PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1980 **295**, 139-149
doi: 10.1098/rsta.1980.0095

Phil. Trans. R. Soc. Lond. A **295**, 139–149 (1980)   [139]
Printed in Great Britain

IV. INTERFACIAL COHESION

Adsorption at grain boundaries and its effect on decohesion

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The energy of decohesion of a grain boundary as influenced by solute adsorption is considered. In the nearly reversible case, the change in this energy, and hence of the likelihood of decohesion, is developed in terms of the thermodynamic description of Gibbs. A distinction is made between the normal separation of a grain boundary, where cohesive force and cohesive energy are interrelated and relevant, and separation at a crack tip where cohesive force is not relevant but where a lattice trapping barrier exists. A number of irreversible decohesion phenomena that can be influenced by solute adsorption are also discussed.

Introduction

With the advent of sophisticated equipment for the study of surface topography, crystallography and chemistry, our understanding of adsorption at internal interfaces and the effects of adsorption on separation of these interfaces has greatly advanced, as reviewed, for example, in Chadwick & Smith (1976). The essential relation of the propensity for grain boundary separation to the sign of the net work per unit area of interface,

$$\phi = 2\gamma_s - \gamma_b, \tag{1}$$

where γ_s and γ_b are the surface energies of the created surfaces and the removed grain boundary, respectively, has been understood since the work of Orowan (1948), see also Inman *et al.* 1963; Hondros & McLean 1974; Seah 1975). However, there remain both differences in the detailed description and conflicting views on the proper interpretation of the terms in (1), particularly for the case where the separation process is irreversible, with local equilibrium not maintained. The purpose of the present work is to attempt to resolve these differences.

In succession, the topics considered are the relation between surface energy and cohesive force; the work of decohesion in a locally reversible, constrained equilibrium mode; lattice trapping and irreversible decohesion with a local activation barrier; and other irreversible effects.

Relation of surface energy to cohesive force

Consider a bicrystal with a planar grain boundary normal to the tensile axis. Suppose that the two crystals, initially at a mean equilibrium separation r_0, are isothermally and reversibly extended at constant pressure and with no change in the number of atoms. The free energy change as a function of separation from r_0 to r_∞ is as shown in figure 1*a*. The free energy change ΔG, divided by the area A, equals the quantity ϕ in (1). Equivalently the slope of the G–r curve is the normal force, required for the extension, and gives the stress–displacement curve in figure 1 *b* when normalized to unit area. The integral of $\sigma \mathrm{d}r$ from r_0 to r_∞ also gives the quantity ϕ. The broken curves in figure 1 represent possible changes accompanying solute adsorption to the grain boundary and free surfaces.

Oriani (1972) and Seah (1975, 1976) have related the maximum stress σ_{m} to the cohesive force for brittle fracture along a grain boundary and imply that changes in σ_{m} with solute adsorption are the dominant impurity effects influencing the brittle fracture stress. This would be true if the *mode* of fracture were one of uniformly stretching the grain boundary in tension. In such a case, the boundary would separate irreversibly when the stress σ_{m} was reached and, provided the compliance of the elastically strained crystal and the machine applying the load were sufficient, attainment of the critical stress σ_{m} would be the fracture criterion. However, invariably, the mode of fracture is one of initiation and propagation of a crack along the boundary, as illustrated in figure 2 *a* where the crack is advancing in the x-direction. While an individual element of the separating surface follows the σ–r curve of figure 1 *b*, this curve is not at all directly connected to the critical local stress for crack propagation and σ_{m} is not the critical stress for decohesion as implied by Oriani (1972) and Seah (1975, 1976).

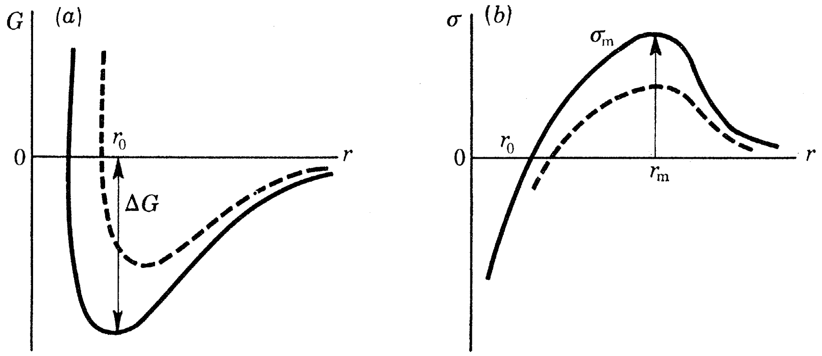

FIGURE 1. (*a*) Free energy–separation diagram for a grain boundary uniformly separating along its boundary plane. (*b*) Corresponding normal stress–separation diagram. Broken lines represent changes with solute adsorption.

Consider first the case of reversible, isothermal, isobaric, isomass extension of the crack. In this case, the details of the crack tip process need not be considered provided the configuration does not change. One could imagine a 'black box' enclosing the tip and moving with it as in figure 2 *a*. Per unit area of advance of the crack, the net change in surface energy is that for the creation of two unit areas of widely separated surface of energy γ_{s} and the destruction of unit area of boundary of energy γ_{b}. Hence, the net work to be supplied by release of elastic energy or external work is ϕ as in (1). Whether or not the process can proceed reversibly depends on the local specimen compliance.

For convenience, the degree of reversibility can be understood in terms of a stretched 'bond' model of the crack tip, but the same qualitative idea would apply for any form of atomic interaction. Consider first figure 2 *b* where three bonds at the tip of the crack are stretched from a displacement r_2 to the value r_{m} corresponding to the maximum stable bond configuration of figure 1 *b*. The centre bond then breaks and irreversibly relaxes to a displacement r_5 while the two neighbouring bonds relax to r_1. Once the broken bond extends from r_5 to r_∞, its contribution to the net work per unit area is again ϕ as in (1), since the state function variation ΔG is determined by the initial and final states alone. However; the bonds adjoining the broken bond also relax irreversibly from r_5 to r_1: the corresponding energy must be supplied in addition to the central bond, so the total energy per unit area will exceed ϕ by this amount. The extra energy will be the integral of $\sigma \mathrm{d}r$ from r_1 to r_{m}, so to this extent the quantity σ_{m} enters the calculation. In general, though, the compliances of neighbouring atoms lead to the situation of figure 2*c* where the adjoining bonds are stretched only to r_4 when the breaking bond is at r_{m}, and relax to r_3. The added energy contribution is then the hatched integral in figure 3*a*, which evidently has no direct relation to σ_{m}. More generally, an integral over all atoms must be performed as a function of x_{c} to determine the magnitude of the energy additional to ϕ, an exact analogue of the determination of the Peierls energy for dislocation motion. Such calculations have been performed for several cases of cracking of otherwise perfect pure crystals (Sinclair 1972, 1975; Hseih & Thomson 1973). These authors found such an additional energy barrier.

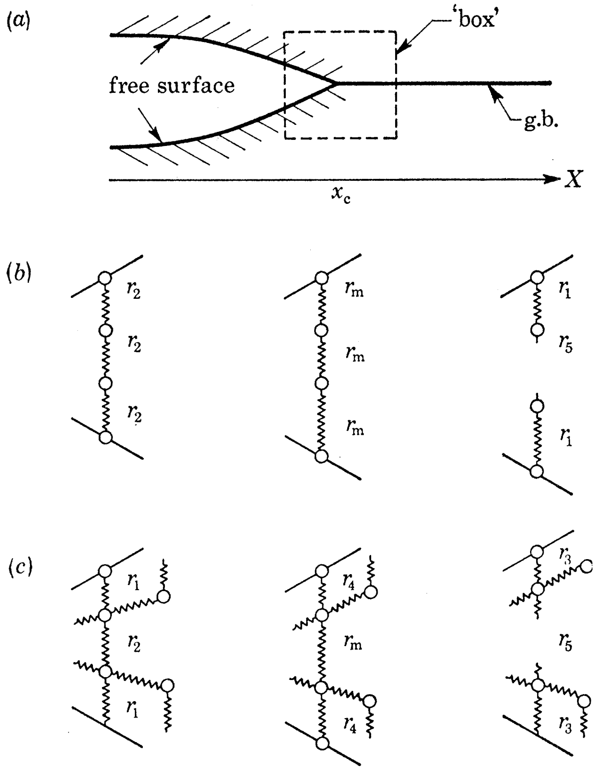

FIGURE 2. (*a*) Separation of a grain boundary by advance of a crack of length x_{c}. (*b*) Three bonds separating at a crack tip. (*c*) Three bonds separating at a crack tip with restraint by lateral bonds.

Limiting cases of the free energy–crack length relation are shown in figure 3*b*. In the limit of little compliance of the region near the crack tip, $r_3 \approx r_4$, the process is nearly reversible, the surface contribution to G is linear in crack area, or for unit length of crack, linear in x_{c} as denoted by curve A. The corresponding release of elastic energy and/or work done by the external device supplying the force is also linear in x_{c}, of the same magnitude but opposite in sign to the surface work, as shown by curve C. Together, curves A + C permit reversible extension with no change in free energy as shown in figure 3*a*. With less local rigidity, relaxations of the $r_4 \rightarrow r_3$ type contribute an excess activation energy and the resulting surface contribution would become the broken curve B. With the same external work term the sum B + C now has a periodic

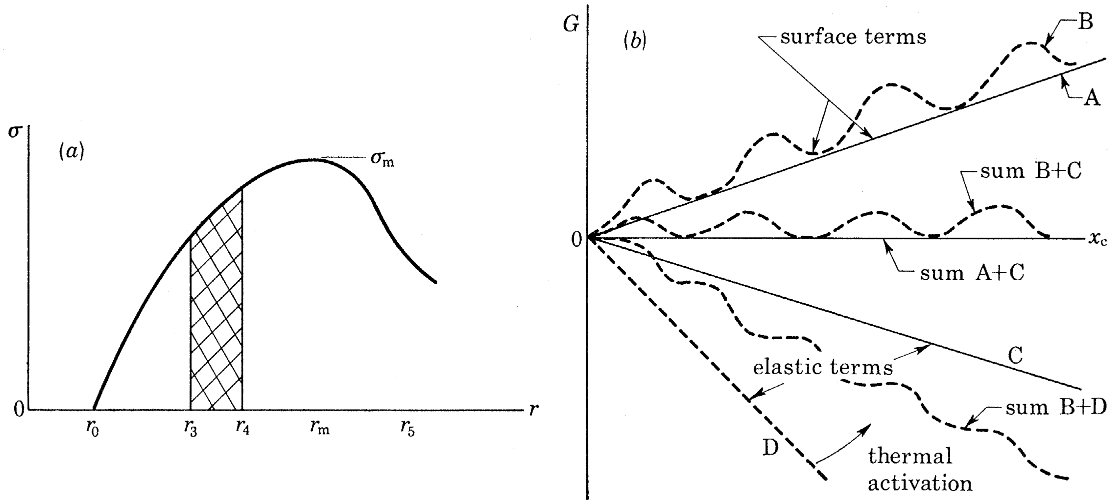

FIGURE 3. (*a*) Normal stress–separation curve corresponding to the processes of figure 2. (*b*) Corresponding total system free energy components – crack length relations. For the reversible case the surface work term A is balanced by the elastic energy release term C and the free energy of the system and the apparatus applying external forces is the horizontal curve. With lattice trapping, the surface term plus the elastic work term C leaves a trapping barrier, the curve B+C. If the barrier is to be overcome athermally, a greater work term D is required, leading to the sum B+D which has zero or negative slope everywhere.

activation barrier (lattice-trapping barrier). This barrier could in principle be surmounted by thermal activation. However, it is more likely for the typical room temperature case that the barrier be surmounted mainly athermally, in which case the external work term would have to be increased in magnitude to the value represented in curve D to remove the barrier effects.

More realistically, the variation of G with x_c in figure 3 would correspond to the cracking of a perfect crystal where the configuration would be regularly periodic with an atomic repeat distance. The variation for a separating boundary might more nearly resemble that in figure 4, with irregularities on the scale of the d.s.c. lattice of the boundary (Bollmann 1970) and an

FIGURE 4. Possible modification of oscillating total free energy curve of figure 3 by solute addition.

overall periodicity corresponding to a coincidence lattice spacing. In this case, the barrier might be overcome by a mixed athermal–thermal activation with the small barriers being surmounted thermally, or even conceivably by the zero-point quantum vibrational energy. Also, for either the case shown in figure 3 or figure 4, it is possible that a partial thermal contribution can be effected by the nucleation of double kinks over the lattice trapping barrier, followed by lateral motion of the kinks along the crack tip. This possibility has been discussed by Sinclair (1975) in analogy to the treatment by Lothe & Hirth (1959) of dislocation motion over the Peierls barrier.

Locally reversible crack extension

We now consider the various descriptions of ϕ as influenced by solute adsorption in the case A of figure 3*b* where no local irreversibility influences the cracking process. As done by Hondros (1965), Seah (1975), Seah & Hondros (1973) and others, we follow the description of Gibbs (1948) in treating surface excess quantities as the difference between quantities in the actual system and a hypothetical one in which bulk properties are uniform up to the surface in question. This model, because of its phenomenological nature, perforce exactly describes the surface energy, as does the closely related model of Guggenheim (1950), who considers the excess quantities to reside in a hypothetical surface phase of finite extent. Alternate statistical mechanical descriptions (McLean 1957; Hondros & Seah 1977; White & Coghlan 1977) or regular solution models (Stark & Marcus 1977; Guttman 1975, 1977), while quite informative in *modelling* solute adsorption at boundaries, are imprecise in describing actual cases because of uncertainties in atomic interactions. A similar situation occurs in the description of solute adsorption to stacking faults (Hirth 1970). Following the specific version of Gibbs treatment given by Hirth (1970, 1973), the differential forms of the combined statement of the first and second laws of thermodynamics for the excess internal energy U^{e} and Gibbs free energy G^{e} are

$$\mathrm{d}U^{\mathrm{e}} = -P\,\mathrm{d}V^{\mathrm{e}} + T\,\mathrm{d}S^{\mathrm{e}} + \gamma\,\mathrm{d}A + \mu_i\,\mathrm{d}n_i^{\mathrm{e}}, \tag{2}$$

$$\mathrm{d}G^{\mathrm{e}} = V^{\mathrm{e}}\,\mathrm{d}P - S^{\mathrm{e}}\,\mathrm{d}T + \gamma\,\mathrm{d}A + \mu_i\,\mathrm{d}n_i^{\mathrm{e}}, \tag{3}$$

where the superscript e indicates surface excess quantity, γ is the surface energy, $i = 1, 2\ldots$ indicates the component, V is volume, P is pressure, A is area, μ is chemical potential and n is number of atoms. The free energy of the hypothetical uniform bulk phases is

$$\mathrm{d}G^{\mathrm{m}} = V^{\mathrm{m}}\,\mathrm{d}P - S^{\mathrm{m}}\,\mathrm{d}T + \mu_i\,\mathrm{d}n_i^{\mathrm{m}} + \mathrm{d}w_{\mathrm{E}}, \tag{4}$$

where the quantities defined earlier refer now to bulk quantities and $\mathrm{d}w_{\mathrm{E}}$ is the elastic work term, including elastic energy stored in the crystal for the process of figure 2*a*, for example. Together, $\mathrm{d}G^{\mathrm{e}}$ and $\mathrm{d}G^{\mathrm{m}}$ give the total variation in free energy of the system:

$$\mathrm{d}G = V\,\mathrm{d}P - S\,\mathrm{d}T + \mu_i\,\mathrm{d}n_i + \gamma\,\mathrm{d}A + \mathrm{d}w_{\mathrm{E}}. \tag{5}$$

The Gibbs fundamental relation conjugate to (2) is

$$0 = V^{\mathrm{e}}\,\mathrm{d}P - S^{\mathrm{e}}\,\mathrm{d}T - A\,\mathrm{d}\gamma - n_i^{\mathrm{e}}\,\mathrm{d}\mu_i. \tag{6}$$

Where it is necessary to denote that (2) to (6) apply to a specific surface, a subscript α, where α = b or s for grain boundary or free surface, respectively, is added to the various thermodynamic state variables. This is obtained from (2) by integrating it over an equilibrated system and then differentiating the resulting expression for U^{e} (note that an equivalent operation cannot be performed for (3) because it contains mixed intensive and extensive variables). With the definition $\Gamma_i^{\alpha} = n_i^{\mathrm{e}}/A_{\alpha}$, and with $V^{\mathrm{e}} = 0$ as in Gibbs' derivation, (5) gives the Gibbs adsorption isotherm

$$(\mathrm{d}\gamma_{\alpha})_T = -\Gamma_i^{\alpha}\,\mathrm{d}\mu_i. \tag{7}$$

In general at least one of the μ_i is not independent because of constraints on bulk phases according to the phase rule.† For a binary system where the Gibbs dividing surface can be chosen so that $\Gamma_1 = 0$,

$$(\partial\gamma_{\alpha}/\partial\mu_2)_{T,P} = -\Gamma_2^{\alpha}, \tag{8}$$

with the constant P constraint applying only to the boundary case.

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† A careful discussion of such constraints as they influence surface thermodynamics is given by Cahn (1978).

As a first example, suppose that the crack extends at constant chemical potential of solute, examples being cracking with equilibration with a gas such as hydrogen at constant pressure or with equilibration by local diffusion between the surface and the underlying bulk phase. The integral form for (8) then gives

$$\begin{aligned}\phi &= 2\gamma_s^A - \gamma_b^A \\ &= 2\gamma_s^0 - \gamma_b^0 - \int_{\mu_2^0}^{\mu_2^A} (2\Gamma_2^s - \Gamma_2^b)\,\mathrm{d}\mu_2,\end{aligned} \tag{9}$$

where the superscript A indicates the equilibrated state, the superscript 0 refers to pure solvent, and the standard state for component 2 is taken as infinite dilution. The form of (9) for the equilibrated case is agreed upon by all who have considered the problem (Hondros & McLean 1974; Fine & Marcus 1971; Seah 1975; Rice 1976).

At elevated temperatures where data are available, Seah (1975, 1976) has found the empirical correlations that $\gamma_b \approx 0.33\gamma_s$ and $\Gamma_2^b \approx 0.40\Gamma_2^s$ and that $\Gamma_2^\alpha \approx$ const. in the dilute n_2 case. Then (9) becomes

$$\phi \approx 1.67\gamma_s^0 - 1.60\Gamma_2^s\,\Delta\mu_2. \tag{10}$$

With positive adsorption of solute, $\Gamma_2^s > 0$, (10) states that the work of separation is reduced by solute adsorption in the equilibrated case. Some reservations about this result are in order. First, one is generally interested in fracture near room temperature, where data on γ_α or Γ_i^α are generally unavailable. There is no fundamental reason why γ_b^0 cannot exceed $2\gamma_s^0$ at low temperature, even though experiment suggests otherwise at elevated temperatures, or why Γ_2^b cannot exceed Γ_2^s, either of which could reverse the trend of ϕ with n_2. While it is convenient to express Γ_2^α in monolayers, one must recall that the excess in the real system is distributed over the bulk phase in the vicinity of the boundary. Indeed, although many elevated temperature cases give Γ_i^α values less than one monolayer (Hondros 1965; Seah 1975), values greater than one monolayer have been found (Seah & Hondros 1973). Contrary to some earlier results, Bitler (1971) and Guttman (1975) have shown that multiple layer values of Γ_i^α are theoretically possible. The range of adsorption has been found (Lehovec 1952) to extend over hundreds of atomic distances in ionic crystals, i.e. over the Debye–Hückel length, and there is no reason this cannot occur in metals over the coherence length of an electron. Finally, entropy terms would tend to favour an increase of Γ_i^α with decreasing temperature, so a rapid buildup of Γ_2^b leading to $\Gamma_2^b > 2\Gamma_2^s$ at low temperatures is possible. The reverse trend, leading to a more rapid decrease of ϕ with solute than expected from high temperature data is also possible.

Seah (1975, 1976) has suggested that at low temperatures, where atom rearrangement by diffusive processes is slow, a constrained separation is possible where the excess Γ_2^b is 'inherited' by the free surface so that $2\Gamma_2^s = \Gamma_2^b$. This situation is feasible, but he proceeds to consider the case of a solution obeying the Henry law and for which $\Gamma_2^\alpha \propto n_2^\alpha$, leading to $\phi = 2\gamma_s^0 - \gamma_b^0$, independent of Γ_2^α: this result is incorrect. The quantity ϕ is a thermodynamic state function with its difference between two states fixed, and the difference, reflected by the integral in (9), can be calculated for a *reversible* path, hypothetical if necessary. We doubt that there is a reversible path that would permit the result $2\Gamma_2^s = \Gamma_2^b$. In terms of the real distribution of excess solute with distance y from the boundary shown in figure 5, the hypothetical excess is given by

$$\Gamma_2^\alpha = \int_0^\infty [n_2(y) - n_2(\infty)]\,\mathrm{d}y. \tag{11}$$

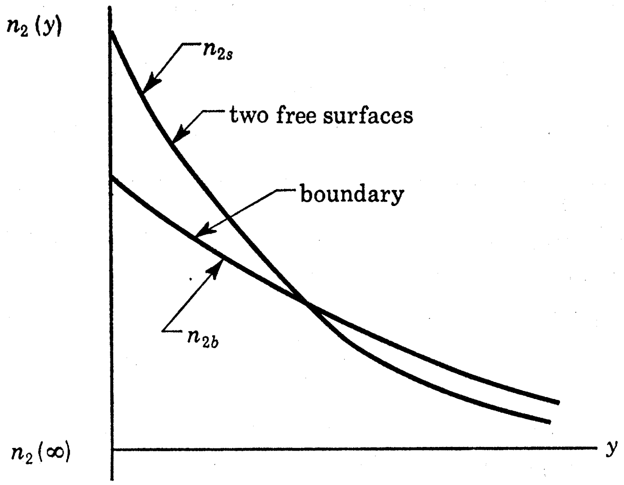

FIGURE 5. Distribution of solute giving rise to the equilibrium excess Γ_2^{α} for the surface and boundary cases.

For the case shown, even if $\Gamma_2^{\mathrm{b}} = 2\Gamma_2^{\mathrm{s}}$ for the local equilibrium situation, the *distribution* of $n_2(y)$ generally differs. Hence if the distribution for the boundary case is 'inherited' by the free surfaces with only local rearrangement in the surface layer permitted, then in addition to the work term ϕ, the elastic term would have to supply an additional 'chemical' term, given by

$$\frac{W_{\mathbf{ch}}}{A} = \int_0^{\infty} \int_{n_i(y)_{\mathrm{b}}}^{n_i(y)_{\mathrm{s}}} \frac{\mu_i}{\Omega}\,\mathrm{d}n_i\,\mathrm{d}y, \tag{12}$$

where Ω is the mean atomic volume of the solution. Here the subscripts on n_i indicate that the integral is to be performed between the two curves in figure 5. If one hypothesized diffusion to equilibrate the local distribution of $n_2(y)$, then diffusion to restore equilibration of the surface and bulk would also occur. In the more likely case, $2\Gamma_2^{\mathrm{s}} \neq \Gamma_2^{\mathrm{b}}$ at a given value of μ_2. Then, even though in the irreversible case the resultant $2\Gamma_2^{\mathrm{s}}$ equals the initial Γ_2^{b}, this result cannot be inserted into (9). Instead one must calculate ϕ by setting up a reversible cycle including the initial and the final states, such as: remove grain boundary at the equilibrium chemical potential μ_2^{A}; create free surface at μ_2^{A}; change chemical potential to μ_2^{B}; that which would be in equilibrium with the free surface created so that $2\Gamma_2^{\mathrm{s}}$ equals the initial Γ_2^{b}; remove free surface at μ_2^{B}; change chemical potential to μ_2^{A}; and recreate grain boundary at μ_2^{A}. The net work in this closed reversible cycle must be zero, which yields the result

$$2\gamma_{\mathrm{s}}^{\mathrm{A}} - 2\gamma_{\mathrm{s}}^{\mathrm{B}} = \int_{\mu_2^{\mathrm{A}}}^{\mu_2^{\mathrm{B}}} \Gamma_2^{\mathrm{s}}\,\mathrm{d}\mu_2,$$

which also could have been deduced directly from (6). Indeed this is simply the Gibbs adsorption isotherm for change of surface energy with adsorbate.

However, concealed in the reversible work cycle is a subtle effect which gives a different result for ϕ. The steps: remove free surface at μ_2^{B}; change chemical potential to μ_2^{A} and recreate grain boundary at this potential are the reversible equivalents of the cracking at constant composition. Hence in addition to the surface work terms the work of adsorption

$$\int_{\mu^{\mathbf{B}}}^{\mu^{\mathbf{A}}} \Gamma_2^{\mathrm{b}^{\mathbf{B}}}\,\mathrm{d}\mu$$

is also performed in this step. Thus, the work of separation in the constant composition case is

$$\phi = 2\gamma_s^A - \gamma_b^A - \int_{\mu_2^A}^{\mu_2^B} (2\Gamma_2^s - \Gamma_2^{b^B})\,d\mu. \tag{13}$$

This result was first obtained by Rice (1976) using a direct analytical development. Integration by parts of the two integrals in (13) gives the actual form $\int (\mu_2 - \mu_2^A)\,d\Gamma_2$ given by Rice (1976).

When $\Gamma_2^\alpha > 0$, $\mu_2^B < \mu_2^A$ and ϕ from (13) will be greater than that from (9), i.e., more work is required in the irreversible case. The value ϕ from (13) may be greater or less than $2\gamma_s^0 - \gamma_b^0$. Interestingly, use of (6) with (13) gives the alternate form for the work of separation in the irreversible case

$$\phi = 2\gamma_s^B - \gamma_b^B + \int_{\mu_2^A}^{\mu_2^B} (\Gamma_2^b - \Gamma_2^{b^B})\,d\mu. \tag{14}$$

That is, irreversible work in the case considered is related to the reversible work of separation of a system equilibrated at potential μ_2^B. This result may be useful in numerical calculations. In any case, as first noted by Rice (1976), Seah's result does not apply to the irreversible case.

Taken together, extrapolation of the high temperature results suggest that it is likely that solute adsorption decreases cohesion and makes cracking easier for the completely equilibrated case or for a case where equilibration begins locally. However, the opposite trend cannot be excluded on the basis of thermodynamics.

IRREVERSIBLE CRACK EXTENSION

Let us first consider irreversible effects other than those associated with the lattice trapping barrier. One example is that of figure 5 leading to the added term of (12). A more extreme variant of this type would occur where the concentrated solute adjacent to the boundary appeared preferentially on one of the two surfaces formed (Stark & Marcus 1977), giving two different integrals of the type in figure 5 and a further increase in w_{ch} as in (12). Another is plastic work w_p associated with dislocation generation and motion in the concentrated stress field at the crack tip, leading to an added required work term as first shown by Orowan (1948). Solute adsorption can increase w_p, for example by making edge dislocation nucleation at the free surface near the crack tip easier by reducing the energy of the surface step created in such nucleation (Rice & Thompson 1974) or by reducing the Peierls stress for dislocation motion (Arsenault 1968). Solute can also decrease w_p, for example by forming rigid surface adsorbate bonds which prevent surface step formation in dislocation nucleation (Gilman 1977) or by increasing the pinning or drag forces which reduce dislocation motion by solid solution effects. Another possibility is that solute changes the tendency for slip inhomogeneity, or local slip band spacing (hydrogen increases this tendency in steel (Lee *et al.* 1978), while carbon decreases it): wider slip band spacing would reduce the blunting tendency at the crack tip and tend to promote a discontinuous mode of brittle separation (Hirth & Thomson 1971). The crack path on an atomic scale can be influenced by solute, either increasing the required work by increasing the surface roughness (more cleavage type steps in the direction of crack advance or a more zig-zag path at the crack tip) or vice versa. For rapid cracking, some of the release of elastic energy may result in local adiabatic heating (Doremus 1976) which would increase the required driving force via the $T\,dS$ term in (2). Doremus also suggests that Orowan (1948) was incorrect in equating a Griffith type (1920) energy approach and a critical stress approach. I disagree with Doremus, in that thermodynamics demands that a local energy release criterion or a local stress criterion at the crack tip must be identical unless thermal activation is involved. The local case may or may not correspond to the reversible case, of course, and one criterion for one of these cases would not correspond to the other criterion for the other case.

A somewhat more subtle effect occurs when the adsorption of solute to the new interfaces occurs after they are effectively separated to $r \gg r_m$ so that their interaction is negligible. Then the 'black box' concept of figure 2*a* would be misleading in that the apparent value of ϕ would be incorrect; the unequilibrated value of γ_s rather than the ultimate equilibrated value would be the appropriate one to use in the work balance. This effect would consistently explain the fact that hydrogen promotes brittle crack extension in iron, while oxygen, which has a greater heat of adsorption, not only does not promote crack extension, but nullifies the effect of hydrogen (Hancock & Johnson 1965). This would be a consistent explanation if oxygen both adsorbs to the pristine surface after it forms and physically blocks hydrogen molecules from the crack tip. A simple view of such a phenomenon would be a size effect with the larger adsorbed oxygen atom or molecule blocking the smaller hydrogen entity. The effect could be more complex: for example with a negative free electron density in the hydrostatic tension field of the crack tip causing oxygen attachment further from the tip, closing the tip region, and blocking hydrogen by the closing. An exactly analogous situation would occur if atomic rearrangement of either solute or solvent (of the type observed in l.e.e.d. measurements; see for example, Guttmann 1977), resulting in a decrease of free energy, occurred subsequent to creation of the free surfaces.

In a somewhat related way, for the situation of figure 2*a*, the stress concentration at the crack tip can influence the chemical potential of solute there and hence the attainment of local equilibrium. For example, for a hydrostatic pressure†, P, (5) for the bulk phase gives

$$(\partial\mu_i/\partial P)_{n_i,\,T,\,A} = (\partial V/\partial n_i)_{P,\,n_j,\,T,\,A} = \Omega_i (i \neq j), \tag{15}$$

where Ω_i is the partial atomic volume of component i. Thus, the presence of the stress field can change the chemical potential in the vicinity of the crack tip. At temperatures at which the solvent phase is mobile (by means of surface or volume diffusion) the hydrostatic tension field at the crack tip decreases the chemical potential of solvent at and near the grain boundary, according to (15), relative to the regions near the free surface, and thus causes atoms to flow to (vacancies to flow away from) the boundary, leading to possible crack tip blunting and advance of the crack under diffusive flow (Robertson 1966; Chuang & Rice 1973). The free energy dissipated by diffusion is an added work term which must be supplied by the elastic energy release and hence causes retardation of cracking.

At lower temperatures, the case of interest is that of an immobile solvent but a mobile interstitial solute (e.g. H in Fe). For such cases, Ω_2 is invariably positive so solute is attracted to the crack tip region. If cracking proceeds reversibly with flow of solute to the boundary region and flow of solute from the created surface back to the bulk or to the vapour to maintain μ_2 constant, the 'black box' model of figure 2*a* holds and the stress effected changes in solute concentration do not change ϕ or the cracking probability. If cracking proceeds intermittently, such that the crack is arrested, permitting flow of solute as above, but then proceeds through the enhanced solute region without equilibration of solute, then Γ_2^s will exceed the value for the

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† For simplicity throughout this treatment, only hydrostatic stress is considered. The same arguments would apply to other stress components and similar relations would apply with σ_{ij} replacing P and $V\epsilon_i$ replacing V, with ϵ_{ij} the strain.

equilibrated case, with the reservations discussed in connection with figure 5. This factor, by (9), reduces ϕ. However, the adsorption in the stress field also changes γ_b:

$$(\partial\gamma_b/\partial P)_{T,\,\mu_2} = V_b^e/A_b, \tag{16}$$

with $\Gamma_2^b > 0$ and the Gibbs surface selected so that $\Gamma_1^b = 0$, one expects $V_b^e/A_b > 0$ (because of the volume occupied by the excess atoms of component 2). This shows that γ_b will also be lowered by the adsorption in a hydrostatic tensile field. Again, it is possible that this effect offsets the effect on γ_s, so that ϕ may be increased or decreased.

An extreme example of this class of behaviour is found in niobium or other b.c.c. transition metals containing hydrogen (Gahr *et al.* 1977). In a crack within a grain, the hydrostatic tension field of the crack stabilizes the hydride phase locally, even though it is unstable in the absence of stress. The consequences in crack extension of this type at a boundary would be as discussed above except that the relevant γ_α values in the irreversible case would be those of the hydride phase.

For either the case of solute adsorption or stabilization of a phase, the influence on cracking could be indirect, of course. For example, then enhanced solute or stabilized phase could suppress plastic flow in the crack tip region, reducing w_p, and hence enhancing the cracking tendency.

Finally, we consider solute effects on the lattice trapping barrier in figures 3*b* and 4. There are no atomic calculations to provide guidance in this case. Analogy with the dislocation case for dilute adsorbate concentrations would suggest that the major effect of solute would be to reduce the periodicity in the boundary region and thus to reduce the barrier. Alternatively, particularly for more concentrated adsorbates, solute interactions could shift the r_4–r_3 lattice compliance effect of figure 2*c* in either direction and thus either increase or decrease the barrier.

Ternary component effects

While most of the specific discussion to this point has focused on binary solutions, the same results and trends apply to ternary solutions. Guttmann (1975) has presented a quasi-chemical model for adsorption in ternary systems. Again, this model gives very useful guidelines to classes of behaviour, but is only an approximation, while the Gibbs result is exact.

Specifically, the Maxwell relation resulting from (6) relates the surface excess of component 2 to that of component 3:

$$(\partial\Gamma_3^\alpha/\partial\mu_2)_{T,\,P,\,\mu_1,\,\mu_3} = (\partial\Gamma_2^\alpha/\partial\mu_3)_{T,\,P,\,\mu_1,\,\mu_2}, \tag{17}$$

from which one can interrelate Γ_2^α and Γ_3^α. Also, (7) expresses the change of γ_α with chemical potential of components 2 and 3, giving the more general form of (9):

$$\phi = 2\gamma_s^0 - \gamma_b^0 - \int_0^{\mu_2^A} (2\Gamma_2^s - \Gamma_2^b)_{\mu_3=0}\,d\mu_2 - \int_0^{\mu_3^A} (2\Gamma_3^s - \Gamma_3^b)_{\mu_2=\mu_2^A}\,d\mu_3. \tag{18}$$

Most of the effects of a third component on irreversible processes would be the same as those of the solute in the binary case and need no further discussion. There is an additional possibility however. One solute could preferentially adsorb to the grain boundary and, when exposed on the nascent crack surface, catalyse the adsorption of a third component from the vapour phase, making the decohesion more nearly approach the reversible, constant μ_i case and hence enhancing the decohesion process.

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SUMMARY AND CONCLUSIONS

For nearly reversible crack extension and equilibration of solute between surface and bulk phases, extrapolation of elevated temperature data indicates that solute adsorption should increase the likelihood of grain boundary decohesion. The probability of decohesion decreases when the crack separates continuously but where solute equilibration does not occur, but the effect has been underestimated in earlier treatments. For all other irreversible effects, solute can either increase or decrease the probability of decohesion. The maximum cohesive force for a boundary separating continuously over its entire area is directly related to the decohesive energy but is not related to the magnitude of the lattice trapping barrier.

The author is grateful to G. R. St Pierre for helpful comments and to the U.S. Office of Naval Research for support of this research under Contract N00014-75-C-0541. The author is pleased also to acknowledge helpful discussions with J. R. Rice and M. P. Seah.

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