Springer Series in Materials Science

Volume 172

Series Editors

Zhiming M. Wang, Fayetteville, AR, USA

Chennupati Jagadish, Canberra, ACT, Australia

Robert Hull, Charlottesville, VA, USA

Richard M. Osgood, New York, NY, USA

Jürgen Parisi, Oldenburg, Germany

For further volumes:

<http://www.springer.com/series/856>

The Springer Series in Materials Science covers the complete spectrum of materials physics, including fundamental principles, physical properties, materials theory and design. Recognizing the increasing importance of materials science in future device technologies, the book titles in this series reflect the state-of-the-art in understanding and controlling the structure and properties of all important classes of materials.

Louissette Priester

Grain Boundaries

From Theory to Engineering

Louissette Priester
Université Paris Sud 11
Paris
France

ISSN 0933-033X
ISBN 978-94-007-4968-9 ISBN 978-94-007-4969-6 (eBook)
EDP ISBN 978-2-7598-0769-7
DOI 10.1007/978-94-007-4969-6
Springer Dordrecht Heidelberg New York London

Library of Congress Control Number: 2012952016

Originally published in French as “Les Joints de Grains” by EDP Sciences. © EDP Sciences 2006.
A co-publication with EDP Sciences, 17, av. du Hoggar, F-91944 Les Ulis, France

© Springer Science+Business Media Dordrecht 2013

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Most current studies tend to present the knowledge on interfaces in crystalline materials by simultaneously considering homophase interfaces or grain boundaries, and hetero-interfaces located either between two crystals of the same material but with two different structures (such as ferrite/austenite in steels), or between two different materials (metal A/metal B, metal oxide, metal–semiconductor). In this work, we deliberately choose to limit our presentation to grain boundaries. Despite the fact that the crystals on both sides of the interface display the same structure and the same composition, these interfaces are not simple. Numerous questions about their structures, their defects, and their organizations in the material still have to be solved. In each chapter, we aim to highlight these questions after having selected well-established data. In particular, we underline the difficulties in going from an ideal grain boundary (akin to a perfect crystal) to a real grain boundary (analogous to a crystal with defects). Subsequently we address the difficulties in going from an isolated grain boundary in a bicrystal to that included in a polycrystal grain boundary network, where each grain boundary is constrained at triple junctions.

Two main ideas prevail in the concept of this work. The first idea is implicitly contained in the book sub-title *From Theory to Engineering*: to know in order to control and even improve. In this perspective, we not only approach the grain boundaries at the current time, but we also try to look into the future of grain boundary research and applications. The underlying question is the grain boundary contribution to the overall material properties, the improvement of which being the final goal in materials science. Now, at the beginning of the twenty-first century, grain boundary engineering, the dream of the 1980s, seems to be taking shape on the horizon. Indeed, with the development of new experimental and computational techniques, progress has been made which enables us to fill the gap between the scales and to move backward and forward between the world of atoms and that of objects. For this reason, the present work is not restricted to a state-of-the-art report, but it moves toward engineering by considering the exchanges between a grain boundary and the other crystalline defects and, moreover, by immersing the boundary in a *practical* environment, i.e. connected with other grain boundaries.

The second idea, strongly associated to the previous one, reveals a constant effort to overcome the dichotomy between the “whole” and the “parts”. It can be summarized as: *from the individual to the collective* or *from the element to the whole*. And again, the objective is to gain a better understanding and an awareness of the practical applications.

In engineering, not only the responses of individual grain boundaries to various stimuli, but also the collective behavior of a grain boundary network must be known. However, grain boundary properties are not explicitly considered in this book for the following reasons. The basic mechanisms at grain boundaries are similar to those occurring in the crystal in several cases such as diffusion and plastic deformation. The reader may find information in specific books dedicated to these properties (references are given at the end of the book). Although the behavior of isolated grain boundaries has been studied extensively, no agreement exists on the elementary processes in cases of migration, corrosion, and wetting. Furthermore, very little is known concerning the grain boundary electric and magnetic properties. Generally, the properties vary with the grain boundary geometry. However, apart from the coherent twins that display very particular behaviors, ambiguities remain about the specific behaviors of other grain boundaries. Most often, the grain boundary chemistry erases the particularities linked to the geometry. In numerous experiments, the difficulty to evaluate the solute content in the intergranular region leads to contradictory results for a same stimulus, a same material, and a same type of grain boundary. The main reason to postpone the consideration of grain boundary properties is the lack of data on the collective grain boundary behaviors in polycrystals. However, the situation could progressively evolve with the simulation of local grain boundary textures and by the percolation approaches of the grain boundary ensemble. Finally, although not treated explicitly in a separate chapter, grain boundary properties are certainly treated implicitly. The mechanical behavior may be understood on the basis of the interactions between lattice dislocations and grain boundaries and of the intergranular stress relaxation under the effects of temperature and time. Other approaches of grain boundary network properties are also briefly stipulated.

The examples treated in this book concern different crystalline materials: metals, ceramics, semiconductors, and superconductors. In earlier times, grain boundary studies mainly developed in the field of metallurgy. Conceptual advances were obtained from high-resolution transmission electron microscopy observations of semiconductor bicrystals. Only the results of experiments and simulations are given in this volume. For the understanding of the electron microscopy images and of the calculated grain boundary structures, the reader may refer to the general references given at the end of the book, which also include books dedicated to grain boundaries and to certain properties often mentioned. Specific references are given at the end of each part and may be repeated from one chapter to the other.

Going *From Theory to Engineering*, three stages need to be passed, constituting the three parts of the book.

Part I deals with the concept of a *perfect grain boundary*, at equilibrium, and questions the maintenance of its crystalline state. The notions of order and disorder always raise questions from a philosophical point of view. *Beauty* is traditionally linked to order and science cannot escape this esthetic connotation. Working on a beautiful object is a noble task. For several years, studies in the grain boundary domain mainly concern grain boundaries that possess symmetry and purity. *Noble* tools such as transmission electron microscopy and atomistic simulations were used to improve understanding of grain boundary order. At the other end of this hierarchy of the beauty, there are ugly and impure grain boundaries, their proportion in polycrystals generally being high. They play a major role in the material properties. This first part presents the notion of *bicrystallography*, followed by the description of grain boundaries in terms of dislocations and in terms of structural units of atoms, with a special focus on the limits of these descriptions. The reasons for which a grain boundary adopts a given structure are also discussed, knowing that order and energy are not necessarily linked.

Part II brings us to the *faulted grain boundary*. It attempts to reveal the influence of the grain boundary structure on its defects, their formation, and their accommodation. Point, line, and volume defects are considered. Interstitial and substitutional solutes in excess in a grain boundary, resulting from a *segregation* phenomenon, strongly change the grain boundary behaviors. They may lead to pre-wetting accompanied by an important widening of the grain boundary region that possibly becomes non-crystalline. In the presence of segregated elements, the differences due to geometrical parameters may be obscured. Segregation may be the origin of the preferential formation of a second phase at grain boundaries that notoriously affects intergranular corrosion, migration, and deformation. Precipitation at grain boundaries and 3D defects well deserve to be analysed in this part. Finally, the interactions between boundaries and lattice dislocations yield strong disturbances at grain boundaries. The elementary mechanisms for the entrance of dislocations in a grain boundary and for the relaxation of the associated intergranular stresses are discussed in greater detail in this part. They constitute the necessary support to allow a good understanding of the mechanical properties of isolated grain boundaries, and subsequently for grain boundaries included in an ensemble.

Part III of the book is specifically devoted to these *grain boundary ensembles* starting from the *triple junction* to real grain boundary networks in polycrystals. To our knowledge, this is the first monograph to sum up the different approaches that have been developed in recent years in an engineering direction. Despite reserves, we take risks to select some mesoscopic and macroscopic studies of grain boundaries that contribute to a better understanding of the grain boundary network configuration in a material. It is an attempt to combine our knowledge of the part and of the whole, aware that there is still a huge territory to explore. In particular, general grain boundaries remain largely unknown. Furthermore, grain boundaries spatially confined in nanocrystals confer specific properties to the material. They also seem to escape order. With the development of Chaos theory, these disordered objects give rise to new interest. Generally, though, the scientific attitude in the

field of grain boundaries remains *classical*: it deals with the research of an hindered order behind an apparent disorder. The approaches developed in that domain are beyond the scope of the deterministic disorder.

The book is addressed to graduate students preparing a thesis, to engineers and to researchers in materials science; it attempts to give basic notions on grain boundaries and to give rise to research subjects in that field. It also tries to interest the scientific community in a major component of the material microstructure, the importance of which increasing as the grain size decreases. This constitutes a real challenge with the development of nanomaterials.

It is my sincere hope and final goal that the knowledge presented and the ideas developed in this work may help future researches on grain boundaries.

Acknowledgments

This book would not exist without the unfailing support and encouragement of the companion of my life since the beginning of my commitment to science:

.....*My very first thanks go to Pierre*

This book is not only the fruit of personal reflection, but also the result of work with students as part of their theses and/or in collaboration with several colleagues. I am indebted to all of them for accompanying me on the route of *Grain Boundaries*, either part of the way or until the end of the road.

Without being exhaustive, I will quote some of them and, primarily, Daniele Bouchet, not to follow a chronological order, but because her work was indirectly responsible for my orientation toward grain boundaries. Indeed, the discovery that electrochemical behavior of iron–chromium alloys is closely related to the microstructure linked to the chemistry of intergranular regions encouraged me to probe further into these areas in order to understand their geography, their history, and their future. My trip did not disappoint me. Professor R. W. Balluffi, at Cornell University, opened to me the border of this region. I warmly thank him for his hospitality in his laboratory and his availability to help me in my initiation.

On my return to the University of Orsay, I had the pleasure of working with two Ph.D. students who have greatly contributed to the launching of the theme Grain Boundaries: Sylvie Lartigue-Korinek and Omar Khalfallah. The many issues raised by them and their enthusiasm to debate have strengthened my resolution to establish a small research group on this subject. Over time, we always kept a strong collaboration with the development of original themes: calculations of elastic image force on a dislocation near the boundary with Omar, grain boundary structures, and behaviors in rhombohedral alumina with Sylvie. From their work, the major concern of all my scientific activity was forged: the interaction of dislocations with grain boundaries. My incursion into the world of ceramics was limited; Sylvie became the specialist. This intransigent researcher has remained my most faithful collaborator; we have not ceased to exchange experiences and ideas and for that I thank her very much.

Then I found again the metal with a multiscale approach, by simultaneously implementing several techniques of transmission electron microscopy. In this approach, I was helped by Brigitte Décamps to whom I am particularly grateful. Together, we supervised two Ph.D. students that I shall not forget in my thanks, Sophie Poulat and Jean-Philippe Couzinié, because their results allowed, among other things, a very promising improvement on general grain boundaries. It is through knowledge of these boundaries that we can hope to move toward a grain boundary engineering.

Finally, I have always appreciated the collaboration of two French colleagues, Jany Thibault -Penisson and Olivier Hardouin Duparc, with whom I have always had fruitful discussions, especially during the writing of this book. I want to thank them for rapid and documented answers they have always given to my questions. I add a special recognition for their contributions to our recent work on nickel and copper. The results obtained by coupling the studies of atomic grain boundary structure by transmission electron microscopy and those by high-resolution simulation, well illustrate the first two chapters of this book.

Other colleagues, French and foreign, have also crossed my path by providing their contributions which have certainly enriched the content of this work and for which I collectively thank them.

L. Priester

Contents

Part I From Grain Boundary Order to Disorder

1	Geometrical Order of Grain Boundaries	3
1.1	Grain Boundary Geometry	3
1.1.1	Crystallographical Parameters	4
1.1.2	Equivalent Rotations: Disorientation	6
1.1.3	Rodrigues Vector and Quaternions	7
1.2	Bicrystallography	8
1.2.1	General Methodology: From the Dichromatic Complex to the Grain Boundary	9
1.2.2	Dichromatic Pattern: Coincidence Site Lattice (CSL)	12
1.2.3	Translation Lattice of the Bicrystal (DSC Lattice)	14
1.2.4	Extension of the Coincidence Notion	16
1.2.5	Generalization of the Coincidence: O-Lattice and O_2 -Lattice	20
1.2.6	Interest and Limit of the Bollmann Approach	22
1.3	Different Types of Grain Boundaries: Terminology	23
1.3.1	Terminology Based on the Macroscopic Parameters	23
1.3.2	Terminology Based on the Microscopic Parameters	25
1.3.3	Practical Distinction Between Grain Boundaries	25
	References	27
2	Mechanical Stress Order of Grain Boundaries	29
2.1	Continuous Approach: The Frank-Bilby Equation	29
2.2	Discrete Approach: The Read and Shockley Model	32
2.3	Bollmann's Discrete Approach: Intrinsic Dislocations	33
2.3.1	Primary Intrinsic Dislocations	33
2.3.2	Secondary Intrinsic Dislocation	37

2.3.3	Interest and Limit of the Intrinsic Dislocation Model	42
2.4	Partial Intergranular Dislocations	44
2.5	Stress Fields Associated to Intrinsic Dislocations	45
	References	47
3	Atomic Order of Grain Boundaries.	49
3.1	Hard Sphere Model: Geometrical Construction.	50
3.2	Structural Unit Model	51
3.2.1	Principle	51
3.2.2	Hierarchy of the Descriptions.	55
3.2.3	Multiplicity of the Descriptions	58
3.2.4	Geometrical Construction of the Grain Boundary Structure.	61
3.2.5	Algorithm for the Determination of the Grain Boundary Structure.	62
3.2.6	Determination of the Grain Boundary Structure by the Strip Method	64
3.3	Interests and Limits of the Structural Unit Model: Any Model has its Exceptions	66
3.3.1	Three-Dimensional Tilt Grain Boundaries in Metals	68
3.3.2	Asymmetrical Tilt Grain Boundaries in Metals	72
3.3.3	Twist Grain Boundaries in Metals	76
3.3.4	Grain Boundaries in Covalent Materials	76
3.3.5	Grain Boundaries in Ionic Materials	79
3.4	Structural Unit Model/Intrinsic Grain Boundary Dislocations	83
3.4.1	Principle of the SU/GBD Model.	84
3.4.2	Characterization of the Dislocations Associated to Structural Units	85
3.4.3	Application of the SU/GBD Model to Tilt Grain Boundaries	88
3.4.4	Limits of the SU/GBD Model for the Twist Grain Boundaries	89
3.5	Structural Unit/Disclination Model	91
	References	92
4	Grain Boundary Order/Disorder and Energy	93
4.1	Grain Boundary Order or Disorder at High Temperature?	93
4.1.1	Solid/Solid Phase Transformations at Grain Boundaries	93
4.1.2	Grain Boundary Pre-melting?	95

4.2	Interfacial Energy: Thermodynamic Aspects and Energy Factors	99
4.3	Macroscopic Degrees of Freedom and Interfacial Energy	100
4.3.1	Variation of the Interfacial Energy with the Misorientation Angle	101
4.3.2	Variation of the Interfacial Energy with the Grain Boundary Plane Inclination	106
4.4	Microscopic Degrees of Freedom and Interfacial Energy	113
4.4.1	Variation of the Interfacial Energy with the in Plane Rigid Body Translation	113
4.4.2	Variation of the Interfacial Energy with the Expansion Normal to the Grain Boundary Plane	115
4.4.3	Variation of the Interfacial Energy with Local Individual Atomic Relaxations	117
4.5	Are There any Geometrical Criteria of Minimum Energy? . . .	117
4.5.1	Low Sigma Value Criterion	118
4.5.2	High Gamma Value Criterion	119
4.5.3	High d Value Criterion	120
4.5.4	High Gamma Value with Constant d Criterion	120
4.6	Energy and Classification of Grain Boundaries: The Limits . .	122
4.6.1	Classification Directly Based on the Grain Boundary Energy	122
4.6.2	Classification Based on the Grain Boundary Interplanar Spacing	123
4.7	Grain Boundary Order or Disorder: What Conclusion?	127
	References	132

Part II From Ideal to Real Grain Boundary

5	Defects in the Grain Boundary Structure	135
5.1	Point Defects	135
5.2	Linear Defects: Extrinsic Dislocations	138
5.2.1	Definition of an Extrinsic Dislocation	138
5.2.2	Geometrical Characteristics of an Extrinsic Dislocation	140
5.2.3	Origin of an Extrinsic Dislocation	142
5.2.4	Extrinsic Dislocation Core	142
	References	146
6	Grain Boundary Segregation	147
6.1	Driving Forces Equilibrium Segregation	148
6.1.1	Elastic Interactions	149
6.1.2	Electronic Effects	151

6.2	Thermodynamic Approaches of Equilibrium Segregation.	151
6.2.1	Gibbs Adsorption Isotherm	152
6.2.2	Segregation in Regular Solid Solution Without Interaction.	153
6.2.3	Segregation in Regular Solid Solution with Interactions.	156
6.3	Segregation Models Based on the Statistical Mechanics	159
6.3.1	Model of Regular Solid Solution with the Bragg-Williams Approximation	160
6.3.2	Mean Field Approximation (MFA) Models	161
6.4	Average Segregation at Grain Boundaries	162
6.4.1	Dependence of the Average Grain Boundary Segregation on the Temperature and the Solute Concentration.	162
6.4.2	Influence of the Interaction Term on the Average Segregation.	163
6.5	Relation Between Segregation and Grain Boundary Structure.	165
6.5.1	Segregation and Grain Boundary Geometrical Parameters.	166
6.5.2	Grain Boundary Segregation and Intrinsic Dislocations.	177
6.5.3	Grain Boundary Segregation and Grain Boundary Atomic Structure	182
6.5.4	Grain Boundary Segregation and Grain Boundary Electronic Structure	192
6.6	Prewetting Transition Upon Segregation at Grain Boundaries	200
6.7	Concept of Complexions	203
6.8	Role of Extrinsic Dislocations in Grain Boundary Equilibrium Segregation	205
6.9	Non-equilibrium Segregation at Grain Boundaries	207
6.10	Concluding Remarks.	213
	References	213
7	Precipitation at Grain Boundaries.	217
7.1	Energetic Aspect	218
7.2	Different Types of Interfaces and Precipitates	220
7.2.1	Coherent Interface	220
7.2.2	Semicoherent Interface	222
7.2.3	Incoherent Interface	223
7.2.4	Different Types of Precipitates.	223

7.3	Generalised Wulff Construction for Nucleus Equilibrium at Grain Boundary	224
7.3.1	Equilibrium Condition for a Nucleus at a Grain Boundary	224
7.3.2	Principle of the Generalised Wulff Construction.	226
7.3.3	Equilibrium Shape of Two-Dimensional Nuclei at Grain Boundaries	227
7.3.4	Influence on the Grain Boundary Plane on the Nucleus Shape	232
7.3.5	Equilibrium Shape of Three-Dimensional Nuclei at Grain Boundaries	233
7.3.6	Grain Boundary Puckering Phenomenon	234
7.4	Grain Boundary Precipitate Growth	235
7.4.1	Migration of a Curved Incoherent Interface	236
7.4.2	Migration of a Planar Interface (Coherent or Semicoherent)	236
7.5	Localisation of Grain Boundary Precipitates on Extrinsic Dislocations.	237
	References	240
8	Interactions Between Dislocations and Grain Boundaries.	241
8.1	Long-Range Elastic Interaction: Image Force.	242
8.2	Dislocation Configurations in the Vicinity of a Grain Boundary.	246
8.3	Short-Range Interactions Between Linear and Planar Defects	248
8.3.1	Combination Processes	249
8.3.2	Decomposition Processes.	250
8.3.3	Transmission Processes	254
8.3.4	Entrance of a Dissociated Dislocation in a Grain Boundary	257
8.3.5	Simulation of the Interaction of a Lattice Dislocation with a Grain Boundary	261
	References	266
9	Intergranular Stress Relaxation	269
9.1	Extrinsic Dislocation Accommodation Models	270
9.1.1	Extrinsic Dislocation Core Delocalisation	270
9.1.2	Extrinsic Dislocation Decomposition and Product Reorganisation	272
9.1.3	Extrinsic Dislocation Incorporation Within the Intrinsic Structure	274

9.2	Evolution of Extrinsic Dislocation Stress Fields	277
9.2.1	Random Disordered Dislocation Wall Model	277
9.2.2	Quasi-Equidistant Grain Boundary Model	279
9.3	Evolution of Extrinsic Dislocation Stress Fields with Time . . .	282
9.4	Experimental Studies of Extrinsic Dislocation Accommodation	284
9.4.1	Accommodation in Symmetrical Tilt Grain Boundaries in Semiconductors	284
9.4.2	Accommodation in Singular, Vicinal and General Grain Boundaries in Metals	286
9.4.3	Accommodation Kinetics	297
9.5	Conclusion on the Extrinsic Dislocation Relaxation Phenomena	300
	References	300

Part III From the Free to the Constrained Grain Boundary

10	The Triple Junction	305
10.1	Triple Junction Geometry	305
10.1.1	Geometrical Parameters and Triple Junction Classification.	305
10.1.2	Tricrystallography.	307
10.2	Triple Junction Equilibrium	310
10.2.1	Thermodynamic Approach: Limits	311
10.2.2	Equilibrium in Terms of Intrinsic Dislocations.	317
10.2.3	Equilibrium in Terms of Structural Units.	319
10.3	Triple Junction Energy	322
10.3.1	Calculation of the Triple Junction Energy	322
10.3.2	Experimental Determination of the Triple Junction Energy.	325
10.4	Triple Junction Defects	326
10.4.1	Intrinsic Defects of a Triple Junction: Geometrical Approach.	327
10.4.2	Extrinsic Defects of a Triple Junction: Mechanical Approach	330
10.5	From Tricrystal to Polycrystal	333
	References	336
11	Grain Boundary Network: Grain Boundary Texture	337
11.1	Criteria for Grain Boundary Distribution	339
11.1.1	Misorientation Criterion	340
11.1.2	Grain Boundary Plane Criterion	341
11.1.3	Non Geometrical Criteria	343
11.2	Calculation of the Misorientation Distribution	344

11.2.1	Crystal Orientation and Grain Boundary Misorientation Distribution Functions	345
11.2.2	Theoretical Misorientation Distributions	347
11.3	Experimental Grain Boundary Misorientation Distributions . . .	353
11.3.1	Different Types of Experimental Misorientation Distributions	355
11.3.2	Effects of the Structure and of the Stacking Fault Energy of the Material	356
11.3.3	Effects of the Material Purity	362
11.3.4	Effects of Thermo-Mechanical Treatments: Relation with Crystal Texture	366
11.4	Grain Boundary Plane Distributions	383
11.5	Five Grain Boundary Macroscopic Parameters Distributions	389
11.5.1	Theoretical Approach	389
11.5.2	Experimental Approach	390
11.6	Grain Boundary Property Distributions	393
11.6.1	Grain Boundary Diffusivity Distribution	394
11.6.2	Grain Boundary Energy Distribution	394
11.7	Triple Junction Distributions	397
11.7.1	Limit for Application of the Coincidence Index Combination Rule	398
11.7.2	Theoretical Approach of the Triple Junction Distribution	402
11.7.3	Experimental Triple Junction Distributions	407
11.7.4	Grain Boundary Energy Distribution Starting from the Dihedral Angle Distribution at Triple Junctions	408
11.8	Local Grain Boundary Texture	411
11.8.1	Different Types of Clusters	411
11.8.2	Observed Cluster Configurations	413
11.8.3	Simulated Cluster Configurations	418
11.9	Percolation Concept Applied to Grain Boundary Networks . . .	424
11.9.1	Infinite Grain Boundary Network	424
11.9.2	Finite Grain Boundary Network	429
11.9.3	Correlated Percolation	429
	References	433
	Epilogue	435
	Recommended Reading	437
	Index	439

Acronyms

CAD	Coincidence Axis Direction
CGBD	Coincidence Grain Boundary Distribution
c.n.i.d.	Cell of Non Identical Displacements
CSL	Coincidence Site Lattice
b.c.c.	Base-centered cubic
f.c.c.	Face-centered cubic
DSC	Displacement Shift Complete ¹ Displacement Symmetry Conserving ²
EAM	Embedded Atom Method
EBSD	Electron Back Scattering Diffraction
EGBD	Extrinsic Grain Boundary Dislocation
GBCD	Grain Boundary Character Distribution
GBD	Grain Boundary Dislocation
GBMD	Grain Boundary Misorientation ³ Distribution
IGBD	Intrinsic Grain Boundary Dislocation
ISDF	Intercrystalline Structure Distribution Function
LDFT	Local Density Functional Theory
MDF	Misorientation Distribution Function
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
HRTEM	High-resolution Transmission Electron Microscopy
MFA	Mean Field Approximation
NNR	Nearest Neighbor Relationship
OCF	Orientation Coherence Function–Orientation Correlation Function

¹ Definition 1 is the original.

² Definition 2 is more explicit.

³ The term “Disorientation” indicates one of the relative orientation relationships between two crystals retained by convention as characteristic of the class of all the equivalent rotations deduced by symmetry operations. The term “Misorientation”, generally used in this book is valid for any one of these relative orientations.

ODF	Orientation Distribution Function
OFE	Oxygen-free Electronic (copper)
OIM	Orientation Imaging Microscopy
S.U.	Structural Unit
YAG	Yttrium Aluminum Garnet

Introduction

Brief History of the Grain Boundary Order Concept

During the first half of the twentieth century, the idea that the grain boundary constitutes an amorphous layer between two crystals prevailed, until some vectorial properties were discovered in around the 1950s. The strong anisotropy of the intergranular penetration of some elements in function of the direction in the grain boundary was found inconsistent with an amorphous grain boundary nature; besides, it was previously argued that a grain boundary may be formed by regions of "*good fit*" separated by regions of "*bad fit*". The first results and models on grain boundary diffusion were obtained at the same time than the first theoretical descriptions of a grain boundary in terms of dislocations which was proposed by [1]. This description historically precedes the geometrical approaches that are first presented in this Part.

The *geometrical models and the intrinsic dislocation models* of the grain boundary structure, described in [Chaps. 1](#) and [2](#) are based, on one hand, on the preservation of the crystalline symmetry and, on the other hand, on the possible modes of intergranular stress relaxation. They are not physical models in that sense that they do not specify the atom arrangement in the grain boundary region.

[Chapter 3](#) deals with the description of *the atomic grain boundary structure*. First predicated by a rigid model that takes into account the sizes and the coordination of atoms, the grain boundary structure was then described as an arrangement of atomic polyhedra; this was deduced from grain boundary energy calculations and minimizations. The calculated structure is, as far as possible, compared to the structure observed by high-resolution transmission electron microscopy. The atom organization in a restricted number of polyhedral clusters is confirmed and the periodic arrangement of these units is formalized in the *structural unit* model. Simultaneously, a strong correlation is established between the latter model and the grain boundary description in terms of intrinsic dislocations, giving rise to the *structural unit / grain boundary dislocation* (SU/GBD) model. But the nature of the grain boundary is more unworkable and cannot be

classified as *ordered* without restriction. Indeed, even when the structural unit model supports the presence of an atomic order in a large number of grain boundaries, it questions this order with its extension to quasi-periodic grain boundaries. Besides, the experiments reveal the existence of three-dimensional (3D) grain boundaries, not theoretically predicted. Finally and more recently, amorphous grain boundaries seem to re-appear. These contradictions justify the title retained for this chapter: From grain boundary order to disorder.

[Chapter 4](#) is dedicated to the *grain boundary order and energy*. First, we deal with the order evolution in function of the temperature; in particular, we are concerned with the possibility of proper grain boundary phase transformations and with that of pre-melting in the intergranular region. The effects of solutes on grain boundary structural transformations are analysed in Part II of the book.

Inherent to the structure calculations, the *grain boundary energy* appears as a factor that may influence the grain boundary behavior. Energetic considerations are the main subject of [Chap. 4](#) with an underlying question: is it possible to predict the grain boundary energy in function of the macroscopic parameters, the only ones available for real grain boundaries. In fact, we show that no reciprocal relationship exists between the grain boundary energy and the grain boundary geometry. Moreover, energy values do not permit to predict intergranular properties. Finally, we raise the problems associated to any classification of grain boundaries based on their energies.

Finally, we attempt to review the fundamental question suggested by the Part I title: what are the limits of the intergranular order? Could the structure of the real grain boundaries be disordered? The responses that we may bring to this question are of great importance for all points developed in the following parts of this book. Indeed, we cannot approach the defects of a grain boundary without knowing its perfect structure. We cannot study triple junctions appearing in polycrystals without knowing the structures of all the abutting grain boundaries. Finally, the grain boundary properties strongly depend on the grain boundary structures.

Reference

1. W.T. Read, W. Shockley, Phys. Rev. **78**, 275 (1950).