HYDROGEN AND INTERFACIAL COHESION

James R. Rice
Division of Engineering
Brown University
Providence, R. I., 02912, USA

Introduction

"Is there a general mechanism capable of explaining (or rational-izing) hydrogen embrittlement effects for the variety of alloy systems and fracture modes which are observed?"

The question was posed by Professor I. M. Bernstein with the sug-gestion that this paper (based on my presentation at the conference panel discussion) should try to address it. Certainly, to the extent that H damage can take the form of high-pressure gas precipitation in cavities or of hydride formation, it is unlikely that a single mechanism exists.

Yet, it does seem that a wide range of H embrittlement phenomena can be explained in terms of the old and somewhat-maligned concept of a "loss of cohesion" due to interstitially dissolved H . Unfortunately, the concept has not yet been made sufficiently quantitative for direct experimental test. Also, discussions in terms of it seem often to bear little relation to the actual topography of fracture: the discussion is usually phrased in terms of a cleavage-like separation of crystal lattice planes whereas instead it seems that interfaces (between grains, inclu-sions and matrix, or phases) are the fracture paths most often sensitized by dissolved H . Finally, a loss-of-cohesion explanation is often con-sidered to imply a cleavage-like macroscopic mode of fracture advance, whereas H can also affect ductile fractures. But here it is important to remark that ductile fracture involves the nucleation and plastic growth and joining of fissures, and certainly the former step will be very much affected by any H-induced alterations of the cohesion between void-nucleating particles and the surrounding matrix.

Indeed, a general observation from a number of Fe, Ni, and Al alloy systems (1,2) is that the types of microstructural fracture paths ob-served in H embrittled material are not greatly different in kind from those which can normally be induced in that material, in the absence of H , by differences in metallurgical treatment and composition of second-

ary elements or in test conditions. Intergranular fractures (e.g., in "temper embrittled" steels), particle-matrix or phase boundary separations, and, in some materials, transgranular cleavages are all normally possible paths, and these must be regarded as competitive in general, with the favored path or combination of paths being controllable, albeit indirectly, by metallurgical treatment and the like. Thus it seems reasonable to view dissolved H as affecting the ease with which all of these could be favored in the final fracture. Normally, all adsorping interfacial paths will exhibit reduced cohesion in the presence of H (although the opposite can happen, at least in principle, for some interfaces), and the path or paths exhibited finally on a fractured surface should indeed be dependent on variables of metallurgical treatment, which might be viewed as setting "initial conditions" on cohesive properties, as well as on the local equilibrating potential of dissolved H, the kinetics of its transport, and on the intensity of local stress concentrations that can be developed on any particular interface.

In supporting cohesion effects as a general mechanism of H embrittlement, I proceed from a tacit assumption that any effects of H on fracture, in the absence of the formation of new solid or high pressure gaseous phases, must be explainable in terms of the effect of H on the cohesive strength of interfaces or of the effect of H on processes of plastic flow, since all normal fracture mechanisms seem explainable (not yet quantitatively!) in terms of these. But in temperature ranges for which H is mobile, there seems to be only a minor effect on plastic flow, if macroscopic stress-strain curves can be taken as indicative, and thus one tends to be left by elimination with cohesion.

Why, however, should H occupy a unique position as an embrittling agent? A partial answer is that H is probably not intrinsically unique as regards its effect on cohesion. Embrittling effects of comparable magnitude would be expected of other dissolved elements (e.g., perhaps Bi in Cu (3), the various "temper embrittling" elements P, Pb, Sn, An, etc. in steels, etc.) which tend to segregate on interfaces, if these had the mobility to make possible physically the separation of an interface at conditions approaching constant equilibrating potential of the segregated species. Such mobility seems to be unique to H at ordinary temperatures. Other elements can be present on an interface only insofar as demanded by equilibrium at some higher prior treatment temperature when the element was mobile. This segregation, per se, may impair cohesion, but the greater impairment of cohesion that results when matter diffuses to an interface, in response to the lowering of its potential by locally elevated stresses, is available only when the element is mobile.

Theory of Interfacial Cleavage

Since apparently brittle, cleavage-like separations of interfaces seem to occur in the presence of dissolved H , one should inquire as to the effect of H on answers to the following questions: (i) What fundamental material properties allow an atomistically sharp crack configuration on a given interface to be stable against crack tip blunting by dislocation emission? In materials for which the configuration is stable, it is presumed that cleavage is possible, and one then wants

additionally to ask (ii) What circumstances allow the generation of sufficiently high local stresses on interfaces, so as to take advantage of the theoretical possibility of cleavage and actually <u>initiate</u> a crack?

Question (i) has been raised previously in connection with the theory of brittle vs. ductile behavior of crystals. Kelly (4) and Kelly, Tyson and Cottrell (5) addressed it in terms of the stress field predicted over atomic dimensions from the elasticity solution for a sharp crack tip, and the issue of whether the theoretical strength for cleavage (σ_c) or shear (τ_c) would first be reached. According to this concept as adapted for a crack on an interface, a sufficient lowering of σ_c for the interface by adsorped H , in circumstances for which τ_c in the adjacent lattice is little changed, would allow an atomistically sharp mode of crack advance on interfaces for which the sharp-tipped configuration would not normally be stable against dislocation blunting. Hondros and McLean (3) analyze embrittlement by Bi segregation on Cu grain boundaries in these terms. Also, some transition of this kind seems to be present in the H embrittlement of fcc polycrystals, e.g. Ni (6) and Al (7). Grain interfaces in these materials are apparently incapable of cleavage under normal conditions, but can sustain brittle cracks in the presence of H at sufficiently high potential.

However, the comparison of σ_c and τ_c with predicted stresses near a sharp tipped crack would seem to be an oversimplified approach, owing to the severe stress gradients, and a more careful assessment of the process of dislocation nucleation from a crack tip seems to be merited. Armstrong (8) and Kitajima (9) have discussed the problem, and a full analysis of nucleation from a crack tip in a crystal has been given by Rice and Thomson (10). Here, I follow that same analysis but generalize it in a manner suitable to the crack on an interface. Still, it is well to remember that the critical sizes and distances involved in the R&T analysis are all comparable to lattice dimensions, and the problem of brittle vs. ductile response will have a full answer only when analyzed by lattice theory.

Consider, then a crack in an interface. This may represent a grain interface as in fig. 1(a) or the interface between a 2nd phase particle, potentially a void nucleator, and the surrounding lattice as in fig. 1(b). In either case, we focus on the crack tip as in fig. 1(c) and follow R&T in assuming that the crack is advancing in an atomistically sharp form, and testing the stability of the tip configuration against plastic blunting. This is done by imagining that local stresses near the crack exist of magnitude sufficient to propagate it according to the Griffith theory (or, equivalently (11,12), to a model based on a curve of cohesive stress vs. separation distance) and computing the energy U_{act} necessary to nucleate a dislocation from the tip.

If $U_{act} < 0$, it is assumed that dislocations are spontaneously emitted from the tip, that the atomistically sharp tip configuration is unstable, and that the interface cannot cleave. On the other hand, if $U_{act} > 0$, an energy barrier exists against dislocation nucleation and the tip can remain atomistically sharp. This means that the interface can cleave, and there remains only the necessity of generating sufficient interfacial stress to generate a crack. The two cases are illustrated in fig. 1(d).

It is worth noting that even if the crack tip remains atomistically sharp, the corresponding critical Griffith elastic crack tip stress field typically involves shear stresses over a size scale of the order of $10^4 b$ or so that are large enough to move existing dislocations (this figure corresponds to a Griffith surface energy of $\mu b/10$ and a shear stress of $3 \times 10^{-3} \mu$ to move existing dislocations, where $\mu =$ shear modulus and $b =$ lattice spacing). Also, dislocations may occasionally intersect the crack immediately at its tip and blunt it, and for these reasons the net energy flux to the crack tip region may far exceed the Griffith value even when the atomistically sharp mode is possible.

Energy of dislocation nucleation from crack tip

The R&T procedure is now directly adopted for the case of a crack on an interface. Equation (17) of their paper gives an expression for the energy U_{act} required to create a semi-circular dislocation loop of radius rb ($b =$ Burgers vector) in a crystal having the core cut-off radius $\xi_0 b$ according to the Hirth and Lothe (13) procedure. The expression about to be given is different only in that I distinguish between the interfacial "surface" energy γ_{int} (where $2\gamma_{int} =$ work of reversible separation of interface) and the lattice surface energy γ_{lat}, associated with the step that forms at the crack tip when the dislocation is nucleated. The R&T analysis treated the crystal as if it were elastically isotropic, and I adopt the same simplification for this first estimate here and neglect also the difference in elastic properties between the materials on the two sides of the interface. Thus, rewriting eq.(17) of R&T with the obvious modifications,

$$U_{act} = \frac{2-\nu}{8(1-\nu)} \mu b^3 r \log \frac{r}{\xi_0} + \frac{2}{\beta'} \gamma_{lat} b^2 (r-\xi_0)$$
$$- \frac{1.395}{\beta} \frac{b^2}{\sqrt{(1-\nu)}} \sqrt{\mu b \gamma_{int}} \; (r^{3/2}-\xi_0^{3/2}) \tag{1}$$

Here $\mu =$ shear modulus, $\nu =$ Poisson ratio, β and β' are orientation factors given by $1/\beta' = \sin \phi \cos \psi$, $1/\beta = (1/\beta') \cos (\phi/2)$, where the crack front is imagined to coincide with the intersection between the slip plane and the interface, ϕ is the angle between the uncracked portion of the interface and the slip plane, and ψ is the angle between the Burgers vector and a line in the slip plane having direction perpendicular to the crack front; see R&T for further details of notation.

In the expression for U_{act}, the first term is the dislocation loop self energy, the second term is the energy of the ledge that is created, and the last term represents the energy decrement due to introducing the dislocation in the stress field of the crack tip. The latter is calculated at critical Griffith conditions, which accounts for its proportionality to $\sqrt{\mu \gamma_{int}}$. While the variation with r is thought to be rather accurate in each term, there is some arbitrariness in choice of the cut-off terms.

It turns out that by redefinition of variables, the calculation of the maximum value of U_{act} (maximized with respect to r) can be made to coincide with that of R&T, and the R&T result given by their fig. 7 is directly applicable here. Thus, the plot of a dimensionless activation energy u_{act}, given by

$$u_{act} = \left[\frac{8(1-\nu)\beta'}{(2-\nu)^2\beta^2}\right] \frac{U_{act}}{\mu b^3} \frac{\gamma_{int}}{\gamma_{lat}} , \tag{2}$$

in terms of the dimensionless parameters

$$S = \left[\frac{16(1-\nu)}{5\beta'(2-\nu)}\right] \frac{\gamma_{lat}}{\mu b} , \quad R = \left[\frac{16\beta'}{5(2-\nu)\beta^2}\right]\xi_0 \frac{\gamma_{int}}{\gamma_{lat}} , \tag{3}$$

has exactly the same form as that in R&T, and the parameters u_{act}, S , R as defined here coincide with those of eqs.(19,20) of R&T when $\gamma_{lat} = \gamma_{int} = \gamma$, say. The result is shown in fig. 2 and, as suggested in the labelling of that figure, the terms within [...] in each of the above expressions are close to unity for typical values of the orientation parameters.

Figure 2 is to be read as follows: For a given interface we identify the parameters S and R , and read off the corresponding value of U_{act} from the figure. If $U_{act} < 0$, dislocation emission is spontaneous and it is presumed that an atomistically sharp crack is not stable against dislocation blunting, but if $U_{act} > 0$ there is an energy barrier against dislocation nucleation and the interface can possibly be subjected to a brittle cleavage separation, the problem then being one of initiation of the interfacial crack.

What does it take to embrittle a fcc polycrystal?

Consider a Ni polycrystal at room temperature. It is known (6) that under a sufficient potential of H charging, a brittle mode of grain boundary cracking can be made to occur. I shall try to analyze this as an interfacial cleavage, explainable in terms of the concepts represented by fig. 2.

Using the same data sources as R&T, and considering first the case in which no H is present, we set $\xi_0 = 2$ for fcc solids, note that $\gamma_{lat}/\mu b \approx .09$ for Ni , and choose $\gamma_{int}/\gamma_{lat}$ as 0.75 . Then, when the bracketed terms in eqs.(3) differ little from unity, we have $S \approx .09$ and $R \approx 1.5$, and it is seen from fig. 2 that U_{act} is negative. Thus grain boundaries in Ni (or, indeed, in Al, for which $S \approx .12$, or in other fcc metals) are not normally capable of a cleavage separation.

Assuming now that the polycrystal is in equilibrium with H at a high potential, the various parameters that make up S and R will be altered. If we assume that the core cut-off and the ratio of surface energies is little altered by H , then R remains unchanged at 1.5 and

S must be reduced from ≈ 0.09 to ≈ 0.05 for brittle cleavage to be possible. Thus, if H reduces γ_{lat} by

$$\Delta\gamma_{lat} \approx (.09-.05)\ \mu b \approx 750\ ergs/cm^2 \quad , \quad \textit{,}$$

the grain boundaries will be embrittled according to the R&T model. This number is certainly attainable from the data given by Petch (14) in fig. 1 of his paper. His plot, while intended for Fe , is actually based on surface adsorption data for Ni , and suggests that reductions of γ_{lat} ranging from 800 to 950 $ergs/cm^2$ are readily obtainable by electrolytic charging with H . For comparison, $\gamma_{lat} \approx 1725\ ergs/cm^2$ normally for Ni .

When the same analysis is applied to Al polycrystals, with R = 1.5 and S = 0.12 in the absence of H , we find that $\Delta\gamma_{lat} \approx (.12-.05)\mu b \approx 490\ ergs/cm^2$ is necessary for embrittlement. This is a large fraction of the normal γ_{lat} of $\approx 840\ ergs/cm^2$, but should presumably be attainable at sufficient H charging. Indeed , experimentally, Al polycrystals can be embrittled (7). The other common fcc solids (Pb, Au, Cu , Ag) should have similar R values to Al and Ni, but have larger S values, ranging from .15 to .21, so that inordinately large reductions of γ_{lat} should be necessary to embrittle their grain boundaries. Hence H should have little effect on these, except perhaps at extremely high charging potential.

By contrast, bcc Fe should have a much tighter core, $\xi_0 \approx 2/3$, and even though S $\approx$ .11 in this case, the grain boundary should always be capable of a brittle separation, the problem being one of obtaining a sufficient stress concentration on the interface to initiate cracking. But fcc Fe polycrystals, assuming R $\approx$ 1.5 and S $\approx$ .11 as above, should not normally be capable of cleavage separations, and it should then be necessary to reduce γ_{lat} by $\Delta\gamma_{lat} \approx 1080\ ergs/cm^2$ to obtain brittleness, where $\gamma_{lat} \approx 1975\ ergs/cm^2$ normally.

Initiation of cleavage separations

Suppose that the interface _is_ capable of cleavage. How can a crack then be _initiated_? As suggested earlier, this question still cannot be answered with great certainty. Smith and Barnby (15) have reviewed theoretical approaches based on dislocation pile-ups. It suffices here to note that the two most important parameters associated with _initiation_ are the cohesive strength σ_c of the interface and its separation energy $2\gamma_{int}$. Essentially, it is necessary that stresses be created on the interface of magnitude equal, locally to σ_c , and that the stress-concentrating sources (pile-ups, plus macro-level applied stress) be able to deliver an energy $2\gamma_{int}$ to unit area of the interface so that the crack can progress along it. This applies to grain interfaces as well as to those between non-deforming particles and a surrounding ductile matrix, where failure leads to a cavity which grows and coalesces in a ductile manner. Hence, alterations of σ_c and/or γ_{int} should affect both the extent of microfracturing and level of stress or deformation at which fracture initiates. Since σ_c and γ_{int} are the important fracture parameters, it is of interest to study the effect of a segregated species

such as H upon them. This can be done through a new approach, that follows, to the thermodynamics of an interface.

Thermodynamics of Interfacial Separation in Presence of a Mobile Species

This will be a brief account of a subject on which a full paper is planned for a later date. See also (16).

Consider a solid interface which is loaded by normal stress σ and is at composition equilibrium with a mobile, soluble substance which, for convenience, I consider to be available in a fluid phase at potential μ per unit mass, fig. 3(a) (μ as used here is not to be confused with its earlier use as a shear modulus). Proceeding in the Gibbs sense of sur- face excesses, we let ϕ be the excess Helmholtz free energy per unit area of interface, we let δ be the excess opening displacement across the interface, and we let Γ be the interfacial concentration excess in units of mass per unit area. I consider temperature as constant in this account, and do not list it explicitly as a variable.

The parameters of greatest interest to fracture models are shown in fig. 3(b), where σ is plotted against δ . Here, however, it is essen- tial to realize that there is no universal relation between the two when a mobile species is present. Instead we write either

$$\sigma = \bar{\sigma}(\delta, \Gamma) \quad \text{or} \quad \sigma = \hat{\sigma}(\delta, \mu) \tag{4}$$

according to whether we wish to take either Γ or μ as the second variable. Thus the fracture parameters σ_c (maximum cohesive stress) and $2\gamma_c$ (work of separation, called $2\gamma_{int}$ in previous sections) will be dependent on the way that μ or Γ varies during the separation and, as Oriani (17) has emphasized in connection with lattice separation, there will be two limiting cases: (i) separation at constant Γ , or "fast" separation, on a time scale which does not allow further matter transport to the interface, and (ii) separation at constant μ , or "slow" separation, on a time scale which allows full composition equilib- rium between the interface and a matter source at constant potential.

Kinetic considerations (diffusion, entry kinetics, etc.) will deter- mine which of the two cases is more nearly followed in some given circum- stance. Indeed, for most dissolved substances at ordinary temperatures, the mobility is so low that only separation at constant Γ is attainable physically, although either case should be attainable for H in the common metals, depending on the time scale, and at sufficiently elevated temper- ature either case may be attainable for other substances.

For separation at constant Γ , the cohesive strength and work of separation are

$$\bar{\sigma}_c(\Gamma) = \bar{\sigma}[\bar{\delta}_c(\Gamma), \Gamma] \quad , \quad 2\bar{\gamma}_c(\Gamma) = [\int \bar{\sigma}(\delta, \Gamma) d\delta]_{\Gamma \text{ const.}} \tag{5}$$

where $\bar{\delta}_c(\Gamma)$ is the separation displacement at which maximum stress

occurs and the integral on δ extends over all values greater than that for an unstressed interface at composition Γ. Similarly, for separation at constant μ, the fracture parameters are

$$\hat{\sigma}_c(\mu) = \hat{\sigma}[\hat{\delta}_c(\mu),\mu] \quad , \quad 2\hat{\gamma}_c(\mu) = [\int \hat{\sigma}(\delta,\mu)d\delta]_{\mu \text{ const.}} \quad (6)$$

where $\hat{\delta}_c(\mu)$ is the separation at maximum stress and the integral on δ extends over all values greater than that for the unstressed interface at potential μ.

The two limiting cases are describable in equilibrium thermostatical terms. Consider the Gibbs equation for the interface and a Lengendre transform of it:

$$\sigma d\delta + \mu d\Gamma = d\phi \quad , \quad \sigma d\delta - \Gamma d\mu = d(\phi - \mu\Gamma) \quad . \quad (7)$$

From these there follow the Maxwell relations

$$(\partial\sigma/\partial\Gamma)_\delta = (\partial\mu/\partial\delta)_\Gamma \quad , \quad (\partial\sigma/\partial\mu)_\delta = -(\partial\Gamma/\partial\delta)_\mu \quad . \quad (8)$$

Thus, by differentiating the expression above for $\hat{\gamma}_c(\mu)$, eq. (6), and applying the latter reciprocal relation, we obtain the following generalization of the Gibbs adsorbtion relation:

$$2d\hat{\gamma}_c(\mu)/d\mu = -[\Gamma_\infty(\mu) - \Gamma_o(\mu)] \quad , \quad (9)$$

where $\Gamma_o(\mu)$ is the surface excess on the unstressed interface at potential μ and $\Gamma_\infty(\mu)$ is the net excess concentration associated with the two completely separated surfaces. This could also be derived by combining the Gibbs adsorption relations for the separated surfaces with that for the unstressed interface, the latter being given by Hondros and McLean (3).

By differentiating the expression for $\bar{\gamma}_c(\Gamma)$ and using the first reciprocal relation, we obtain an analogous expression for the rate of change, with Γ :

$$2d\bar{\gamma}_c(\Gamma)/d\Gamma = [\mu_\infty(\Gamma) - \mu_o(\Gamma)] \quad , \quad (10)$$

where $\mu_o(\Gamma)$ is the potential corresponding to excess concentration Γ on the unstressed interface, and $\mu_\infty(\Gamma)$ the potential corresponding to net excess concentration Γ on the two completely separated surfaces. Hence, a specification of the adsorption isotherms for the unstressed interface and for the separated surfaces suffices for computation of both $d\hat{\gamma}_c(\mu)/d\mu$ and $d\bar{\gamma}_c(\Gamma)/d\Gamma$.

Also, differentiating the expressions above for $\hat{\sigma}_c(\mu)$, $\bar{\sigma}_c(\Gamma)$, noting that $\partial\sigma/\partial\delta$ vanishes at the maximum stress point, and using the reciprocal relations, the following relations are obtained for the alterations of maximum cohesive strength:

$$d\hat{\sigma}_c(\mu)/d\mu = -[\partial\Gamma(\delta,\mu)/\partial\delta]_{\delta=\hat{\delta}_c(\mu)}, \quad d\bar{\sigma}_c(\Gamma)/d\Gamma = [\partial\mu(\delta,\Gamma)/\partial\delta]_{\delta=\bar{\delta}_c(\Gamma)} \quad (11)$$

Finally, in the interest of brevity, I leave it to the reader to derive the following interesting result: Let an unstressed interface be at equilibrium at composition Γ' and potential μ' . Then the difference between the "fast" $(\Gamma=\Gamma')$ and "slow" $(\mu=\mu')$ fracture separation energies is

$$2\bar{\gamma}_c(\Gamma') - 2\hat{\gamma}_c(\mu') = \int_{\Gamma'}^{\Gamma''} [\mu_\infty(\Gamma'') - \mu_\infty(\Gamma)]d\Gamma \quad , \quad (12)$$

where $\mu = \mu_\infty(\Gamma)$ is again the equation of the adsorption isotherm for the two completely separated surfaces, and where Γ'' is the final excess concentration on the completely separated surfaces when these are separated at constant potential [thus $\mu' = \mu_\infty(\Gamma'')$] . Under very general conditions, one may assert that Γ on the free surfaces increases monotonically with μ , so that the integral is non-negative and

$$2\bar{\gamma}_c(\Gamma') \geq 2\hat{\gamma}_c(\mu') \quad , \quad (13)$$

with strict inequality holding whenever Γ'' differs from Γ' . Hence, while segregation per se may embrittle an interface, the greater embrittlement occurs when the segregant is mobile so that conditions of separation at constant μ can be approached.

Indeed, there seems to be no reason, in principle, why all mobile solutes should embrittle all interfaces on which they segregate. Whether the segregant embrittles or strengthens depends on the sign of the bracketed terms in eqs. (9,10). But the inequality of eq. (13) remains valid in either case.

Acknowledgement

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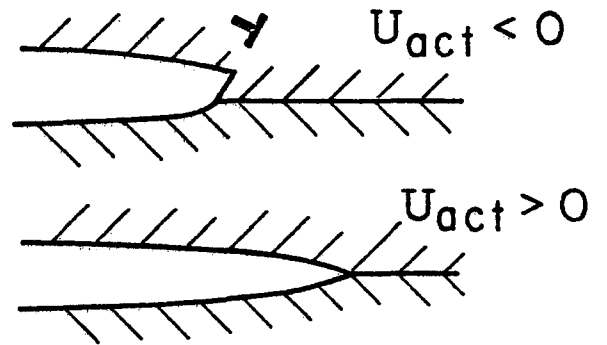17. R. A. Oriani: Berichte der Bunsen-Gesellschaft für phys. Chem., 1972, Vol. 76, p. 848.
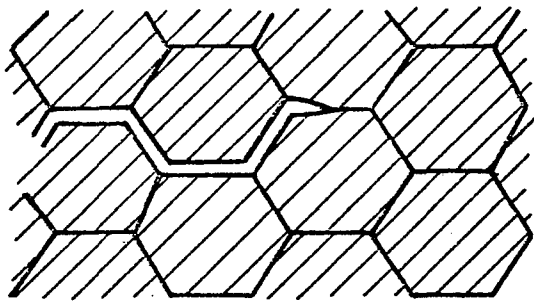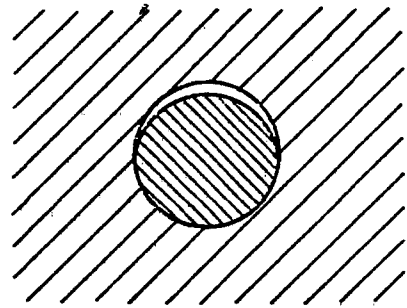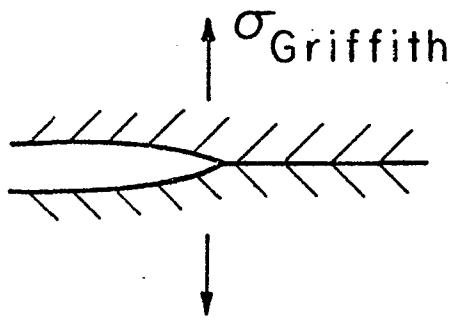
FIG. 1 (a) INTERGRANULAR CRACKING. (b) CRACKING OF PARTICLE/ MATRIX INTERFACE IN FORMATION OF DUCTILE RUPTURE CAVITY.

(c) ATOMISTICALLY SHARP CRACK TIP STRESSED TO CRITICAL CONDITIONS. (d) DUCTILE BLUNTING BY DISLOCATION NUCLEATION IF $U_{act} < 0$; CLEAVAGE IF $U_{act} > 0$.
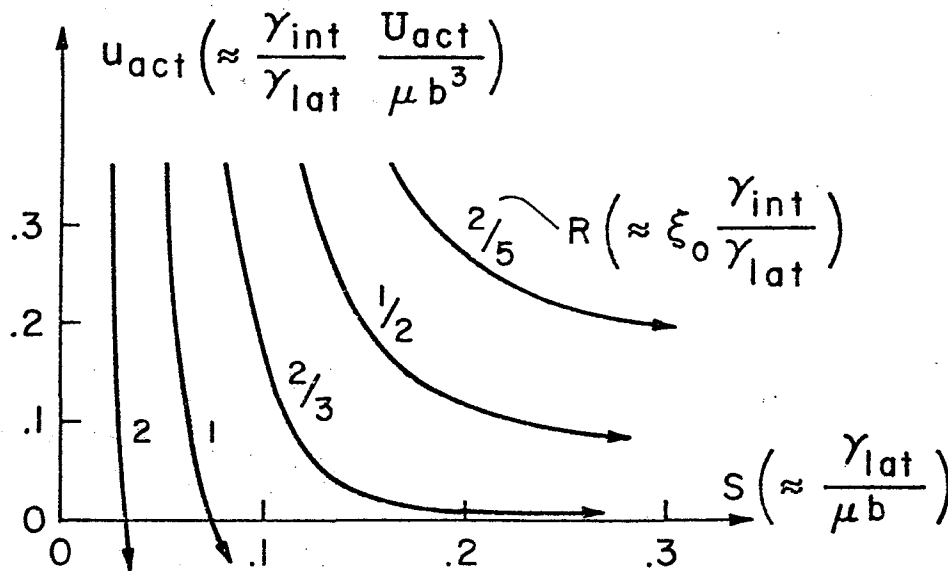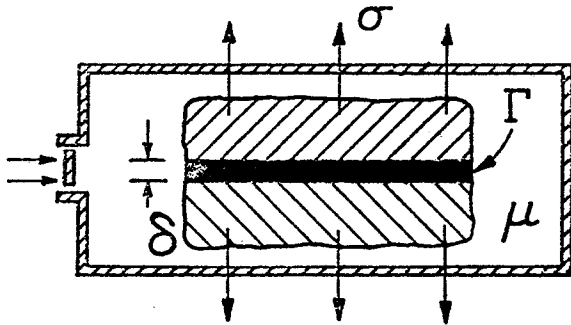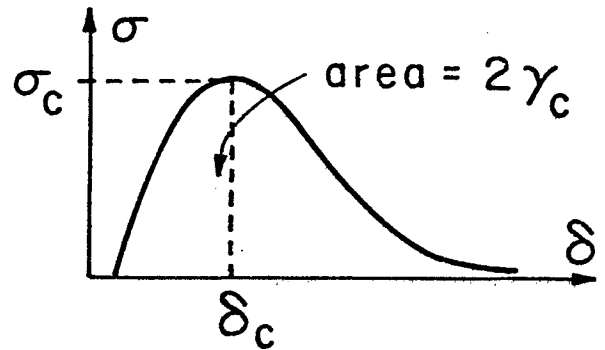
FIG. 2 ENERGY U_{act} OF DISLOCATION NUCLEATION FROM TIP OF INTERFACIAL CRACK AT CRITICAL CONDITION; SEE TEXT EQS. (2,3) FOR EXACT DEFINITIONS OF U_{act}, R, AND S. CLEAVAGE POSSIBLE IF $U_{act} > 0$.

FIG. 3 (a) INTERFACE UNDER STRESS σ, WITH EXCESS
SEPARATION δ AND EXCESS CONCENTRATION Γ
OF MOBILE SPECIES AT POTENTIAL μ. (b) STRESS
VERSUS SEPARATION; LATER CURVES FOR Γ CON-
STANT AND FOR μ CONSTANT ARE CONSIDERED.