MECHANISM FOR DIFFUSION INDUCED
GRAIN BOUNDARY MIGRATION

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ABSTRACT

Grain boundaries are found to migrate under certain conditions when solute atoms are diffused along them. This phenomenon, termed diffusion induced grain boundary migration (DIGM), has now been found in six systems. The observed phenomenon and empirical data are used to discard certain concepts for the driving force and the mechanism. We propose a mechanism in which differences in the diffusion coefficients of the diffusing species along the grain boundary cause a self-sustaining climb of grain boundary dislocations and motion of their associated grain boundary steps.

1. INTRODUCTION

There is now clear experimental evidence [1-6] that grain boundaries can be induced to migrate under certain conditions when solute atoms are diffused along them. This process, which has been termed diffusion induced grain boundary migration (hereafter referred to as DIGM), is illustrated schematically in Fig. 1. If solute atoms are diffused into a region of a boundary from some source as in Fig. 1(a) under conditions where the lattice diffusion length is relatively short, the boundary is observed to migrate with a velocity v leaving behind an alloyed zone in its wake. Alternatively, if solute atoms are diffused out of a boundary to some sink as in Fig. 1(b) the boundary is again observed to migrate leaving behind a zone with reduced alloy content (termed de-alloyed) in its wake. Clearly, the overall motivation for such an effect is the change in chemical potential of the diffusing atoms when they engage in either solid solution mixing or un-mixing as a result of the combined grain boundary diffusion and migration. This effect is of considerable interest since it may lead to significant bulk alloying, or de-alloying, and grain boundary migration under conditions where lattice diffusion is negligible.

The present authors have described and discussed DIGM in a previous note [4] in which they concluded that the unequal diffusion of solute and solvent atoms is an essential factor in this phenomenon. They also reported that an effort was underway to construct a model in which the boundary migration occurs by the climb of grain boundary dislocations (GBDs) and their associated steps as a result of an inequality in the grain boundary diffusivities of the solute and solvent atoms.

The purpose of the present paper is to present a detailed account of the results of that work. We begin by summarizing the important experimentally observed features of DIGM which are relevant to the construction of a suitable model. The model, based on the existence of a grain boundary Kirkendall Effect as described above, is then developed in some detail, and the experimental evidence which supports it is discussed. It is stressed throughout that the proposed model is closely related to currently proposed GBD models for: (a) grain boundary migration [7]; and (b) grain boundaries as point defect sources/sinks [8].

2. SUMMARY OF EXPERIMENTALLY OBSERVED FEATURES OF DIFFUSION INDUCED GRAIN BOUNDARY MIGRATION (DIGM)

2.1 The effect is found in a variety of diffusion systems [1-6] including those in which either mixing (alloying) or un-mixing (de-alloying) take place and those in which the solid solutions exhibit either positive or negative deviations from the ideal free energy of mixing [9]. A listing of selected data is given in Table 1.

2.2 In every case in which the effect has been observed [1-6] it has been associated with some type of chemical diffusion of solute atoms along the grain boundary, and it is clear [3-6] that no significant migration would have occurred without diffusion.

2.3 Measurements [3-5] show that the alloy composition exhibits step function discontinuities across the interfaces separating the alloyed (or de-alloyed) zones from the matrix. [see Fig. 1(a,b) and Table 1].

2.4 The effect is observed [1-6] only over a range of relatively low diffusion temperatures (see Table 1) where lattice diffusion is essentially frozen out but where significant diffusional transport along

the grain boundary still occurs during the time of the experiment. (We note that this observation is consistent with the sharp discontinuities in concentration across the zones described above in Section 2.3.)

2.5 The effect is observed [5] only for large angle grain boundaries and is not observed for small angle boundaries possessing crystal misorientations less than about 15° . (Boundaries of the latter type generally consist of an array of discrete lattice dislocations, rather than a continuous slab of core material.)

2.6 A limited amount of data [5] suggests that the extent of the migration depends upon the type of boundary which is involved, i.e., the crystal misorientation across the boundary and the inclination of the boundary plane. For [111] tilt boundaries in the Au(Cu) system the extent of migration varies significantly as the tilt angle is varied [5].

2.7 The effect is observed [4,5] for initially symmetric as well as asymmetric grain boundaries.

2.8 The boundary migration is initiated in a number of systems [1,3-6] by the formation and expansion of bulges in the boundary which grow into the adjacent grains in either direction as is illustrated in a highly idealized manner in Fig. 2. The spatial distribution and directions of the bulges seem fairly random. (See data for ℓ and L in Table 1.) The depth of the alloyed (de-alloyed) zone in thick specimens after more extensive DIGM is several microns [see distance D in Fig. 3(b)]. The zone extends over the entire specimen thickness in specimens that are less than about $10\ \mu$ in thickness [see distance d in Fig. 3(a)] [3,6].

2.9 The average apparent rate of migration is erratic and shows large variations from boundary to boundary in the same polycrystalline specimen even when the boundaries are similar in type [5].

2.10 There is considerable evidence that a net number of atoms is either added to or removed from the alloyed or de-alloyed zone by grain boundary diffusion during DIGM. Associated with this effect is either an expansion or contraction of volume elements in this region in a direction perpendicular to the boundary plane. When zinc is diffused into massive copper specimens from the vapor phase along grain boundaries transverse to the surface to produce alloyed zones consisting of the α -phase by DIGM, it is observed [6] that whiskers and hillocks are formed on the surface. This result provides evidence for the existence of a compressive stress parallel to the surface due to the tendency of the specimen to expand in a direction perpendicular to the grain boundaries as a result of the addition of a net number of atoms to the specimen by boundary diffusion. (Here, only the surface region of the specimen is penetrated as a result of the grain boundary diffusion, and any transverse expansion of the alloyed regions is resisted by the non-diffused bulk of the specimen.) This result can be explained only if zinc atoms diffuse into the boundary more rapidly than copper atoms diffuse out. When the reverse experiment is carried out by diffusing zinc out of a massive α -brass specimen containing transverse boundaries into the vapor phase via DIGM, extensive porosity is observed [6] in the de-alloyed zone. This result provides evidence for a net loss of atoms by unequal boundary diffusion. Again, we must conclude that the effect is due to the more rapid diffusion of zinc than copper in the grain boundary.

In other work evidence has been found that the average apparent rate of DIGM is reduced when the restraints on expansions or contractions normal to the boundary plane are increased. In thin film solid-solid

couples consisting of evaporated layers of copper and gold, and silver and gold, it is found [5] that the rate of DIGM of boundaries transverse to the plane of the thin film is reduced when any dimensional changes normal to the boundaries are restrained by leaving the thin film specimens attached to massive substrates.

We note that the extensive surface bulging observed [3] to result from DIGM at the intersections of alloyed zones with the specimen free surface when zinc is diffused from the vapor phase into iron specimens containing grain boundaries transverse to the surface (see Fig. 1 in [3]) would occur with, or without, unequal grain boundary diffusion rates.

3. ESTABLISHMENT OF MODEL

A somewhat surprising aspect of the diffusion induced grain boundary migration phenomenon is that it occurs at all. At a first glance the initial state has considerable symmetry, and the prediction that the boundary would remain stationary with a symmetric diffusional profile on either side of it would seem valid. Asymmetries in boundary structure are common, but then the phenomenon also occurs apparently undiminished with specially created symmetric tilt boundaries which, however, may still contain imperfections that break the symmetry.

The initiation does not seem to depend on a degree of asymmetry related to the orientation of the boundary plane. Most of the boundary area remains stationary until a bulge expands and "tears" the boundary loose. The symmetry keeps the boundary stationary except at nucleation sites where symmetry breaking occurs to initiate the process. Once the boundary is migrating, the migration seems self-sustained. The grain boundary is no longer compositionally symmetric, but it must be explained how the diffusional process couples to drive the

motion and provides a driving force large enough to expand a bulge against radii of curvature as small as $0.1 \mu\text{m}$.

At the low temperatures of the DIGM experiments little diffusional mixing would occur unless the boundary migrates. However, the increased rate of free energy decrease due to the migration can be totally uncoupled as a driving force for the migration. That the free energy decrease is necessary, but not sufficient, to drive the migration can be illustrated, as follows, by a hypothetical ideal diffusion couple. Consider two species with identical properties that form ideal solutions in which there is no difference between the species in any kinetic parameter or in their preference for any defect. The atoms therefore differ only in the labeling. A mixture of isotopes is a close approximation of this ideal system. In a given structure the same atomic motions would occur regardless of how the atoms are labeled. Consider next a diffusion couple of these two species with grain boundaries. The onset of DIGM would indeed enhance the mixing and lead to an increased rate of free energy decrease. But any motion of the boundary would be the same in two hypothetical experiments that have the same arrangement of atoms but have them labeled differently. If there is no grain boundary motion apart from that corresponding to random fluctuations in a homogeneous alloy, there will be none in the diffusion couple. In this respect we note that even the smaller hemispherical grain boundary bulges observed ($\sim 0.1 \mu$ in diameter) increase the free energy by $(\pi/4)(1 \times 10^{-7})^2 \text{ J}$ which is 10^6 kT and would never be observed in the homogeneous sample, and, thus, also not in the diffusion couple. (Here, we assumed 1 J/m^2 as the grain boundary free energy.) Since the mere relabeling of atoms in this ideal

system cannot induce grain boundary migration, we must look for factors in real systems for clues to the coupling that leads to DIGM.

Real systems differ from this ideal system in three major ways: thermodynamic, structural and kinetic. The ideal system has a purely entropic mixing free energy. Real systems can deviate positively or negatively from ideality (or Raoult's Law). The ideal system has no enthalpy or volume change on mixing. On the other hand, real systems do. Positive heats of mixing tend to correlate with positive deviations from Raoult's Law [9]. If we assume DIGM to be caused by the non-ideal part of the enthalpy or free energy of mixing, one would predict no DIGM on alloying (mixing) for positive deviations, since the energy that has to be supplied to mix the alloys must also come from the entropy of mixing, and no DIGM on de-alloying (un-mixing) for negative deviations for the same reasons. Table 1 lists how the six systems in which DIGM has been observed differ from ideal solutions and whether or not DIGM has been observed on mixing and/or un-mixing. We conclude that neither ideal solution behavior nor deviations from ideal solution behavior can be a universal factor in the coupling that leads to DIGM.

Components of real systems differ in their interactions with grain boundaries. Meyrick [10] has proposed that if one species raises the boundary energy, migration that leaves it behind would be spontaneous. In a given system this might explain DIGM during either mixing or un-mixing but not for both. The observation in Fe(Zn) and Cu(Zn) of DIGM for both mixing and un-mixing rules this out as a universal mechanism.

In real systems, the lattice parameter is a function of composition leading to lattice mismatch across diffusion zones. In DIGM, the original

position of the grain boundary is observed to be marked by a lattice dislocation network that accommodates the abrupt lattice parameter change due to the abrupt composition change [3-5]. It is difficult to see how this factor could initiate, or sustain, DIGM. In any case, DIGM is observed in the Au(Ag) system where this factor must be negligible.

Manning has suggested that if composition gradients rather than compositions raise a boundary energy, boundaries would tend to move from diffusion zones. The physical basis that might lead to such an effect is presently unknown but is being examined [11].

Components of real systems differ in their mobilities and how they interact with vacancies and dislocations. If a concentration gradient exists along a grain boundary we may therefore expect a net flow of atoms due to the unequal diffusion of the two species in a manner consistent with the experimental observations cited in Section 2.1. We believe that the net deposition or removal of atoms in the grain boundary due to this unequal diffusion is the only plausible and universal cause of DIGM.

The observations of hillocks and whiskers (or porosity) in the Cu(Zn) system can be accounted for by a net deposition (removal) of atoms. The accompanying stresses could produce plastic deformation and dislocations which could in turn contribute to the maintenance of DIGM if the boundary migrated to remove the dislocations in a manner analogous to recrystallization, or, if the boundary migrated as a result of a direct interaction with the stress field. However, these effects are caused by DIGM, and, therefore, cannot initiate DIGM. As

we now point out, there is a much more direct interaction of the grain boundary with the unequal diffusion process through the climb of grain boundary dislocations.

There is now extensive evidence [12] that dislocations can exist in grain boundaries and that such dislocations, i.e., grain boundary dislocations (GBDs), can climb in the boundary and provide the necessary sources and sinks for the divergences in the net flow [8]. Furthermore, steps in the boundary are generally intrinsically associated with GBDs [8,12], and, therefore, climbing GBDs will carry the boundary with them as a result of the associated step migration. In view of all the factors examined for real systems, it appears that this is the only basic model which is consistent with the absence of DIGM in the ideal system, with our empirical observations, and with the existence of a coupling mechanism consisting of well-established physical principles. The other factors considered might be important in some systems under certain conditions but they could not explain all the presently known cases of DIGM.

Our proposed model is therefore the following:

- (i) different chemical species diffuse at different rates along the boundary when a chemical gradient is established;
- (ii) the unequal diffusion induces the climb of GBDs in the boundary which act as sources/sinks for divergences in the net current of atoms which are developed;
- (iii) the climbing GBDs cause the boundary to migrate via the motion of the grain boundary steps which are intrinsically associated with them.

At the present time there is no conclusive evidence from other experiments reported in the literature for the existence of unequal chemical diffusion rates in grain boundaries. The DIGM evidence is therefore the first indicating the existence of this effect. The conclusion that such an effect exists is a natural extension of the well-established observation that solute and solvent atoms generally diffuse at different rates in the lattice causing the bulk Kirkendall effect [13], and it would actually be surprising, therefore, if it did not occur in grain boundaries. Furthermore, it should be pointed out that the existence of unequal grain boundary diffusion rates appears to be consistent with our rather limited current knowledge of the mechanism (mechanisms) of grain boundary diffusional processes. For example, it is known that a net current of atoms can be induced to flow in grain boundaries, as during diffusional (Coble) creep [14], and it has been considered likely on the basis of this, and additional considerations [15], that grain boundary diffusion occurs by a vacancy mechanism. More recently it has been found by computer simulation [8,16] that vacancy and interstitial point defects in the grain boundary core are often considerably relaxed. Nevertheless, the extended region over which the relaxation occurs around the defect is still associated with a missing atom (or extra atom), and the defect can therefore still be considered as a bona fide point defect. So far, interstitial defects appear to have considerably higher formation energies in boundaries than vacancies (as is the case in the lattice), and it therefore appears likely that vacancies should be the main equilibrium point defects present. Furthermore, relaxed vacancies in the boundary should be capable of relatively easy migration. This behavior is consistent with the observed low

activation energy for the diffusion of atoms in grain boundaries [17]. In view of all of these considerations we proceed by assuming that the unequal grain boundary diffusion occurs by a vacancy mechanism.

The climb of GBDs and their associated steps across the boundary* causing grain boundary migration is analogous to the well-known surface step mechanism for single crystal growth. In such a mechanism the line defects can move without incurring large energy changes in the overall system by means of localized fluctuations which involve relatively small numbers of atoms. This is consistent with the current idea that each grain boundary possesses a unique structure which tends to be preserved during migration. An extensive discussion of the operation of grain boundaries as sources/sinks by the climb of GBDs has been given recently by Balluffi [8]. A discussion of grain boundary migration by the migration of GBDs and their associated steps has been given by Smith [7] and Balluffi [8].

The process is illustrated simply in two dimensions in Fig. 4 for the simple case of an edge GBD and its associated step in a symmetric tilt boundary with tilt angle $\theta = 36.9^\circ$ in a simple cubic structure. As is well known [12], such GBDs possess Burgers vectors which are vectors of the DSC-Lattice produced by Crystals I and II and are therefore

* It should be pointed out at this juncture that the interface which migrates in DIGM must have changed structure somewhat in order to accommodate the discontinuity in chemical composition across it. To keep the present model as simple as possible we consider only the case where the diffusion occurs in a one-phase system and the variation of lattice parameter with composition is negligible. In this manner we avoid problems associated with possible lattice parameter differences across the boundary. This procedure results in only a slight loss of generality, since we are neglecting only the small mismatch in lattice parameter which can always be compensated for by adding an intrinsic array of GBDs.

clearly revealed within the framework of the DSC-Lattice as is seen in Fig. 4(a). Grain boundary steps are generally associated with such GBDs since the overall pattern produced by the atoms in the two crystals adjoining the boundary is translated when one crystal is shifted with respect to the other by the Burgers vector, i.e., a vector of the DSC-Lattice. The GBD in Fig. 4(a) is sessile in the plane of the boundary. If it climbs in the boundary plane, Crystal II will translate relative to Crystal I by a displacement given by the Burgers vector, and the boundary will migrate as a result of the motion of the associated step. Specifically, if the GBD in Fig. 4(a) absorbs a vacancy it will climb upwards by the distance s , three atoms will be removed from Crystal II, and two atoms will be added to Crystal I. In this manner one vacancy is destroyed, two atoms are transferred from Crystal II to Crystal I, and Crystal I grows at the expense of Crystal II. At the same time, Crystal II will undergo a rigid body translation with respect to Crystal I in the direction along $-\vec{b}$. These results can be easily generalized to three dimensions and to include GBDs of mixed character possessing Burgers vectors making arbitrary angles with the grain boundary normal. In such cases motion in the boundary plane by combined glide and climb is required. More extensive discussions of the details of this mechanism have been presented recently by Balluffi [8], King and Smith [18] and Smith [7].

Since DIGM occurs under conditions where the atomic mobility in the grain boundary is high compared to the mobility in the lattice (Section 2.4), we assume that there is appreciable mobility in the grain boundary core and no mobility in the lattice. Also, we take the grain boundary core to be a slab of material a few atom distances wide;

i.e., the region of width, λ , illustrated in Fig. 4. If the boundary in Fig. 4(b) is producing an alloyed zone by DIGM during the inward diffusion of a solute as illustrated in Fig. 1(a), the detailed situation in the grain boundary core will appear as in Fig. 5. Here, solute atoms (filled circles) are diffusing in the core, and an alloyed zone is being left behind by the migrating boundary. If the solute atoms diffuse faster than the solvent atoms in the core the boundary acts as a sink for atoms in order to accommodate the net inward diffusive flux of atoms. This is achieved by the downward climb of GBDs of the type shown. This climb motion accommodates the incoming atoms and at the same time causes the boundary to migrate into the pure solvent lattice. The continued climb of the GBDs and their associated steps brings a continuous fresh supply of solvent atoms into the boundary core due to the atomic shuffles at the advancing steps. This tends to depress the solute atom concentration in the core in the vicinity of the climbing GBDs which in turn stimulates the further inward diffusion of solute atoms, and the entire process becomes self-sustaining. This process is analyzed in more detail in the next section.

4. DETAILED BEHAVIOR OF MODEL

We begin by formulating the behavior of a single climbing GBD during DIGM as illustrated, for example, in Fig. 5. In the simplest model we assume that the grain boundary fluxes (volume/distance time) of the two species, J_A and J_B , are given by Fick's Law expressions in terms of the atomic fraction C of the B component,

$$J_A = D_A \lambda \frac{\partial C}{\partial x} ; \quad -J_B = D_B \lambda \frac{\partial C}{\partial x} , \quad (1a,b)$$

where D_A and D_B are intrinsic boundary diffusion coefficients (distance²/time), and λ is the boundary thickness. The net flux of atoms, $J_A + J_B = (D_A - D_B) \lambda (\partial C / \partial x)$, must be constant between GBDs, since there can be no net deposition of atoms except at GBDs. At the GBDs there can be a discontinuous change in concentration gradient, $\Delta(\partial C / \partial x)$, which leads to a net deposition rate of atoms, with volume/length of dislocation line given by

$$-\Delta(J_A + J_B) = (D_B - D_A) \lambda \Delta(\partial C / \partial x) \quad , \quad (2)$$

which must result in a GBD climb velocity, v_d ,

$$v_d b_n = (D_B - D_A) \lambda \Delta(\partial C / \partial x) \quad , \quad (3)$$

where b_n = component of Burgers vector normal to grain boundary plane.

When a GBD possessing a step of height ξ climbs down by the addition of atoms, as in Fig. 4, a layer of thickness ξ in one crystal (I) will be converted to a layer of thickness $(\xi + b_n)$ in the other crystal (II). Conversely, for climb by a net loss of atoms a layer of thickness $(\xi + b_n)$ in Crystal II will be converted to one of thickness ξ in Crystal I. If the compositions of Crystals I and II are C_I and C_{II} respectively, a balance on B atoms at the GBD is

$$\Delta J_B - v_d \xi C_I + v_d (\xi + b_n) C_{II} = 0 \quad (4)$$

$$\text{or } v_d [(\xi + b_n) C_{II} - \xi C_I] = D_B \lambda \Delta(\partial C / \partial x) \quad (5)$$

This equation indicates that the moving step in a boundary between crystals of different compositions produces a discontinuity in concentration gradient as illustrated in Fig. 5(b), which in turn causes the climb that will sustain the discontinuity.

While the two physical concepts embodied in Eqs. (3) and (5) explain DIGM as a self-sustaining mechanism in which a discontinuity in gradient causes the climb which perpetuates the discontinuity, the equations are probably too simple. This may be seen by solving the two equations for the composition difference,

$$C_{II} - C_I = \frac{b_n}{\xi} \left[\frac{D_B}{D_B - D_A} - C_{II} \right], \quad (6)$$

which in this simple model is independent of either v_d or the boundary concentration. For down climb, the factor $D_B/(D_B - D_A)$ is related to the fraction of B atoms deposited, while the factor b_n/ξ is the dilution ratio of the deposit to the matter transferred from one grain to the other. The composition difference is an unstable steady state one. A larger composition difference will lead to an increased discontinuity and higher velocities, and, in turn, a higher composition difference, while a smaller composition difference will eventually lead to the cessation of motion. Thus, start-up is difficult, but once a threshold has been crossed the motion is self-sustaining. The actual magnitudes must come from more complicated, and, probably, non-linear models.

A linear model of slightly increased complexity would use vacancies in the boundary to permit some atom-flux divergences between dislocations. The non-equilibrium vacancy gradients would then act as back stresses to regulate the atom fluxes, and from the vacancy supersaturation a GBD climb force would be obtained. This climb force is a small fraction of the available free energy decrease.

A complete solution of the DIGM problem would now require a solution of the entire diffusion problem along the boundary in the presence of a distribution of climbing GBDs of the type just described. The solution of such a problem poses a number of formidable problems such as, for example, the determination of the distribution of GBDs (see below), and the establishment of the diffusion boundary conditions which apply at the GBDs. In view of the present state of our knowledge we shall not attempt to deal quantitatively with these difficult problems. Instead, we proceed with a rather general discussion of a number of additional aspects of the model, as below.

5. DISCUSSION

The continuous operation of the present model requires the continuous generation of GBD line length. Mechanisms for producing this line length have been discussed by Balluffi [8] for the closely related problem of the operation of grain boundaries as point defect sources/sinks in chemically homogeneous systems. It was concluded [8] that the required line length can be generated by the nucleation of GBDs in the boundary core and/or by the development of GBD growth spirals depending upon the nature of the boundary and the magnitude of the driving force. In the former case GBD loops are nucleated in the presence of the non-equilibrium vacancy concentration which is present in the boundary (which in the case of DIGM is due to the unequal chemical diffusion rates in the boundary). In the latter case lattice dislocations which impinge on the boundary plane act as poles for the development of GBD growth spirals by climb in the presence of non-equilibrium point defects. Further details are given

in [8]. A major conclusion is that these processes occur relatively easily for general grain boundaries which possess structures which are not too highly ordered and that such boundaries therefore act as highly efficient sources/sinks over a wide range of driving forces. For example, generally occurring boundaries have been found to operate as point defect sources/sinks with high efficiencies when the chemical potential of the point defects is as low as $\sim 10^{-5}$ eV. In a number of cases, however, threshold effects for source/sink action become apparent at chemical potentials in the range 10^{-4} to 10^{-5} eV. These have been attributed to a variety of effects which are connected with difficulties in nucleating and climbing the necessary GBDs. However, it seems likely that the point defect chemical potentials developed by the unequal diffusion in the present cases with large composition changes are large enough to drive the various source/sink processes at a sufficient rate to cause the boundaries to act as efficient overall sources/sinks.

It is apparent that, at the beginning of the process, once any section of the boundary undergoes any migration whatsoever by the GBD-step mechanism, it can only continue to advance in the same direction. The direction in which any segment of the boundary migrates then depends upon the direction of the first successful fluctuation or increment of GBD climb which "imprints" the system locally. This direction should therefore depend upon the initial intrinsic structure of the boundary and the particular arrangement of GBDs which might be present.

For any given boundary a considerable number of GBDs with differing Burgers vectors and associated steps is geometrically possible. The Burgers vectors include at the least the primitive vectors of the

three-dimensional DSC-Lattice, and the steps include a number of possibilities dictated by the energies of the configurations which are involved [18]. All of these GBD-step configurations are therefore at least conceivable candidates for service in promoting boundary migration. In the general case the boundary will not lie parallel to, or perpendicular to, any of the Burgers vectors, and, therefore, we should be most concerned with cases where the GBDs migrate in the boundary by combined glide and climb.

It is interesting to speculate that each bulge which develops (as shown in Fig. 2) corresponds to a region of the boundary which is initially dominated by a group of GBDs of the same type such as could be the case if the GBDs multiplied by the growth of spirals, and that different GBDs may dominate at different depths in the diffusion zone to reflect the changing ΔC .

We note that the magnitudes of the quantities required by Eq. (6) for our simplest model are not unreasonable in view of its elementary aspects. When $C_I = 0$, equation (6) takes the form

$$\Delta C = C_{II} = \frac{(b_n/\xi)}{(1 + b_n/\xi)} \left(\frac{D_B/D_A}{D_B/D_A - 1} \right) \quad (7)$$

The ratio D_B/D_A is probably substantially larger than unity, and $(D_B/D_A) / [D_B/D_A - 1]$ is therefore probably of order unity. From Table 1, $\Delta C \approx 0.1$. Values of $b_n/\xi \approx 0.1$ are therefore required. Such values appear possible for the GBDs in general grain boundaries where the magnitudes of the primitive Burgers vectors are relatively small, and the heights of the associated steps tend to be relatively large. Also,

we recall that the boundary plane will not generally be normal to $\vec{b}$, and, therefore, $b_n < |\vec{b}|$. Recent work by King [19] indicates that the upper limit of the ratio b/ξ for stable GBDs tends to increase as the degree of coincidence (as measured inversely by the size of the Coincidence Site Lattice) increases. It therefore might be difficult for certain high coincidence boundaries, i.e., boundaries with relatively large b_n/ξ ratios, to engage in DIGM. There are some indications in [5] that this may indeed be the case.

We conclude by emphasizing that considerably more work needs to be done to establish the model. For example, it would be highly desirable to have direct observation of GBD climb activity in the boundary. More measurements are needed of all of the DIGM parameters listed in Table 1 over a wide range of conditions for a variety of systems, and further experiments with controlled grain boundaries containing well characterized GBDs would be valuable.

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TABLE 1
Summary of DIGM Data

Investigators	Alloy System	$(\frac{T}{T_m})^*$	$t(h)^{**}$	$L(\mu m)^\dagger$	$\ell(\mu m)^\dagger$	$\Delta C^\ddagger$ (at.fr.)	Mixing (m), or Unmixing (u)	Positive (+), or Negative (-) Deviation
den Broeder [1]	W(Cr)	≈ 0.50	≈ 16	≈ 15	≈ 3	$\approx 0.1-0.3$	(m)	(+)
Tu [2]	Ag(Pd)	≈ 0.33	≈ 48	--	≈ 1	≈ 0.2	(u)	(-)
Hillert and Purdy [3]	Fe(Zn)	≈ 0.50	≈ 3	≈ 18	≈ 8	≈ 0.05	(m) and (u)	(+)
Cahn, Pan and Balluffi [4]	Au(Cu)	≈ 0.34	≈ 48	≈ 1	≈ 0.1	$\approx 0.1-0.3$	(m)	(-)
	Au(Ag)	≈ 0.40	≈ 64	--	≈ 0.05	≈ 0.2	(m)	(-)
Cahn [6]	Cu(Zn)	≈ 0.50	1-16	3-100	3-100	≈ 0.2	(m) and (u)	(-)

* Fraction of absolute melting temperature.

** Diffusion time.

† See Fig. 2.

‡ Composition difference across migrating boundary.

FIGURE CAPTIONS

- FIG. 1 Schematic diagram of DIGM in a region of a grain boundary.
(a) Solute atoms are deposited during grain boundary diffusion, and the boundary migrates while leaving behind an alloyed zone.
(b) Solute atoms are removed during grain boundary diffusion, and the boundary migrates while leaving behind a de-alloyed zone.
- FIG. 2 Schematic diagram of the grain boundary bulging which occurs during early stages of DIGM. Diffusion direction perpendicular to the paper.
- FIG. 3 Schematic diagram of alloyed (de-alloyed) zone after more extensive DIGM than that shown in Fig. 2. Diffusion direction in plane of paper. (a) thin specimen, and (b) thick specimen.
- FIG. 4 Climb of GBD in symmetric tilt boundary in simple cubic structure. Tilt angle = 36.9° ; $\vec{b}$ = Burgers vector; λ = grain boundary core width. (a) Initial structure. (b) GBD after climb by annihilation of a vacancy. (See text.)
- FIG. 5 (a) Schematic diagram of grain boundary core during DIGM by GBD-step climb. Alloyed zone is being left behind. Filled circles = solute atoms; open circles = host atoms. λ = core width. (b) Schematic diagram of solute atom concentration along grain boundary in vicinity of climbing GBD.

FIG. 1

FIG. 2

FIG. 3

FIG. 4