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GRAIN BOUNDARY DIFFUSION - STRUCTURAL EFFECTS AND MECHANISMS

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Abstract - This paper considers the available evidence for relationships between grain boundary structure and diffusion. In any one material the boundary structure is a function of geometry, solute segregation and, in the case of compounds (e.g. oxides), non-stoichiometry. The effect of these parameters on boundary diffusion in some fcc materials is examined and comparisons made between bicrystal and polycrystalline material and between metals and ceramics.

All experiments from which inferences can be made concerning the mechanism of grain boundary diffusion suggest that it takes place by an enhanced concentration of point defects segregated preferentially to the boundary core where they are also more mobile than in the lattice.

INTRODUCTION

There is now in existence a large body of data concerning diffusion in crystalline solids and a corresponding understanding of the atomistic mechanisms which are involved. Thus, for bulk diffusion, the relationships between structure and diffusion are described by the energies required to form and move point defects, such as vacancies or interstitials, and their mutual interactions. A similar situation has not yet been reached for diffusion along grain boundaries despite the fact that such diffusion often controls many technologically important processes, particularly at 'low' temperatures. The data which do exist for grain boundary diffusion are relatively sparse and of lower quality and poorer reproducibility than the corresponding data for lattice diffusion because of experimental difficulties. Nevertheless, in recent years there have been considerable improvements in understanding and observing the structures of grain boundaries. Can these lead to a link between grain boundary structure and diffusion?

In this paper we first consider the phenomenological description of grain boundary diffusion and then survey the evidence for variation of diffusion properties with
misorientation across the boundary. We then consider the relationship between diffusion in individual bicrystal boundaries and diffusion in a polycrystalline mass and the influence of segregation on boundary diffusion. The differences in behaviour between metals and ceramic materials are then explored and finally the implications concerning likely diffusion mechanisms are discussed. Many of the experimental data considered here are not new and have been discussed in several earlier reviews [1-4]. In this paper the emphasis is on what new data are available and looking at the older results in a slightly different way.

1. GRAIN BOUNDARY DIFFUSION EXPERIMENTS

The usual phenomenological description of grain boundary diffusion represents the boundary as a slab of width \( \delta \) in which the diffusion coefficient \( D' \) is greater than \( D \) in the surrounding lattice. Thus the first structural aspect of a boundary that we must consider is its width. All evidence from calculations, direct observations and the diffusion experiments themselves now indicates that \( \delta \lesssim 1 \text{ nm} \) (wherever a value for \( \delta \) is required in the subsequent discussion it will be assumed to be 1 nm). Since \( \delta \) is so small the 3-dimensional slab model is rather questionable. Nevertheless, the model does allow all observable features of diffusion experiments to be described (e.g. profiles of tracer concentration versus depth) and is therefore a convenient way in which to summarise the experiments.

The experiments themselves may be carried out in different kinetic regimes and use a variety of techniques. In the regime of negligible lattice diffusion, \((Dt)^{1/2} \ll \delta \) and named type C by Harrison [5], the boundary diffusion coefficient, \( D' \), may be measured directly. To operate in this regime low temperatures and short anneal times, \( t \), are required because \( \delta \) is so small. When \((Dt)^{1/2} \gg \delta \), which is more usual and named type B, then experiments yield the diffusion parameter \( P = D'\delta \). In a solid solution for which there is segregation to the slab with a segregation coefficient \( \alpha \), then \( P = \alpha D'\delta \) and the condition for type C diffusion is \((Dt)^{1/2} \ll \alpha \delta \).

The best data come from those experiments in which a tracer depth profile is measured since in this case \( P \) is practically independent of the effective boundary condition at the specimen surface [6]. In some experiments, only that depth of penetration at which the tracer can just be detected is measured (e.g. by autoradiography). This is not an accurate method, but probably gives reasonable comparative values. The results of early experiments were analysed using Fisher's approximate solution of the diffusion equations rather than the more accurate solutions of Suzuoka (thin film boundary condition) and Whipple (constant surface concentration). LeClaire [6] compared the three solutions and estimated the likely errors that could arise from using Fisher's solution. He concluded that in sectioning experiments the likely errors in \( P \) are typically a factor of 4 and in activation energy, \( Q' \), 0.2 to 0.3 eV.

2. INFLUENCE OF MISORIENTATION ACROSS THE BOUNDARY

This topic has been little studied in recent years and the only new data are those of Osenbach and Stubican [7] for Cr diffusion in (100) tilt boundaries in MgO. In this section the earlier work is summarised and compared with these more recent results.

2.1 \( P \) as a function of misorientation

The key questions to be answered here are "do all workers observe similar effects?" and "is there any evidence for low values of \( P \) at some misorientations?" In order to address these questions the available data for a variety of systems with fcc structures, and for both (100) and (110) tilt boundaries in bicrystal specimens, have been assembled in Figures 1 and 2. In some experiments [8,9,14] the data are only available as penetration depth, \( y \), of diffusant as a function of tilt angle, \( \phi \). Since under most conditions the concentration in the boundary is a function of \( P/y^2 \) [6], relative values of \( P \) were obtained by assuming them proportional to \( y^2 \).
Furthermore, in order to make the comparison between different systems easier, each data set has been normalised with respect to $P$ at a tilt angle of $30^\circ$ (or the maximum value of $\theta$ if this is less than $30^\circ$).

Figure 1 shows that for diffusion parallel to the [100] tilt axis the general tendency is for $P$ to increase with $\theta$ to a maximum value at approximately $45^\circ$ and then to decrease. $P$ must be zero at $0^\circ$ and $90^\circ$ and there is no evidence of low values of $P$ at intermediate misorientations. The structures of some of these boundaries in Cu have been calculated by Sutton and Vitek [15] and rationalised in terms of structural units in the boundary core.

The calculations indicate that certain boundaries are structurally 'favoured' and are composed entirely of a basic core structural unit. At misorientations between two favoured ones the boundary structure is a mixture of the two favoured units. According to Sutton and Vitek the favoured boundaries should show up in grain boundary diffusion as discontinuities in $dD'/d\theta$ with $dD'/d\theta$ being nearly constant for intermediate values of $\theta$. (They also point out that the same boundaries are not necessarily favoured in different metals having the same crystal structure and therefore generalisation can be misleading.) Whether $D'$ is large or small at the favoured boundary depends on the actual core structure. In metals it is reasonable to assume that the denser the core the lower is $D'$, but this is not necessarily so for ionic materials. For Cu the calculations indicate that the $\Sigma = 5$ coincidence boundaries ($\theta = 36.9$ and $53.1^\circ$) are favoured and that the structural units are lattice dislocation cores. The experimental results in Figure 1 for the fcc metals are reasonably in accord with these predictions and there are no misorientations in these boundaries (other than the perfect lattice) which show low diffusivity.

The data for Zn in Al [9] are very different from the other systems in that the most rapid diffusion was observed at the smallest misorientation, $\theta = 9^\circ$. This is not consistent with the data for Cu in Al [8] nor with the dislocation pipe model of low angle boundaries.

For a symmetrical tilt boundary with $\theta < 36.9^\circ$ the boundary may be approximated by an array of individual lattice dislocations (Burgers vector $b$) with a spacing $\lambda = b/(2 \sin \theta/2)$ and radius $a$. If we assume that fast diffusion is restricted to the core, $P$ is related to the dislocation diffusion coefficient, $D_d$, by

$$P = \pi a^2 D_d/\lambda = \pi a^2 D_d \theta/b$$  \hspace{1cm} (1)

The data in Figure 1 show that the proportionality between $P$ and $\theta$ holds approximately, even up to much higher angles than might initially be expected i.e. when the cores are no longer well separated. The dependence of $P$ on $\theta$ for Cr diffusing in MgO is seen to be somewhat different from that observed in the metals in that $P(\theta)/P(30)$ is larger at low values of $\theta$. Calculations of [100] tilt boundary structures in NiO [16] (which is isostructural with MgO) indicate in common with metals a similar basis of structural units comprising dislocation core configurations. However, in ionic materials the core configurations are very different because of the requirement to prevent ions of like charge being too close together. Furthermore, all diffusion in MgO is thought to be dominated by impurity effects and therefore different behaviour may be expected for either reason.

Figure 2 shows data for [100] tilt boundaries in the same format as in Figure 1. For these boundaries all the data agree in finding a smooth increase of $P$ with $\theta$ up to about $30^\circ$. Calculations for Al [15] indicate that $\Sigma = 27$ ($\theta = 31.6^\circ$) is the favoured boundary with lowest $\theta$ and has an open structure in which $D'$ is likely to be large which is consistent with the experimental data. Thereafter the results diverge and at $40^\circ$ are in wide disagreement. The data sets do tend to converge in the region $70-80^\circ$ and this is close to the $\Sigma = 3$ coherent twin boundary ($\theta = 70.5^\circ$) along which fast diffusion is expected to be unlikely. At higher angles the data are very sparse, but there is an indication of another region of slow diffusion close to the $\Sigma = 11$ ($\theta = 129.5^\circ$) misorientation which is also a favoured boundary.
Figure 1 - Grain boundary diffusion ($P = \alpha D'$) in [100] bicrystal tilt boundaries parallel to the tilt axis as a function of misorientation and normalised with respect to $P$ at $\Theta = 30^\circ$ (Refs. 7-12). Data is identified by authors' initials e.g. HBG = ref. 9).

Figure 2 - As Figure 1 but in [110] bicrystal tilt boundaries. (Refs. 9, 13, 14).

Figure 3 - Anisotropy of diffusion in [100] tilt boundaries in MgO and Ag. (Refs. 7 and 17).
However, the only boundary for which there is general agreement on its having a low diffusivity is the $\Sigma = 3$ coherent twin boundary.

2.2 Anisotropy as a function of misorientation

Anisotropy in $D'$ is to be expected in general and to be particularly evident in low angle tilt boundaries since diffusion parallel to the dislocation cores (tilt axis) described by equation (1) will be much easier than perpendicular to them. As $\Theta$ increases and the cores become closer together the anisotropy would be expected to decrease. This general behaviour has been observed for [100] tilt boundaries in both Ag and MgO bicrystals (Figure 3). Again, there is a significant quantitative difference between the oxide and the metal.

2.3 Activation energy as a function of misorientation

In their original work Upthegrove and Sinnott [10] claimed to observe a decrease in activation energy, $Q'$, as $\Theta$ increased, for Ni diffusion parallel to the tilt axis in [100] Ni tilt boundaries. This was subsequently shown to be erroneous and an artefact of using Fisher's approximate solution for analysing the experiments. Re-analysis [18] indicates that $Q'$ is approximately independent of $\Theta$ in these boundaries. $Q'$ is also approximately independent of $\Theta$ for self diffusion of Ag in [100] tilt boundaries [11] for $\Theta$ up to 16°, but $Q'$ is slightly greater for $\Theta = 28°$ which is rather surprising. The analogous experiments for Cr diffusion in MgO [7] also show $Q'$ to be independent of $\Theta$ over the range of the measurements i.e. up to 20°.

There is thus no real evidence of a systematic variation of $Q'$ with misorientation in any system. All the results just cited are consistent with the lattice dislocation model of low angle boundaries and therefore $Q'$ is to be identified with the activation energy for dislocation pipe diffusion.

3. DIFFUSION IN POLYCRYSTALLINE MATERIALS

Boundaries of the type considered thus far are rarely encountered in polycrystalline material. It is therefore instructive to compare data for diffusion in these simple bicrystal boundaries with data for diffusion in polycrystalline 'general' boundaries in systems where both types of experiment have been carried out. This is possible for self diffusion in Ni, Ag and Pb and the data are shown in Figure 4. The data indicate that, in terms of absolute values, the disagreement between bicrystal and polycrystalline specimens is usually less than a factor of 5 and much of this may result from the poor precision of the autoradiographic technique used in some of the experiments with bicrystals.

However, there is one qualitative trend which is difficult to understand and that is a tendency for $Q'$ measured in polycrystalline specimens to be greater than $Q'$ for [100] tilt boundaries, (this is particularly evident in the case of Pb). Since $Q'$ for the [100] tilt boundaries is the activation energy for dislocation diffusion this implies that dislocation diffusion has a lower activation energy than 'random' boundaries. This does not seem consistent at first sight with other experiments in which diffusion along low angle boundaries has been measured in 'single crystal' specimens for Au in Au [25] and Ni in NiO [26]. The ratio $Q'$ (high angle)/$Q'$ (low angle) was 0.76 for Au and 0.89 for NiO. This may be because low angle boundaries formed by recrystallisation of cold work contain dislocations having the Burgers vector of isolated lattice dislocations (or may be dissociated), whereas those grown into bicrystals will be constrained by the boundary geometry.

4. SEGREGATION AND DIFFUSION

In recent years several studies of this phenomenon in polycrystalline metals have been reported and a wide range of effects has been observed [27]. These include all combinations of enhancing or retarding grain boundary diffusion of the solvent or solute and the effect can be both strong and weak.
Figure 4 - Comparison between self diffusion in bicrystal and polycrystalline specimens of Ni, Ag and Pb. (Refs. 10-12 and 19-24).

Figure 5 - The influence of Sb segregation to Fe boundaries on the boundary diffusion of Fe and Sb and the coverage of the boundary by Sb (Ref. 28).

Figure 6 - Comparison between lattice and grain boundary diffusion for some fcc metals and oxides (Refs. 7, 19-22 and 33).
Figure 5 [28] is an example of a retarding effect in which a bulk concentration of $3 \times 10^{-5}$ atom fraction of Sb in Fe is seen to reduce $D'$ for both Fe and Sb diffusion by a factor of 70 with respect to its value in pure Fe. In Figure 5 is also shown the fractional coverage of the boundary plane by Sb. The form of this isotherm indicates strong attractive forces between Sb atoms in the boundary.

It has been suggested [27] that in such cases the decrease in atomic mobility in the boundary is because the segregant preferentially occupies those sites which would otherwise have high mobility and that the strong interactions between segregant atoms produce a relatively immobile two-dimensional structure.

In other cases, such as Ag(Ni) [29], even a strong segregation of solute has very little effect on boundary diffusion (and boundary energy) and this is presumably because different boundary sites and interactions are involved.

The only studies of doping on boundary diffusion in a ceramic material are for Cr diffusion in MgO(Cr) bicrystals [7] and U in UC polycrystals [30]. In MgO(Cr) $P$ increases linearly with bulk Cr concentration as does the bulk diffusivity of Cr (due to Cr$^{3+}$-doping creating charge-compensating Mg vacancies). Studies of Cr segregation in polycrystalline MgO [31] indicate that the segregation of Cr is relatively weak ($\Delta$ ~ 3) and that strong 'structural' effects would not perhaps be expected. In UC some dopants (Y, Zr, Ce) change both $P$ and $D$ (for U diffusion) in the same sense whilst others (W, V, Ta) have opposing effects on $P$ and $D$.

5. DIFFUSION IN CERAMICS

We have already drawn attention to some similarities and differences between metals and the ceramics MgO and NiO and these are explored further in this section. Grain boundary diffusion in a range of ceramic materials has also been the subject of a recent review [32].

5.1 Comparison with metals

The lack of a large concentration of highly mobile electrons in ionic compounds emphasises the importance of the charge on defects and the possibility of interactions via long range electric fields. Thus in such materials grain boundaries will in general be charged and a compensating space charge will extend into the crystals on each side of the boundary. There then exists the possibility of $\delta$ being considerably larger than 1 nm, as normally assumed for metals.

Diffusion experiments in both type B and C conditions, from which $\delta$ can be deduced, have been carried out for Ni in both low and high angle boundaries in NiO [26,27] and for Cr in low angle boundaries in Cr$_2$O$_3$ [34]. They indicate that $\delta$ is also approximately 1 nm in these materials and that any enhanced diffusion in the space-charge region is negligible compared to that in the boundary core.

In Figure 6 both $D$ (for the lattice) and $P$ (for high angle boundaries) have been plotted as a function of $T_m/T$ for some fcc metals and oxides ($T_m$ = melting temperature). This shows that grain boundary diffusion of Ni in NiO is very similar to that in polycrystalline metals at an equivalent temperature. (The relative scales of $P$ and $D$ have been chosen so that if $\delta$ is assumed to be 1 nm, $D'$ can be read on the $D$ scale.) However, it is also evident that, as a function of $T_m/T$, $D$ is greater for Ni in NiO than in the metals. This results in some practical problems in measuring $P$ in an oxide such as NiO since experimentally we require good differentiation between lattice and grain boundary diffusion. For example, $D'/D = 10^2$ for Ni at $T_m/T = 1.5$, but for Ni in NiO at $T_m/T = 2.25$. The corresponding $D'$ in Ni is approximately $10^6$ that in NiO and the practical consequence is that Ni grain boundary diffusion in NiO can only be accurately measured at relatively low temperatures and small diffusion depths.

Another practical problem when working with ceramic materials is that their diffusion properties are very sensitive to impurities and the materials themselves are generally less pure than metals. Impurity problems are so severe in the alkali
halides that there are no reliable data for these materials [35]. The data for Cr diffusion in MgO quoted extensively in this paper are not characteristic of pure MgO since even D in MgO is known to be always controlled by impurities. This may account for the high values of P for Cr in MgO when compared with other materials. The data in Figure 6 indicate that D' for Cr in MgO is of a magnitude characteristic of a liquid at only half the melting temperature of MgO. On the other hand there are good reasons to conclude that the data for NiO (and some to be referred to later for Cr₂O₃) are characteristic of the pure material.

Being compounds, ceramics differ from metals in that both components of the compound may have enhanced diffusion in grain boundaries. The only material in which both components have been studied is NiO and Figure 7 summarises diffusion data for both Ni and O in this oxide. (Again the scales are offset so that D' is given by the D scale when δ = 1 nm.) The more mobile ion in the lattice (Ni) is also the more mobile in the grain boundaries and D' for oxygen boundary diffusion is approximately equal to D for nickel lattice diffusion.

The importance of ionic charge in determining mobility in oxide boundaries is illustrated in Figure 8, which shows D' for some solute tracer ions in high angle NiO boundaries. The more highly charged ions have the lower diffusion coefficients whereas in metal boundaries it is the atoms of larger radius which have the lower diffusion coefficients.

5.2 Effect of deviation from stoichiometry

Ceramic compounds are in general not of exact stoichiometric composition and the extent of non-stoichiometry can vary widely. In the case of oxides the composition can be controlled by the oxygen activity in the gas phase, a(0₂), and consequently D and P are functions of a(0₂). Moreover, for lattice diffusion D ~ a(0₂)^n and n is characteristic of the point defect which is responsible for diffusion. Thus for lattice diffusion of Ni in NiO at high temperatures n ≈ 1/5 which indicates diffusion by a mixture of doubly and singly charged Ni vacancies.

In Figure 9 D and D'δ, for both high and low angle boundaries, are shown as a function of a(0₂) for Ni diffusing in NiO at relatively low temperatures. At these temperatures it is not possible to deduce a value for n, but the increase of D with increasing a(0₂) at the higher oxygen activities indicates that D at these temperatures is still characteristic of pure NiO and that Ni is diffusing via Ni vacancies. A similar dependence on a(0₂) is also observed for D'δ, which suggests a similar mechanism for grain boundary diffusion.

This similarity between D'δ and D as a function of composition has been observed in other systems. This is illustrated in Figure 10 where both D and D'δ for Cr diffusion in Cr₂O₃ are plotted as a function of a(0₂). In this case diffusion in the lattice at high a(0₂) is by Cr vacancies and at low a(0₂) perhaps by Cr interstitials. Furthermore, in UC Routbort and Matzke [40] observed that for U diffusion both D and D'δ were greater in UC₄₋ₓ than at the stoichiometric composition.

6. MECHANISM OF GRAIN BOUNDARY DIFFUSION

The experimental evidence which gives information concerning the mechanism of grain boundary diffusion in metals has been discussed at length in other reviews [1,2] and is only briefly summarised here. The fact that mass transport along boundaries takes place in such processes as sintering and creep shows that a place exchange mechanism is not involved since this is incapable of giving a net transport of matter. The influence of a hydrostatic pressure on D'δ for Ag self diffusion has been measured by Martin et al. [24]. From these experiments they deduced an activation volume for boundary diffusion of approximately 1 atomic volume which is close to the value of 0.9 for lattice diffusion by a vacancy mechanism (0.1 would be expected for an interstitial). Again for Ag self diffusion, Robinson and
Figure 7 - Lattice and grain boundary diffusion of Ni and O in NiO. \( a(O_2) = 1 \) for Ni and 0.2 for O (refs. 26, 33, 36 and 37).

Figure 8 - Solute tracer diffusion in NiO grain boundaries (refs. 33, 38, 39 and, for Cr, to be published).

Figure 9 - The influence of oxygen activity on diffusion of Ni in the lattice, low angle boundaries and high angle boundaries in NiO. (Refs. 26 and 33).

Figure 10 - The influence of oxygen activity on diffusion of Cr in the lattice and low angle boundaries in Cr2O3 (ref. 34).
Peterson [20] measured the isotope effect for $D'\delta$ and found it to be only slightly different from that observed for $D$. From this they concluded that tracer motion in the boundary is not highly correlated (i.e. a single row of atoms is not involved) and that the atomic jump itself only involves a small number of atoms. All these observations support the concept of grain boundary diffusion in Ag taking place via 'vacancies' which are more easily formed in the boundary and are more mobile than in the lattice.

The experiments on ceramic materials described in Section 5.2 lend further support to this mechanism. They also suggest in addition that the 'defect' responsible for boundary diffusion may be an interstitial when lattice diffusion occurs by an interstitial, and mechanistic experiments in such a system would be worthwhile.

In conclusion it would appear that the link between grain boundary structure and diffusion will probably be made through computer simulations and calculations of the formation and migration enthalpies of these grain boundary 'point defects'.

An attempt along these lines was recently reported by Riscondi [41] for tilt and twist boundaries in Al. The approach used was to estimate the mean reciprocal jump frequencies along 'easy' pathways through the core structures. The results for $D'$ both parallel and perpendicular to the tilt axis of $[100]$ and $[110]$ tilt boundaries are shown in Figures 11 and 12 and may be compared with the experimental data in Figures 1 and 2. In neither case do the calculations predict all the general features discussed in Section 2.1. They do successfully predict large anisotropy at low $\Theta$ and low diffusivity in the $\Theta=3$ and $\Theta=11$ [110] boundaries. However, they are not successful in predicting the proportionality between $D'$ and $\Theta (\leq 45^\circ)$ in [100] boundaries, or the gradual rise to a maximum at about $30^\circ$ in [110] boundaries.

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![Figure 11](image1.png)  
![Figure 12](image2.png)

**Figure 11** - Calculated self diffusion coefficients for [100] tilt boundaries in Al at 250°C as a function of misorientation (ref. 41).  

**Figure 12** - As Figure 11 but for [110] tilt boundaries (ref. 41).
A.P. Sutton: In the case of impurity ions diffusing in boundaries in NiO how can one know the charge state of the impurity?

A. Atkinson: There is experimental evidence from bulk diffusion studies that Cr$^{3+}$
and Co$^{2+}$ are reasonable charge states for these ions in NiO. However, no such data are available for Ce (because there is negligible solid solution) and this is referred to as Ce$^{2+}$ on the grounds that CeO$_2$ is the phase which coexists with NiO.

T. Watanabe: You have mentioned that the activation energy for grain boundary diffusion is independent of the boundary misorientation, and the activation energy is larger for polycrystals than for bicrystals. I do not understand why there is a difference in the activation energy between polycrystals and bicrystals. So I would like to have your comment on the difference.

A. Atkinson: I cannot explain this difference. One would expect that in a polycrystalline mass the grain boundaries which have the fastest diffusivity and lowest activation energy would dominate. However, the observations that activation energy is independent of misorientation only apply to a narrow range of 001 symmetrical tilt boundaries which may not be sufficiently numerous in a polycrystalline mass to dominate the average behaviour even though they may have lower activation energy. An additional point is that the errors in activation energy are likely to be greater in the bicrystals than the polycrystals and they may in fact be closer than they seem.

M. Schlüter: You showed a measured dependence of diffusivity vs $T$ on the apparent charge state of the diffusing atom. These curves seemed to show identical or similar slopes. How can one understand this apparent independence of activation barriers?

A. Atkinson: The apparent activation energies for Ce and Cr are both greater than for Co and Ni. However, the approximations used in analysing the raw diffusion profiles are such that the activation energy differences are less significant than the differences in the diffusion coefficients themselves.

M. Biscondi: At the end of your talk, you have hinted at my calculations of intergranular diffusion coefficients, which are derived from computed grain boundary structures. I must make two remarks about your appreciation: 1) The agreement of these calculated estimations with our experimental results concerning grain boundary diffusion of Zn in Al bicrystals are not bad, for the $<100>$ tilt axis as well as for the $<110>$ tilt axis. 2) According to the simulations, the core structure of the dislocations which constitute low angle tilt boundaries around $<100>$ depends on the misorientation, at least from $\sim 10^\circ$ (by core structure, I mean the precise position of atoms, the stress field, the distribution of grain boundary excess energy on the atomic sites). Therefore, it is not a priori shocking that the grain boundary diffusion coefficient along the tilt axis does not grow.
with misorientation in the range 10-30°.

A. Atkinson: Your calculations for diffusion in <100> tilt boundaries in Al do indeed show maximum diffusion at \( \theta = 10^\circ \) and this you find experimentally for Zn diffusion in Al boundaries. However, the calculations are for Al self diffusion whereas the experiments are for Zn interdiffusion. It does not seem reasonable to argue that Zn and Al will behave similarly, since other data for Cu diffusion in Al show a very different behaviour (Fig. 1). Furthermore, the experimental data for Ag, Pb and Ni are all consistent in that they show a gradual increase in diffusivity for \( \theta \) increasing to 45°. It seems strange that diffusion in Al is predicted not to show similar behaviour.