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ON THE EMBRITTLEMENT OF GRAIN BOUNDARIES BY IMPURITIES

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ABSTRACT

The segregation of impurities to grain boundaries is shown to produce a reduction in the grain boundary energy, but that this does not necessarily coincide with a tendency toward embrittlement caused by decohesion. Indeed, it is shown that only when certain relationships occur between the composition dependence of the surface and grain boundary energies can there be a true decohesion of the boundary. The criterion for embrittlement, based on boundary decohesion, requires that the ratio of the changes in surface and boundary energies increase with concentration of the impurity, or equivalently, that the ratio of the amount of impurity segregated to the surface to the amount of impurity segregated to the boundary increase with increasing impurity concentration. However, since impurity segregation to grain boundaries occurs independent of whether or not decohesion results, an effect of impurities in the vicinity of the grain boundary on localized plasticity is likely to be the dominant factor in intergranular embrittlement of otherwise ductile materials.

INTRODUCTION

It is well known that the presence of certain solute elements in various materials can lead to intergranular embrittlement, with the explanation often given that segregation of these impurities to grain boundaries has reduced the cohesive strength of the boundary through a reduction in interfacial energy. Numerous examples of this phenomenon can be cited: Pb in Sn,¹ Sb in Cu,² Al in Cr,³ O, P and Sb in Fe,⁴⁻⁶ Sb, As, Sn, and P in steel.⁷⁻¹³ Interestingly, most of these embrittling impurities come from Groups 4A, 5A, and 6A of the periodic table, suggesting that some form of electronic interaction is responsible. Only recently, with the advent of Auger spectroscopy, has reliable quantitative data on the extent of segregation to grain boundaries begun to be available, but there is as yet no concomitant data on the reduction in interfacial energy caused by the segregation of impurities.

The qualitative argument for the effect of impurities on intergranular decohesion appears to be crudely based on Griffith's model for crack extension¹⁴ which states that the stress to propagate a crack is related to the energy to create two new fracture surfaces. Balancing the potential energy release rate with the rate at which new surface is generated leads to the relation

$$\sigma = (2E\gamma/\pi c)^{1/2} \quad (1)$$

where σ is the fracture stress, E is the elastic modulus, $2c$ is the crack length and γ is an appropriate surface energy term. This is found to give a fair representation of the behavior of brittle materials,¹⁴⁻¹⁸ but when one inserts a

1. KALISH, H. S., and DUNKERLEY, F. J. *The Low Temperature Properties of Tin and Tin-Lead Alloys*. Trans. AIME, v. 180, 1949, p. 637-656.
2. McLEAN, D. *The Embrittlement of Copper-Antimony Alloys at Low Temperatures*. J. Inst. Metals, v. 81, 1952-1953, p. 121-123.
3. SULLY, A. H., BRANDES, E. A., and MITCHELL, K. W. *The Effect of Temperature and Purity on the Ductility and Other Properties of Chromium*. J. Inst. Metals, v. 81, 1952-1953, p. 585-598.
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reasonable value for metal surface energies into Equation 1, the calculated fracture stress turns out to be too low by at least an order of magnitude. This prompted Orowan¹⁹ to suggest that the Griffith fracture criterion should be modified for metals to include a term p expressing the plastic work required during crack extension:

$$\sigma = [2E(\gamma + p)/\pi c]^{1/2}. \quad (2)$$

Estimates of the plastic work term are about two to three orders of magnitude greater than the surface energy γ , so it would seem that γ should have a negligible effect upon the fracture stress. Nevertheless, the attitude persists that the Griffith-type argument, based upon a reduction in interfacial energy due to segregated impurities, is not invalidated since the plastic work term will in some way be related to the interfacial energy.

This paper analyzes the effect that impurities will have on grain boundary and fracture surface energies, from which is qualitatively derived a criterion for intergranular embrittlement based on boundary decohesion. The validity of the analysis is greatest for the inherently less ductile materials, where the plastic work term is small, or for those ductile materials for which there is a direct relation between the plastic work of crack extension and interfacial energy, as is often assumed. The likelihood that the latter condition will not be achieved is also discussed.

GRAIN BOUNDARY THERMODYNAMICS

To clarify the origins and the physical significance of some of the terms and concepts to be utilized later, the following brief discussion of surface thermodynamics is offered. Compare a heterogeneous system of i components containing a grain boundary with a homogeneous system of the same volume with no grain boundary. The energy of the heterogeneous system may be written

$$E = TS - PV + \sum_i \mu_i N_i + \gamma A \quad (3)$$

where T = temperature

S = entropy

P = pressure

V = volume

μ_i = chemical potential of component i

N_i = number of atoms of component i

γ = specific grain boundary energy

A = grain boundary area

19. OROWAN, E. *Notch Brittleness and the Strength of Metals*. Trans. Inst. Engrs. Shipbuilders Scotl., v. 89, 1945, p. 165-215.

The energy of the homogeneous system may be written

$$E' = TS' - PV + \sum_i \mu_i' N_i' \quad (4)$$

The Gibbs-Duhem relations corresponding to Equations 3 and 4 are

$$SdT - VdP + \sum_i N_i d\mu_i + Ad\gamma = 0 \quad (5)$$

$$\text{and } S'dT - VdP + \sum_i N_i' d\mu_i' = 0 \quad (6)$$

Assuming that the concentration of the homogeneous system and of the heterogeneous system away from the grain boundary are the same, then

$$\mu_i = \mu_i', \text{ and } d\mu_i = d\mu_i' \quad (7)$$

Subtracting Equation 6 from Equation 5 and making use of Equation 7 yields

$$(S - S')dT + \sum_i (N_i - N_i')d\mu_i + Ad\gamma = 0 \quad (8)$$

At constant temperature Equation 8 can be written

$$\begin{aligned} d\gamma &= - \sum_i [(N_i - N_i')/A]d\mu_i \\ &= - \sum_i \Gamma_i d\mu_i \end{aligned} \quad (9)$$

where Γ_i is the excess number of atoms of component i per unit area of the boundary. This is the Gibbs adsorption equation²⁰ relating the change in surface energy with surface composition.

The surface excesses Γ_i are the excess number of atoms of the i components at (or near) the boundary, over and above the number that would have been present had the concentration of each component remained constant right up to an imaginary geometric dividing surface. This definition is illustrated in Figure 1 where the concentrations C_i refer to the number of atoms per unit volume. Because the atoms near a grain boundary are less densely packed than within the bulk of the grain, the concentration of component 1 (here taken to be the dominant matrix component) is shown decreasing at the grain boundary. Interestingly, it is unnecessary to

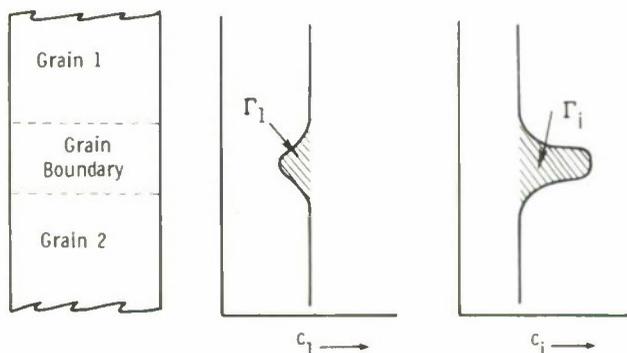


Figure 1. The distribution of components of a solid solution in the vicinity of a grain boundary. Component 1 might typically represent the solvent, component i might represent any solute.

20. GIBBS, J. W. *Collected Works, Vol. 1.* Longmans, Green, New York, 1928, p. 230, Eq. 507.

define the actual position of the boundary in the derivation of Equation 9. Since the bulk concentrations in the adjoining grains are both equal, the boundary excess (or deficiency) is simply the shaded area shown in Figure 1 regardless of where the boundary is drawn.* At equilibrium the Γ 's can be either positive or negative depending on whether the element tends to segregate to or away from the boundary, respectively. Increasing the bulk solute concentration will cause a decrease in the equilibrium boundary energy for those solutes for which $\Gamma > 0$, an increase for those for which $\Gamma < 0$.

For simplicity all subsequent discussion will consider only a two-component system. For a system of two components Equation 9 becomes

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2. \quad (10)$$

The two chemical potentials are related by Equation 6, which at constant temperature and pressure can be expressed as

$$d\mu_1 = - (N_2/N_1)d\mu_2 = - (C_2/C_1)d\mu_2 \quad (11)$$

Substitution in Equation 10 gives

$$d\gamma = - [\Gamma_2 - (C_2/C_1)\Gamma_1]d\mu_2 \quad (12)$$

$$= -\Gamma_{2(1)}d\mu_2 \quad (13)$$

where $\Gamma_{2(1)}$ is the relative adsorption of component 2 with respect to component 1. Experimental measurements of the composition dependence of boundary energy are unable to separate the individual Γ 's according to Equation 12, but rather can measure only $\Gamma_{2(1)}$. Our later discussion will therefore be in terms of this relative adsorption parameter also.

There are two conditions for which $d\gamma/d\mu_2 = 0$, and hence for which a slight change in bulk composition has no effect upon the boundary energy: (1) when $\Gamma_1 = \Gamma_2 = 0$, i.e., the boundary composition (expressed in atoms or moles per unit volume) is the same as that in the bulk; and (2) when the ratio of the excess concentrations at the boundary equals the ratio of the bulk concentrations, i.e., $\Gamma_2/\Gamma_1 = c_2/c_1$. Both of these represent narrow restrictions on the boundary composition which are unlikely ever to be encountered. The far more common situation is for an equilibrium boundary composition different from that in the bulk to develop. As the system proceeds from the unsegregated to the segregated state, a reduction in grain boundary energy will occur, regardless of whether the grain boundary is becoming more enriched with the segregating solute ($\Gamma > 0$) or the grain boundary is becoming depleted of solute ($\Gamma < 0$).

*In the case of an interphase boundary, the bulk concentrations in the two phases joined at the boundary are not equal, and the surface excesses will depend on the definition adopted for the geometric position of the boundary. The convention introduced by Gibbs calls for locating the boundary at a position which makes one of the boundary excesses zero. For a grain boundary there is no boundary position for which this can be done, and therefore the geometric boundary location cannot be defined in this manner. Nevertheless, there is no ambiguity in defining the Γ 's.

GRAIN BOUNDARY DECOHESION

When one considers the propagation of a crack along a grain boundary as in Figure 2, one realizes that the energy to produce two new fracture surfaces is reduced by the presence of the grain boundary in that the grain boundary energy must be deducted from the energy of the two fracture surfaces. Thus the surface energy term in the Griffith equation (Equation 1) is really $(2\gamma_{FS} - \gamma_B)/2$, and it is a reduction in this term which leads to decohesion. Ignoring the plastic work done in crack extension (or assuming that it will be directly related to the surface energy term), the criterion for embrittlement on this admittedly oversimplified basis is

$$d(2\gamma_{FS} - \gamma_B) = 2d\gamma_{FS} - d\gamma_B < 0 \quad (14)$$

where a distinction must be made between the impurity-induced change in the fracture surface energy γ_{FS} and what would be the corresponding change in the energy of the free surface γ_S at this same composition. The physical meaning of this distinction is apparent from Figure 2.

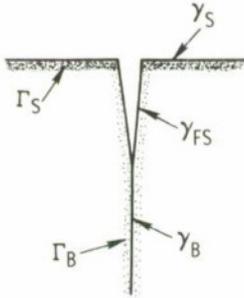


Figure 2. A schematic representation of a grain boundary crack, illustrating the distinction between the grain boundary, the free surface, and the fracture surface. Impurity excesses are shown at each type of interface.

Presumably the changes in surface and grain boundary energies could be calculated from Equation 13 if the corresponding relative surface excesses were known. For example, should the equilibrium surface and grain boundary excesses vary with composition as shown in the upper curves in Figure 3, the corresponding free surface energy and grain boundary energy would be those shown qualitatively in the lower curves in Figure 3. In Figure 3a it was assumed that Γ_S will be greater than Γ_B ; Figure 3b illustrates the case for which $\Gamma_B > \Gamma_S$. One cannot judge *a priori* which condition is more likely to occur.

A critical assumption in the following analysis is that the fracture surface can be treated as a free surface which is in equilibrium with a bulk composition different from the actual bulk composition. Thus, allowing that the surface excess at the uncracked grain boundary will divide itself equally between the two fracture surfaces, i.e., $\Gamma_{FS} = \Gamma_B/2$, the energy of the fracture surface will be taken to be equal to the energy of that equilibrium free surface for which $\Gamma_S = \Gamma_B/2$, even though this latter condition would be achieved at equilibrium only at an entirely different composition. *The fracture surface, therefore, is not in thermodynamic equilibrium with the actual bulk composition.*

Referring to Figure 3, if X_0 is the alloy composition for which $\Gamma_B(x = X_0)$ is the equilibrium grain boundary excess, then Γ_{FS} is $\Gamma_B(x = X_0)/2$, which is the equilibrium free surface excess if the alloy composition were X' . The change in

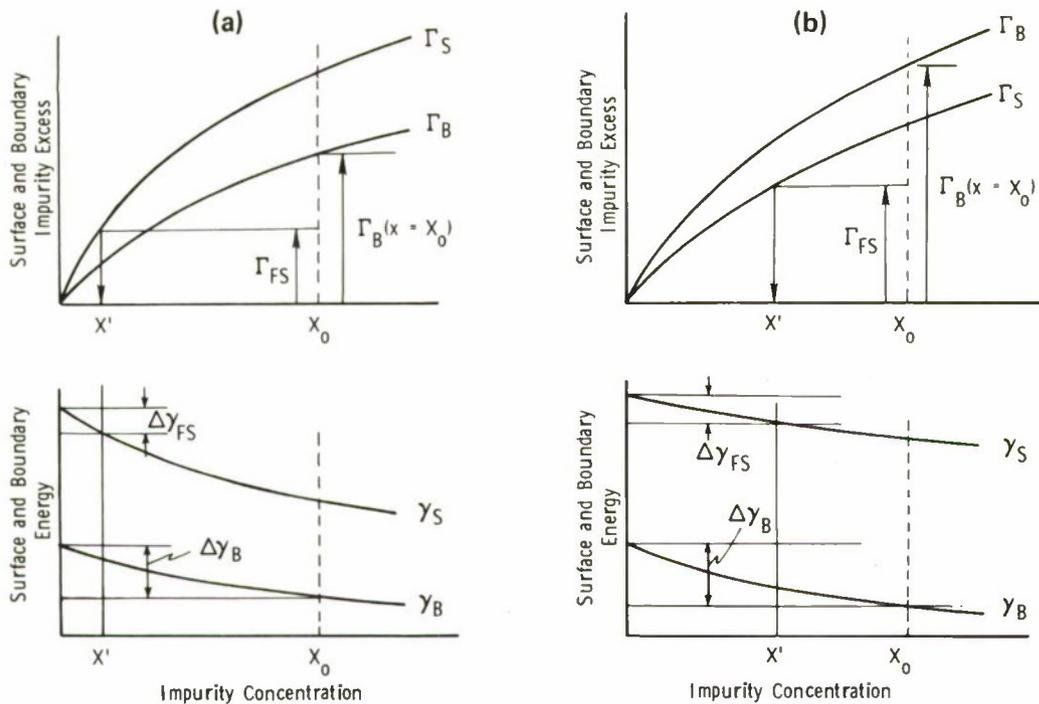


Figure 3. The effect of impurity concentration on the surface and grain boundary excess (upper). The corresponding effect of impurity concentration on the surface and grain boundary energy (lower). (a) $\Gamma_S > \Gamma_B$; (b) $\Gamma_S < \Gamma_B$.

grain boundary energy produced by the addition of an impurity element up to composition X_0 (compared with the total absence of that impurity) is simply $\Delta\gamma_B$ in the figure. The change in fracture surface energy produced by the addition of an impurity element up to composition X_0 is the same as the change in equilibrium free surface energy produced by the addition of an impurity element up to composition X' , namely $\Delta\gamma_{FS}$ in Figure 3. The relative magnitudes of $\Delta\gamma_{FS}$ and $\Delta\gamma_B$ are thus controlled by the composition dependence of Γ_S and Γ_B , which therefore determine whether or not a particular impurity element will be embrittling.

The composition dependence of the surface and boundary excess have been shown, via thermodynamic arguments, to lie within certain bounds,²¹ but there have been no experimental measurements reported of surface or boundary segregation as a function of composition. It therefore will be necessary to assume a simple functional relationship for the composition dependence of the Γ 's which is consistent with the thermodynamic limits, and then to assess the effect which that assumed functional relationship has upon the embrittlement criterion stated earlier. In addition, however, there have been data reported on surface and grain boundary energies as a function of composition²² which can be used to verify the reasonableness of the assumed functional relationship between Γ and composition.

21. CAHN, J. W., and HILLIARD, J. E. *On the Equilibrium Segregation at a Grain Boundary*. Acta Met., v. 7, 1959, p. 219-221.

22. HONDROS, E. D. *The Influence of Phosphorus in Dilute Solid Solution on the Absolute Surface and Grain Boundary Energies of Iron*. Proc. Roy. Soc. London. v. A286, 1965, p. 479-498.

Since the problem of impurity-induced embrittlement deals mainly with trace amounts of impurities, the alloy can be treated as a dilute solution for which

$$d\mu/dx = kT/x \quad (15)$$

Equation 13 can then be written

$$d\gamma/dx_2 = -\Gamma_{2(1)} (d\mu_2/dx_2) = -(kT/x_2)\Gamma_{2(1)} \quad (16)$$

It will be assumed that the relative surface and boundary excesses depend upon composition in a manner given by the relations

$$\Gamma_S = Ax^n \quad (\text{for the free surface}) \quad (17)$$

$$\text{and } \Gamma_B = Bx^m \quad (\text{for the grain boundary}) \quad (18)$$

where A and B are temperature-dependent coefficients and n and m are constants having values less than one. Substitution of Equations 17 and 18 into Equation 16 and carrying out the integration gives the result

$$\gamma_S = \gamma_S^0 - (kTA/n)x^n \quad (19)$$

$$\text{and } \gamma_B = \gamma_B^0 - (kTB/m)x^m \quad (20)$$

The data of Hondros²² on the effect of phosphorus on the absolute surface and grain boundary energies of iron are shown in Figures 4 and 5 for the gamma and delta phases. The solid lines are equations of the form given in Equations 17 and 18, i.e.,

$$\gamma_S^\gamma = 2130 - 740 x^{1/3} \quad (\text{Figure 4a}) \quad (21a)$$

$$\gamma_B^\gamma = 745 - 265 x^{1/3} \quad (\text{Figure 4b}) \quad (21b)$$

$$\gamma_S^\delta = 2090 - 1535 x^{1/2} \quad (\text{Figure 5a}) \quad (21c)$$

$$\gamma_B^\delta = 845 - 635 x^{1/3} \quad (\text{Figure 5b}) \quad (21d)$$

It can be seen that these equations are a reasonable representation of the experimental data, so that the assumed form of the relationship between composition and the interfacial excess also is reasonable.

For an alloy of composition X_0 , the change in grain boundary energy relative to that of pure solvent is given by Equation 20:

$$\Delta\gamma_B \equiv \gamma_B^0 - \gamma_B(x = X_0) = (kTB/m)X_0^m \quad (22)$$

Similarly, the change in fracture surface energy is given by Equation 19:

$$\begin{aligned} \Delta\gamma_{FS} &\equiv \gamma_S^0 - \gamma_{FS}(x = X_0) \\ &= \gamma_S^0 - \gamma_S(x = X') = (kTA/n)(X')^n \end{aligned} \quad (23)$$

where X' is defined as that composition for which the surface excess $\Gamma_S(x = X')$, is equal to half the boundary excess, $\Gamma_B(x = X_0)/2$. Combining this definition of X' with Equation 17 leads to

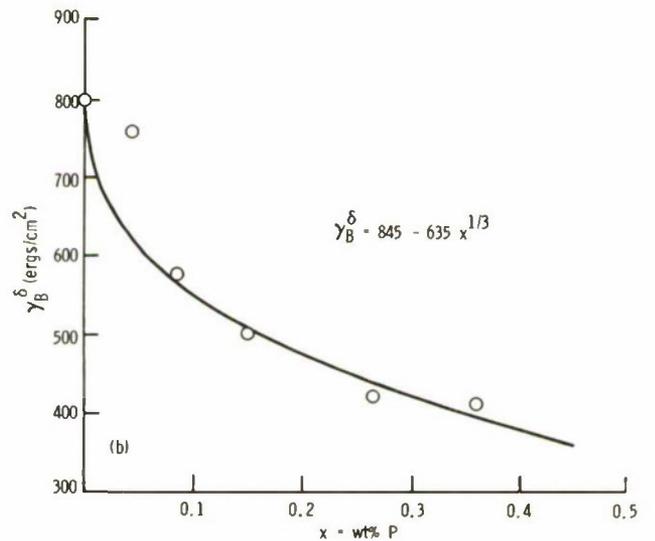
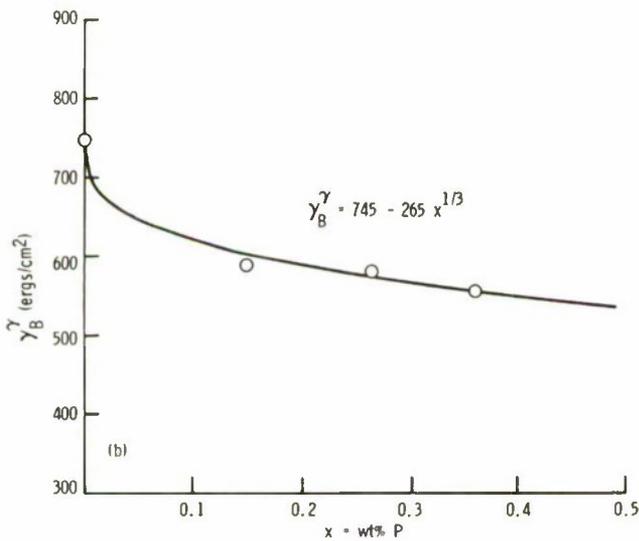
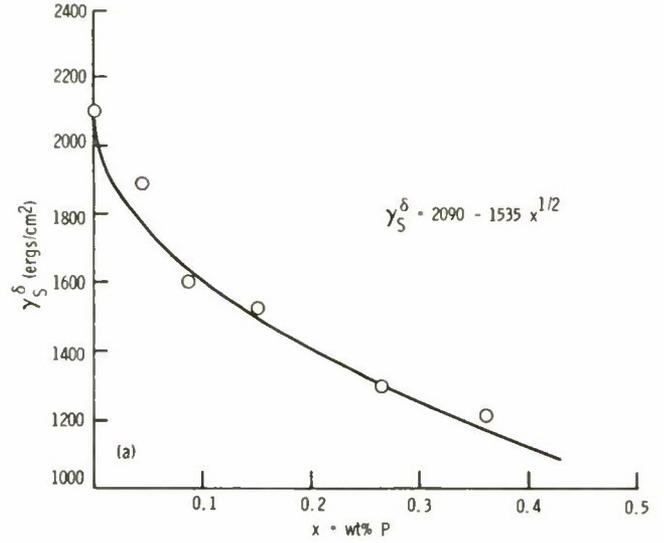
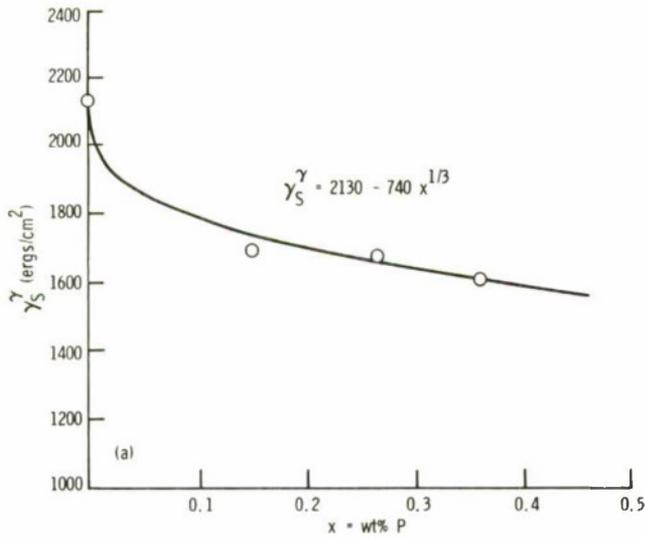


Figure 4. The effect of phosphorus concentration on (a) the surface energy and (b) the grain boundary energy of γ -iron.

Figure 5. The effect of phosphorus concentration on (a) the surface energy and (b) the grain boundary energy of δ -iron.

$$\begin{aligned}\Gamma_{FS} &= A \cdot (X')^n = \Gamma_B(x = X_0)/2 \\ &= BX_0^m/2\end{aligned}\tag{24}$$

Therefore,

$$(X')^n = BX_0^m/2A\tag{25}$$

Substituting back in Equation 23 gives

$$\Delta\gamma_{FS} = (kTA/n)(BX_0^m/2A) = (kTB/2n)X_0^m\tag{26}$$

Utilizing Equations 22 and 26, the embrittlement criterion then becomes

$$2\Delta\gamma_{FS} - \Delta\gamma_B = kTBX_0^m(1/n - 1/m) < 0\tag{27}$$

from which m must be less than n for embrittlement to occur. For $m \geq n$, the energy required to make two fracture surfaces by splitting one grain boundary in the alloy is equal to or greater than the energy to do the same thing in pure solvent, so that the impurity element has no embrittling effect whatsoever, even though it may be adsorbed on the grain boundaries. For $m < n$, there will be an embrittling effect, the severity of which is greater the higher the concentration of the impurity (i.e., the higher the value of X_0) and the higher the value of the constant B (i.e., the stronger the tendency for the impurity to segregate to the grain boundary). This is in qualitative agreement with our intuition and with those few experimental observations which do exist.

Based upon the values of m and n inferred from Hondros' data described in Equation 21(a-d), one would expect δ -iron to possibly be embrittled by phosphorus but γ -iron not. It is known that γ -iron is not embrittled by adsorbed phosphorus, and although it is not known if δ -iron is embrittled,* the other body-centered cubic form of iron, α -iron, is indeed embrittled by phosphorus.⁵⁻⁶ In addition, several alloying elements are known to segregate to grain boundaries in iron or steel, where they reduce the boundary energy but cause no embrittlement.²³⁻²⁵ This analysis provides at least one rationale for this type of behavior also.

An attempt was made to select fairly general functions to describe the composition dependence of the surface and boundary excesses. Obviously other selections could have been made which would have modified the specifics of the embrittlement criterion. Nevertheless, after trying some other reasonable functions, certain general qualitative characteristics of the embrittlement criterion emerge:

(1) If the ratio Γ_S/Γ_B increases with increasing concentration of impurity, the impurity will have an embrittlement tendency. If that ratio decreases the impurity is nonembrittling.

*Since B is inversely related to temperature, the high temperature range over which δ -iron exists most likely prevents any substantial segregation of phosphorus to the grain boundaries and an embrittling effect would probably be absent as a result.

23. HARRIS, L. A. *Some Observations of Surface Segregation by Auger Electron Emission*. J. Appl. Phys., v. 39, 1968, p. 1428-1431.
24. STEIN, D. F., JOSHI, A., and LaFORCE, R. P. *Studies Utilizing Auger Electron Emission Spectroscopy on Temper Embrittled of Low Alloy Steels*. Trans. ASM, v. 62, 1969, p. 776-783.
25. MARCUS, H. L., and PALMBERG, P. W. *Auger Fracture Surface Analysis of a Temper Embrittled 3340 Steel*. Trans. TMS-AIME, v. 245, 1969, p. 1664-1666.

(2) If the ratio $\Delta\gamma_S/\Delta\gamma_B$ increases with increasing concentration of impurity, the impurity will be embrittling. If not it will be nonembrittling. Actually this condition is a corollary of condition (1).

Unfortunately, very accurate measurements of boundary and surface energies or of boundary and surface excesses would be required as a function of composition to check this prediction, and very few are available, especially of the required accuracy.

Combining Equations 22 and 27, the embrittlement criterion can be written

$$2\Delta\gamma_{FS} - \Delta\gamma_B = \Delta\gamma_B(m/n - 1) < 0 \quad (28)$$

Thus, at least for the functions assumed here for the composition dependence of the surface and boundary excesses, the net change in interfacial energy (Equation 14) is proportional to but less than the change in grain boundary energy induced by impurities. However, since it is not likely that m will be much different than n , the net change in interfacial energy can probably be expected always to be much less than $\Delta\gamma_B$, and the degree of boundary decohesion actually experienced on this basis is unlikely, therefore, ever to be large.

The preceding discussion has looked solely at the potential for embrittlement caused by an impurity-induced reduction in the grain boundary energy, with no attention paid the effect which impurities might have on the plastic work term in Equation 2. Undoubtedly the plastic work involved in crack extension in ductile metals also is affected by impurities, and one could argue convincingly that it is this term which must be substantially reduced for embrittlement to occur. For those that would believe that a reduction in the plastic work term will be directly related to a reduction in the surface energy, the embrittlement criterion might in fact be similar to that stated previously. However, it is more likely that the effect of impurities on the plastic work term is incidental to their presence in the vicinity of the crack tip and does not depend directly on the effect of the impurities on boundary energy. The role of impurities in inherently ductile materials may simply be to locally raise the yield strength near the boundary, restricting plastic flow at the crack tip. The consequences of such an increased flow stress might be described in terms of a reduced strain to fracture, or a resistance to blunting of the crack, or in a reduced plastic zone size, lessening the energy converted to plastic work. Whatever the case, it is worth noting that all the known embrittling elements in iron are potent solid solution strengtheners. There currently is no model which explains the effect of adsorbed impurities on the plastically deformed region around the tips of grain boundary cracks, but this would appear to be the place to look for the explanation of impurity-induced intergranular embrittlement of otherwise ductile metals.

SUMMARY

The well-known embrittling effects of certain solute elements in various materials have been discussed from the standpoint of their effect on interfacial energy. It was shown that essentially all solutes can cause a reduction in grain boundary energy, but that only when certain relationships occur between the

composition dependence of the surface and grain boundary energies can there be a true decohesion of the boundary. The conditions for embrittlement on this basis are described in terms of the ratio of the surface and boundary excesses or equivalently in terms of the ratio of the changes in surface and boundary energies. The net change in the interfacial energy produced by crack extension (i.e., $2\gamma_{FS} - \gamma_B$) is likely never to be large.

The applicability of the stated embrittlement criterion is greatest for those materials in which the plastic work associated with crack extension is small, or in which that plastic work is directly related to boundary cohesion. It is pointed out, however, that impurities present in the vicinity of a grain boundary crack can affect the plastic work of crack extension independent of an effect on boundary energy. In ductile materials, therefore, the indiscriminate and broadly used explanation for grain boundary embrittlement based upon an impurity-induced reduction in boundary energy is not well founded.

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The segregation of impurities to grain boundaries is shown to produce a reduction in the grain boundary energy, but that this does not necessarily coincide with a tendency toward embrittlement caused by decohesion. Indeed, it is shown that only when certain relationships occur between the composition dependence of the surface and grain boundary energies can there be a true decohesion of the boundary. The criterion for embrittlement, based on boundary decohesion, requires that the ratio of the changes in surface and boundary energies increase with concentration of the impurity, or equivalently, that the ratio of the amount of impurity segregated to the surface to the amount of impurity segregated to the boundary increase with increasing impurity concentration. However, since impurity segregation to grain boundaries occurs independent of whether or not decohesion results, an effect of impurities in the vicinity of the grain boundary on localized plasticity is likely to be the dominant factor in intergranular embrittlement of otherwise ductile materials.

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