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A.M. Glaeser and J.W. Evans

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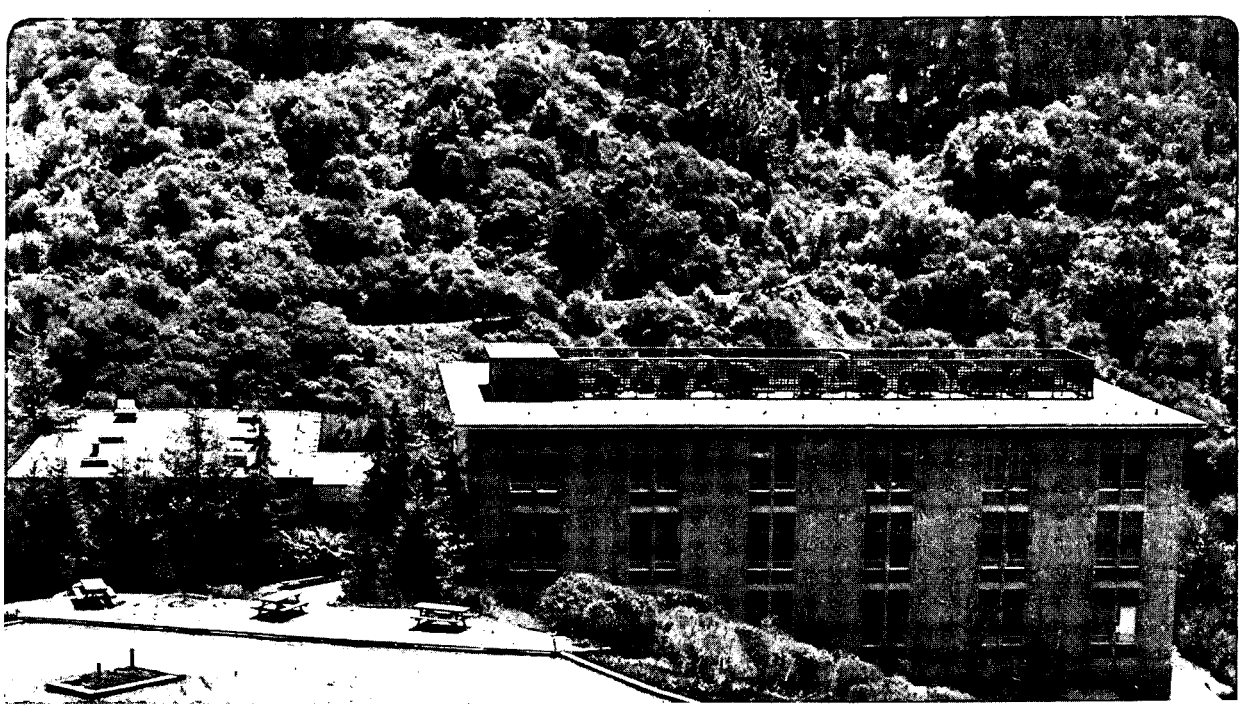

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Effect of Grain Boundary Migration on Apparent Boundary Diffusion Coefficients

by A. M. Glaeser[†] and J. W. Evans[*]

Department of Materials Science and Mineral Engineering
and
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley

ABSTRACT

The effect of grain boundary migration on the tracer concentration depth profiles that develop during a diffusion experiment is evaluated. An expression for the average tracer concentration within a plane at depth x and time t for a boundary migrating with velocity V is derived. This average concentration is compared to that expected for a stationary boundary. Results indicate that considerable errors in both the magnitude and temperature dependence of the apparent diffusion coefficient may arise if grain boundary migration is neglected.

[†] Assistant Professor of Ceramic Engineering, to whom correspondence should be addressed

[*] Professor of Metallurgy

Symbols:

$\bar{C}$	- mean concentration in a plane parallel to the surface at depth x
C_o	- tracer concentration at surface
D, D_b	- grain boundary diffusivity
D_ℓ	- lattice diffusivity
D_o	- pre-exponential term in boundary diffusivity
E	- activation energy for boundary diffusion
E_{AD}	- activation energy for boundary diffusion alone
E_ℓ	- activation energy for lattice diffusion
E_{AV}	- activation energy for boundary velocity (migration)
(E/kT_m)	- reduced (normalized) activation energy
L	- grain boundary displacement ($= Vt$)
M_t	- quantity of tracer diffused into the boundary per unit of grain area perpendicular to the x-axis
R	- ratio of $\partial \ln \bar{C}/\partial x$ for the moving boundary $[\partial \ln \bar{C}/\partial x]_V$ to $\partial \ln \bar{C}/\partial x$ for the stationary boundary $[\partial \ln \bar{C}/\partial x]_{V=0}$
s	- separation distance between grain boundaries
T	- temperature
T_m	- melting temperature
(T_m/T)	- reduced reciprocal temperature
t	- time
V	- grain boundary velocity
V_o	- pre-exponential term in velocity
W	- grain boundary thickness
x, X	- depth below sample surface
y	- distance normal to the boundary plane
η	- $(\equiv X\sqrt{\frac{V}{WD}})$, η^2 may be regarded as dimensionless grain boundary velocity
λ	- $(\equiv \frac{L}{W})$ dimensionless boundary displacement
ξ	- $(\equiv \frac{y}{W})$ dimensionless distance normal to boundary plane
τ	- dimensionless time $(= \lambda/\eta^2)$

Background:

Grain boundaries and their associated properties are of both considerable scientific interest and technological importance. Grain boundaries play essential roles in a broad range of kinetic phenomena in polycrystals, e.g., as preferential diffusion paths, sites for nucleation of second phases (precipitates and voids), as vacancy sources and sinks during sintering and creep, etc.. Grain boundary self-diffusion and/or heterodiffusion along both stationary and moving boundaries plays an important role in many of these phenomena. Thus, characteristics of boundary diffusion processes are of interest.

Several theoretical models and complimentary experimental techniques have been developed for measurement of grain boundary diffusion coefficients. Theoretical treatments of Fisher[1], Whipple[2], and Suzuoka[3] model the grain boundary as a **stationary** slab of thickness W perpendicular to the free surface, with negligible concentration gradients within the boundary slab in a direction parallel to the sample surface (the y-direction), and a transport coefficient D_b characterizing diffusion within the boundary. Diffusion within the boundary is assumed to obey Fick's Law; the boundary diffusivity is assumed to be much larger than the lattice diffusivity. Fixed surface concentration $C = C_o$ at $x = 0$ and $t > 0$ is assumed in both the Fisher and Whipple analyses. Fisher's solution is approximate, the Whipple solution exact. In contrast, Suzuoka modelled diffusion of a finite amount of tracer into the material by grain boundary and lattice diffusion in the absence of surface diffusion accomodated tracer redistribution.

All three solutions yield expressions for the tracer concentration as a function of depth below the surface x, distance normal to the

boundary plane y, and anneal time t. These expressions may be used to deduce the average tracer concentration within a plane at a depth x below the surface at time t. Alternatively, shapes of isoconcentration contours may be calculated as a function of the boundary diffusivity:lattice diffusivity ratio.

Information of this type may be experimentally determined and employed to evaluate D_b, or more specifically, the product WD_b. The boundary tracer concentration at depth x may be measured, the angle which isoconcentration contours make with the boundary plane may be determined, or the total amount of tracer within thin slices cut parallel to the surface may be analyzed. Experiments of the latter type, involving serial sectioning, are commonly used.

Such experimental measurements have been used to determine WD_b in a wide variety of materials, with numerous combinations of host material and tracer. Considerable attention has been given to grain boundary diffusion in metals, particularly fcc metals. Experiments have been conducted on both bicrystals and polycrystals. For some materials, data from both types of samples are available.

Diffusivities obtained using bicrystals often indicate variability in the magnitude of the diffusivity and the activation energy for boundary diffusion E. Grain boundary misorientation, boundary plane orientation, dislocation dissociation, and other factors have been shown to influence grain boundary diffusion. For a discussion of these effects, the reader is referred to the review by Peterson[4].

Within a polycrystal, both boundary misorientation and boundary plane orientation will be statistically distributed. Results of boundary diffusion experiments on a polycrystal are assumed to provide

average values of WD_b, representative of "general" or random grain boundaries. Consequently, the boundary diffusivity and activation energy appropriate to polycrystals may differ from those of a particular set of bicrystals. For example, when diffusivities for lead bicrystals and polycrystals are compared, the activation energy E varies between 4.7 and 15.7 kcal/mole, while calculated values of WD_b vary by up to two orders of magnitude. For silver, E varies between 11.8 and 30 kcal/mole, and the pre-exponential factor varies by several orders of magnitude.

Even when sets of polycrystal boundary diffusion data for nominally the same material are compared, scatter in diffusivities and activation energies is sometimes evident. Differences between calculated diffusivities may to some extent reflect differences in crystallographic texture, or the manner in which concentration depth profiles were converted into diffusivities, i.e., use of the Fisher analysis as opposed to the Whipple or Suzuoka analysis.

When boundary diffusion characteristics of a wide variety of materials are compared, additional factors contribute to variability. Hwang and Balluffi[5] compiled grain boundary diffusion data for polycrystalline metals. To compensate for materials differences, D_b was plotted versus a reduced reciprocal temperature (T_m/T) where T_m is melting temperature. A band of data spanning a wide range of homologous temperature results.

Hwang and Balluffi also plotted reduced (normalized) activation energy (E/kT_m) versus homologous temperature (T/T_m). Although the reduced activation energies vary, the data indicate the apparent activation energy for grain boundary diffusion decreases with decreasing

temperature. For $T > 0.42T_m$ the average normalized activation energy is 9.35, while at $T < 0.42T_m$ the activation energy is 6.93. Two explanations are proposed: 1) contributions from jump paths (mechanisms) with high activation energies are "frozen out" at low T and/or 2) contributions from boundaries with high E are frozen out as T decreases.

Grain boundary migration, either accompanying recrystallization or chemically induced (DIGM),[6] may also affect the apparent boundary diffusivity. Experimental studies[7,8] suggest diffusion in migrating boundaries may occur more rapidly than in stationary boundaries. Enhancements of up to 10^4 in WD_b and changes in E of up to 50% were reported. Differences in the diffusion mechanism in moving and stationary boundaries were suggested as an explanation for the increased diffusivity and change in activation energy.

Two factors complicate a comparison of these high diffusivities with those obtained from more conventional experiments. First, the misorientation of the migrating boundary was not determined, and misorientation may have a significant effect on the diffusivity. Second, the experiments involved diffusion of an impurity in a chemical potential gradient, and the results were compared to self-diffusion in a pure material with stationary boundaries.

Although changes in grain boundary diffusion mechanism as a result of simultaneous grain boundary migration have been proposed, the potential effect of grain boundary migration on tracer penetration and concentration-depth profiles in the **absence** of any mechanistic change has received relatively little attention[9]. The analyses of Fisher, Whipple, and Suzuoka assume stationary boundaries. Application of these analyses to samples with moving boundaries may result in apparent

diffusivities differing considerably from those appropriate to stationary boundaries.

Some amount of grain boundary migration is expected even at low temperatures in polycrystals. A driving force for grain growth is present in all polycrystals. To minimize this driving force, microstructures may be stabilized by grain growth anneals prior to tracer application. However, even in cases where the average grain size is large, small grains are also present, and the driving force for their disappearance can be quite large. In addition to boundary motion directly associated with grain disappearance, shifts in the positions of adjoining boundaries are necessary to re-establish equilibrium dihedral angles along triple junctions (triple points in two-dimensional sections) following grain elimination. This latter motion may not be readily apparent, and does not of itself contribute to grain growth. Finally, grain boundaries with non-perpendicular free surface intersections experience a driving force for migration[10].

The extent of grain boundary migration will depend on several factors. The range of anneal temperature will obviously be important. Reduction in grain boundary migration with decreasing temperature may introduce an apparent temperature dependence to the activation energy for boundary diffusion. Average grain size as well as grain size distribution will affect the driving force for migration. Sample purity may modify boundary mobility, and affect grain boundary migration rates. Study to study variations in any of these factors may contribute to scatter in reported or extrapolated boundary diffusivities.

The ensuing theoretical treatment assesses grain boundary migration effects on tracer penetration. An expression is derived describing the

average tracer concentration within a plane at depth x at time t for a boundary migrating with velocity V. This average concentration is compared to that expected for a stationary boundary. The modifying effect of a temperature dependent boundary velocity (mobility) on the apparent temperature dependence of the boundary diffusivity is evaluated. Although the results are most nearly applicable to grain boundary self-diffusion, the indicated trends and effects are expected to manifest themselves in a broader range of situations.

Mathematical Formulation:

Consider an idealized grain boundary as depicted in Fig. 1. The boundary is perpendicular to the surface of the solid (at which the tracer concentration is held at C_o) and has width W. The boundary is considered to be large in the direction perpendicular to the plane of the figure. It is moving with a constant velocity component V in a direction perpendicular to itself. It is assumed that diffusion in the grain boundary obeys Fick's first law (diffusivity of tracer = D) and that diffusion rates in the lattice are negligible. It is further assumed that any point in the lattice is swept no more than once by the moving grain boundary, and that the concentration at that point is equal to the concentration in the grain boundary as it sweeps through. Thus, diffusion occurs only when the region is encompassed by the boundary; the instantaneous boundary concentration profile is frozen in as the boundary migrates.

A differential balance on tracer within the grain boundary (assumed to be sufficiently narrow that concentration gradients in the y-direction are negligible) yields:

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} - \frac{VC}{W} \qquad (1)$$

Initial and boundary conditions are

$$C = 0 \quad \text{at} \quad t = 0 \quad \text{for } x > 0 \qquad (2)$$

$$C = C_o \quad \text{at} \quad x = 0 \quad \text{for } t > 0 \qquad (3)$$

$$C \to 0 \quad \text{as} \quad x \to \infty \qquad (4)$$

The partial differential equation and associated equations (2)-(4) are identical in form with those for unsteady state diffusion in one

direction coupled with first order reaction within semi-infinite solids. The solution for the latter problem is available[11] and can be used for the present case:

$$\frac{C}{C_o} = \frac{1}{2} \exp\left\{ -x \sqrt{\frac{V}{WD}} \right\} \operatorname{erfc}\left\{ \frac{x}{2\sqrt{Dt}} - \sqrt{\frac{Vt}{W}} \right\}$$

$$+ \frac{1}{2} \exp\left\{ x \sqrt{\frac{V}{WD}} \right\} \operatorname{erfc}\left\{ \frac{x}{2\sqrt{Dt}} + \sqrt{\frac{Vt}{W}} \right\} \qquad (5)$$

This equation gives the concentration at position x in the grain boundary at time t. The quantity of tracer diffused into the boundary at time t is given by:

$$M_t = C_o \sqrt{\frac{DW}{V}} \left\{ \left(\frac{Vt}{W} + \frac{1}{2} \right) \operatorname{erf}\sqrt{\frac{Vt}{W}} + \sqrt{\frac{Vt}{\pi W}} \exp\left(- \frac{Vt}{W} \right) \right\} \qquad (6)$$

where M_t is the quantity per unit of grain boundary area perpendicular to the x-axis.

The quantity in parenthesis {} in Eq. 6 increases more rapidly than $V^{\frac{1}{2}}$ on increasing V and consequently M_t is an increasing function of V. In other words, movement of the grain boundary increases the total amount of tracer diffused into the solid.

Of greater experimental interest than M_t is the amount of tracer measured along a plane (say x = X) parallel to the surface of the solid, i.e., the quantity:

$$\bar{C}s = \int_0^s C \, dy \qquad \text{at } x = X \qquad (7)$$

where $\bar{C}$ is the mean concentration in the plane and s is the separation between grain boundaries. The integral on the right of Eq. 7 can be

rewritten:

$$\bar{C}s = \int_{o}^{L} C\ dy + WC\Big|_{y=L} \tag{8}$$

where L = Vt is the present position of the left hand side of the grain boundary. The first term on the right of Eq. 8 represents tracer in the lattice, the second tracer in the grain boundary.

Recalling that the concentration at any point in the lattice is the concentration in the grain boundary when it sweeps through that point, Eq. 5 yields the lattice concentration:

$$\frac{C}{C_o} = \frac{1}{2} \exp\left\{ -X \sqrt{\frac{V}{WD}} \right\} \operatorname{erfc}\left\{ \frac{X}{2} \sqrt{\frac{V}{Dy}} - \sqrt{\frac{y}{W}} \right\}$$

$$+ \frac{1}{2} \exp\left\{ X \sqrt{\frac{V}{WD}} \right\} \operatorname{erfc}\left\{ \frac{X}{2} \sqrt{\frac{V}{Dy}} + \sqrt{\frac{y}{W}} \right\} \tag{9}$$

for $0 \leq y \leq L$

Equation 9 can now be substituted into Eq. 8 (in two places) yielding

$$\frac{s\bar{C}}{C_o} = \frac{1}{2}\exp\left\{-X\sqrt{\frac{V}{WD}}\right\}\int_0^L \operatorname{erfc}\left\{\frac{X}{2}\sqrt{\frac{V}{Dy}} - \sqrt{\frac{y}{W}}\right\}dy$$

$$+ \frac{1}{2}\exp\left\{X\sqrt{\frac{V}{WD}}\right\}\int_0^L \operatorname{erfc}\left\{\frac{X}{2}\sqrt{\frac{V}{Dy}} + \sqrt{\frac{y}{W}}\right\}dy$$

$$+ W\left[\frac{1}{2}\exp\left\{-X\sqrt{\frac{V}{WD}}\right\}\operatorname{erfc}\left\{\frac{X}{2}\sqrt{\frac{V}{DL}} - \sqrt{\frac{L}{W}}\right\}\right.$$

$$\left. + \frac{1}{2}\exp\left\{X\sqrt{\frac{V}{WD}}\right\}\operatorname{erfc}\left\{\frac{X}{2}\sqrt{\frac{V}{DL}} + \sqrt{\frac{L}{W}}\right\}\right] \qquad (10)$$

Putting $\xi \equiv \frac{y}{W}$, $\lambda \equiv \frac{L}{W}$, and $\eta \equiv X\sqrt{\frac{V}{WD}}$, Eq. 10 becomes

$$\frac{s\bar{C}}{WC_o} = \frac{1}{2}\exp(-\eta)\left[\int_0^\lambda \operatorname{erfc}\left(\frac{\eta}{2\sqrt{\xi}} - \sqrt{\xi}\right)d\xi + \operatorname{erfc}\left(\frac{\eta}{2\sqrt{\lambda}} - \sqrt{\lambda}\right)\right]$$

$$+ \frac{1}{2}\exp(\eta)\left[\int_0^\lambda \operatorname{erfc}\left(\frac{\eta}{2\sqrt{\xi}} + \sqrt{\xi}\right)d\xi + \operatorname{erfc}\left(\frac{\eta}{2\sqrt{\lambda}} + \sqrt{\lambda}\right)\right] \qquad (11)$$

The right hand side is a function only of η and λ.

Consider the case of large λ. The first integrand on the right of Eq. 11 $\rightarrow 2$ as $\xi \rightarrow \lambda$, while the second integrand $\rightarrow 0$. Hence

$$\frac{s\bar{C}}{WC_o} = \lambda\exp(-\eta) \qquad (12)$$

which is consistent with the result obtained by substituting Eq. 8.49 of Crank's book[11] in Eq. 8.

Now consider the case of small λ. The integrands on the right of Eq. 11 are zero at $\xi = 0$ and increase monotonically (first integrand),

or to a maximum at $\xi = \eta/2$ (second integrand) on increasing ξ. Since the upper limit, λ, is small i.e. $<\eta/2$, then throughout the integration the integrand is less than or equal to its value at the upper limit. The value at the upper limit coincides with the second term in each square parenthesis and therefore, for small λ, each integral is negligible compared to the second term. Hence

$$\frac{s\bar{C}}{WC_o} \rightarrow \frac{1}{2}\,\mathrm{erfc}\left(\frac{\eta}{2\sqrt{\lambda}}\right)[\exp(-\eta) + \exp(\eta)]$$

$$\approx \mathrm{erfc}\left(\frac{\eta}{2\sqrt{\lambda}}\right) = \mathrm{erfc}\left(\frac{X}{\sqrt{4Dt}}\right) \qquad (13)$$

for η small., i.e., the classical result for unsteady state diffusion in one dimension into a semi-infinite solid.

Using these asymptotic solutions it is possible to discern the effect of temperature. Consider a series of experiments each carried out for the same time and in each of which the concentration $\bar{C}$ is measured at the same depth below the surface X; the experiments are carried out at different temperatures. It is assumed that grain boundary diffusion of tracer and grain boundary movement obey the usual activation energy equations

$$D = D_o\exp(-E_{AD}/RT) \qquad (14)$$

$$V = V_o\exp(-E_{AV}/RT) \qquad (15)$$

For low temperature, V and therefore λ are small and Eq. 13 applies. A plot of ln $\bar{C}$ against reciprocal temperature should yield the usual straight line of slope $-E_{AD}/2R$.

For high temperature, V and λ are large, and Eq. 12 applies. Substituting (14) and (15) in (12) and taking logarithms:

$$\ln \bar{C} = \text{constant} - \frac{E_{AV}}{RT} - X \sqrt{\frac{V_o}{WD_o}} \exp\left(\frac{E_{AD} - E_{AV}}{RT} \right) \qquad (16)$$

Typically $E_{AV} > E_{AD}$ and the last term on the right of this equation is negligible; a plot of $\ln \bar{C}$ versus reciprocal temperature yields a straight line of slope $-E_{AV}/R$. It should be noted that this also holds true for the case $E_{AV} = E_{AD}$ and the slope is then twice the slope at low temperature.

Results:

The right hand side of Eq. 11 was evaluated using an IBM XT microcomputer. The error function was approximated using 7.1.26 of Abramowitz and Stegun[12]. The integrations were carried out by twelve point Gaussian quadrature. As a check on the precision of the integration, each integral was re-evaluated as the sum of two subintervals over ranges of $\lambda/2$. Parameter values for which these two integrations differed by more than 3% are indicated by a dashed line in Fig. 2. The ordinate in Fig. 2 is $s\bar{C}/WC_o$ from Eq. 11 divided by erfc $(X/\sqrt{4Dt})$, the asymptotic solution for small λ and η predicted by Eq. 13. The ordinate is therefore the ratio of the mean concentration in the plane at depth X to that which would have existed in the plane if grain boundary movement had been negligible. The curves are computed for constant dimensionless time:

$$\tau = \lambda/\eta^2$$

The abscissa is η^2 which can be regarded as a dimensionless grain boundary velocity. We see that the asymptotic solution (Eq. 13) is approached at low grain boundary velocities while at high grain boundary velocities, the effect of grain boundary movement on the mean concentration becomes large. It is seen that the effect becomes large (approximately doubles the mean concentration) at values of η^2 equal to approximately $1/\tau$, i.e., for $\eta^2\tau = \lambda > 1$. Therefore, grain boundary movement will have a significant effect on diffusion in solids even if

the grain boundaries move only by one width during the course of the diffusion*.

In Fig. 3 the ordinate is $s\bar{C}/C_oW$ and this is plotted versus the grain boundary movement (expressed in grain boundary widths) for various dimensionless grain boundary velocities. The broken lines correspond to the asymptote for high λ (Eq. 12), and this asymptote is reached approximately at values of $\lambda = 10$. Therefore, the convenient analytical solution of Eq. 12 can be used when grain boundary movement is more than ten grain boundary widths during the course of diffusion. Note that for large λ and small η, Eq. 12 becomes

$$\frac{s\bar{C}}{WC_o} = \lambda \qquad (17)$$

and that this is borne out by the computed results.

Figure 4 presents the relationship between dimensionless mean concentration and inverse temperature. The activation energy for diffusion alone (E_{AD}) is fixed at 10^4R; three activation energies for boundary migration are considered: $E_{AV} = E_{AD}$, $2E_{AD}$, $3E_{AD}$. The value of V_o for each E_{AV} was adjusted to equalize V at 1000K.

In each case, the apparent activation energy for the mean concentration (at fixed t and X) increases with temperature. The higher E_{AV}, the more pronounced the change in activation energy. If V_o is

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*This result is partly a consequence of the assumption that lattice diffusion is negligible, however it is reasonable to conclude that in cases where the lattice diffusivity is well below the grain boundary diffusivity, even small grain boundary movements may be significant. This point is given further consideration in the Discussion.

fixed, the temperature at which the activation energy increases shifts to higher temperature as E_{AV} increases.

Discussion:

The analysis predicts that both the total tracer penetration and average tracer concentration at depth X increase due to grain boundary migration. The magnitude of the increase depends on the fraction of tracer within the boundary left in the boundary's wake, and the number of times a particular spatial coordinate (x,y) is passed by boundaries. In the present analysis, the lattice concentration is assumed equal to that of the boundary when it passed the point; a modification to fractional dropoff is possible. Furthermore, it is assumed that each point is swept only once. Thus, the analysis is applicable to a situation where the extent of grain boundary migration L is less than the interboundary spacing s. It is specifically in this situation that grain growth during diffusion may be difficult to detect.

Figure 2 demonstrates that the mean concentration ratio at depth X increases with t when D_b, W and V are held constant. Thus, the greater the anneal time, and hence boundary displacement, the more significant the difference between the actual average subsurface concentration and that predicted using a stationary boundary model.

When $\lambda > 10$, the mean concentration at time t is proportional to the boundary displacement, and hence scales with V. For a boundary core width of order 5-10Å, only a 100Å displacement significantly changes $\bar{C}$. Assuming an average grain size of 100μm, a boundary energy of 200 erg/cm^2, and an anneal time of one hour, a displacement of 100Å results when the boundary mobility exceeds $\approx 4 \times 10^{-14}$ cm^3/dyne·sec. The estimated **room temperature** mobility in high-purity oxygen-free lead is of order 10^{-10} cm^3/dyne·sec, and mobilities at higher temperature are consistently above 10^{-9} cm^3/dyne·sec. Although boundary mobilities in

lower purity lead and other materials may be considerably lower, the result indicates the potential for considerable (in comparison to 100Å) boundary displacements even in relatively coarse grained material during short anneals.

When boundary migration occurs during the diffusion anneal, errors in the magnitude of the calculated diffusivity are to be anticipated. The nature of the error will depend on the experimental method of data collection and the manner in which the concentration depth profile is converted into a WD_b product; both over- and underestimates of the diffusivity are possible.

The Fisher analysis predicts that the average tracer concentration at depth x and time t is described by

$$\ln \bar{C}\ (x,t) = -(4/\pi)^{\frac{1}{4}}\ [D_\ell^{\frac{1}{4}}/(WD_b)^{\frac{1}{2}}]t^{-\frac{1}{4}}\ x + \text{constant}$$

where D_ℓ is the lattice diffusivity, and thus

$$\partial \ln \bar{C}/\partial x = -(4/\pi)^{\frac{1}{4}}\ (D_\ell/t)^{\frac{1}{4}}/(WD_b)^{\frac{1}{2}}.$$

The asymptotic solution for $\lambda > 10$ in the present analysis predicts

$$\ln \bar{C}\ (x,t) = \ln\ (VtC_o) - (V/WD_b)^{\frac{1}{2}}\ x + \text{constant}.$$

Consequently,

$$\partial \ln \bar{C}/\partial x = -(V/WD_b)^{\frac{1}{2}}.$$

A comparison of these results reveals a number of interesting features. First, if the Fisher analysis is used to convert specific values of $\bar{C}$ (X,t) to diffusivities, boundary migration will increase $\bar{C}$ (X,t) and WD_b will be overestimated. If W is assumed to be of order

one or two lattice parameters, D_b will be overestimated. In contrast, if the measured value of WD_b and a "known" value of D_b for a stationary boundary are compared, a large apparent boundary width is suggested.

In contrast, if the actual **boundary** tracer concentration depth profile is measured, C at any depth x will be smaller than for a stationary boundary, while the tracer concentration gradient will be larger. In this case, a lower value for the grain boundary diffusivity would be inferred.

In both the Fisher and the moving boundary analyses, a linear relationship between $\ln \bar{C}$ and x is predicted. Consequently, the general "shape" of the concentration-depth profile provides no indication of whether the boundary was stationary or mobile during the diffusion anneal.

In the moving boundary case, the slope of a $\ln \bar{C}$ versus x plot is boundary velocity dependent, i.e., $\partial \ln \bar{C}/\partial x \propto -(V)^{\frac{1}{2}}$. Therefore as V increases, $\partial \ln \bar{C}/\partial x$ becomes **more** negative, or equivalently, the concentration **gradient** steepens. In the Fisher solution, $\partial \ln \bar{C}/\partial x \propto -(1/WD_b)^{\frac{1}{2}}$. Thus, an increase in $\partial \ln \bar{C}/\partial x$ due to boundary migration would be interpreted as a decrease in WD_b. If diffusivities are analyzed from plots of $\partial \ln \bar{C}/\partial x$, the onset of grain boundary motion may reduce $(WD_b)_{apparent}$ to a value smaller than that which would have been deduced from a stationary boundary. Although grain boundary migration may increase $\bar{C}$ at each x, the gradient in $\bar{C}$ may be reduced.

Since $\partial \ln \bar{C}/\partial x$ is independent of x for both the stationary and migrating boundary cases, the ratio of the slopes can be used to identify the potential effects of time, temperature, etc., on the

apparent diffusivity. The ratio **R** of $\partial \ln \bar{C}/\partial x$ for the moving boundary $[\partial \ln \bar{C}/\partial x]_V$ to $\partial \ln \bar{C}/\partial x$ for the stationary boundary $[\partial \ln \bar{C}/\partial x]_{V=0}$, may be expressed as

$$\mathbf{R} \equiv [\partial \ln \bar{C}/\partial x]_V/[\partial \ln \bar{C}/\partial x]_{V=0} \approx 0.94\ [Vt/(D_\ell t)^{\frac{1}{2}}]^{\frac{1}{2}}.$$

Consequently, when the boundary displacement (Vt), exceeds the lattice diffusion distance $\approx (D_\ell t)^{\frac{1}{2}}$, $[\partial \ln \bar{C}/\partial x]_V > [\partial \ln \bar{C}/\partial x]_{V=0}$, and $(WD_b)_{apparent} < (WD_b)_{stationary}$. Plausibly, **R** can assume a wide range of values, and thus grain boundary migration may be the source of considerable error in estimated boundary diffusivities.

The extent to which the apparent WD_b is increased or decreased will depend on the extent of migration, and thus on temperature. Fig. 4 indicates that the onset of significant grain boundary migration increases the temperature dependence of $\ln \bar{C}\ (X,t)$. Thus, if the boundary diffusivity were determined by measuring the temperature dependence of the tracer concentration at some fixed depth X, the onset of (undetected) grain boundary migration would lead to an apparent increase in the activation energy for grain boundary diffusion.

If in contrast, boundary diffusivities are determined by examining tracer concentration depth profiles obtained at different temperatures, the apparent temperature dependence of the diffusivity will depend on that of **R**. When $d\mathbf{R}/dT > 0$, and the boundary displacement is becoming progressively larger than $(D_\ell t)^{\frac{1}{2}}$, $(WD_b)_{apparent}/(WD_b)_{stationary}$ is decreasing with increasing T. In this case, the apparent activation energy for boundary diffusion is lower than that for the stationary boundary. In contrast, in materials for which $E_{AV} < E_\ell/2$, where E_ℓ is the activation energy for lattice diffusion, $V/D_\ell^{\frac{1}{2}}$ decreases as T

increases. Normally, the anneal time t will also be reduced as T increases. Both factors contribute to a decrease in **R** with increasing T, and would result in an apparent increase in E_{AD}. In materials for which $V/D_\ell^{\frac{1}{2}}$ increases with T, the magnitude of the decrease in t will determine the sign of d**R**/dT.

In addition to temperature, the purity, grain size and grain size distribution of polycrystals will influence the extent of migration. A decrease in sample purity may have a number of effects on grain boundary diffusion. Impurity segregation will modify grain boundary chemistry and possibly alter the nature of jump processes in the boundary core. In addition however, segregation will impair grain boundary migration through solute drag effects. Consequently, the effect of sample purity on apparent diffusivities may also reflect modification of grain boundary migration rates. Similarly, differences in grain size and grain size distribution among nominally identical specimens may have a modifying effect on the apparent grain boundary diffusivity, and contribute to scatter in reported values.

The simultaneous occurrence of grain boundary and lattice diffusion will also modify concentration depth profiles from those predicted by the present analysis. As the ratio of $(D_\ell t)^{\frac{1}{2}}$ to Vt increases from zero to values much greater than unity, one would expect a corresponding transition in concentration depth profiles from those predicted by the present analysis to those predicted by the Fisher, Whipple, Suzuoka analyses. It seems reasonable to assume that the effect of lattice diffusion will be important when $(D_\ell t)^{\frac{1}{2}}$ is comparable to or greater than Vt. For fcc metals at $T/T_m \approx 0.5$, the lattice diffusivity is of order 10^{-16} cm^2/s.[13] For diffusion anneals of duration 10^4 to 10^6 s, the

lattice diffusion distance varies from 100 to 1000Å. Consequently, even in samples with mm size grains, with a boundary energy of order 200 erg/cm^2, grain boundary mobilities of order 10^{-13} to 10^{-14} are sufficient to produce comparable grain boundary displacements. As pointed out previously, mobilities exceeding these values are not unusual, particularly in high purity materials. Consequently, even though lattice diffusion will modify the results, tracer penetration due to grain boundary migration alone may well represent a major fraction of the total tracer penetration in a wide range of situations.

In conclusion, the analysis indicates that considerable errors in both the magnitude and temperature dependence of the apparent diffusion coefficient may arise when the effects of grain boundary migration on tracer penetration are neglected. In addition to affecting the results of grain boundary diffusivity measurements, grain boundary migration may also have an important modifying effect on a broad range of kinetic phenomena during which diffusion along grain boundaries and grain boundary migration occur simultaneously.

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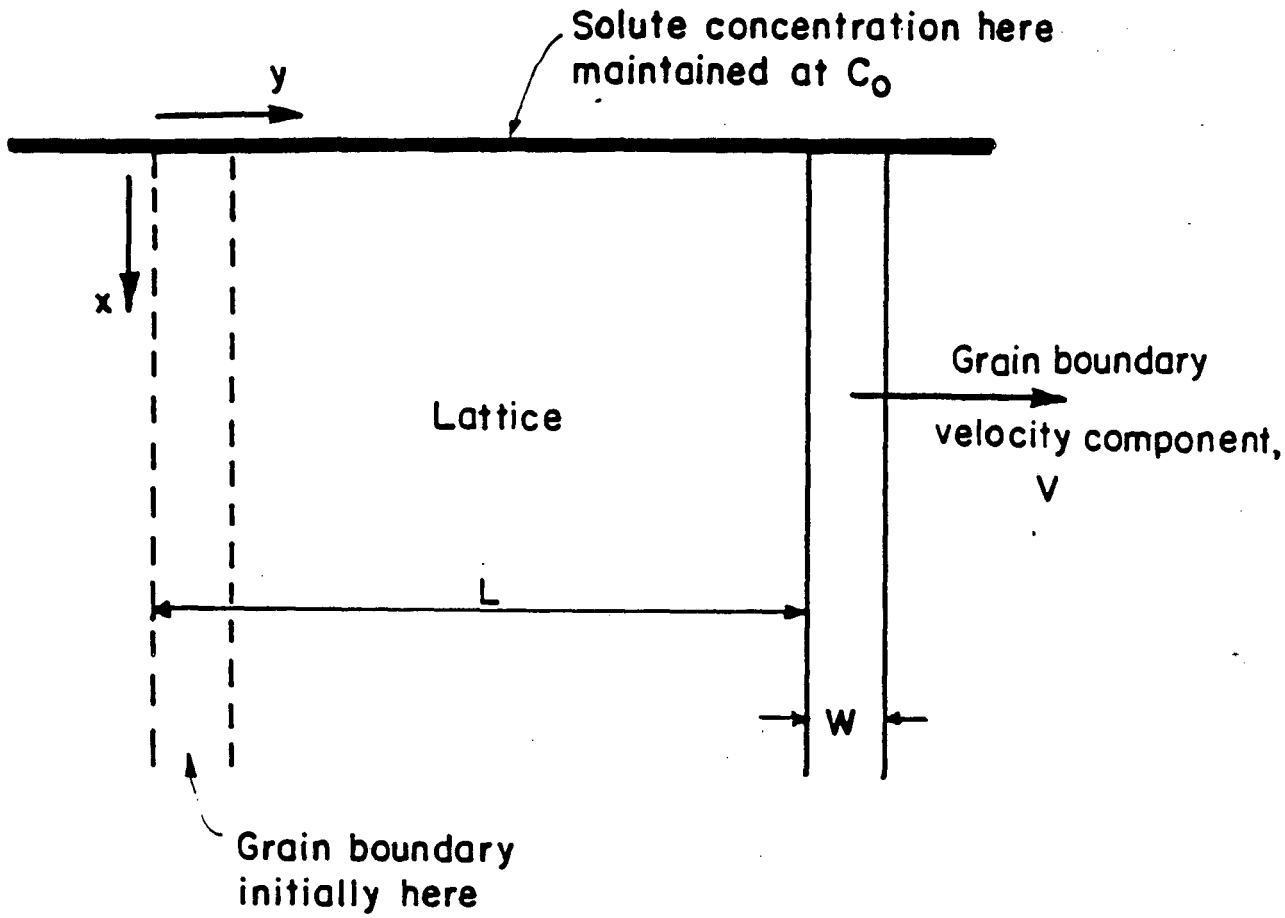
Figure Captions:

Figure 1. Coordinate system and schematic illustration of geometry assumed in the analysis. The grain boundary of width W is perpendicular to the sample surface at which the tracer concentration is held at C_o, and moves with velocity V is the y-direction.

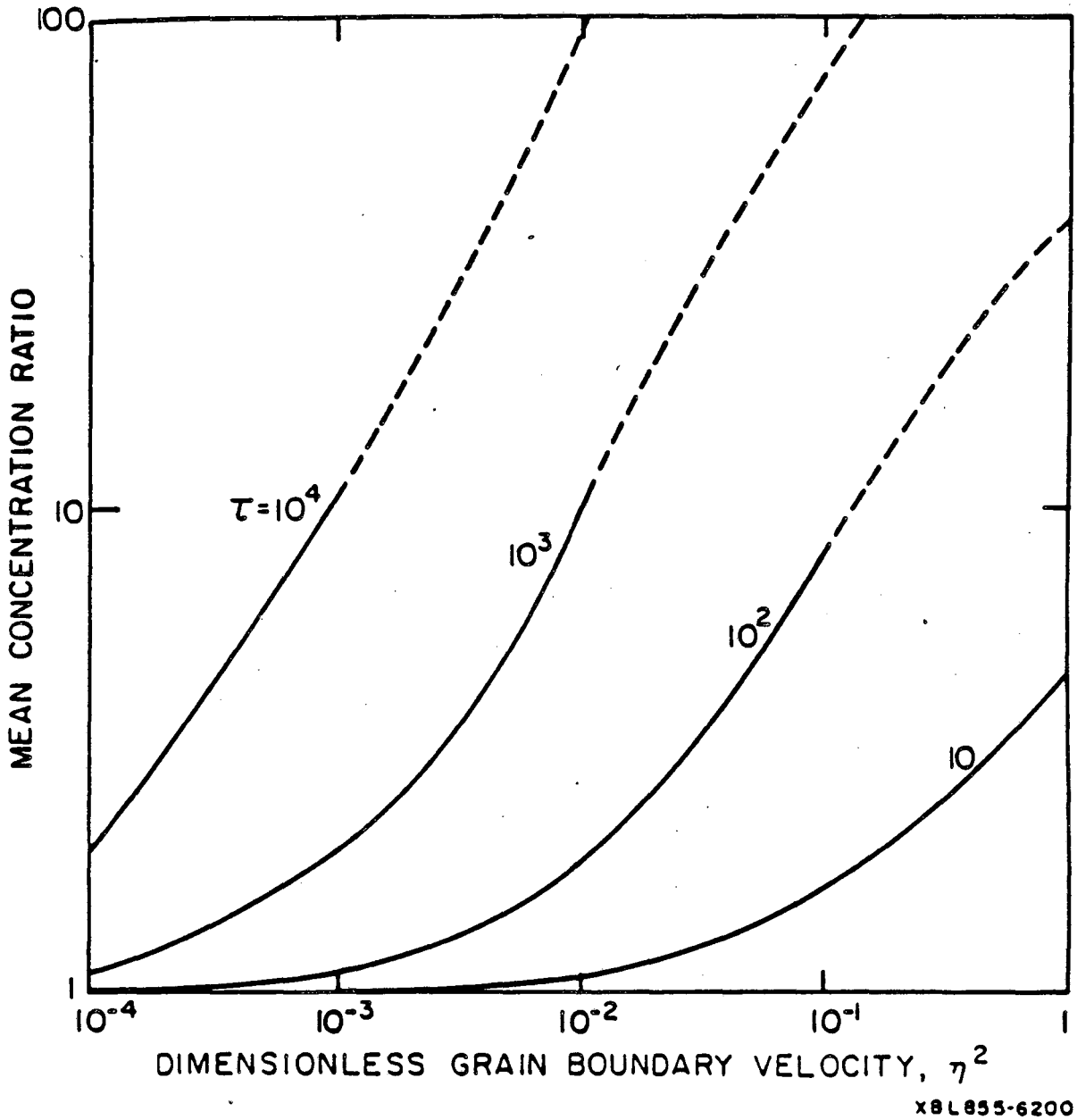
Figure 2. Plot of $s\bar{C}/WC_o$ (from Eq. 11) divided by erfc $(X/\sqrt{4Dt})$, versus dimensionless grain boundary velocity η^2. The ordinate is the ratio of the mean concentration in the plane at depth X to that which would have existed in the plane if grain boundary movement had been negligible. Curves are computed for constant dimensionless time τ.

Figure 3. Plot of $s\bar{C}/C_oW$ versus grain boundary movement (expressed in grain boundary widths) for various dimensionless grain boundary velocities. The broken lines appearing in this plot correspond to the asymptote for high λ.

Figure 4. Temperature dependence of the dimensionless mean concentration for constant anneal time and depth X. The activation energy for diffusion alone (E_{AD}) is fixed at 10^4R; three activation energies for boundary migration are considered: $E_{AV} = E_{AD}$, $2E_{AD}$, $3E_{AD}$. The value of V_o for each E_{AV} was adjusted to equalize V at 1000K.


Solute concentration here
maintained at C_o
y
x
Lattice
Grain boundary
velocity component,
V
L
W
Grain boundary
initially here

XBL 855-6195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10
1
MEAN CONCENTRATION RATIO
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10^2
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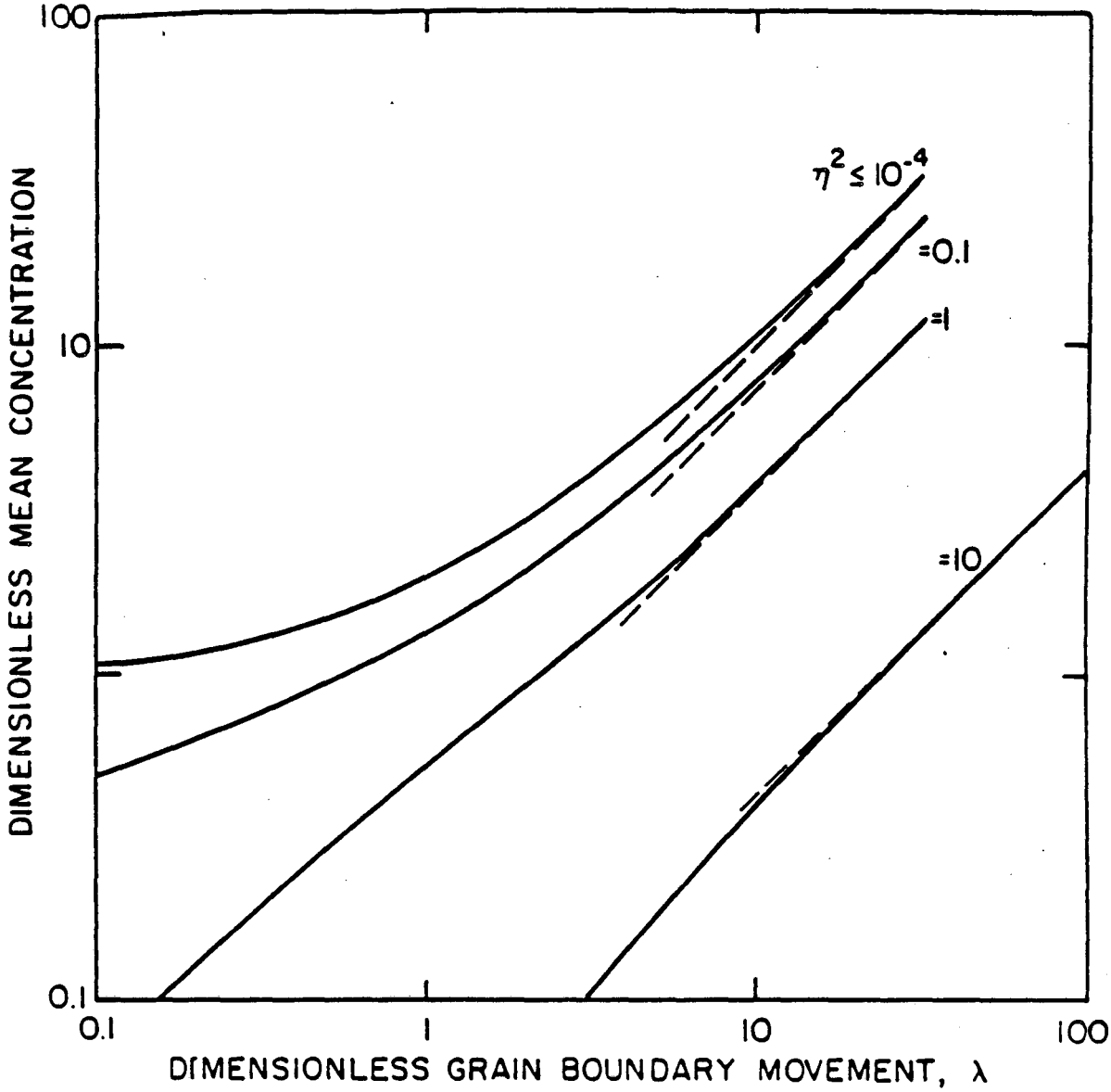
10^-3
10^-2
10^-1
1
DIMENSIONLESS GRAIN BOUNDARY VELOCITY, η^2
XBL855-6200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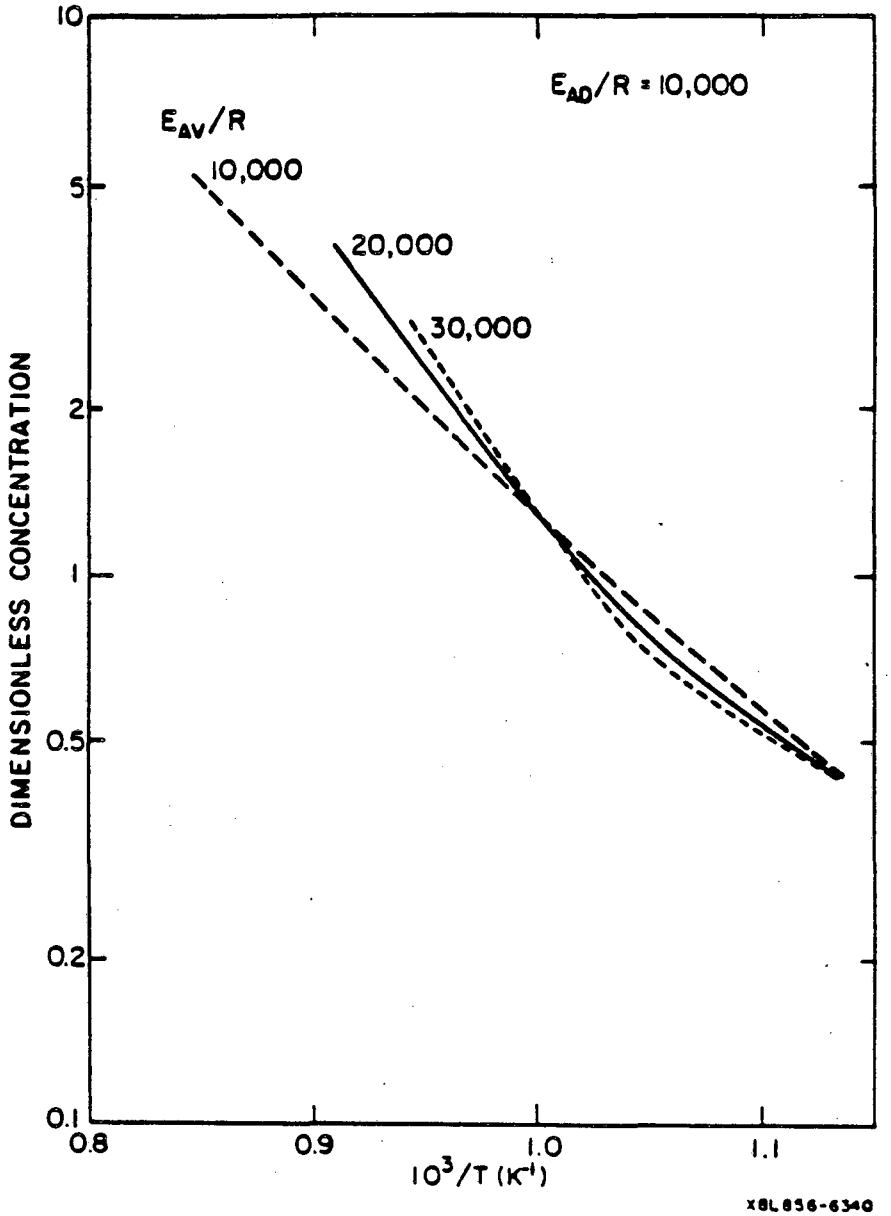
10
0.1
0.1
1
10
100
DIMENSIONLESS MEAN CONCENTRATION
DIMENSIONLESS GRAIN BOUNDARY MOVEMENT, λ
$\eta^2 \leq 10^{-4}$
=0.1
=1
=10

XBL 855-6201


$E_{AD}/R = 10{,}000$
E_{AV}/R
10,000
20,000
30,000
DIMENSIONLESS CONCENTRATION
10
5
2
1
0.5
0.2
0.1
0.8
0.9
1.0
1.1
$10^3/T\ (K^{-1})$
XBL856-6340

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