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Theory of chemically assisted fracture

Part 1 *General reaction rate theory and thermodynamics*

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In this first of a two-paper series, we develop a theoretical formulation for chemically assisted brittle fracture in materials. The external environment is assumed to be a diatomic gas, and the chemical attack is at the crack tip. The crack is presumed to be atomically sharp, and the adsorbing chemical species lowers the energy of bond breaking at the crack tip. The formalism is couched in the language of chemical absolute reaction rate theory, and the results bear a close resemblance to the reaction rate theory of atomic diffusion in solids. Expressions are derived for thermally activated crack growth. The thermodynamic limit is derived, and the connection made to previous macroscropic mechanical treatments. A qualitative discussion is given of more complex forms of fracture chemistry. General conclusions are that atmospherically assisted fracture should be associated with changes in adsorbed surface energy; that details of kinetics will vary widely from one chemical system and material to another; and that cleavage experiments should be a quantitative tool for surface and interfacial energy measurements. Finally, bridging reactions at the crack tip are shown to lead to possibilities for chemical toughening of the material.

1. Introduction

Lattice theories of fracture have been developed* which account for the atomistic character of fracture in crystal lattices. These theories describe in a fundamental, but qualitative, way how brittle materials can sustain slow crack growth by thermally activated processes of the atoms at the crack tip at stresses above the thermodynamic Griffith stress, but below the stress required for fast fracture. Although these theories have demonstrated the existence of energy barriers to crack motion and the stress dependence of these barriers, they have not developed a complete kinetic theory of the atomic processes at the tips of cracks. More importantly, they have not treated the effect of chemical reactions at the crack tip, which are known to have dramatic effects on slow crack growth [2, 3]. Lawn and Wilshaw ([4] p. 162) have adapted ideas from chemical molecular kinetics of these theories in a qualitative manner and has derived expressions for the stress dependence of crack growth, but a satisfactory theoretical framework is still lacking. It is this framework which we address in this paper. The ideas proposed here are also analogous to the "stress sorption" mechanism as discussed by Uhlig, e.g. [5].

We shall, however, not confine this discussion to a purely general approach. Indeed we shall argue that the reactions which can occur at a crack tip have a wide variety: at least as wide as those which are observed on surfaces themselves. Nevertheless, there is a class of simple reactions treated here in which, for each fracture-unit event (a single bond breaks at the crack tip), a molecule of the external gaseous atmosphere is adsorbed, with half the molecule attached to each half of the severed bond. The prototype molecule is H_2, although our treatment is, of course, not limited to hydrogen. As we shall see, the phenomena associated with this simple class of reactions will not only served as an introduction to a much broader field, but will also be seen to have important connection to a wide class of observations about fracture.

We adopt the view of the classical "absolute

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*For a recent review of this work with references to earlier papers, see [1].

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reaction rate theory" as it has been developed in chemical kinetics [6]. In the next section, for purposes of didactic clarity, we apply this scheme to the cracked solid under stress in a vacuum (intrinsic fracture). We consider the path in the configuration space of the entire solid as the bond between a pair of atoms breaks at the crack tip. The result of the breakage of this bond is to translate the crack by one atomic position, and the crack surface is increased by two atomic areas (one on top and one on the bottom). The new configuration of the crystal is entirely similar to the old, except for the additional broken bond. By computing the probability flux of the system through the saddle between these two positions, we shall have a result for the velocity of the crack.

In Section 3, we consider the more complex system consisting of the cracked solid in equilibrium with an external gaseous environment which chemisorbs in the open surface of the solid, and which attacks the highly stretched bonds at the crack tip. We assume that the unit process is a gaseous diatomic molecule interacting directly with the two atoms of the lattice at the tip of the crack (most probably at a kink site on the crack).

In Section 4, we investigate the thermodynamic limit of the kinetic theory, and derive the condition for the equilibrium crack. This leads to suggestions discussed in Part 2 for direct measurement of the surface energy of solids. In Section 5, we consider qualitatively some limitations of the theory and effects to be expected from more complex chemical reactions at crack tips.

A complete theory of atmospherically assisted fracture would be exceedingly complex. It would involve knowledge not now available of force laws between pairs of lattice atoms, and between lattice atoms and adsorbing species. It would involve more knowledge about surface configurations and mobility than we yet have. It would also involve detailed knowledge of the activated states at the crack tip, which probably will never be obtainable. The results of this work, then, will not be complete in the sense that detailed chemical specific predictions will be made or attempted. On the other hand, we believe it will be useful to have a theoretical framework constructed for these processes. Such a framework will allow one to assign the role of the various parameters, and it will allow one to think about fracture processes in a physically correct way which may suggest qualitative results and serve as a guide for interpreting experimental findings. It will also allow us to construct simple models which may permit some semiquantitative predictions.

In the present paper, Part 1, we shall present general results, with a minimal reliance on specific models. In Part 2 we shall look at detailed but highly simplified models of the activated state. Taken together, these two papers then provide the general framework which we seek.

2. Slow crack growth in vacuum (intrinsic crack growth)

Our basic assumption is that the system, composed of a cracked solid under stress, possesses a configuration space with a series of local energy minima corresponding to successive positions of the crack, each position differing from its neighbour by the breaking of one atomic bond at the tip. We shall assume for simplicity that the crack is growing homogeneously at all atomic positions along the crack line. If the growth is inhomogeneous, then the analysis is modified in a straightforward way if the density of inhomogeneities (kink sites) is known.

The configuration space we visualize is sketched in Fig. 1. According to the lattice theories, if we draw a reaction path through the minima and saddle points of Fig. 1, we obtain the "dinosaur back" function sketched in Fig. 2. The broad maximum in this function corresponds to the thermodynamically quiescent point also specified by the Griffith critical length condition. On the left side of the maximum, the crack heals, on the right, it grows.

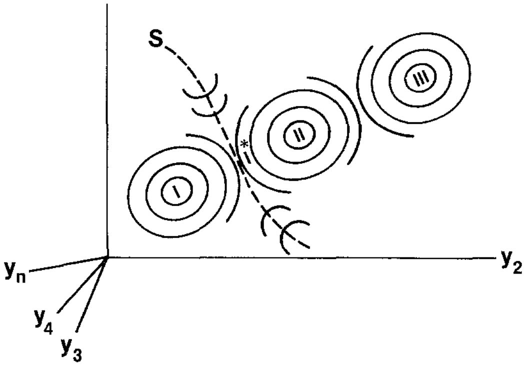

Figure 1 A schematic representation of the configuration space of a crack. As the crack tip moves forward from one atomic position to the next it moves over energy barriers as shown. I and II label neighbouring stable positions, while I* is the saddle point between them. *S* is the hypersurface separating I from II.

In Fig. 1, we compute the jump rate from one local minimum (labelled I) to the next (labelled II), through the hypersurface at the saddle point labelled I*) which separates the neighbourhood of I from that of II. The rate of transition is given by the general flux equation

$$\nu^* = \int \rho(S) v \, \mathrm{d}S \qquad (1)$$

where $\rho(S)$ is the probability density function evaluated on the hypersurface S; and v is the average positive hypervelocity of the system. The integral is evaluated in precisely the manner as originally performed by Vineyard in his classic paper on diffusion in solids [7]. First, the normal co-ordinates, y and y^*, of the system must be calculated both at the local minimum, and at the saddle point, respectively. With these, the energy of the two points is

$$\begin{aligned} E(\mathrm{I}) &= \sum_{n=1}^{N_\mathrm{L}} \tfrac{1}{2}(\dot{y}_i^2 + (2\pi\nu_i)^2 y_i^2) \\ E(\mathrm{I}^*) &= \sum_{n=2}^{N_\mathrm{L}} (\dot{y}_i^{*2} + (2\pi\nu_i^*)^2 y_i^{*2}). \end{aligned} \qquad (2)$$

The sum is over the degrees of freedom of the system. ν and ν^* are the respective frequencies. We note that these normal co-ordinates include the mass of the lattice atoms. If all atoms are the same, then $y_i = \sqrt{m} x_i$, where x_i has the dimension of length. If the masses are not all the same, then the normal co-ordinate transformation mixes these masses together in sometimes complicated ways. Since the hypersurface has one less dimension than the total configuration space, the number of degrees of freedom in the hypersurface is one less than at position I. We also note that these normal modes include the surface modes. Using Equation 2, we can write for the average value of v normal to the hypersurface

$$v_\perp = \frac{\int_0^\infty \dot{y}_1^* e^{-\dot{y}_1^{*2}/2kT} \, \mathrm{d}\dot{y}_1^*}{\int_{-\infty}^{\infty} e^{-\dot{y}_1^{*2}/2kT} \, \mathrm{d}\dot{y}_1^*}. \qquad (3)$$

The density $\rho(y)$ integrated over the hypersurface is given by the expression

$$\int \rho(y) \, \mathrm{d}y = \frac{\prod_{i=2}^{N_\mathrm{L}} \left[\int_{-\infty}^{\infty} e^{-(2\pi\nu_i^*)^2 y_i^{*2}/2kT} \, \mathrm{d}y_i^* \int_{-\infty}^{\infty} e^{-\dot{y}_i^{*2}/2kT} \, \mathrm{d}\dot{y}_i^* \right] e^{-E/kT}}{\int_{-\infty}^{\infty} e^{-(2\pi\nu_1)^2 y_1^2/2kT} \, \mathrm{d}y_1 \prod_{i=2}^{N_\mathrm{L}} \left[\int_{-\infty}^{\infty} e^{-(2\pi\nu_i)^2 y_i^2/2kT} \, \mathrm{d}y_i \int_{-\infty}^{\infty} e^{-\dot{y}_i^2/2kT} \, \mathrm{d}\dot{y}_i \right]}. \qquad (4)$$

Carrying out the integrations,

$$\begin{aligned} \nu^* &= \frac{kT}{h} \frac{Z(\mathrm{I}^*)}{Z(\mathrm{I})} = \frac{\prod_{i=1}^{N_\mathrm{L}} \nu_i}{\prod_{i=2}^{N_\mathrm{L}} \nu_i^*} e^{-E/kT} \\ &= \nu_\mathrm{L} e^{-E/kT} \end{aligned} \qquad (5)$$

where E is the difference in potential energy between the saddle configuration and the local energy minimum at I. The similarity to Vineyard's result for diffusion is striking.

An interesting subtlety arises in the fracture case regarding the frequency factor difference between forward and backward jumps of the crack. As the crack jumps forward, one bond is broken and as it closes, a bond is reconnected. However, the number of non-zero frequencies is the same in both cases, because two bulk modes have been converted to surface modes. Hence, rigorously, the forward and backward frequency factors are unequal. This means that the quiescent point, where the crack is precisely in equilibrium (equal backward and forward jump rates), will not occur at the precise top of the dinosaur function, but at a temperature-dependent position displaced from it. However, as a practical matter, this shift will not be large.

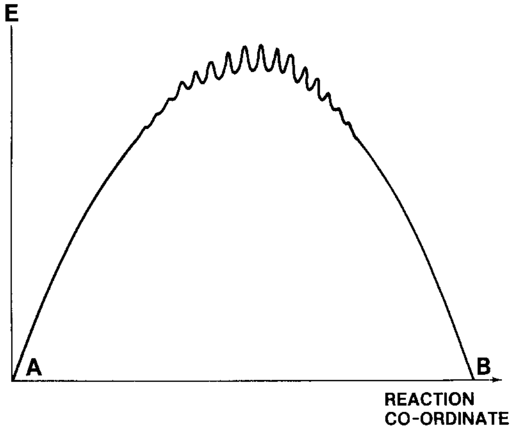

Figure 2 The energy of a crack as a function of its length. As the crack grows from one stable configuration to another along a reaction co-ordinate, it traces out in average a parabolic energy curve with local energy barriers superimposed. The parabola is that derived first by Griffith for a continuum.

Finally, we note that as in diffusion, we expect the numerical value of the frequency quotients to be something like the geometric mean of the frequency spectrum weighted by the vibration mode density of states. This will be a number near the Debye limit. Intuitively, however, one could not predict this result before the derivation because the low frequency opening mode of the crack is the intuitive guess for the proper attempt frequency, not a Debye mode.

3. Chemically assisted fracture

In the previous case, where the only process is the opening and closing of bonds during fracture, the analysis is step-by-step analogous to Vineyard's diffusion model. When an external atmosphere is present, we must include the adsorption step in the analysis.

In this case, state I of Fig. 2 differs from state II by one broken bond at the crack tip and two additional adsorbed atoms at the new surface site. The activated state includes a molecule of the gas in intimate contact with the critically stretched atoms at the crack tip. We cannot model this activated state exclusively in terms of the two critically stretched solid atoms in contact with the gas molecule, because the total cracked solid and interacting gas participate in the activation process in a nonseparable fashion.

We proceed from Equation 1 in the form

$$\nu^* = \frac{kT}{h}\frac{Z(\mathrm{I}^*)}{Z(\mathrm{I})} = \sqrt{\left(\frac{kT}{2\pi}\right)}\int \rho(y^*)\,\mathrm{d}S \quad (6)$$

where

$$\rho(y^*) = \frac{e^{-E(y^*)/kT}}{Z(\mathrm{I})}\prod_{i=2}^{N_\mathrm{L}}\int e^{-\dot{y}_i^{*2}/2kT}\,\mathrm{d}\dot{y}_i^* . \quad (7)$$

ρ is the system probability density function evaluated on the hypersurface. y_i^* is the normal co-ordinate which is arbitrarily chosen orthogonal to the hypersurface S at the saddle point. Z is the total partition sum of the system. Z can be evaluated in the neighbourhood of position I of Fig. 1 with small error. The y_i^* are the N normal co-ordinates of the system, including the co-ordinates of the external gas molecules. There is an immediate cancellation of the $N-1$ kinetic energy integrals in the numerator with corresponding terms of Z. Since Z contains N such factors, there is a single term. ($2mkT$), remaining in the denominator from all kinetic energy integrals. In the integration over S, *except for the molecule interacting with the crack tip*, the external gas terms again cancel exactly with the corresponding terms in Z. The integration over y_i^* is immediate, giving a factor, kT. We are thus left with the integration.

$$\nu^* = \sqrt{\left(\frac{kT}{2\pi}\right)} \times N_\mathrm{g}\int_S \frac{e^{-E(\mathrm{I}^*)/kT}}{\zeta_\mathrm{g}}\,\mathrm{d}S \Big/ \prod_{i=1}^{N_\mathrm{L}}\int e^{-E_\mathrm{L}(\mathrm{I})/kT}\,\mathrm{d}y_i . \quad (8)$$

The factor N_g arises because the probability of finding a single gas molecule interacting at the crack tip is proportional to the total number of gas atoms in the system. Integration over S is over that part of S which contains the original lattice plus the interacting gas molecule at the tip. ζ_g is the single molecule free gas partition sum in volume V, and the integral over position I is the potential energy part of the partition sum of the original solid. This integral is evaluated in the neighbourhood of region I of Fig. 1, and we note that the integral includes the co-ordinates of the previously adsorbed gas atoms, but not the interacting gas molecule at the tip.

In a way analogous to Vineyard's calculation, the potential energy function of the lattice, $E_\mathrm{L}(\mathrm{I})$ is evaluated using the normal co-ordinates of the system near its ground state at I, and

$$E_\mathrm{L}(\mathrm{I}) = \sum_{i=1}^{N_\mathrm{L}(\mathrm{I})} (2\pi\nu_i y_i)^2 \quad (9)$$

where $N_\mathrm{L}(\mathrm{I})$ is the number of atoms (including adsorbed atoms) in the lattice at I. ν_i as before are the normal mode frequencies. The integral in the denominator of Equation 6 then becomes

$$\prod_{i=1}^{N_\mathrm{L}}\int e^{-E_\mathrm{L}(\mathrm{I})/kT} = \sqrt{\left(\frac{kT}{4\pi}\right)}\prod_{i=1}^{N_\mathrm{L}}\frac{1}{\nu_i}. \quad (10)$$

The factor ζ_g is simply

$$\zeta_\mathrm{g} = \left[\left(\frac{4\pi m_\mathrm{g} kT}{h^2}\right)^{3/2} V\right]\left[\frac{8\pi^2\lambda IkT}{h^2}\right]\left[\frac{1}{1-e^{-h\nu_\mathrm{g}/kT}}\right]. \quad (11)$$

The first bracket is the partition sum of a free particle, where we have assumed that the gas is composed of diatomic molecules of a single chemical element where the atomic mass is m_g. V is the volume of the gas. The second bracket is the rotational partition sum, where I is the moment of inertia of the gas molecule, and λ is the nuclear spin factor which is a number of order unity. The third bracket is the vibrational term.

We remember that S contains all the coordinates of the atoms of the condensed solid (including the chemisorbed atoms on the crack surfaces), as well as those of the interacting molecule at the crack tip. If we count the independent frequencies of all these atoms, there are $N_L + 5$, and in the corresponding integral over I there are only N_L. We finally have

$$\nu^* = \frac{rp \prod_{i=1}^{N_L} \nu_i}{\prod_{i=2}^{N_L+6} \nu_i^*} e^{-E/kT}$$

$$r = \frac{h^5 (1 - e^{-h\nu_g/kT})}{64\pi^{7/2} I (kT)^{7/2} m_g^{3/2} \lambda} \cdot \qquad (12)$$

Here p is the pressure of the gas, E is the total activation energy of the process, and ν_g is the vibration frequency of the gas molecule. In the general case, the pre-exponential is complicated by the branch of frequencies associated with the adsorbed layer to which the reacting molecule contributes. Although the number of these frequencies is given rigorously by the limits displayed in the products of Equation 10, the values of the various frequencies are complicated by modes moving back and forth from bulk to surface branches.

The general subject of surface modes is one which has received a great deal of study, and we can draw on this work to break down Equation 10 into more useful approximations. Numerical work [8, 9] in pure monatomic solids shows that there are a number of localized modes – some localized in layers adjacent to, but not at the surface itself. Unless there is extensive reconstruction, the surface always represents a loosening of the atomic bonding, and thus surface modes are lowered in comparison to the bulk modes. This statement is true even though surface modes appear in gaps within the bulk mode distributions, or even though surface modes overlap bulk modes when the two types of modes belong to non-mixing classes. The number of surface localized modes depends upon the symmetry of the surface and the strength and range of the atomic forces.

When an adsorbed layer is present, the variety of modes possible is greater. If the ratio of force constant to mass, α/m_g, of the adsorbed species is larger than the same ratio for the pure solid, then the surface frequencies are increased by the adsorbed layer. For ratios α/m_g sufficiently large, the Rayleigh mode which is present below the band at all frequencies for the pure solid disappears, and a corresponding set of optical modes appears above the bulk modes.

These general results bear on this work in the following way. The surface opened by the crack has a mode which is reflected by the crack tip, and which we shall term a "crack mode". These modes have all the attributes described above for ordinary surface modes, except that they are truncated at the crack tip itself. Their number, of course, is increased when the crack is lengthened in proportion to the number of atoms transferred from the bulk to surface positions. Therefore, it is possible to partition the products over frequencies into the surface (including the crack modes) and bulk portions. Thus, for the three separate types of product which have appeared in Equations 3 and 10, we have

$$\prod_{i=1}^{N_L} \nu_i = \prod_{i=1}^{N_s} \nu_i(\mathrm{s}) \prod_{i=1}^{N_B} \nu_i(\mathrm{B}) \qquad (13a)$$

$$\prod_{i=1}^{N_L} \nu_i^* = \prod_{i=1}^{N_s} \nu_i^*(\mathrm{s}) \prod_{i=2}^{N_B} \nu_i^*(\mathrm{B}) \qquad (13b)$$

$$\prod_{i=2}^{N_L+6} \nu_i^* = \prod_{i=1}^{N_L+6} \nu_i^*(\mathrm{s}) \prod_{i=2}^{N_B} \nu_i^*(\mathrm{B}) \qquad (13c)$$

where $\nu(\mathrm{s})$ is a surface mode and $\nu(\mathrm{B})$ is a bulk mode. Some of the added modes in Equation 13c due to the adsorbing atom at the saddle point may in fact be bulk modes, depending on masses and force constants, but generally we expect these modes to be primarily localized at the surface. When the crack is moving forward (breaking additional bonds), the frequency which goes to zero at the saddle will be a bulk mode, and when the crack moves backward, the frequency going to zero will be a surface mode.

Two special cases exist. In the first, the adsorbing atom is assumed to be a very light atom compared with the substrate atoms. Then the optical mode branches become separated and distinct from the bulk mode branch. When $kT > h\nu$ for these modes, the classical approximation is valid. If the main bonding of the adsorbed atoms is with the surface, then the optical modes are flat, and one can approximate them with a single Einstein frequency.

In this case, we can write

$$\nu^*_{\text{forward}} = \frac{n_g(kT)^{5/2}}{(4\pi m_g)^{3/2}8\pi^2\lambda I}\,\frac{\prod_{i=1}^{N_L}\nu_i}{\prod_{i=2}^{N_L+6}\nu_i^*}\,\nu_{go}\,e^{-E/kT} \tag{14}$$

$$= \frac{n_g(kT)^{5/2}}{(4\pi m_g)^{3/2}8\pi^2\lambda I}\,\frac{\nu_{go}}{\prod_{i=1}^{6}\nu_i^*(\text{s})} \times \frac{\prod_{i=1}^{N_L}\nu_i(\text{B})}{\prod_{i=2}^{N_L}\nu_i^*(\text{B})}\,e^{-E/kT} \tag{15}$$

where ν_i^* is partitioned over the optical modes at the crack tip for the interacting molecule. These will, of course, be at somewhat softer frequencies then the fully formed surface modes. ν_{go} is the frequency of vibration of the free gas molecule.

In the second simple case, we assume that the crack reactions occur at temperatures where the light gas molecule is frozen in its lowest state both in the gaseous and adsorbed states. Hydrogen at normal temperatures, for example, would be such a case. Then we have the simple result

$$\nu^* = \frac{n_g h^5}{(4\pi m_g)^{3/2}8\pi^2\lambda(kT)^{5/2}I}\,\frac{\prod_{i=1}^{N_L}\nu_i(\text{B})}{\prod_{i=2}^{N_L}\nu_i^*(\text{B})}\,e^{-E/kT}. \tag{16}$$

When the adsorbing atom is heavier than the solid bulk atoms, then the various surface modes have large dispersion, and no simple form is possible. The general expression of Equation 12 must then be used, with the surface modes lying at lower frequencies than their pure crystal counterparts.

We note that in Equations 10 to 13 in the limit of low pressure, the jump frequency of the crack goes to zero. Of course, there is a parallel route for crack advance provided by Equation 3, because the crack can advance without chemical assist. Thus, the actual velocity is a sum given by Equations 3 and 10.

4. Chemical and thermal equilibrium at a crack tip

The previous analysis refers to the forward motion of a crack, and if one is interested in the point at equilibrium, this is only half the problem.

The reverse reactions lead from state II to state I* in Fig. 1. For the pure crack at state II, the number of modes is exactly the same as at I, because the total number of particles contained in the solid is unchanged. Hence, formally, we have

$$\nu_b^* = \frac{\prod_{i=1}^{N_L}\nu_i(\text{II})}{\prod_{i=2}^{N_L}\nu_i(\text{I}^*)}\,e^{-(E(\text{I}^*)-E(\text{II}))/kT}. \tag{17}$$

Even though this result is formally the same as Equation 5, the *numerical value* of the rate of transition from I to II is not in general equal to the rate of transition from II to I, because not only may the activation energies differ, but the frequency factors are different. In going from I to II, a bond is broken, thus a set of bulk modes are converted to surface modes with the consequent change in frequency.

When an external atmosphere is present, the molecule which in state II is part of the covered surface at the tip, moves back to the saddle point. Beyond the saddle point, as the system falls back to state I, the molecule becomes a part of the free gas again. In the backward transition, the external gas does not enter the analysis, so the rate of transition is simply

$$\nu_b^* = \frac{\prod_{i=1}^{N_L+6}\nu_i(\text{II})}{\prod_{i=2}^{N_L+6}\nu_i(\text{I}^*)}\,e^{-(E(\text{I}^*)-E(\text{II}))/kT}. \tag{18}$$

In this case, because of the two additional atoms covering the opening surface at II than at I, there are six additional modes at II. N_L is taken to be the number of modes in state I.

We could find the condition for the quiescent point by setting the detailed expressions above for the reverse transitions equal to the forward transitions. However, there is a general statement of the result which derives from the fundamental relationship between statistical mechanics and thermodynamics. In particular, we note that Equations 6 and 7, and their counterparts for the pure solid can be written in the form

$$\nu^* = \frac{kT}{h}\,\frac{Z(\text{I}^*)}{Z(\text{I})}. \tag{19}$$

Here $Z(\text{I}^*)$ is the partition sum of the system evaluated in the hypersurface intersecting the saddle point, and $Z(\text{I})$ is the partition sum of the system evaluated in the neighbourhood of I. We take the definition

$$Z = \frac{1}{N!}\sum e^{-E_i/kT} \tag{20}$$

to account for the indistinguishability of the molecules. Likewise, a similar expression can be written for the backward transition,

$$\nu_{\mathrm{b}}^* = \frac{kT}{h}\frac{Z(\mathrm{I}^*)}{Z(\mathrm{II})}. \tag{21}$$

The system is quiescent or in equilibrium when Equations 19 and 21 are equal. Thus,

$$Z(\mathrm{II}) = Z(\mathrm{I}) \tag{22}$$

from which it follows with the relation

$$F = -kT\ln Z$$

that

$$F(\mathrm{I}) = F(\mathrm{II}), \tag{23}$$

where F is the free energy of the total system. This result is, of course, almost tautological from thermodynamics for two states which are in equilibrium with each other. However, by displaying it explicitly from our kinetic analysis, we are assured that the analysis contains the correct thermodynamics.

The quiescent point at equilibrium has an important fracture meaning, because the quiescent point also specifies the stress condition called in fracture mechanics K_{ISCC}. That is, above the quiescent point, the crack grows by slow crack growth through the lattice trapping regime to the point where mechanical stability at the crack tip cannot be maintained, and the solid then undergoes unstable fast fracture. This latter stress is defined as the stress condition called K_{IC} in fracture mechanics.

The stress condition at K_{ISCC} is also traditionally related to the Griffith criterion for brittle materials, and this is couched in terms of the surface energy. Since our analysis includes temperature effects in a general way, it is of interest to sort out the bulk from the surface and chemical effects at the crack tip. We can do so from the condition 22, or 21. We first write the free energy of the vibrating pure solid as

$$F = E_0 + kT\sum_i \ln h\nu_i/kT, \tag{24}$$

where E_0 is the internal energy referred to some reference state. E_0 will contain the zero point energy of the oscillators plus any strain energy of the system, but will not contain contributions from vibrations. Then for the equilibrium of the crack,

$$E(\mathrm{I}) - E(\mathrm{II}) = kT\left[\sum_i \ln h\nu_i(\mathrm{II})/kT - \sum_i \ln h\nu_i(\mathrm{I})/kT\right]. \tag{25}$$

For the pure solid when the system at I and II has the same number of modes,

$$E(\mathrm{I}) - E(\mathrm{II}) = kT\sum_{i=1}^{N_{\mathrm{L}}} \ln \frac{\nu_i(\mathrm{II})}{\nu_i(\mathrm{I})}. \tag{26}$$

When the external reacting gas is present, the condition for equilibrium is obtained from Equation 22 and the partition sums for states I and II. State I has N_{g} gaseous molecules in the external atmosphere, and N_{L} total vibration modes in the solid, while state II has $N_{\mathrm{g}} - 1$ gaseous molecules in the atmosphere, and $N_2 + 6$ modes of vibration. In our previous notation, Equation 22 becomes

$$\frac{\zeta_{\mathrm{g}}}{N_{\mathrm{g}}} Z_{\mathbf{xtal}}(\mathrm{I}) = Z_{\mathbf{xtal}}(\mathrm{II}). \tag{27}$$

Taking logarithms, and from the relations $\mu_{\mathrm{g}} = -kT\ln \zeta_{\mathrm{g}}/N_{\mathrm{g}}$, where μ_{g} is the chemical potential of the gas,

$$\mu_{\mathrm{g}} + F_{\mathbf{xtal}}(\mathrm{I}) = F_{\mathbf{xtal}}(\mathrm{II}) \tag{28}$$

or

$$\mu_{\mathrm{g}} + E(\mathrm{I}) - E(\mathrm{II}) = kT\left(\sum_{i=1}^{N_{\mathrm{L}}+6} \ln\frac{h\nu_i(\mathrm{II})}{kT} - \sum_{i=1}^{N_{\mathrm{L}}} \ln\frac{h\nu_i(\mathrm{I})}{kT}\right). \tag{29}$$

Equations 26 and 29 are not yet in the desired form, because the partition of free energies into surface and bulk portions is not yet made, and requires additional discussion. The partition is simply made by the Gibbs definition of surface excess quantities when the surface is a simple infinite planar form. However, for the cracked solid, where the cleavage surface is terminated in a tip region of the crack, the Gibbs surface excess argument must be reconsidered. In particular, near the crack tip, it is impossible to partition contributions to the free energy into portions which are separately bulk and surface contributions. Consider first the strain energy of the lattice. The difficulty at the crack tip is apparent when one considers that in the tip region, atoms interact with distant neighbours, i.e. across the opening surface, and there is no clear way to separate bulk from surface energies. Thus, we consider the following strategem. Fig. 3 depicts a cracked lattice in which we have drawn an

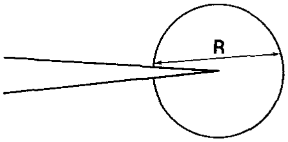

Figure 3 Schematic drawing of a crack tip with a core region. The core is composed of many atoms, but is small compared with the crack length and the size of the crystal.

arbitrary, but small, core boundary around the tip region which contains N_c atoms. We consider the limit of very long cracks, that is the length l is very many atom spacings long, and where no other surfaces or inhomogeneities are atomically close by, and assume that the distance R is very small compared to these lengths. Thus, $N_c \ll N_L$, where N_L is the number of atoms in the lattice. In this limit, when the crack increases by one atom spacing, say from one of the minima sketched in Fig. 1 to a neighbour, the energy of the atoms in the core is arbitrarily equal to the two states. However, the cracked surface area of the solid has increased by exactly one atomic area. Hence, in comparing two states, I with II, the difference in surface area between the two states in the Gibbs sense is one atomic area. All surface quantities, since they are by definition scaled by their area, are then well defined. So are the bulk quantities. The core atoms are a "wash" item in this bookkeeping since in states I and II they have exactly congruent configurations. With this construction, the partition into bulk and surface terms can be carried through for the cracked solid just as it was done with the Gibbs construction.

We can now write the final form of the equilibrium expressions. For the crack in pure material, we have

$$\Delta F_{\text{bulk}} = \Delta F_{\text{surf}} \tag{30}$$

where we have partitioned in the following way

$$\begin{aligned} \Delta F_{\text{bulk}} &= E_{\text{bulk}}(\text{II}) - E_{\text{bulk}}(\text{I}) = \Delta E_{\text{bulk}} \\ \Delta F_{\text{surf}} &= E_{\text{surf}}(\text{II}) - E_{\text{surf}}(\text{I}) \\ &\quad + kT \sum_{\substack{\text{all}\\ \text{modes}}} \ln\left(\frac{\nu(\text{II})}{\nu(\text{I})}\right). \end{aligned} \tag{31}$$

In this expression, all the entropy change terms are carried in the surface portion of ΔF. This is because the bulk frequencies are not changed by the changes in stress distribution as the crack moves. On the other hand, as the crack advances, because of the increasing area of the cleavage surface, some bulk modes are converted to surface modes. Since this is an effect which is proportional to the change in surface area and does not involve a change in bulk volume or strain in the crystal, it is by definition an exclusive contribution to the surface free energy. The remaining bulk term, ΔE_{bulk} is, however, essentially related to the (isothermal) crack extension force, G, as defined in fracture mechanics. Indeed, we have

$$GL = -\frac{\partial E_{\text{bulk}}}{\partial l} \tag{32}$$

where L is the thickness of the cracked solid, assuming the crack is a "through the thickness" crack, and l is the crack length.

In this expression, it is important to remember that E_{bulk} includes not only the strain energy of the solid, but also the work done by externally applied stress. Although not mentioned explicitly till now, the external stress on the solid is required in order for the cracked solid to be mechanically stable.

When a single bond is broken to generate the energy change E_{bulk}, in terms of G we have

$$\Delta E_{\text{bulk}} = \frac{\partial E_{\text{bulk}}}{\partial l}\frac{b^2}{L} = -Gb^2 \tag{33}$$

where b^2 is an atomic area of the cleavage surface. From Equations 30 and 31,

$$\begin{aligned} G &= 2\gamma \\ \gamma &= E_{\text{surf}}(\text{II}) - E_{\text{surf}}(\text{I}) + kT \sum_{\substack{\text{all}\\ \text{modes}}} \ln\left(\frac{\nu(\text{II})}{\nu(\text{I})}\right). \end{aligned} \tag{34}$$

Thus the thermodynamic macroscopic Griffith relation for finite temperature is derived.

Where external reacting gases are present, the results are of considerably more interest. Using the surface-bulk partition as performed above for the pure homogeneous solid, Equation 38 becomes

$$-\mu_g + \Delta E_{\text{bulk}} = \Delta F_{\text{surf}}. \tag{35}$$

As before

$$Gb^2 = \Delta F_{\text{surf}} + \mu_g. \tag{36}$$

From thermodynamics, the surface energy of a surface containing various chemical species is given by

$$\gamma = f_s + \sum_i \Gamma_i \mu_i \tag{37}$$

where Γ_i is the coverage density of the ith component, μ_i the chemical potential of that species, and f_s the area density of surface excess free energy.

We have implicitly assumed in our work that $\Gamma_i = \Gamma_g$, the gas atom coverage, was unity in atomic units. Hence Equation 36 becomes

$$G = 2\gamma \qquad (38)$$

as before. There is no reason henceforth to assume that the surface coverage is complete, and in this more general condition, the surface energy derived from Equation 29 can be written so that the usual combinatorial surface terms are present. Then in the atomic model we have constructed, we have

$$\gamma b^2 = \Delta E_{\mathrm{surf}} + kT\left[\sum_{i=1}^{N_L+6} \ln\frac{h\nu(\mathrm{II})}{kT} - \sum_{i=1}^{N_L} \ln\frac{h\nu(\mathrm{I})}{kT}\right]$$

$$+ \Gamma_g\mu_g - kT\ln Z_{\mathrm{comb}}. \qquad (39)$$

Z_{comb} is the combinatorial partition sum for exchanging gas atoms and vacant sites on the surface carried out typically in the calculation of the Langmuir surface coverage theory.

Again, connection is made in Equation 36 between the microscopic theory and the macroscopic world of fracture. The temperature and pressure dependence of γ can be found by either thermodynamic calculations of γ in Equation 38 or microscopic calculations as implied in Equation 39.

5. Other forms of chemical interaction

In the previous discussion, we have calculated the rate of fracture on the basis of the simplest form of reaction kinetics at the crack tip. It is our purpose here to explore qualitatively the limits of this treatment, by outlining two broad classes of quite different crack tip chemical effects. In particular, we note that geometrical or steric constraints on the gas molecule may make it difficult to fit the molecule easily into the restricted space available at the crack tip, and chemical reactions at the tip can be more complex than we have so far envisioned. We shall discuss each of these possibilities in turn.

5.1. Steric hindrance

This effect relates to the possibility that the cohesive region of the crack may be buried in the "sub-surface" portion of the crack tip. Then the critical chemical reactants which assist in opening the bonds at the tip cannot reach the critically stretched bonds. We shall refer to this effect as "steric hindrance" or "size factor".

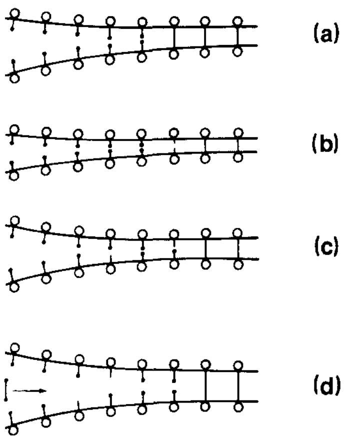

Figure 4 Vacancy mechanism for atmospherically assisted fracture: The black circles represent adsorbed atoms and the dangling bonds represent vacancies. The crack grows when a bond breaks and the vacancies migrate out of the crack core, as shown in the sequence (b), (c). Finally in (d), the original configuration (a) is restored when new molecules chemisorb on the surface.

Under these conditions, there still remains a mechanism by which slow crack growth can occur, which we shall call the vacancy mechanism, and which is depicted in Fig. 4. In this mechanism, the first step is to snap a bond at the tip spontaneously. In the second step, adsorbed atoms migrate to the open bonds at the tip, forming a vacancy in the adsorbed layer on each surface. Finally, the vacancy population on the surface is kept in equilibrium by adsorption of additional molecules from the gas.

Fig. 5 shows the energy of the surface as a

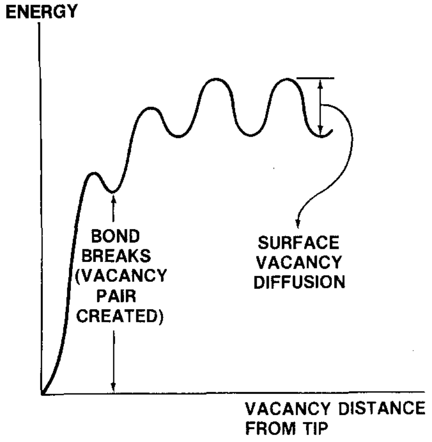

Figure 5 Energy of the crack as vacancies are formed at the tip and migrate out of the core region. The first barrier in which the bond breaks is the energy of formation of the vacancy pair. In this process, the external atmosphere has little influence on the energy of the system.

function of the reaction co-ordinate corresponding to the formation and migration of the vacancy. In the first step sufficient energy is supplied to open two bonds at the stress imposed on the crystal. This bond breakage, of course, must be accomplished without assistance from the external atmosphere, and requires a high energy. After the vacancy wanders out of the crack-tip region, the free energy is lowered by adsorption of a gas molecule, and the final surface energy increment is that appropriate to the covered surface. Thus, the surface energy to be used in the thermodynamic specification of the quiescent point is that of the covered surface, but the activation energy for the formation and motion of the vacancies creates a large barrier in the kinetics of the crack growth process. Consequently, one would not expect ever to be able to measure K_{ISCC}, because of the externally slow rates there.

For all practical purposes, the growth of the crack takes place without help from the external molecules, and the forward reaction rate for crack growth is formally analogous to the crack growth rate in vacuum, (Equation 5)

$$\nu = \frac{\prod_{i=1}^{N_{\mathrm{L}}} \nu_i}{\prod_{i=2}^{N_{\mathrm{L}}} \nu_i^*} e^{-E/kT}. \qquad (40)$$

This expression is independent of external gas pressure, in clear contrast to the direct chemical process. A small pressure effect does appear when one includes the possibilities for backward flow of vacancies at the tip, but to first order this flow can be neglected.

Clearly, steric effects will be a strong function of the crack opening geometry, and should vary widely from one material to another. Indeed, computer simulations have been performed in Fe [10] and Si [11] which show contrasting results. In the case of Fe, the simulation shows the tip region to have a relatively open geometry with plenty of room for atmosphere molecules of modest size to maneuver. For Si, however, the crack is in the shape of a long narrow slit, so that steric effects should be very important. These contrasting configurations must be traceable to the strength of the bonds in tension in relation to their strength in bending. Thus, the dimensionless parameter, $\mu a/\gamma$ (where μ is the shear modulus, a the lattice spacing, and γ half the bond energy or surface energy (whichever is deemed most appropriate)), should be a qualitative measure of the steric factor for cracks in materials. We show in Table I a list of representative materials correlated with this parameter. Si and Fe are seen to have significantly different values of this parameter, as confirmed by the computer simulations. We offer Table I as a rough qualitative guide in predicting the size factor trend from one material to another in chemically assisted fracture.

TABLE I

Cu	5.76
Al	8.51
Ni	10.8
Fe	8.73
W	25.8
LiF	26.1
NaCl	30.0
MgO	28.7
Al_2O_3	18.4
Si	19.3
Ge	32.8
C	23.7
Be	34.2
Zn	32.9

5.2. Toughening reactions by chemical bridging of the crack

Our approach in this work has been to analyse the effect on fracture of the simplest chemical reaction of a diatomic molecule at the crack tip in which each bond that breaks adsorbs two atoms from the molecule. More complex reactions are easy to imagine, and are probably the rule. For example, adsorbing atoms need not correspond one-for-one to each broken bond on the surface. However, the most striking kind of contrasting reaction is afforded by the possibility of bridging reactions *across the crack tip.**

Such a bridging reaction is schematically depicted in Fig. 6. In this case the adsorbing atom forms a link across the crack, binding two atoms of the solid together, which have been cleared from one another by the crack. Most atomic species are capable of bonding to more

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*We are indebted to R. Gomer of the University of Chicago, and J. Kruger of NBS for enlightening discussion of the varieties of chemical interactions with solid surfaces and in particular to R. Gomer for first pointing out to us the possibility of bridging reactions.

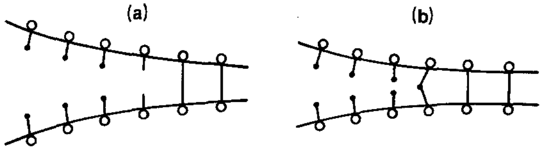

Figure 6 Bridging reaction at a crack tip. In (b) an atom (or it could be a molecular fragment) bonds the two sides of the fracture surface together.

than one atom. Indeed, such bridging reactions are by no means limited to single atoms, but molecular fragments and molecular radicals can also be attached across the crack opening to each cleavage surface. In this case, the only necessary requirement is that a reactive site is present on each end of the bridge.

Such reactions at the crack tip can be expected to have profound effects on the fracture process. Aside from the fact that the bridging bond may be even stronger than the original bonds of the solid atoms for one another, there is a second more important effect. Any bridging bond corresponds to a mechanical blunting of the crack. Even when the bridging bond is formed by only one atom, the crack opening displacement (COD) at the tip is doubled over that of the intrinsic sharp crack. For example, the COD for the intrinsic crack is one atomic spacing, while (leaving aside differences in atomic radii) with the bridging atom, the COD increases to two atomic spacings.

A more dramatic effect on DOC comes about if a molecular bridge can be fashioned between the two sides of the crack. In this case, the COD becomes the length of the bridging molecule. In particular, if chains can be fashioned of varying lengths so that voids are not left behind the molecular bridge, the bridging reaction can multiply the toughness of the material by many fold.

We know of no clear cases of bridging reactions at the crack tip of the sort proposed here. However, the craze formed at the tip of a fracture in a polymer is a similar phenomenon, because in that case also, molecular bridges are formed across the crack by the stretched polymer chains which toughens the material drastically [12].

6. Implications and general conclusions

6.1. Kinetics of chemically assisted fracture

The principle result of our work is that chemically assisted fracture should be a widespread phenomenon associated with the lowering of the surface energy of the material by the external environment. Two important qualifiers of this conclusion exist. Steric or size effects can restrict the external molecules from entering the "cohesive region" of the crack where chemical reactions must occur if they are to affect fracture rates, and a variety of complex chemical effects can occur at the crack tip whose effect can be to strengthen the crack or to slow down its growth. Thus, chemically assisted fracture, and especially its rate, is expected to be highly specific as to the chemical species and material involved.

Our work only addresses cases where the crack tip region is atomically sharp. In cases of fibrous fracture (fracture by hole growth), and of fracture by chemical dissolution [6], the geometry of the crack tip is thought to be blunt on an atomic scale, and a different treatment is required. Our results also do not directly address the effects of dislocations which are present in the deformation regions of most cracks. However, in an extensive class of fracture phenomena, an atomically sharp crack can be associated with, and is consistent with, a large amount of plastic flow in the vicinity of the crack tip, and the features we have described should apply to the behaviour of that crack tip. For quantitative results, the line of thought of a previous paper [13] should be followed, with the forces holding the crack together described approximately by the brittle solutions developed here. Additional formulas would have to be developed connecting forces and stresses in this region characterized by atomic and chemical phenomena to those in the macroscopic regions outside it within which plasticity occurs and which are governed by continuum time-dependent plasticity and elasticity. This task has been accomplished in the static limit by the present author [13]. and Hart [14] has developed a formalism which can be applied to time-dependent ductility when the time dependence of the tip is included as we have outlined it here.

Thus, we suggest that a general experimental survey of brittle fracture in gaseous environments would be desirable in order to delineate those solids which can be described by the simple form of chemically assisted fracture discussed here. In such a survey, one goal should be to separate steric effects from such effects as molecular bridging at the crack tip. A detailed study of the rates of crack growth in model systems would also serve to check the specific quantitative predictions we have made, and begin to throw light on the specific chemical processes involved.

Unfortunately, a systematic knowledge base is not now available, in spite of the vast extant literature on fracture. Water is known to be a general cause of slow crack growth in glasses [2]; however, the amorphous structure of the glass and the possibility of complex reactions on the surface with the water make this not a very promising model system, at least initially. Likewise, hydrogen gas is known to be a ubiquitous embrittler of metals [3]. We believe the mechanism, at least in high strength steels, is that which we have studied in an earlier paper [13]; however, rates of crack growth in steels are probably modified drastically by the deformation surrounding the crack. The action of oxygen [15] in poisoning the effect of hydrogen could be a case of steric interference at the crack tip, or an example of a bridging reaction. More suitable model systems would be those where dislocation effects are negligible, and where an extensive lore of surface knowledge exists. Silicon appears to be one possible model solid, certain ceramic materials another, and hexagonal metals a third.

We note in passing the interesting situation regarding liquid metal embrittlement (LME) [16]. In that case, the low interfacial energy between solid and liquid metal as contrasted to the vacuum–solid surface energy would have the same effect on fracture as adsorption from the gas phase which we have treated. In the same way as we have seen for gaseous adsorption at the crack tip, steric effects in the liquid metal case should be important. However, although this line of thought is very suggestive for LME, a detailed treatment analogous to that performed here for gases has not been performed.

6.2. Surface energy, and thermodynamics

We have shown that the Griffith result, $G = 2\gamma$, rigorously specifies the quiescent point where the slow crack growth velocity goes to zero in thermal equilibrium. Since there are a number of cases known where fracture is completely brittle with no dislocation involvement, we propose that careful measurement of the quiescent point in vacuum should be a fundamental measure of surface and interfacial energies in those solids. In the past, measurement of surface energy by cleavage methods has been unreliable for a number of reasons. Dislocations associated with the crack, in particular, have been a well recognized source of error. However, from our derivation, it is also necessary that the crack be at its quiescent point as well. We believe that with modern microscope techniques and the possibility they offer of observing crack sharpness and quiescence directly, the cleavage method should be capable of being made into a powerful tool for the direct measurement of surface and interfacial energies. The effects of temperature, surface coverage, and of interfacial segregation should all be observable.

6.3. Bridging reactions and chemical strengthening

Finally, we have suggested that an important class of chemical reactions at the tip is that when an adsorbed atom or molecular fragment forms a bridge across the opening wedge at the crack tip. Whereas the straightforward surface energy argument always predicts a weakening of the solid by chemical adsorption, in principle, a bridging reaction has the potential of *strengthening* the solid. The authors are unaware of specific cases where such reactions have been observed, but the peculiar craze formation in polymers where the crack is held together by stretched polymer chains is an analogous effect. In this case, the material is indeed toughened by the formation of molecular bridges. Similarly, in non-polymeric materials, a configuration can be envisioned in which molecular species form a set of oriented chains at the crack tip holding the wedge at the crack together. But even if only one atom bridges at the tip, in practice, if the bridging bond is strong, this will have an effect on the material toughness and could lead to significant effects even in materials containing deformation zones around the crack [14]. The demonstration of a bridging reaction in a model system would be an indicator that more interesting cases might be possibly of practical value.

References

1. E. R. FULLER Jr and R. THOMPSON, "Fracture Mechanics of Ceramics", Vol. 4, edited by R. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum, New York, 1978) p. 157.
2. S. WIEDERHORN, *ibid*, Vol. 2, p. 613.
3. R. ORIANI and P. JOSEPHIC, *Acta Met.* 22 (1974) 1065.
4. B. LAWN and T. WILSHAW, "Fracture of Brittle

Solids", (Cambridge University Press, 1975).

5. H. H. UHLIG, "Corrosion and Corrosion Control" (Interscience, New York, 1972).
6. S. BENSON, "Thermochemical Kinetics" (Wiley, New York, 1977).
7. G. VINEYARD, *J. Phys. Chem. Solids* 3 (1957) 121.
8. D. CASTIEL, L. DOBRZYNSKI and D. SPANJAARD, *Surface Sci.* 60 (1976) 269.
9. R. ALLEN, G. ALLDREDGE and F. DEWITTE, *Phys. Rev. B* 4 (1971) 1648, 1661, 1682.
10. P. GEHLEN and M. F. KANNINEN, "Inelastic Behaviour in Solids", edited by M. F. Kanninen (McGraw-Hill, New York, 1970) p. 587.
11. J. SINCLAIR and B. LAWN, *Proc. Roy. Soc.* A329 (1972) 83.
12. R. KAMBOUR, *J. Polymer Sci. Macromol: Rev.* 7 (1973).
13. R. THOMSON, *J. Mater. Sci.* 13 (1978) 128.
14. E. HART, *Int. J. of Solids and Structures,* to be published.
15. J. H. JOHNSON, A.J. KUMNICK and N. QUICH, "Effect of Hydrogen on Behavior of Materials", edited by W. Thompson *et al.* (Met. Soc. AIME, 1975).
16. M. NICHOLAS and C. OLD, *J. Mater. Sci.* 14 (1979) 1.

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