Grain Boundaries and Crystalline Plasticity
Grain Boundaries
and
Crystalline Plasticity

Edited by
Louisette Priester
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Preface

This book highlights the significant role played by the grain boundaries in the plastic behavior of crystalline materials. The need to understand this role increases with the development and the use of materials (metals, ceramics, etc.) with submicron sized grains. From well-established models to new experimental and simulation approaches, this book gives the state of the art on the relationship between the “grain boundary” object and its contribution to the mechanical properties of a material. The authors, amongst the best experts in the various fields addressed, give readers a comprehensive overview of their specialties, from the theoretical basics to the recent developments due to the appearance of new techniques.

Starting from the behavior of a grain boundary then going back to the contribution of a grain boundary network to the plasticity of a polycrystalline set, requires a multi-scale approach. This approach begins with the description of the grain boundary on an atomic scale and then details the elementary reactions – on a nano- and microscopic scale – between point defects, dislocations and grain boundaries, and finally takes an interest in the material behaviors – on mesoscopic and macroscopic scales – and in the laws ruling these behaviors. The project also requires coupling of physical, chemical and mechanical approaches.

These various approaches are discussed without excessive mathematical formality and are supported by many references. The presentation of the definitions, mechanisms and theoretical models is followed by the description of experiments and numerical simulations, which support the models. The examples cover various types of crystalline materials: metals
and metal alloys, ceramics, semiconductors, etc. The properties involved are:
hot and cold deformation, creep, fatigue and fracture.

Each chapter holds stand-alone interest and is a good reference to acquire
basic knowledge in a specific field, at the discretion of the reader. However,
only reading the book as a whole provides the reader with an understanding
of the role of the grain boundary in crystalline plasticity. The book is divided
into six chapters:

– Chapter 1 discusses the basic notions of grain boundaries: their
  geometry, their structures and their defects. This chapter focuses on
  intergranular dislocations, which are deformation vectors;

– Chapter 2 details the elementary processes involved between
dislocations and grain boundaries during deformation and the relaxation of
the resulting stresses;

– Chapter 3 describes deformation and the stress states in the boundaries
  and in their vicinity during deformation; it discusses the material behavior as
  a function of the grain size and it quickly tackles recrystallization
  phenomena;

– Chapters 4 to 6 successively discuss:

  1) the role of the grain boundaries in creep and in high temperature
     plasticity with an extension to the superplasticity phenomenon,

  2) the behavior of the boundaries subjected to high and low temperature
     fatigue efforts on bi- and polycrystals, with a few key-elements: iron,
     stainless steel, copper, superalloys, etc.,

  3) the response of grain boundaries to the fracture with particular focus
     on the effect of segregation on intergranular brittleness, but also focusing on
     embrittlement caused by liquid metals.

Providing an understanding of the influence of grain boundaries on
crystalline plasticity has not yet been the subject of a dedicated book,
although the subject constitutes a challenge for controlling material
performances.

Louisette Priester
University of Paris Sud 11
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Chapter 1

Grain Boundary Structures and Defects

1.1. Equilibrium structure of grain boundaries

A grain boundary is an interface between two crystals of the same structure. The mechanical properties of industrial materials are driven, not only by the properties of their component crystals, but also by those of the boundaries between those crystals, in particular the structure and chemical composition of the boundaries. The structural materials are generally polycrystalline and their mechanical properties are directly linked not only to the grain size but also to the grain boundaries. Moreover, since materials used in the electronics industry are to be as free from defects as possible, then it is no less true that complex manufacturing processes introduce stresses which are most often released by defects, among them dislocations, twins and also grain boundaries.

These grain boundary “objects” are therefore encountered in numerous materials; their structures and their mechanical, chemical and electrical properties have for decades been the subject of in-depth studies and they are becoming of fundamental importance in the new so-called nanomaterials. Before describing the defects found in grain boundaries during mechanical or chemical processes, we will, in this section, present three approaches which have been used in order to describe equilibrium boundaries; the purely

Chapter written by Jany Thibault-Penisson and Louisette Priester.
geometric approach, the dislocation approach, historically the first, and finally the structural unit approach originally based on energy calculations. Here, two reference works are recommended: [PRI 06] and [SUT 95].

1.1.1. Geometric description and elements of bicrystallography

1.1.1.1. Degrees of freedom

A grain boundary is defined geometrically using nine parameters, or degrees of freedom: six parameters define the interface operation, which links two adjacent crystals, and three define the interface plane. Of these nine parameters, five are said to be macroscopic and four are said to be microscopic. In cubic systems, where the operation of grain orientation is always rotational, the three macroscopic parameters defining this operation are the angle of rotation \( \theta \) and the directional cosines of the rotation axis \([u \ v \ w]\); the final two macroscopic parameters are those which define the orientation of the interface plane given by its normal. The four microscopic parameters are, on the one hand, three parameters which define the translation between grains (translation within the boundary plane and expansion perpendicular to the boundary) and, on the other, the parameter which enables the interface to be positioned along the normal to the boundary plane. These microscopic parameters are, in fact, “energy” parameters, generally defined from the calculated atomic structure which is the most energetically stable and/or experimentally observed using electron microscopy. In non-cubic materials, the interface operation is not a simple rotation, but is often accompanied by a deformation.

1.1.1.2. Tilt, twist, mixed, symmetrical and asymmetrical grain boundaries

In the interests of simplification, this terminology is used to define grain boundaries according to the relative orientations of the rotation axis \([u \ v \ w]\) with respect to the boundary plane \(\{h \ k \ l\}\).

A grain boundary is said to be a tilt boundary if the axis \([u \ v \ w]\) is contained within the boundary plane, a twist boundary if the axis \([u \ v \ w]\) is perpendicular to the plane and mixed if the axis is inclined. Boundaries are said to be symmetrical if the plane between two grains, for instance 1 and 2, can be defined by the expression \(\{h \ k \ l\}_1 = \{h \ k \ l\}_2\), otherwise they are said to be asymmetrical.
1.1.1.3. Bicrystallography and coincidence

The concept of coincidence and the definition of a coincidence index were proposed by G. Friedel in 1920 and 1926 [FRI 20, FRI 26] in order to describe twins. Bollmann [BOL 70] developed this concept towards a more complete geometric description for grain boundaries, by using the notion of bicrystallography, where two lattices are interpenetrated: a bicrystal is obtained by the interface operation, then the positioning of the interface and finally by suppression, within each grain, of atoms from the other grain. Away from the interface, grain atoms occupy their position of equilibrium in the crystal. For some interface operations, the lattice nodes of the two crystals are coincident (Figure 1.1). We therefore define the CSL (coincidence site lattice) which is in fact the intersection of translation subsets of the two crystal lattices. The coincidence is characterized by a coincidence index $\Sigma$ which is equal to the ratio between the volume of the coincidence unit cell and the volume of the primitive unit cell of the crystal. $\Sigma$ is a whole number (an odd number for cubic materials) which varies discontinuously with $\theta$. A description of coincidences based on the indices $\Sigma$ in cubic materials has been provided by Mykura [MYK 80]. A 3D coincidence only exists for cubic or hexagonal materials for a particular c/a ratio. In other cases, most grain boundaries are described as “close to specific orientations” [GRI 89].

![Figure 1.1](image_url)

Figure 1.1. Coincidence lattice unit cells viewed along the rotation axis a) of a $\Sigma = 5$ bicrystal: rotation around the 001 axis in a body-centered cubic lattice; b) of a $\Sigma = 3$ bicrystal: rotation around 011 in a face-centered cubic lattice (here, four coincidence cells are represented). The common points of the lattices are bicolored. Different point sizes indicate different positions along the normal to the scheme. The projection of the crystalline lattices is indicated by dashed lines.
1.1.1.4. DSC lattice

Boundaries encountered within materials are not necessarily coincidence boundaries; the deviation from the coincidence has been geometrically defined by Bollmann [BOL 70] by introducing the DSC (displacement symmetry conserving) lattice, which leaves the CSL invariant. This lattice is the combination of translation subsets of the two crystals; it enables the Burgers vectors of perfect boundary dislocations to be defined, i.e. those which leave the boundary structure unchanged.

The higher the coincidence index, the shorter the elementary vectors of the DSC lattice. Figure 1.2 shows a projection along the rotation axis 011 of the DSC lattice associated with the CSL lattice of the $\Sigma = 3$ boundary in the face-centered cubic material from Figure 1.1b. Dislocations which are not associated with a Burgers vector belonging to the DSC lattice are named “partial” and they are situated between two boundary sections of different structures.

![Figure 1.2. DSC lattice (thin lines) associated with the $\Sigma = 3$ bicrystal obtained by rotation around [011] in a face-centered cubic system. Vectors $b_1$ and $b_2$ are two of the three elementary DSC vectors and the third is parallel to the axis 011: here $b_1 = \frac{1}{3}[1 \overline{1} \overline{1}]$, $b_2 = \frac{1}{6}[\overline{1}1\overline{1}]$ and $b_3 = \frac{1}{2}[011]$](image)

1.1.1.5. Limit of the geometric approach

The concepts of tilt and twist or symmetry and asymmetry are highly relative. Indeed, a tilt boundary can also be described as a twist boundary
through the symmetrical operations of the crystals. The description chosen is generally the one which, from all possible descriptions, corresponds to the smallest rotation. The description of a boundary also depends on the extent to which it is observed: a micron-scale linear boundary may turn out to be multifaceted if observed over an atomic scale.

It should also be noted that a step perpendicular to the rotation axis in a tilt grain boundary corresponds to a facet of twist character (Figure 1.3). In the image obtained by high resolution transmission electron microscopy (HRTEM) we see a moiré pattern which corresponds to the superposition of two crystals which are rotating relative to each other and which is an image of the CSL lattice along the 001 axis.

The “bicrystallographic” description only provides a geometric reference to the orientation between lattices, not information about the boundary plane, and therefore describes nothing of the lower energy boundary structure. The equilibrium boundary structure, which is locally defined by the relative translation of crystals and the position of the boundary plane, is determined either from experimental observations, mostly by HRTEM, or from digital simulation.

Note that no correlation exists between the coincidence index and the grain boundary energy.

Finally, we note that a more complete approach to bicrystallography has been developed and is used to describe intergranular defects [PON 89]; this is briefly presented in Appendix 1.

Figure 1.3. HRTEM image of the $\Sigma = 5$ boundary in Ge around 001. The tilt boundary plane is (310); nanometric facets of plane (001) can be seen along the boundary, which confers on it a local twist character
1.1.2. Grain boundary structure in terms of intrinsic dislocations

1.1.2.1. The Read-Shockley model

The first model of low misorientation tilt grain boundaries, or sub-boundaries, was proposed by Read and Shockley [REA50] and consists in a periodic distribution of dislocations which enables a small misorientation to be accommodated between two adjacent grains. This model was later extended to cover any misorientation.

The dislocations introduced are said to be “intrinsic”, since they are necessary in order to reproduce the sub-boundary structure. A wall of edge dislocations which are a distance \( d \) apart and with the same Burgers vector \( b \) therefore accommodates a misorientation \( \theta = b/d \) (Figures 1.4 and 1.5a); it forms a symmetrical tilt sub-boundary.

![Figure 1.4. Read-Shockley sub-boundary model](image.png)

Asymmetry of the boundary plane necessarily gives rise to facets and is accommodated by various Burgers vector dislocations (Figure 1.5b). A twist sub-boundary is accommodated by a wall of two perpendicular families of screw dislocations (Figure 1.6) [PRI79].

Recent numerical simulations [CHE09] have shown that the dislocation content varies according to the boundary plane and have thus confirmed the observations of sub-boundaries in germanium [BOU79] and aluminum [PEN79], which had previously been validated by elastic calculations.
Figure 1.5. a) TEM image of tilt sub-grain boundary around 011 in Ge highlighting primary intrinsic dislocations. b) Detail of the boundary showing a facet: the symmetrical boundary is accommodated by edge dislocations (A) and the asymmetrical facet by dissociated 60° dislocations (B).

Figure 1.6. TEM image showing a planar view of the square array of screw dislocations which accommodates a 4° twist boundary around 001 in Au.

The Read-Shockley model has also enabled the boundary energy (per surface unit) to be calculated as the sum of the energies from the constitutive dislocations:

$$\gamma = \gamma_0 \theta (A - \ln \theta)$$  \[1.1\]

where $\gamma_0$ and $A$ are constants. At low angles, the energy increases linearly with the misorientation angle.
This Read-Shockley formula is valid for misorientation angles less than around 15°, the value above which the distance between dislocations is generally such that their cores are overlapping.

1.1.2.2. Dislocation model generalization: the continuous Frank-Bilby model

The model described by Frank [FRA 50] and Bilby [BIL 55] is the generalization of the Read-Shockley model. However, it does not rest on isolated dislocations, but is based on a continuous distribution of dislocations which accommodate the misorientation.

The dislocation density \( B \) over a boundary section of length \( X \) which is necessary in order to accommodate rotation \( R \) is given by:

\[
B = (1 - R^{-1})X \tag{1.2}
\]

where \( B \) is determined by a Frank circuit (Figure 1.7) equivalent to the Burgers circuit. This model is applicable to all high angle grain boundaries.

**Figure 1.7.** Frank circuit. A closed circuit is traced onto one of the crystals around the vector \( X_i \). This circuit is reported around the boundary, such that \( X_I = X_{II} \). It no longer closes and the boundary dislocations content over the length \( X \) is given by the closure failure \( B \).
1.1.2.3. *Dislocation model generalization: Bollmann’s discrete 0-lattice model*

In the purely bicrystallographic approach presented above, the concept of dislocation has not been explained. The bicrystal comprises zones of good and bad coincidence. Intrinsic dislocations are placed in the bad coincidence zones. Bollmann [BOL 70] introduced two mathematical lattices in order to determine the position and character of these dislocations.

The 0-lattice continually varies according to the misorientation angle between the two crystalline lattices; the coincidence sites therefore have internal coordinates in the crystalline unit cells, unlike the example of the CS Lattice, where only lattice nodes may be coincident. A planar section of the 0-lattice enables to describe the so-called primary intrinsic dislocation content which accommodates the $\theta$ angle between the two grains. Intrinsic primary dislocations are identical to those taking place in the matrix. This approach explains the presence of different dislocation types in order to accommodate facets very well, as in Figure 1.5b.

![Figure 1.8](image-url)  
*Figure 1.8. TEM observations of secondary intrinsic dislocations: a) Observation by the weak beam technique, in $\Sigma = 9$ (122) tilt boundary around 011; b) HRTEM observation of the cores of the secondary dislocations with $bc = 1/9 [122]$ Burgers vector (the elementary vector of the DSC) in a near coincidence $\Sigma = 9$ GB in Ge*
The 02-lattice enables the deviation from the exact coincidence of high angle boundaries to be accommodated in terms of secondary intrinsic dislocations. These dislocations can be described as having a Burgers vector belonging to the associated DSC lattice. Figure 1.8 shows – using two different TEM modes – observations of secondary intrinsic dislocation distributions, which account for small deviations from the coincidence in a \([011] \Sigma = 9 \ (221)\) tilt bicrystal of Cu [COU 06] and in a \([011] \Sigma = 9 \ (221)\) twist bicrystal of Ge [THI 90].

1.1.2.4. Limitations of the “dislocation” model

The structural approach to grain boundaries in terms of dislocations is very rich and has enabled numerous observations to be explained. However, the continuous Frank-Bilby model and the 0-lattice discrete model are essentially geometric. They do not take any account of local relaxations which might occur. In particular, while the discrete model gives possible distributions and types of dislocations which enable misorientation between two adjacent grains to be accommodated, it does not provide data on the boundary plane and/or dislocation distributions so as to better minimize the energy of the system.

1.1.3. Grain boundary atomic structure – structural unit model

The atomic structures of grain boundaries have been the subject of many studies. The arrangement of atoms was firstly described in terms of structural units (SU), particularly in diamond cubic structures [HOR 59, HOR 60], where covalent bonds enable a simple representation of structural units.

Then came atomic calculations [HAS 72], which made use of the potential between atoms to calculate the grain boundary energy and the more stable structure.

Extending the structural unit concept has enabled a more systematic atomic approach [SUT 83] for all materials in both symmetrical and asymmetrical boundaries.

1.1.3.1. Structural unit model

A boundary is entirely composed of structural units, which are more or less complex regular polyhedra. If the boundary is periodic, then the
structural units are produced periodically. A simple classification [SUT 83] of symmetrical periodic boundaries has been proposed, supported by atomic calculations.

AAA-type boundaries are composed of a single structural unit which is said to be favored and correspond to energy minima; examples of these are \( \Sigma = 3 \) (111) symmetrical tilt boundaries in face-centered cubic (and diamond cubic) materials and \( \Sigma = 11 \) (113) boundaries in face-centered cubic materials.

Unfavored coincidence grain boundaries, some of them being singular, have a short period, containing several structural units, e.g. ABAB.

General boundaries have a complex sequence of structural units.

As a matter of fact, the range of long period symmetrical grain boundaries of angle \( \theta \) can be described (Figure 1.9) from the periods of two delimiting boundaries of angles \( \theta_1 \) and \( \theta_2 \) such that \( \theta_1 < \theta < \theta_2 \), with shorter periods and which share the same rotation axis and the same median plane [PRI 06]. These delimiting boundaries are not necessarily low in energy.

Figure 1.9. Construction of a symmetrical grain boundary from structural units

Observation using HRTEM has enabled the approach in terms of structural units of a boundary structure to be confirmed. Figure 1.10 shows two examples of observations of “intermediate” boundaries and their structural unit descriptions [HAR 00, THI 93].
Figure 1.10. Observed (a, d) and simulated (b, d) atomic structures of the $\Sigma = 11 \{332\}$ boundary in nickel (a, c) and the $\Sigma = 11 \{332\}$ boundary in germanium (b, d). The white arrows in image (a) indicate the presence of extrinsic dislocations. The atomic columns are shown in white in (a) and in black in (d).
It should be noted, however, that the structural units which make up an intermediate boundary are not rigorously identical to those in delimiting boundaries, since the environment is different. This deformation contributes to elastic energy.

It has even been observed that in AAAAB intermediate boundaries, the A structural units, which are topologically identical, could present different deformations throughout the period of the boundary. This is the same for boundaries where the adjoining planes are not commensurate, like those found in gold [PEN 99], where the planes are \{001\}//{110} and where the quasi-periodicity of the boundary results from structural units which are differently deformed according to their position along the boundary (Figure 1.11).

![Figure 1.11. a) HRTEM of a {001}//[110] quasi-periodic boundary with a common axis 011 in Au. b) Atomic simulation. Deformation of the SU is emphasized](image)

1.1.3.2. Structural unit model applied to grain boundary dislocations

In AAAABAAB intermediate symmetrical tilt grain boundaries the B units correspond to secondary intrinsic dislocation cores which accommodate the deviation from the coincidence of the AAAA boundary. Similarly, it has been shown that secondary dislocations are linked to structural units which are compatible with the boundary structure.

The general, but periodic tilt grain boundary can in fact be considered as an AAAAAA boundary where a tilt sub-boundary is superimposed: as secondary dislocations have structural unit B cores [THI 93], the Burgers vectors linked to structural unit B do not necessarily correspond to the elementary vector of the DSC array.
Note that the structural unit which is compatible with the boundary structure has a Burgers vector which is variable along the boundary in which it is placed.\footnote{1}

A single B unit (which is therefore linked to an extrinsic dislocation) which is placed in the delimiting AAAA boundary can be described by a Burgers vector linked to the DSC lattice of the AAAA boundary; placed in an intermediate AAABAAAB boundary, this supplementary B unit is associated with a DSC lattice Burgers vector of the AAABAAAB boundary. Finally, if it is placed in the delimiting BBBB boundary, its Burgers vector is null. These points will be explained in section 1.2.2.2.

1.1.3.3. Limitations of the approach in terms of structural units

The description in terms of structural units is principally applied to tilt grain boundaries around low index axes; it is more difficult to describe twist boundaries in these terms [SCH 85].

\textbf{Figure 1.12.} HRTEM image of the \{011\} $\Sigma = 33 (144)$ tilt grain boundary. The structure of the boundary presents a glide mirror and is described in structural unit terms by LCCLCC. The model proposed by calculations was a pure LCLCC mirror. Only HRTEM has been able to propose a model which has in fact turned out to be the lowest energy structure.

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1. The Burgers vector of a defect depends on the perfect lattice reference chosen. For a crystal this reference is “naturally” the perfect crystal. For a boundary, the reference lattice may be chosen in different ways: crystal I, crystal II or bicrystal. The Burgers vector will therefore be a vector from lattice I, lattice II or from the DSC, respectively (see also Appendix 1).
This description is relatively easy to manipulate for tilt grain boundaries, but, for high index boundary planes, it is not possible to determine which of the multiple possible structures would be the most probable. An example is given in Figure 1.12, where the HRTEM has been able to validate an LCLCC glide mirror boundary model [LAM 01], whereas the calculated models have all been based on the LCLCC distribution, which presented a pure mirror. L is the structural unit comprising two 5- and 7-atom rings and C is the structural unit comprising two 6-atom rings, placed side by side laterally and which represent the perfect crystal.

1.1.4. Energetic atomic description

Energetically favorable boundary structures can only be revealed as a result of bicrystal energy calculations. Numerical simulations have few restrictions regarding the types of boundaries studied. They can be 3D and then enable changes in temperature to be tackled. As we saw in the last section, the comparison with the observations is the key to validating realistic models. Indeed, the local atomic structure, in particular the determination of microscopic parameters, can only be studied experimentally using HRTEM or HAADF, which are the projection techniques used in atomic column imaging. Whichever method is used, electron microscopy observations of atomic columns are limited to grain boundaries where the common axis is a single axis for which the projected interatomic distances are greater than the resolution of the device used. Not all boundaries are therefore accessible using these techniques. Nevertheless, under good conditions, the comparative approach reveals itself to be very powerful. Recent developments from the perspective of electron microscopy have enabled the atomic positions in complex materials such as YBaCuO [HOU 06] to be refined and the oxygen levels in Cu-O chains and changes in the bond length between Cu and the apical oxygen to be measured. In this context, a useful article from 1998 on the comparisons between calculations and observations is [PRI 98].

Static simulations enable the energy from configurations of an ensemble of atoms, interacting via interatomic potential, to be minimized. It is not always easy to determine this potential; methods from “molecular dynamics”, which take into account temperature and which are derived from an ensemble of atoms with position x and speed v, lead to the final equilibrium configuration and also evaluate atom displacement; this enables
problems relating to fusion [CIC 83] or diffusion [HAR 96] of the boundary to be tackled.

Figure 1.13 shows two examples of energy calculated for symmetrical tilt grain boundaries around the 011 axis. The curves showing the relationship between energy and misorientation angle are not the same for diamond [KOH 02] or face-centered [HAS 72] material structures. If the (111) $\Sigma = 3$ boundary corresponds to a minimum energy in both cases, this is not the case for all boundaries. (122) $\Sigma = 9$ corresponds to a minimum in Si or Ge while it is (113) $\Sigma = 11$ for Ni, Al or Cu.

Boundary energy therefore varies in a range from 0.5 to 1.5 J/m$^2$. It can be compared to stacking fault energy: 0.250 J/m$^2$ in Ni, 0.120 J/m$^2$ in Al, 0.060 J/m$^2$ in Si and 0.045 J/m$^2$ in Cu.

It is clear that boundary energy is not linked to the coincidence index. The principal factor is the coupling of the $\{h_1k_1l_1\}$ and $\{h_2k_2l_2\}$ planes side by side. It should be noted that asymmetrical facets may also reduce energy [HAR 07].

An example comparison between experimental and simulation results has led to the validation of the (112) $\Sigma = 3$ symmetrical boundary structure around 011 in body-centered cubic Mo [BAC 97]. For BCC materials, it is the (112) $\Sigma = 3$ boundary which corresponds to minimum energy. This boundary presents expansion and rigid translation which can be validated by HRTEM and simulation.

Boundaries, even at equilibrium, may present a structure which is laterally extended, particularly for low stacking fault energy materials [RIT 96]. HRTEM boundary observations in Ag [ERN 92] and Cu [WOL 92] have effectively highlighted the stability of a 9R rhombohedral structure at the boundary.

An interesting example result obtained through simulation, which would not be obtained using transmission microscopy, is the description of high twist angle grain boundaries in silicon, interest in which has been revived when considering the possibility of producing collages of platelets. Simulations of twist boundaries around the 001 axis show that their energy is elevated, in the order of 1.4 J/m$^2$, compared with tilt boundaries (see Figure 1.13) and their structure is highly disordered and may contain numerous