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|-----|---|-----|---|
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| 102 | Photonic Crystal Fibers
Properties and Applications
By F. Poli, A. Cucinotta, and S. Selleri | 112 | Atomistic and Continuum Modeling of Nanocrystalline Materials
Deformation Mechanisms and Scale Transition
By M. Cherkaoui and L. Capolungo |
| 103 | Polarons in Advanced Materials
Editor: A.S. Alexandrov | 113 | Crystallography and the World of Symmetry
By S.K. Chatterjee |
| 104 | Transparent Conductive Zinc Oxide
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Editor: H.R. Huff | 116 | Einstein Relation in Compound Semiconductors and Their Nanostructures
By K.P. Ghatak, S. Bhattacharya, and D. De |
| 107 | Organic Semiconductors in Sensor Applications
Editors: D.A. Bernards, R.M. Ownes, and G.G. Malliaras | 117 | From Bulk to Nano
The Many Sides of Magnetism
By C.G. Stefanita |
| 108 | Evolution of Thin-Film Morphology
Modeling and Simulations
By M. Pelliccione and T.-M. Lu | 118 | Extended Defects in Germanium
Fundamental and Technological Aspects
By C. Claeys and E. Simoen |

Volumes 50–98 are listed at the end of the book.

Mohammed Cherkaoui • Laurent Capolungo

Atomistic and Continuum Modeling of Nanocrystalline Materials

Deformation Mechanisms and Scale
Transition



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Preface

This book was motivated by the extensive amount of literature dedicated to nanocrystalline (NC) materials published over the last two decades. The authors have been greatly interested in this new emerging field and wished to provide a comprehensive state-of-the-art text on the matter. Therefore, this oeuvre is suited for graduate students and research scientists in mechanical engineering and materials science. All chapters are written such that they can be read independently or consecutively.

Since their discovery in the early 1980s, NC materials have been the subject of great attention, for they revealed unexpected fundamental phenomena, such as the breakdown of the Hall-Petch law, and suggested the possibility of reaching the ever-so-challenging large-ductility/high-yield stress compromise. Although the problem of describing the behavior of NC materials is still challenging, numerous fundamental, computational, and technological advances have been accomplished since then. Most of these are presented in this book. By raising the difficulties and remaining problems to solve, the book highlights new directions for research to develop rigorous and complete multi-scale methods for NC materials.

The introduction of this book chronologically summarizes the different advances in the field. Chapter 1 is dedicated to the presentation of the most commonly employed processing methods. Chapter 2 presents the microstructures of NC materials as well as their elastic and plastic responses. Additionally, Chapter 6 introduces a discussion of several plastic deformation mechanisms of interest. In all other chapters, modeling techniques and advanced fundamental concepts particularly relevant to NC materials are presented. For the former, continuum micromechanics, molecular dynamics, the quasi-continuum method, and nonconventional finite elements are discussed. For the latter, grain boundary models and interface modeling are discussed in dedicated chapters. Given the vast diversity of subjects encompassed in this book, references are provided for readers interested in more specialized discussion of particular subjects. Applications of each concept and method to the case of NC materials are presented in each chapter. The last two chapters of this book are dedicated to more advanced material and aim at showing original methods allowing multi-scale material's modeling.

The authors wish to thank the editor and the formidable group of – unfortunately anonymous – reviewers for their support, rigorous comments, and insightful discussions.

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Contents

1 Fabrication Processes	1
1.1 One-Step Processes	3
1.1.1 Severe Plastic Deformation	3
1.1.2 Electrodeposition	9
1.1.3 Crystallization from an Amorphous Glass	10
1.2 Two-Step Processes	12
1.2.1 Nanoparticle Synthesis	12
1.2.2 Powder Consolidation	22
1.3 Summary	25
References	25
2 Structure, Mechanical Properties, and Applications of Nanocrystalline Materials	29
2.1 Structure	29
2.1.1 Crystallites	30
2.1.2 Grain Boundaries	33
2.1.3 Triple Junctions	37
2.2 Mechanical Properties	37
2.2.1 Elastic Properties	39
2.2.2 Inelastic Response	42
2.3 Summary	50
References	51
3 Bridging the Scales from the Atomistic to the Continuum	53
3.1 Introduction	53
3.2 Viscoplastic Behavior of NC Materials	54
3.3 Bridging the Scales from the Atomistic to the Continuum in NC: Challenging Problems	58
3.3.1 Mesoscopic Studies	59
3.3.2 Continuum Micromechanics Modeling	65
References	75

4 Predictive Capabilities and Limitations of Molecular Simulations.	81
4.1 Equations of Motion	82
4.2 Interatomic Potentials	85
4.2.1 Lennard Jones Potential	86
4.2.2 Embedded Atom Method	87
4.2.3 Finnis-Sinclair Potential	89
4.3 Relation to Statistical Mechanics	90
4.3.1 Introduction to Statistical Mechanics	91
4.3.2 The Microcanonical Ensemble (NVE)	93
4.3.3 The Canonical Ensemble (NVT)	95
4.3.4 The Isobaric Isothermal Ensemble (NPT)	97
4.4 Molecular Dynamics Methods	97
4.4.1 Nosé Hoover Molecular Dynamics Method	97
4.4.2 Melchionna Molecular Dynamics Method	100
4.5 Measurable Properties and Boundary Conditions	101
4.5.1 Pressure: Virial Stress	101
4.5.2 Order: Centro-Symmetry	102
4.5.3 Boundaries Conditions	102
4.6 Numerical Algorithms	105
4.6.1 Velocity Verlet and Leapfrog Algorithms	105
4.6.2 Predictor-Corrector	106
4.7 Applications	108
4.7.1 Grain Boundary Construction	108
4.7.2 Grain Growth	110
4.7.3 Dislocation in NC Materials	112
4.8 Summary	115
References	116
5 Grain Boundary Modeling	117
5.1 Simple Grain Boundaries	118
5.2 Energy Measures and Numerical Predictions	119
5.3 Structure Energy Correlation	121
5.3.1 Low-Angle Grain Boundaries: Dislocation Model	122
5.3.2 Large-Angle Grain Boundaries	126
5.4 Applications	138
5.4.1 Elastic Deformation: Molecular Simulations and the Structural Unit Model	138
5.4.2 Plastic Deformation: Disclination Model and Dislocation Emission	139
5.5 Summary	141
References	142

6	Deformation Mechanisms in Nanocrystalline Materials.	143
6.1	Experimental Insight	143
6.2	Deformation Map	145
6.3	Dislocation Activity	147
6.4	Grain Boundary Dislocation Emission	151
6.4.1	Dislocation Geometry	153
6.4.2	Atomistic Considerations	154
6.4.3	Activation Process	155
6.4.4	Stability	157
6.5	Deformation Twinning.	157
6.6	Diffusion Mechanisms	159
6.6.1	Nabarro-Herring Creep.	161
6.6.2	Coble Creep.	162
6.6.3	Triple Junction Creep	163
6.7	Grain Boundary Sliding	163
6.7.1	Steady State Sliding.	163
6.7.2	Grain Boundary Sliding in NC Materials.	165
6.8	Summary	167
	References	167
7	Predictive Capabilities and Limitations of Continuum Micromechanics	169
7.1	Introduction	169
7.2	Continuum Micromechanics: Definitions and Hypothesis	170
7.2.1	Definition of the RVE: Basic Principles	171
7.2.2	Field Equations and Averaging Procedures	175
7.2.3	Concluding Remarks	182
7.3	Mean Field Theories and Eshelby's Solution.	183
7.3.1	Eshelby's Inclusion Solution	184
7.3.2	Inhomogeneous Eshelby's Inclusion: "Constraint" Hill's Tensor	186
7.3.3	Eshelby's Problem with Uniform Boundary Conditions	188
7.3.4	Basic Equations Resulting from Averaging Procedures	190
7.4	Effective Elastic Moduli for Dilute Matrix-Inclusion Composites	193
7.4.1	Method Using Equivalent Inclusion	193
7.4.2	Analytical Results for Spherical Inhomogeneities and Isotropic Materials	196
7.4.3	Direct Method Using Green's Functions	199
7.5	Mean Field Theories for Nondilute Inclusion-Matrix Composites	201

- 7.5.1 The Self-Consistent Scheme 202
- 7.5.2 Interpretation of the Self-Consistent 206
- 7.5.3 Mori-Tanaka Mean Field Theory 208
- 7.6 Multinclusion Approaches 215
 - 7.6.1 The Composite Sphere Assemblage Model 215
 - 7.6.2 The Generalized Self-Consistent Model
of Christensen and Lo 216
 - 7.6.3 The $n + 1$ Phases Model of Herve and Zaoui 219
- 7.7 Variational Principles in Linear Elasticity 220
 - 7.7.1 Variational Formulation: General Principals 221
 - 7.7.2 Hashin-Shtrikman Variational Principles 230
 - 7.7.3 Application: Hashin-Shtrikman Bounds for Linear
Elastic Effective Properties 237
- 7.8 On Possible Extensions of Linear Micromechanics
to Nonlinear Problems 243
 - 7.8.1 The Secant Formulation 246
 - 7.8.2 The Tangent Formulation 256
- 7.9 Illustrations in the Case of Nanocrystalline Materials 272
 - 7.9.1 Volume Fractions of Grain and Grain-Boundary
Phases 273
 - 7.9.2 Linear Comparison Composite Material Model 273
 - 7.9.3 Constitutive Equations of the Grains and Grain
Boundary Phase 277
 - 7.9.4 Application to a Nanocrystalline Copper 278
- References 282

8 Innovative Combinations of Atomistic and Continuum:

- Mechanical Properties of Nanostructured Materials 285**
- 8.1 Introduction 285
- 8.2 Surface/Interface Structures 289
 - 8.2.1 What Is a Surface? 289
 - 8.2.2 Dispersion, the Other A/V Relation 289
 - 8.2.3 What Is an Interface? 290
 - 8.2.4 Different Surface and Interface Scenarios 290
- 8.3 Surface/Interface Physics 293
 - 8.3.1 Surface Energy 294
 - 8.3.2 Surface Tension and Liquids 295
 - 8.3.3 Surface Tension and Solids 299
- 8.4 Elastic Description of Free Surfaces and Interfaces 300
 - 8.4.1 Definition of Interfacial Excess Energy 301
 - 8.4.2 Surface Elasticity 301
 - 8.4.3 Surface Stress and Surface Strain 302
- 8.5 Surface/Interfacial Excess Quantities Computation 302
- 8.6 On Eshelby’s Nano-Inhomogeneities Problems 303
- 8.7 Background in Nano-Inclusion Problem 304

- 8.7.1 The Work of Sharma et al. 304
- 8.7.2 The Work by Lim et al. 305
- 8.7.3 The Work by Yang 307
- 8.7.4 The Work by Sharma and Ganti 310
- 8.7.5 The Work of Sharma and Wheeler 313
- 8.7.6 The Work by Duan et al. 315
- 8.7.7 The Work by Huang and Sun 318
- 8.7.8 Other Works 319
- 8.8 General Solution of Eshelby’s Nano-Inhomogeneities Problem 320
 - 8.8.1 Atomistic and Continuum Description of the Interphase 320
 - 8.8.2 Micromechanical Framework for Coating-Inhomogeneity Problem 328
 - 8.8.3 Numerical Simulations and Discussions 336
- Appendix 1: “T” Stress Decomposition 344
- Appendix 2: Atomic Level Description 346
- Appendix 3: Strain Concentration Tensors: Spherical Isotropic Configuration 347
- References 349

- 9 Innovative Combinations of Atomistic and Continuum: Plastic Deformation of Nanocrystalline Materials 353**
 - 9.1 Quasi-continuum Methods 354
 - 9.2 Thermal Activation–Based Modeling 358
 - 9.3 Higher-Order Finite Elements 361
 - 9.3.1 Crystal Plasticity 363
 - 9.3.2 Application via the Finite Element Method 366
 - 9.4 Micromechanics 370
 - 9.5 Summary 377
 - References 377

- Subject Index 379**

Introduction

Major technological breakthroughs engendering significant impact on modern society have occurred during this past century. These novelties have emerged in areas as diverse as transportation, telecommunications, construction, etc. Recall that only 20 years ago, the Internet, global positioning, electric-powered cars, and so forth were either pure theory or reserved to a then much-envied small pool of the population. In the early 20th century, automotive and aerospace engineering were the stuff of popular and scientific fantasy and interest because they literally created a revolution, contributing to the “flattening of the world.” The last part of the past century has seen the same sort of interest being directed towards device minimization, in its general sense. An unquestionable example is that of cellular phones and computers, whose dimensions and weight have been substantially optimized since their introduction on the market. Recently, a summit was reached with the creation of micro-electromechanical systems (MEMS). Devices such as resonators, actuators, accelerometers, and gyroscopes can already be fabricated with micrometer dimensions. These are already used in industry. The “trend” to minimize devices and structures and the subsequent successes has led to new fields of science all encompassed in the generic term *nanotechnologies*. In a general way, one could define nanotechnologies as all devices and materials with either dimensions or characteristic dimensions in the range of several nanometers up to several hundred nanometers.

The reader is certainly aware of what a nanometer represents in terms of units. However, it is important to assess the physical “smallness” of the nanometer. For example, a single particle of smoke still has dimensions more than a thousand times larger than a nanometer. A nanometer is approximately equal to three interatomic distances in a copper crystal. Keeping the above remark in mind, one can easily suspect nanomaterials and nanotechnologies to reveal novel and never-before-observed phenomena.

Interestingly, the “infinitesimal” has been a perpetual subject of fascination, intensive reflection, and often the source of advances in all fields of science. In mathematics, the not-so-simple yet crucial, idea of integration results from the conceptualization of the infinitesimally small. Indeed, supposing a function f from the real line to the real line, the integration of this

function is based on the consideration that the real line is an infinite sequence of real values and the distance between two consequent values is infinitesimal. Similarly, the concept of atom, the etymology of which is from the Greek word *atomos* “non-cut,” attributed to Leucippus of Miletus and Democritus of Abdera, is dated from 500 B.C. and is clearly still subject to ongoing studies. Nowadays, owing to the increase in computing resources and to the amelioration of experimental apparatus such as the transmission electron microscope, the observation and numerical modeling of atoms and groups of atoms with complex arrangements are commonly performed in most research laboratories. Even nanotechnologies that may seem recent and whose early development is often assumed to date from the late 1990s can actually be traced back to the middle of the 20th century. Indeed, in 1959, Richard Feynman discussed in detail in a talk entitled, “There Is Plenty of Room at the Bottom,” the possibility of encrypting the totality of the *Encyclopedia Britannica* on the head of a pin. During World War II, nanoparticles smaller than ~ 5 nm could already be synthesized in Japan.

Although unremarkable to the “untrained eye,” simultaneously to the minimization of devices, materials have also been the subject of massive investigations aiming at refining their microstructure. The idea being that most phenomena are dependent on characteristic dimensions (e.g., time, length). Indeed, let us consider the following experiments: (1) a person walks slowly into the ocean and (2) the same person falls at high speed from a wakeboard into the ocean. The perception of the reaction of the water on the body of the subject will clearly be different due to the change in characteristic dimensions: time. Similar reasoning can be applied to the reaction, or more precisely to the behavior of materials which can largely differ depending on the characteristic dimensions. One of the most notable effects observed in polycrystalline materials (i.e., materials composed of agglomerates of crystals) is that predicted by the Hall-Petch law describing the increase in yield strength proportional to the inverse of the square root of the grain size. With the above size-dependent yield strength, decreasing the characteristic dimensions (e.g., crystal size) of a copper sample from 100 microns down to 1 micron would lead to an increase in the yield strength on the order of 250%. This example brings to light the importance of size effects in materials which are unquestionably an efficient way to improve the response of materials. The second route of improvement typically results from the addition of different substances in an initially pure material. This is the case of dopants in semiconductors. The remarkable size effect mentioned in the above has driven the scientific community to further refine the microstructure of materials down to nanometric dimensions. These materials are referred to as nanostructured (NS) materials.

Since the early 1990s, a broad range of NS materials – exhibiting outstanding mechanical, electrical, and magnetic properties – have been synthesized. For example, ZnO nanorods and nanobelts, typically obtained via solid-vapor thermal sublimation, exhibit high piezoelectric coefficient, on the order of 15–25 pm/V, which suggest promising applications in sensors and actuators.

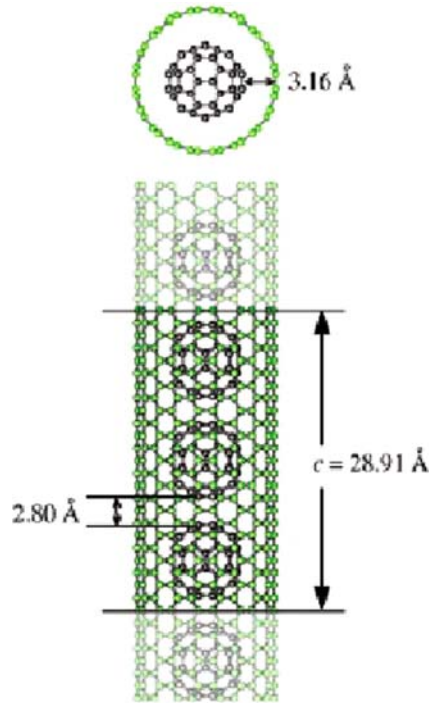


Fig. 1 Multiwalled carbon nanotube

Similarly, multiwalled carbon nanotubes (see Fig. 1), whose tensile properties are measured by attaching them to tips of AFM cantilever probes, exhibit tensile strength ranging from 11 to 63 GPa [1]. Hence, multiwalled carbon nanotubes are outstanding candidates for reinforcement in composite materials.

The appeal of NS materials is not limited to the potential applications that may result from the adequate use of their superior properties but is also driven by the novel fundamental phenomena occurring solely in these materials. The most renowned example is the breakdown of the Hall Petch law which will be discussed in more details throughout this book.

These novel phenomena, underlying the occurrence of unknown deformation mechanisms, have suggested a particular interest in the scientific community. This is especially the case of nanocrystalline materials, to be introduced in the following section, for which numerous technical papers debating on their structure, mechanical response and deformation mechanisms were published since their creation in the late nineteen eighties.

Let us first clearly define the type of NS material this book is dedicated to, and present a short history of the advances in the field in order to help the reader better comprehend and judge of the many remaining challenges to be faced in the area.

What Are Nanocrystalline Materials?

Owing to the large variety of fabrication processes, which will be discussed in detail in the following chapter, a vast diversity of NS materials can be synthesized. Indeed, NS materials present an opportunity to mix substances which were so far not miscible. As an example, Ag-Fe alloys, which are typically immiscible substances in the solid state, can be fabricated via inert gas condensation using two evaporators [2] (this technique will be discussed in the following chapter).

A classification of nanocrystalline materials (see Fig. 2), based on their chemical composition and crystallite geometry, was proposed in Gleiter's pioneering work [3]. NS materials can be divided in three families: (1) layer shaped, (2) rod shaped, and (3) equiaxed crystallite. For each family the composition of the crystallites can vary. All crystallites can have same structure, or a different composition. Also, the composition of the crystallites can be different from that of the boundaries, or more generally of that of the interphase (the phase between crystallites). Finally, the crystallites can be dispersed in a matrix of different composition.

Different fabrication processes are used to fabricate different families and categories of nanostructured materials. For example, nanocrystalline Ni Co/CoO functionally graded layers with mean grain size ranging from ~ 10 to

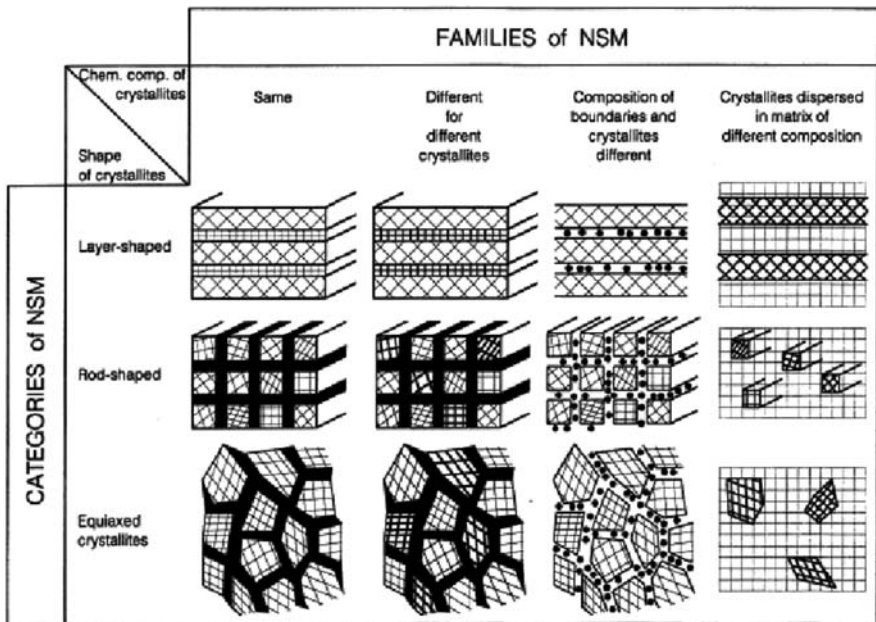


Fig. 2 Classification of nanostructured materials as proposed by Gleiter [3]

~40 nm are processed via electrodeposition followed by cyclic oxidation and quenching [4], while nanocrystalline Ni can be processed solely via electrodeposition (among others).

This book focuses on equiaxed nanostructured materials with crystallites having similar constitution. Depending on the size of the crystallites (also referred to as grain cores), a particular nomenclature, generally accepted by the community, is used. Hence, throughout this book, nanostructured materials with equiaxed crystallites and mean grain size larger than ~100 nm and smaller than 1 micron will be referred to as ultrafine grain materials, while nanostructured materials with equiaxed crystallites and mean grain size smaller than ~100 nm will be referred to as nanocrystalline materials.

Although the microstructure of nanocrystalline (NC) materials is to be presented in detail in a later chapter, let us briefly comment on the particular features of NC materials. Three constituents compose NC materials: (1) grain cores also referred to as crystallites, (2) grain boundaries, and (3) triple junctions also referred to as triple lines. Grain cores exhibit a crystalline structure (e.g., face center cubic, hexagonal compact, body center cubic). Grain boundaries correspond to regions of junction between two grains. It has a structure that depends on the orientations of the adjacent grains and on the shape of the grains. Therefore, grain boundaries can exhibit either an organized structure, yet different from that of the crystallites, or a much less ordered structure. This is dependent on several factors. One of the most influential factors is the fabrication process. Also, most defects (e.g., impurities, pores, vacancies) are localized within the grain boundaries and triple junctions. The latter are regions where more than two grains meet. Interestingly, they typically do not exhibit particular atomic order. Grain boundaries and triple junctions constitute an interphase and have a more or less constant thickness on the order of ~1 nm. This means that a decrease in the grain size leads to an increase in the volume fraction of interphase. In the case of coarse grain polycrystalline materials, with grain size larger than 1 micron, the volume fraction of interphase is typically less than 1% while in the case of NC materials, the volume fraction of interphase can be as high as 40–50% (depending on the grain size). This is one of the most striking features of NC materials.

A Brief History

In order to build appreciation for the critical modeling and experimental issues and points of interest concerning NC materials, it is appropriate here to present a brief history of NC materials which obviously does not have the vocation to be exhaustive.

Nanocrystalline materials were first fabricated in 1984 in pioneering work of Gleiter and Birringer, who first produced samples with grain sizes ranging from 1 to 10 nm and immediately discussed the extremely high ratio of volume

fraction of interface to grain core [5, 6]. Let us note that successful synthesis of nanoparticles could already be achieved in the late 1940s (for further details the reader is encouraged to read the review by Uyeda). The microstructure of these novel materials was also the subject of interest because neither long-range nor short-range structural order in the interphase was revealed by X-ray diffraction and Mössbauer microscopy.

In 1987, the first diffusivity measures at relatively low temperature (~ 360 K) on 8 nm grain size NC materials produced by vapor condensation reported a self-diffusion coefficient 3 orders of magnitude larger than that of grain boundary self-diffusion [7, 8]. Similarly, studies on the diffusivity of silver in NC copper with 8 nm grain size revealed diffusivity coefficients 2–4 orders of magnitude higher than measured in a copper bicrystal. Hence, the existence of a novel solid state structure in the interphase was suggested [9]. Moreover, the mixture of apparently nonmiscible elements was already discussed.

These first results were quickly followed by an extensive series of experiments (e.g., positron annihilation, X-ray diffraction) revealing what was referred to as an “open structure” for grain boundaries and characterized by the presence of voids and vacancies within the interphase region [10, 11]. Let us note here that these experiments were performed on nanocrystalline metals with grain size smaller than 10 nm.

In 1989, hardness measurements on NC Cu and Pd produced by inert gas condensation (to be presented in a later chapter) reveal a deviation from the Hall-Petch law. Precisely, these experiments revealed that below a critical grain size NC metals exhibit a negative Hall-Petch slope. This means that, contrary to the prediction given by the Hall-Petch law (i.e., a decrease in the grain size leads to an increase in the yield strength proportional to the inverse of the square root of the grain size), the yield strength can decrease with decreasing grain size providing the crystallites are smaller than a critical value. This “breakdown” of the Hall-Petch law was suggested to result from rapid diffusion throughout grain boundaries, similar to the process predicted by Coble but activated at room temperature.

The experimental results mentioned in the above are of primary importance because NC materials appeared, then, to be capable of reaching an excellent strength/ductility compromise. This would emerge from the high-yield strength obtained prior to the breakdown of the Hall-Petch law and from exceptional diffusion coefficients at room temperature (suggesting the possibility of superplastic deformation). Consequently, NC materials were soon considered by many as a technological niche.

Simultaneously, the novel properties of nanocrystalline materials brought to light numerous fundamental questions. Among others, limited data available in the early 1990s were not sufficient to establish, on the basis of rigorous statistical analysis, the certainty of the occurrence of the breakdown of the Hall-Petch law, or the abnormal diffusivity coefficients reported. Similarly, considering the high interphase-to-grain-core volume fraction ratio, one may wonder what is the role of grain boundaries and triple

junctions to the viscoplastic deformation of NC materials? Does the inter-phase region actively participate in the deformation? What is the structure of grain boundaries in nanocrystalline materials? Typically, in coarse-grained metals, dislocation activity (nucleation, storage, annihilation) drives the plastic deformation. Is it the case in nanocrystalline materials? Precisely, how is dislocation activity affected by grain size? What is the relationship to superplastic deformation?

Since the early 1990s, the scientific community has focused on simultaneously improving the fabrication processes and models (both computational and theoretical) in order to elucidate the long list of challenging questions listed in the above (among others). As will be shown throughout this book, considerable progress was achieved since the appearance of NC materials. For example, molecular dynamics simulations (both two-dimensional columnar and fully three-dimensional) and quasi-continuum studies, to be discussed in detail in upcoming chapters, revealed some of the details of NC deformation (e.g., grain boundary dislocation emission, grain boundary sliding). NC materials are particularly well suited for numerical simulations via molecular dynamics. Indeed, performing a back-of-the-envelope calculation, a cubic 20 nm sized copper grain contains approximately 220,000 atoms, which is well below the maximum number of atoms that one would simulate with molecular statics (at zero Kelvin) or molecular dynamics. From a purely theoretical standpoint, numerous phenomenological models were developed to investigate the effect of particular mechanisms (e.g., grain boundary sliding, vacancy diffusion, grain boundary dislocation emission). Also, particular attention was paid to the theoretical description of grain boundaries from structural unit models for example.

Finally, the fabrication processes have been systematically improved over the past decade in order to produce defect-free samples (e.g., low porosity, low contamination, etc.). As a result, the mechanical response of NC materials has clearly improved over the 20 years or so since the synthesis of the first sample. Indeed, early traction tests on NC Cu samples in the quasi-static regime exhibited limited ductility (tensile strain < 5%) while the latest experiments on cold-rolled cryomilled NC Cu exhibit more than 40% ductility.

Modeling Tools

One of the particularities of NC materials is that their characteristic lengths and time scale stand at the crossroads of that of several modeling techniques (micromechanics, molecular statics, molecular dynamics, and nonconventional finite elements). Consequently, detailed understanding of size effects and novel phenomena occurring in nanocrystalline materials can be reached solely via the use of complimentary approaches relying on detailed observations,

fundamental models at the atomic and mesoscopic scale (the scale of the grain), and complex computer-based models.

Figure 3 presents the range of application of the most commonly used modeling techniques as a function of characteristic length (vertical axis) and time scale (horizontal axis). First, computational models based on molecular statics (at 0 K) and dynamics are typically used to predict the displacements, position, and energies of a given number of atoms, ranging from a few to several hundred thousand, subjected to externally applied boundary conditions (e.g., temperature, displacement, pressure). These simulations rely on the description

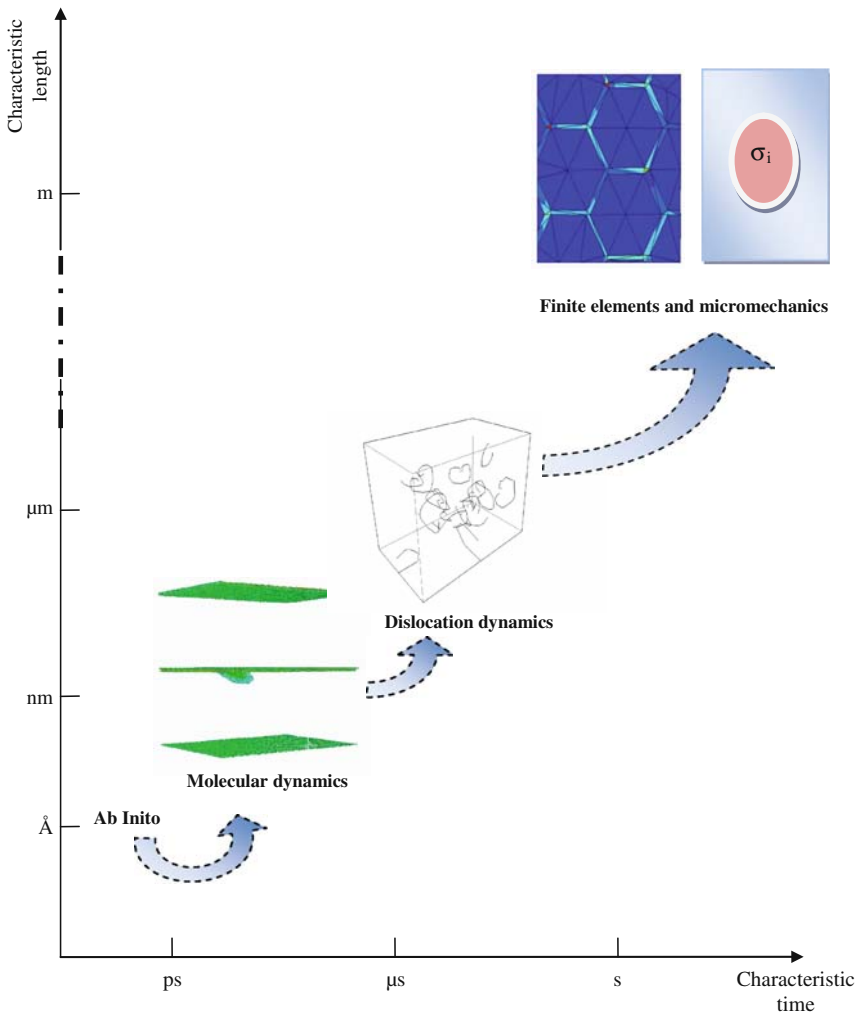


Fig. 3 Schematic of the range of applications of the most commonly used computational and theoretical modeling techniques

of the interatomic potential from which the attractive or repulsive forces can be calculated. The interatomic potentials are typically based on *ab initio* calculation. It is fitted to a relatively large number of parameters (e.g., interatomic distance, stacking fault energies, etc.). Owing to the large number of operations to be performed simultaneously, the characteristic lengths and time of molecular simulations are limited. For example, simulations are rarely performed in real time larger than ~ 200 ps. This is due to the limitation on the calculation time-steps which must remain smaller than the period of vibration of atoms (on the order of the femtosecond). Hence, molecular dynamics simulations aiming at studying viscoplastic deformation mechanisms are limited to extremely high strain rates or applied stresses on the order of several GPa. Alternatively, molecular static simulations present the clear advantage of not being limited to small computation steps. However, the simulations are limited to zero Kelvin. Nonetheless, molecular simulations are crucial for they provide valuable information on the motion of atoms which cannot be trivially observed via transmission electron microscopy.

At the microscopic scale, dislocation dynamics simulations can provide useful information as to the intricacies of the dislocation interactions in nanocrystalline materials. Dislocation dynamics are based on the equations of motion of dislocation lines which are typically modeled as a concatenation of smaller dislocation segments. The nodes, or junction between the segments, are the points of interest where the equations of motions are applied. Considerable progress was made in the field such that, nowadays, dislocation dynamics can be applied to complex problems (e.g., cracks). However, to date, dislocation dynamics models are limited to low dislocation densities and representative volume elements on the order of a couple micrometers cubed. One of the major remaining limitations of discrete dislocation dynamics is that of the treatment of interfaces, which has yet to be addressed. Clearly, this limits the application of such methods to study NC materials. Similarly, models based on phase field theory (e.g., constrained energy minimization of a variational formulation) can successfully predict the details of dislocation interactions. While these models present the advantage of being less computationally intense than dislocation dynamics simulations, published work in the literature is often limited to single slip.

At much larger time and length scales, micromechanics and finite elements analyses can predict macroscopic properties and responses of NC materials from a set of parameters extracted from both experiments and models based on the techniques mentioned earlier. In the case of finite elements, precise predictions of stress and strain fields can be obtained. However, the description of the statistical distribution of grain and grain boundary misorientations is often prevented due to computational times. On the other hand, micromechanical models (e.g., mixture rules, Taylor's model, Mori-Tanaka, self-consistent schemes, generalized self-consistent schemes) inherently account for the statistical microstructural features of the material. However, a rigorous description of the grain geometry is typically not obtained with these models. Recently, micromechanical models were solved via Fast Fourier Transform (FFT)

coupled with Voronoi tessellation. This has allowed us to overcome the limitations mentioned above – at the expense of calculation time.

The transfer of information between the different time and length scales, corresponding to the range of applications of each modeling technique, is the keystone to successful modeling of NC materials. One of the major difficulties is bridging information from the scale of atomistic simulations to the micron scale, where large quantities of defects interact. This challenge is often referred to as the micron gap (see Fig. 3). In the last decade, several techniques, which will be presented in this book, have been proposed to perform scale transitions between the different time and length scales.

This book aims at summarizing some of the most important advances in the field in terms of modeling, both theoretical and computational, and fabrication process prospective. The objective here is clearly not to make an exhaustive list of all published work to date but to present and discuss the foundations, limitations, and possible evolutions of existing techniques.

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