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Theory of chemically assisted fracture

Part 2 *Atomic models of crack growth*

E. R. FULLER Jr, ROBB THOMSON
National Bureau of Standards, Washington, D.C., USA

In Part 2 we have applied the one-dimensional model of a crack to the problem of the simple form of chemically assisted fracture when the external atmosphere is composed of diatomic molecules. Predictions of the stress dependence can be made on the basis of this model which show a power law dependence whose exponent varies from $\frac{3}{2}$ to 2 depending on the form of the atomic bonds of the solid. General conclusions are that chemical activity accentuates and extends the intrinsic slow crack growth phenomenon because of the surface adsorbtion activation barrier, and that the "chemical" and "mechanical" contributions to the activation energy for slow crack growth are not separable.

1. Introduction

In Part 1 [1], we have developed a general statistical mechanical framework for brittle crack growth in a solid, including the effects of external diatomic gaseous environments. One of the parameters in this framework was the energy of the activated state, about which little was said. Whereas the treatment of the previous paper was rather general in character, in any discussion of the activation energy, we become immediately immersed in detailed models, and we turn to this subject here.

The reader will be aware that a realistic treatment of the energies and atomic configurations of the processes at the crack tip is well beyond current theoretical capabilities. We shall therefore attempt to extract qualitative results from the simplest models available. Since the one-dimensional model is easily manipulated and yields analytic solutions, it is nicely suited to our task. From it we can extract the main physical features of the chemical processes at the tip, develop an understanding of the factors governing the stress dependence, and separate out local effects on the bond breaking atoms from contributions of the whole lattice. Hence, in section 2, we shall present these analytical results for the one-dimensional model. This model has been worked out in some detail in an earlier paper [2], but in Section 2 we present some additional results for non-linear forces at the crack tip which will be useful in our analysis of the atmosphere-assisted cracking problem. In Section 3, we make use of the analytical results from the one-dimensional model to sketch a physical picture of atmosphere-assisted fracture as we believe it can occur in nature.

Before turning to the details, however, it is first of all important to repeat that we envision chemical attack of the atmosphere molecules as taking place at the critically stretched bond at the tip of the crack for the reasons discussed at length in Part 1. In this assumed mechanism, bond breaking at the crack tip and chemisorption take place in one reaction step. We shall further assume that the cleavage surface is completely covered by adsorbed atoms, but these already adsorbed atoms play no important role in the in the forward fracture growth process. In Part 1 we gave reasons why the surface vacancy mechanism of crack growth (where adsorption takes place at sites other than the crack tip) would be slow compared with direct chemical action at the crack tip.

2. One-dimensional model of atmosphere-assisted fracture

The one-dimensional chain model is depicted in Fig. 1 and has been worked out in a previous paper [2]. In terms of the bendable and stretch-

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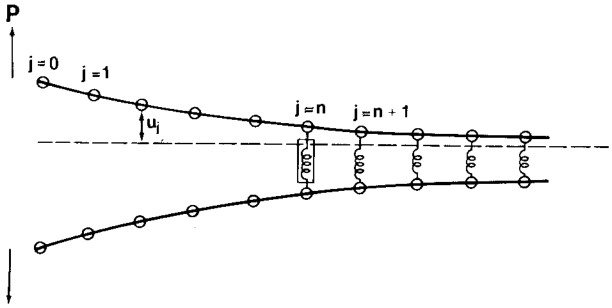

Figure 1 One-dimensional model of fracture. Two chains are held together by a combination of stretchable and bendable bonds. The external force P applied to the end atoms holds the crack open. The first stretchable spring is attached at $j = n$. This bond is also assumed to be different from the rest because of the influence of the external atmosphere.

able springs of Fig. 1, the potential energy of the system is given by

$$u = -2Pu_0 + \beta \sum_{j=1}^{\infty} (u_{j+1} - 2u_j + u_{j-1})^2$$

$$+ 2\gamma_0(u_n) + 2\alpha \sum_{j=n+1}^{\infty} u_j^2 + 2n\gamma_0 \qquad (1)$$

where P is the external force, u_i is the vertical displacement of each atom from equilibrium, $2\gamma_0(u_n)$ is the bond energy of a non-linear spring at $j = n$ and α and β are the stretchable and bendable spring constants. The last term is the surface bond energies of the broken bonds, $j < n$. In the analysis, we shall allow the properties of the stretchable spring at $j = n$ to be a variable which reflects the influence of the external atmosphere.

The solution of the problem is depicted in Fig. 2 for one value of n ($n = l$) in heavy line, and for several other values of n (crack length) self consistently patched together. The horizontal line at a given external force crosses the solution at a number of values, which depicts the fact that the crack possesses a number of mechanically stable configurations. For the branch of the solution $n = l$, the horizontal line crosses at three places, noted as I, I*, II. State I* is an unstable equilibrium configuration; I and II are stable. The activated state between I and II is therefore I* (see Part 1, Fig. 1), and the activation energy for crack growth is given by:

$$\tfrac{1}{2} E_+ = \int_{\mathrm{I}}^{\mathrm{I}^*} P(u_0)\,\mathrm{d}u_0 - P\Delta u_0$$

$$\tfrac{1}{2} E_- = \int_{\mathrm{II}}^{\mathrm{I}^*} P(u_0)\,\mathrm{d}u_0 - P\Delta u_0. \qquad (2)$$

The first term is the strain energy induced in the springs in going from I to I* or II to I*, respectively. However, as is typical of elastic calculations of this kind, we must consider the total system which also includes external weights which might be considered to be attached by pulleys to the atom at $n = 0$, and whose potential energy is thus changed by the displacement Δu_0. The change in the energy of the external weights is simply $-2P\Delta u_0$, as shown by the second term in Equation 2 above. The two cross-hatched areas in Fig. 2 correspond to the forward and reverse activation energies.

The bond forces are related directly to the intrinsic surface energy. That is, when the crack advances by one atom spacing, exactly one new open bond pair is added to the surface, and this energy is given by

$$2\gamma_0 = 2 \int_0^{\infty} f(u_n)\,\mathrm{d}u_n. \qquad (3)$$

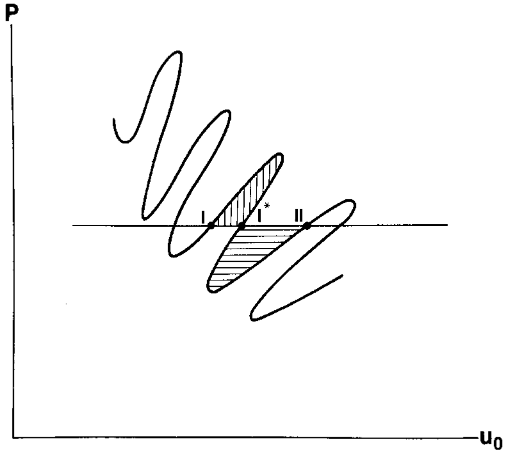

Figure 2 Solution of the one-dimensional model. For a set length of crack, $n = l$, the compliance (P versus u_0) is an increasing function. When the bond breaks, the curve bends back on itself to another branch, $n = l + 1$, and the process starts over. The horizontal line cuts the solution for $n = l$ at point I, and at $n = l + 1$ at II. The area given by the vertical cross-hatches represents the strain energy to move the system to the metastable position I*, which is the saddle point. The reverse fluctuation strain energy is given by the horizontal cross-hatched area.

In this model, γ_0 is the surface energy per unit length at zero temperature.

We shall now calculate the activation energy explicity. From Equation 1 and Fig. 1, the displacement of the nth atoms is given by [2]

$$\left(\frac{n+\xi}{\xi}\right)P = f(u_n) + (\xi - 1)\alpha u_n$$

$$\xi = \left[\frac{1+\surd(1+8\beta/\alpha)}{2}\right]^{\frac{1}{2}}. \qquad (4)$$

The function $f(u_n)$ is the (non-linear) restoring force in the nth bond defined by

$$f(u_n) = \frac{\partial\gamma_0(u_n)}{\partial u_n}. \qquad (5)$$

For $n \gg 1$, the displacement of the 0th atom is [2]

$$u_0 = \left(\frac{n+\xi}{\xi}\right)u_n + \frac{Pn^3}{3\beta}. \qquad (6)$$

We substitute Equations 6 and 4 for u_0 in Equation 2, and find

$$E_+ = \int f(u_n)\,\mathrm{d}u_n + \alpha(\xi-1)\int u_n\,\mathrm{d}u_n$$

$$-\left(\frac{n+\xi}{\xi}\right)P\int \mathrm{d}u_n + \frac{n^3}{3\beta}\int P\,\mathrm{d}P. \qquad (7)$$

In the integration of Equation 7, we note that in going from I to I*, the final and initial states have equal values of the external force, P, but differing values of u_0 and u_n (see Fig. 2). Thus the last term in Equation 7 is strictly zero. Also, the first term has a simple meaning; it is just the change in bond energy of the atom at the tip between the two states. Thus,

$$\tfrac{1}{2}E_+ = [\gamma_0]_{\mathrm{I}}^{\mathrm{I}^*} + \frac{\alpha(\xi-1)}{2}[u_n^2]_{\mathrm{I}}^{\mathrm{I}^*} - \frac{(n+\xi)}{\xi}P[u_n]_{\mathrm{I}}^{\mathrm{I}^*}. \qquad (8)$$

To make further progress, we must invert Equation 4 to find u_n in terms of the external force, P, which means that the form of the bond function at the tip must be known. From the form of Equation 8, we note that E_+ will have a strongly non-linear dependence on the external stress.

In order to try to learn more about the activation process, we shall assume a simple non-linear force law for the bond at the crack tip.

$$f(u_n) = 2\alpha u_n(1-\eta u_n). \qquad (9)$$

Then Equation 4 can be inverted, and we find for large n

$$\frac{K}{\xi} = \frac{nP}{\xi} = \alpha(\xi+1)u_n - 2\alpha\eta u_n^2. \qquad (10)$$

Here K has the meaning of stress intensity factor for the one-dimensional model [2]. If we define a set of quantities, P^+, K^+, u^+, etc., to correspond to the point of maximum force, were $\mathrm{d}K/\mathrm{d}u_n = 0$, then

$$u^+ = \frac{\xi+1}{4\eta}$$

$$K^+ = \alpha(\xi+1)^2\xi/8\eta. \qquad (11)$$

From its definition, K^+ is what is called in a fracture mechanics K_{IC}. ($K^+ \equiv K_{\mathrm{IC}}$). Then

$$u = u_+[1 \pm \surd(1 - K/K^+)]. \qquad (12)$$

When we substitute all these quantities in Equation 8 and perform the necessary manipulations, we finally obtain the simple result

$$E_+ = \frac{8}{3}\,\frac{K^{+2}}{\alpha\xi^2(\xi+1)}\left(1-\frac{K}{K^+}\right)^{\frac{3}{2}}. \qquad (13)$$

This expression is to be contrasted with the stress dependence obtained for the snapping bond linear model [2]

$$E_+\,(\text{snapping bond}) \propto \left(1-\frac{K}{K^+}\right)^2. \qquad (14)$$

Because the P versus u_0 function is rounded without a cusp by the non-linear force law, we expect the activation energy to disappear at $K^+ = K_{\mathrm{IC}}$ with zero slope. Equations 13 and 14 represent opposite extremes from one another, and yet the exponent of $(1 - K/K_+)$ only changes from $\frac{3}{2}$ to 2. Perhaps the stress dependence of more realistic force laws is thus bracketed by these extremes. Most force laws, for example, should be linear over a greater range than Equation 9, but of course not be so brittle as a snapping bond.

At small values of K/K^+, Equations 13 and 14 can be linearized so that the activation energy is linear in K/K^+. Of course, for the reasons discussed in Part 1, at still lower values of stress, as $K \to K_{\mathrm{ISCC}}$, the crack velocity itself becomes linear in the stress because of reverse fluctuations, and crack healing.

3. Physical description of chemically assisted fracture

Having the analytical apparatus of the one-

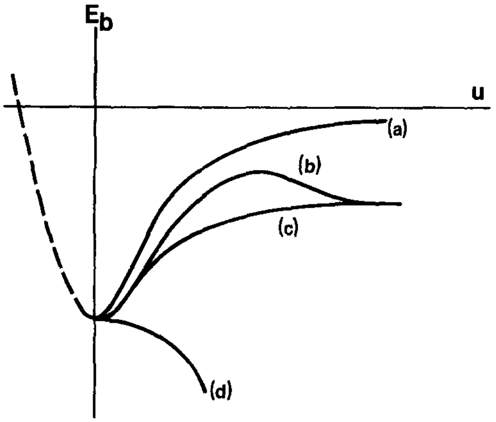

Figure 3 Schematic Morse functions for the bond at the tip of the crack. (a) Intrinsic fracture, no external atmosphere; (b) Morse function as modified by chemical reaction with external atmosphere with adsorbtion activation barrier; (c) Morse function with adsorbtion, no barrier; and (d) corrosion reaction corresponding to negative surface tension.

dimensional model in hand from the last section, we now turn to how to interpret the effects of chemical attack at the crack tip. In this discussion, we shall use a language borrowed from that describing the gaseous reactions of two chemical gaseous species, even though the chemical bond at the surface is usually greatly modified by the underlying crystal. In important ways, our discussion has also already been anticipated by Lawn and Wilshaw [3] in their treatment of chemically assisted fracture.

The bond energy function $E_b(u)$ is depicted in Fig. 3a for two atoms A-A of the intrinsic crystal as they are separated at the crack tip (Equation 3). When a foreign molecule, B-B is brought to the vicinity of A-A, this bond function is modified. In Fig. 3b, c and d, we have plotted schematically the total energy ("Morse function") of the four A-A and B-B atoms as a function of the separation of the A-A atoms. In these curves, we assume that for a particular A-A separation, the B atoms take a configuration which minimizes the total energy. The "Morse function" thus generated is drawn for several different possibilities. In b, c, and d the energy of the covered surface (in its ground state) is less than that of $2A + B_2$, so that the surface tension of γ_0 of the surface at $T = 0$ is lowered by the gaseous reactants, and for all of these cases, the chemical reaction should decrease the stiffness of the A-A bond. In b, however, an activation barrier also exists for the chemical reaction, while at c, it does not. This activation barrier from the chemical adsorbtion reaction itself adds to the activation energy for crack growth over and above the lattice effects proper which give rise to lattice trapping for the intrinsic case. In d, the reaction becomes exothermic, and the surface energy goes negative, indicative of spontaneous corrosive attack.

The chemical activation energy indicated in b arises from the nature of the quantum mechanics of molecules adsorbing on a surface. In general, but not always, molecules must transverse an activation barrier when they pass from a weakly physisorbed state to a more strongly chemisorbed state characterized by molecular break-up and chemical binding of the fragments to the surface. There are also cases like NO where complex molecular species are tightly bound on the surface. In our case, because of the considerable constraints imposed by the narrow confines of the crack-tip region, we expect substantial activation barriers to be the rule.

We make contact with the one-dimensional model through the force function which is related to γ_0 by means of Equation 5 and the general solution, Equation 4. From the Morse functions of Fig. 3, we can draw the appropriate force laws to use in Equation 4, etc. These are depicted correspondingly in Fig. 4.

The general solution of the one-dimensional problem is then depicted in Figs. 5 and 6 for a particular crack length. In Figs. 5a and 6a, we show the intrinsic solution already given in Fig. 2 for comparison. Even though the bond at the tip

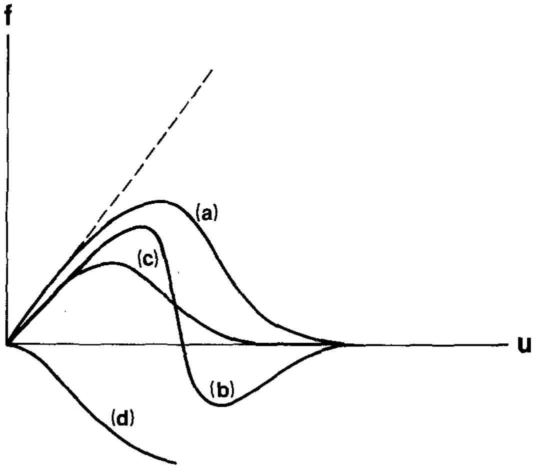

Figure 4 Bonding force laws of attraction corresponding to Morse functions as given in Fig. 3. These curves are plotted as the slopes of the corresponding curve in Fig. 3.

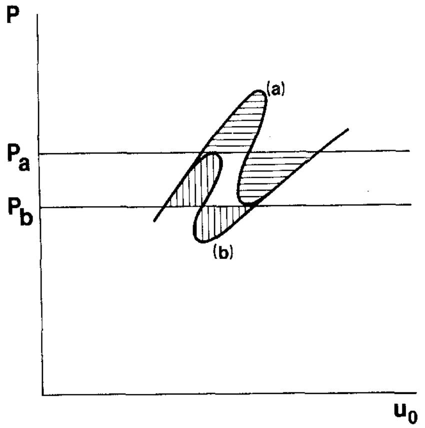

Figure 5 Effect of chemical interaction on solution of one-dimensional model. (a) the solution (see Fig. 2) without external chemical interactions; (b) shows the result of a chemical interaction of the type shown in Fig. 3c (no adsorbtion barrier).

has a different stiffness than the rest of the chain, the overall compliance of the chain is only changed by an infinitesimal amount. However, the whole construction of the solution in Fig. 5a is lowered in stress and displacement, as shown in Fig. 5b. Also, a look at the analysis for this case shows that the activation energy at the quiescent point, the quiescent point itself, and the range of activated crack growth all decrease in value monotonically within the decrease in surface energy. In the case of activated chemisorbtion, as in Fig. 6b, the solution of the model is further modified as shown for the reverse reaction in a way which increases the reverse activation energy. Increasing the reverse activation energy lowers the quiescent point (still fixed by the surface energy as shown in Part 1). Thus, two contrasting effects operate for activated adsorbtion. The activation energy and activated growth regime are lowered by the lowered surface energy, but increased by the activation barrier of adsorbtion. We have shown these effects operating in Fig. 6b. In both Figs. 5 and 6, we have indicated the quiescent point by an equal area construction for forward and backward fluctuations, shown by P_a and P_b.

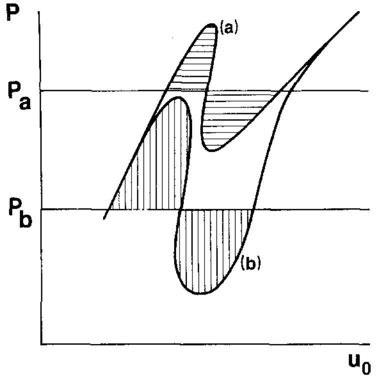

Figure 6 Effect of chemical interaction on solution of one-dimensional model. Same as Fig. 5, except that (b) corresponds to Fig. 3b (adsorbtion barrier).

From the analysis, and from the graphical construction, the appearance of adsorption activation barriers is indistinguishable from the lattice trapping barriers of the intrinsic discrete lattice, except that when chemical reactions are occurring, the barriers are different. From the data so far available, there appears to be no *a priori* way of saying how strong the effects of adsorption barriers will be relative to intrinsic lattice trapping. In general, we expect these to be intimately related to the force laws and the detailed molecular process at the tip; in one case lattice trapping is more important, and in another the chemical barriers are the more important. For very brittle bonds which break almost discontinuously in a bond snapping mode, we have shown in an earlier paper [2] on the one-dimensional model that the activation barriers at the quiescent point are roughly equal to half the bond energy. On the other hand, for soft force laws, the lattice barriers will be a small fraction of this value. No detailed calculations have explored this question, however, because of the uncertain character of atomic force laws in materials. Experimentally, however, intrinsic lattice barriers have not been widely observed (though we hasten to add that an extensive search has not been made). On the other hand, activated crack growth is widely observed in a variety of materials. We are thus tempted to suggest that the dominant effect at the crack tip is most often contributed by the activated adsorption barrier as depicted in Fig. 6b. Unfortunately, there is no way of measuring these barriers independently of a fracture experiment, since they are likely to be considerably higher than physiosorption to chemisorption reactions on free surfaces because of the additional constraints and unique configurations of the crack tip. Also, they should be analogous to, but quantitatively different from bimolecular gaseous reactions for the same reasons.

These expected results are summarized in Fig. 7. This figure shows the total (free) energy of the system as a function of crack length or reaction co-ordinate, and is an extension of Fig. 2 of Part 1.

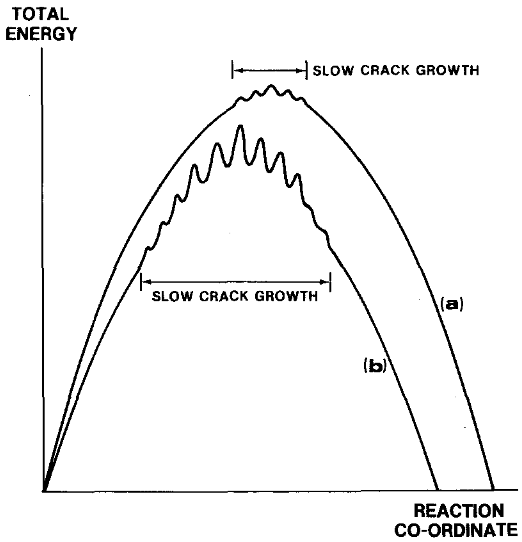

Figure 7 **Energy as a function of crack length. The total elastic energy (or total free energy) is plotted as a function of that reaction co-ordinate of the system that correlates with crack length. (a) Intrinsic fracture, no external chemical atmosphere. (b) Same material and stress with external chemical interaction. The regime of slow crack growth is indicated as that region where the crack is trapped by the wiggly energy function.**

Curve a represents the intrinsic energy curve for a fractured solid in vacuum at a given stress, and shows a small region of slow crack growth about the maximum value of the energy given by the Griffith relation. When this same solid with the same stress is subjected to an external chemically embrittling atmosphere, the surface energy of the solid is lowered by the adsorbtion of the atmosphere on its cleavage faces and the Griffith critical crack length is shorter. Also, because of the activated adsorbtion reaction at the crack tip, the barriers become much larger, and the region of thermally activated slow crack growth is extended.

Additional important conclusions about the activation energy can be drawn from the one-dimensional analysis. One might have expected that the activation energy is mainly due to the necessity of breaking the critical bond at the tip. However, the energy to snap this critical bond is given by the first term in Equation 8, and we note from inspection of the relative sizes of the various terms in this equation that the other terms are of roughly equal magnitude. These other terms are contributions to the activation energy which are not localized at the crack tip bond, but are due to bond stretching of the other atoms in the near region surrounding the crack tip. In fact, these additional terms have the effect of multiplying the adsorbtion activation barrier at the tip atom. Thus, the "chemistry" at the crack tip and the "mechanics" of the larger region around the tip are intimately mixed together, and one cannot obtain correct results by focussing attention merely on the processes occurring at the single bond tip.

The importance of the non-local contributions is accentuated in two and three dimensions. In one dimension, the strain beyond the crack tip falls off exponentially with distance from the crack tip, while in two dimensions it goes as the inverse square root of distance. Thus, the core region in two dimensions is much larger than in one, and the non-local effects will dominate the local bond at the tip. However, in spite of these strong non-local effects, we expect that the activation energy for crack growth will be strongly correlated with the chemisorption barriers which would be measured on a clean surface.

In Section 2, we have derived quantitative results for the stress dependence of the crack growth and how this varies with force law type. It would be desirable if some connection could be made between these results and the more general case of activated adsorbtion reactions and higher dimensionality.

An effective force law corresponding to an activated reaction such as in Fig. 3b, possesses regions of negative force as we have shown in Fig. 4b. Actually, such a region of negative force could well be included in the force law given in Equation 9 if displacements at the tip become larger than $1/\eta$. However, for a forward fluctuation of the crack, the negative region of the force law will not be traversed in going to the top of the activation barrier. Indeed, so long as the force constants satisfy the absurdly easy requirement $\beta/\alpha < 188$, no region of negative force will be experienced in getting to the top of the barrier. (The negative portion of the force, of course, contributes in an essential way to the reverse fluctuation). Hence, the precise form of the force law is unimportant in the negative region, and the general results we have derived for soft quadratic and hard linear snapping force laws will stand. That is to say in one dimension, we still expect a stress dependence of crack growth to lie between the square law (Equation 14) and the $\frac{3}{2}$ law (Equation 13) already discussed.

The question of the effect of higher dimensionality is a more difficult one and its solution remains for a later paper. Intuitively, however, since the core effects in one dimension are stronger than in two dimensions, because of the different ranges of the strain with distance from the crack, we expect the effects of changing force laws to be less drastic in two dimensions than in one. Thus, the conclusions drawn above on the basis of a one-dimensional model may remain valid in two-dimensions. A more rigorous demonstration of this statement is, however, obviously needed.

One final important consequence of our derivation of the stress dependence is that with a power law stress dependence in the activation energy term as given in Equations 13 and 14, activation volume is not a useful concept for crack growth. If we derive an expression for the activation volume from its thermodynamic definition, then it will be stress dependent in an essential way. Also, there is no particularly simple physical meaning for it in terms of the parameters of our models. Instead, the stress dependence of crack growth is a complex phenomenon which depends weakly upon the particular force laws of the atoms and configuration of the solid and the adsorbing molecules.

We close this section with a comment regarding the form of the typical K/V curve as measured for slow crack growth. Fig. 8 is a typical representation. First, there must be a "stress corrosion limit" where the velocity goes to zero (I). Above this is a region (region I) where the velocity is thermally activated and controlled by chemical reactions at the tip. At higher stresses (region II) the crack outruns the atmosphere, and the fracture jumps to the intrinsic fracture (region III) curve which is independent of chemical interactions and is the same as one would measure in vacua.

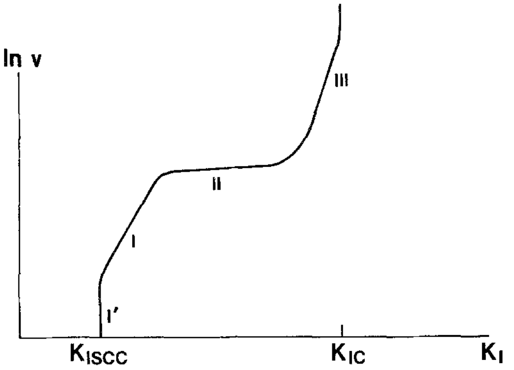

Figure 8 Velocity versus K. Region I′ is where the crack is stable without growth. This point is called K_{ISCC}. (I) Chemically assisted fracture, (II) diffusion-limited fracture, (III) intrinsic crack growth. Independent of external chemical interactions.

Additional details can be elucidated regarding the slopes of the K versus v curves in regions I and III. Typical experimental results show the slope in I to be shallower than that in III. We assume that at the respective (but different) quiescent points, region I has a higher activation energy than III for the reasons discussed. However, these curves are typically not measured near the quiescent points, but closer to $K_{\text{IC}} = K^+$. From Equation 13, we note that always $(K^+)_{\text{chem}} < (K^+)_{\text{intrinsic}}$. Hence, where $K \to K^+$, we have $\mathrm{d}\ln v/\mathrm{d}K \propto \mathrm{d}E_+/\mathrm{d}K$ is expected to be lower for region I than for region III.

Actual materials, of course, often exhibit additional complexities – most notably plastic deformation – which must be accounted for before a final K/v law can be predicted. In the case of extensive plastic deformation, the considerations here only apply to the underlying crack which "sees" a stress which is strongly shielded by the plastic deformation field [4–6].

4. Conclusions

The one-dimensional model predicts a stress-dependent activation energy for slow crack growth when assisted by chemical reactions at the tip. The stress dependence in one dimension does not vary strongly with the form of the force laws ($\frac{3}{2}$ power to 2nd power for quadratic force laws to snapping bonds). It is, however, strongly dependent and correlated with chemisorbtion barriers at the crack tip. The barriers which would be measured for chemisorption on a clean planar surface will be enhanced by non-local "mechanical" effects in the core region surrounding the crack tip. We can interpret this by saying that in order for the crack tip bond to snap with chemisorption of an atmosphere molecule, the atoms surround the crack tip must also relax their configurations. Since the process is strongly stress dependent, the observed activation energy barriers will not be exactly the same as for clean surface adsorbtion, but will be strongly correlated with it.

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