Chapter 5

THE MOBILITY AND MIGRATION OF BOUNDARIES

5.1 INTRODUCTION

The structure and energy of grain boundaries were discussed in chapter 4. In this chapter we examine the models and mechanisms of boundary migration and in particular the mobilities of boundaries, in order to provide a foundation for the discussions of recovery, recrystallization and grain growth in later chapters. More detailed discussion of some of the issues raised in this chapter can be found in the recent books about boundaries and interfaces by Sutton and Balluffi (1995) and Gottstein and Shvindlerman (1999).

5.1.1 The role of grain boundary migration during annealing

The migration of low angle (LAGB) and high angle grain boundaries (HAGB) plays a central role in the annealing of cold worked metals. Low angle boundary migration occurs during recovery and during the nucleation of recrystallization, and high angle boundary migration occurs both during and after primary recrystallization.

Despite the importance of grain boundary migration during annealing, the details of the process are not well understood. This is mainly because boundary migration involves atomistic processes occurring rapidly, at high temperatures, and under conditions
which are far from equilibrium. It is therefore very difficult to study boundary migration experimentally or to deal with it theoretically. Although there is a wealth of experimental evidence accumulated over many years, in many cases results are contradictory and few clear patterns emerge. However, it is evident that even very small amounts of solute have an extremely large influence on the boundary mobility and it is therefore very difficult to determine the intrinsic mobility of a boundary. Although a great deal is now known about the structure of grain boundaries (chapter 4), and models for grain boundary migration based on boundary structure have been formulated, there is as yet little evidence of quantitative agreement between the models and the experimental results.

5.1.2 The micromechanisms of grain boundary migration

Low angle and high angle grain boundaries migrate by means of atomistic processes which occur in the vicinity of the boundary. In this section we briefly outline the various mechanisms which have been proposed, in order to prepare for the more detailed considerations which appear later in this chapter.

The mechanism of boundary migration depends on several parameters including the boundary structure which, in a given material, is a function of misorientation and boundary plane. It also depends on the experimental conditions, in particular the temperature and the nature and magnitude of the forces on the boundary, and it is also strongly influenced by point defects in the material such as solutes and vacancies.

It is well established that low angle grain boundaries migrate through the movement by climb and glide of the dislocations which comprise the boundary, and many aspects of LAGB migration may therefore be interpreted in terms of the theory of dislocations.

The basic process during the migration of high angle boundaries is the transfer of atoms to and from the grains which are adjacent to the boundary, and models based on such thermally activated atomic jumps constitute the earliest models of boundary migration. As discussed in §4.4.2, the structure of a grain boundary is related to its crystallography, and there is evidence that boundaries may migrate by movement of intrinsic boundary defects such as ledges or steps or grain boundary dislocations. In some cases boundary migration may involve diffusionless shuffles, which are processes involving the cooperative movement of groups of atoms (cf. diffusionless phase transformations). In certain circumstances combined sliding and migration of boundaries may also occur.

Because the atomic packing at grain boundaries is less dense than in the perfect crystal, grain boundaries are associated with a free or excess volume which depends on the crystallography of the boundary (§4.4.3). This leads to a strong interaction with solute atoms and to the formation of a solute atmosphere which, at low boundary velocities, moves with the boundary and impedes its migration. The range of boundary velocities is very large. For example, in the case of grain growth the boundary may move relatively slowly through almost perfect crystal. However, during recrystallization the boundary moves at a very high velocity (often much higher than during diffusion-controlled phase transformations). In this case, the boundary migrates into highly defective material, leaving perfect crystal behind it. The mechanism by which the boundary removes the defects during recrystallization is not known, but it is reasonable to suppose that the
boundary energies and structures may differ for the cases of grain growth and recrystallization.

### 5.1.3 The concept of grain boundary mobility

A grain boundary moves with a velocity ($v$) in response to the net pressure ($P = \Sigma P_i$) on the boundary (§1.3). It is generally assumed that the velocity is directly proportional to the pressure, the constant of proportionality being the **mobility ($M$)** of the boundary, and thus

$$v = MP$$

This type of relationship is predicted by reaction rate theory (§5.4.1) if the mobility is independent of the driving force and if $P \ll kT$, and should be independent of the details of the mechanism of boundary migration.

There are however proposed boundary migration mechanisms such as step or boundary dislocation controlled migration (Gleiter 1969b, Smith et al. 1980) where the mobility depends on the driving force, and under certain conditions it is then predicted that this relationship may not hold. If the boundary mobility is controlled by solute atoms then, as discussed in §5.4.2, the **retarding pressure due to solute drag ($P_{\text{sol}}$)** may be a function of the boundary velocity. Although a complex relationship between driving pressure ($P_d$) and velocity may be found (e.g. fig. 5.32), equation 5.1 may still be obeyed if $P$ in equation 5.1 is replaced by ($P_d - P_{\text{sol}}$).

Surprisingly, there are comparatively few experimental measurements of the relationship between velocity and driving pressure. Results consistent with equation 5.1 have been obtained by Viswanathan and Bauer (1973) for copper and by Demianczuc and Aust (1975) for aluminium. More recently, Huang and Humphreys (1999a) have confirmed this relationship by in-situ SEM measurements of boundary mobility during the recrystallization of aluminium. Although Rath and Hu (1972) and Hu (1974) fitted their data for zone refined aluminium to a power law relationship $v \propto P^n$ with $n \gg 1$, Gottstein and Shvindlerman (1992) argued that the Rath and Hu experiments were strongly influenced by thermal grooving and by re-analysing their data and taking this into account, showed that they were consistent with equation 5.1. A re-examination of the early experimental results by Vandermeer and Hu (1994) has also concluded that they can be reconciled with equation 5.1.

The mobility of grain boundaries is temperature dependent and is usually found to obey an Arrhenius type relationship of the form

$$M = M_0 \exp\left(-\frac{Q}{RT}\right)$$

The slope of a plot of $\ln(M)$ or $\ln(v)$ (for constant $P$), against $1/T$ therefore yields a value of $Q$, the apparent activation energy which, as is further discussed below, may be related to the atom-scale thermally activated process which controls boundary migration.
However, this is not always the case, and great care should be taken in the interpretation of experimentally measured activation energies.

5.1.4 Measuring grain boundary mobilities

Our current knowledge of grain boundary mobility is very much limited by the lack of good experimental data. In addition to the problems arising from the effects of trace amounts of impurities on mobility (§5.3.3), the actual measurements are extremely difficult to make (appendix 2.7.2).

Measurements of boundary mobility are made by determining the velocity of a boundary in response to a well defined driving force. Experiments in which the velocity of a boundary is measured during recrystallization may be difficult to interpret, because the driving pressure which arises from the stored energy, and is typically 10–100 MPa, is not easy to measure accurately, varies throughout the microstructure and does not remain constant with time, decreasing as recovery proceeds. However, in a subgrain-forming material such as aluminium, subgrain sizes and misorientations in well-recovered materials can now be determined quite accurately by EBSD (Humphreys 2001) and therefore the driving pressure can be calculated from these parameters according to equation 2.8 (Huang and Humphreys 1999a). Many measurements of boundary mobility have been carried out on materials with a better characterised driving force, such as an as-cast substructure or by using bicrystals of carefully controlled geometry (e.g. Masteller and Bauer 1978, Gottstein and Shvindlerman 1999). In such experiments however the driving pressure is much lower (around $10^{-2}$ MPa), and it is not clear to what extent measurements of boundary mobility in materials with such low driving forces are directly applicable to migrating boundaries in recrystallizing material. In addition, there is evidence that moving boundaries interact with dislocations, and that defects affect boundary mobility (§5.3.4), indicating that there may be a real physical difference between boundary migration in deformed and undeformed material.

It should be noted that many of the measurements of boundary migration are conducted under conditions where the driving force is constant and the results are expressed as boundary velocities rather than mobilities (e.g. fig. 5.9). As equation 5.1 is expected to be obeyed, the mobility will be directly proportional to the velocity, and it is therefore reasonable to discuss such results in terms of boundary mobility even though this parameter has not actually been measured.

5.2 THE MOBILITY OF LOW ANGLE GRAIN BOUNDARIES

5.2.1 The migration of symmetrical tilt boundaries under stress

Although boundaries migrate during recovery, recrystallization and grain growth under driving pressures arising from defects or boundary curvature, it has long been known that symmetrical tilt boundaries, such as shown in figure 4.4 can move readily under the influence of stress (Washburn and Parker 1952, Li et al. 1953). The mobility of such
boundaries has been shown to depend on both temperature and boundary misorientation, and the effect of misorientation on the migration under constant stress of symmetrical tilt boundaries in zinc is shown in figure 5.1. It may be seen that as the misorientation increases and the dislocations in the boundary become closer together (equation 4.4), the mobility decreases. It is presumed that the dominant mechanism during boundary migration is glide of the edge dislocations which comprise the boundary, although dislocation boundaries in real materials will be more complicated than that of figure 4.4, and their migration will require some dislocation climb.

Recent investigations of the migration of planar symmetrical $<111>$ and $<112>$ tilt boundaries in very high purity aluminium under the influence of small shear stresses (Winning et al. 2001) have revealed a number of interesting features. As shown in figure 5.2, there is a sharp transition in mobilities at misorientations ($\theta$) of $\sim 14^\circ$. The mobilities of the lower angle boundaries are found not to depend significantly on the boundary misorientation, although there is very limited data for $\theta < 10^\circ$. The activation enthalpy for migration of the low angle boundaries is close to that for self diffusion, which is consistent with dislocation climb control, whilst that for high angle boundaries is lower, and close to that for boundary diffusion. The relative mobilities of high and low angle boundaries under stress therefore depends on temperature as shown in figure 5.2, where it is seen that at very high homologous temperatures, low angle boundaries move more rapidly than high angle boundaries. A comparison of boundary migration under stress with that driven by curvature (Winning et al. 2002), indicates that although the low angle boundary mobilities are similar, those for high angle boundaries may differ greatly and depend on the tilt axis.

There are two factors which need to be considered in applying the above results to recovery, recrystallization and grain growth of polycrystals.

If a boundary moves by dislocation glide under the influence of an applied stress, this implies that such movement must inevitably lead to a shape change. In unconstrained single crystals such as were used for these experiments, this may have little effect, but in a grain constrained within a polycrystal this will lead to the generation of internal

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**Fig. 5.1.** The effect of misorientation on the mobility of symmetrical tilt boundaries in zinc at 350°C under a constant stress, (after Bainbridge et al. 1954).
stresses which will oppose further boundary migration. A grain or subgrain microstructure contains many types of boundary, and the behaviour of symmetrical tilt boundaries may be untypical of the more general low angle boundaries found in a deformed and recovered metal (§6.4.2). Further work is therefore required on the behaviour of ‘random low’ and high angle boundaries under stress before the relevance of the above results to annealing processes in polycrystals can be established.

5.2.2 General low angle boundaries

5.2.2.1 Measurements of the mobility of low angle boundaries

It has long been recognised that the mobilities of general low angle boundaries are significantly lower than those of high angle boundaries. However, there are few systematic investigations of the mobility of such boundaries and of the effect of
misorientation. This is a major problem, because, as discussed in §6.5.3, a knowledge of the mobility of general low angle boundaries is a critical factor in developing an understanding of the annealing of deformed metals.

Early work which has shown that low and medium angle boundaries have a low mobility includes that of Tiedema et al. (1949) who found that recrystallized grains oriented within a few degrees of the matrix grew very slowly and were left as island grains, Graham and Cahn (1956) on aluminium, Rutter and Aust (1960) on lead, and Walter and Dunn (1960b) on iron. It should be emphasised that the references cited provide only a few largely qualitative observations and do not include a systematic investigation of the effect of misorientation on mobility.

Sun and Bauer (1970) and Viswanathan and Bauer (1973) used a bicrystal technique, in which the boundary energy provided the driving force for migration, to measure the mobility of high and low angle boundaries in NaCl and copper. Their results were reported as a mobility parameter $K'$ which is the product of the mobility $M$ and the boundary energy $\gamma$. This parameter is similar to the ‘reduced mobility’, which is often used in investigations of curvature driven grain growth.

$$K' = 2\gamma M$$  \hspace{1cm} (5.3)

The results for sodium chloride are shown in figure 5.3 and for copper in figure 5.4. Both figures clearly show a large difference in mobility between low and high angle boundaries. From figure 5.4 it may be seen that $K'$ for the high angle boundaries in copper is some three orders of magnitude greater than that for low angle ($2\degree$–$5\degree$) boundaries. As the boundary energy for $20\degree$ tilt boundaries in copper is only around four times that of $2\degree$ boundaries (Gjostein and Rhines 1959), the difference in mobility between high and low angle boundaries is therefore a factor of $\sim 250$. It is also seen that the activation energies for migration of the low angle boundaries are in both materials very much higher than for the high angle boundaries. In the case of copper, the value of $\sim 200$ kJ/mol for the low angle boundaries is close to that for self diffusion (table 5.1) and for NaCl, the value of 205 kJ/mol is close to that for the diffusion of Na$^+$ in NaCl.

![Fig. 5.3.](image_url)  

Fig. 5.3. a) Displacement of a curved boundary with time at 750°C in a NaCl bicrystal as a function of misorientation about a $<100>$ axis. b) Activation energy for boundary migration, (after Sun and Bauer 1970).
Measurements on high purity zinc and aluminium bicrystals by Fridman et al. (1975) have confirmed that the mobility of medium angle boundaries increases with increasing misorientation as shown in figure 5.13. Figure 5.13c also confirms that the activation energy for LAGB migration is higher than that for HAGB migration, although the reported activation energies for migration of LAGBs appear to be considerably higher than those for self diffusion.

Several investigations of the mobilities of low angle boundaries in aluminium have recently been reported. Huang and Humphreys (2000) measured the growth rates of subgrains in deformed single {110} <001> crystals of Al–0.05%Si. Crystals of this orientation are stable during plane strain compression and do not recrystallize, thereby allowing extensive subgrain growth to occur (§6.5.2). The mobilities of low angle boundaries of misorientations between 2.5–5.5° were calculated, and are shown in figure 5.5, where it is seen that the mobility increases by a factor of ≈50 as the misorientation rises by ≈3° in this range.

Investigation of cube-oriented crystals of the same material enabled the range of LAGB misorientations to be increased (Huang, Humphreys and Ferry 2000), and the combined effects of temperature and misorientation on mobility are shown in figure 5.6.
The activation energy for boundary migration was found to be a function of misorientation up to $^{1/2}/C16$, above which it remained constant (fig. 5.7). The activation energies were all in the range 125–154 kJ/mol, consistent with values for the lattice diffusion of Si in Al, and suggesting that the boundary migration is controlled by lattice diffusion of a solute atmosphere (§5.4.2).

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_m$ (K)</th>
<th>$G$ (GPa)</th>
<th>$b$ (nm)</th>
<th>$Q_S$ (kJ/mol)</th>
<th>$Q_C$ (kJ/mol)</th>
<th>$Q_B$ (kJ/mol)</th>
<th>$\gamma_B$ (Jm$^{-2}$)</th>
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<tr>
<td>Al</td>
<td>933</td>
<td>25.4</td>
<td>0.286</td>
<td>142</td>
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<td>0.324a</td>
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<td>Au</td>
<td>1336</td>
<td>27.6</td>
<td>0.288</td>
<td>164</td>
<td></td>
<td></td>
<td>0.38a</td>
</tr>
<tr>
<td>Cu</td>
<td>1356</td>
<td>42.1</td>
<td>0.256</td>
<td>197</td>
<td>117</td>
<td>104</td>
<td>0.625a</td>
</tr>
<tr>
<td>$\alpha$-Fe</td>
<td>1810</td>
<td>69.2</td>
<td>0.248</td>
<td>239</td>
<td>174</td>
<td>174</td>
<td>0.79a</td>
</tr>
<tr>
<td>$\Gamma$-Fe</td>
<td>1810</td>
<td>81</td>
<td>0.258</td>
<td>270</td>
<td>159</td>
<td>159</td>
<td>0.76a</td>
</tr>
<tr>
<td>NaCl</td>
<td>1070</td>
<td>15</td>
<td>0.399</td>
<td>217 ($\text{Na}^+$)</td>
<td>155</td>
<td>155</td>
<td>0.5c</td>
</tr>
<tr>
<td>Pb</td>
<td>601</td>
<td>7.3</td>
<td>0.349</td>
<td>109</td>
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<td>66</td>
<td>0.2b</td>
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<td>37b</td>
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<td>49.3</td>
<td>0.267</td>
<td>91.7</td>
<td>60.5</td>
<td>60.5</td>
<td>0.34a</td>
</tr>
</tbody>
</table>

Data are from Frost and Ashby (1982) unless otherwise indicated.

a) Murr (1975)
b) Friedel (1964)
c) Sun and Bauer (1970)

Fig. 5.5. The effect of misorientation on the mobility of low angle boundaries in Al–0.05%Si at 300°C, measured from subgrain growth in single crystals, (data from Huang and Humphreys 2000).

The activation energy for boundary migration was found to be a function of misorientation up to $\sim14^\circ$, above which it remained constant (fig. 5.7). The activation energies were all in the range 125–154 kJ/mol, consistent with values for the lattice diffusion of Si in Al, and suggesting that the boundary migration is controlled by lattice diffusion of a solute atmosphere (§5.4.2).
Yang et al. (2001) determined the mobilities of low angle boundaries in 99.98% Al from detailed analysis of the geometry of triple junctions in thin foils. Their results are quite similar to those shown in figures 5.5 and 5.6.

The determination of boundary mobilities either by subgrain growth or from triple junction geometry is based on the premise that the microstructural evolution is controlled by the mobility of the boundaries and not the triple junctions. The circumstances under which triple junction mobility may be rate limiting are discussed in §5.5.

5.2.2.2 Mechanisms of low angle boundary migration

The mechanisms of low angle boundary migration are poorly understood, and the few systematic investigations of the mobilities of low angle boundaries discussed above, provide the following clues to the mechanisms of low angle boundary migration:

- Low angle boundaries migrate at a rate consistent with equation 5.1, showing that the mobility is a constant for a particular boundary during isothermal annealing.
- Low angle boundary migration is controlled by a bulk diffusion process.
- The boundary mobility increases significantly with increasing misorientation.

Nes (1995a) has discussed various possible rate controlling mechanisms, including thermally activated glide, cross-slip, climb and solute drag. Furu et al. (1995) have suggested that the subgrain growth kinetics which they measured in polycrystalline commercial aluminium alloys were most consistent with a process of thermally activated glide and solute drag. In such a situation the apparent activation energy for migration is dependent on subgrain size and will not remain constant during growth or for different microstructures. The experimental results discussed in §5.2.2.1 which show that the
activation energy remains constant for a range of subgrain sizes and boundary misorientations, are more consistent with earlier suggestions (e.g. Sandström 1977b) that the boundary movement occurs by climb of the dislocations comprising the boundary, at a rate controlled by the lattice diffusion of solute. Although it has been suggested (Ørsund and Nes 1989) that at low temperatures boundary migration may be controlled by dislocation pipe or core diffusion, there is currently no experimental evidence of this.

5.2.2.3 Theories of the mobility of low angle boundaries

As the energy and structure of low angle boundaries are sensitive to misorientation, the intrinsic boundary mobility is also expected to depend on these parameters. The migration of low angle boundaries in general requires climb of dislocations in the boundary and this is expected to be the rate determining process. The theory of the mobility of low angle grain boundaries has been discussed by Sandström (1977b) and Ørsund and Nes (1989), and these authors suggest that the mobility of low angle boundaries is given by

\[ M = \frac{CD_s b}{kT} \]  

(5.4)

where \( C \) is a constant of the order of unity and \( D_s \) is the coefficient of self diffusion.

An important factor discussed by Hirth and Lothe (1968), and not considered by the above investigators, is that there is no net flow of matter as the boundary moves and therefore the vacancy source-to-sink spacing is approximately equal to the dislocation spacing (\( h \)) in the boundary, which is related to the boundary misorientation (equation 4.4).
In view of the large orientation dependence of the boundary structure on misorientation ($\theta$), the mobility of low angle boundaries is likely to show some dependence on $\theta$, which is not found in equation 5.4, and the following approximate analysis (Humphreys and Hatherly 1995), which was based on discussions with E. Nes, and has some similarity to that presented by Furu et al. (1995), is suggested.

Consider a boundary bowing to a radius of curvature $R$. The pressure ($P$) on the boundary due to the curvature is given by

$$P = \frac{2\gamma_s}{R}$$

(5.5)

where $\gamma_s$ is the boundary energy as given by equation 4.5. For small values of $\theta$ we use the approximation $\gamma_s \sim c_1 Gb \theta$, where $c_1$ is a small constant.

If we assume that equation 5.1 applies, the boundary velocity is given by

$$v_b = \frac{dR}{dt} = \frac{2M \gamma_s}{R} = \frac{2c_1 MGb \theta}{R}$$

(5.6)

**Case A – Very low angle boundaries ($\theta \to 0$)** We first consider the movement of boundaries in which the dislocations are spaced far apart. In this limiting situation we can assume that the behaviour of the individual dislocations in the boundary is dominant. An individual dislocation in the boundary is bowed to a radius of curvature $R$ and the force on unit length of the dislocation is given approximately by

$$F = \frac{Gb^2}{2R}$$

(5.7)

For dislocation climb under conditions of negligible vacancy supersaturation, $Fb^2 \ll kT$ and the climb velocity ($v_d$) of a dislocation under the influence of a force $F$ is given approximately (Friedel 1964, Hirth and Lothe 1968), as

$$v_d = D_s c_j \left(\frac{Fb}{kT}\right)$$

(5.8)

Where $c_j$ is the concentration of jogs. Substituting for $F$ as given by equation 5.7

$$v_d = \frac{D_s c_j Gb^3}{2kTR}$$

(5.9)

As the dislocations are assumed to be essentially independent in such a low angle boundary, the velocity of all the dislocations in the boundary is given by equation 5.9 and therefore $v_d = v_b$. Thus from equations 5.6 and 5.9

$$v_b = \frac{2c_1 MGb \theta}{R} = \frac{D_s c_j Gb^3}{2kTR}$$

(5.10)
and hence

$$M = \frac{D_s c_b b^2}{4c_1 kT\theta}$$

(5.11)

i.e. in this limiting case:

- The dominant mechanism is climb of individual dislocations
- $v = M.P$ is expected to hold
- $M$ is inversely proportional to $\theta$

**Case B** – Boundaries where the dislocation cores overlap ($\theta > 15^\circ – 20^\circ$) In this situation we have effectively reached the case of a high angle boundary, and for a general boundary we can reasonably assume (§5.4.1.1)

- The dominant mechanism is atom jumps across the boundary
- $v = M.P$ is expected to hold
- $M$ is independent of $\theta$

**Case C** – The intermediate case This is probably the most important regime for the recovery of deformed polycrystals, but the most difficult to analyse.

**C1 (medium angles)** When the boundary angle is large and $h$ is small, the movement of the boundary is probably dominated by atom transfer over a distance $h$, and the process is analogous to the diffusion of atoms through a membrane of thickness $h$, which would result in $M$ being inversely proportional to $h$, i.e. $M \propto h$.

**C2 (low to medium angles)** This is a transition regime in which the dominant mechanism is not clear. There are two opposing factors.

- The decrease in mobility with increasing $\theta$ due to the factors discussed for case A will tend to decrease the mobility as $\theta$ increases.
- As $\theta$ increases, $h$, the vacancy source-to-sink distance decreases, and this, as discussed above, will increase the dislocation climb rate and hence the mobility.

It is expected that the second effect will eventually dominate as $\theta$ increases, leading to a minimum mobility at some small misorientation. The extent to which a theory based on the behaviour of individual dislocations can be applied is also unknown, because reactions at dislocation nodes may become a dominant factor (Hirth and Lothe 1968). In the absence of a specified mechanism, it is not known if the mobility is independent of driving force as is assumed by equation 5.1. On the basis of the above analysis, it is suggested that the variation of the mobility of a general low angle boundary with misorientation may be as shown in figure 5.8.

**Comparison with experiment** Measurements of the activation energies for LAGB migration or recovery generally indicate control by lattice diffusion as predicted by the model.

The heavy lines in figure 5.8 indicate regions for which there is significant experimental evidence as detailed below.
REGION A. There are no recent experimental data for this region, but a decrease in mobility with increasing misorientation for $\theta < 1^\circ$, for the special case of symmetrical tilt boundaries under stress, is shown in figure 5.1.

REGION B. There is reasonable evidence that the mobility of random HAGBs is high and independent of $\theta$.

REGION C1. There is evidence, e.g. figures 5.3 to 5.6, that the mobility of boundaries in the range 5–20$^\circ$ increases with $\theta$ and saturates at about 14–20$^\circ$. There is a change in the misorientation dependence of the activation energy for migration at $\sim$14–15$^\circ$ (e.g. figs. 5.2, 5.6 and 5.7) which is consistent with a change in boundary structure, i.e. from a low angle to a high angle boundary.

REGION C2. For misorientations in the range 2–5$^\circ$, there is evidence in aluminium, that the boundary mobilities increase rapidly with increasing $\theta$ (fig. 5.5). Mobilities in this range are typically 10–500 times lower than for a random high angle boundary.

In summary, it is quite clear that although considerable progress has been made in the past decade, further experimental and theoretical work is needed before our understanding of the mobilities of low angle grain boundaries can adequately provide a sound basis for the development of detailed models of annealing.

5.3 MEASUREMENTS OF THE MOBILITY OF HIGH ANGLE BOUNDARIES

5.3.1 The effect of temperature on grain boundary mobility in high purity metals

5.3.1.1 The activation energy for boundary migration
Measurements of the temperature dependence of boundary mobility are often analysed in terms of equation 5.2 to determine the activation energies (Q) and pre-exponential factors ($M_0$), in the expectation that the values of Q may provide information as to atomic-scale thermally activated processes which control boundary migration.
Figure 5.4 is typical of data found for metals of very high purity, where the linear relationship between the logarithm of mobility and 1/T implies a single activation energy over the range of conditions investigated, and Table 5.2 shows some experimental data for the mobility of high angle boundaries, obtained by several techniques in a variety of high purity metals. Comparison of the activation energies for boundary migration in Table 5.2 with the activation energies for diffusion given in Table 5.1 shows that the activation energy for boundary migration in high purity metals is often close to that for grain boundary diffusion, i.e. about half that for bulk diffusion.

5.3.1.2 Transition temperatures

In impure metals or alloys, as will be discussed in §5.3.3, the variation of mobility with temperature is more complicated than that of Figure 5.3, with more than one apparent activation energy being found over a range of temperatures. However, even in high purity metals a change in mobility and activation energy is sometimes found at very high homologous temperatures. There are two likely explanations for this:

(a) Changes in boundary structure, in which coincidence site or ordered boundaries may become more disordered and therefore lose their special properties, may occur at elevated temperatures.

There is some evidence from experiments on high purity lead (Rutter and Aust 1965) and copper (Aust et al. 1963, Ferran et al. 1967) that the higher mobility of special boundaries is lost at high temperatures, and this has been interpreted in terms of a change in grain boundary character at high temperatures (see also §4.4.3). Maksimova et al. (1988) have measured a discontinuous change in mobility with increasing temperature for $\Sigma 17, 28^\circ <001>$ boundaries in 99.99999% tin. Boundaries within $\sim 1^\circ$ of this were found to show a discontinuous drop in mobility with increasing temperature.
at temperatures between 0.94 and 0.98 $T_m$ as shown in figure 5.9, whereas boundaries misoriented by more than this amount from $\Sigma 17$ did not show a transition. Boundaries in the higher temperature regime had a higher activation energy, and the authors claimed that this was due to the transition from a special boundary to a general boundary at high temperatures. Wolf and colleagues (e.g. Wolf 2001) have recently provided convincing evidence, using molecular dynamics modelling, of a reversible change in structure of special boundaries, to a disordered ‘liquid-like’ state at high temperature.

(b) The mechanism of boundary migration may change at high temperatures.

Other work has shown a discontinuous transition to a high temperature regime of higher boundary mobility and low activation energy for migration. Gleiter (1970c) has detected a discontinuous change in properties for $<100>$ tilt boundaries in high purity lead at temperatures in the range 0.7 to 0.8 $T_m$, the actual temperature depending on the crystallography of the boundary. The high temperature regime is characterised by a very low activation energy for migration (26 kJ/mol) whereas at the lower temperatures the activation energy is 58 kJ/mol which is close to that for boundary diffusion (table 5.1). In zinc, there have been reports of a transition to a very low activation energy of $\sim 17$ kJ/mol at $T > 0.91 T_m$ (Gondi et al. 1992) which is comparable with that for liquid diffusion, and Kopetski et al. (1979) have found a sharp transition to a regime of zero activation energy for boundary mobility in zinc at temperatures above $\sim 0.9 T_m$ as shown in figure 5.10. Although Gleiter (1970c) interpreted his results in terms of a
transition to a different boundary structure, there is a similarity between all three sets of measurements, and the last two have been interpreted in terms of a change in the mechanism of boundary migration from one controlled by diffusion to one involving cooperative atomic shuffles (§5.4.1.4). Further evidence for such transitions and discussion of the mechanisms can be found in Sutton and Balluffi (1995) and Gottstein and Shvidlerman (1999).

5.3.2 The effect of orientation on grain boundary migration in high purity metals

Because boundary migration involves diffusion processes in and across the boundary, it is to be expected that the structure of the boundary should affect its mobility. In order to define the relationship between two grains it is necessary to specify both the orientation relationship between the grains and the orientation of the boundary plane (§4.1). Although, as discussed below, there are some data on the effect of these parameters on grain boundary migration, the information is far from complete.

5.3.2.1 The orientation dependence of grain boundary mobility

There is extensive evidence that not only do high angle grain boundaries have a greater mobility than low angle boundaries (§5.2.2) but that the mobilities and activation energies for migration of high angle boundaries are dependent on orientation. Early work in this area includes that of Cook and Richards (1940) and Bowles and Boas (1948) who found rapid growth of certain orientations in copper, and Beck et al. (1950) who showed that in lightly rolled high purity aluminium, grains with a misorientation of $\sim 40^\circ$ about a $<111>$ axis exhibited the largest growth rate. Kronberg and Wilson (1949) who carried out recrystallization experiments on copper, found that grains related to the deformed matrix by a rotation of $22^\circ$–$38^\circ$ about a common $<111>$ axis, and by $19^\circ$ about a $<100>$ axis grew most rapidly. They postulated that there was a relationship between the fast-growing orientations and boundary structure and that special boundaries, (later known as Kronberg-Wilson boundaries), which had a high

![Graph showing temperature dependence of reduced mobility of <1120> tilt boundaries in zinc, for two values of misorientation, showing a transition to a high temperature regime of zero activation energy.](after Kopetski et al. 1979).
density of **coincidence sites** (§4.4.1) often exhibited fast rates of growth. One of the best known early investigations of the effect of misorientation on mobility is that by Liebmann et al. (1956) who measured the migration rate of \(<111>\) tilt boundaries during the recrystallization of 99.8% aluminium crystals which had been lightly deformed. They found the mobility to be a maximum for a misorientation of \(\sim 40^\circ\) about a \(<111>\) axis, a result which has proved to be of great importance to the theory of recrystallization texture development in fcc metals (§12.3.2). Their results were obtained on lightly strained material in which the impurities were present as dispersed phases. In experiments on similar material in which the impurities were retained in solid solution, a high mobility of \(40^\circ <111>\) boundaries was not observed (Green et al. 1959). However, at larger strains (e.g. 80% by rolling), high mobility of these boundaries was observed irrespective of microstructure, for a wide range of purity levels (from 99.97%–99.9999%) (Parthasarathi and Beck 1961, Gleiter and Chalmers 1972). Growth selection experiments on aluminium (Ibe and Lücke 1966) showed similar results, although such experiments must be interpreted with some caution as they do not directly yield boundary mobilities or velocities. Figure 5.11 shows the results of a more recent investigation of the effect of orientation on boundary mobility during the recrystallization of aluminium, in which the effects of both the misorientation angle and axis on mobility are shown. The very broad peak (\(\pm 10^\circ\)) of figure 5.11a is in agreement with the earlier, more limited results of Liebmann et al. (1956), and contrasts with the much sharper peaks (\(\pm 0.2^\circ\)) which are typically obtained from curvature-driven grain growth (e.g. fig. 5.12).

Although it is normally found in aluminium alloys that the only fast growing boundaries are those around \(40^\circ <111>\), recent investigation of recrystallization in high purity aluminium have shown that at low temperatures (\(<150^\circ C\)), there is a transition to preferential growth of grains with a relationship of \(28–38^\circ\) about \(<100>\) to the deformed matrix (Huang and Humphreys 1999b).

The existence of certain orientation relationships which are associated with a rapid growth rate is well established for a large number of metals (Gleiter and Chalmers 1972), and a summary of the early observations is given in table 5.3. The fact that a boundary has a large number of coincidence sites is not necessarily an indication that it has a high mobility and it is well known that the high angle boundary with the most coincidence sites, the \(\Sigma 3\) twin boundary, has an extremely low mobility (Graham and Cahn 1956). It was shown in chapter 4 that although some low \(\Sigma\) boundaries have a low energy, this is not universally the case, and this is reinforced by the data in table 5.3 which show that high mobility has only been identified for a few values of \(\Sigma\). As is discussed in §5.3.3, the orientation dependence of boundary migration is closely linked to solute effects, and therefore some care must be taken in interpreting the data of table 5.3.

Extensive measurements of boundary mobilities have been carried out by Shvindlerman and colleagues using curvature driven growth in high purity bicrystals of aluminium and other materials. Figure 5.12 shows data for the migration of \(<111>\) tilt boundaries in very high purity aluminium and figure 5.13 shows the effects of both misorientation and purity for \(<100>\) tilt boundaries in aluminium.

Such experiments enable the relationships between mobility and misorientation to be studied with great precision. It is seen from figure 5.12a that there are two distinct and narrow peaks, at \(38.2^\circ\) and \(40.5^\circ\). Figures 5.12a and b show that the relative strength of
the peaks varies with temperature, and at low temperatures the 38.2° peak is important, whereas at higher temperatures the 40.5° peak dominates. The different temperature dependence of the mobilities of the two types of boundary are evident in figure 5.12b, and this is also expressed as a difference in activation energy as shown in figure 5.12c. The 38.2° <111> boundary is the coincidence site boundary Σ7, for which special properties might be expected. The reason for the shift at high temperatures to a peak at 40.5° is not clear, but may be associated with a transformation to a more random boundary structure (Molodov et al. 1995), or may be associated with impurities. In high purity materials, the effects of small amounts of impurity may have a very large influence on the activation energy for boundary mobility as seen in figure 5.13.

Fig. 5.11. The relative migration rates of recrystallizing grain boundaries as a function of (a) misorientation angle, for boundaries with axes within 10° of <111>, (b) deviation from a <111> axis, for boundaries with misorientations between 30 and 50°, (Huang and Humphreys 1999a).
Table 5.3
Orientations for which rapid growth is commonly found.

<table>
<thead>
<tr>
<th>Sigma</th>
<th>Rotation</th>
<th>Axis</th>
<th>Rotation</th>
<th>Axis</th>
<th>Metal</th>
<th>Structure</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Σ7</td>
<td>38.2</td>
<td>&lt;111&gt;</td>
<td>35–45</td>
<td>&lt;111&gt;</td>
<td>Al</td>
<td>fcc</td>
<td>Liebmann et al. (1956)</td>
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<td></td>
<td>38</td>
<td>&lt;111&gt;</td>
<td></td>
<td></td>
<td>Cu</td>
<td>fcc</td>
<td>Kronberg and Wilson (1949)</td>
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<td></td>
<td>36–42</td>
<td>&lt;111&gt;</td>
<td></td>
<td></td>
<td>Pb</td>
<td>fcc</td>
<td>Aust and Rutter (1959a)</td>
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<tr>
<td>Σ13a</td>
<td>22.6</td>
<td>&lt;100&gt;</td>
<td>23</td>
<td>&lt;100&gt;</td>
<td>Al</td>
<td>fcc</td>
<td>May and Erdmann (1959)</td>
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<td></td>
<td>19</td>
<td>&lt;100&gt;</td>
<td></td>
<td></td>
<td>Cu</td>
<td>fcc</td>
<td>Kronberg and Wilson (1949)</td>
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<tr>
<td>Σ13b</td>
<td>27.8</td>
<td>&lt;111&gt;</td>
<td>30</td>
<td>&lt;111&gt;</td>
<td>Cu</td>
<td>fcc</td>
<td>Beck (1954)</td>
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<td>30</td>
<td>&lt;111&gt;</td>
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<td></td>
<td>Ag</td>
<td>fcc</td>
<td>Ibe and Lücke (1966)</td>
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<tr>
<td></td>
<td>20–30</td>
<td>&lt;111&gt;</td>
<td></td>
<td></td>
<td>Nb</td>
<td>bcc</td>
<td>Stiegler et al. (1963)</td>
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<tr>
<td>Σ13</td>
<td>30</td>
<td>&lt;0001&gt;</td>
<td>30</td>
<td>&lt;0001&gt;</td>
<td>Zn</td>
<td>cph</td>
<td>Ibe and Lücke (1966)</td>
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<td></td>
<td>30</td>
<td>&lt;0001&gt;</td>
<td></td>
<td></td>
<td>Cd</td>
<td>cph</td>
<td>Ibe and Lücke (1966)</td>
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<tr>
<td>Σ17</td>
<td>28.1</td>
<td>&lt;100&gt;</td>
<td>26–28</td>
<td>&lt;100&gt;</td>
<td>Pb</td>
<td>fcc</td>
<td>Aust and Rutter (1959)</td>
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<td></td>
<td>30</td>
<td>&lt;100&gt;</td>
<td></td>
<td></td>
<td>Al</td>
<td>fcc</td>
<td>Fridman et al. (1975)</td>
</tr>
<tr>
<td>Σ19</td>
<td>26.5</td>
<td>&lt;110&gt;</td>
<td>27</td>
<td>&lt;110&gt;</td>
<td>Fe–Si</td>
<td>bcc</td>
<td>Ibe and Lücke (1966)</td>
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</table>
It is often found that for a particular type of boundary, there is a relationship between changes of the activation energy \( Q \) and the pre-exponential factor \( M_0 \) as the misorientation is varied, and this is known as the ‘\textit{compensation effect}’ (Molodov et al. 1995). The relationship is

\[
Q = Q_{11} \ln(M_0) + Q_{12}
\]  

(5.12)

where \( Q_{11} \) and \( Q_{12} \) are constants.

Figure 5.12d shows that the relationship between \( Q \) and \( M_0 \) for boundaries close to \( \Sigma 7 \) in high purity aluminium is in agreement with equation 5.12. Such a relationship means that in a plot of \( \ln(M) \) against \( 1/T \), as in figure 5.12b, the various straight lines intersect at a common point (the \textit{compensation temperature}). Such a relationship implies a coupling between the enthalpies and entropies of activation (Molodov et al. 1995, Fig. 5.12. The mobility of \(< 111>\) tilt boundaries in 99.999 at% Al determined by curvature-driven growth experiments. (a) The effect of temperature on the reduced mobility, (b) The temperature dependence of the reduced mobility of 38.2° and 40.5° \(< 111>\) tilt boundaries, (c) The activation energy for migration, (d) The relationship between activation energy and pre-exponential factor, (after Molodov et al. 1995).
The relationship of equation 5.12 has also been found to hold for low angle grain boundaries (\(\Sigma 1\)) in aluminium (Huang et al. 2000a). This type of relationship only applies to boundaries of similar type. For example, molecular dynamic simulations predict that boundaries close to either \(\Sigma 7\) or \(\Sigma 13\) will produce relationships in accord with equation 5.12, but that the constants \(\alpha\) and \(\beta\) will be different for the two cases (Upmanyu et al. 1999).

It should be noted that a compensation effect may also be found for other thermally activated grain boundary processes such as diffusion (Sutton and Balluffi 1995).

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**Fig. 5.13.** The mobility of \(<100>\) tilt boundaries in aluminium. (a) The effect of temperature and misorientation on the mobility of boundaries in 99.9992 at% aluminium, (b) The effect of temperature and misorientation on the mobility of boundaries in 99.99995 at% aluminium, (c) The orientation dependence of the activation energy for migration in samples of different purity, (Fridman et al. 1975).
The orientation dependence of grain boundary migration has implications for the texture developed during recrystallization and grain growth (§12.3.2). In the case of primary recrystallization, it is impossible to define accurately, other than on a very local scale, the relationship between the growing grain and the deformed matrix, because any grain of the deformed material will contain a highly misoriented substructure (§2.4). Therefore caution must be exercised in the application of mobility-orientation relationships to recrystallizing material, and in particular in relating a high boundary mobility to a specific boundary structure. The boundary misorientation is normally defined by an axis/angle pair (§4.2) and there is abundant evidence that, as indicated by figure 5.11a and table 5.3, there is a significant spread of angles for which a high mobility is found. There is less information as to the importance of deviation from a $<111>$ axis, although figure 5.11b shows that this peak is also very broad.

5.3.2.2 The effect of boundary plane on mobility

It has long been known that for a particular misorientation, the boundary mobility may depend on the actual boundary plane (Gleiter and Chalmers 1972). An extreme example is the $\Sigma 3$ twin orientation in fcc metals where the coherent $\{111\}$ plane boundary is very immobile, whereas the incoherent twin boundary has much greater mobility. It is noticeable that in many cases, grains with an orientation relationship for rapid growth show very anisotropic growth, and an early and very clear example of this is seen in the work of Kohara et al. (1958). For fcc metals the anisotropy is such that the faces parallel to the $<111>$ rotation axis (i.e. the twist boundaries) grow much more slowly than the tilt boundaries (Gottstein et al. 1978), and thus an unconstrained grain tends to become plate-shaped as seen in figure 5.14.

The mobility of $40^\circ <111>$ tilt boundaries during recrystallization has been found to be some ten times larger than that of the twist boundaries (Huang and Humphreys 2000), and it has also been shown (Huang and Humphreys 1999a) that the mobilities of the $40^\circ <111>$ twist boundaries are similar to those of ‘random’ high angle boundaries.

During the recrystallization of high purity aluminium at temperatures below $\sim 150^\circ C$, grains with an orientation relationship of $\sim 30^\circ$ about a $<100>$ direction to the matrix (close to $\Sigma 17$), may develop an approximately octahedral shape during recrystallization (figure 5.15) and this has been shown to be due to the growth being most rapid in $<100>$ directions (Huang and Humphreys 1999b). Growth is rapid in all the $<100>$ directions and not just in the direction parallel to the misorientation axis.

In all three of the cases discussed above, $\Sigma 3$, $\Sigma 7$ and $\Sigma 17$, the grains develop asymmetric shapes which are determined by the orientation relationships between the deformed matrix and the recrystallizing grain, and which are the result of anisotropic boundary mobilities.

A quite different example is the crystallographic faceting of recrystallizing grains. There is some evidence from x-ray topography (e.g. Gastaldi, Jourdan and Grange 1992, Sutton and Balluffi 1995) of faceting parallel to low index planes of the new grains during the later stages of recrystallization in pure aluminium, although this behaviour is not commonly observed in recrystallizing aluminium. However, a recent investigation of nickel alloys which had been internally oxidised (Humphreys 2000), has shown evidence of very strong faceting parallel to $\{100\}$ planes of the recrystallizing grains as shown in
Fig. 5.14. Optical micrograph of lenticular grains, viewed edge-on in a recrystallizing single crystal of Al–0.05%Si. The grains are rotated by \( \sim 40^\circ \) to the deformed matrix about the marked \(<111>\) axis, and the broad face of the plate is parallel to the rotation axis, (Ardakani and Humphreys 1994).

Fig. 5.15. SEM micrograph showing recrystallization in high purity aluminium at 50°C. The grains are misoriented by \( \sim 30^\circ \) to the deformed matrix and grow preferentially in directions parallel to \(<100>\) of the recrystallizing grains, resulting in an approximately octahedral grain shape, (Huang and Humphreys 1999b).
The facets are on the recrystallizing grain, and are not affected by the orientation relationship to the deformed matrix. The growth of the grains is therefore somewhat similar to the growth of crystals from the melt, i.e. crystallization rather than recrystallization. As the facets are not evident in the fully recrystallized material, such microstructures appear to be the result of faceted growth rather than anisotropic boundary energies. A reasonable interpretation of such growth behaviour is that the recrystallization is controlled by a ledge mechanism akin to that which occurs for crystal growth from the melt or during vapour deposition. Although it is not yet clear why such a mechanism should control recrystallization in this material, the recent report of similar faceting in electrodeposited nickel with sulphur impurities (Hibbard et al. 2002), suggests that it may be due to impurity segregation at the recrystallizing boundaries.

5.3.3 The influence of solutes on boundary mobility

Solute elements have an enormous effect on boundary migration and very small amounts of impurity may reduce the mobility by several orders of magnitude (Dimitrov et al. 1978) as shown in figure 5.17a. Because the effects of solute are so strong, particularly at low concentrations, it is very difficult to be confident that the mobilities measured in ‘pure’ metals and discussed in §5.3.1 and §5.3.2 actually represent the intrinsic behaviour of boundaries.

5.3.3.1 The effect of solute concentration

From figure 5.17 it may be seen that the relationship between mobility and solute content shows two distinct regimes separated by a transition region:-

(a) At high solute concentrations the mobility is low and decreases with increasing solute concentration. In this low mobility regime it is thought that an atmosphere of solute
atoms is associated with the boundary. The boundary velocity is then controlled by the rate of diffusion of the impurity atoms (§5.4.2). Gordon and Vandermeer (1966) have shown that for aluminium containing small amounts of copper, in the low mobility regime the boundary velocity at constant driving force is inversely proportional to the solute concentration as shown in figure 5.18.

(b) At low solute concentrations the mobility is higher and solute has little influence on the mobility. In this high mobility regime, the boundary mobility is little affected by solute and it is thought that the boundary has broken away from its solute atmosphere (§5.4.2).

For the cases of copper and magnesium in aluminium shown in figure 5.17a, there is a very sharp transition between the two regimes. However, similar experiments have shown more gradual transitions for silver (fig. 5.17c) or iron (Montariol 1963) in aluminium. In the same solvent, different solutes may, as shown in figure 5.17a affect...
the critical concentration at which the transition occurs and, as is apparent in figure 5.17a may also reduce the mobility in the slow regime by different amounts.

The apparent activation energy for boundary migration is also a function of the solute content, exhibiting a transition at the critical solute content at which boundary breakaway occurs as shown in figures 5.17b and c. The details of the transition are different in both cases. For the magnesium solute (fig. 5.17b) the transition is abrupt, whereas for the silver solute (fig. 5.17c) it is gradual.

In most cases it is found that the activation energies at low solute concentrations are essentially solute independent and correspond to those found for materials of very high purity as shown in table 5.2. The apparent activation energy at higher solute concentrations is typically close to that for self diffusion or for diffusion of the solute in the solvent, and, as seen from figures 5.17b and c, may depend on solute concentration.

5.3.3.2 The effect of temperature
The combined effects of temperature and solutes on mobility are best seen from plots of the logarithm of mobility against 1/T. As shown in figure 5.19 for boundary mobility in Au with 20ppm Fe (Grunwald and Haessner 1970), such a plot may show both a change to a lower apparent activation energy and a sharp increase in mobility at a higher temperature. Similar results have been reported for lead (Aust 1969) and copper (Grewe et al. 1973). In most cases it is found that the activation energies at high temperatures
correspond to those found for materials of very high purity and the activation energy at low temperature is typically close to that for self diffusion.

In many cases (Gordon & Vandermeer 1962, Fridman et al. 1975) a peak is found in the activation energy at the transition, as is shown in figure 5.20. The origin of this peak can be seen in figure 5.19, where during the transition, the slope of the line (i.e. apparent activation energy) increases. This is clearly an apparent activation energy due to a transition in the effect of solutes on the boundary and does not correspond to the activation energy of a physical mechanism.

Fig. 5.19. The effect of temperature on the migration velocity of a 30° <111> tilt boundary in gold, (after Grunwald & Haessner 1970).

Fig. 5.20. The effect of copper additions on the activation energy for boundary migration in aluminium, (after Gordon and Vandermeer 1962).
5.3.3.3 The effect of orientation

It has been known for a long time that the effects of solutes on boundary mobility are dependent on the crystallography of the boundary, and that special boundaries, i.e. those which are close to a coincidence relationship, are less susceptible to effects of solute than are random boundaries (Kronberg and Wilson 1949, Aust and Rutter 1959a,b). The well-known results obtained by Aust and Rutter on tin-doped lead are shown in figure 5.21. At low impurity concentrations the mobilities of the special and general boundaries are similar. As the impurity level is increased the mobility of the random boundaries is affected much more by the impurities. The combined effects of misorientation and solute have also been demonstrated for tilt boundaries in <111> and <100> rotated grains in aluminium, as shown in figures 5.12 and 5.13. For aluminium of 99.9992 at% purity, except at the highest temperature, the mobility fluctuates with misorientation, with maximum growth rates occurring near coincidence rotations (fig 5.13a). However as shown in figure 5.13b, for material of 99.9995 at% purity, the mobility is found to be almost independent of orientation for \( \theta > 20^\circ \). These results confirm those of Aust and Rutter (1959a,b) and indicate that:

The orientation dependence of grain boundary mobility (§5.3.2.1) arises primarily from an orientation dependence of solute segregation to the boundary rather than an intrinsic structure dependence of grain boundary mobility.

There is some evidence, such as that shown in figure 5.13c, that the orientation dependence of mobility disappears not only at high purities, but also at lower purity levels. Experiments on zinc (Sursaeva et al. 1976, Gottstein and Shvindlerman 1992), demonstrate a similar effect, which indicates that the window within which orientation dependence of mobility is found, may be determined by both the boundary structure and the purity level as shown schematically in figure 5.22.
The evidence for the disappearance of the orientation dependence of boundary mobility at lower purities is not conclusive, and, as discussed by Haessner and Hoffmann (1978), the results of Fridman et al. (1975) for the lowest purity material in figure 5.13c contradict those of Demianczuc and Aust (1975) who found an orientation dependence of mobility in aluminium of similar purity. In addition, much of the evidence for the orientation dependence of mobility in aluminium (Liebmann et al. 1956, Yoshida et al. 1959) was obtained in material of much lower purity. The effect of solutes on the orientation dependence of migration warrants further investigation.

Gordon and Vandermeer (1966) and Gottstein and Shvindlerman (1992) speculate that with lower impurity levels than have yet been achieved, it is conceivable that random grain boundaries would move more easily than special boundaries because the lower energy of the special boundaries would provide a greater barrier to the transitory structure modification required when a boundary moves. However, this argument does not take account of the possibility discussed in §5.4.1 that special boundaries in high purity materials may move by a low energy mechanism involving atomic shuffles, a mechanism which would not be available to random boundaries.

5.3.3.4 The effects of temperature and orientation
There is evidence that in copper (Aust et al. 1963) and lead (Rutter and Aust 1965), the higher mobility of special boundaries in materials of moderate purity may disappear at high temperatures as shown in figure 5.23. This may be due to the evaporation of the solute atmosphere at boundaries at high temperatures (§5.4.2).

5.3.4 The effect of point defects on boundary mobility
The interaction of vacancies and other point defects with static high angle grain boundaries has been extensively investigated (e.g. Ballufí 1980), and it has been shown

Fig. 5.22. Schematic diagram showing the dependence of the activation energy of grain boundary mobility for different purity levels, (after Gottstein and Shvindlerman 1992).
that boundaries may act as sources and sinks for point defects and that point defects interact with grain boundary dislocations. The effect of point defects on a migrating boundary is less clear, although there is evidence (Hillert and Purdy 1978, Smidoda et al. 1978) that the diffusion coefficient of a moving boundary is several orders of magnitude larger than that of a stationary boundary.

5.3.4.1 The effect of vacancies on boundary mobility
The role of defects on boundary mobility has been extensively discussed e.g. Cahn (1983), Gleiter and Chalmers (1972), Haessner and Hofmann (1978). Although these reviewers are in general agreement that a vacancy flux or supersaturation enhances boundary mobility, the experimental evidence for this is not extensive. Evidence which indicates that vacancies enhance migration was obtained by Haessner and Holzer (1974), who showed that neutron irradiation increased the boundary velocity in recrystallizing copper single crystals as shown in figure 5.24. In this material the irradiation produces Frank vacancy loops, and although this increases the driving force for recrystallization, the authors claim that calorimetric measurements showed that this effect was negligible and that the vacancy loops increased the boundary mobility. Support for this is provided by the work of Atwater et al. (1988), who attributed increased grain growth rates in ion-bombarded thin films of gold, germanium and silicon to the effect of the point defects on boundary mobility.
Other indirect evidence indicating that vacancies affect boundary mobility comes from the sintering of copper wires, when the presence of pores on a boundary is found to increase its mobility (Alexander and Balluffi 1957), and from the sintering of alumina, when small pores are found to be consumed by slowly migrating boundaries (Coble and Burke 1963).

The basic concept that the vacancies swept up by a moving boundary will increase the free volume of the boundary and therefore aid atom movement across the boundary is plausible (Gordon and Vandermeer 1966), but has not been backed by rigorous theory. Such a model implies that the structure of static and moving boundaries will be different and also suggests that boundary structure and hence mobility may be dependent on boundary velocity. This problem is most likely to be resolved ultimately by dynamic computer simulations of boundary migration.

It may be difficult to separate the effects of vacancies on the boundary mobility and on the driving pressure for boundary migration. Estrin et al. (1999, 2000) have discussed the thermodynamic effects of vacancies during grain growth. During grain growth, the boundary area per unit volume decreases, and the consequent elimination of the excess free volume associated with the boundaries will lead to injection of vacancies into the grains. As this increases the energy of the grains, there will therefore be a reduction in the driving pressure for grain growth. This effect is only likely to be important for very fine-grained materials, but is predicted to have a significant influence on the stability of nanocrystalline materials against grain growth. This is a similar argument to that advanced for a solute-limited grain size (§11.4.2.5).

5.3.4.2 Generation of defects by moving boundaries
A moving boundary may act as a source of defects, and there is evidence (Gleiter 1980) that in material of low dislocation density, a higher dislocation density may be left behind a migrating boundary. This is attributed to the formation of dislocations by
growth accidents rather than to the emission of dislocations by stress relaxation at the boundary. Gleiter suggests that in a similar manner, growth accidents will lead to vacancies being left behind a moving boundary, and cites experimental evidence of a vacancy supersaturation behind moving boundaries in aluminium and nickel alloys.

5.3.5 The scope of experimental measurements

It should be emphasised that for a number of reasons we cannot confidently draw general conclusions about the mobility of high angle grain boundaries during recrystallization.

- It is extremely difficult to carry out reliable experimental investigations of boundary mobility.
- There are a large number of variables to be investigated including solvent, solute, concentration, misorientation, boundary plane, temperature and driving force, and therefore there have been few systematic investigations.
- The most detailed systematic investigations have been carried out by curvature driven grain growth, with driving pressures which are a significantly lower than those found in recrystallization, at very high temperatures, and on special boundaries.

5.4 THEORIES OF THE MOBILITY OF HIGH ANGLE GRAIN BOUNDARIES

In this section we examine the extent to which the migration of high angle boundaries in pure and solute-containing alloys can be accounted for theoretically. This subject is discussed in more detail in the recent books by Sutton and Balluffi (1995) and Gottstein and Shvindlerman (1999).

5.4.1 Theories of grain boundary migration in pure metals

A schematic diagram of a grain boundary is shown in figure 5.25a. Models of grain boundary migration are generally based on the assumption that atoms are continually detached from the grains (e.g. A and B) by thermal activation and move into the more disordered region of the boundary itself (e.g. C), which is shown exaggerated in figure 5.25a. The atoms are then re-attached to one of the grains. If the atom flux in both directions is equal then the boundary is static. However, if there is a driving force for migration then the flux will be greater in one direction. There are several proposed variants on this general model, the main variables being:

Single or group activation. Migration may occur either by the activation of single atoms or by the collective movement of a group of atoms.

The role of atoms in the boundary region. Atoms detached from a parent grain are either immediately reattached to a grain or may remain or move in the boundary region.

Preferential sites. If the crystallography of the boundary is taken into account then there may be preferential sites for detachment and attachment of atoms.
5.4.1.1 Thermally activated boundary migration – early single-process models

The theory of boundary migration based on reaction rate theory, in which boundary movement is controlled by single atom movements, was proposed by Turnbull (1951), and in this section we use this type of approach to illustrate the nature of the problem. Consider the boundary of figure 5.25a, which is considered to have a thickness $\delta$, moving to the left under the influence of a free energy difference of $\Delta G$. In order for an atom to break away from its parent grain it must acquire, by thermal activation, an activation energy of $\Delta G^a$ as shown in figure 5.25b. If the frequency of atomic vibration is $v_0$, then the number of times per second that the atom acquires this energy is $v_0 \exp(-\Delta G^a/kT)$. If there are $n$ atoms per unit area of boundary which are suitable sites for a jump, then the number of jumps per second from a grain is $nv_0 \exp(-\Delta G^a/kT)$. However, they will not all be in favourable positions to jump, and therefore we include a grain boundary structure dependent factor $A_J$, which is the fraction of atoms able to jump. As not all atoms may find a suitable site for attachment to the other grain, then we introduce an accommodation factor $A_A$, which is the fraction of successful attachments. The effective flux of atoms from grain 1 to grain 2 will thus be

$$A_J A_A n v_0 \exp\left(-\frac{\Delta G^a}{kT}\right)$$

In the same manner, there will be a flux of atoms from grain 2 to grain 1, given by

$$A_J A_A n v_0 \exp\left(-\frac{\Delta G^a + \Delta G}{kT}\right)$$

There will therefore be a net flux from grain 1 to grain 2 of

$$J = A_J A_A n v_0 \exp\left(-\frac{\Delta G^a}{kT}\right)\left(1 - \exp\left(-\frac{\Delta G}{kT}\right)\right)$$  \hspace{1cm} (5.13)

Fig. 5.25. Grain boundary migration by means of atom jumps. (a) The mechanism of migration, (b) The free energy of an atom during a jump across the boundary.
If the boundary velocity is $v$, and the interatomic spacing is $b$, then,

$$v = \frac{J}{n} b = A_J A_A v_0 b \exp\left(\frac{-\Delta G^a}{kT}\right)\left(1 - \exp\left(\frac{-\Delta G}{kT}\right)\right)$$  \hfill (5.14)

As the free energy changes during recrystallization are small, we may assume that $\Delta G \ll kT$ and expand $\exp(-\Delta G/kT)$ giving

$$v = A_J A_A v_0 b \exp\left(\frac{-\Delta G^a}{kT}\right)\frac{\Delta G}{kT}$$  \hfill (5.15)

As the driving pressure $P = \Delta G$ then

$$v = A_J A_A v_0 b \exp\left(\frac{-\Delta G^a}{kT}\right)\frac{P}{kT}$$  \hfill (5.16)

and substituting $\Delta G = \Delta H - T\Delta S$ then

$$v = A_J A_A v_0 b \exp\left(\frac{-\Delta H^a}{kT}\right)\exp\left(\frac{\Delta S}{k}\right)\frac{P}{kT}$$  \hfill (5.17)

Equation 5.17 is therefore identical in form to equation 5.1 with

$$M = \frac{A_J A_A v_0 b}{kT} \exp\left(\frac{-\Delta H^a}{kT}\right)\exp\left(\frac{\Delta S}{k}\right)$$  \hfill (5.18)

The model discussed above is very general and not specific enough to allow prediction of the parameters such as the activation energy ($\Delta H^a$). For example, although the activated process is often identified with grain boundary diffusion, in this model the atoms move **across** the boundary rather than **within** it and the two processes are not necessarily identical. Also, a better defined basis for the parameters $A_J$ and $A_A$ needs to be developed. These problems, and the question of whether atoms migrate within the boundary region have been addressed more specifically in later theories which take account of the boundary structure and which attempt to relate the mobility to movements in grain boundary defects such as **steps** or **dislocations** as discussed below.

### 5.4.1.2 Early group-process theories

In the earliest group-process theory by Mott (1948), groups (islands) of atoms move from one grain into the boundary region and similar groups attach themselves to the other grain. Later developments of this type of model are reviewed by Gleiter and Chalmers (1972). The attractiveness of such models was that because groups of atoms were thermally activated, this required a much larger activation energy than that for a single atom (equation 5.18), which was at that time in accord with experimental observations. However, when it was later shown that such large activation energies were due to impurities (§5.3.3), and were not characteristic of boundaries in pure materials (table 5.2), attention switched to single-process theories. As discussed below, there is now some evidence that cooperative atomic movements are important in boundary...
5.4.1.3 Step models

An early attempt to incorporate the effects of boundary structure into a model for boundary mobility was made by Gleiter (1969b) who proposed a detailed atomistic model in which boundary migration occurred by the movement of steps or kinks in the boundary as shown in figure 5.26. Evidence for the existence of such steps had been found from transmission electron microscopy (Gleiter 1969a). The steps move by the addition or removal of atoms from the steps, and the atoms are assumed to diffuse for short distances within the grain boundary. This is an analogous process to that occurring during the growth of crystals from a vapour, and interface migration by ledge movement is a well established mechanism for the movement of interphase boundaries during phase transformations (Aaronson et al. 1962).

For driving pressures of the magnitude encountered during annealing, Gleiter calculates the boundary velocity to be

\[ v = b v_0 \Psi \exp \left( \frac{\Delta G^a}{kT} \right) \frac{P}{kT} \]  

(5.19)

This is similar to equation 5.15, but modified by a factor \( \Psi \) which is a function containing details of the step configuration in a boundary of thickness \( \delta \), and which is of the form

\[ \Psi = \frac{c}{\delta} \left( 1 + \frac{b}{\delta} \left( \frac{1}{f_1} - \frac{1}{f_2} \right) \right) \]  

(5.20)

where \( c \) is a constant and \( f_1 \) and \( f_2 \) are functions of the step density on the crystals either side of the boundary. The mobility of the boundary is predicted to be dependent on both the misorientation and the boundary plane through the terms \( f_1 \) and \( f_2 \). For example for the case of crystals rotated about a \(<111>\) axis in fcc metals, the ledge density and hence the mobility is predicted to be lowest for the \{111\} twist boundaries as is found in practice (§5.3.2.2).

Fig. 5.26. The ledge mechanism of boundary migration. An atom is detached from a kink in the ledge, migrates along the ledge and into the boundary, (after Gleiter 1969b).

migration of pure materials and newer versions of group-process models are currently being developed.
5.4.1.4 Boundary Defect Models

An improvement in the understanding of the defect structure of high angle grain boundaries, and recognition that steps and intrinsic boundary dislocations are common features, has led to experimental and theoretical investigations into the role of these defects in the processes of boundary migration. There is a very close relationship between boundary steps and boundary dislocations, and in general, boundary dislocations have steps in their cores (King and Smith 1980). The example shown in figure 5.27 is of a $1/10<310>$ dislocation in a boundary close to $\Sigma 5$ in an fcc material. The height of these steps depends on the Burgers vector of the dislocation, the boundary plane and the crystallography of the boundary. When such dislocations move, then the steps move and boundary migration inevitably occurs. There is extensive evidence that boundary dislocations move and multiply and that they retain their core structure at elevated temperatures (e.g. Dingley and Pond 1979, Rae 1981, Smith 1992).

In special cases, the dislocations can glide in the boundary plane and therefore athermal boundary migration is possible. A well known example of this is the case of $1/6<112>$ twinning dislocations in fcc materials. These dislocations move by glide on the \{111\} planes and the twin plane advances by one \{111\} planar spacing for the passage of each dislocation. In the more general case, the dislocation cannot glide in the boundary and a combined glide/climb movement of the boundary dislocations is required.
If boundary movement is accomplished by the collective movement of a density $\rho$ of boundary defects each moving at velocity $v$ and having a step height $h$, then the boundary velocity ($v_b$) will be given (Smith 1992) by an expression of the form

$$v_b = h\rho v$$  
(5.21)

Glide of boundary dislocations is of course associated with shear deformation and the process of boundary dislocation motion results in a combined migration and sliding of the boundary. Such a combined process has been modelled by Bishop et al. (1980) and has been observed in zinc bicrystals by Ando et al. (1990), and on near $\Sigma 5$ boundaries in gold bicrystals by Babcock and Balluffi (1989a), who found good correlation between the movement of boundary dislocations and the migration and sliding of a boundary under stress. It should however be noted that such dislocation motion results in a shape change, which if not relaxed can exert a back-stress such as to cancel out the driving pressure for boundary migration (Smith et al. 1980). This suggests that the behaviour of unconstrained bicrystals may be different from that of the constrained polycrystals which are of more general importance in recrystallization and grain growth (cf. §5.2.1).

Further experiments of Babcock and Balluffi (1989b) in which the boundaries migrated under the influence of capillary forces at high temperature showed quite different behaviour. The boundaries migrated in a jerky fashion and the movement of boundary dislocations was found to account only for a negligible part of the boundary migration, particularly for more general boundaries. Whether or not such jerky boundary migration is genuine or is an artefact of the experiment is not yet clear, although similar behaviour has been found by a number of workers. On the basis of their experiments and from computer simulations (Majid and Bristowe 1987) and Babcock and Balluffi (1989b) have interpreted these experiments in terms of local cooperative shuffling of atoms in a process similar to that proposed by Bauer and Laxner (1986). This mechanism is shown schematically for a $\Sigma 5 <001>$ twist boundary in figure 5.28.

Fig. 5.28. Proposed mechanism of migration of $\Sigma 5 [001]$ twist boundary by atomic shuffling. (a) View along [001] showing first planes of crystal 1 (O) and crystal 2 (+) facing the boundary. Vectors show the atomic shuffles of atoms in crystal 1 required to displace the boundary by $a/2$ and produce the square boundary ledge shown obliquely in (b), (after Babcock and Balluffi 1989b).
Babcock and Balluffi (1989b) argue that this is a more important mechanism of boundary migration than is the movement of boundary dislocations. However, the number of atoms which must move in a coordinated manner in such a shuffle is large for high order CSLs, and therefore this type of mechanism is only likely to be effective in a highly ordered boundary and not in a general boundary.

5.4.1.5 The status of boundary migration models
Theoretical and experimental work in recent years has largely concentrated on the behaviour of low $\Sigma$ boundaries, and in particular on symmetrical tilt boundaries in materials of very high purity. As such simple boundaries are not typical of more general boundaries, this has probably led to an over-emphasis on the importance of boundary structure and defects in interpreting the migration of boundaries as was concluded by Smith (1992).

Although the movement of steps or boundary dislocations certainly occurs, and can explain some properties of some boundaries, the important process in the more general case appears to be the thermally activated transport of atoms across boundaries and the migration would seem to be controlled by the activation energy for this process. Apart from special cases, there is no good evidence that the sites of attachment and detachment have any significant effect.

It has long been recognised that in general boundaries the local excess volume or porosity of the boundary is a very important parameter which may determine not only the energy of the boundary (§4.4.2), but also the migration behaviour (Seeger and Haasen 1956, Gordon and Vandermeer 1966), and that except for low $\Sigma$ boundaries, this is likely to be more important than the atomistic details of the boundary structure. The concept of excess boundary volume can explain a number of important factors which are related to the boundary crystallography, including the higher mobility of tilt boundaries than twist boundaries (§5.3.2.2) and the relative effect of solutes on general and special boundaries (§5.3.3).

5.4.2 Theories of grain boundary migration in solid solutions
Most theories of the effects of solutes on boundary mobility are based on that proposed by Lücke and Detert (1957) for dilute solid solutions. The theory was further developed independently by Cahn (1962) and by Lücke and Stüwe (1963), and later extended to include higher solute contents by Lücke and Stüwe (1971).

There are several other earlier theories which are reviewed by Lücke and Stüwe (1963), Gordon and Vandermeer (1966) and Gleiter and Chalmers (1972) and there have been several later models, notably those proposed by Bauer (1974) and by Hillert and Sundman (1976) and Hillert (1979) who extended the theory to include high solute contents. However, the Cahn–Lücke–Stüwe (CLS) model is still widely accepted as giving a good semi-quantitative account of the effects of solute on boundary migration, and this is the basis for the following discussion.

The CLS theory is based on the concept that atoms in the region of a boundary have a different energy ($U$) to those in the grain interior because of the different local atomic
environment. There is therefore a force \( \frac{dU}{dx} \) between the boundary and a solute atom which may be positive or negative, depending on the specific solute and solvent. The total force from the boundary on all solute atoms is \( P = \sum \frac{dU}{dx} \), and an equal and opposite force is exerted by the solute atoms on the boundary. The result of this interaction is an excess or deficit of solute (an atmosphere) in the vicinity of the boundary, and the solute concentration \( c \) is given by

\[
c = c_0 \exp\left(-\frac{U}{kT}\right)
\]

(5.22)

where \( c_0 \) is the equilibrium solute concentration.

For a stationary boundary and a solute which is attracted to the boundary, the interaction energy \( U \), force \( F \), solute concentration \( c \) and diffusion coefficient \( D \) are shown in figure 5.29 as a function of distance \( x \) from the boundary.

The extent to which an element segregates to a stationary boundary is usually related to its solubility, and as a general rule the tendency for segregation increases as the solubility decreases as is shown in figure 5.30. It is therefore to be expected that the force exerted by solute atoms on a boundary, which is a function of the solute concentration in the boundary and solute diffusivity, will depend strongly on the specific solute and solvent combination.

![Schematic diagrams of the interaction of solute with a boundary. (a) The potential U(x), (b) The interaction force F(x) between a solute atom and the boundary, (c) The resulting distribution of solute atoms for a stationary boundary (full line) and a boundary moving from left to right (dotted line), (d) Diffusivity in the boundary region D(x).](image-url)
If moving boundaries have a larger free volume than stationary boundaries (§5.3.4), then it is to be expected that solubility in a moving boundary will be greater than in a static boundary. There is some indirect evidence for this from a study of Pb–Au alloys by Simpson et al. (1970) who found that precipitation occurred at grain boundaries in specimens undergoing grain growth which were quenched and aged, whereas this effect was not found in material with stationary boundaries.

### 5.4.2.1 Low boundary velocities

For a moving boundary, the solute profile becomes asymmetric as shown in figure 5.29c such that the centre of gravity of the distribution lags behind the boundary.

For the case illustrated in figure 5.29c, where the boundary is moving from left to right, there is therefore a net force due to the solute, dragging the boundary to the left. As the boundary velocity increases, the solute lags further behind the boundary.

The relationship between the driving pressure (P) and boundary velocity (v) at low velocities is found to be

\[
P = \frac{v}{M} + \alpha c_0 v \tag{5.23}
\]
where $M$ is the mobility of the boundary in the absence of solute, and $\alpha$ is a constant which depends on the details of the model.

It may be seen from equation 5.23 that the velocity is predicted to be inversely proportional to the solute concentration ($c_0$). The apparent activation energy for boundary migration will be the mean value for solute diffusion in the boundary region, which will depend both on the value of $U$ and the assumed $U$-x and $D$-x profiles (fig. 5.29). Hillert (1979) has shown that the choice of these parameters has a large effect on the results. For example, the CLS model assumed a wedge shaped energy-well rather than that shown in figure 5.29a, and it also assumed that diffusivity is constant throughout the material. It should be emphasised that this theory is limited to dilute solid solutions ($c_0 < 0.1\%$). Hillert (1979) calculated the boundary mobility using a model which allows the boundary diffusivity to differ from that of the bulk and found that the maximum value of the solute drag was much smaller than predicted by equation 5.23 if an increased boundary diffusivity was assumed.

5.4.2.2 High boundary velocities

The relationship between boundary velocity and driving pressure at intermediate velocities is very difficult to calculate as it depends critically on the details and parameters of the model. However a limiting case is reached at high boundary velocities when the solute atoms can no longer keep up with the boundary, which then breaks away from its atmosphere. In this case

$$P = \frac{v}{M} + \frac{c_0}{\alpha'v}$$

(5.24)

where $\alpha'$ is a constant.

It is estimated that the first term is dominant and therefore the solute atoms have only a small effect. The mobility and activation energy are then expected to be similar to the intrinsic values for a boundary in a pure metal (§5.3.1).

Equations 5.23 and 5.24 are combined by Cahn (1962) and Lücke and Stüwe (1963) to give

$$P = \frac{v}{M} + \frac{\alpha c_0 v}{1 + \alpha' v}$$

(5.25)

5.4.2.3 Predictions of the model

This model predicts that the retarding force due to solute drag varies with boundary velocity, reaching a maximum value as shown in figure 5.31. This figure also shows that the solute drag becomes less effective at high temperatures, and this is because under these conditions the solute concentration near the grain boundary decreases in accord with equation 5.22, so that the atmosphere effectively evaporates.

Although, for the reasons discussed above, it is difficult to fully quantify the CLS model, it is of interest to look at the qualitative predictions regarding the relationships
between driving pressure, solute concentration and temperature and boundary velocity, as shown schematically in figure 5.32. In figure 5.32a the effect of three levels of solute content on the relationship between velocity and driving pressure is shown and compared with the behaviour of the pure material in which the velocity is proportional to the driving pressure (equation 5.1). It may be seen that for very low solute concentrations the curve is continuous, and deviates only slightly from that predicted for the pure material. However, for high solute concentrations, the curve is S-shaped and predicts a discontinuous change of velocity (dotted lines) from the lower branch (equation 5.23) and the upper branch (equation 5.19). In figure 5.32b, the boundary velocity is plotted as a function of temperature for the cases of low solute A, high solute B and no solute C. The slope of the plot of ln(\(v\)) vs 1/\(T\) may be interpreted in terms of an apparent activation energy. The straight lines D and E superimposed on A and B, represent the limiting cases for low velocity as given by equation 5.23.

5.4.2.4 Correlation of experiment and theory

Although the experimental data are very limited and the theories cannot as yet be fully quantified, it appears that many features of the experimental results can be qualitatively explained in terms of the CLS model.

- **At low velocities the velocity is inversely proportional to the solute concentration**

This result, which is predicted by equation 5.23, is consistent with the experimental results shown in figure 5.17.

- **At higher driving forces or lower solute concentrations, there is a transition to a high velocity regime in which the boundary velocity is independent of solute content**

This is clearly shown in the results of figures 5.17 and 5.19.
The apparent activation energy will decrease as the temperature increases.

This result, which is predicted by the model as shown in figure 5.32b, is in accord with many of the experimental results discussed in §5.3.3. The model predicts that at low boundary velocity, the mobility is controlled by solute diffusion and therefore an activation energy appropriate for this process is expected. Figure 5.32b predicts that in moving from the low to high velocity regimes, the apparent activation energy should exhibit a peak. The data shown in figures 5.17, 5.19 and 5.20 are consistent with this. In some cases, e.g. figure 5.17, the activation energy in the low velocity regime is a function of solute content. This may be due to the effect of solute on the boundary free volume and hence on the activation energy for solute diffusion. The model predicts (fig. 5.32b) that in the high velocity regime, the activation energy for boundary migration should be similar to that for high purity material. The experimental results show that this is often the case.

The nature of the transition depends on the solute concentration and driving force

Figure 5.32b shows that the nature of the velocity transition with increasing temperature is predicted to be gradual for low solute concentrations and sharp for higher concentrations. There is evidence that both gradual (figs. 5.19 and 5.20) and discontinuous transitions (fig. 5.17) can occur, although a change in the nature of the transition as a function of solute content has not yet been demonstrated in a single investigation.

The effect of solute is less at higher temperatures

Equation 5.22 shows that at higher temperatures the solute atmosphere will be much weaker. The results shown in figure 5.23 are in agreement with this.
5.4.2.5 Development of the theory

Although the CLS model appears to be in reasonable qualitative agreement with many of the experimental results, it is generally agreed that it cannot make realistic quantitative predictions. The CLS approach is based on the segregation of impurities to grain boundaries, and the activation energy for migration, is predicted to be dependent on the solute and solvent, but independent of the solute concentration. However, recent experiments have shown the activation energy to increase significantly with the addition of small solute concentrations to high purity aluminium, (Molodov et al. 1998), and these authors have suggested that this is due to an interaction between the solute atoms at the boundary. Taking this into account by applying the Bragg-Williams theory of regular solutions, they showed that the boundary migration enthalpy includes the enthalpy of impurity migration, the adsorption energy of solutes in the boundary and the energy of interaction between adsorbed atoms, and that the theory gives a better account of the experimental results.

There are a number of other factors which will need to be incorporated into quantitative theories of grain boundary migration in solute-containing alloys. These include the effect of solutes on boundary structure, energy and diffusivity and the interaction of solutes and boundary crystallography.

5.5 THE MIGRATION OF TRIPLE JUNCTIONS

5.5.1 Introduction

This chapter has been concerned with the migration and mobility of grain boundaries. However, in a 3-D polycrystal (or a subgrain structure), the grains are joined not only at boundaries, but also at triple junction lines (§4.5) and quadruple junction points. The triple junctions are defects which will have particular atomic structures and energies (Palumbo and Aust 1992, King 1999).

Galina et al. (1987) first suggested that triple junctions might have a finite mobility and that under some circumstances this, rather than the boundary mobility might limit the rate of growth of a grain assembly. It is postulated that by analogy with equation 5.1, the triple junction velocity \( v_{TJ} \) is proportional to the driving pressure \( P_{TJ} \) and the mobility \( M_{TJ} \)

\[
v_{TJ} = M_{TJ} P_{TJ} \quad (5.26)
\]

The mobilities of the triple junctions can only be accurately measured experimentally for a very limited set of geometrical configurations and have been reported for 99.999% zinc (Czubayco et al. 1998), and 99.999% aluminium (Protasova et al. 2001) in tri-crystals containing symmetrical tilt boundaries.

It is found that the temperature dependence of boundary and triple junction mobilities is markedly different as shown in figure 5.33, with the activation energy for triple junction migration being approximately twice that for self diffusion.
Molecular dynamic simulations (Upmanyu et al. 2002) and 2-D vertex models (Weygand et al. 1998a) are in general agreement with the limited experimental data, and it is significant that the molecular dynamic simulations indicate that the mobility of a triple junction depends also on its direction of motion.

5.5.2 The importance of triple junction mobility

Both experiments and simulations show that triple junction mobility is finite and may be sufficiently small to limit the rate of grain boundary migration. In such circumstances, the usual assumption that the rate of subgrain (§6.5) or grain (§11.1) growth is controlled by boundary mobility would be incorrect. The effects of finite triple junction mobility on the grain growth of a polycrystal have been examined theoretically (Gottstein et al. 2000) and by computer simulation (Weygand et al. 1999), and the main conclusions are that when triple junction drag is significant,

- The isothermal grain growth kinetics are similar to those for boundary control, i.e. $R \propto t^{1/2}$ (§11.1)
- The scaling behaviour for grain size distribution (§11.1.1) disappears
- The von Neumann-Mullins law (§11.1.5) is no longer valid

Because of the limited data available, it is difficult to ascertain the conditions under which triple junction drag will be a significant factor in grain growth, but it is expected that this will be for small grain sizes, low temperatures and near high symmetry misorientations. The simulations (Upmanu et al. 2002) suggest that triple junction drag may only be significant in materials of grain size up to ~50 interatomic spacing, and therefore important only for nanocrystalline materials. The large differences in the activation energies for boundary and triple junction migration

Fig. 5.33. Temperature dependence of triple junction (●) and grain boundary (▲) mobilities in 99.999%Al, (Protasova et al. 2001).
(figure 5.33) should enable the controlling mechanism to be identified from measurements of the temperature dependence of the grain growth kinetics of polycrystals.

Although there is currently little data available for materials of very small grain sizes, the measured activation energies for both grain growth and subgrain growth (5.2.2.1) are typically close to those for self diffusion, corresponding to control by boundary rather than triple junction migration. The grain growth kinetics of an Al–Mg alloy (fig. 14.12), measured over a large range of sizes, appear to be similar at both small (<0.5 μm) and large grain sizes (Hayes et al. 2002), suggesting that a common mechanism operates.