

THE IMPURITY-DRAG EFFECT IN GRAIN BOUNDARY MOTION*

JOHN W. CAHN†

The drag on a grain boundary produced by an impurity atmosphere is examined in detail, and is found to depend on the velocity of the grain boundary relative to the diffusivity of the impurity and its interaction with the grain boundary. At high velocities the faster diffusing impurities have the greater drag; whereas at low velocities the reverse is true. With increasing impurity concentration or with decreasing temperature a boundary may experience a transition due to a changing interaction with its impurity atmosphere. The nature of the transition depends on driving force and may give rise to a large apparent activation energy, as well as jerky boundary motion due to the existence of a range of conditions where two boundary velocities are possible. Special orientation effects that may result in textures are expected to occur more easily at high velocities.

DIE BREMSWIRKUNG VON VERUNREINIGUNGEN AUF DIE KORNGRENZENWANDERUNG

Die Behinderung der Korngrenzenbewegung durch Verunreinigungen wird im einzelnen untersucht; sie hängt demnach vom Verhältnis der Korngrenzengeschwindigkeit zur Diffusionsgeschwindigkeit der Verunreinigungen und deren Wechselwirkung mit der Korngrenze ab. Bei hohen Geschwindigkeiten bremsen die leichter diffundierenden Verunreinigungen stärker, bei kleinen Geschwindigkeiten ist es umgekehrt. Mit zunehmender Konzentration der Verunreinigungen oder mit abnehmender Temperatur kann eine Korngrenzenumwandlung eintreten, bedingt durch eine veränderte Wechselwirkung mit den Verunreinigungen. Die Art der Umwandlung hängt von der treibenden Kraft ab und bewirkt eine große, scheinbare Aktivierungsenergie, sowie eine ruckweise Korngrenzenbewegung, deren Ursache ein Bereich ist, in dem zwei Korngrenzengeschwindigkeiten möglich sind. Spezielle Orientierungseffekte, die zu Texturbildung führen können, sollten bei hohen Geschwindigkeiten leichter eintreten.

In recent years a number of authors⁽¹⁻⁷⁾ have reported a large reduction in grain boundary mobility when small amounts of soluble impurities were added to high purity metals. The main theoretical paper in this area has been that of Lücke and Detert⁽⁸⁾, which predicts the following:

(1) At high concentration or low driving force, the velocity V is determined by an impurity drag effect in which the impurities are dragged along by the grain boundary

$$V = \frac{PD(\infty)}{kT\Gamma} \quad (1)$$

where P is the driving force, $D(\infty)$ the bulk diffusion coefficient, and Γ the number of adsorbed impurity atoms per unit area of grain boundary. $D(\infty)$ is given by them as $D_0 e^{-Q/kT}$ and Γ by $4\sqrt{2}C_0/a^2 e^{-E/kT}$ where C_0 is the bulk impurity concentration, a the lattice parameter and E the interaction energy between an impurity atom and the grain boundary. (We shall

take E as negative if there is adsorption. Its sign is thus opposite to Lücke and Detert's interaction energy V .)

(2) Under low concentration-high driving force conditions defined by

$$P \geq N_v C_0 E e^{E/kT} \quad (2)$$

where $N_v = 4/a^3$ is the number of atoms per unit volume, the boundary breaks away from its atmosphere and its rate of motion is "determined by the rate of diffusion of foreign (*sic*) atoms across the boundary. Therefore the activation energy of recrystallization for very pure material or at high enough temperatures should be equal to the activation energy of grain boundary diffusion". Lücke and Detert suggest that at the transition between these two extremes there is a discontinuity in velocity, although in their schematic diagrams they show the velocity continuous through a broad transition region.

One of the main failures in the theory is the inability to explain Aust and Rutter's results⁽⁵⁾ on the relative effect of silver, gold and tin in high purity lead. According to equation (1), silver⁽⁹⁾ and gold,^(9,10) which in

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† General Electric Research Laboratory, Schenectady, New York.

lead diffuse faster than tin,⁽⁹⁾ should exert less of drag and permit the boundary to move faster. In fact just the reverse is true. Furthermore, although the theory suggests a discontinuous break-away, the observed transition in velocity is more gradual. In addition there are a number of serious approximations in the theory, many^(5,11) of which have been questioned. The purpose of the present paper is to remove a number of these approximations, keeping, however, their main assumption that it is the force exerted by an impurity atmosphere which is responsible for the observed phenomena.

In the present paper we will (Section 1) solve for the composition profile of a boundary moving at a specified velocity. From this composition profile we can (Section 2) calculate the force exerted by the impurity atoms. We shall find that this force initially rises with increasing velocity and then decreases as the velocity becomes high. By adding to this impurity drag force the force needed to keep a boundary moving with that velocity in the pure material, we obtain (Section 3) the total force necessary to move the boundary with that velocity in the impure material. Thereby we obtain a velocity-driving force relation for that composition and temperature, from which the velocity can be obtained as a function of temperature and composition.

1. THE COMPOSITION PROFILE

Let us assume that, as far as the impurity atoms are concerned, the boundary is represented by an interaction energy $E(x)$ and a diffusion coefficient for motion normal to the boundary $D(x)$, both of which are functions of the distance from an arbitrarily chosen center plane of the boundary.

The chemical potential of the impurity species is assumed to be given by

$$\mu = kT \ln C(x) + E(x) + \text{const.} \quad (3)$$

where the constant is so chosen that $E(\infty) = 0$. The flux of atoms is assumed to be

$$-J = \frac{DC}{kT} \frac{\partial \mu}{\partial x} = D \frac{\partial C}{\partial x} + \frac{DC}{kT} \frac{\partial E}{\partial x} \quad (4)$$

and

$$\begin{aligned} \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \left[\frac{\partial D}{\partial x} + \frac{D}{kT} \frac{\partial E}{\partial x} \right] \frac{\partial C}{\partial x} \\ + \frac{1}{kT} \left[\frac{\partial D}{\partial x} \frac{\partial E}{\partial x} + D \frac{\partial^2 E}{\partial x^2} \right] C. \end{aligned} \quad (5)$$

If the boundary moves with a steady velocity then the

composition profile is expected to reach a steady state value for which

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} \quad V > 0$$

and therefore

$$\begin{aligned} 0 = D \frac{\partial^2 C}{\partial x^2} + \left[\frac{\partial D}{\partial x} + \frac{D}{kT} \frac{\partial E}{\partial x} + V \right] \frac{\partial C}{\partial x} \\ + \frac{C}{kT} \left[\frac{\partial D}{\partial x} \frac{\partial E}{\partial x} + D \frac{\partial^2 E}{\partial x^2} \right]. \end{aligned} \quad (6)$$

This equation describes the composition profile at steady state for an arbitrary $E(x)$ and $D(x)$. It is general and involves only the assumptions inherent in equation (3) (dilute solution everywhere) and in equation (4). Strictly the assumption in equation (4) is that D defined as the ratio $-JkT/(\partial\mu/\partial x)$ is for a given temperature a function only of x the position relative to the boundary.

Equation (6) has the solution

$$\begin{aligned} C = C_0 V \exp \left\{ -\frac{E(x)}{kT} - V \int_{x_0}^x \frac{d\eta}{D(\eta)} \right\} \\ \times \int_{-\infty}^x \exp \left\{ \frac{E(\xi)}{kT} + V \int_{x_0}^{\xi} \frac{d\eta}{D(\eta)} \right\} \frac{d\xi}{D(\xi)}. \end{aligned} \quad (7)$$

It is seen from the form of the solution that the composition at a point x is only influenced by the part of the boundary still approaching and that it reflects no influence of the parts already past. The composition profile trailing the boundary at steady state is identically C_0 .

Because of this asymmetry in the form of the solution, equation (7) does not hold for $V < 0$ and $V = 0$ represents a singularity in the solution. For $V = 0$ we have from equation (3)

$$C = C_0 \exp \left[-\frac{E(x)}{kT} \right]. \quad (8)$$

2. THE IMPURITY DRAG

An impurity atom will exert a force $-(dE/dx)$ on the boundary. The total force exerted by all the impurity atoms on the boundary is therefore given by

$$P_i = -N_v \int_{-\infty}^{+\infty} (C - C_0) \frac{dE}{dx} dx. \quad (9)$$

In order to find P_i we must obtain and evaluate C from equation (7) and perform the integration. Because of the complexity of equation (7) and our lack of knowledge about $E(x)$ and $D(x)$ we will be concerned with limiting cases or with additional assumptions.

These follow here:

(1) *High velocity limit*

If the velocity is so high that

$$V \gg - \frac{D(x)}{kT} E'(x) \tag{10}$$

for all x , we can by expanding $D(\xi)$ and $E(\xi)$ and $\int_{x_0}^{\xi} \frac{dn}{D(n)}$ in equation (7) as in Taylor's series about $\xi = x$, obtain that the composition is given approximately by

$$C(x) \cong \frac{C_0}{1 + \frac{DE'}{kTV}} \tag{11}$$

and the impurity drag is given by

$$P_i \cong \frac{C_0 N_v}{kTV} \int_{-\infty}^{+\infty} E'^2 D dx. \tag{12}$$

In contrast to this Lücke and Detert's equation (1) (in the notation of this paper) has P proportional to V and inversely proportional to D . Equation (12) is therefore of the proper form for explaining Aust and Rutter's results on silver and gold in lead, if their samples satisfied the high velocity criterion.

(2) *Low velocity limit*

If we assume that there exists a distance Λ from the boundary beyond which $E = 0$ and $D = D(\infty)$, we can for V small, that is,

$$1/V > \int_{-\Lambda}^{\Lambda} \frac{dx}{D(x)} \tag{13}$$

expand the part of the exponential involving V in equation (7) and obtain for $-\Lambda < x < \Lambda$

$$C = C_0 e^{-E/kT} \left\{ 1 + V \int_{-\Lambda}^x \frac{e^{\frac{E(\xi)}{kT}} - 1}{D(\xi)} d\xi + O(V^2) \right\}. \tag{14}$$

We can, in equation (14), replace the lower limit by $-\infty$. Thus the exact location of Λ is not significant. Equation (14) corrects several misconceptions one might have about what happens to the atmosphere at small velocities. The atmosphere does not remain undiminished with only a lag, as is assumed in Lücke and Detert's treatment. Instead, if E is nowhere positive, the composition is everywhere reduced. Desorption begins immediately at small velocities. Similarly if E is nowhere negative, the composition is everywhere raised.

For the impurity drag we obtain upon substituting equation (14) into equation (9)

$$P_i = 4N_v C_0 V kT \int_{-\infty}^{+\infty} \frac{\sinh^2 [E(x)/2kT]}{D(x)} dx. \tag{15}$$

Comparison of equation (15) with equation (1) indicates several important similarities and differences:

(1) Equation (15) reduces to equation (1) if $E(x)$ is large and negative at the grain boundary and if $D(x)$ is constant and equal to the bulk diffusion coefficient.

(2) Equation (15) is independent of the sign of E , and predicts that drag for impurities which avoid the boundary is the same as it is for impurities which are adsorbed. The former are pushed ahead of the boundary; the latter are dragged along by the boundary.

(3) Equation (15) clearly specifies which diffusion coefficient is appropriate if $D(x)$ is not constant.

(3) *Assumed profile*

In order to present graphically some of the features of these equations, D was assumed constant and E was assumed to vary with x in the manner shown in Fig. 1. Fig. 2 gives a series of composition profiles for E_0 negative, and Fig. 3 gives the same for E_0 positive. Fig. 4 gives the corresponding impurity drag. The limiting laws are also given.

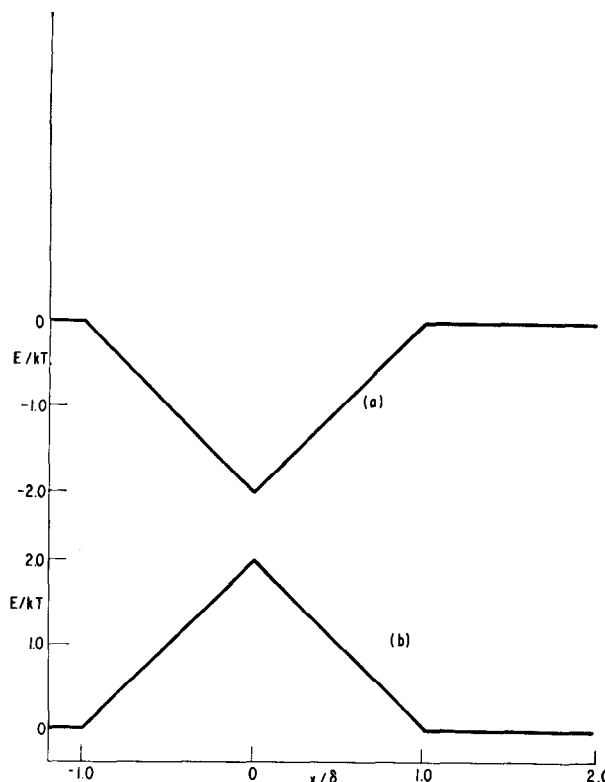


FIG. 1. The interaction energy profile $E(x)$ used in computing Figs. 2-4. (a) $E < 0$; (b) $E > 0$.

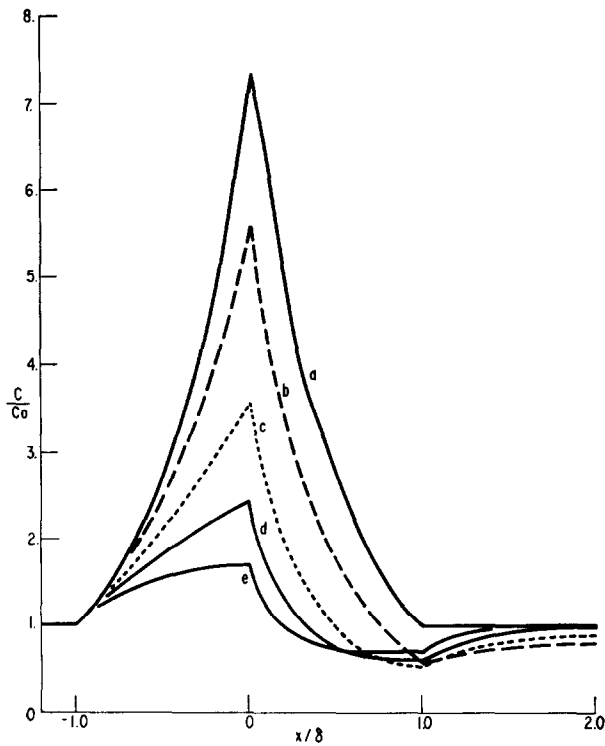


FIG. 2. Composition profiles for E negative for various velocities. (a) $V\beta = 0$ equilibrium; (b) $V\beta = \frac{1}{3}$ low velocity. Note that desorption occurs everywhere but is higher at the leading half; (c) $V\beta = 1$; for this velocity the impurity drag is a maximum; (d) $V\beta = \sqrt{3}$, the inflection in the drag-velocity curve. Note that the desorption ahead of the interface is beginning to diminish, while desorption behind the interface is continuing, leading to diminishing drag; (e) $V\beta = 3$, a high velocity. The composition profile is beginning to approach the step function predicted by equation (11) for this boundary.

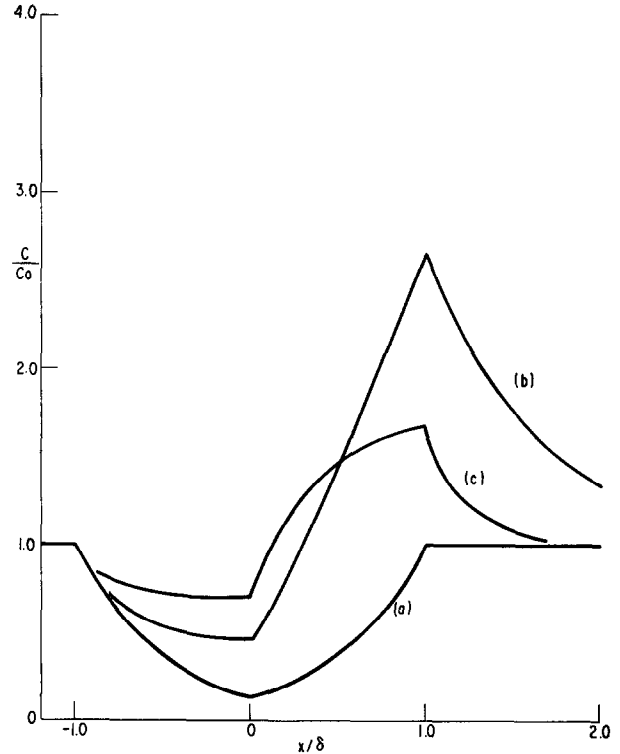


FIG. 3. Composition profiles for E_0 positive for various velocities. (a) $V\beta = 0$ equilibrium; (b) $V\beta = 1$ maximum drag. Note pile-up ahead of interface; (c) $V\beta = 3$, high velocity. Approach to step function predicted by equation (11).

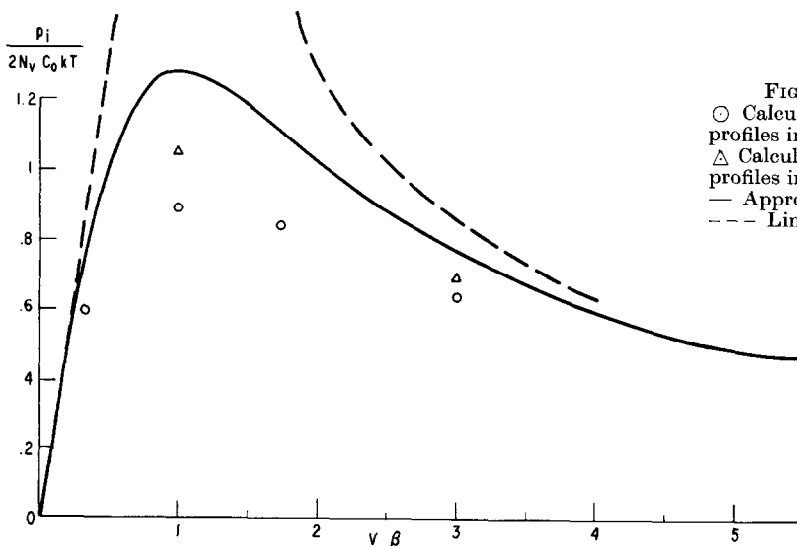


FIG. 4. Impurity drag for various velocities.
 ○ Calculated from equation (9) using composition profiles in Fig. 2 ($E < 0$);
 △ Calculated from equation (9) using composition profiles in Fig. 3 ($E > 0$);
 — Approximate equation (16)
 --- Limiting laws, equations (12) and (15).

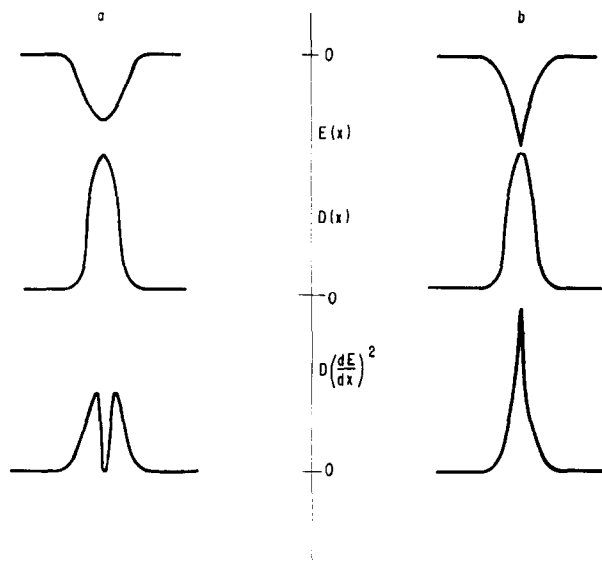


FIG. 5. The contributions to impurity drag at high velocities from various parts of the impurity atmosphere shown schematically for two cases. (a) Energy of interactions has flat minimum at center of boundary; (b) Energy of interaction has pointed minimum at center. Top curves shows interaction energy; middle curve, diffusion coefficient; bottom curve, contribution to drag; all as functions of distance from center of boundary.

Although equation (9) defines the force exerted by the impurity atoms as an integral across the boundary it does not show directly what features of the boundary are responsible. For example, at equilibrium when C is given by a Boltzmann factor, equation (9) integrates to zero indicating that the forces pulling and pushing cancel. In order to see where the net forces originate, it is simpler to consider equations (12) and (15) in which the dependent variable C does not appear in the integrand.

From equations (12) and (15) we see that drag develops everywhere across the boundary regardless of whether E or dE/dx is positive or negative. Regions, where dE/dx is positive and where, according to equation (9), the impurities pull the boundary forward, nevertheless contribute to the drag simply because the impurity concentration there is falling off more rapidly with increasing velocity than regions where dE/dx is negative. This is shown in Figs. 2 and 3.

Thus equation (12) and (15) show where in the boundary the drag originates. A closer examination of equation (12) reveals that at high velocity we must distinguish between two kinds of boundaries, one in which $E(x)$ reaches a flat extremum at the center and for which dE/dx is zero there, and the other in which $E(x)$ has a pointed extremum. The integrand of equation (12) for the former case is shown schematically in Fig. 5(a), for the latter case in Fig. 5(b). In the latter

case the drag comes from the center of the boundary and the appropriate diffusion coefficient is a grain boundary diffusion coefficient. In the former case the center contributes little, and most of the drag comes from the transition region where both E and presumably D also are changing. Thus the diffusion coefficient there is neither a bulk nor a grain boundary diffusion coefficient.

At low velocities the situation is even more complicated, for both the numerator and denominator of the integrand increase as we approach the center of the boundary. The numerator goes from zero to something probably no greater than 10^4 ; the denominator increases⁽¹²⁾ typically by a factor of 10^6 . We thus can think of two cases: in one the range over which $E(x)$ is altered is greater than the range over which $D(x)$ is altered. This might be because the elastic interactions between boundary and impurity extend far, whereas the disordered liquid-like region in which the diffusivity is high is narrow. In that case the integrand will appear as in Fig. 6(a) and most of the drag will come from a region away from the center of the boundary with a diffusivity much below that of the grain boundary. On the other hand, if numerator and denominator have similar ranges we obtain a situation in which the center contributes most heavily to the drag as shown in Fig. 6(b). In this case we expect a very small impurity drag.

Approximate equation for impurity drag

By comparing equations (12) and (15), we see that it is possible to construct an approximate equation for the drag which fits the high and low velocity extremes

$$P_i = \frac{\alpha V C_0}{1 + \beta^2 V^2} \quad (16)$$

where

$$\alpha = 4N_v kT \int_{-\infty}^{+\infty} \frac{\sinh^2 \frac{E(x)}{2kT} dx}{D(x)} \quad (17)$$

$$\alpha/\beta^2 = \frac{N_v}{kT} \int_{-\infty}^{+\infty} \left(\frac{dE}{dx} \right)^2 D(x) dx. \quad (18)$$

Both α and β are approximately inversely proportional to diffusivity. With increasing velocity, P_i first increases, reaches a maximum at $V\beta = 1$ and then decreases. It has an inflection point at

$$V\beta = \sqrt{3} \quad (19)$$

for which

$$\frac{dP_i}{dV} = -\alpha C_0/8 \quad (20)$$

and for which

$$P_i = \sqrt{3}\alpha C_0/4\beta \quad (21)$$

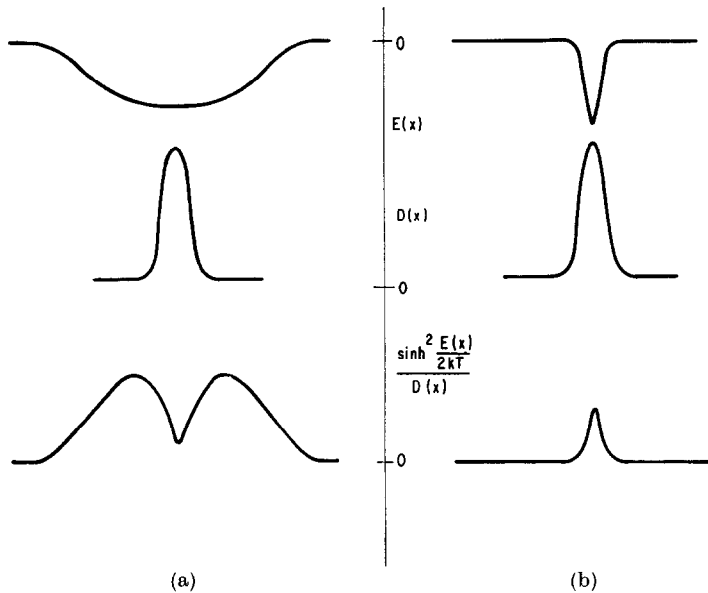


FIG. 6. The contributions to impurity drag at low velocities from various parts of the impurity atmosphere shown schematically for two cases. (a) Range of energy interaction greater than range of enhanced diffusivity; (b) Range of energy interaction smaller than range of enhanced diffusivity. Top curve shows interaction energy; middle curve, diffusion coefficient; bottom curve contribution to drag; all as functions of distance from center of boundary.

For the assumed profile of the previous section

$$\alpha = \frac{N_v(kT)^2}{E_0 D} \left(\sinh \frac{E_0}{kT} - \frac{E_0}{kT} \right)$$

$$\beta^2 = \frac{\alpha K T \delta}{2N_v E_0^2 D}$$

Fig. 4 shows how well the approximate equation (16) fits the impurity drag of this boundary.

3. THE VELOCITY AS A FUNCTION OF TEMPERATURE, COMPOSITION AND DRIVING FORCE

We have so far considered only the impurity drag. When the specimen is pure this becomes negligible and one is then able to measure a driving force-velocity relation which takes into account all other factors. Let us call these other factors the intrinsic drag and denote it by $P_0(V)$. There exist several theories^(13,14) for $P_0(V)$. Since most of these theories give a linear relation between the driving force and velocity, $P_0(V)$ is probably proportional to V . For our present purposes, the exact form is not important, provided that it does not curve strongly. It is hoped that experimentally determined values of $P_0(V)$ will be used whenever these are available, rather than the linear form assumed here.

When we come to impure materials, we may still define the intrinsic drag $P_0(V)$ to be the difference between the actual driving force $P(V, C)$ which gives a velocity V in a material with impurity concentration, C , and the impurity drag $P_i(V, C)$. We now come to an important assumption. Let us assume that P_0 is approximately independent of composition in the composition range of interest, or to put it another way

that the composition variation of P_0 is negligible compared to P_i . Under these conditions we can measure $P(V, C)$, $P_0(V)$ and thus obtain $P_i(V, C)$ which may be compared with the calculated. This assumption is made because, in the absence of any data, it seems reasonable. But its validity may be checked* and if it is found invalid, the same experiment would probably suggest suitable modifications.

With this assumption we now have an expression relating the velocity to composition, temperature and driving force

$$P(V, C) = P_0(V) + P_i(V, C). \quad (22)$$

Unfortunately this is an implicit relation for V and even after simplifying by assuming that P_i is given by equation (16) and that

$$P_0 = \lambda V \quad (23)$$

we still obtain a cubic algebraic equation in V

$$P = \lambda V + \frac{\alpha C_0 V}{1 + \beta^2 V^2}. \quad (24)$$

Here λ is intrinsic drag coefficient and is the reciprocal of the intrinsic mobility. Thus it is easier to discuss the results in terms of what driving force or what composition is necessary to obtain a given velocity than it is to ask what is the velocity for a given set of conditions. Therefore we begin with the various extremes and the transitions between them.

* Several experiments suggest themselves, but the simplest would be to measure the grain boundary velocity as a function of composition at very high driving forces and velocities. Under these conditions the impurity drag is small, and any large composition effect in the intrinsic drag will be most pronounced here.

The low velocity and low driving force extreme

When $V < 1/\beta$, equation (24) becomes

$$P = (\lambda + \alpha C_0)V$$

or

$$V = \frac{P}{\lambda + \alpha C_0}. \quad (24)$$

This low velocity is attained either by low driving force $P/\lambda < 1/\beta$ or high impurity content $P/\alpha C_0 < 1/\beta$. The low driving force is particularly simple since it lies within the low velocity extreme over the whole composition range, and equation (24) should hold. It predicts that $1/V$ should be a linear function of composition with slope α/P and intercept λ/P . Alternatively it predicts that for relatively high purity the velocity is independent of concentration and that with increasing concentration it approaches being inversely proportional to concentration. The transition between these should be continuous with no inflection.

The high velocity extreme

When $V \gg 1/\beta$ equation (24)* becomes

$$P = \lambda V + \frac{\alpha C_0}{\beta^2 V}.$$

This velocity requires a driving force

$$P \gg \lambda \beta^2 + \alpha C_0$$

or a

$$C_0 \ll (P - \lambda \beta^2)/\alpha.$$

Solving for V when C_0 is small

$$V = \frac{P}{\lambda} - \frac{\alpha C_0}{P \beta^2} = \frac{P}{\lambda} \left(1 - \frac{\alpha \lambda C_0}{\beta^2 P^2} \right). \quad (25)$$

For comparison the low-driving force extreme for C_0 small may be written

$$V = \frac{P}{\lambda} - \frac{\alpha P C_0}{\lambda^2} = \frac{P}{\lambda} \left(1 - \frac{\alpha C_0}{\lambda} \right) \quad (24a)$$

This illustrates the basic difference between the impurity effect at high and low driving forces respectively.

(1) At low driving forces the relative decrease in velocity produced by an impurity is insensitive to driving force. At high driving forces it is inversely proportional to the square of the driving force.

(2) At low driving force a slowly diffusing species has a greater composition effect. At high driving forces just the reverse is true, and the fast diffusing solute has the larger composition effect.

* I am very grateful to Dr. J. W. Rutter for the useful observation that, according to equation (24), the high velocity branch is limited to velocities not less than one-third the intrinsic velocity. Once the impurities have reduced the velocity by a factor exceeding 3, one is either in the low velocity region or in the transition region.

The transition region

We have seen that for very long driving forces, the transition between pure and impure boundary behavior should be continuous with no inflection point. At higher driving forces the boundary is capable of going at such velocities where the impurity drag has an inflection point. This inflection point has considerable effect on the nature of the transition region.

The inflection point occurs at

$$V = \sqrt{3}/\beta.$$

At this inflection point

$$\frac{dP}{dV} = \lambda - \frac{1}{8} \alpha C_0. \quad (26)$$

For $C_0 < C^* = 8\lambda/\alpha$ this slope will be positive and the $P(V)$ curve will increase monotonically. However, for $C_0 > C^*$ the slope will be negative at the inflection point and over a range in driving force there appear to be three velocities which satisfy the steady state conditions (Fig. 7).

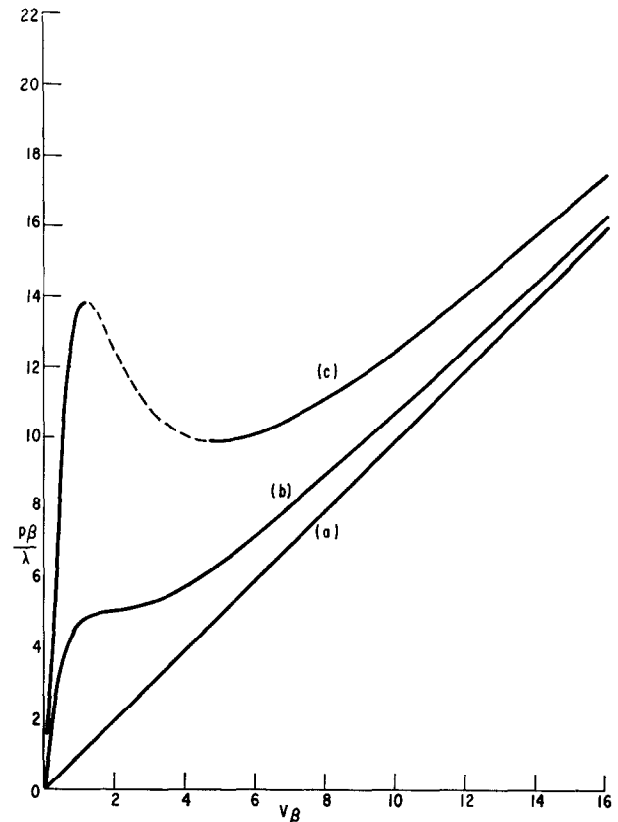


FIG. 7. The driving force versus velocity curve for various composition. (a) Pure material; (b) Impurity concentration less than c^* . Note that near inflection the velocity increases rapidly for small changes in driving force; (c) Impurity concentration approximately $3c^*$. The unstable part of this curve is broken. The two stable branches already conform well to the high and low velocity approximations.

The middle velocity, however, represents an unstable solution. This can be seen by considering a small variation in velocity. If the boundary momentarily goes faster, it will lose enough impurities, that the total drag will decrease, allowing the boundary to accelerate still further. Similarly if the boundary slows down momentarily, the total drag will increase, slowing the boundary down further.

The other solutions are stable for the total drag increases with increasing velocity, even though for the highest velocity solution, the impurity drag component decreases. Thus either of these two solutions, being stable to small velocity fluctuation, can be expected to maintain themselves for fairly long periods. It would take a fairly large perturbation to alter a boundary behavior from the high velocity solution to the low velocity solution or vice versa. For example, consider a fast moving boundary momentarily halted by an impurity particle. Locally impurities have gathered, and it now would proceed with the slow velocity. However, it is surrounded by fast moving regions that are moving ahead and it will find that the driving force is now increased by a surface tension times curvature term, which may be sufficient to raise the driving above the maximum driving force for which the slow solution exists. If the surface tension term is insufficient to do this, then the slow moving boundary has been "nucleated".

The region of two stable solutions thus may represent a region where boundary motion is jerky and measurements are not reproducible. In order to locate this region it is sufficient to remember that the inflection point in the unstable solution lies within it. Thus we expect to find such behavior at a composition in the vicinity of

$$C_0 = \frac{4\lambda}{\alpha} \left(\frac{\beta P}{\lambda\sqrt{3}} - 1 \right) \quad (27)$$

and the two possible velocities will straddle

$$V = \sqrt{3}/\beta.$$

The magnitude of driving force required is

$$P > \sqrt{3}\lambda/\beta. \quad (28)$$

At driving forces

$$\sqrt{3}\lambda/\beta < P < 3\sqrt{3}\lambda/\beta \quad (29)$$

the slope at the inflection point is positive and there will be a unique velocity for each composition over the entire composition range. The velocity will be a continuous function of composition through the transition region, although it will have an inflection point at

$$C_0 = \frac{4\lambda}{\alpha} \left(\frac{\beta P}{\lambda\sqrt{3}} - 1 \right) \quad (27)$$

The temperature coefficient and "activation energy"

The temperature dependence of velocity for a given sample (constant composition and driving force) has been interpreted in terms of an "activation energy". This "activation energy" is a complicated quantity and in the transition region is of little physical significance.

At the two extremes the activation energy is relatively simple. For the high purity material the activation energy refers to the intrinsic drag term only and is probably of the order of the activation energy for grain boundary self diffusion.

$$-\frac{d \ln V}{d(1/T)} = -\frac{d \ln \lambda}{d(1/T)} = Q_0. \quad (30)$$

For the high concentration extreme we obtain from equation

$$-\frac{d \ln V}{d(1/T)} = -\frac{d \ln (\lambda + \alpha C_0)}{d(1/T)} \cong -\frac{d \ln \alpha}{d(1/T)} = Q_\alpha. \quad (31)$$

Examination of the definition of the quantity α reveals that Q_α is a complicated quantity, which depends on which of the two situations depicted schematically in Fig. 6 is at hand. If the range over which $E(x)$ is changing is comparable to the range over which $D(x)$ is changing as in Fig. 6(b) then Q_α is approximately the sum of the activation energy of grain boundary diffusion and the adsorption energy of the impurity on the boundary. If, however, the range over which $E(x)$ is changing is much greater than the range of enhanced diffusivity, Q_α is much more complicated but would consist mainly of an activation energy for diffusion in this intermediate region which is probably close to bulk diffusion. The temperature dependent term arising from the hyperbolic sine, which for small values of the argument is no longer an exponential, would happily be small.

The activation energy for the transition region depends on the driving force. For extremely low driving forces it should go continuously from Q_0 at high temperatures to Q_α at low temperatures, provided that the transition occurs in the interval. For extremely high driving forces the activation energy is not defined since there will be a discontinuity in velocity in the transition region. For the intermediate driving forces the activation energy will reach a maximum at the temperature where the velocity is at the inflection in the isothermal curve.

$$\frac{d \ln V}{d(1/T)} = \frac{\frac{d \ln \lambda}{d(1/T)} - \frac{3\alpha C_0}{16\lambda} \frac{d \ln \beta}{d(1/T)} + \frac{C_0}{4\lambda} \frac{d \alpha}{d(1/T)}}{1 - \frac{\alpha C_0}{8\lambda}}. \quad (32)$$

Comparison with equation (26) indicates that the denominator is proportional to the slope of the P, V curve and that the apparent activation energy approaches infinity as this slope approaches zero. Thus in the intermediate range of driving force the apparent activation energy has a maximum in the transition region which becomes very large as P approaches $3\sqrt{3}\lambda/\beta$. Thus there is little physical significance to the "activation energy" in the transition region.

For extremely high driving forces, in the region of two steady state velocities, one might be tempted to measure some average velocity, in which case one obtains a continuous curve through the transition region and report an apparently finite activation energy maximum, which increases with decreasing driving force and approaches infinity as P approaches $3\sqrt{3}\lambda/\beta$.

DISCUSSION

The impurity drag phenomena have been classified according to boundary velocity and according to driving force.

(1) At very low velocities the impurity drag is given by a single parameter

$$\alpha = 4N_v kT \int \frac{\sinh^2 \frac{E(x)}{2kT}}{D(x)} dx \quad (17)$$

and the velocity by

$$V = \frac{P}{\lambda + \alpha C_0} \quad (24)$$

Thus the theory predicts that: (1) The velocity is proportional to driving force at constant composition; (2) That the reciprocal of the velocity is a linear function of composition, whose slope should permit evaluation of the parameter α and (3). That the impurity effect is independent of the sign of $E(x)$. This is contrary to the prediction of Lücke and Detert who predict a very small effect if $E(x)$ is positive.

(2) At very high velocities the impurity drag is also given by a single parameter

$$\alpha/\beta^2 = \frac{N_v}{kT} \int D(x) \left(\frac{dE}{dx} \right)^2 dx \quad (18)$$

and the velocity by

$$V = \frac{P}{\lambda} - \left(\frac{\alpha}{\beta^2} \right) \frac{C_0}{P} \quad (25)$$

Thus the theory predicts that: (1) The velocity is no longer strictly proportional to driving force, except under those conditions where the second term is negligible, that is, high purity or very large driving forces; (2) That the impurity drag diminish with higher driving force, or conversely that at higher driving forces greater impurity levels are required for equivalent effects; (3) That impurities having greater diffusivity will have the greater drag.

All the high velocity phenomena can be qualitatively understood by remembering that at these velocities the boundary sweeps through so fast that it produces only little change in the initially constant impurity concentration. Whatever change does occur contributes to the drag and altering the conditions to allow greater change, as, for example, lower velocity and higher impurity diffusivity, will give greater drag.

(3) There are three types of transition behavior to be expected in going from pure to impure material. The kind of transition depends on the driving force. (a) At very low driving forces the transition is smooth with no inflection in the variation of velocity with composition and no maximum in the apparent activation energy; (b) At intermediate driving forces the transition is still continuous, but there is an inflection in the variation of velocity with composition and a maximum in the apparent activation energy; (c) At high driving forces there are two branches to the velocity-composition curve, and a range of composition where two velocities are possible.

The magnitudes of driving force separating these three regions is of the order of $3\lambda/\beta$.

How does one determine whether one is dealing with high or low driving forces or high or low velocities? Due to our present lack of knowledge of the quantities $D(x)$ and $E(x)$ it is difficult from first principles to decide what is a low driving force or a low velocity. We must therefore rely on the experimentally determined behavior of a grain boundary to decide which of the extremes we are dealing with or what transition we are observing. Such measurements then will serve to evaluate the parameters α and β and permit predictions to be made for other driving forces and other compositions. At present we can only guess at the order of magnitude of the transition velocity $\sqrt{3}/\beta$.

(1) If the center contributes little to the drag at either high or low velocities, the transition velocity is approximately $10^{-1} D/\delta$, where D is a diffusion coefficient intermediate in magnitude between bulk and grain boundary diffusion coefficients. This velocity was obtained by setting

$$\alpha = 4N_v kT \left(\frac{E_0^2}{4kT} \right) \delta/D$$

and

$$\alpha/\beta^2 = \frac{N_v}{kT} \frac{DE_0^2}{\delta}$$

(2) For the case in which the center of the boundary contributes most heavily to the drag both at high and low velocity, the transition velocity is

$$\frac{D_B E_0 K^{1/2}}{\delta kT} \quad \text{if } K < 1 (E_0 > 0)$$

or

$$-\frac{D_B E_0}{\delta k T K^{1/2}} \quad \text{if } K > 1 \quad (E_0 < 0).$$

Here α was set equal to

$$\frac{4N_V k T \delta K}{D_B} \quad \text{if } K > 1$$

or

$$\frac{4N_V k T \delta}{D_B} \frac{1}{K} \quad \text{if } K < 1$$

where K is the partition coefficient (if $K > 1$, $\Gamma = N_V K C_0 \delta$) and $\alpha/\beta^2 \cong E^2 D_B N_V / \delta k T$.

In case (1) transition velocities are less than 10^{-3} cm/sec, assuming $D < 10^{-9}$ cm²/sec and in case (2) it is of the order of 10^{-1} cm/sec, assuming $D_B = 10^{-7}$ cm²/sec, $\delta = 10^{-7}$ cm, $K = 10^{+4}$, $E_0/kT = -10$. These estimates, although crude, indicate that the velocities Aust and Rutter encountered are greater than the transition velocity if the conditions for case (1) hold. These conditions were a flat extremum in $E(x)$ at the center of the boundary and that the range of enhanced diffusivity was smaller than the range of interaction of boundary with impurity. Their observation that the faster diffusing species exerted a greater drag indicates that their velocities are indeed greater than the tin transition velocity.* It also indicates that their relatively small driving force of 3000 ergs/cm³ is not a small driving force, in the sense of this paper, but a large one. Almost all work involving recrystallization of plastically strained crystals, in which the driving force is orders of magnitude greater, is therefore comfortably in the high driving force extreme.

Special boundaries

Aust and Rutter found that boundaries of certain special orientations were markedly less influenced by impurity atoms. Since these are boundaries for which a certain degree of matching of lattice exist, we expect better packing of atoms and resulting alterations in $D(x)$ and $E(x)$. We expect that $D(x)$ would be drastically reduced. This results in a reduction in transition velocity so that Aust and Rutter's boundaries were growing even further in the high velocity extreme than

* The reversal in relative drag of two species of widely differing diffusivities occurs at velocities only slightly greater than the transition velocity of the slower species. For all higher velocities the faster diffusing species exerts the larger drag, even though it may still be in its low velocity region.

were their ordinary boundaries. Equation (12) is thus applicable and the lowering of $D(x)$ should result in a lowering of impurity drag consistent with observations.

At very high concentrations, in the low velocity extreme, the change in $D(x)$ would have just the reverse effect and one might expect a reversal of the relative rates of growth of the two boundaries. The exact magnitude depends on the relative values of E of the two types. The energy factor is much more important at low velocities where it occurs as an exponential than it is at high velocities. The energy factor can, however, be obtained from surface tension measurements. The fact that Aust and Rutter⁽¹⁵⁾ fail to observe the development of special boundaries at high impurity levels of tin in lead seems to support this reversal.

At the sort of driving forces used in recrystallization, that is orders of magnitude greater than those used by Aust and Rutter, the special boundaries and the resulting texture should persist to much higher impurity concentrations, as found, for example, by Parthasarathi and Beck⁽¹⁶⁾.

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