, for the series I–II transition:

$$v/v_I + v/v_{II} = 1 \quad (8)$$

so that the slower of the two steps is rate limiting. Similarly, for the parallel II–III transition:

$$v = v_{II} + v_{III} \quad (9)$$

so that the faster step is rate limiting. Together with $v_I(G)$ and $v_{III}(G)$ from Eqn. (4), Eqns. (7)–(9) may be used to generate the entire composite $v(G)$ curve in Fig. 1.

4. Concluding Remarks

Subcritical crack growth occurs in most brittle solids. It is especially evident in solids with a substantial component of ionic bonding, so that polar environmental species like water can interact with the crack walls in a rate-dependent manner. The generic analysis outlined in Sect. 2 is able to account for the dependence of these interactions on such variables as chemical concentration, temperature, and above all applied stress (G or K).

In all the models outlined in Sect. 3 it is implicit that the crack front advances by sequential rupture of bonds, so that the tip remains atomically sharp. It is this atomic sharpness that explains the intrinsic brittleness of ceramic materials. The kinetic states associated

with subcritical crack growth are consistent with the thermodynamically-based Griffith energy-balance concept of fracture: at $G = 2\gamma$ the crack is in equilibrium with its environment (threshold); at $G > 2\gamma$ the crack extends at increasing velocity as G increases; at $G < 2\gamma$ the crack can retract and, provided the crack walls are able to recontact, heal (albeit with trapped environmental species). Such thresholds are consistent with the existence of “fatigue limits” in engineering strength data. In this picture, dissipative processes may occur around an advancing crack front, but not change the essential bond-rupture mode of crack extension.

See also: Crack Growth in Multiphase Materials; Brittle Materials : Flaw Assessment

Bibliography

- Charles R J, Hillig W B 1962 The kinetics of glass failure by stress corrosion. In: *Symp. sur la Résistance Mécanique du Verre et les Moyens de L'Améliorer*. Union Scientifique Continentale du Verre, Charleroi, Belgium, p. 511
- Glasstone S, Laidler K J, Eyring H 1941 *The Theory of Rate Processes*. McGraw-Hill, New York
- Israelachvili J N 1985 *Intermolecular and Surface Forces*. Academic Press, London
- Lawn B R 1974 Diffusion-controlled subcritical crack growth. *Mater. Sci. Eng.* **13**, 277–83
- Lawn B R 1983 Physics of fracture. *J. Am. Ceram. Soc.* **66**, 83–91
- Lawn B R 1993 *Fracture of Brittle Solids*. Cambridge University Press, Cambridge
- Lawn B R, Hockey B J, Wiederhorn S M 1980 Atomically sharp cracks in brittle solids: an electron microscopy study. *J. Mater. Sci.* **15**, 1207–23
- Lawn B R, Roach D H, Thomson R M 1987 Thresholds and reversibility in brittle cracks: an atomistic surface force model. *J. Mater. Sci.* **22**, 4036–50
- Maugis D 1985 Subcritical crack growth, surface energy, fracture toughness, stick-slip and embrittlement. *J. Mater. Sci.* **20**, 3041–73
- Michalske T A, Freiman S W 1981 A molecular interpretation of stress corrosion in silica. *Nature* **295**, 511
- Orowan E 1944 The fatigue of glass under stress. *Nature* **154**, 341
- Wiederhorn S M 1967 Influence of water vapor on crack propagation in soda-lime glass. *J. Am. Ceram. Soc.* **50**, 407–14
- Wiederhorn S M, Bolz L H 1970 Stress corrosion and static fatigue of glass. *J. Am. Ceram. Soc.* **53**, 543–8

Brian R. Lawn

Copyright © 2001 Elsevier Science Ltd.

All rights reserved. No part of this publication may be reproduced, stored in any retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the publishers.

Encyclopedia of Materials: Science and Technology
ISBN: 0-08-0431526
pp. 3286–3290