Interface Morphology Development During Stress Corrosion Cracking:
Part I. Via Surface Diffusion

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The initiation of a crack in a specimen under tensile or compressive stresses is treated from the point of view of perturbation analysis. A surface distortion is Fourier analyzed into a series of waves and the amplitude response of a single component of varying frequency is theoretically investigated. The response of the individual components yields a Griffith-type criterion for wave amplitude growth. The model is applied to alloy systems undergoing stress corrosion cracking via surface diffusion.

THE present scientific understanding of stress corrosion is very fragmentary and the need for a more detailed mechanistic understanding of the overall process has been evident for some time.[1-3] The lack of generality or comprehensive foundations in the existing descriptions has led to a very empirical assessment of the stress corrosion phenomena and has not provided the fundamentals on which a basic quantitatively predictive theory can be founded.

In this series of papers, the theoretical approach is to treat the interface between a material under stress and its environment as a phase front that is capable of motion either as a smooth regular front or as a chaotic rumpled front. The first case corresponds to that of uniform corrosion, the second to that of cracking. The phase front changes position and shape via both surface and volume diffusion processes and is analyzed via what is essentially a perturbation procedure not too unlike the problem of Taylor instability[4] of a fluid with surface tension. All of the elementary processes are quite general and the question of which mechanism leads to cracking in a particular instance is purely a matter of kinetics.

At least four categories of choice appear to be necessary for an overall analysis; these are: 1) either a perfect solid plus loading or a heterogeneously imperfect solid (grain boundaries, two-phase boundaries, and so forth) plus loading; 2) either small amplitude or large amplitude surface distortion; 3) shape change either by surface diffusion, surface reaction, or volume diffusion, and 4) presence or absence of a tarnish film. A fifth category would obviously distinguish the environmental conditions. In this first paper, we restrict ourselves to the treatment of a perfect solid without surface film in tensile and shear modes and discuss the growth of small amplitude distortions via surface diffusion.

In the next section, we treat the necessary and sufficient conditions for crack growth. Section II deals with a linear stability analysis of a smooth solid surface and Section III discusses the results and implications of the treatment.

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I) NECESSARY AND SUFFICIENT CONDITIONS FOR CRACK GROWTH

The second law of thermodynamics naturally provides us with the necessary condition for crack growth. This one condition is that the entropy of an isolated system (in this case the elastic body plus its loading mechanisms) be maximized. This is, of course, equivalent to specifying extremum conditions on the free energy of the elastic body while imposing constraints on the loading mechanisms. A theorem of this sort is well known in the theory of elasticity—the theorem of minimum potential energy.[5] In Appendix I, a formal development produces a result in complete harmony with classical thermodynamics,[7,8] namely that, for a species residing in the lattice, the chemical potential defined only at the surface is given by

$$\mu = \mu_0 + V°\Delta F + V° P \qquad [1]$$

where ΔF is the strain energy density (Helmholtz free energy change), $V°$ the atomic volume, and P the normal pressure at that point on the surface. A somewhat simple heuristic argument can also be used to calculate the chemical potential at a free surface as well as at a surface where a normal traction T_n acts. It is that the two types of work we must consider in adding an element of mass, from an unstrained reference state, to the stressed body are i) strain energy or work necessary to produce a coherent match and ii) a PV or $T_n \times V$ term which is the work required to "push back" the loading mechanism. This leads again to Eq. [1] or in the case of a free surface to Eq. [12] in Appendix I.

It should be realized at this point just how useful is the concept of chemical potential in treating the energetics of crack growth since, in using the commonly accepted approach of minimum potential energy as is commonly done, the analysis is limited to specific geometries. Indeed, authors[6] have found it difficult to set "precise conditions for more general configurations". These problems are purely computational and are eliminated by the use of the differential quantity μ. It is interesting to note that the speculations concerning general configurations of Rice and Drucker[6] seem to be in harmony with the thermodynamic formulation.

After taking into account the release of mechanical energy, we must consider such processes as surface creation plus the work required to drive other proc-
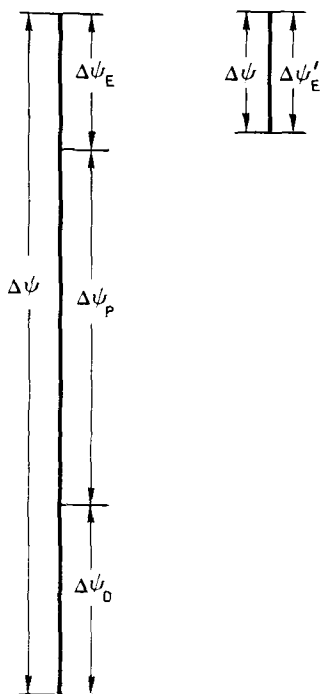
Fig. 1—Schematic representation of a coupling equation for crack growth.

esses, which will provide sufficiency, such as plastic deformation. The analysis of these processes is really what our understanding of crack growth depends upon.

In the full analysis of crack growth, the requirement of decreasing free energy (entropy production) is rarely sufficient to insure crack growth. For example, the Griffith criterion for infinitely sharp brittle cracks is both necessary and sufficient for crack growth if, and only if, we interpret the meaning of brittle as the complete absence of plastic deformation (which tends to blunt sharp cracks). However, for cracks with a tip radius of the order of a few atomic spacings and larger, the Griffith criterion no longer remains sufficient since the Griffith critical stress is then lower than that required to exceed the cohesive stress at the crack tip. The effect of plastic deformation is, in this case, to decrease greatly the concentrated stress at the tip. If, as a result of the introduction of even a mildly corrosive environment, the region just ahead of the crack is embrittled, then, at that point, we examine possible mechanisms by which the crack can either propagate or sharpen to reinstall the Griffith criterion as a sufficient condition. Examples of the former might be microdissolution, surface diffusion, vapor diffusion or void formation while examples of the latter are also dissolution, surface and/or volume diffusion. Thus, in addition to creating surface, the cracking process generally must also drive such processes as plastic deformation and defect formation or be kinetically limited by alternative cracking modes such as surface diffusion. This can be diagrammed by a coupling equation as shown in Fig. 1. Here, in both cases (a) and (b), the entire reversible work (driving force) is represented by $\Delta\psi$. This is the amount of energy required to actually propagate a crack. The various terms determined by the actual mode of cracking account for surface creation $(\Delta\psi_E)$, plastic deformation $(\Delta\psi_P)$ and also, for example, defect formation $(\Delta\psi_D)$. If we do not supply the

means (applied stress or chemical free energy) to achieve $\Delta\psi$, where $\Delta\psi = \Delta\psi_E + \Delta\psi_P + \Delta\psi_D$, no cracking is observed. However, in environmental phenomena there are several alternatives available, namely the elimination of those processes corresponding to $\Delta\psi_P$ and $\Delta\psi_D$ through surface embrittlement. In addition, as is well known, the necessary conditions for crack growth are also altered so that in (b) we represent $\Delta\psi_E$ $\Delta\psi'_E$, where $\Delta\psi'_E < \Delta\psi_E$. Changes in $\Delta\psi_E$ will be both real—reduction in surface energy, and apparent—chemical free energy supplied by the corrosion process.*

*By corrosion process we do not necessarily imply that the body is undergoing any massive weight loss through corrosion—we are thinking more in terms of a microdissolution process.

Consequently, in the case at hand where we are essentially trying to install the Griffith criterion as both necessary and sufficient, we are led to a study of the morphology of growing cracks. The relevance of such an approach has already been suggested by Hillig and Charles[14] and Creager and Paris.[9] Their approach accounting only for dissolution is identical with the analysis of dendritic growth.[10] They show that if the dissolution rate is a stronger function of the applied stress, σ, then $\sigma^{1/2}$ a parabolic notch should tend to sharpen.

II) AN INTERFACE INSTABILITY MODEL FOR STRESS CORROSION CRACKING

Cracks are usually modeled as either singularities or as thin elliptical notches in an elastic continuum. In certain restricted cases these shapes lend themselves to analytic treatment. However, the amount of flexibility in these solutions is insufficient to be compatible with our generalized model. On the other hand, to consider the completely arbitrary shape is beyond the ability of applied mathematics. We are then forced by practical necessity to consider something less than completely arbitrary shapes which, while possessing all the correct qualitative characteristics, are such as to allow thorough mathematical analysis. We can easily imagine such a shape if we consider any real crack (or notch) as being Fourier analyzed into harmonic components and choosing any one of these components (fully specified by a wavelength λ_i and amplitude a_i) as our model.[15] Under suitable conditions the full response of the crack can be calculated by linear superposition of the response of each wave. This condition is that, for all those waves where a_i is nonzero but infinitesimal, $a_i/\lambda_i \ll 1$. To be more precise, we can state the proposition as follows. Physical systems are described by their spatial domain and the various fields in this region, D, and on the boundary, Fig. 1. These fields are usually coupled either in the domain or on the boundary or both. This coupling (aside from the purely static case) imparts a time dependence to the various quantities associated with these fields. The changes in time can be i) monotonic or ii) oscillatory. In addition, in the case of oscillatory behavior, the oscillations may be linear or nonlinear. In the physical theories involved with fracture mechanics, we are mainly concerned with those cases involving monotonic changes in say i) the boundary Σ of D (crack propagation), ii) the elasto-static field, iii) thermal fields, iv) coupled elasto-static fields related to moving defects, and so forth.

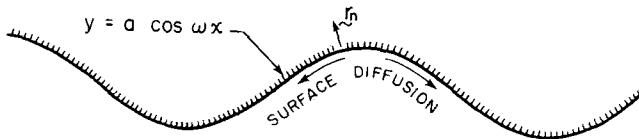In our case, the way in which linear fields change

Fig. 2—Elastic solid containing a sinusoidal surface profile. Note that the wave grows by surface diffusion which is driven by the applied stress.
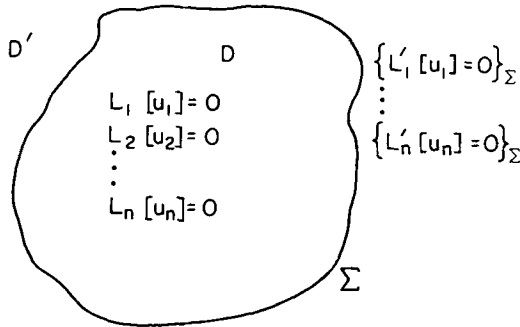

Fig. 3—Schematic representation of metal-environment field governed by differential operators L and boundary conditions L'.

through coupling is typically nonlinear even though the fields themselves are described by linear differential equations. Monotonic changes are produced by the thermodynamic driving forces discussed in the previous section. Thus, in combination, thermodynamics and kinetic phenomenology provide the coupling laws.

We are studying here the situation of the response of an elastic continuum to applied stress. We impose the condition that our elastic body, being a material one, be subject to the usual phenomenological laws such as mass transport, heat transfer, and so forth. The important equations are those governing the elastostatic field, the total potential field, the transport field and the coupling between them. Since we are dealing only with a linearized version of this problem, we shall not be able to represent the coupling exactly. In this way, the analysis is like those used in the theory of hydrodynamic stability. However, there are important differences that are explained in Appendix II. There it is shown that, without losing any generality, we may confine our considerations to surface shapes represented by only even harmonics; viz., $y = a \cos \omega x$.

Consider a sinusoid of the form $y = a \cos \omega x$, where the solid in the region $a \cos \omega x \leq y < \infty$ and infinite in the x-direction, Fig. 3. In addition, we consider two types of loading; Mode I or tensile and Mode III or shear loading. The solutions for Mode I with applied stress $\sigma_{xx} = \sigma_0$ are

$$\sigma_{xx} = \sigma_0 - a\sigma_0(\omega^2 y - 2\omega) e^{-\omega y} \cos \omega x \qquad [2a]$$

$$\sigma_{yy} = -\omega^2 a\sigma_0 y \, e^{-\omega y} \cos \omega x \qquad [2b]$$

$$\tau_{xy} = -\omega a\sigma_0(1 - \omega y) e^{-\omega y} \sin \omega x \qquad [2c]$$

and for Mode III with applied shear stress $\tau_{xz} = \tau_{xz}^0$

$$\tau_{xz} = \tau_{xz}^0 + \tau_{xz}^0 a\omega \cos \omega x \, e^{-\omega y} \qquad [3a]$$

$$\tau_{yz} = -a\omega \, \tau_{xz}^0 \sin \omega x \, e^{-\omega y} \qquad [3b]$$

It is easily verified that the form of Eqs. [2] and [3] is consistent with the asymptotic scheme outlined in Appendix II.

To study the dynamics of this wave, we need the chemical potential expressions and the rate laws. As discussed earlier the chemical potential is given by

$$\mu = \mu^0 + \Delta W V^0 + \gamma K V^0$$

where ΔW is the strain energy, γ is the surface free energy, and K is the mean curvature. For our governing equations we will restrict ourselves here to surface diffusion. We first note that the strain energy is given to first order in $a\omega$, for Mode I as

$$\Delta W(x) = \sigma_0^2(1 + 4a\omega \cos \omega x)/2E \qquad (a) \qquad [4]$$

and for Mode III as

$$\Delta W(x) = (1 + \sigma) \tau_{xz}^{02}(1 + 2a\omega \cos \omega x)/E \qquad (b) \qquad [5]$$

The mean curvature is given by

$$K = -a\omega^2 \cos \omega x \qquad [6]$$

The boundary value problem associated with the growth of the crack can be developed along the same lines as those used by Mullins[16] to describe grain boundary grooving. The flux of matter along the surface of the wave can be written in the familiar phenomenological form

$$\mathbf{J} = -\nu D/kT \, \nabla \mu \qquad [7]$$

where, for simplicity, we assume the existence of a single diffusion constant (i.e., D is isotropic), and where ν is the surface density. The gradient operator is one, in principle, that operates over the surface but to remain consistent with our first order treatment we may assume $\nabla \approx \partial/\partial x$. If we multiply the divergence of Eq. [7] by $+V^0$, the atomic volume, dimensional analysis proves the result to be the rate of normal motion of the surface,

$$\mathbf{r}_n = -D\nu/kT \cdot V^0 \nabla_x^2 \mu \qquad [8]$$

Geometry suggests that[16]

$$\mathbf{r}_n = (1 + y')^{-1/2} \frac{\partial y}{\partial t} \qquad [9]$$

Equating Eqs. [8] and [9] the differential equation is, for $y(x, t)$,

$$\frac{\partial y}{\partial t} = - \frac{D\nu V^0}{kT} \nabla_x^2 \mu \qquad [10]$$

where again we have neglected terms of $\sigma(a^2\omega^2)$ and greater. Substituting into Eq. [10] from Eqs. [6] and [4] or [5], evaluating the result at $x = 0$ (the tip) and calling the result V, the initial crack velocity,* we

*Solutions of Eq. [10] are of the form $a(t) = a(0) e^{Vt}$ where V is actually an exponential amplification factor. By forming $a'(t) = a(0)V e^{Vt}$ we mean by V [or $a(0)V$] the initial velocity.

obtain for Mode I loading,

$$V = B(-\gamma\omega^4 + \omega^3\sigma_0^2/E) \qquad [11]$$

where $B = aV^{02}\nu D/kT$. For instability we must have $V > 0$. This will be true if

$$\sigma_0 \geq (E\gamma\omega)^{1/2} = \left(\frac{2\pi E\gamma}{\lambda}\right)^{1/2} \qquad [12]$$

Eq. [12] is by its nature both a necessary and sufficient condition for growth (initial instability) of the harmonic component of wavelength λ. However, it is not necessarily sufficient for instability of the crack since
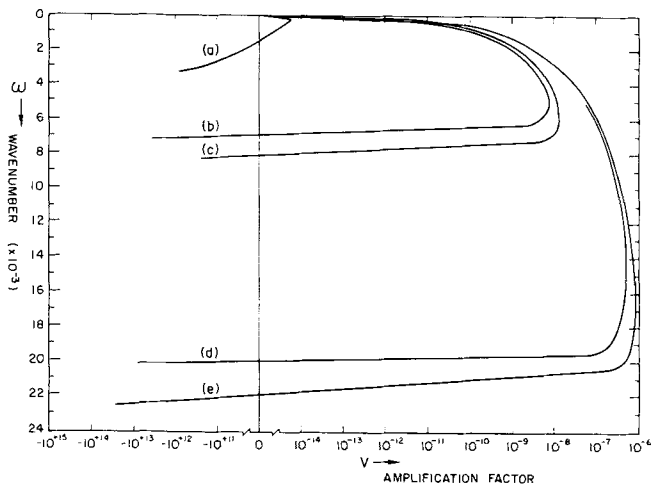
Fig. 4—Amplification factor, V (velocity), as a function of frequency, ω. Plots are for various values of applied stress, σ: (a) $\sigma = 10{,}000$ psi, (b) $\sigma = 50{,}000$ psi, (c) $\sigma = 75{,}000$ psi, (d) $\sigma = 87{,}500$ psi, and (e) $\sigma = 100{,}000$ psi. Physical constants used are listed in Table I.

one of two possibilities is present: i) the velocity of the wave is negligible, or ii) harmonic degeneration takes place such that the resulting waves are stable. The latter possibility is not considered in the theory of initial instability since all the time dependence is contained in the amplitudes. We adopt the logical point of view that the wavelengths involved in breakdown (crack growth) are those that grow with appreciable velocities. With this in mind, we examine the maximum velocity wave; *i.e.*, we examine the conditions

$$\frac{\partial V}{\partial \omega} = 0 \quad \text{and} \quad \frac{\partial^2 V}{\partial \omega^2} < 0$$

which yield

$$\omega^* = \frac{3}{4} \frac{\sigma_0^2}{E\gamma} \quad [13]$$

The stability equation, Eq. [12], then becomes, using Eq. [13], an identity while the equation for the velocity becomes for Mode I loading,

$$V_I = 0.1 \, B\sigma_0^8/\gamma^3 E^4 \quad [14]$$

For Mode III loading the result is

$$V_{III} = B \, \tau_{xz}^{08}/\gamma^3 E^4 \quad [15]$$

One can represent this information in two ways. One can plot the amplification factor, V, as a function of wave number, Fig. 4, treating σ_0 (or τ_{xz}^0) as a parameter. The result is that as σ_0, the applied stress, is increased, higher frequency waves fall to the right of $V = 0$. In addition, ω^* moves downward (increases as σ_0 increases). It should be noted that higher frequencies correspond to smaller wavelengths or sharper geometries. This is the origin of crack sharpening. The velocities given by Eqs. [14] and [15] should not be directly associated with the crack rate *a priori*. These quantities relate to the overall stability of the planar surface in that they indicate that while some waves vanish others are growing. This means that, in time, the surface will take on the morphology of those waves that grow the fastest and thus initiate or resharpen a crack. Only in the event that the distribution of growing waves is sharply peaked about the critical
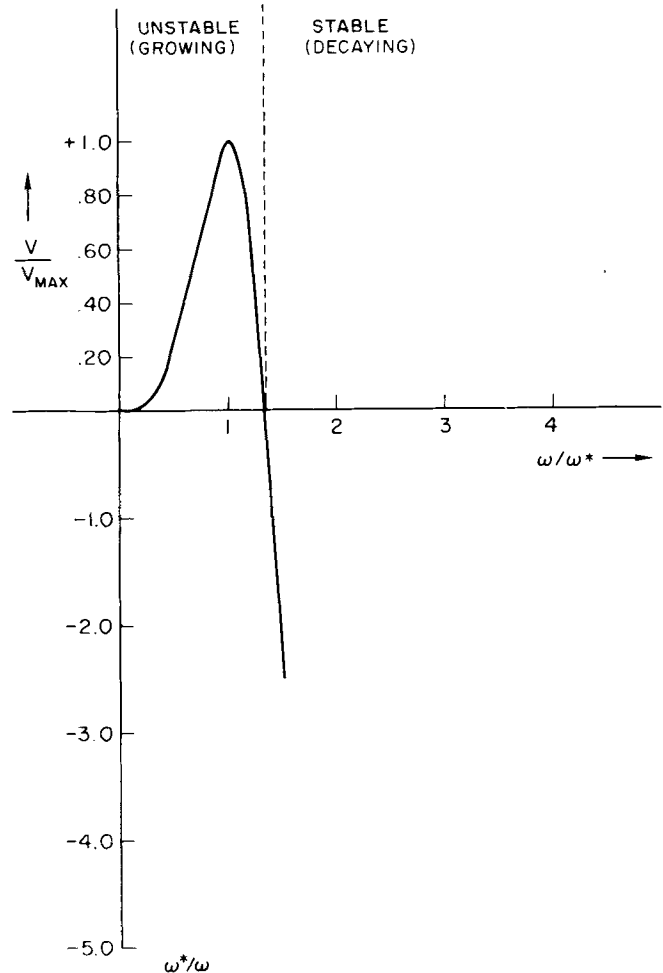

Fig. 5—Amplification factor, V, normalized to V_{max}, as a function of frequency, ω, normalized to ω^*.

wave number ω^* would we be able to predict quantitatively the actual surface morphology and growth law for these small cracks. This is actually the case for the above system as depicted in Fig. 5. Here waves with appreciable velocities have wave numbers near ω^*. Furthermore, Fig. 4 shows how the amplification factor, Eq. [11], varies with applied stress. Note that the peak value is correctly going as σ_0^8 and that, for appreciable stresses, the curves begin to flatten about the summit at ω^*. This is entirely consistent with the preceding discussion concerning Fig. 5. In other words, $V \approx V_{max}$ for all waves that grow. A listing of physical constants used to calculate Fig. 4 is presented in Table I; the reader will understand that Fig. 5 depends only upon the functional form of the growth law (or amplification factor). Note that the value of $D_S = 10^{-10}$ used in calculating V is not to be considered high for the very rough surfaces normally encountered in stress corrosion.

IV) DISCUSSION

Although the very strong dependence of interface stability on applied stress seems rather startling at first, it has a relatively simple physical explanation. At first glance, one might have expected a dependence like σ_0^2 since increases in strain energy are expected

$$a = 10^{-4} \text{ cm}$$
$$V^{\circ} = 2 \times 10^{-23} \text{ cm}^3$$
$$\nu = 3 \times 10^{15} \text{ per/cm}^2$$
$$D = 10^{-10} \text{ cm}^2/\text{sec}$$
$$E = 1.2 \times 10^{12} \text{ dynes/cm}^2$$
$$\gamma = 1500 \text{ ergs/cm}^2$$

to increase the rate of stress corrosion. However, here, we are interested in the gradients of the strain energy rather than in just the magnitude of the quantity. For the case of a wave, the gradients in strain energy are magnified by a factor of ω and the rate of change, *i.e.*, the divergence, introduces an additional factor of ω. This, combined with another factor of ω, associated with stress concentration, yields an overall dependence of $\omega^3 \sigma_0^2$ as given in Eq. [11]. The correspondence between ω and σ_0 is made by looking at the selective amplification of individual waves; *i.e.*, by looking at $V_{\max}$ by Eq. [13]. Thus, in combination, elasticity, morphology, and kinetics combine to produce a much more profound effect than might ordinarily be expected.

The foregoing treatment can be applied equally well to pure metals in a vacuum as to alloyed systems in fluid environments. In the former case, Fig. 4 shows us that the kinetics of notch formation would be quite negligible; *i.e.*, an initial velocity of 10^{-8} cm per sec would produce a penetration of 10^{-2} cm in 10^3 years assuming an initial amplitude of 10^{-4} cm. However, in the latter case, the kinetics can be appreciably altered by the changes in material constants as a result of the adverse environment. For example, the surface diffusion coefficient could be expected to increase by several orders of magnitude as a result of a) the rough (porous) nature of the selectively corroding alloy surface, and b) the presence of a fluid medium at the surface. In fact, using a simple model for surface diffusion,[11] the activation energy for a rough surface which has a high population of adatoms is about one-quarter of that for a normal surface. This can lead to values of $D_S \sim 10^{-5}$ sq cm per sec. One might also expect surface energy changes as a result of environmental changes to be significant. Reductions in surface energy, γ, can be both real (adsorption induced) and apparent (due to chemical free energy supplied by the environment). If the effective surface energy were somehow reduced by a factor of 3, notch penetrations of 10^{-2} cm could occur in a matter of 1 to 2 hr. Thus, in adverse environments, $V \sim 10^{-5}$ cm per sec can be attained and rapid notch growth follows.

The basic objectives of the approach set forth here are to gain insight into the possible and probable mechanisms operative in stress corrosion and to focus attention on those material parameters that could significantly influence the kinetics of the process. This is done, not so much to prescribe a general mechanism, but rather to single out common denominators and describe the cracking characteristics in limiting cases. In this way, one can hope to provide a theoretical framework wherein any particular set of stress corrosion conditions can be evaluated in terms of cracking susceptibility utilizing understanding gained from consideration of a set of fairly simple processes

like the one presented here. To fill out the picture, one must evaluate the processes of microdissolution and volume diffusion on initial instability of the surface. Likewise, all three processes must be evaluated for the case of a sharp notch in relatively perfect material and a notch located at a grain boundary or two-phase boundary. These additional studies will be presented in subsequent papers.

As a final comment on the merits of the present approach, it should be noted that an experimental technique exists for continuously monitoring the amplitude of surface waves of any given frequency.[12,13] Thus, experimental values of D_S in the unstressed condition can be obtained and the change in wave amplitude as a function of stress determined and compared with theoretical predictions. This comparison of theory and experiment should be of great value in isolating the key processes involved in morphology changes in specific environments. Experiments of this kind are now in progress.

NOTATION

A_i Surface area of body in state i

a Amplitude of harmonic wave

B Numerical constant in rate equations

D Surface diffusion coefficient

E Young's Modulus

f_i ith component of the body force vector

G Gibbs free energy

J Surface flux of atoms

K Mean curvature

L Differential operator

r_n Rate of advance of a surface normal to itself

s Surface area

T_i ith component of the traction vector

u_i ith component of the displacement vector

V Mechanical potential energy and amplification factor

$V_{\max}$ Largest value of amplification factor

W Strain energy density

γ Surface free energy

ϵ_{ij} Elastic strain tensor

σ_{ij} Elastic stress tensor

ν Volume element

ω Wave number of harmonic wave $(= 2k/\lambda)$

APPENDIX I

FORMAL DEVELOPMENT OF CHEMICAL POTENTIAL IN STRESSED SYSTEMS

Classical elasticity[5,7] requires that the equilibrium state of a body is the one in which the quantity, V, defined as

$$V = \int_{\nu} W d\tau - \int_{\nu} f_i \cdot u_i \, d\tau - \int_{A} T_i \cdot u_i \, ds \qquad [\text{I-1}]$$

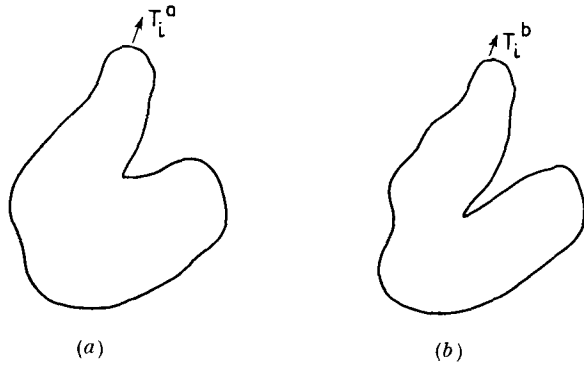Fig. I-1—Linear elastic body under surface tractions T_i. States a and b correspond to before and after crack extension by mass removal.

Fig. I-2—Regions $\nu_i'(i = a, b)$ in the immediate vicinity of the point of mass removal.

is minimized with respect to all kinematically acceptable displacement fields, u_i, to find the equilibrium displacement field as a function of the functionals $\int W d\tau$, the integrated strain energy, $\int T_i \cdot u_i \, ds$, the surface traction work, and $\int f_i \cdot u_i \, d\tau$, the body force work. In Eq. [I-1] ν and A are the volume and boundary of the body, respectively, while f_i and T_i are the components of the body force and surface tractions, respectively. The quantities $d\tau$ and ds are volume and surface elements, respectively. It may be easily seen from first principles that, if the loading is performed slowly enough to preserve constancy of temperature, $V = G + C$, where G is the Gibbs free energy and C is a reversible work due to effects other than mechanical loading. This being the case, what needs to be shown is that V is reduced upon crack opening. Consider the two states a and b of a linearly elastic body shown in Fig. I-1. We will neglect body forces for the time being since they typically are not significant. The potential energy for state a is

$$V_a = \int_{\nu_a} W(\epsilon_{ij}^a) d\tau - \int_{A_a} T_i^a \cdot u_i^a \, ds \qquad [\text{I-2a}]$$

while for state b it is

$$V_b = \int_{\nu_b} W(\epsilon_{ij}^b) d\tau - \int_{A_b} T_i^b \cdot u_i^b \, ds \qquad [\text{I-2b}]$$

Examining the second integral in both these potential expressions, we note that (i) on that part of the surface of b common to a, $T_i^a = T_i^b$, while on the newly created surface in the notch, $T_i^b = 0$, so that

$$\int_{A_a} T_i^a \cdot u_i^a \, ds - \int_{A_b} T_i^b \cdot u_i^b \, ds = -\int_{A_a} T_i^a \cdot (u_i^b - u_i^a) \, ds$$

Eqs. [I-2a] and [I-2b] may be combined and rewritten as

$$V_b - V_a = \int_{\nu_b} W(\epsilon_{ij}^b) d\tau - \int_{\nu_a} W(\epsilon_{ij}^a) d\tau - \int_{A_a} T_i^a$$
$$\times (u_i^b - u_i^a) \, ds$$
$$= \int_{\nu_b - \nu_a} W(\epsilon_{ij}^b) d\tau + \left\{ \int_{\nu_a} W(\epsilon_{ij}^b) d\tau - \int_{A_a} T_i^a \right.$$
$$\left. \times u_i^b \, ds \right\} - \left\{ \int_{\nu_a} W(\epsilon_{ij}^a) d\tau - \int_{A_a} T_i^a \cdot u_i^a \, ds \right\}$$
$$[\text{I-3}]$$

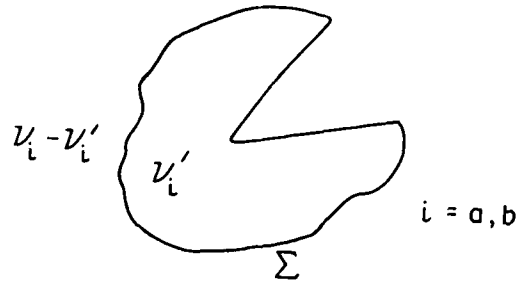Now both T_i^a, u_i^a and T_i^b, u_i^b are stationary (equilib-

rium) states for the functional $V[T_i, u_i]$, $i.e.$, they minimize it. Thus, following Rice and Drucker,[6] if we replace u_i^b and thus ϵ_{ij}^b in the first term and first bracket of Eq. [I-3] and note that $V_b[T_i^a, u_i^a] \geq V_b[T_i^b, u_i^b]$, then Eq. [I-3] becomes the inequality

$$V_b - V_a \leq \int_{\nu_b - \nu_a} W(\epsilon_{ij}^a) d\tau \qquad [\text{I-4}]$$

Eqs. [I-3] and [I-4] lead to the following two important results. The first is that, during crack growth, extension by removal of material from the free surface of the crack reduces the potential energy. The second provides an important link with classical thermodynamics. We focus our attention on a region in the immediate vicinity of the crack tip, Fig. I-2, bounded by the surface Σ and realize that this is where both volume and surface area are created and/or destroyed. Rewriting Eq. [I-3] we obtain

$$V_b - V_a = \overline{W(\epsilon_{ij}^b)} \int_{\nu_b'} d\tau + \int_{\nu_b - \nu_b'} W(\epsilon_{ij}^b) d\tau - \int_{A_a} T_i^a$$
$$\times u_i^b \, ds - \overline{W(\epsilon_{ij}^a)} \int_{\nu_a'} d\tau - \int_{\nu_b - \nu_b'} W(\epsilon_{ij}^a) d\tau$$
$$+ \int_{A_a} T_i^a \cdot u_i^a \, ds \qquad [\text{I-5}]$$

where ν_i' denotes that portion of volume ν_i considered as the immediate neighborhood of the tip. Our aim is to make $\nu_b - \nu_a \rightarrow 0$, $i.e.$, we wish to calculate the differential change in free energy as we remove material. Eq. [I-5] can be written as

$$V_b - V_a = \overline{W(\epsilon_{ij}^b)} \nu_b' + \int_{\nu_b - \nu_b'} W(\epsilon_{ij}^b) d\tau - \overline{W(\epsilon_{ij}^a)} \nu_a'$$
$$- \int_{\nu_a - \nu_a'} W(\epsilon_{ij}^a) d\tau - \int_{\nu_b} \sigma_{ij}^a \epsilon_{ij}^b \, d\tau + \int_{\nu_a} \sigma_{ij}^a \epsilon_{ij}^a \, d\tau$$
$$[\text{I-6}]$$

This may also be written as

$$V_b - V_a = \overline{W(\epsilon_{ij}^b)} \nu_b' - \overline{W(\epsilon_{ij}^a)} \nu_a' + \int_{\nu_b} \{ W(\epsilon_{ij}^b) - W(\epsilon_{ij}^a) \}$$
$$- \sigma_{ij}^b \epsilon_{ij}^a + \sigma_{ij}^a \epsilon_{ij}^a \} \, d\tau - \int_{\nu_b'} \{ W(\epsilon_{ij}^b) - W(\epsilon_{ij}^a) \} d\tau$$
$$[\text{I-7}]$$

The above is equivalent, after combining terms, to

$$V_b - V_a = \overline{W(\epsilon_{ij}^a)}(\nu_b' - \nu_a') + \int_{\nu_b} \left\{ \int_{\epsilon_{ij}^b}^{\epsilon_{ij}^a} (\sigma_{ij}^a - \sigma_{ij}) d\epsilon_{ij} \, d\tau \right\}$$
$$[\text{I-8}]$$

or, after applying the divergence theorem, to

$$V_b - V_a = W(\epsilon_{ij}^a)(v_b' - v_a') + \int\limits_{\Delta A} \int\limits_{u_i^b}^{u_i^a} (T_i^a - T_i)\,du_i\,dA$$

[I-9]

Since ΔA may be made closed with no further contribution to the integral in [I-9], we obtain

$$V_b - V_a = W(\epsilon_{ij}^a)(v_b' - v_a') + \int\limits_{v_a'-v_b'} \int\limits_{\epsilon_{ij}^b}^{\epsilon_{ij}^a} (\sigma_{ij}^a - \sigma_{ij})d\epsilon_{ij}\,d\tau$$

[I-10]

Dividing by $(v_b' - v_a')$, we obtain the important result that

$$\frac{(V_b - V_a)}{(v_b' - v_a')} = \frac{\delta V}{\delta v} = W(\epsilon_{ij}^a) + \int\limits_{\epsilon_{ij}^b}^{\epsilon_{ij}^a} (\sigma_{ij}^a - \sigma_{ij})\,d\epsilon_{ij}$$

$$= W(\epsilon_{ij}^a) + \sigma(\delta v^n)$$

[I-11]

where $n > 0$. In the limit where $\delta v \to 0$, Eq. [I-11] reads

$$\frac{\partial V}{\partial v} = W(\epsilon_{ij}^a)$$

[I-12]

APPENDIX II

RESOLUTION OF THE COUPLED FIELD PROBLEM

Our elastic field is represented by the linear operator L_1 in D operating on a suitable stress function, u. Since the derivatives of u are related to stress, the boundary conditions can be expressed by the operation of another linear operator L_1' on Σ as suggested in Fig. 1. The phenomenon of fracture can be represented by a density field in $D + \Sigma + D'$ such that the density, given by $p(x, y, z)$, vanishes outside D. The actual rate of change in density, corresponding to a change in the size and shape of D, constitutes the Cauchy problem involving the linear parabolic operator L_2, where $L_2[\phi] = 0$ and $\phi(t = 0) = f(x, y, z)$. In the above, ϕ represents the position of Σ and changes in ϕ with time (i.e., Cauchy solution) represent boundary changes.

To solve this coupled field problem, we propose the following linearized self-consistent scheme. Suppose that the eigenfunctions of L_2 can be expressed as a linear combination of momentum eigenfunctions; i.e.,

$$u = \int\limits_0^\infty a(\boldsymbol{\omega})\,e^{i\boldsymbol{\omega}\cdot\boldsymbol{r}}\,d^3h(\boldsymbol{\omega})$$

[II-1]

where the integral is of the Riemann-Stieltjes type. In addition, let the integrand, I, itself satisfy $L_1[I] = 0$ and also satisfy the boundary conditions

$$\{L_1[I] = 0\}_\Sigma$$

This is not the same situation that arises in the typical homogeneous eigenvalue problem since, in the present case, the boundary Σ is not coincident with any natural coordinate in D and therefore, satisfying the boundary conditions in this fashion is impossible. In other words, the equations $\{L_1[I] = 0\}_\Sigma$ are only approximately satisfied and, for the cases we are discussing, this approximation consists of retaining only terms linear in $a\omega$ and an approximation to be discussed shortly. It should be noted that this type of lin-

earization is separate from the linearization scheme we shall adopt in coupling the field L_1 to L_2. For reasons to be made clear shortly, Eqs. [II-1] and [II-2] we can rewrite [II-1] in the form

$$u = \int\limits_0^\infty g(y)\,a(\omega)\,e^{i\omega x}dh'(\omega)$$

[II-2]

where we have i) assumed a two dimensionality for the system and ii) extracted the y dependence in this particular way.* Now for the boundary ϕ we suppose the

*This presupposes that L_1 is separable.

form

$$\phi(\equiv y \ni \Sigma) = \int\limits_0^\infty \delta(\omega, t)\,e^{i\omega x}dh''(\omega_x)$$

[II-3]

where the entire time dependence is contained in the amplitudes $\delta(\omega, t)$. If we now rewrite the operator L_2 as $L_{2t} + L_{2x}$ where L_{2t} is the time part and L_{2x} the spatial part, and substitute the right side of [II-3], we obtain

$$L_{2t}\left\{\int\limits_0^\infty \delta(\omega t)\,e^{i\omega x}dh''(\omega)\right\} = \int\limits_0^\infty L_2\,\delta(\omega,t)\,e^{i\omega x}dh''(\omega)$$

$$= \int\limits_0^\infty \delta(\omega, t)\,L_2\,e^{i\omega x}dh''(\omega)$$

[II-4]

The orthogonality of the Fourier components allows us to rewrite [II-4] as

$$L_{2t}\,\delta(\omega, t)\,e^{i\omega x} = \delta(\omega, t)\,L_{2x}\,e^{i\omega x}$$

[II-5]

Furthermore, if we substitute the form [II-2] into the equation $\{L_1'[u] = 0\}_\Sigma$, we find that,

$$L_1'\left[\int\limits_0^\infty g(y)a(\omega)\,e^{i\omega x}dh'(\omega)\right]_{y=\int\limits_0^\infty \delta(\omega,t)\,e^{i\omega x}dh''(\omega)} = 0$$

leads to, if we retain only terms linear in $a\omega$ and $\delta\omega$, relations of the form $a(\omega) = d\delta(\omega)$, where d is a function that may depend upon ω. This result is common to perturbation methods[4] and is impossible to show in general. The validity of the procedure depends upon the differential operators L_1 and L_2 and the boundary conditions. The procedure is now outlined but without losing any generality we shall confine considerations to only the even harmonics; viz., $a\cos\omega x$.

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