Thermally activated fracture of glass

The fracture of glass is often presented as an ideal illustration of classic fully brittle failure; Griffith himself demonstrated his energy criterion for brittle failure by experiments with glass [1]. However, the Griffith theory is essentially a static one, no allowance being made for slow crack growth below the fracture stress. Such sub-critical crack growth can lead to catastrophic failure, and is well known to occur in glass as reviewed by Wachtman [2]. The phenomenon is observed in a wide range of environments, including vacuum.

A stress corrosion model due to Charles and Hillig [3] has often been used to explain slow crack growth in glass. Limitations of this theory have been pointed out by Lawn [4], who has developed an alternative model based on the ideas of lattice trapping combined with thermal activation. It is the purpose of the present paper to apply these ideas to observations of crack growth in glass in vacuum.

Essentially, the theory of lattice trapping introduces atomistic effects into crack propagation in the same way as the Peierls–Nabarro theory of lattice friction introduces such considerations into dislocation motion. As a consequence, the surface energy term U_s in the energy balance equation

$$U = (-W_L + U_E) + U_s$$

of the Griffith theory where W_L represents external work and U_E represents stored elastic energy is not linearly proportional to crack area, but contains a periodically varying part reflecting the discrete breaking of atomic bonds at the crack tip. Hence, in a crystalline solid containing a crack of unit width and length c parallel to an atomic row of spacing a_x in the direction of crack motion, we have [4],

$$U_s = 2\gamma c - \left(\frac{\gamma_{tx} a_x}{\pi}\right) \sin\left(\frac{2\pi c}{a_x}\right)$$

where γ_{tx} is a trapping term. For an amorphous solid in which the crack moves by breaking of individual bonds of area a, the analogous expression is

$$U_s = 2\gamma A - \left(\frac{\gamma_t a}{\pi}\right) \sin\left(\frac{2\pi A}{a}\right). \qquad (1)$$

Proceeding according to fracture mechanics,

$$\frac{dU}{dA} = -G + 2\Gamma,$$

where G is the mechanical energy release rate or crack extension force, and Γ is the fracture surface energy. Then the surface energy may be written as

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

The crack is in mechanical equilibrium when $dU/dA = 0$, and hence is "lattice trapped" within the range $2\Gamma_- \leqslant G \leqslant 2\Gamma_+$ where $\Gamma_\pm = \gamma \pm \gamma_t$. Within this range, the activation energies for forward and backward motion of the crack ΔG_f and ΔG_b vary between a maximum and zero, with $\Delta G_f = \Delta G_b$ at $G = 2\gamma$. The detailed form of the variation depends ultimately on the interatomic forces, but it is reasonable to assume that at least over part of the range a linear approximation

$$\Delta G_f = \Delta G_0 \left(1 - \frac{G}{G_t}\right) \qquad (2)$$

is adequate where ΔG_0 and G_t are constants. For values of G toward the upper end of the trapping range, only forward motion need be considered and we can write for the velocity $v = v_f - v_b$ of crack motion

$$v \simeq v_f = v_0 \exp(-\Delta G_f/RT). \qquad (3)$$

The constant v_0 will be given by

$$v_0 = Na\nu$$

where N is the number of stretched bonds along the crack front and ν is the attack frequency.

The crack extension force G is related to the stress intensity K and may be written as $G = K^2/E$ where E is Young's modulus. Hence, from Equations 2 and 3,

$$\ln(v/v_0) = -[\Delta G_0(1 - K^2/K_t^2)]/RT \qquad (4)$$

where the constant K_t is the stress intensity at which $\Delta G_f = 0$, which give the condition for spontaneous crack propagation.

Slow crack growth in a variety of glasses under vacuum has been investigated by Wiederhorn *et al.* [5]. Their data have been used to determine the parameters of Equation 4; the agreement of the data with Equation 4, as may be judged by the typical data in Fig. 1, is somewhat better than

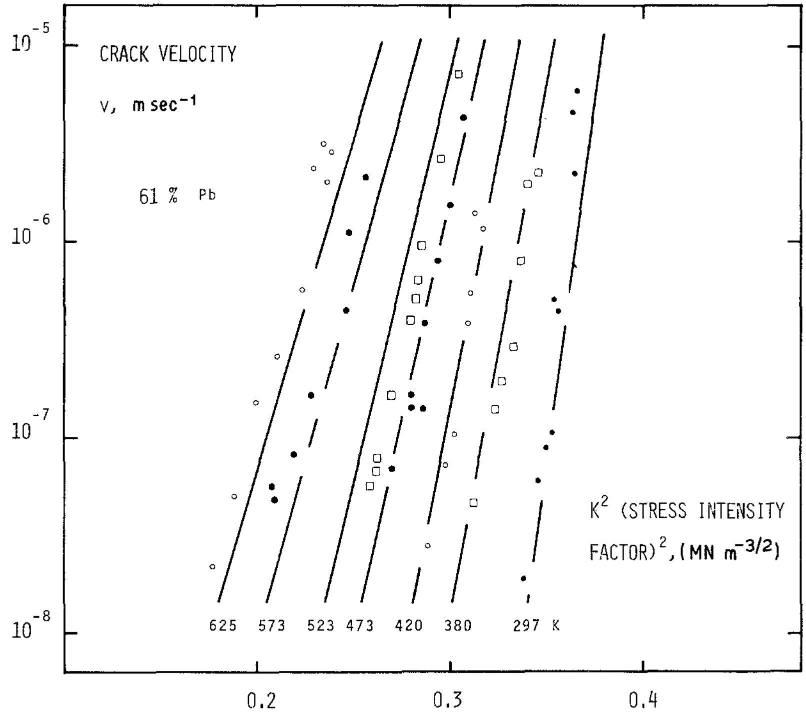

Figure 1 Crack growth velocity of 61% lead glass in vacuum as a function of (stress intensity)^2; data from S. M. Wiederhorn *et al.* [5].

achieved by Wiederhorn *et al.* using an equation relating ln v linearly to K rather than K^2. The parameters obtained are listed in Table I. In order to explain the observation of slow crack growth to very small values of K, particularly for borosilicate crown glass, it has been necessary to assume that $(\gamma + \gamma_t) = 2\gamma$ and that backward motion of the crack is inhibited in some way so that $v_b = 0$. Under these assumptions, ΔG_0 represents the activation energy for bond rupture under zero stress, and $K_t^2 = 4E\gamma$. In obtaining γ from K_t^2 in Table I, E has been taken as 8×10^{10} Nm^{-2}.

The values in Table I are in good agreement with expectation. Single bond energies vary in the range $\simeq 1$ to $\simeq 4 \times 10^8$ J (kg mol)$^{-1}$ ($\simeq 30$ to $\simeq 100$ kcal (g mol)$^{-1}$) for modifiers (i.e. Na) and glass formers (i.e. Si) respectively [7]. The expected value of v_0, taking $N \simeq l/b$, $a \simeq b^2$, and $\nu \simeq \nu_E$, where l is the length of the crack tip, b is the average interbond distance along the crack front ($\simeq 5 \times 10^{-10}$ m), and ν_E is the Einstein frequency ($\simeq 10^{13}$ sec^{-1}), is $v_0 \simeq 5 \times 10^3$ m sec^{-1} which is close to the sound velocity $v_s \simeq \sqrt{(E/\rho)}$ where ρ is the density (~ 2.5 g cm^{-3}). The surface energy can be estimated from $\gamma \simeq N'Q/2$ where N' is the number of bonds crossing unit area of surface ($\simeq 1/b^2 = 4 \times 10^{18}$ m^{-2}) and Q is the bond energy ($\simeq 100$ kcal (g mol)$^{-1} = 70 \times 10^{-20}$ J per bond) as $\gamma \simeq 1.4$ J m^{-2}. The critical stress intensity K_t has been measured directly by Wiederhorn [6] as 0.96 and 0.82 MN m$^{-3/2}$ for aluminosilicate and soda-lime silicate glasses respectively. All these measurements are in reasonable agreement with the values reported in Table I.

TABLE I Activation parameters for slow crack growth in vacuum. [1 J (kg mol)$^{-1}$ = 2.37×10^{-7} kcal (g mol)$^{-1}$]

Glass	v_0 (m sec^{-1})	ΔG_0 [J (kg mol)$^{-1}$]	K_t (MN m$^{-3/2}$)	γ (J m^{-2})
61% lead	5.7×10^2	2.05×10^8	0.70	1.52
Aluminosilicate	3.6×10^6	3.96×10^8	0.92	2.66
Borosilicate crown	9.6×10^6	2.28×10^8	1.09	3.69
Soda-lime silicate	7.0	3.49×10^8	0.74	1.72

Several simplifying assumptions have been made above, which warrant comments. First, it has been assumed that backward crack motion does not occur, even below $G = 2\gamma$. This could be rationalized in terms of local rearrangement of the atoms after bond breaking; due to the lack of long-range order in glass, it is not unreasonable to expect some local rearrangement after bond rupture [8]. Lateral relaxation of atoms across the fracture plane would make it more difficult to re-form broken bonds. Although there is evidence for crack healing in glass [8], no complete strength recovery has been observed. Secondly, γ_t has been assumed equal to γ, which implies rather severe lattice trapping; this would follow if the crack tip were very narrow, so that the crack tip stresses are essentially localized in one bond. Finally, the whole treatment rests on the assumption that crack motion in glasses occurs by the breaking of single bonds and the resulting increase of crack area by $\sim b^2$; by contrast, if the crack were perfectly straight and moved rigidly through the solid, for an amorphous material $\mathrm{d}U_s/\mathrm{d}A$ would be independent of the position of the crack and no lattice trapping would be expected.

In summary, the present paper has shown that slow crack growth of glass in vacuum can be explained by the thermally activated breaking of bonds at the crack tip within the framework of the "lattice trapping" theory.

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Comment on "Dielectric behaviour and morphology of poly(vinylidene fluoride)"

The recent paper by Baird *et al.* [1] presents some novel data on oriented poly(vinylidene fluoride) (PVDF) which is particularly interesting since measurements are made both parallel and perpendicular to the orientation direction. Whilst not questioning the validity of this data we would like to suggest a very different interpretation of the anisotropy observed.

The authors of this paper, in common with other investigators, suggest that the anisotropy of $\epsilon^{\parallel}$ at -20° C implies an oriented amorphous phase, Since the samples were drawn at 169° C and T_g is $\sim -40^\circ$ C this is extremely unlikely. We prefer to view the data as an extreme example of form birefringence, that is, the anisotropy is a consequence of the shape and orientation of the crystallites rather than arising from an anisotropic amorphous phase.

A detailed analysis is prohibitive since it would require a knowledge of the lamellar shape factors and orientation functions which is not easily obtainable from low-angle X-ray data. In particular, the line-collimated low-angle X-ray data used by the authors do not easily yield data on the orientation of the lamellae. Similar samples studied by us, however, using a point-collimated low-angle apparatus yield a typical pattern consisting of two arcs of half angle ~ 35° indicating a concentration of lamellar normals along the draw direction. Measurements made perpendicular to the draw direction, therefore, tend to see the two phases