

# Grain-boundary migration in single-phase and particle-containing materials

EVAN GRANT, ANGUS PORTER\*, BRIAN RALPH†

*Department of Metallurgy and Materials Science, University of Cambridge, UK*

---

An understanding of the detailed mechanisms which control the migration of grain boundaries through multiphase materials is limited. In this article, the forces which may cause grain-boundary migration (such as those due to recrystallization, grain growth and a redistribution of chemical species) together with effects which oppose this motion (such as solute drag and particle pinning) are reviewed. Theories of grain-boundary migration are presented and, in particular, the influence of grain-boundary structure on these models is discussed. It is shown that experimental studies of grain-boundary migration in bicrystals offer the best opportunity of relating migration mechanisms to the grain-boundary structure. In the light of this an attempt is made to develop an experimental approach by which the interaction of a migrating boundary with a dispersion of particles might be studied.

---

## 1. Introduction

Grain-boundary migration can be defined as the movement of a grain boundary perpendicular to its tangent plane, and it occurs when the boundary is subjected to a force large enough to cause its motion. The movement results in a reduction of free energy. The driving force can take many forms, but technologically the most significant are the removal of the stored energy of deformation (as in primary recrystallization), the reduction of grain-boundary area (as in grain growth), and the removal of excess chemical free energy (as, for example, in discontinuous precipitation). Owing to the vast technological importance of these, and related processes, and to the rich fundamental interest in them, the characterization of the structure and properties of migrating grain boundaries has been the subject of intensive research (e.g. [1-12]).

Given this importance, and the effort put into the field, there is a remarkable degree of ignorance about the fundamental processes which occur when a grain boundary migrates. This serves to highlight the difficulty of the problem: the

processes of interest are atomistic, and, in most cases, they occur at well above ambient temperature. The situation is further complicated by the fact that impurities at concentrations of the order of parts per million are sufficient to alter drastically the properties of migrating grain boundaries (e.g. [13]). A clear picture of the structure of a migrating grain boundary has yet to emerge; the limitations are largely imposed by the available experimental techniques, and the principal advances in the theoretical understanding of grain-boundary phenomena have coincided with development of improved techniques.

One unquestionable observation is that grain boundaries are able to migrate with widely varying velocities. For instance, it is known that low-angle grain boundaries migrate much more slowly than do all high-angle boundaries except coherent twins (e.g. [14]). In this paper we concern ourselves with the migration of high-angle boundaries and before this migration can be fully understood and predicted, it is necessary to characterize how the boundary migrates in different conditions. Explicitly, it is necessary to determine how the

\*Present address: Plessey Research (Caswell) Ltd, Towcester, UK.

†Present address: Department of Metallurgy and Materials Science, University College, Cardiff, Wales, UK.

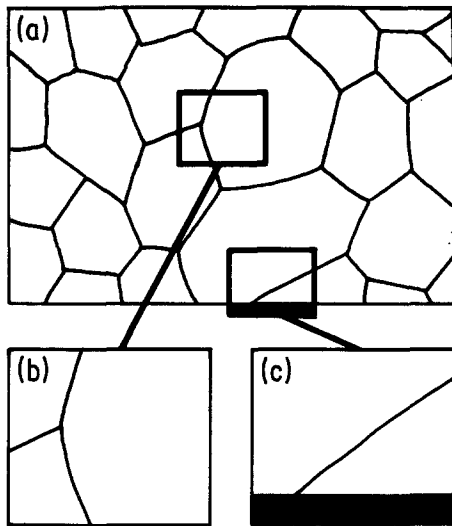


Figure 1 (a) "Average" data concerning grain-boundary migration can be obtained from polycrystalline samples. (b) Such specimens can also be used to study the behaviour of single boundaries in the presence of others. (c) Bicrystals cut from coarse-grained polycrystals allow the examination of isolated single boundaries.

boundary velocity depends on driving force, temperature, material composition and boundary crystallography (e.g. [15]).

No single experimental approach has proved universally applicable to the study of grain-boundary migration in all circumstances. Each method, however attractive in some ways, has its disadvantages in others. Many different classifications of these methods are possible, but generally the distinction is drawn between experiments revealing data related either to a specific single boundary or to "average" boundary behaviour. This distinction is emphasized in Fig. 1.

The ultimate aim of this article is to consider how the presence of particles in an alloy modifies the migration process and, indeed, how the particles and migrating interface interact. To understand interactions (Section 6) it is first necessary to review the forces acting on a migrating boundary in a single-phase system, what is known about the migration process and the structure of the migrating interface. An attempt is made to develop an approach which would lead to an ideal experimental study of the interaction between a migrating grain boundary and a dispersion of particles. This ideal experiment would involve knowing all the geometrical parameters describing the boundary, since it is known that

these parameters affect the structure and hence the properties of the boundary. Thus in this paper, whilst data relevant to the "average" boundary referred to above are discussed, a considerable stress is given to experimental techniques which involve the migration of well-characterized boundaries, for instance in bicrystal experiments.

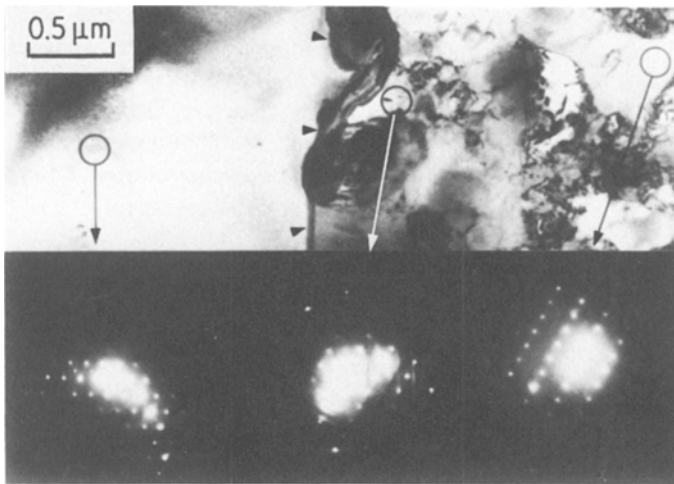
## 2. Driving forces for grain-boundary migration

There are two distinct ways of causing a boundary to migrate. If a difference in free energy per unit volume exists between adjoining grains, there will be a pressure on the boundary between them to move away from the lower energy grain into the higher energy one; an example is recrystallization. Alternatively, if a gradient of any quantity on which the total grain-boundary energy depends can be established, there will be a driving force for boundaries to move and so reduce the total energy. Grain growth is an example of this situation. The nature of the driving force largely determines the scope of the experiments possible, and in the following sections the quantities which can be used to create a driving force for migration, and the ways in which they can be exploited experimentally, will be considered.

### 2.1. Primary recrystallization

In these experiments the driving force is generated by the difference in the density of dislocations and other defects across the boundary. To follow the migration of these grain boundaries some property which can be related to the recrystallized fraction is measured. The difficulty then is calculating the recrystallized fraction from the property measured and relating this fraction to some mean boundary velocity. To extract details about the velocity, it is necessary to make assumptions about the three-dimensional grain structure, based on some model, on empirical observations, or, preferably, on a combination of these (e.g. [16]).

The principal advantage of recrystallization is the high driving force available. For a typical case the driving pressure is of the order of  $10^7$  to  $10^8$  Pa. Moreover, by controlling the amount of prior deformation, the driving force can be controlled within limits. The upper limit is determined by the maximum amount of energy that can be stored in the worked state and corresponds to the driving pressure given above. The lower limit is dependent on the minimum amount of deformation required



*Figure 2* Microdiffraction patterns obtained from a partially recrystallized sample of a nickel-base superalloy (recrystallization interface arrowed). The zone axis of (a) is near  $\langle 110 \rangle$ ; of (b) and (c) near  $\langle 211 \rangle$ . Diffraction patterns (b) and (c) indicate a lattice rotation in the unrecrystallized material corresponding to a rotation of the beam direction of approximately  $1^\circ \mu\text{m}^{-1}$ .

for recrystallization. The net result is that this method enables work to be done on migrating boundaries in pure materials over the temperature range  $0.25$  to  $0.75 T_m$  ( $T_m$  is the absolute melting temperature of the material). Above this range, recrystallization may occur too fast to reveal any quantitative information about the evolution of the recrystallized fraction.

The stored energy of deformation is, however, inhomogeneous (see e.g. [7]), and the boundary sees local variations in driving force as it migrates. Also, processes of recovery occurring in parallel with recrystallization tend to reduce the total stored energy in an unknown, unquantifiable way, as the experiment proceeds (e.g. [17]). However, it is possible to stabilize the deformed structures against recovery to some extent by doing pre-experiment anneals to effectively bring all recovery processes to completion (e.g. [18, 19]).

In addition to the accumulation of “average” data, it is possible to study the migration rate of a single recrystallization interface within a polycrystalline sample (Fig. 1b) – for example with dynamic experiments in a transmission electron microscope (e.g. [20]). However, in such cases the behaviour of each boundary is likely to be modified by that of adjoining interfaces. Further, the crystallographic parameters describing the misorientation across any recrystallization interface will change as it migrates, due to the lattice curvature associated with the dislocation content of the unrecrystallized grain; this point is illustrated in Fig. 2.

Some control of the boundary crystallography is possible using the methods of Rutter and Aust

[21, 22] who utilized the subgrain structure found in melt-grown single crystals to induce grain-boundary migration. The as-cast crystal contained a uniform, thermally stable network of subgrain boundaries, and the development of a single recrystallization interface permitted the study of a boundary of controllable misorientation, migrating under a constant known driving pressure. The available driving pressure is however low, around  $10^2$  Pa, and this restricts the useful experimental range to temperatures above  $0.8 T_m$ . The small magnitude of the driving force is one disadvantage of this method, and another is the inability to vary the driving force widely. Further, the misorientation between the subgrains means that the precise crystallographic parameters of the migrating boundary change continuously as it moves through the striated crystal.

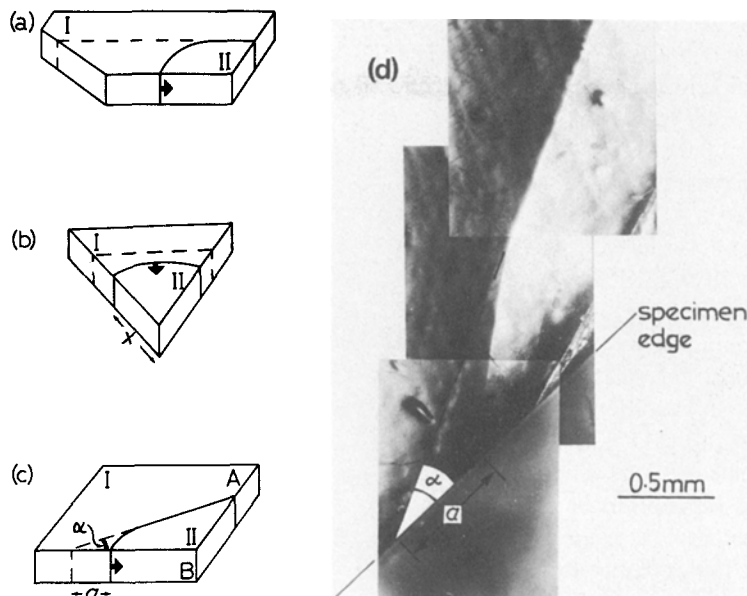
It may be concluded that complete characterization of the behaviour of single boundaries cannot be achieved via recrystallization studies.

## 2.2. Grain growth

The driving force for grain-boundary migration in this case is the reduction in total grain-boundary area. Depending on experimental conditions this pressure can be from  $10^2$  to  $10^5$  Pa.

### 2.2.1. Polycrystals – average properties

In these investigations the mean grain size is determined metallographically at various stages during growth and the rate of change of grain size with time gives the mean boundary velocity (see e.g. [23–25]). The lower driving forces available restrict the useful experimental temperature



**Figure 3** Bicrystal specimen geometries. (a) A constant driving force geometry. (b) Wedge geometry. (c) Reverse capillarity geometry. In all cases the boundary is migrating from grain I into grain II, as indicated; the original boundary position is shown by a dashed line. Other parameters are referred to in the text. (d) An experimental example of geometry (c), in 99.999% pure aluminium, after migration for a distance  $a$ .

range to higher temperatures. They also mean that this type of experiment is more susceptible to the influence of impurities and other drag forces (e.g. thermal grooving) which may alter grain-boundary migration behaviour ([26] and see Section 3).

### 2.2.2. Bicrystals – single boundaries

These experiments provide a method of studying the migration of a single grain boundary of well-characterized crystallography, under the action of a known driving force. The driving force for migration is the reduction of grain-boundary area with displacement, and to exploit this, special bicrystal geometries are required. Considerable ingenuity has been applied to devising various geometries, each of which is suitable for certain types of experiment.

One particular approach is to use evaporated single-crystal thin films which are welded together to form a bicrystal. Much information on the structure of static grain boundaries has been generated from the study of these bicrystals using transmission electron microscopy and X-ray diffraction (e.g. [27, 28]). Further, it is possible to heat these bicrystals *in situ* in the electron microscope and observe the grain-boundary migrate so that it has a lower total area (e.g. [29]).

It is difficult to make kinetic observations this way because of interactions with the surfaces of the welded specimen and it is likely that their presence dominates the effects observed. Furthermore, while the boundary axis and angle of misorientation may remain constant, the boundary plane clearly changes. This difficulty tends to arise with the other methods which are of a more macroscopic nature and are described below.

**2.2.2.1. Constant driving force geometries.** Such bicrystals are suitable for studying the motion of a grain boundary at constant velocity, as, for instance, in comparing mobilities of grain boundaries in alloys with different solute concentrations. To achieve constant driving force the boundary must migrate without changing shape, so that the curvature remains constant. One method that has been employed followed from the original suggestion of Dunn [30] and is illustrated in Fig. 3a. The boundary decelerates until the constant width region of crystal II is reached (cf. Section 2.2.2.3. below) and then migrates under the influence of a constant driving force. A development of this geometry has been used by Shvindlerman and co-workers [31–33] to study grain-boundary migration in aluminium. It is essentially a doubled-up version of the first

geometry discussed, and eliminates some of the problems associated with the free surfaces. The maximum practicable driving pressure with this geometry is of the order of  $10^4$  Pa [34].

**2.2.2.2. Wedge geometry.** Rath and Hu first successfully adopted a wedge technique to study grain-boundary migration in bicrystals, and this is illustrated in Fig. 3b [35]. Previous attempts to utilize this geometry failed because of the inability to produce sufficiently pure material [36] and because unintentional deformation of one of the crystals provided an additional unquantifiable driving force for migration [37].

On initial movement, if the variation of boundary energy,  $\gamma$ , as a function of boundary plane is negligible, the boundary takes up the shape of a cylindrical arc, the radius of curvature being  $x$ , the distance to the apex. The pressure,  $P$ , is given by

$$P = \gamma/x \quad (1)$$

Thus the driving force increases as the boundary approaches the tip of the bicrystal. The study of the variation of mobility with driving force is facilitated. The major disadvantage is the low driving pressure; this may be as low as 10 Pa (see e.g. [38]). Because the boundary is subject to the minimum driving force at the beginning of the experiment, it is unlikely to move at all if there are any pinning forces acting on it. Thus, the method is clearly not suited to the study of migration as a function of drag forces.

**2.2.2.3. Reverse capillarity geometry.** The most commonly used bicrystal geometry, and the one which offers the most flexibility, is the one developed by Sun and Bauer [39, 40] and termed by them the reverse capillarity geometry. The specimen geometry is illustrated in Figs. 3c and d. Sun and Bauer first studied the migration of boundaries in sodium chloride bicrystals [40] and their technique has since been used in studies of migration in cadmium [41, 42], zinc [43], copper [44, 45], aluminium [46–48] and ice [49].

The technique is based on an analysis of two-dimensional grain boundaries made by Mullins [50]. Two simplifying assumptions are made: that the grain-boundary velocity is proportional to the driving force ( $M$ , the boundary mobility, is defined as the constant of proportionality); and that the driving force on a grain boundary at any point is directly proportional to the local curvature. The

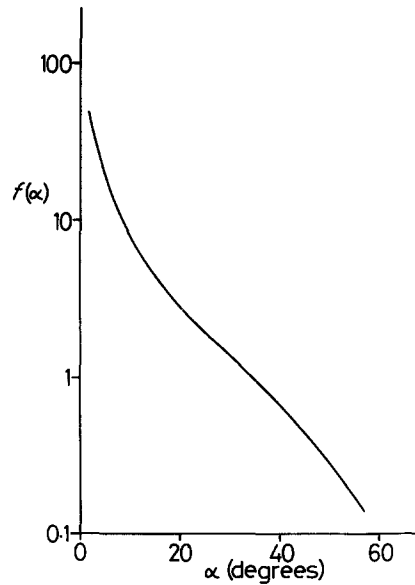


Figure 4 The driving force amplification factor  $f(\alpha)$  associated with the reverse capillarity geometry as a function of  $\alpha$  (see Figs. 3c and d; after Sun and Bauer [39]).

result of the analysis is that a planar grain boundary which meets a free surface at an acute angle will, on annealing, assume a hyperbola-like shape, and will migrate to continually reduce the radius of curvature [39, 50] under a driving pressure given by

$$P = \gamma f(\alpha)/a \quad (2)$$

Sun and Bauer show the equivalence of the migration of the hyperbola-like shape to the expansion of a circular boundary, with the hyperbola-like shape migrating  $f(\alpha)$  times faster, because of its greater curvature. There is unfortunately no analytical solution for  $f(\alpha)$ , but Sun and Bauer [39] have calculated the function numerically, and their result is replotted in Fig. 4.

Assuming that there are no extrinsic drag forces or pinning forces on the boundary and that  $M$  and  $\gamma$  are isotropic, the displacement,  $a$ , after time,  $t$ , is given by the equation

$$a^2 = 2M\gamma f(\alpha)t \quad (3)$$

A parabolic relationship between displacement and time is thus predicted, and has often been observed (e.g. [40, 46]).

A circular-arc shape has sometimes been observed on face A of Fig. 3c [43]. It is possible to allow for this, and the non-perpendicular intersection of the boundary with face B. Also, the fact that the boundary energy is anisotropic

leads to faceting of the boundary in some experiments (e.g. 45, 47]). An analysis of these different shapes is given by Masteller and Bäuer [34].

The most important advantages of this geometry are:

1. high driving forces are available. From Fig. 4 it is clear that  $f(\alpha)$  is large, especially for  $\alpha < 10^\circ$ , and driving pressures as large as  $10^5$  Pa have been obtained;

2. by varying  $\alpha$ , the driving force can be changed easily, and over a large range. This facilitates investigations of the variation of mobility with driving force;

3. the highest driving force is present at the beginning of the experiment, and it decays as the boundary migrates. Migration ceases when the net driving force can no longer overcome the pinning forces. There are two benefits here: for any moderate degree of pinning, some migration will always occur before the boundary is pinned; and the decay of driving force with time is analogous to the situation of grain growth. Thus, this geometry allows the investigation of pinning forces, and promises to be more relevant to grain growth.

Despite all this, the technique does have important limitations; some are common to all bicrystal experiments, others are more specific. It has been consistently emphasized that the bicrystal techniques described provide the only method of measuring the properties of specific grain boundaries. Yet, the nature of the driving force demands that the boundary under investigation be curved, and thus there is no well-defined boundary plane. Furthermore, except in the constant velocity geometries, the curvature changes during the experiment, so the effect of anisotropy is not even a constant over the duration of migration. In common with the vast bulk of work on grain-boundary migration, bicrystal experiments have, in general, been unable to reveal the motion of the boundary, as it moves (work of Hondoh and Higashi [49] with ice is an exception). Most workers have employed multi-anneal techniques to enable the maximum yield of data to be obtained from each bicrystal; the specimen is prepared, heated, cooled, examined metallographically, reheated, etc. The heating/cooling cycle is liable to influence the results, particularly in the presence of solutes, and is a serious limitation on the data obtained.

## 2.3. Other driving forces for grain-boundary migration

### 2.3.1. Chemical forces

In this class the phenomena of discontinuous precipitation and of diffusion-induced grain-boundary migration (DIGM) can be considered: both involve the migration of high-angle grain boundaries under the action of a chemical driving force. In the former a grain boundary migrates through a supersaturated solid solution, or an unstable two-phase alloy, and leaves behind it a two-phase alloy much nearer to equilibrium. In the latter, concentration gradients are removed by the passage of a grain boundary. The common feature is the use of migrating grain boundaries as high diffusivity paths that enable the movement of solute to occur much more quickly than it could if only bulk diffusion were operative (see Section 5). The processes have been considered in detail by Cahn and Balluffi, by Hillert, and by Smith and their respective co-workers (e.g. [51–56]).

The exact magnitude of the driving pressure in discontinuous precipitation is difficult to calculate, but it is large, a value of  $5 \times 10^8$  Pa being quoted in one review [15]. The situation with DIGM is even less clear, but again high driving forces are available [54]. One limitation is that solute must always be present in sufficient quantity to generate the driving force, and so the study of the influence of solute concentration on grain-boundary migration can only be done over a restricted range. With discontinuous precipitation there is the further complication that a phase is being precipitated at the interface, and this must alter the grain-boundary properties in some way. Thus, despite the high driving forces available, there are really too many complicating features for these methods to be suited to primary investigations of grain-boundary mobility. Clearly though, any model of migrating grain boundaries that develops out of other experiments must be capable of explaining these phenomena.

### 2.3.2. Magnetic forces

The existence of magnetocrystalline anisotropy can be exploited to generate a driving force for grain-boundary migration. The method is restricted to materials which have a high degree of anisotropy, and which suffer negligible secondary effects, resulting from magnetostriction and anisotropic thermal expansion, for example. Grain-growth experiments with bismuth in a

magnetic field have been performed [57]. The driving pressure is known and can be controllably varied up to a limit of approximately  $10^3$  Pa. Moreover, there is no absorption of dislocations or other defects, so the driving force does not affect the boundary crystallography.

### 2.3.3. Radiation damage

The defects introduced when a material is subjected to irradiation can also be used to induce grain-boundary migration. The principle is analogous to recrystallization: a high-angle grain boundary can migrate through the damaged crystal leaving strain free material with a much lower defect density behind it.

The nature of the defect structure is very different from that introduced by deformation, with a much higher proportion of vacancies and interstitials. This fact has been exploited to study the effect of vacancies on grain-boundary migration [19]. The unusually high concentration of vacancies ahead of the grain boundary is likely to alter the properties of the grain boundary. Furthermore, as in recrystallization, parallel recovery processes will tend to reduce the stored energy as the experiment goes on, and the driving force is thus not always well known.

### 2.3.4. Other driving forces

1. In the same way that grain-boundary energy depends on the precise boundary parameters, the energy of the interface between a crystal and its environment depends on the interface plane. Grains with low-energy surfaces can thus grow at the expense of grains with higher energy surfaces. This is sometimes known as tertiary recrystallization (e.g. [38]) and the driving pressure available is of the order of  $10^3$  Pa. Clearly the surface effects will be more important for experiments on smaller samples: in particular, bicrystals are likely to suffer more than bulk polycrystals.

2. The existence of elastic anisotropy can be exploited to create a pressure difference across a grain boundary. Although widely applicable in principle, this technique has never been able to produce measurable high-angle grain-boundary migration, and this is probably due to the small magnitude of the driving force that can be applied to the boundary.

3. The mechanism is uncertain, but the migration of grain boundaries under the influence of an electric field has been observed (e.g. [58]).

4. Grain-boundary energy varies with temperature (see e.g. [59]): a temperature gradient should therefore result in a driving force for grain-boundary migration. Some work has been done in this field (e.g. [3]) but the driving forces are low and no quantitative data have been measured using this method.

5. Some work indicates that grain-boundary energy varies with pressure (e.g. [60]). This is a reasonable hypothesis, as a grain boundary has an associated free volume (i.e. an excess volume compared with perfect crystal) and the energy, and possibly the structure, would thus be expected to change with applied pressure. A boundary in a pressure gradient should, therefore, be subject to a driving force for migration.

## 3. Forces which oppose grain-boundary migration

If a grain boundary were subject only to driving forces, it would migrate with increasing velocity until it left the specimen. Boundaries are, however, subject to pinning and drag forces. The former are independent of grain-boundary migration velocity and must be exceeded by the net driving force before any grain-boundary migration can occur; the latter only act on a moving boundary and depend on the migration velocity. Once the boundary has broken away from the pinning forces it is accelerated by the driving forces until the drag forces have built up to balance them and a steady state is achieved. In a real material of course, the velocity will continually change as, due to inhomogeneity, local driving and drag forces vary.

The two main sources of velocity-independent resistive forces are surfaces and impurities (e.g. [61]). Local equilibrium where a grain boundary meets a surface results in groove formation. The geometry of the groove results in a force resisting boundary migration [26]. Pinning forces arise because the presence of a particle on the grain boundary reduces grain-boundary area and hence grain-boundary energy. This is generally known as Zener pinning (see e.g. [62] and Section 6).

Surfaces and impurities are also sources of drag forces. Furthermore, even in a pure, very large sample (i.e. one with negligible surface and impurity effects) grain boundaries are seen to exist. There is an intrinsic drag force which results from the thermodynamically irreversible atom transport across the boundary. Thus boundaries,

when migrating, have their upper speed set by an intrinsic drag force (see e.g. [61]).

### 3.1. The effect of solute on grain-boundary migration

The mobility of grain boundaries is very sensitive to the presence of solute and it was only after ultra-pure, zone-refined metals became available that quantitative evaluation of the effects became possible. The extreme care required in measuring purity is illustrated by an experiment performed by Aust and Rutter [13]. This compared mobilities of grain boundaries in aluminium that had been zone-refined in four passes and some that had been given twelve passes. Grain boundaries in the purer sample were found to have double the mobility of those in the less pure sample. In addition, the activation energy for migration in the purer metal was a sixth of that in the less pure. Clearly, impurities have a large effect on grain-boundary properties and it is not sufficient to define the purity of a sample by saying it is zone-refined. Several theories to explain the impurity drag effect have been proposed, and the work has recently been reviewed by Hillert [55].

First ideas on impurity drag were based on the work of Lucke and Detert [63]. Cahn [64] and Lucke and Stuwe [65] independently developed the theory, and arrived at essentially identical results\*. The model is based on the assumption that a force of interaction exists between dissolved solute and the grain boundary. This may be positive or negative, and results in the presence of an excess or a deficit of solute at the grain boundary compared to the bulk. Lucke and Detert pointed out that as the boundary exerts a force on the solute, then the solute must also exert a force on the boundary. When a boundary is in "equilibrium" and at rest, the profile is symmetrical, and there is no net force on the boundary.

The situation is more difficult when a migrating boundary is considered. Two regimes of migration are envisaged. At low migration velocities and high solute concentrations the solute profile can be calculated and there is now a net force on the boundary, as the symmetry has been lost. For the case of a positive interaction energy, the segregated solute "cloud" tries to keep up with the boundary, and the profile has its centre of mass

behind the boundary. For the case of a negative interaction energy, the solute is pushed in front of the boundary so that the profile is biased ahead of the migrating interface. In both cases there is a retardation force on the boundary.

At high velocities, and low solute concentrations, it is anticipated that the boundary can leave its solute atmosphere, and migrate as if it were in pure material. This phenomenon is known as breakaway. Note that it assumes the presence of the solute will not change the basic atomistic processes that occur as the boundary migrates.

This theory has produced qualitative agreement with many experimental results (e.g. [66]), but detailed comparison is difficult as many values must be estimated. The predicted variation of velocity with driving force, temperature and amount of solute is illustrated in Fig. 5.

Lucke and Stuwe [67] later extended their model, changing principally the interaction energy function to make some allowance for the atomic structure of crystalline solids. The predicted variation of velocity with driving force is very similar. Once again we have a loaded boundary regime, a free boundary regime and a driving force-dependent transition between them.

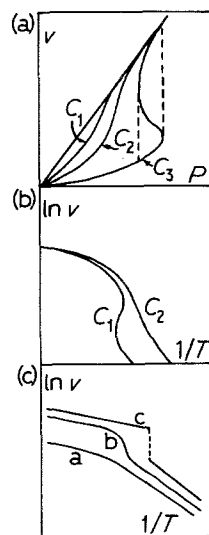


Figure 5 Schematic illustrations of the grain-boundary velocities predicted by the Cahn–Lucke–Stuwe theories of solute drag as a function of: (a) driving pressure ( $P$ ), for solute levels,  $C_1 < C_2 < C_3$ ; (b) temperature ( $T$ ), for solute levels  $C_2 < C_1$ ; (c) temperature ( $T$ ), for driving forces  $a < b < c$ .

\*The interaction between a migrating boundary and vacancies may be treated in the same way as is mentioned in Section 4.2.5.



Bauer [61, 68] has pointed out that the Cahn–Lucke–Stuwe theories allow only for interaction forces perpendicular to the boundary. In his more general treatment, Bauer also allows lateral diffusion, and he has developed a dynamic model of grain-boundary migration. The grain boundary is pictured gradually aiding the formation of solute clusters. Eventually, the cluster spacing becomes large enough that the boundary can move off. It is then slowed by solute drag once more and the cluster formation process is repeated. Boundary motion is thus predicted to be “jerky”. In addition to the usual loaded and free regimes of boundary migration that are common to most models, Bauer predicts the existence of an intermediate regime where a planar grain-boundary shape is unstable.

Hillert has been responsible for a different approach to understanding the nature of the solute–boundary interaction [55, 69]. He argues that the drag on a moving boundary must correspond to some work being done on that boundary, and this is identified as being the dispersion of free energy resulting from the irreversible nature of the diffusive processes occurring. This method of calculating the drag force is not restricted to low solute concentrations, but in the limit of low concentrations, it gives the same result as the Cahn–Lucke–Stuwe theories. It is also predicted that a high diffusivity in the interface relative to the bulk will reduce the magnitude of the solute drag, and make it constant over many orders of magnitude of boundary velocity. Such a phenomenon has not been observed, and it will be interesting to see if it can be found.

### 3.2. Summary of the forces acting on a migrating boundary

Section 2 considered the many possible ways of creating a driving pressure for grain-boundary migration and described the associated experimental approaches. It has been shown that only the bicrystal techniques described in Section 2.2.2. offer the opportunity of studying the migration of boundaries of well known and controlled crystallography. Forces which resist the migration of grain boundaries have been considered in Section 3 and in particular the drag created by the presence of solutes has been considered in some detail in Section 3.1. To develop these ideas of solute drag further will be impossible until the structure of the migrating grain boundary is understood sufficiently well to calculate the constants in the

drag equation. It is only very recently that more detailed interpretations of the atomic structure have become possible (see Section 4). Smith and co-workers [15] have made tentative proposals about the effect of solutes limiting migration by pinning the glide/climb motion of dislocations.

## 4. Theories of grain-boundary migration

As an introduction, current ideas about the structure of stationary grain boundaries will be briefly summarized. Many different descriptions have been proposed, and although these vary widely in detail, most of the current models of grain-boundary structure can be considered complementary. The disparities are largely in emphasis; ultimately the models provide a similar picture of the structure. The key feature is that the structure of the large majority of grain boundaries is periodic; in broad terms, most boundaries can be considered to be made up of regions of good fit separated by regions of poor fit.

### 4.1. The structure of static grain boundaries

Earlier models of grain-boundary structure tended to concentrate on explaining observed properties (e.g. [70]). Great advances have been made since Kronberg and Wilson [71] first focused attention on the geometry of grain boundaries by realizing the importance of the coincidence site lattice (CSL) (e.g. [72]). Furthermore, detailed geometric models based on the O-lattice and the displacement shift complete (DSC) lattice of Bollmann have since been developed (e.g. [73–75]). More recently much work has been done on simulating grain-boundary structure by computer modelling (e.g. [76–79]).

A fairly clear picture of the structure of a static grain boundary has now emerged. The structure, and consequently energy, of grain boundaries is seen to be a sensitive function of misorientation between grains. Certain misorientations give rise to periodic structures of short wavelength, and these have special properties. The CSL and O-lattice theories enable some of these misorientations to be predicted. The periodic structures can be preserved for small deviations from the precise misorientation by superimposing a dislocation network, and the dislocations can be described with the DSC lattice (e.g. [80]). Computer simulations enable the atomic arrangement in the boundary to be predicted, but it is not yet possible to check these predicted structures against experimental observation.

## 4.2. Grain-boundary migration

For the theoretical description of grain-boundary migration, a detailed knowledge of the grain-boundary structure is required. As has been seen above, geometrical and computer-based simulations of static grain-boundary structure have made great advances, but they still only provide, in the best cases, an approximate description of grain-boundary structure. Furthermore, it is likely that ideas of static structure can only serve as a guideline for theories of grain-boundary migration.

All the prevailing models of grain-boundary migration are based on absolute reaction rate theory. A static boundary is pictured as being in dynamic equilibrium. As a result of thermal fluctuations, atoms are continually being detached from grains and thus freed to move into the grain-boundary region. Depending on the model, the atom is then immediately joined to the abutting grain, or it may be pictured as free to move around in the grain-boundary region by thermally activated jumps, before attaching itself once more to a grain. For a static boundary, the flux in each direction is equal, and the boundary does not move. However, if there is a driving force for grain-boundary migration, the flux in one direction will be greater.

The main points that have to be decided, and thus create distinctions between models are:

1. single or multiple activation: does migration occur by the movement of single atoms or by the collective movement of a group of atoms?
2. “narrow” or “wide” boundary: once detached from the parent grain do atoms immediately attach themselves to a grain again, or are they free to exist “in the boundary”, and if so, what freedom do they have to move?
3. preferential sites: are these available for detachment and attachment of atoms? Are all atoms at the crystal–boundary interface equally likely to be thermally activated to jump into the boundary, or are some more favourably positioned than others? Similarly, are there favoured sites for the attachment of atoms on the growing crystal?

On the basis of reaction rate theory an expression can be derived for migration velocity (e.g. [81]):

$$v = \nu KP \left[ \exp \left( \frac{\Delta S_a}{k} \right) \exp \left( \frac{-Q}{kT} \right) \right] \quad (4)$$

where  $\nu$  is the attack frequency,  $P$  is the driving pressure,  $\Delta S_a$  is the entropy of activation for

transfer of one atom (or a group),  $Q$  is the activation enthalpy for the transfer of one atom (or a group), and  $K$  is a constant which depends on atomic volume, temperature and the distance a boundary migrates when one atom (or a group) is transferred. Whether one atom or a group of atoms is considered depends on whether the model is based on a single or multiple process theory. For the specific models described below, Equation 4 is modified by allowance for detailed predictions of how material is transported across the boundary.

### 4.2.1. Group process theories

The earliest of these is due to Mott [82], and it was related to his island theory of static grain-boundary structure. Groups of atoms are envisaged simultaneously detaching themselves from the shrinking grain and moving into a disordered boundary region, while similarly sized groups move from this region and attach themselves to the growing grain. Developments of this theory took into account macroscopic grain-boundary energy and were thus able to account qualitatively for variation of grain-boundary migration with misorientation between grains (see e.g. [3]).

Mott assumed a collective process because it enabled the observed high activation energies for grain-boundary migration to be explained. When it became apparent that the high values could also be explained by impurity drag, the theory was no longer required, and it became generally assumed that the single process theories offered a better insight into grain-boundary migration. Recently, however, Haessner has focused attention on the multiple process theories once more [83, 84]. While there is no suggestion that the particular theory of Mott is still relevant, Haessner does believe that single process theories cannot account for the observed high migration velocities in pure metals, and that some sort of cooperative atomic movement must be occurring. He suggests a process with a very large pre-exponential factor rather than a high activation energy.

### 4.2.2. Early single process theories

Turnbull [81] was responsible for the first of the single process theories of grain-boundary migration. The theory was based on the assumption that every atom on the surface of either grain was equally likely to be thermally activated, and could move in a single jump to the other grain (narrow boundary). The migration velocity is given by a

relationship of the form of Equation 4, but the model is not sufficiently specific to allow prediction of the values of  $Q$ ,  $\Delta S_a$  etc. The proposed migration process has often been identified with grain-boundary diffusion, but note that in the diffusion case, atoms move along the grain-boundary, whereas in this model the only atomic jumps are across the boundary. Comparisons of the two phenomena must be made with care.

This simple model can be extended by considering the proposed structure of the migrating boundary in greater detail. It is reasonable to expect that, due to the atomic arrangement of the crystal–boundary interface, some atoms will need less thermal activation to move into the boundary region than others. Further developments concern what might happen to an atom that has left one grain before it attaches itself to another, and what sites at the interface might be favoured for attachment and detachment. Varying degrees of mobility for the detached atom in the boundary layer have been proposed in the wide boundary models. Note that this is now true grain-boundary diffusion. With a wide boundary, three different stages can be distinguished: detachment from one grain; movement in the interface; and re-attachment to a grain. The migration process is no longer a simple singly activated process and any of the three stages can be rate-limiting.

#### 4.2.3. Step models

Gleiter [85, 86] first proposed a detailed atomistic mechanism of grain-boundary migration. The model of migration pictured atoms being detached from steps on the shrinking grain, and making a few diffusive jumps in the grain boundary before being attached to steps on the growing grain (Fig. 6). Gleiter was able to make quantitative predictions about migration velocity by assuming the growing grain behaved like a crystal growing by vapour deposition. It does not seem plausible that atoms would be free to migrate in the boundary as in a vapour and the model has been criticised on this basis (e.g. [87]). Haessner [83, 84] has extended the model, and emphasized that either the removal/attachment of atoms or diffusion in the boundary may be rate-limiting.

This model becomes more acceptable if less restraint is placed on the nature of the atomistic jumps which occur in the boundary, and on the exact nature of the steps at the surface of a grain (e.g. [15]). The model is necessarily less specific,

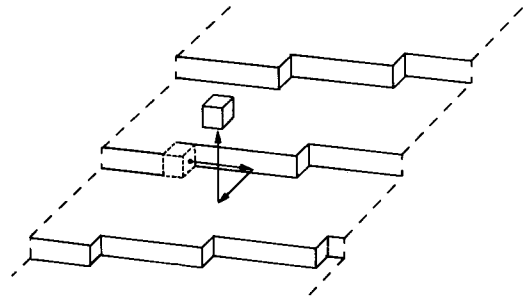


Figure 6 The atomic movements considered by Gleiter to play a part in determining grain-boundary migration rates. An atom detaches from a kink site; migrates along a ledge; detaches onto a terrace site; migrates along the terrace; and moves into the grain boundary (after Gleiter [85, 86]).

and does not enable precise elucidation of quantities in Equation 4 to the same extent as Gleiter's model, but it does provide a more realistic picture of how one grain might grow at the expense of another.

#### 4.2.4. Dislocation mechanisms

The general recognition of the importance of dislocations, and hybrid line defects (e.g. dislocations with steps at their cores; see e.g. [15]) in static grain-boundary structure has led to much conjecture on their possible role in grain-boundary migration. For special cases migration can occur by pure glide. The situation is analogous to twinning in hexagonal metals, and the only adjustment in atomic positions can be achieved by diffusionless shuffles. In the more general case, a combination of glide and climb is required, and migration is diffusion-limited. The glide/climb process accompanied by the appropriate shuffles produces boundary migration. Note that each diffusive jump is associated with several atomic shuffles, and thus the addition of several atoms to the growing grain. Note also that we are now describing a group process mode of migration (cf. Section 4.2.1. and [84]).

Grain-boundary migration and grain-boundary sliding are both high-temperature phenomena, and it is not unreasonable to expect them to be related (e.g. [88, 89]). Indeed, grain growth has sometimes been observed to occur with the production of shears between grains (e.g. [15]). However, grain-boundary migration is not always accompanied by shear. In order for a dislocation model to satisfy the demand for no shear, the sum of all Burgers vectors that pass along the interface must be zero: the shear components cancel, and the necessary

flux of defects can be supplied by short range diffusion between dislocations, so there is no requirement for long-range diffusion either. The problem now is that if a dislocation network satisfies this demand, it cannot also accommodate a deviation from a low-energy boundary misorientation. So, in general, the observed equilibrium dislocation structure of grain boundaries cannot provide a mechanism for migration.

One proposed mechanism describes migration in terms of the motion of spiral arrays of dislocations; there is no requirement for long-range diffusion and the net Burgers vector is zero. Dislocation mechanisms provide, in general, a faster migration rate than step mechanisms because one jump leads to the transfer of many atoms. The exact crystallography of the boundary and the nature of the dislocations determine how many atoms are involved [90, 91].

One of the factors that limits grain-boundary migration theories is the inability to image the structure of a migrating grain boundary. Evidence from the structure of static boundaries before and after migration has supported the belief that the migrating boundary has a related structure and that grain-boundary dislocation motion does occur when the boundary migrates [15, 90–92]. While the observed dislocation displacements cannot always account for all the observed migration, it is becoming clear that the dislocations do play an important role, and this will have to be accounted for by any definitive model of grain-boundary migration.

#### 4.2.5. Other models

The precise role of vacancies and other defects in grain-boundary structure is not clear, but has been the subject of much discussion (e.g. [3, 12, 84, 93–95]). Gleiter, in particular, has worked on the structure of defects in boundaries, and has developed an atomistic picture of relaxed vacancies and dislocations. There is general agreement that increased vacancy content makes a boundary more “porous” and hence more mobile. This point is difficult to investigate, as it is not possible to determine easily the local vacancy content in the boundary. There is also a possibility that a boundary needs a supply of vacancies from the matrix to enable it to migrate at all (e.g. [66]). Again, emphasis is placed on boundary porosity [16, 19].

The question of the porosity of grain boundaries connects up with the often made suggestion

that different grain-boundary structures may be stable under different conditions. In particular, it has often been suggested that a migrating boundary should have a different structure from a static one, that the structure of both static and migrating grain boundaries should be temperature dependent, and that the structure of migrating grain boundaries should be velocity dependent.

The thermodynamics of grain boundaries as a distinct two-dimensional phase, have been developed by Hart [96] following Gibbs’ general treatment of surfaces. The possibility of a phase change has parallels in the occurrence of allotropic transformations in three-dimensional phases, and must be treated with an open mind; there is no reason to believe that a grain boundary should have one unique structure, stable under all conditions. Indeed, the evidence from computer simulations is that alternative structures for some grain boundaries, all having very similar energies, do exist (e.g. [77]). It must be borne in mind, though, that these simulations are for structures at absolute zero, and are of restricted application to higher temperatures. Dynamic simulations, which allow for temperature are being developed (e.g. [89, 97]).

### 5. The properties of an “average” boundary during migration

Several studies have been performed which suggest that the properties of migrating grain boundaries are quite different from those of the equivalent static interfaces. Since, as has already been discussed, the dynamic observation of a migrating boundary is difficult, these observations have tended to compare microstructures before and after migration, in multi-component systems. Inferences about the behaviour of the interfaces can then be made. In Section 6, the effects of grain-boundary migration on the microstructure of particle-containing alloys will be discussed. However, some studies of initially single-phase alloys are pertinent to that discussion, and these will be considered here.

#### 5.1. Solubility

Simpson *et al.* [98], in a study of a lead–0.01% gold alloy, demonstrated that solubility in a migrating boundary is very high compared with a stationary boundary. This was inferred from the fact that when specimens undergoing grain growth were quenched and then aged at room temperature, substantial precipitation was observed to

occur on the grain boundaries. Stationary boundaries (i.e. ones in specimens where the grain structure was stable) did not exhibit similar effects.

## 5.2. Diffusivity

Hillert and Purdy [54] induced grain-boundary migration using a chemical driving force, by placing specimens of iron in an atmosphere of zinc vapour. Diffusion of zinc along the grain boundaries resulted in boundary migration via a discontinuous precipitation-type reaction. Evaluation of zinc levels some distance from the specimen surface indicated that diffusivity in a moving boundary was four orders of magnitude greater than that reported for stationary boundaries.

Smidoda *et al.* [99] examined the discontinuous production of  $\gamma'$ (Ni<sub>3</sub>Al) precipitates at a recrystallization interface in a solid solution of aluminium in nickel. By relating the velocity of the migrating boundary to the diffusion distance for  $\gamma'$ -forming elements in the boundary, they suggested that diffusion rates in the moving interface were three orders of magnitude faster than in stationary boundaries.

The mechanism by which rapid diffusion may occur within a migrating boundary is by no means clear. In addition, it has been indicated that these two sets of observations involve experimental details which are far from ideal [100, 101]. In particular, the type of boundary involved has not been determined in either case, nor have completely direct comparisons of migrating and static boundaries been made. Nonetheless, the indications of many studies of multiphase materials (see below) are that it is essentially correct to say that solubility and diffusivity are very high in migrating interfaces.

## 6. Particle effects

When the motion of a boundary is opposed by an array of particles, there are several possibilities: the boundary may be pinned by the particles (see e.g. Fig. 7); it may drag them with it; it may cause them to coarsen until it can escape from them; or, if the driving force is large enough, it will migrate through the field of particles just like a boundary in a single-phase, pure material, but subject to a reduced net driving force. In this latter case, the microstructure of the material may be modified in a radical manner, particularly if the particle/matrix interface is coherent prior to boundary migration.

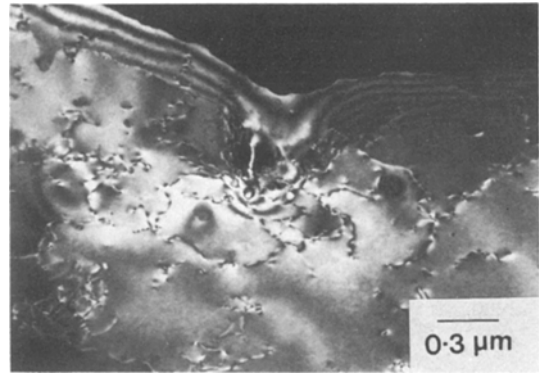


Figure 7 Centred dark-field electron micrograph showing pinning of a grain boundary during grain growth by a  $\delta'$ (Al<sub>3</sub>Li) particle in an Al–Li binary alloy.

### 6.1. Pinning by a stable array of incoherent particles

The magnitude of the pinning force was first calculated by Zener [102]. The boundary was assumed to move rigidly through the particle array, and to experience a retarding force,  $F$ , from each particle. If the volume fraction of particles is  $V_v$ , and they are spheres of radius  $r$ , then the area,  $A$ , associated with each particle is  $2\pi r^2/3V_v$ . If the boundary energy per unit area is  $\gamma$ , the force exerted by each particle on the boundary is  $\pi r\gamma$ . Thus the pinning force per unit area of boundary,  $P_z$ , is given by

$$P_z = \frac{F}{A} = \frac{3V_v\gamma}{2r} \quad (5)$$

The boundary is, of course, flexible and bows out between particles when a driving force is applied, so Zener's treatment is only an approximation. However, corrections to this treatment have been made and these give results of the same order of magnitude (e.g. [103, 104]).

The analysis of Zener can be applied to estimate, during grain growth, the grain size at which the driving and pinning pressures are equal, and hence the point at which growth will cease. This limiting grain size ( $R_z$ ) is given by the equation:

$$R_z = 4r/3V_v \quad (6)$$

However, this grain size has been shown to be a substantial overestimate of the true limiting grain size. Gladman [105, 106] has developed a detailed geometrical model of grain growth in particle-containing materials. This analysis indicates that for a growing grain, radius  $R$ , surrounded by grains of radius  $R_0$ , grain growth is inhibited by a uniform

distribution of particles, radius  $r$ , when their size is less than a critical value given by:

$$r = \frac{6R_0V_v}{\pi} \left( \frac{3}{2} - \frac{2R_0}{R} \right)^{-1} \quad (7)$$

This geometrical approach is complemented by an analysis due to Hillert [107] which is essentially kinetic in foundation. He too showed that the grain-growth behaviour observed depends on details of the particle and grain-size parameters. An experimental investigation of the validity of these models has recently been performed [108].

Gladman [106] has considered the onset of abnormal grain growth (secondary recrystallization) to be due, at least in part, to instability in the second-phase particle distribution, manifested by particle coarsening or partial dissolution. This, and other observations, of boundary-induced modifications to particle distributions will now be discussed.

## 6.2. An unstable array of incoherent particles

Ashby [62] has recently reviewed the possible interactions between a migrating boundary and incoherent particle distributions. Under conditions where the particles are stable, migration of the boundary is subject to Zener-type pinning. However, the boundary may, in certain circumstances, drag the particles with it as it moves; or alternatively, particle coarsening may allow a pinned boundary to “escape” as the Zener pinning parameter ( $V_v/r$  in Equation 5) falls.

Observations of particles being dragged by grain boundaries have been made by Ashby and Centamore [109], and mechanism maps describing the rate-controlling step for the process (be it diffusion within the matrix, interface, or particle, or the kinetics of the interfacial reaction) have been compiled (see e.g. [62] and Fig. 8). In general, particle dragging is only observed in cases where the particle radius and volume fraction are small. For a more effective pinning dispersion, the boundary is likely to be pinned completely. In such cases, particles lying on the boundary will coarsen rapidly with the remainder of the particle population (e.g. [110]). Eventually, as long as the volume fraction of particles on the boundary is constant,  $V_v/r$  will fall to a point at which the boundary can break away. Then, the boundary migrates a small distance, is pinned by a new set of particles, and the process repeats [62]. If, on

the other hand, the particles in the boundary coarsen at the expense of those near the interface, the parameter  $V_v/r$  may not decrease as a result of coarsening. In such cases, the boundary may become permanently pinned, and, in the case of recrystallization, re-nucleation becomes necessary (see e.g. [17, 111] and Fig. 9).

A final possibility, if the driving force for migration is much larger than the pinning force, is that the boundary may migrate virtually unhindered through the particle distribution. In such circumstances, the resultant microstructure is similar before and after grain-boundary migration, as long as the particle–matrix interface is incoherent and the orientation relationship is random (see Section 6.3). Some change to the volume fraction and size distribution of particles may be observed, due to high solubility and accelerated coarsening of particles in contact with the interface (e.g. [112]).

## 6.3. Grain-boundary migration through a coherent precipitate distribution

If one considers the unhindered migration of a grain boundary through a dispersion of coherent second-phase particles, it immediately becomes apparent that the energy of the system after migration is much higher than that beforehand, because of the replacement of a low-energy precipitate–matrix interface with an incoherent boundary of much higher energy (e.g. [103]). It is this simple fact that makes the range of boundary–particle interaction types broader than for incoherent particles. In addition, the possession of a rational particle–matrix orientation relationship prior to boundary migration allows these interactions to be closely monitored.

### 6.3.1. Changes to particle morphology and orientation

Most observations have been made in nickel-base superalloys, where the second-phase particles ( $\gamma'$  – essentially  $\text{Ni}_3(\text{Al}, \text{Ti})$ ) are of fundamental importance in determining high-temperature strength, and grain-boundary migration (in the form of recrystallization) plays an important part in thermomechanical processing routes.

Four processes have been reported to occur during recrystallization of such alloys (e.g. [111, 113–116]).

1. The boundary migrates with no effect on the precipitate distributions; the particles thus

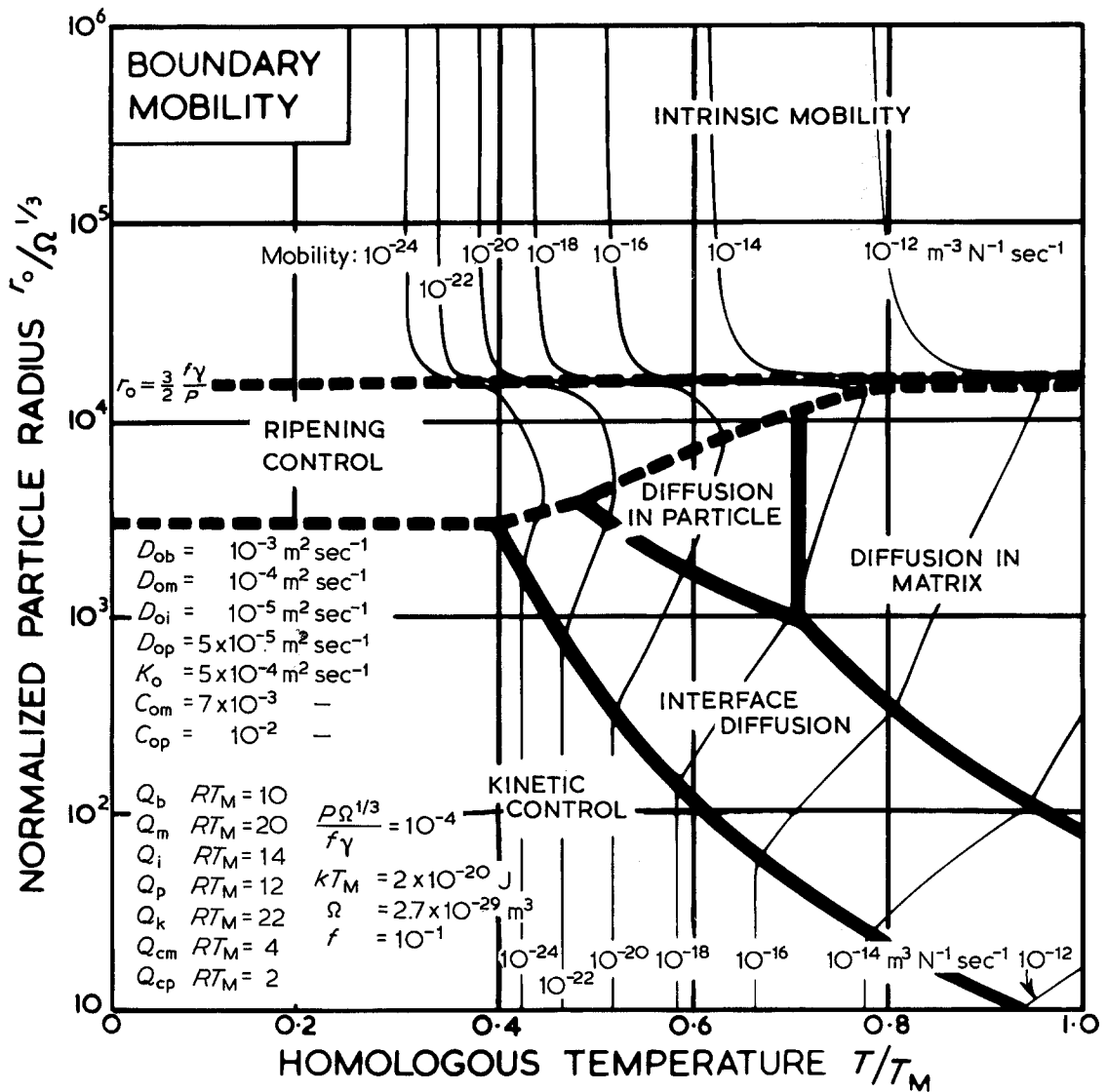


Figure 8 A boundary mobility diagram showing the dominant mechanism controlling grain-boundary migration rate in an alloy containing a volume fraction of particles of 0.1 (courtesy Ashby [62]).

become incoherent after migration, as discussed above.

2. The precipitates dissolve while in contact with the migrating boundary, and re-precipitate coherently within the new grain. This reprecipitation may occur discontinuously at the interface, or homogeneously behind it.

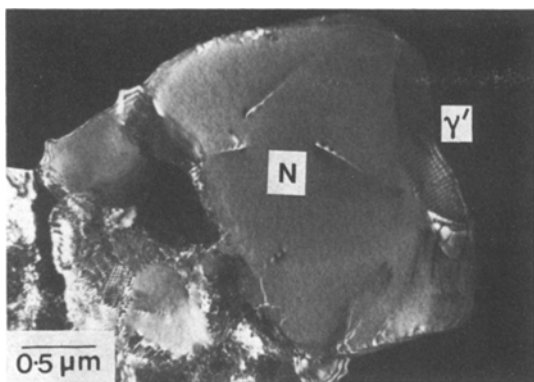
3. The boundary may be pinned completely by the particles. The precipitates may then coarsen with either of two results. Firstly, if coarsening is not accompanied by a change in precipitate volume fraction at the interface, boundary "break-away" will eventually occur, with a result equivalent to (1) above. If coarsening occurs with an

accompanying increase in volume fraction, the boundary may become permanently pinned, as discussed in Section 6.2.

4. The precipitate can be cut by the boundary, and undergo the same orientation change as the grain surrounding it. This appears to be a rare occurrence in the case of superalloys [116].

The elements of these four points are summarized in Fig. 10.

Doherty [117] has considered the thermodynamics of the interaction between a migrating boundary and a coherent particle distribution. Perhaps the most significant result of this analysis is that the Zener pinning drag is approximately



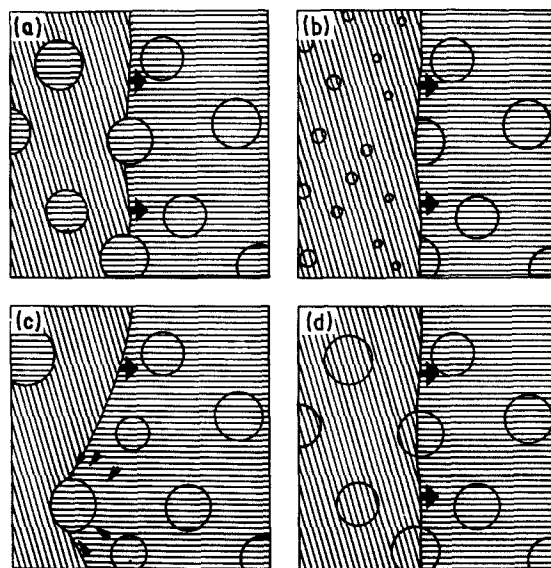
**Figure 9** Centred dark-field electron micrograph of a partially recrystallized nickel-base superalloy. The boundary has been pinned by a  $\gamma'$  particle (out of contrast), and the migration process has continued by formation of a new recrystallization nucleus (indicated N) [17].

four times bigger for a coherent particle than an incoherent one; hence very large driving forces are required if migration is to occur. Doherty also suggests that interaction type (4) is observed infrequently due to the kinetic difficulty of the process; each particle cut by the boundary must essentially re-nucleate in its new orientation, and this process is likely to be slow compared with the rate of boundary migration.

### 6.3.2. Other observations

Two other observations of boundary–particle interactions are relevant here. First, it has been observed that phases not normally observed to occur may be produced discontinuously at a migrating interface [118, 119]. This behaviour has been interpreted as indicating that there is “time and space” within a migrating boundary for atoms to be arranged onto their thermodynamically most favourable sites. During bulk precipitation, the kinetics of atom transfer across a coherent matrix–particle interface may result in a lower degree of ordering being achieved (see Figs. 11a and b).

Secondly, it has recently been observed that precipitates produced discontinuously at a moving interface will become partially coherent as they grow; this may occur more readily than an equivalent process for matrix-nucleated precipitates (see e.g. [120] and Fig. 11c). Thus, not only does a recrystallization interface act as an efficient sink for dislocations, but such interfaces may also act as dislocation sources while migrating, as has been suggested by Gleiter for the case of a grain bound-



**Figure 10** The possible interactions between a migrating grain boundary and a coherent particle distribution (see text). (a) Precipitate by-pass. (b) Precipitate dissolution and reprecipitation. (c) Boundary pinning, with coarsening of pinning particles at the expense of those near the interface. (d) Particle cut-through.

ary moving under the driving forces of grain growth [121].

## 7. Future prospects

It has been shown that migrating grain boundaries may act very radically in the modification of microstructure in metallic systems. Much remains to be established however. Peterson [101] has suggested that quantitative comparisons of the behaviour of migrating and static boundaries can only be achieved with carefully controlled bicrystal experiments. Such experiments might also be extended to multi-phase materials. If the reverse capillarity method is employed (see Section 2.2.2), migration of a boundary through a dispersion of particles should proceed until the driving pressure is equally opposed by the pinning pressure. Combining Equations 2 and 5 gives:

$$\frac{f(\alpha)}{a} = \frac{3V_v}{2r} \quad (8)$$

For a value of  $f(\alpha)$  of 20 (corresponding to  $\alpha \approx 5^\circ$ ) and a volume fraction  $V_v$  of 0.01 of 100 nm diameter particles, this condition implies a boundary migration distance of approximately  $70 \mu\text{m}$  (see Fig. 12). This distance should be perfectly adequate to study boundary–particle interactions.



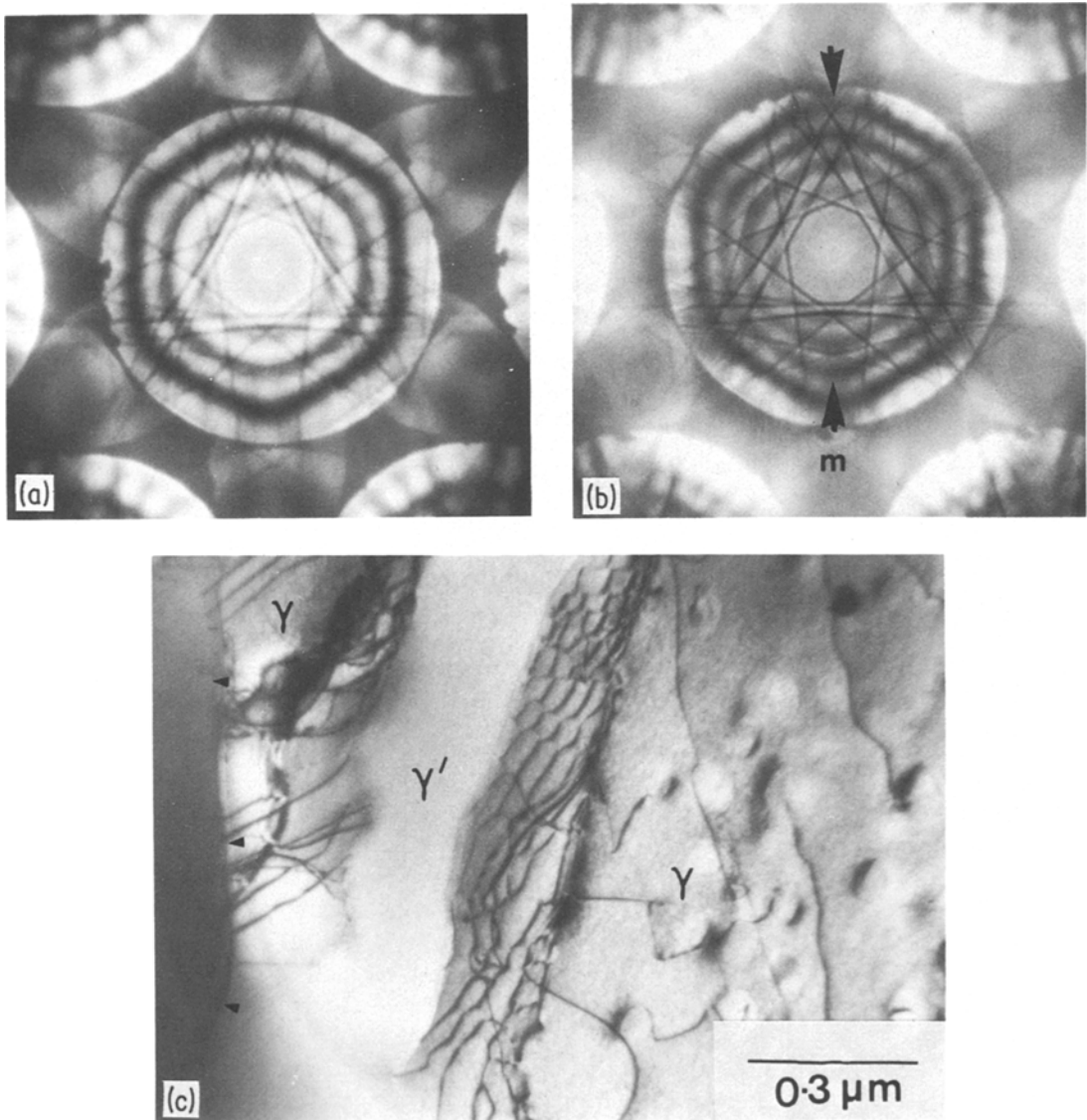


Figure 11 (a)  $(111)$  zone axis convergent beam diffraction pattern from bulk-precipitated  $\gamma'$  in a nickel-base superalloy, possessing  $3m$  point symmetry, corresponding to a cubic unit cell. (b) A similar pattern from  $\gamma'$  precipitated discontinuously at a recrystallization interface. The pattern has only mirror symmetry ( $m$ ), indicative of a higher degree of ordering, point group symmetry  $4/m\bar{m}m$  [118]. (c) A  $\gamma'$  particle precipitated by a discontinuous mechanism in a nickel-base superalloy. Arrays of misfit dislocations have been incorporated into the  $\gamma/\gamma'$  interface from the migrating boundary (arrowed) [120].

Three limitations of such bicrystal experiments should be noted:

1. the pinning capability of coherent particles is approximately four times that of incoherent particles;

2. if the precipitates are susceptible to coarsening with an increase in volume fraction, complete boundary pinning may result;

3. bicrystal techniques require high tempera-

tures, which are likely to be above the solvus temperature for a precipitate distribution.

Such experiments are thus likely to be restricted to the examination of systems containing inert particle distributions (e.g. a dispersion of oxide particles). However, they should provide valuable insight into the characteristics of well-defined migrating interfaces, and into their interaction with minor phase distributions.

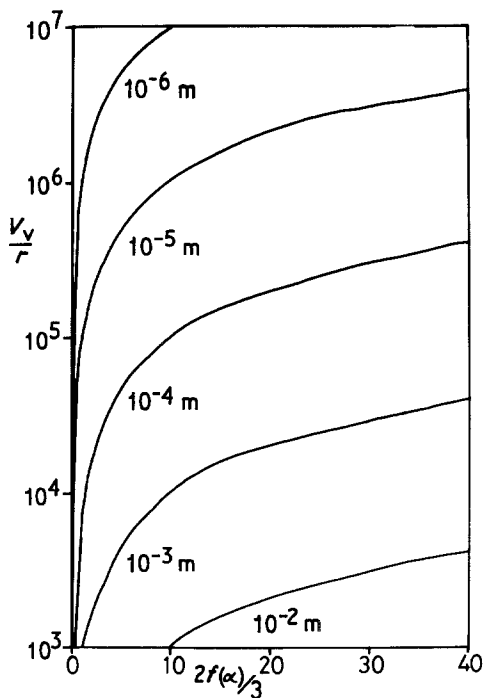


Figure 12 Predicted boundary migration distances for the reverse capillarity bicrystal geometry (see Figs. 3c and d) as a function of particle pinning parameter ( $V_p/r$ ) and driving force amplification factor ( $f(\alpha)$ ), calculated from Equation 8.

### Acknowledgements

The authors are grateful to Professor R. W. K. Honeycombe FRS for the provision of laboratory facilities. Financial support for this work at Cambridge from the Science and Engineering Research Council and the Risø National Laboratory, Denmark is gratefully acknowledged. The authors also acknowledge with gratitude a maintenance award for one of us (EG) from the Risø National Laboratory and a fellowship for another (AP) from the Churchill College Cambridge during the course of which this article was prepared. It is a particular pleasure to be able to thank Mrs Carole Bishop for her patience in preparing the manuscript. Valuable discussions with a number of their colleagues including Dr R. A. Ricks, Ms V. L. Kohler, Miss P. L. Makin and Mr C. G. Shelton are acknowledged. Constructive suggestions as to how to improve the text were offered by Dr W. M. Stobbs, Dr C. M. F. Rae and Dr N. Hansen.

### References

1. H. HU, (Ed.), "The Nature and Behaviour of Grain Boundaries" (Plenum, New York, 1972).

2. P. CHAUDARI and J. W. MATTHEWS, (Eds.) *Surf. Sci.* **31** (1972) 1.
3. H. GLEITER and B. CHALMERS, *Prog. Mat. Sci.* **16** (1972) 127.
4. J. M. TOGURI (Ed.), *Can. Met. Q.* **13** (1974) 1.
5. M. BISCONDI and C. GOUX, (Eds.), *J. de Physique Colloq.* **36** (1975) C4.
6. J. C. WALTER, J. H. WESTBROOK and D. A. WOODFORD (Eds), "Grain Boundaries in Engineering Materials" (Claitor's Publishing Division, Baton Rouge, 1975).
7. P. COTTERILL and P. R. MOULD, "Recrystallisation and Grain Growth in Metals" (Surrey University Press, Guildford, 1976).
8. G. A. CHADWICK and D. A. SMITH (Eds), "Grain Boundary Structure and Properties" (Academic Press, London, 1976).
9. F. HAESSNER (Ed.), "Recrystallisation of Metallic Materials", 2nd edn (Dr Riederer-Verlag GmbH, Stuttgart, 1976).
10. R. W. BALLUFFI (Ed.), "Grain Boundary Structure and Kinetics" (ASM, Metals Park, Ohio, 1980).
11. H. HU, in "Metallurgical Treatises", edited by J. K. Tien and J. F. Elliott (The Metallurgical Society AIME, New York, 1981) p. 385.
12. H. GLEITER, *Mat. Sci. Eng.* **52** (1982) 91.
13. K. T. AUST and J. W. RUTTER, in "Ultra-High Purity Metals" (ASM, Metals Park, Ohio, 1962) p. 115.
14. S. P. BELLIER and R. D. DOHERTY, *Acta Metall.* **25** (1977) 521.
15. D. A. SMITH, C. M. F. RAE and C. R. M. GROVENOR, in "Grain Boundary Structure and Kinetics", edited by R. W. Balluffi (ASM, Metals Park, Ohio, 1980) p. 337.
16. R. A. VANDERMEER, in "The Nature and Behaviour of Grain Boundaries", edited by H. Hu (Plenum, New York, 1972) p. 285.
17. A. J. PORTER and B. RALPH, *Mat. Sci. Eng.* **59** (1983) 69.
18. B. B. RATH and H. HU, *Trans. AIME* **245** (1969) 1243.
19. F. HAESSNER and H. P. HOLZER, *Scripta Metall.* **4** (1970) 161.
20. R. F. RAY, W. B. HUTCHINSON, F. M. C. BESAG and R. E. SMALLMAN, *J. Microsc.* **97** (1973) 217.
21. J. W. RUTTER and K. T. AUST, *Acta Metall.* **6** (1958) 375.
22. *Idem*, *Trans. AIME* **221** (1961) 641.
23. G. F. BOLLING and W. C. WINEGARD, *Acta Metall.* **6** (1958) 283, 288.
24. E. L. HOLMES and W. C. WINEGARD, *Trans. AIME* **224** (1962) 945.
25. P. NIESSEN and W. C. WINEGARD, *J. Inst. Metals* **94** (1966) 31.
26. W. W. MULLINS, *Acta Metall.* **6** (1958) 414.
27. T. SCHOBBER and R. W. BALLUFFI, *Phil. Mag.* **24A** (1971) 165.
28. S. L. SASS and P. D. BRISTOWE, in "Grain Boundary Structure and Kinetics", edited by R. W. Balluffi (ASM, Metals Park, Ohio, 1980) p. 71.
29. P. J. GOODHEW, *Met. Sci.* **13** (1979) 108.

30. C. G. DUNN, F. W. DANIELS and M. J. BOLTON, *Trans. AIME* **185** (1949) 708.
31. V. Yu. ARISTOV, Ye. M. FRIDMAN and L. S. SHVINDLERMAN, *Phys. Met. Metall.* **35** (1973) 187.
32. E. M. FRIDMAN, C. B. KOPEZKY, L. S. SHVINDLERMAN and V. Yu. ARISTOV, *Z. Metallkunde* **64** (1973) 458.
33. V. Yu. ARISTOV, C. V. KOPEZKY and L. S. SHVINDLERMAN, *Scripta Metall.* **11** (1977) 109.
34. M. S. MASTELLER and C. L. BAUER, in "Recrystallization of Metallic Materials", edited by F. Haessner (Dr Reiderer-Verlag GmbH, Stuttgart, 1978) p. 251.
35. B. B. RATH and H. HU, *Trans. AIME* **245** (1969) 1577.
36. K. T. AUST, unpublished work, quoted by C. J. Simpson and K. T. Aust, *Surf. Sci.* **31** (1972) 479.
37. W. E. BRON and E. S. MACHLIN, *Trans. AIME* **206** (1956) 513.
38. H. P. STUWE, in "Recrystallisation of Metallic Materials", edited by F. Haessner (Dr. Reiderer-Verlag GmbH, Stuttgart, 1978) p. 11.
39. R. C. SUN and C. L. BAUER, *Acta Metall.* **18** (1970) 635.
40. *Idem, ibid.* **18** (1970) 639.
41. E. A. GREY and G. T. HIGGINS, *Scripta Metall.* **6** (1972) 253.
42. *Idem, Acta Metall.* **21**, (1973) 309.
43. A. V. ANTONOV, Ch. V. KOPEZKII, L. S. SHVINDLERMAN and Ya. M. MUKOVSKII, *Phys. Status Solidi (a)* **10** (1972) 121.
44. R. VISWANATHAN and C. L. BAUER, *Acta Metall.* **21** (1973) 1099.
45. *Idem, Met. Trans.* **4** (1973) 2645.
46. D. W. DEMIANCZUK and K. T. AUST, *Acta Metall.* **23** (1975) 1149.
47. M. S. MASTELLER and C. L. BAUER, *Phil. Mag.* **38A** (1978) 697.
48. *Idem, Acta Metall.* **27** (1979) 483.
49. T. HONDOH and A. HIGASHI, *Phil. Mag.* **39A** (1979) 137.
50. W. W. MULLINS, *J. Appl. Phys.* **27** (1956) 900.
51. J. W. CAHN and R. W. BALLUFFI, *Scripta Metall.* **13** (1979) 499.
52. J. W. CAHN, J. D. PAN and R. W. BALLUFFI, *ibid.* **13** (1979) 503.
53. R. W. BALLUFFI and J. W. CAHN, *Acta Metall.* **29** (1981) 493.
54. M. HILLERT and G. R. PURDY, *ibid.* **26** (1978) 333.
55. M. HILLERT, *Met. Sci.* **13** (1979) 118.
56. D. A. SMITH and A. H. KING, *Phil. Mag.* **44A** (1981) 333.
57. W. W. MULLINS, *Acta Metall.* **4** (1956) 421.
58. G. LOMARD, J. C. RONAIS, M. LALLEMAND and C. EYRAUD, *C. Mem. Sci.* **64** (1967) 59.
59. U. ERB and H. GLEITER, *Scripta Metall.* **13** (1979) 61.
60. H. MEISER, H. GLEITER and R. W. MIRWALD, *Scripta Metall.* **14** (1980) 95.
61. C. L. BAUER, *Canad. Met. Q.* **13** (1974) 303.
62. M. F. ASHBY, in "Recrystallisation", Proceedings of the 1st Risø International Symposium on Metallurgy and Materials Science, edited by N. Hansen, A. R. Jones and T. Leffers (Risø National Laboratory, Denmark, 1980) p. 325.
63. K. LUCKE and K. DETERT, *Acta Metall.* **5** (1957) 628.
64. J. W. CAHN, *ibid.* **10** (1962) 789.
65. K. LUCKE and H. P. STUWE, in "Recrystallisation of Metals", edited by L. Himmel (Interscience, New York, 1963) p. 171.
66. C. J. SIMPSON, W. C. WINEGARD and K. T. AUST, in "Grain Boundary Structure and Properties", edited by G. A. Chadwick and D. A. Smith (Academic Press, London, 1976) p. 201.
67. K. LUCKE and H. P. STUWE, *Acta Metall.* **19** (1971) 1087.
68. C. L. BAUER, *J. de Physique Colloq.* **36** (1975) C4-333.
69. M. HILLERT and B. SUNDMAN, *Acta Metall.* **24** (1976) 731.
70. D. MCLEAN, "Grain Boundaries in Metals" (Clarendon Press, Oxford, 1957).
71. M. L. KRONBERG and F. H. WILSON, *Trans. AIME* **185** (1949) 501.
72. D. G. BRANDON, B. RALPH, S. RANGANATHAN and M. S. WALD, *Acta Metall.* **12** (1964) 813.
73. W. BOLLMANN, "Crystal Defects and Crystalline Interfaces" (Springer-Verlag, Berlin, 1970).
74. D. A. SMITH and R. C. POND, *Int. Met. Rev.* **21** (1976) 61.
75. B. RALPH, R. C. ECOB, A. J. PORTER, C. Y. BARLOW and N. R. ECOB, in "Polycrystals", Proceedings 2nd Risø International Symposium on Metallurgy and Materials Science, edited by N. Hansen, A. Horsewell, T. Leffers and H. Lilholt (Risø National Laboratory, Denmark, 1981) p. 111.
76. V. VITEK, A. P. SUTTON, D. A. SMITH and R. C. POND, in "Grain Boundary Structure and Kinetics", edited by R. W. Balluffi (ASM, Metals Park, Ohio, 1980) p. 115.
77. A. P. SUTTON and V. VITEK, *Phil. Trans. Roy. Soc. (London)* **309A** (1983) 1.
78. M. F. ASHBY, F. SPAEPEN and S. WILLIAMS, *Acta Metall.* **26** (1978) 1647.
79. R. C. POND, D. A. SMITH and V. VITEK, *Scripta Metall.* **12** (1978) 699.
80. J. J. BACCMANN, G. SILVESTRE and M. PETTIT, *Phil. Mag.* **43A** (1981) 189.
81. D. TURNBULL, *Trans. AIME* **191** (1951) 661.
82. N. F. MOTT, *Proc. Phys. Soc.* **60** (1948) 391.
83. F. HAESSNER, *J. de Physique Colloq.* **36** (1975) C4-345.
84. F. HAESSNER and S. HOFMANN, in "Recrystallisation of Metallic Materials", 2nd edition, (Dr. Reiderer-Verlag GmbH, Stuttgart, 1970) p. 63.
85. H. GLEITER, *Acta Metall.* **17** (1969) 565.
86. *Idem, ibid.* **17** (1969) 853.
87. K. LUCKE, R. RIXEN and F. W. ROSENBAUM, in "The Nature and Behaviour of Grain Boundaries", edited by H. Hu (Plenum, New York, 1972) p. 245.
88. M. F. ASHBY, *Surf. Sci.* **31** (1972) 498.

89. G. BISHOP, R. J. HARRISON, T. KWOK and S. YIP, *Prog. Mat. Sci. Chalmers Anniversary Volume* (1981) 49.
90. D. A. SMITH and C. M. F. RAE, *Met. Sci.* **13** (1979) 101.
91. C. M. F. RAE and D. A. SMITH, *Phil. Mag.* **41A** (1980) 477.
92. C. M. F. RAE, *ibid.* **44A** (1981) 1395.
93. Y. ESTRIN and K. LUCKE, *Scripta Metall.* **15** (1981) 799.
94. *Idem*, *Acta Metall.* **29** (1981) 791.
95. H. GLEITER, *Prog. Mat. Sci. Chalmers Anniversary Volume* (1981) 125.
96. E. W. HART, in "The Nature and Behaviour of Grain Boundaries", edited by H. Hu (Plenum, New York, 1972) p. 155.
97. R. M. S. COTTERILL, T. LEFFERS and H. LILHOLT, *Phil. Mag.* **30A** (1974) 265.
98. C. J. SIMPSON, K. T. AUST and W. C. WINEGARD, *Met. Trans.* **1** (1970) 1482.
99. K. SMIDODA, C. COTTSCALK and H. GLEITER, *Met. Sci.* **13** (1979) 146.
100. W. GUST, M. B. HINTZ, A. LODDING, H. ODELIUS and B. PREDEL, *Acta Metall.* **30** (1982) 75.
101. N. L. PETERSON, *Int. Met. Rev.* **28** (1983) 65.
102. C. ZENER, private communication (1948), quoted by C. S. Smith, *Trans. AIME* **175** (1948) 15.
103. M. F. ASHBY, J. HARPER and J. LEWIS, *Trans. AIME* **245** (1969) 413.
104. P. M. HAZZELDINE, P. B. HIRSCH and N. LOUAT, in "Recrystallisation", Proceedings 1st Risø International Symposium on Metallurgy and Materials Science, edited by N. Hansen, A. R. Jones and T. Leffers (Risø National Laboratory Denmark, 1980) p. 159.
105. T. GLADMAN, *Proc. Roy. Soc. (London)* **294A** (1966) 298.
106. *Idem*, in "Recrystallisation", Proceedings 1st Risø International Symposium on Metallurgy and Materials Science, edited by N. Hansen, A. R. Jones and T. Leffers (Risø National Laboratory, Denmark 1980) p. 193.
107. M. HILLERT, *Acta Metall.* **13** (1965) 227.
108. C. J. TWEED, N. HANSEN and B. RALPH, *Met. Trans.* **14A** (1983) 2235.
109. M. F. ASHBY and R. M. A. CENTAMORE, *Acta Metall.* **16** (1968) 1081.
110. A. J. ARDELL, *ibid.* **20** (1972) 601.
111. P. R. HOWELL and J. V. BEE, in "Recrystallisation", Proceedings 1st Risø International Symposium on Metallurgy and Materials Science, edited by N. Hansen, A. R. Jones and T. Leffers (Risø National Laboratory, Denmark, 1980) p. 171.
112. A. R. JONES and B. RALPH, *Acta Metall.* **23** (1975) 355.
113. F. HAESSNER, E. HORNBOGEN and N. MUKHERJEE, *Z. Metallkde* **57** (1966) 270.
114. V. A. PHILLIPS, *Trans. AIME* **239** (1967) 1955.
115. A. J. PORTER and B. RALPH, in "Recrystallisation", Proceedings 1st Risø International Symposium on Metallurgy and Materials Science, edited by N. Hansen, A. R. Jones and T. Leffers (Risø National Laboratory, Denmark, 1980) p. 147.
116. A. J. PORTER and B. RALPH, *J. Mater. Sci.* **16** (1981) 707.
117. R. D. DOHERTY, *Met. Sci.* **16** (1982) 1.
118. A. J. PORTER, M. P. SHAW, R. C. ECOB and B. RALPH, *Phil. Mag.* **44A** (1981) 1135.
119. M. P. SHAW, R. C. ECOB, A. J. PORTER and B. RALPH, in "Proceedings of Conference on Microanalysis with High Spatial Resolution", edited by G. W. Lorimer, M. H. Jacobs and P. Doig (Metals Society, London, 1981) p. 229.
120. R. A. RICKS and A. J. PORTER, in Proceedings of 41st Annual Meeting of EMSA, edited by G. W. Bailey (Claitor's Publishing Division, Baton Rouge, 1983) p. 244.
121. H. GLEITER, in "Grain Boundary Structure and Kinetics", edited by R. W. Balluffi (ASM, Metals Park, Ohio, 1980) p. 427.

*Received 12 December 1983  
and accepted 10 January 1984*