SEGREGATION INDUCED EMBRITTLEMENT OF GRAIN INTERFACES^{*}

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ABSTRACT

Conditions are discussed under which an interface, possibly containing an adsorbed species, is capable of sustaining an atomistically sharp cleavage crack, rather than having any such crack blunt out via dislocation nucleation. Two models for ductile versus brittle interface response are discussed. One of these is applied to model grain boundaries in face centered cubic materials, and is used to compare predictions with experimental observations on the embrittlement of Cu polycrystals by the addition of dilute concentrations of Bi. The general results are in qualitative agreement, although the model predicts behavior that is, in general, more ductile than that observed experimentally. Several possible reasons for this excess ductility are discussed. An appendix presents an analysis of the work of reversible separation of an interface containing a segregated species. This is intended to clarify some issues recently raised in the literature on interfacial embrittlement, especially concerning the distinctions that must be drawn between expressions for cohesive energy reductions for interfacial separation at constant chemical potential, μ , versus separation with constant concentration, Γ , of the adsorbate species.

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I. INTRODUCTION

There exist normally ductile materials which exhibit brittle behavior when impurity atoms segregate to their grain boundaries. Examples of this occur in such phenomena as: (i) temper embrittlement of alloy steels -- embrittling elements such as phosphorous, tin, and antimony segregate to prior austenite grain boundaries during prolonged exposure to high temperatures (McMahon [1968]); (ii) the intergranular embrittlement of some alloys -- for example, a small Bi concentration in normally ductile Cu leads to observations of grain boundary segregation of the Bi, and intergranular fracture (Hondros and McLean [1974]); (iii) hydrogen embrittlement -- one possible mechanism of hydrogen embrittlement is thought to be a loss of cohesion of interfaces, due to augmented hydrogen concentrations at these sites (Rice [1976]).

The segregation generally occurs during heat treatment when the impurity atoms have some degree of mobility in the parent lattice. (Presumably, hydrogen could be mobile even at ordinary temperatures). The cause of the resultant brittleness is not yet definitively established, but it is often attributed to a decohesion of the grain boundaries, i.e., a reduction in the work required to reversibly separate these interfaces.

Some criterion is required to determine what is "brittle" or "ductile" behavior. Kelly, Tyson, and Cottrell [1967] proposed as a criterion for brittle fracture that if the ratio of the maximum tensile stress to the maximum shear stress in a crack tip stress field exceeded the ratio of the theoretical cleavage stress to the theoretical shear stress of the material in question, then brittle failure was possible, assuming that there were no thermally activated processes which would blunt the crack.

In this work, we have used a criterion developed by Rice and Thomson [1974] for ductile versus brittle behavior of crystals, and later extended by Rice [1976] to the case of interfaces. The essence of the Rice and Thomson approach is as follows: the existence of an "atomistically" sharp crack is postulated, and the question of the stability of this configuration against blunting via dislocation nucleation is posed as a necessary condition for brittle cleavage to be possible. The crack is loaded normal to its plane so that the Griffith criterion ($\mathcal{U} = 2\gamma$) is just short of being satisfied. The Rice and Thomson criterion involves the concept of an activation energy (U_{act}) which is the work required to nucleate a metastable loop of dislocation from the tip of the crack, thus blunting the crack. For now, it suffices to note that U_{act} is a function of the angular orientations of the slip plane and slip direction with respect to the crack front, the material's elastic constants, and 2γ , which is the reversible work, per unit area, necessary to separate two layers of atoms in the material lattice. If the activation energy is positive, the work required for dislocation nucleation is greater than that needed to form new surfaces via crack advance (2γ). We would then expect the crack to advance in a brittle manner. If, on the other hand, the activation energy is a negative quantity, we would expect that upon loading, the crack would blunt via dislocation nucleation before the critical Griffith conditions could be attained at the tip.

This approach was later extended by Rice [1976] to the case of a crack on a grain boundary. Here, the activation energy is still a function of orientation parameters, but it now depends on two different surface energy terms; $2\gamma_{int}$ which is the work per unit area necessary to reversibly split

open the grain boundary, and γ_{step} which is the work per unit area of new surface to form the "step" or "ledge" left behind at the crack tip after nucleation of the dislocation loop. This modification is especially useful if we may indeed consider the effect of impurity segregation to be a decohesion of the grain boundaries with a lowering of γ_{int} .

An alternate approach to the brittle versus ductile question is also discussed here. This asks: as the crack is loaded, and K , the stress intensity factor, is increased, which value is the first reached -- a K corresponding to the Griffith load (the crack propagates), or one corresponding to a load at which dislocation nucleation is possible (the crack blunts). As will be discussed later, a relationship between two dimensionless parameters, R_0 and S , from the modified Rice and Thomson criterion, is developed to define the limits of the brittle or ductile regions in the R_0 versus S plane. Predictions of brittle or ductile behavior of an interfacial crack are then possible.

Since the face centered cubic lattice has well defined slip systems, and since experimental data due to Hondros and McLean [1974] was available detailing the ductile or brittle behavior of Cu-Bi alloys, in cases for which the Bi is present in small concentrations and seems to be atomistically segregated to the grain boundaries, it was considered a good system for checking the validity of Rice and Thomson's criterion. The system also provided an opportunity to examine the orientation dependence, among grain interfaces of random orientation relative to the basic fcc lattice, of the question of brittle versus ductile response. For example, the experiments suggest that with increasing Bi segregation at the grain boundaries, a greater proportion of the interfaces sustain what appear to be brittle cleavage cracks.

II. MODEL OF A CRACK ON A GRAIN BOUNDARY

A grain boundary in our fcc material is modeled as a planar interface in a bicrystal. The grains are of arbitrary orientation, and the tensile axis is normal to the interface plane. Figure 1 shows the model and various orientation parameters. We assume the pre-existence of an atomistically sharp crack on the interface. [Several mechanisms for the nucleation of such a crack have been proposed; for example, dislocation pile-ups at grain boundaries or matrix-inclusion interfaces (Stroh [1954] and Hondros [1975])].

The essential question is: "Can a given interface cleave?" i.e., "Can the crack maintain its atomistically sharp configuration?" In this model, only one slip system intersecting the grain boundary needs to be activated for the crack to blunt.

Since we assume that the two grains in our model are independently of arbitrary orientation, it suffices to restrict our attention to one grain and the interface. We still must consider what constitutes an "arbitrary orientation". In this model, we chose to represent a single orientation by specifying the normal to the interface relative to the cell edge directions of the fcc lattice. This specifies the orientation of the grain with respect to the interface up to an arbitrary rotation about the chosen normal direction. To sample the range of possible orientations, about fifty points were indexed on the standard triangle of the (100) stereographic projection; these were used to represent different normal directions.

For each orientation, we consider each of the twelve slip systems, and determine the angles ϕ and ψ which are as previously indicated

in Figure 1. Here we make another assumption: the crack line is allowed to rotate so as to align itself with the intersection line of the interface and the slip plane in question. [It is important to note that this rotational freedom probably introduces some extra ductility into the model, for we allow the crack to find the most favorable position for dislocation nucleation before we ask whether that nucleation is possible]. It is now possible to make some prediction as to the ductile or brittle behavior of this orientation, based on the criteria of the next section.

III. CRITERIA FOR DUCTILE VS. BRITTLE RESPONSE OF A CRACK ON AN INTERFACE

Rice and Thomson Criterion

As we noted previously, the ductile versus brittle response criterion as developed for crystals by Rice and Thomson [1974] and later extended to interfaces between grains by Rice [1976] involves determining whether the activation energy for dislocation loop nucleation is positive or negative.

In the following discussion, $U(r)$ is a function whose value is the energy necessary to form a dislocation loop of radius rb , where b is the Burger's vector. U_{act} is the maximum value, on r , of $U(r)$, and hence is the "activation energy" necessary to nucleate a metastable dislocation loop. This activation energy consists of three parts -- the self energy of the dislocation loop, the energy required to form the ledge or step at the tip of the crack as the dislocation loop is formed, and the decrease in energy due to the fact that the dislocation is introduced into the stress field near the crack tip.

For the case of a crack on an interface, Rice [1976] gives the following expression:

$$U_{act} = \frac{2-v}{8(1-v)} \mu b^3 r \ln \left(\frac{8}{e^2} \frac{r}{\xi_0} \right) + \frac{2}{b} \gamma_{step} b^2 (r - \xi_0) - \frac{1.395}{b} \frac{b^2}{\sqrt{1-v}} \sqrt{\mu b \gamma_{int}} (r^{3/2} - \xi_0^{3/2}) \quad (1)$$

Here, ϕ , ψ , γ_{int} and γ_{step} are as previously defined; μ is the shear modulus, v is Poisson's ratio, rb is the radius of the dislocation loop, and $\xi_0 = r_0/b$ is the non-dimensional dislocation core cut off, with r_0 as defined by Hirth and Lothe [1968].

Also,

$$\frac{1}{\beta'} = \sin\phi \cos\psi ; \frac{1}{\beta} = \sin\phi \cos\psi \cos(\phi/2) \quad (2)$$

Rice also defined two dimensionless parameters and a dimensionless activation energy.

$$R_o = \left[\frac{16 \beta'}{5(2-\nu)\beta^2} \right] \epsilon_o \frac{\gamma_{int}}{\gamma_{step}} \quad S = \left[\frac{16(1-\nu)}{5\beta'(2-\nu)} \right] \frac{\gamma_{step}}{\mu b} \quad (3)$$

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

Or, expressing $U(r)$ in terms of R_o and S , letting $r' = r/\epsilon_o$, and noting that $8/e^2 \approx 1$

$$U(r') = \frac{5R_o}{16} \left\{ r' \ln r' + 5S(r'-1) - 1.395 \frac{5}{2} \sqrt{R_o S} \left[(r')^{3/2} - 1 \right] \right\} \quad (4)$$

In the grain boundary model, we calculated the parameters R_o and S , used an iteration procedure to solve $dU(r)/dr = 0$ for the value of r' that maximized the energy $U(r')$ then calculated that maximum value.

Figure 2 shows plots of dimensionless activation energy u_{act} versus S , for several different values of R_o . If we ignore the orientation dependence, choosing more or less representative values for ϕ , ψ , and ν ,

$$S \approx \frac{\gamma_{step}}{\mu b} \quad R_o \approx \frac{\epsilon_o \gamma_{int}}{\gamma_{step}} \quad u_{act} \approx \frac{\gamma_{int}}{\gamma_{step}} \frac{U_{act}}{\mu b^3}$$

Figure 2 should be understood as follows: for a given set of R_0 and S , calculated from material properties and orientation parameters via Eqns. (3), $u_{act} > 0$ implies cleavage is possible (if there is some means of nucleating the crack), and $u_{act} < 0$ implies that cleavage is not possible.

Alternate Approach to Brittle versus Ductile Criterion

An alternate approach to the determination of brittle versus ductile behavior asks the following question: as the crack is loaded, and the stress intensity factor is increased, which condition is first reached -- a K corresponding to the Griffith load (in which case the crack propagates in a brittle configuration); or a K corresponding to a load at which dislocation nucleation is possible (in which case the crack blunts)?

Writing the energy for a loop of radius r , nucleated under a general stress intensity K -- so that $2\gamma_{int}$ in Eqn. (1) is replaced by $\bar{U} \equiv (1-\nu)K^2/2\mu$:

$$U(r) = \mu b^3 r \frac{(2-\nu)}{8(1-\nu)} \ln \left(\frac{8}{e^2} \frac{r}{\xi_0} \right) + \frac{2}{B^2} \gamma_{step} b^2 (r - \xi_0) - \frac{1.395}{B} \frac{b^2}{\sqrt{1-\nu}} \sqrt{\mu b \bar{U} / 2} \left(r^{3/2} - \xi_0^{3/2} \right). \quad (5)$$

The first term is the self energy of the dislocation loop; the second is the ledge energy; the third is the decrease in energy due to introducing the dislocation into the crack tip stress field. Rearranging the last term of (5) with $\bar{U} = (1-\nu)K^2/2\mu$,

$$U(r) = \frac{2-\nu}{8(1-\nu)} \mu b^3 r \ln \left(\frac{8}{e^2} \frac{r}{\xi_0} \right) + \frac{2\gamma_{step} b^2 r}{B^2} - \frac{.986}{\sqrt{2}} \frac{K b^{5/2} r^{3/2}}{B} \quad (6)$$

when the additive constants, irrelevant to the present development, are deleted.

To calculate the K that would be sufficient to nucleate a metastable dislocation loop, we must satisfy two conditions. First, the forces acting on the dislocation loop ("force" being the derivative of energy with respect to r) at equilibrium, are given by

$$\frac{dU}{dr} = \frac{2-\nu}{8(1-\nu)} \mu b^3 \ln \left(\frac{8}{e} \frac{r}{\xi_0} \right) + \frac{2\gamma_{\text{step}} b^2}{\beta'} - \left(\frac{3}{2} \right) \frac{.986}{\sqrt{2}} \frac{K b^{5/2} r^{1/2}}{\beta} = 0. \quad (7)$$

And second, we are seeking a critical radius for the dislocation loop -- one corresponding to an instability. In such a case, we must also have

$$\frac{d^2U}{dr^2} = \frac{2-\nu}{8(1-\nu)} \frac{\mu b^3}{r} - \frac{3}{4} \frac{.986}{\sqrt{2}} \frac{K b^{5/2}}{\beta r^{1/2}} = 0. \quad (8)$$

Rearranging (8) yields, for the critical value of r ,

$$\frac{1}{2} \left(\frac{3}{2} \frac{.986}{\sqrt{2}} \frac{K b^{5/2} r^{1/2}}{\beta} \right) = \frac{2-\nu}{8(1-\nu)} \mu b^3. \quad (9)$$

Substitution of (9) into (7) and rearrangement yields

$$\frac{2-\nu}{8(1-\nu)} \mu b^3 \ln \left(\frac{8r_{\text{crit}}}{e^3 \xi_0} \right) + \frac{2\gamma_{\text{step}} b^2}{\beta'} = 0. \quad (10)$$

Solving for the critical value of r ,

$$\begin{aligned} \frac{r_{\text{crit}}}{\xi_0} &= \frac{e^3}{8} \exp \left\{ \frac{-2\gamma_{\text{step}} 8(1-\nu)}{\mu b \beta' (2-\nu)} \right\} \\ r_{\text{crit}} &= \frac{e^3 \xi_0}{8} e^{-5S}, \end{aligned} \quad (11)$$

where S is as previously defined in Eqn. (3). Solving (9) for the corresponding critical K value for the instability,

$$K_{crit} = \frac{2-\nu}{6(1-\nu)} \frac{\sqrt{2} \beta}{.986} \frac{\mu b^{1/2}}{r_{crit}^{1/2}} \quad (12)$$

The corresponding value of the energy release rate is

$$\mathcal{J}_{crit} = \frac{(1-\nu) K_{crit}^2}{2\mu} = \frac{2\beta^2}{9(.986)^2 e^3} \frac{(2-\nu)^2}{(1-\nu)} \frac{\mu b}{\xi_o} e^{5S} \quad (13)$$

Griffith's criterion gives us the value $\mathcal{J} = 2\gamma_{int}$ for brittle (reversible) crack growth. We form, therefore, the ratio of the critical energy release rate for dislocation nucleation to that required for crack growth:

$$\begin{aligned} \frac{\mathcal{J}_{crit}}{2\gamma_{int}} &= \frac{\beta^2 (2-\nu)^2}{9(.986)^2 e^3 (1-\nu)} \frac{\mu b}{\xi_o \gamma_{int}} e^{5S} \\ &= \left(\frac{16}{5}\right)^2 \frac{1}{9(.986)^2 e^3} \frac{1}{R_o^* S} e^{5S} = \frac{0.058}{R_o^* S} e^{5S} \quad (14) \end{aligned}$$

We observe that if $\mathcal{J}_{crit} > 2\gamma_{int}$, the load necessary for dislocation nucleation cannot be reached, since it is greater than the maximum load the interface can carry without cleaving. Thus $\mathcal{J}_{crit}/2\gamma_{int} > 1$ is an indication of brittle behavior, and the converse implies ductile behavior. Equation (14) may be solved for values of R_o^* which correspond to a dividing line between the ductile and brittle behavior on the $R_o - S$ plane,

$$R_o^* = \frac{0.058}{S} e^{5S} \quad (15)$$

This is shown in Figure 3. For a given S , a value of $R_o < R_o^*$ is an indication of brittle behavior, and conversely, $R_o > R_o^*$ implies ductile behavior.

Hence, a prediction of ductile, or brittle behavior for a particular orientation is reduced to calculating values of R_o and S via Eqns. (3), and comparing this value of R_o with the critical value R_o^* obtained from Eqn. (15).

It is also possible to obtain a dividing line from the Rice and Thomson approach. For some S value, using an iteration procedure, we have determined the value of R_o for which $U_{act} = 0$. For greater R_o values, $U_{act} < 0$ (implies ductile behavior), and for smaller R_o values, $U_{act} > 0$ (implies brittle behavior). This line is also shown in Figure 3. Note that based on Figure 3, the modified Rice and Thomson criterion predictions are probably more ductile than those of the alternate approach.

IV. RESULTS

Hondros and McLean [1974] used a thin foil zero creep technique and dihedral angle measurements at 927°C and 1040°C to deduce the surface and grain boundary energies γ_s and γ_b for pure copper and several Cu-Bi alloys with Bi concentrations in the range of .002 to .02 weight percent Bi. For the pure copper, this resulted in $\gamma_s \approx 1640$ ergs/cm² and $\gamma_b \approx 460$ ergs/cm². By plotting surface energy versus log of concentration, for several systems besides Cu-Bi, they deduced the average minimum energies were about 54% of the values for the pure metals, which for Cu-Bi lead to $\gamma_s^{\min} \approx 885$ ergs/cm² and $\gamma_b^{\min} \approx 218$ ergs/cm² -- these at 927°C. This approximating technique was necessary due to the extreme difficulty encountered in forming 10 μ m foils for zero creep tests from the very brittle Cu-Bi alloys.

They also performed tensile tests at room temperature on pure copper and several Cu-Bi alloys in the composition range above. The Cu-Bi alloys with .006 or greater weight percent of Bi exhibited varying degrees of intergranular failure, while cracks were never seen in the pure copper. We sought to compare our brittle versus ductile predictions with their experimental observations. However, calculation of the two dimensionless parameters R_o and S involves $2\gamma_{\text{int}}$ -- the work to reversibly separate an interface, and γ_{step} -- the work to form the step or ledge at the crack tip. For purposes of our numerical calculations, these two energies are approximated by

$$\gamma_{\text{step}} \approx \gamma_s \quad 2\gamma_{\text{int}} \approx 2\gamma_s - \gamma_b \quad (16)$$

However, the latter equation only holds for the case of interfacial separation when the interface is in chemical composition equilibrium with the

bulk phase at potential μ throughout the process of separation (see Rice [1976]; or Appendix). This is not so in the present case, so that generally $2\gamma_{int} > 2\gamma_s - \gamma_b$, and our estimate of $2\gamma_{int}$ represents some sort of lower bound on the actual value.

Using the approximate values of γ_{step} and γ_{int} , we calculated values of R_o and S using other data appropriate to pure copper; $\mu = 4.05 \times 10^{11} \text{ (cgs)}$, $b = 2.55 \text{ \AA}$, $\nu = 0.324$.

Continuum dislocation theory gives rise to an arbitrary core cut-off, r_o , when calculating the self energy of a line of dislocation. (Hirth and Lothe [1968], p. 212). The precise value of this cut-off is unknown, but estimates range from $b/2$ to $2b$ for close packed metals. R_o and S values were calculated for two different values of the non-dimensional core cut-off $\xi_o (= r_o/b) = 1$ or $= 2$, using both pure copper, and minimum estimated values of surface and grain boundary energies with the Bi segregate, for each of the slip systems associated with about fifty crack plane normal directions.

For clarity, the results of only nine orientations are plotted in Figures 4 through 7. These particular points were chosen for two reasons: (i) they are a good representation of the scatter pattern on the $R_o - S$ plane; (ii) they are distributed throughout the standard triangle and are probably representative of any possible orientation, (i.e., choice of normal direction). In each of the figures, the solid line given by Eqn. (15) as $R_o^* = (0.058/S) \exp(5S)$, represents the dividing line between the brittle region -- $R_o(S) < R_o^*(S)$; and the ductile region -- $R_o(S) > R_o^*(S)$. Figures 4 and 5 show the results for $\xi_o = 2$ with energy values for Cu and the most brittle Cu-Bi alloy respectively. Figure 6 and 7 show similar results

for $\xi_0 = 1$. Each set of points on these plots (indicated by a single symbol) represents the R_0 and S values calculated for each of the different slip systems for one particular choice of the crack plane normal.

Note that those directions with a high degree of crystallographic symmetry have fewer points, since values of R_0 and S are identical for slip systems with identical orientation angles ϕ and ψ .

If a particular set of R_0 and S for some slip system falls in the brittle region, we assume an atomistically sharp crack configuration is stable against dislocation nucleation on that slip system, and the material could possibly exhibit brittle behavior if no other system was active. If the R_0 , S set for some other slip system falls in the ductile region, presumably the crack would blunt.

For both values of ξ_0 , the lowering of γ_{step} and γ_{int} via Bi segregation to the grain boundaries results in a decrease in the ductility of the predicted behavior, i.e., fewer sets of R_0 and S fall in the ductile range implying fewer slip systems are activated. The trend toward brittle behavior is much more pronounced in the $\xi_0 = 1$ case, and, in general, choosing $\xi_0 = 1$ leads to more brittle overall behavior, and thus, probably serves to counteract some of the excess ductility introduced via our model's assumptions -- i.e., unlimited crack rotation. This will be discussed further in the next section. Note that for the $\xi_0 = 1$ case, three of the represented normal directions (100), (111), and (110) have all sets of R_0 and S in the brittle range, and all of the other normals have, at most, one R_0 and S point left in the ductile range.

V. DISCUSSION

The model predicts behavior that is generally more ductile than the tensile tests by Hondros and McLean indicate. For example, even with the most severe reductions in surface and grain boundary energies, our model indicates that some slip systems might be active, whereas metallographic examination of Hondros and McLean's tensile specimens reveals intergranular cracking for Cu-Bi alloys with surface energies much higher than the minimum estimated values, i.e., systems for which the embrittlement is much less severe than the worst case suffer extensive intergranular cracking. There are several causes of the model's excess ductility: (i) We allow unlimited crack line rotation, so that the crack front is in the most favorable position for dislocation nucleation before we ask whether that nucleation is possible. This freedom of rotation was necessitated because we chose to represent an orientation by aligning one crystallographic direction with the crack plane normal. Since this only determines the orientation up to an arbitrary rotation, it is a bit ambiguous if we ask how many orientations are actually represented by that one choice of normal direction. (ii) We ask questions such as: what reductions in γ_{int} are necessary so that all of the slip systems are inactive? This is a rather stringent criterion for determining brittle behavior. Perhaps some alternate question would be more accurate, but finding such a question is an open-ended problem. (iii) Our model is not a discrete lattice model. We have accounted for some crystallographic effects, (i.e., the orientations of the slip systems); but in accounting for the effects of the segregate at the interface, we have only allowed reductions in γ_{int} and γ_{step} .

There has been no consideration of problems related to misfits of larger or smaller segregate atoms, or the possibility of a two dimensional segregate phase with its own crystallography existing at the grain boundaries.

[Note: for the case of Bi in Cu, spectroscopic studies by Joshi and Stein [1971] and Johnson et. al. [1976] have tended to rule out the possibility of the segregated Bi existing as a three dimensional phase, since the Bi is localized to within a few atomic distances of the Cu grain boundaries]. (iv) There is a problem in determining the energy of the step or ledge that is left behind at the crack tip as the dislocation is nucleated. In the model, we assumed that the energy to form a unit area of the step (γ_{step}) was equal to the energy required to form a unit area of new surface by splitting the lattice (γ_s).

For the Cu-Bi alloys under discussion, Hondros and McLean measured grain boundary Bi excess concentrations of up to three equivalent monolayers of Bi located within about $10\text{\AA}$ of the interface. Thus, it is possible that as the edge is formed, the new surface consists entirely of Bi atoms, or alternatively, of some population of atoms more closely representing the composition of the grain boundary than a free surface. It is possible that the work required to form the step is closer to γ_{int} than to γ_s , which would lead to lower S values, and more "brittle" predictions.

Despite all of these problems, it is important to note that the model does predict a trend toward brittle behavior as γ_{int} is lowered by increased segregation. This is consistent with the cited experiments, although the changes in ductile versus brittle behavior that our model predicts are not as drastic as the experimental observations.

Appendix: Comments on the Work of Separation of an Interface Containing an Adsorbed Species

There seems to be a general lack of appreciation for the significance of using the equation

$$2\gamma = 2\gamma_s - \gamma_b \quad (1)$$

as the work of separation of a grain boundary in a system with surface adsorption (Seah [1975,1976]; Inman and Tipler [1963]; Joshi and Stein [1971]; Hondros and McLean [1974]; Hondros [1975]). Here γ_b is the grain boundary energy and γ_s is the surface energy, both being defined by expressions of the form $\gamma_s = \phi_s - \mu\Gamma_s$, with ϕ_s being the surface Helmholtz free energy, μ the chemical potential of the adsorbed species, and Γ_s the concentration of adsorbate on one free surface.

As has been pointed out by Rice [1976] in his discussion of the thermodynamics of interfaces, a careful distinction must be made between two limiting cases of reversible interfacial separation. These are:

(i) separation of constant chemical potential μ , or separation that is slow when compared with diffusion times so that the surface excess of the adsorbate on the separating interface is always at chemical composition equilibrium with a bulk phase at potential μ ; and (ii) separation at constant excess concentration, Γ , of the adsorbate, or separation that is rapid when compared with diffusion times so that no more adsorbate diffuses to (or from) the interface during the separation process. As will be shown, Eqn. (1) is valid only for the case of separation at constant μ .

Following Rice [1976], we consider the case of an interface between two identical solid phases, loaded by a normal stress σ . Define δ as

the excess opening displacement of the interface, following Gibbs' notion of surface excesses. A representative plot of σ versus δ is shown in Figure 8. In the case of a system with adsorption, σ depends not only on δ but also on a variable characterizing the state of the adsorbate. Thus the expression relating σ to δ (at fixed temperature) must depend additionally on either μ or Γ . Accordingly, we introduce functions

$$\sigma = \hat{\sigma}(\delta, \mu) \quad \text{and} \quad \sigma = \bar{\sigma}(\delta, \Gamma) . \quad (2)$$

The first mode of description is most convenient for separation at constant μ ; the second for separation at constant Γ . The area under the σ versus δ curve is the reversible work of separation (or, for an ideally brittle body, the "work of fracture"); we have two expressions. We define the work of separation at constant μ as $2\hat{\gamma}_c(\mu)$, where it is noted that

$$2\hat{\gamma}_c(\mu) = \int_{\hat{\delta}_0(\mu)}^{\infty} \hat{\sigma}(\delta, \mu) d\delta . \quad (3)$$

Similarly, we define $2\bar{\gamma}_c(\Gamma)$ as the work of separation at constant Γ and note that

$$2\bar{\gamma}_c(\Gamma) = \int_{\bar{\delta}_0(\Gamma)}^{\infty} \bar{\sigma}(\delta, \Gamma) d\delta . \quad (4)$$

Here, $\hat{\delta}_0(\mu)$ or $\bar{\delta}_0(\Gamma)$ represents the initial excess displacement of an unstressed interface at adsorbate potential μ or composition Γ , respectively. Here, Γ is the total amount of adsorbate on the interface

and thus, when the interface is infinitely separated to form two free surfaces, we have $\Gamma = 2\Gamma_g$ where Γ_g is the amount of adsorbate on each surface.

The Gibbs relation for the interface is

$$\sigma d\delta + \mu d\Gamma - s dT = d\phi ; \phi = u - Ts \quad (5)$$

(where s and u are respectively the specific surface entropy and internal energy), and, by a Legendre transformation,

$$\sigma d\delta - \Gamma d\mu - s dT = d(\phi - \mu\Gamma) \quad (6)$$

and holding temperature fixed, we have the following Maxwell relations:

$$\left(\frac{\partial \sigma}{\partial \Gamma}\right)_\delta = \left(\frac{\partial \mu}{\partial \delta}\right)_T \quad \left(\frac{\partial \sigma}{\partial \mu}\right)_\delta = - \left(\frac{\partial \Gamma}{\partial \delta}\right)_\mu \quad (7)$$

Differentiating (3) and (4) with respect to μ and Γ , respectively, and using the Maxwell relations (7), we obtain Rice's generalizations of the Gibbs adsorption theorem in the form:

$$2 \frac{d\hat{\gamma}_c(\mu)}{d\mu} = - \left[\Gamma_\infty(\mu) - \Gamma_0(\mu) \right] \quad (8)$$

$$2 \frac{d\tilde{\gamma}_c(\Gamma)}{d\Gamma} = \left[\mu_\infty(\Gamma) - \mu_0(\Gamma) \right] \quad (9)$$

where $\Gamma_0(\mu)$ is the adsorbate concentration on the unstressed interface in equilibrium with potential μ ; $\Gamma_\infty(\mu)$ is the equilibrium concentration on two free surfaces in equilibrium with μ ; $\mu_0(\Gamma)$ is the chemical potential that would equilibrate concentration Γ on the unstressed interface; and, $\mu_\infty(\Gamma)$ is the potential to equilibrate a total excess Γ on the two free surfaces.

Consider an unstressed interface containing adsorbate of amount Γ' at equilibrium with a potential μ' . The difference in the work of fracture between the two cases of slow ($\mu = \text{constant} = \mu'$) and fast ($\Gamma = \text{constant} = \Gamma'$) separation of the interface is (Rice [1976]):

$$2\bar{\gamma}_c(\Gamma') - 2\hat{\gamma}_c(\mu') = \int_{\Gamma'}^{\Gamma''} [\mu_{\infty}(\Gamma'') - \mu_{\infty}(\Gamma)] d\Gamma \quad (10)$$

where, using our previous definitions, $\Gamma'' = \Gamma_{\infty}(\mu')$ which may be obtained from the adsorption isotherm for a free surface, and $\mu_{\infty}(\Gamma'') \equiv \mu'$.

Note that so long as the adsorption isotherm of the completely separated surfaces, namely $\Gamma = \Gamma_{\infty}(\mu)$, is such that Γ increases with μ , the right side of (10) is non-negative and hence:

$$2\bar{\gamma}_c(\Gamma') \geq 2\hat{\gamma}_c(\mu') \quad (11)$$

We may note in addition that, from (6) (with constant T),

$$\hat{\sigma}(\delta, \mu) = \left[\frac{\partial(\phi - \mu\Gamma)}{\partial\delta} \right]_{\mu} \quad (12)$$

Thus, from (3):

$$2\hat{\gamma}_c(\mu) = [\phi_{\infty}(\mu) - \mu\Gamma_{\infty}(\mu)] - [\phi_0(\mu) - \mu\Gamma_0(\mu)] \equiv 2\gamma_s - \gamma_b \quad (13)$$

according to the definitions of γ_s and γ_b given at the outset.

Accordingly, Eqn. (1) gives the work of separation at constant μ and, as we have remarked, this is in general different from the work of separation at constant Γ .

In recent papers, Seah [1975, 1976] suggested that segregation might

not affect the low temperature work of separation of a grain boundary, i.e., he considered a constant Γ process. Our Eqn. (9) implies that $2 d\bar{\gamma}(\Gamma)/d\Gamma = 0$ only if at some value of Γ , the corresponding equilibrating value of μ is the same for the separated surfaces as it is for the original, unstressed, coherent interface. This is not true in general (for example, the interface and free surfaces are not likely to have identical adsorption isotherms which is what would be implied by $d\bar{\gamma}(\Gamma)/d\Gamma = 0$). Thus, via this analysis of the process of separation, we are led to a different conclusion than the possibility suggested by Seah -- namely that adsorption does alter the work of separation.

Seah's proposed model was for a system with dilute bulk concentration, X_c , of the segregating species. The surface and grain boundary adsorbate concentrations were in equilibrium with the bulk chemical potential μ ; i.e., $\Gamma_s = \Gamma_s(\mu)$; $\Gamma_b = \Gamma_b(\mu)$. The surface and grain boundary energies were given by:

$$\begin{aligned} \gamma_s &= \gamma_{so} - kT\Gamma_s \\ \gamma_b &= \gamma_{bo} - kT\Gamma_b \end{aligned} \quad (14)$$

These are valid expressions for the case of dilute bulk concentrations, for surfaces that are formed from the coherent lattice via a constant μ process. Or, alternatively, they are valid if there has been time enough for the surface and grain boundary excess concentrations to reach equilibrium with the bulk chemical potential, μ , via solute segregation to (or away from) the surfaces or grain boundaries, γ_{so} and γ_{bo} are respectively the energies of the surface and grain boundary with no adsorbate.

The grain boundary in Seah's model was split open at low temperatures. As there was no time for further solute segregation, these two new surfaces each were assumed to have the adsorbate concentration $\Gamma'_s = 1/2 \Gamma_b$, i.e., a constant Γ separation. He then assumed that the energy of each of the new surfaces could be expressed as in Eqn. (14) and wrote:

$$\gamma'_s = \gamma_{so} - kT(1/2 \Gamma_b) . \quad (15)$$

However, as we mentioned, an equation of this form is only valid for surfaces formed from the coherent lattice via a constant μ separation, and, further, $1/2 \Gamma_b$ is not the surface excess in equilibrium with that potential μ .

Seah then used an expression equivalent to our Eqn. (1) and found $2\gamma = 2\gamma'_s - 2\gamma_b = 2\gamma_{so} - \gamma_{bo}$, i.e., that the work of separation was not altered by segregation. But, as has been shown in Eqn. (13), $2\gamma = 2\gamma_s - \gamma_b$ is only a valid expression for the work of separation at constant μ .

In what follows, we will calculate and compare the work for constant μ and constant Γ grain boundary separations using assumptions that are appropriate for comparison with Seah's work, and valid for dilute bulk concentrations, X_c , of the segregating species. Specifically, we adopt the dilute concentration form for the potential μ at equilibrium with X_c ,

$$\mu = \mu_s(T) + kT \ln X_c , \quad (16)$$

and following Seah, we assume that for an unstressed interface at composition equilibrium with the bulk phase, the adsorbate concentration is

$$\Gamma_o = \beta_o(T)X_c . \quad (17)$$

Similarly, for a pair of free surfaces at composition equilibrium with the bulk, we assume a form consistent with (17):

$$\Gamma_{\infty} = \beta_{\infty}(T)X_c \quad [= 2\Gamma_s = 2\beta_s(T)X_c] \quad (18)$$

Here $\beta_o(T)$ and $\beta_{\infty}(T)[= 2\beta_s(T)]$ are regarded as empirical coefficients, in the spirit of Raoult's Law. These expressions allow us to write the adsorption isotherms for the completely separated surfaces and the unstressed interface, respectively, as

$$\mu_{\infty}(\Gamma) = \mu_{\infty}(T) + kT \ln \left[\frac{\Gamma}{\beta_{\infty}(T)} \right] \quad (19)$$

$$\mu_o(\Gamma) = \mu_o(T) + kT \ln \left[\frac{\Gamma}{\beta_o(T)} \right] \quad (20)$$

The inverted forms of these two isotherms are

$$\Gamma_{\infty}(\mu) = \beta_{\infty}(T) \exp \{ [\mu - \mu_{\infty}(T)] / kT \} \quad (21)$$

$$\Gamma_o(\mu) = \beta_o(T) \exp \{ [\mu - \mu_o(T)] / kT \} \quad (22)$$

From these expressions and Eqns. (8) and (9) we calculate the work of separation at constant μ :

$$2\hat{\gamma}_c(\mu) = 2\gamma_o + 2 \int_{-\infty}^{\mu} \frac{d\hat{\gamma}(\mu)}{d\mu} d\mu = 2\gamma_o - \int_{-\infty}^{\mu} (\beta_{\infty} - \beta_o) e^{(\mu - \mu_{\infty})/kT} d\mu$$

or

$$2\hat{\gamma}_c(\mu) = 2\gamma_o - kT(\beta_{\infty} - \beta_o) e^{(\mu - \mu_{\infty})/kT} \quad (23)$$

Similarly, the work of separation at constant Γ is:

$$2\tilde{\gamma}_c(\Gamma) = 2\gamma_0 + 2 \int_0^\Gamma \frac{d\tilde{\gamma}(\Gamma)}{d\Gamma} d\Gamma = 2\gamma_0 - \int_0^\Gamma kT \ln\left(\frac{\beta_\infty}{\beta_0}\right) d\Gamma$$

or

$$2\tilde{\gamma}_c(\Gamma) = 2\gamma_0 - kT\Gamma \ln\left(\frac{\beta_\infty}{\beta_0}\right). \quad (24)$$

Here, $2\gamma_0$ is the work required to separate reversibly an interface with no adsorbate.

It is enlightening to consider the reductions in the work of separation due to segregation for the two cases of constant μ and constant Γ separation. Accordingly, for an interface with, in its unstressed state, initial concentration Γ' at equilibrium with a potential μ' , the alteration for the constant μ separation is:

$$2\gamma_0 - 2\hat{\gamma}(\mu') = kT(\beta_\infty - \beta_0)e^{(\mu' - \mu_k)/kT}$$

or, using Eqn. (22) as an expression for Γ' :

$$2\gamma_0 - 2\hat{\gamma}(\mu') = kT \Gamma' \left(\frac{\beta_\infty}{\beta_0} - 1 \right), \quad (25)$$

and, the alteration for the constant Γ separation is:

$$2\gamma_0 - 2\tilde{\gamma}(\Gamma') = kT \Gamma' \ln\left(\frac{\beta_\infty}{\beta_0}\right). \quad (26)$$

Using equations (25) and (26), we may write an expression for the difference between the work of separation at constant $\Gamma = \Gamma'$ and constant $\mu = \mu'$ (for dilute X_c):

$$2\tilde{\gamma}(\Gamma') - 2\hat{\gamma}(\mu') = kT \Gamma' \left[\left(\frac{\beta_\infty}{\beta_0} - 1 \right) - \ln\left(\frac{\beta_\infty}{\beta_0}\right) \right] \quad (27)$$

and note that the right hand side of (27) is, in general, non-negative for all values of β_∞/β_0 . This demonstrates in a particular case the result quoted in Eqns. (10, 11), namely that the work of separation at constant Γ is generally greater than that for constant μ .

Alternatively, we may rewrite Eqns. (25) and (26) to obtain two non-dimensional expressions for the reduction in the work of separation; for the constant $\mu = \mu'$ process:

$$\frac{2\gamma_0 - 2\hat{\gamma}(\mu')}{kT\Gamma'} = \left(\frac{\beta_\infty}{\beta_0} - 1 \right). \quad (28)$$

And similarly for the constant $\Gamma = \Gamma'$ process,

$$\frac{2\gamma_0 - 2\hat{\gamma}(\Gamma')}{kT\Gamma'} = \ln \left(\frac{\beta_\infty}{\beta_0} \right). \quad (29)$$

These are plotted as non-dimensional energy reduction versus the ratio β_∞/β_0 in Figure 9. Note that the constant μ energy reduction is always greater than the constant Γ reduction. [In principle, there seems to be no reason to rule out the possibility of segregation increasing the work of separation, as is shown for values of (β_∞/β_0) less than 1. From the inverted isotherms, Eqns. (19) and (20), $\beta_\infty/\beta_0 < 1$ implies that the equilibrium adsorbate concentration on an unstressed interface is greater than the equilibrium concentration on two free surfaces]. The only case where segregation does not affect the energy required for separation of the interface is when $\beta_\infty \equiv \beta_0$ -- i.e., when the adsorption isotherms for the unstressed interface and the pair of free surfaces are identical. As we have noted previously, this is an unlikely case.

We conclude that segregation, even if dilute, does indeed affect the work of reversible separation of an interface, even when the separation takes place at constant adsorbate concentration. At the same time, we conclude that the work of separation at constant adsorbate potential μ will, in general, be less than that at constant adsorbate concentration Γ . Further, only the former of these is properly computed by Eqn. (1), given the interpretations of the kind $\gamma_s = \phi_s - \mu\Gamma_s$ normally attached to the quantities γ_s and γ_b .

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Figure 1. Grain boundary model and crystallographic parameters.

Figure 2. Energy U_{act} of dislocation nucleation from tip of interfacial crack at critical condition; from Rice [1976], cleavage possible if $U_{act} > 0$.

Figure 3. Regions of brittle and ductile behavior on $R_0 - S$ plane from criteria of Rice and Thomson [1974] and alternate approach discussed in the text.

Figure 4. R_0 and S values for pure copper surface energies, core cut off $\xi_0 = 2$; points indicated on (100) standard triangle are crack plane normal directions.

Figure 5. R_0 and S values for most brittle Cu-Bi alloy surface energies; core cut off $\epsilon_0 = 2$; symbols as indicated in Figure 4.

Figure 6. R_0 and S values for pure copper surface energies, core cut off $\epsilon_0 \approx 1$; symbols as indicated in Figure 4.

Figure 7. R_0 and S values for most brittle Cu-Bi alloy surface energies; core cut off $\xi_0 = 1$; symbols as indicated in Figure 4.

Figure 8. Stress, σ , versus separation, δ , for an interface, δ_0 is the excess separation for an unstressed interface; exact curve shape is a function of δ and either Γ or μ .

Figure 9. Reduction of energy required for interfacial separation for a system with segregation; Γ' is the initial excess interfacial concentration in equilibrium with potential μ' on an unstressed interface.