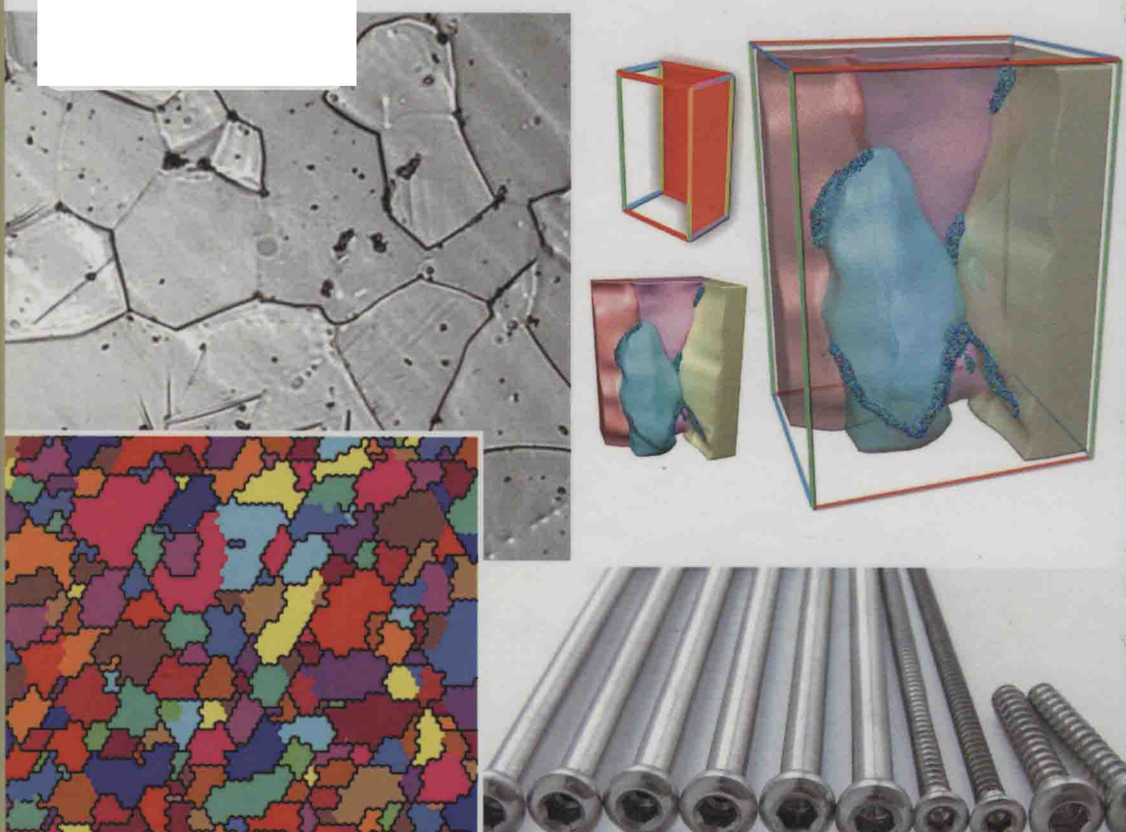
Bulk Nanostructured Materials:

Fundamentals and Applications

Ruslan Z. Valiev • Alexander P. Zhilyaev • Terence G. Langdon



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To Marina, Tatiana and Mady for their support during the writing of this book and throughout our scientific careers

Preface

In recent years, the development of bulk nanostructured materials (BNM) has become one of the most topical directions in modern materials science. Nanostructuring of various materials paves the way to obtaining unusual properties that are very attractive for different structural and functional applications. In this research topic, the use of both "bottom-up" and "top-down" approaches for BNM processing/synthesis routes has received considerable attention. In the "bottom-up" approach, bulk nanomaterials are fabricated by assembling individual atoms or by consolidating nanoparticulate solids. The "top-down" approach is different because it is based on grain refinement through heavy straining or shock wave loading. During the last two decades, grain refinement by severe plastic deformation (SPD) techniques has attracted special interest since it offers new opportunities for developing different technologies for the fabrication of commercial nanostructured metals and alloys for various specific applications. Very significant progress was made in this area in recent years. The generation of new and unusual properties has been demonstrated for a wide range of different metals and alloys: examples include very high strength and ductility, record-breaking fatigue endurance, increased superplastic forming capabilities, as well as multifunctional behavior when materials exhibit enhanced functional (electric, magnetic, corrosion, etc.) and mechanical properties.

The innovation potential of this research area is outstanding, and now a transition from laboratory-scale research to industrial applications is starting to emerge. In addition, the subject of BNM is now entering the textbooks on materials science and related subject areas and therefore it is very important to have a single treatise that comprises the fundamental as well as applied aspects of bulk nanomaterials. At the same time, although the processing of BNM by assembling individual atoms/particles has been described in several books, there is at present no international monograph devoted exclusively to bulk nanomaterials produced by severe plastic deformation. This omission forms the background for the present work. Equally, it is now apparent that research on BNM has developed so rapidly in recent years that the terminology needs some clarification, and it is necessary to provide a clearer definition of the terms widely used within this field. This information is given in Chapter 1.

Acknowledgments

The use of bulk nanostructured metals and alloys as structural and functional materials of the next generation has remained an open question until recently, when a breakthrough has been outlined in this area associated both with the development of new processing routes for the fabrication of bulk nanostructured materials and with investigations of the fundamental mechanisms that lead to novel properties for these materials. Our understanding of these issues has naturally developed through our many close interactions with colleagues and associates around the world. We would like to express our sincere gratitude and appreciation to all who provided support, offered comments, discussed, allowed quoting of their remarks and publications, and otherwise assisted in the preparation of this book, particularly our reputable colleagues and friends from the International NanoSPD Steering Committee—Profs. Yuri Estrin, Zenji Horita, Michael Zehetbauer, Yuntian Zhu (www.nanospd.org), and other members of the materials science community actively working with us to publish many joint works. Many of these papers are cited in the reference sections, and we take this opportunity to offer our sincere apologies to all collaborators who have been with us over the course of many years and whose contributions we have failed to mention.

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Contents

Chapter 1

Introduction

Although the mechanical and physical properties of all crystalline materials are determined by several microstructural parameters, the average grain size of the material generally plays a very significant, and often a dominant, role. Thus, the strength of all polycrystalline materials is related to the grain size, *d*, through the Hall–Petch equation, which states that the yield stress, σ_y, is given by

$$\sigma_y = \sigma_0 + k_y d^{-1/2}, \tag{1.1}$$

where σ_0 is termed the friction stress and k_y is a constant of yielding [1, 2]. It follows from Equation 1.1 that the strength increases with a reduction in the grain size, and this has led to an ever-increasing interest in fabricating materials with extremely small grain sizes.

It is now over 25 years since Herbert Gleiter presented the first concepts for developing nanocrystalline (NC) materials (i.e., materials with a grain size of less than 100 nm) and the potential for producing special properties [3]. Since that time, the field of nanomaterials has flourished over the last two decades, owing to the considerable interest in this topic and the scientific and technological importance.

At the same time, it is now apparent that research on nanomaterials has developed widely in recent years, and the terminology needs some clarification. The three terms actively used within this field are ultrafine-grained (UFG), NC,

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and nanostructured (NS) materials, and it is initially useful to provide a clearer definition of these three terms, which have been discussed at several conferences and in reviews [4–10].

With reference to the characteristics of polycrystalline materials, UFG materials can be defined as polycrystalline materials having very small and reasonably equiaxed grains with average grain sizes less than ~1 μm and grain boundaries with predominantly high angles of misorientation. In practice, the presence of a large fraction of high-angle grain boundaries is important in order to achieve advanced and unique properties [5]. Thus, the grain sizes of UFG materials lie both within the submicrometer (100–1000 nm) and the nanometer (less than 100 nm) ranges. For grain sizes below 100 nm, the latter are termed nanocrystalline materials or nanocrystals. In practice, UFG materials also exhibit other structural elements having sizes of less than 100 nm including second-phase particles or precipitates, dislocation substructures, and pores. These nanometer-sized features also have a considerable influence on the properties of the materials. For example, in severe plastic deformation (SPD) processing, nanostructural elements such as nanotwins, grain boundary precipitates, and dislocation substructures may form within the ultrafine grains of 100–300 nm in size, and their formation will have a significant effect on the mechanical and functional properties [7]. Materials containing these nanostructural elements are designated "nanostructured materials." In order to qualify as bulk nanostructured materials (BNM), the only additional requirements are that there exists a homogeneous distribution of nanostructural elements in the entire sample and the samples typically have 1000 or more grains/nanostructural elements in at least one direction.

To date, two basic and complementary approaches have been developed for the synthesis of BNM, and these are known as the "bottom-up" and the "top-down" approaches [11, 12].

As was already noted earlier, in the "bottom-up" approach, BNM are fabricated by assembling individual atoms or by consolidating nanoparticulate solids. Examples of these techniques include inert gas condensation [6, 11], electrodeposition [13], ball milling with subsequent consolidation [14], and cryomilling with hot isostatic pressing [15, 16], where cryomilling essentially denotes mechanical milling in a liquid nitrogen environment. In practice, these techniques are often limited to the production of fairly small samples that may be useful for applications in fields such as electronic devices but are generally not appropriate for large-scale structural applications. Furthermore, the final products from these techniques invariably contain some degree of residual porosity and a low level of contamination, which is introduced during the fabrication procedure. Recent research has shown that large bulk solids, in an essentially fully dense state, may be produced by combining cryomilling and hot isostatic pressing with subsequent extrusion [17], but the operation of this combined procedure is expensive, and at present it is not easily adapted for the production and utilization of structural alloys for large-scale industrial applications.

The "top-down" approach is different because it is dependent upon taking a bulk solid with a relatively coarse grain size and processing the solid to produce a UFG microstructure through SPD. Processing by SPD refers to various experimental procedures of metal forming that may be used to impose very high strains on materials