A RATIONALIZATION OF THE DATA ON
GRAIN BOUNDARY MIGRATION
IN ZONE-REFINED METALS

by

Paul Gordon

Technical Report Number 10
to
Office of Naval Research
Contract No. NONR 1406 (03)

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Department of
Metallurgical Engineering
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Page 9, last paragraph, the words "Figure la" and "Figure lb" should be interchanged.
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Abstract. It is shown that equations for grain-boundary migration given by Gordon and Vandermeer---based on the idea first advanced quantitatively by Löcke and Detert---satisfactorily explain the data on boundary migration obtained with polycrystalline material. Reasons for the apparent lack of agreement between the equations and data from single-boundary migration measurements are discussed.
A RATIONALIZATION OF THE DATA ON GRAIN BOUNDARY MIGRATION IN ZONE-REFINED METALS AS INFLUENCED BY DISSOLVED IMPURITIES

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Paul Gordon*

(Submitted to Trans. Met. Soc. AIME)

I INTRODUCTION

Grain boundary migration in recrystallization and in post-recrystallization grain growth has been the subject of extensive studies for many years. Only with the advent of zone-refining, however, has it been possible to carry out such studies on high-purity metals, and thus to delineate quantitatively the major effect on the migration rates of very small percentages of dissolved impurities. Earlier experimental work almost invariably gave migration rate parameters which disagreed with theoretical predictions by many orders of magnitude. It is now apparent that this was primarily because even the "pure" experimental materials contained appreciable quantities of impurities whereas the theoretical equations implicitly assumed no impurity effects.

During the past five years three groups of workers have made sufficiently detailed studies of boundary migration in zone-refined metals and in these metals with small additions of solute elements to permit meaningful comparison with theory.

*Professor, Department of Metallurgical Engineering, Illinois Institute of Technology
Winegard, Bolling and Holmes\textsuperscript{1,2,3,4,5} and \textsuperscript{6} investigated grain growth in zone-refined polycrystalline tin and lead as influenced by the solute elements lead, bismuth and silver; Gordon and Vandermeer\textsuperscript{7,8} and \textsuperscript{9} studied recrystallization in zone-refined, polycrystalline aluminum and in dilute alloys of copper with this aluminum; and Aust and Rutter\textsuperscript{10,11} and \textsuperscript{12} investigated the migration of individual boundaries on single crystals of zone-refined lead as affected by minute additions of tin, silver and gold. All three groups compared their results with the predictions of theory---on the one hand with the older theories where no account was taken of impurity effects, and on the other with a theory of solute-dependent boundary migration advanced by Lücke and Detert\textsuperscript{13} in 1957.

In general, it was found that, as might be expected, the experimental results did not agree with the older theories except for migration in the zone-refined metals to which no solute additions had been made. In addition, however, the Winegard and Aust groups concluded that the Lücke-Detert theory also did not correlate well with their solute-influenced experimental results.

Gordon and Vandermeer\textsuperscript{9} presented modified equations for both solute-independent and solute-dependent boundary migration based on the concept proposed by Lücke and Detert, and showed that their experimental results and the predictions of their equations agreed quite well. It is the purpose of this...
paper to discuss the three sets of data in terms of the LDGV (Ldcke-Detert, Gordon-Vandermeer) equations. It will be shown that not only the Gordon-Vandermeer data on recrystallization but also the Winegard et al data on grain growth are satisfactorily explained by the theory. A brief discussion will also be presented on the reasons why the Aust and Rutter data cannot be successfully correlated with the theory.
II THE LDGV THEORY OF BOUNDARY MIGRATION

The equations for boundary migration as given by Gordon and Vandermeer are:

for solute-independent (SI) migration

\[ G^{SI} = Z \frac{D_0^{GB}}{\lambda} \exp\left[\frac{-Q^{GB}}{RT}\right] \]  \hspace{1cm} (1)

and for the solute-dependent (SD) migration

\[ G^{SD} = Z \frac{D_0^{1}}{\lambda C_0} \exp\left[-\frac{Q^{1} + E}{RT}\right] \]  \hspace{1cm} (2)

where

- \( G \) = boundary migration rate
- \( Z \) = driving energy per mole
- \( R \) = gas constant per mole
- \( T \) = absolute temperature
- \( \lambda \) = width of the boundary

- \( D_0^{GB}, Q^{GB} \) = pre-exponential factor and activation energy per mole for grain boundary diffusion
- \( C_0 \) = atomic fraction of solute added
- \( A \) = a vibrational entropy factor \( \approx 1/4 \)

- \( D_0^{1}, Q^{1} \) = pre-exponential factor and activation energy per mole for volume diffusion of solute in distorted region near boundary

- \( E \) = internal energy gain per mole of solute atoms transferred to boundary from bulk material

Assuming that data for isothermal grain growth obey the equation

\[ \delta = Kt^n \]  \hspace{1cm} (3)

where \( \delta \) is the average grain diameter, \( t \) the annealing time
n a temperature-independent constant and K a temperature-
dependent constant, then the equations corresponding to (1) and (2) for the rate of change of the average grain diameter at a given annealing time in grain growth are:

\[
G_{SI} = \left[\frac{Z}{RT} \frac{n\delta D_0 GB}{\gamma} \exp\left(-\frac{Q_{GB}}{RT}\right)\right]^{1/2} \tag{4}
\]

\[
G_{SD} = \left[\frac{Z}{RT} \frac{n\delta D_{A}}{\Lambda_{ACO}} \exp\left(-\frac{Q_1 + E}{RT}\right)\right]^{1/2} \tag{5}
\]

Here, the driving energy per mole, Z, is

\[
Z = \frac{2\sigma V_m}{\delta} \tag{6}
\]

where \(\sigma\) is the specific grain boundary energy and \(V_m\) is the molar volume of the parent material*.

For a fixed alloy composition and constant driving energy, equations (1) and (2) or (4) and (5) predict variations of \(G\) with temperature as shown in Figure 1. The lines marked cd in Figure 1 represent solute-independent migration according to equations (1) or (4), those marked ab indicate solute-dependent migration in accordance with equation (2) or (5). The latter are slightly curved because, as the temperature changes, the ratio of the impurity content in the boundary, \(C_B\), to that in the bulk material, \(C_O\), changes according to the relation

\[
\frac{C_B}{C_O} = A \exp\left(\frac{E}{RT}\right) \tag{7}
\]

*\(G\) and \(\delta\) are assumed to be identical in deriving equations (4) and (5).
leading to a change in $Q^1$, as discussed by Gordon and Vandermeer.9

The temperature, $T_c$, at which the two curves $ad$ and $cd$ cross, can be obtained by setting the migration rates in equations 1 and 2 or 4 and 5 equal to one another, yielding

$$T_c = \frac{Q_{GB}^B - (Q^1 + E)}{R \ln(D_{0GB}^B / D_{0}^1 AC_0)}$$

Boundary migration for constant $Z$ and $C_0$ will, in general, proceed according to equation (1) or (4) at low temperatures (line $ab$ in Figure 1), but as the temperature is raised and $C_B$ becomes smaller*, a migrating boundary will break away from its excess solute atom array at some temperature, $T_B$. This temperature is given by the condition that the total restraining force due to the excess solute array at the boundary has decreased until it is just equal to the driving force for boundary migration. When this happens the boundary will migrate according to equation (4) or (5) (line $cd$ in Figure 1). Generally, the breakaway can be expected to take place over a narrow temperature band, rather than at a sharply defined temperature, since there will usually be local inhomogeneities in composition and

*It is assumed that $C_B > C_0$, i.e., extra solute atoms are absorbed in the boundary.
driving force. As a result, if the experimental temperature range includes $T_B$, the variation of $G$ with temperature may show the behavior depicted by the heavy line in Figure 1a. However, this type of behavior will be observed only if $T_B$ is well below $T_c$. If $T_B \geq T_c$, the behavior illustrated in Figure 1b will be found whenever the experimental temperature range includes $T_B$. The condition $T_B > T_c$ need not be considered, for it can be shown by the following reasoning that the upper limit of $T_B$ is $T_c$: according to the basic concept of the theory, the line $ab$ in Figure 1 actually represents the rate at which solute atoms can migrate in the region near a boundary. As long as this rate is less than the rate at which a solute-free boundary can migrate (as given by line $cd$), then the solute atoms will restrain the boundary—provided there are enough solute atoms in the excess array. Under these conditions---$T_B \leq T_c$---the boundary migrates at the same rate as the solute atoms, and the line $ab$ can be considered to give the velocity of the boundary as well as that of the solute atoms. If, on the other hand, it is stipulated that $T_B > T_c$, this means that above $T_c$ the solute atoms can migrate faster than a solute-free boundary. Since, however, the driving force for the migration of the solute atoms comes only from the moving boundary, these atoms cannot precede the boundary and their velocity will now be fixed by the more slowly moving boundary. Thus, above $T_c$, the solute
atoms do not exert a drag on the boundary, but rather the boundary limits the motion of the solute atoms. The velocity of both, then, is that of a solute-free boundary. In other words, there is no breakaway phenomenon above $T_c$---both a solute-laden and a solute-free boundary migrate at the same rate! This rate is given by the line cd in Figure 1.

Accordingly, in the figure, the portion of ab lying above $T_c$ is drawn dotted.

The nature of the migration rate-temperature curve is, thus, seen to depend on the ratio, $T_B/T_c$. The breakaway temperature, $T_B$, may readily be shown to be given by

$$T_B = \frac{E}{R \ln \left( \frac{Z}{EAC_0} \right)}$$

and therefore

$$\frac{T_B}{T_c} = \frac{E}{(Q^1 + E) - Q^GB \log \left( \frac{D_0}{D_{c0}} \right)}$$

It should be noted that because driving energies in grain growth are typically several orders of magnitude smaller than those in recrystallization, equation (10) predicts that the behavior shown in Figure 1a is much more probable for grain growth than for recrystallization, and vice versa for the behavior depicted in Figure 1b. For example, taking the typical values $A \approx 1/4$, $D_{c0}/D_0 \approx 1/5$, $E \approx 3000$ cals/mole, $E/(Q^1 + E - Q^GB) \approx .15$
E/Z for grain growth $\approx 10^6$ and E/Z for recrystallization $\approx 10^3$, then $T_B/T_c$ is equal to unity for all $C_0 \approx 10^{-7}$ in grain growth and for all $C_0 \approx 10^{-4}$ in recrystallization. Thus, in recrystallization it is not difficult to make $C_0$ small enough to place $T_B$ well below $T_c$, but to accomplish this in grain growth requires solute contents about three orders of magnitude smaller.
III. CORRELATION OF THEORY WITH EXPERIMENTAL DATA FOR
BOUNDARY MIGRATION IN POLYCRYSTALLINE MATERIALS

The most comprehensive research of the Winegard group
was carried out on growth in zone-refined tin and in alloys
of this tin containing 0.002, 0.005, 0.010, 0.02, 0.03, 0.05
and 0.10 atomic percent lead, respectively. The discussion
of their results will, thus, be based primarily on these
Pb-Sn alloys, although the less complete results on bismuth
in tin will be dealt with briefly. Henceforth, in all
cases the zone-refined base metal will be referred to as
"pure", and the alloys will be designated by the number
 correspon-
ding to the atomic percent of solute added and the
solute symbol.

Figure 2 presents the data of Holmes and Winegard\(^6\) for
pure tin and for tin with lead addition\(^5\). The data points in
the figure were read from the Holmes-Winegard plots; the
lines were drawn through the points by this writer in ac-
cordance with the concepts discussed in the previous section.
The data clearly indicate that in these materials the beha-
vior shown schematically in Figure 1b (\(T_B = T_C\)) was observed.
For the pure tin and the 0.002, 0.005, 0.01 and 0.02 alloys
\(T_C\) (and \(T_B\)) is within the experimental temperature range
studied. For the 0.03, 0.05 and 0.10 alloys \(T_C\) lies above
the highest temperatures studied, and, as a matter of fact,
could not in any case be attained since melting intervenes.

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Holmes and Winegard interpreted this observed behavior as indicating a failure of the theory, since they assumed that the theory predicted only the type of behavior indicated in Figure 1a. It is seen, however, that the data does in fact follow the prediction of the LDGV equations for $T_B=T_C$. Furthermore, the values of $T_C$ calculated from equation (8) agree quite well with the experimental values, as shown in Table I.

Table I
Experimental and Calculated Quantities for Pb and Sn

<table>
<thead>
<tr>
<th>Co atom fraction</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. Range</td>
<td>Type*</td>
</tr>
<tr>
<td>Pure (Est. $10^{-5}$)</td>
<td>385-490</td>
<td>lb</td>
</tr>
<tr>
<td>2 x $10^{-5}$</td>
<td>395-490</td>
<td>lb</td>
</tr>
<tr>
<td>5 x $10^{-5}$</td>
<td>440-490</td>
<td>lb</td>
</tr>
<tr>
<td>1 x $10^{-4}$</td>
<td>385-490</td>
<td>lb</td>
</tr>
<tr>
<td>2 x $10^{-4}$</td>
<td>460-490</td>
<td>SD</td>
</tr>
<tr>
<td>3 x $10^{-3}$</td>
<td>415-490</td>
<td>SD</td>
</tr>
<tr>
<td>5 x $10^{-4}$</td>
<td>425-490</td>
<td>SD</td>
</tr>
<tr>
<td>1 x $10^{-3}$</td>
<td>455-490</td>
<td>SD</td>
</tr>
</tbody>
</table>

*lb indicates solute-dependent migration at low temperatures, solute-independent at high temperatures; Figure 1b behavior; temperature range includes $T_B,T_C$

SD indicates solute-dependent migration; below $T_B,T_C$
A summary of the migration rate-temperature behavior for the Pb in Sn alloys and also for the Bi in Sn alloys as calculated from equations (8), (9) and (10) is presented in Figure 3 and in Table I. For these calculations the values in Table II were assigned the various quantities in the equations.

Table II
Values of quantities in Equations (8), (9) and (10)
Used in Pb-Sn and Pb-Bi calculations

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Pb in Sn</th>
<th>Bi in Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q^i+E) - Q^GB</td>
<td>19.0 kcal/mole (a)</td>
<td>(Q^i+E) - Q^GB for Pb in Sn plus 2.0 (b)</td>
</tr>
<tr>
<td>D_0^GB</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>A</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>E</td>
<td>1.5 kcal/mole (c)</td>
<td>3.8 kcal/mole (c)</td>
</tr>
<tr>
<td>\sigma</td>
<td>10^{-5} cals/cm^2</td>
<td>10^{-5} cals/cm^2</td>
</tr>
<tr>
<td>\delta</td>
<td>0.2 cm (d)</td>
<td>0.2 cm</td>
</tr>
<tr>
<td>V_m</td>
<td>16.3 cm^3</td>
<td>16.3 cm^3</td>
</tr>
</tbody>
</table>

Notes to Table II

(a) average of values taken from Figure 1
(b) indicated by Holmes and Winegard to be 2 kcal/mole greater than for Pb in Sn
(c) values given by Holmes and Winegard
(d) estimated, private communication with Winegard
For comparison, the experimental temperature ranges investigated are indicated in Figure 3 by the horizontal full lines for Pb in Sn and the dashed lines for Bi in Sn. It is seen that in both systems all the experimental compositions lie well above the range for the type of behavior shown in Figure 1a (TB<Tc). To obtain such behavior in Pb-Sn, the lead content would have to be considerably less than 10^-6, and for Bi-Sn less than 10^-8, with the driving force available from the prevailing grain sizes of about 0.2 cm. The actual behavior observed (see Figure 2) correlates quite well with the relative positions of the experimental ranges studied and the calculated values of TB and Tc.

A further test of the theory is provided by the prediction from equation (5) that at constant temperature and driving force the rate of change, G^{SD}, of the average grain diameter for a given parent metal and solute should be proportional to C_o^{-1/2}. That this is actually the case is shown in the upper portion of Figure 4 for Pb in Sn and Bi in Sn at 450^0K. Equation (5) also indicates that if the proper values of (Q^1+E) are known for different solutes in the same parent metal, then at constant temperature and driving force one common line with slope = -1/2 should result for all solutes when log G is plotted against log C_o + (Q^1+E)/4.6RT. Again, this prediction is borne out by the data for Pb in Sn and Bi in Sn as illustrated in the lower portion of Figure 4.
The agreement between the LDGV theory and the Gordon-Vandermeer data for boundary migration during recrystallization in aluminum and aluminum with copper additions has been described in detail previously\(^9\). In the present discussion only one further point will be made concerning this data in order to emphasize the difference in behavior to be expected for recrystallization as compared with grain growth.

Figure 5 presents the Al-Cu data as given by Gordon and Vandermeer\(^9\). The experimental temperature ranges studied, the apparent activation energies found and the type of migration rate-temperature behavior observed are listed in Table III. Also in Table III are the calculated values of \(T_B\), \(T_c\) and \(T_B/T_c\), and the migration rate-temperature behavior predicted by the theory. The calculated values were obtained using the following quantities: 

\[
(Q^1 + E) = 30 \text{ kcal/mol} \\
(\text{from curves 3,4,5,6 and 7 in Figure 5}); \\
Q^{GB} = 15 \text{ kcal/mol} \\
(\text{from curve 10 in Figure 5}); \\
D^0_{\text{GB}}/D^0_0 = 0.2; \\
A = 0.25; \\
Z = 4 \text{ cals/mole} \text{ (as given by Gordon and Vandermeer}^9\text{).} \\
\] 

The value of \(E\) to be used was calculated from the fact that the data indicate the curve for the 0.0017 alloy lies just below or at \(T_B\). Assuming, then, that \(1/T_B\) for this alloy is approximately \(2.4 \times 10^{-3} K^{-1}\), \(E\) was found from equation (9) to be 4.4 kcal/mol. It is interesting to note parenthetically that this value of \(E\) for Cu in Al is about 1 to 2 kcal/mol higher than the corresponding values calculated.
from dislocation theory (see, for example, McLean\textsuperscript{14})—probably an indication that there is an appreciable contribution to $E$ from valency effects not included in the dislocation calculations.

Table III
Experimental and Calculated Quantities for Recrystallization in Aluminum with Copper Additions

<table>
<thead>
<tr>
<th>Co Atom Fraction</th>
<th>Experimental</th>
<th>Calculated</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp.Range</td>
<td>Type</td>
<td>$Q$</td>
</tr>
<tr>
<td>Zone-Refined (Est. $5 \times 10^{-7}$)</td>
<td>273-350</td>
<td>SI</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>354-412</td>
<td>la</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>383-412</td>
<td>la</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td>383-428</td>
<td>la $\rightarrow$ SD</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>398-443</td>
<td>SD</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>412-462</td>
<td>SD</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>428-483</td>
<td>SD</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>412-473</td>
<td>SD</td>
<td>29.8</td>
</tr>
</tbody>
</table>

*SI - solute-independent migration, above $T_B$ but below $T_c$

SD - solute-dependent migration, below $T_B$

la - temperature range studied is above $T_B$ but below $T_c$, behavior as indicated in Figure la
The satisfactory agreement between experiment and theory shown by the data in Table III is pictured graphically in Figure 6. Comparison with Figure 3 clearly shows the effect of the larger driving energies available in recrystallization. In the latter region of $T_B/T_C < 1$ extends to much higher solute contents; as a result, the probability of observing the type of behavior in Figure 1a is much greater for recrystallization than for grain growth.
IV. SINGLE BOUNDARY MIGRATION

Aust and Rutter, by means of an extensive series of elegant measurements on single boundary migration, have established on a firm experimental basis the expectation that boundary orientation and relative crystal orientation have a pronounced influence on grain boundary migration rates. However, the very extensiveness of their work has itself emphasized the tremendous difficulties involved in attempts to isolate these orientation variables. Aust and Rutter have managed to separate their boundaries very roughly into three groups with respect to orientation variables, a not inconsiderable accomplishment. Yet, a detailed study of their data reveals that there are undoubtedly very large differences in orientation effects within each of the three groups. In spite of these significant differences both Aust and Rutter, and others\textsuperscript{15,16} have attempted to use this data exclusively to test theories which do not specifically take orientation effects into account. It is not surprising that the theories have either been found wanting\textsuperscript{11} or have been left to stand as top-heavy theoretical superstructures on flimsy experimental under-pinnings\textsuperscript{15,16}.

There is little doubt that any really complete theory of boundary migration will ultimately have to account not only for the profound effects of dissolved and undissolved impurities on migration rates but also for the effects of
the five degrees of orientation freedom involved in boundary motion. There is also little doubt that in testing the predictions of such a theory with regard to orientation effects, single boundary migration measurements will be, and are, far superior to measurements in polycrystalline materials. For the present, however, it is apparent that the experimental isolation of these variables by means of single boundary migration measurements is a task of almost forbidding complexity, particularly if at the same time variations in solute content are also purposely introduced. Furthermore, it makes little sense to regard such otherwise significant measurements as the exclusive means of testing theories designed to explain only solute effects. If, as is the case without exception to date, the theories specifically ignore orientation effects, then measurements in polycrystalline materials will more readily give data appropriate to the testing of the theories. This is a consequence of the fact that the experimental techniques used in polycrystalline boundary migration measurements incorporate a statistical assurance that only boundaries with approximately the same environment present themselves for measurement. Thus, properly prepared and treated polycrystalline samples automatically maintain the orientation variables essentially constant, a task which must be pieced out variable by variable and sample by sample in single boundary migration work.

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It is, therefore, the considered opinion of the writer that, valuable as the Aust and Rutter data are with respect to orientation effects, the lack of agreement between their data and the theory discussed here is only apparent rather than real, and is primarily the result of the incomplete isolation of the orientation variable. It seems probable that, if and when a sufficiently large number of individual boundaries are examined to give a good statistical separation of the orientation variables, the single boundary migration data will also be found to be in agreement with this theory.
ACKNOWLEDGEMENTS

The author takes this opportunity to express his thanks to the Office of Naval Research for their financial support of this work.


16. E.S. Machlin, "Theory of Solute Atom Limited Grain Boundary Migration", to be published
Figure 1. Schematic illustration of migration rate-temperature curves in break away region for a) $T_B \ll T_c$ and b) $T_B \not\approx T_c$. 
Figure 2. Experimental data for grain growth in tin and in Pb-in-Sn alloys.
Figure 3. Comparison of experimental T and C₀ ranges with calculated positions of Tₜ and Tₐ for Pb-in-Sn and Bi-in-Sn grain growth.
Figure 4. Growth rates at 450°K for Pb-in-Sn and Bi-in-Sn.
Figure 5. Experimental data\textsuperscript{9} for recrystallization in aluminum and in Cu-in-Al alloys.
Figure 6. Comparison of Experimental $T$ and $C_0$ ranges with calculated positions of $T_B$ and $T_C$ for Cu-in-Al recrystallization.