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Bulk Nanostructured Materials with Multifunctional Properties

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Preface

The fact that the bulk nanostructured metallic materials have been one of the hottest topics in materials science in the last decade clearly shows their growing importance as future materials. For example, small-diameter dental implants made from nanostructured pure titanium are to replace standard ones made from Ti–4Al–6V alloy, since the nanostructured pure titanium is characterized not only by increased mechanical strength and fatigue life, but also by better biocompatibility compared to the conventional Ti–4Al–6V alloy. In other words, one can say that the nanostructured pure titanium is characterized by better multifunctional properties. Despite the significant body of experimental and theoretical research on nanostructured materials in the literature, investigations of their multifunctional properties began within last few years. Many new developments in the area of nanostructured metallic materials have recently occurred, and important new applications are planned, particularly in electrical engineering. Thus, it is hoped that the appearance of this first book is timely.

In preparing this book, we have sought to cover the various features of generation and application of bulk nanostructured metallic materials with multifunctional properties. This book begins with the introduction of bulk nanostructured metallic materials, main techniques developed for their fabrication, and importance of multifunctional approach attempting to enhance their multiple properties at the same time (Chap. 1). The main concepts of a nanostructural design to achieve superior properties are presented and thoroughly discussed in Chap. 2. Multifunctional properties of bulk nanomaterials are considered in detail in Chap. 3. Particular attention is devoted to microstructure—property relationships and the role of individual microstructural features, which provides the central theme. Finally, advantages of current and potential innovative applications of bulk nanomaterials in various engineering sectors are described in detail in Chap. 4.

This book has been written primarily for the researchers working on materials science and engineering of bulk nanostructured metallic materials with superior properties, although we believe it will also serve as a useful guide to both current and potential producers and users of nanostructured materials. For this reason, books and articles for further reading are listed at the end of each chapter and are augmented by the references included with many of the figures and tables.

The authors would like to acknowledge gratefully numerous collaborators around the world, whose names are presented in the reference list.

Contents

Chapter 1
Introduction

1.1 What Are Bulk Nanostructured Metallic Materials and How Are They Processed?

We would like to begin this book with introduction to the concept of bulk nanostructured metallic materials and the modern techniques for their fabrication. Bulk nanostructured metallic materials have been the object of extensive research for the past 25 years [1]. In 1988, the first report was published demonstrating the potential for achieving ultrafine grains within the submicrometer range through the application of severe plastic deformation (SPD) to bulk coarse-grained metallic materials, resulting in the enhancement of their properties [2]. Nowadays, this approach is generally termed SPD processing. After the first publications, the SPD-processed materials with submicrocrystalline structure attracted a lot of attention that led to the initiation and development of many research activities around the world devoted to processing and measuring their characteristics [3, 4]. The research activity in this field has both continued to develop and very much expanded up to the present day [4–7].

The SPD concept is based on the fact that a metal specimen is subjected to very high plastic strains ($\varepsilon > 4$–6) under complex stress state and very high hydrostatic pressure, leading to refining the coarse grains down into submicro- and nanograins [3]. Thus, the SPD has often been referred to as ‘top–down’ approach. Depending on the final grain size, the materials with ultrafine-grained (UFG) structure were classified as follows [4]:

1. Submicrocrystalline materials are those with a grain size in the range of 100–1000 nm;
2. Nanocrystalline materials are those with a grain size below 100 nm.

However, as it is shown in Chap. 2, the UFG metallic materials processed by SPD techniques are characterized not only by grains with size below 1 μm, but also by a number of nanoscale structural elements such as nanoclusters of solute atoms and

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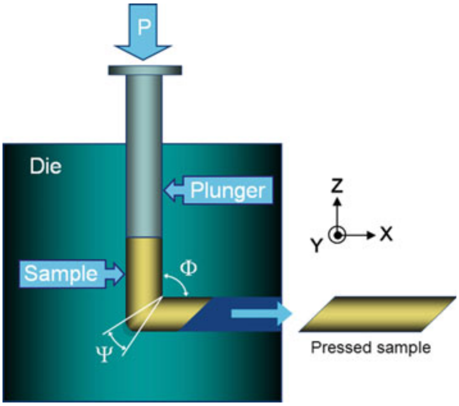
nanoparticles that can considerably influence their properties. Therefore, these materials are often referred to as a class of 'bulk nanostructured materials' and this definition has been widely used by the international research community (www.nanospd.org) [5, 6].

Numerous SPD techniques were developed for grain refinement in metallic materials, and their detailed list can be found in the recent comprehensive overviews [4, 7]. Below, we shortly describe three most popular SPD techniques mastered at many research laboratories around the world.

1. **Equal channel angular extrusion (ECAP)**. This technique was first introduced by Segal et al. in the earlier 1980s [8], later in the beginning of 1990 was developed by Valiev et al. for producing UFG metals, and now has become as the most important and the most widely used SPD method [4, 9]. The ECAP technique imposes large plastic deformation on a large billet by simple shear [8]. The billet is pressed through a special die which has two channels having the same cross sections and intersecting at an angle Φ in the range of 90°–120° (Fig. 1.1). The billet can be subjected to several ECAP passes in order to increase the total strain induced into the billet. There are four basic processing routes in ECAP, and these routes introduce different slip systems during the pressing operation, so that they lead to significant differences in the microstructures produced by ECAP [10–12]. These processing routes are schematically represented in Fig. 1.2 [13]: Thus, in route A, the sample is pressed without rotation, in route B_A, the sample is rotated by 90° in alternate directions between consecutive passes, in route B_C, the sample is rotated by 90° in the same sense (either clockwise or counterclockwise) between each pass, and in route C, the sample is rotated by 180° between passes.

In the early works on ECAP processing of Al alloys aiming at producing UFG microstructures [14–17], it was shown that 1–2 ECAP passes (inserting strain of ~1–2 into processed billets) were usually sufficient for considerable grain refinement. However, the dislocation cell structures formed exhibited predominantly low-angle grain boundaries (LAGBs). Significant increase in the number of ECAP

Fig. 1.1 Schematic presentation of ECAP die



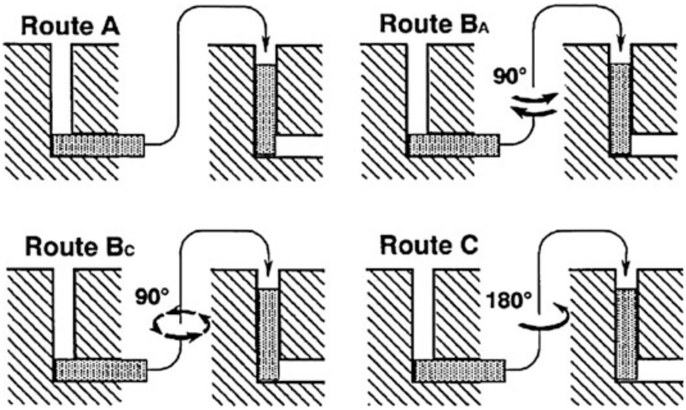


Fig. 1.2 The four fundamental processing routes in ECAP. The figure is reproduced from [13] with permission from the publisher

passes up to 8–12 resulted in the formation of homogeneous UFG microstructure containing predominantly high-angle grain boundaries (HAGBs) due to the transformation of LAGBs into HAGBs [18]. It was demonstrated that route B_C contributes to this microstructure evolution most efficiently leading to the formation of ultrafine equiaxed grains/subgrains, whereas processing through routes A and C resulted in microstructure mainly consisting of elongated grains/subgrains [16, 17]. Other parameters to control the microstructure evolution during ECAP processing include geometrical parameters of ECAP die (Fig. 1.1), processing temperature and pressing speed [9].

The main shortcoming of the conventional ECAP technique is low efficiency and high wastage of processed material. To reduce the processing cost and to save the material, a continuous ECAP processing technique (a combination of ECAP with the well-established Conform process) was developed for the production of long-length rods and wires [19]. This process is illustrated in Fig. 1.3. It is based on using a rotating shaft containing a groove so that the workpiece is fed into the groove and is driven forward by frictional forces. This approach has been employed for processing bulk nanostructured metals on a commercial scale through continuous large-scale production, as demonstrated in Chap. 4.

2. **High-pressure torsion (HPT)**. In HPT, a small disk is placed between two anvils and one of them is able to rotate under the pressure of several GPa, thus deforming the disk by pure shear [20]. Schematic illustration of the HPT processing is presented in Fig. 1.4. Although the fundamental principles of this procedure were first proposed more than 70 years ago [21], processing by HPT gained significant importance only within the last 20 years when it was recognized that this metal-forming process provides an opportunity for producing ultra-fine grained structures [2, 3]. The main advantage of HPT is that under high pressure, very high strains can be induced into sample without its failure, so other mechanisms of microstructure evolution can be evolved once high

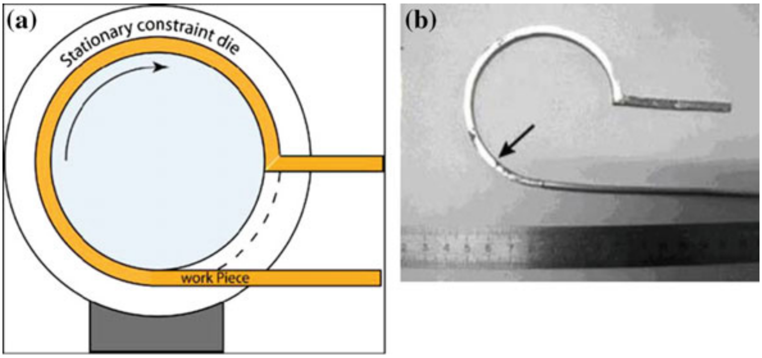
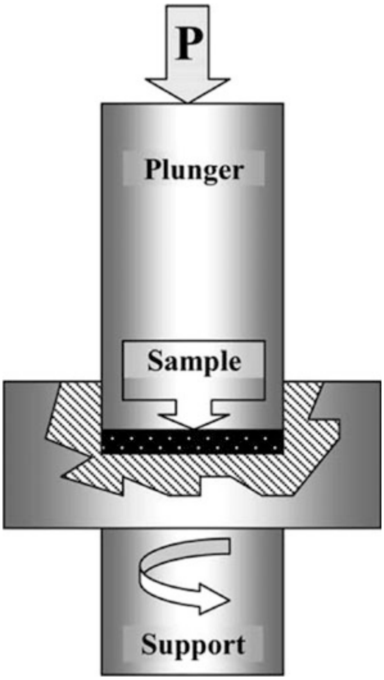


Fig. 1.3 **a** A schematic illustration of an ECAP-Conform setup; **b** an Al workpiece in the process of ECAP-Conform where the arrow denotes the transition to a square cross section. The figure is reproduced from [19] with permission from the publisher

Fig. 1.4 Schematic illustration of HPT processing. The image is reproduced from [22] with permission from the publisher



strains are reached and microstructures with smaller grain sizes can be generated [22, 23]. Even hard to deform metallic materials, such as tungsten [23], can be subjected to HPT processing due to very high pressures applied. Two main shortcomings of standard HPT are a small sample size and inhomogeneous strain induced into processed disks leading to inhomogeneous microstructure along the disk radius [20, 24]. The latter can be solved via increase of

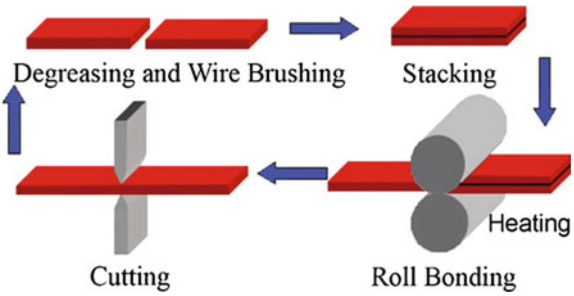


Fig. 1.5 Schematic illustration of the procedure of ARB process. The image is reproduced from [30] with permission from the publisher

deformation strain (number of HPT turns) leading to a more homogeneous microstructure along the disk radius [25] though a small unprocessed area might remain in the center of disk.

3. **Accumulative roll bonding (ARB)**. It is a method of rolling a stack of metal sheets, which is repeatedly rolled to a severe reduction ratio, sectioned into two halves, their surfaces are degreased and brushed, and the halves are piled again and rolled, as shown in Fig. 1.5 [26, 27]. It should be noted that ARB involves not only deformation, but also bonding (roll bonding). Only sheets can be produced via ARB method. The UFG microstructures developed in metallic materials by ARB technique are usually characterized by strong anisotropy. First, the grains are often elongated along the rolling direction, though it was shown that annealing of the ARB-processed highly pure Al can lead to the formation of more equiaxed UFG microstructure [28]. Second, ARB results in the formation of crystallographic texture, and the overall texture intensity is determined by strain induced into sample [29, 30]. Crystallographic texture can vary through the sheet thickness due to high friction between the roll and the material during ARB. This is an ideal method for fabrication of metal sheets with UFG microstructures. Very recently, it was also demonstrated that multi-layered nanolamellar composites [31] and particle-reinforced nanocomposites [32] can be successfully produced via this technique. However, ARB has a few disadvantages in comparison with other SPD methods: (1) The ARB processing requires high degree of technological precision and it is time-intensive; (2) quality of bonding between layers might affect mechanical and service properties of the final nanostructured sheets.

Another approach that can be used for the production of bulk nanostructured materials is based on fabrication and consolidation of nanopowders [33]. It has also been often referred to as ‘bottom-up’ approach. The main challenge in using this technology is the retention of nanostructures of the sintered materials [34]. In particular, cold isostatic pressing (CIP) (which allows to avoid the grain growth during long hot sintering) is a promising technology for the fabrication of bulk nanocrystalline materials. Still, CIP should in some cases be combined with hot isostatic pressing, or other technological routes, to ensure the required strength and density of specimens. The main shortcomings of the bottom-up approach include (1) porosity typically present in the samples produced via this technique, (2) contamination induced into samples during fabrication [33], and (3) very high manufacturing labor costs. Therefore, this approach does seem to have a potential for a wide commercialization at industrial scale.

1.2 About Importance of Multifunctional Approach in Studies on Metallic Materials

Materials design has traditionally involved selecting a suitable material for a given application. Materials are often chosen by 'trial and error' or simply on the basis of what has been used before. While this approach frequently works, it does not always lead to optimization or innovation. Presently, a paradigm shift is underway in which this classical materials selection approach is replaced by design of material microstructure to achieve certain performance requirements, subject to constraints on individual properties such as strength, conductivity, and corrosion resistance. Here, we would like to refer to the book by Prof. Michael Ashby of Cambridge University as the most authoritative source of information [35]. The Ashby approach for materials selection starts by asking three key questions:

- What is the *function* of the component in the design?
- What *objectives* need to be optimized?
- What *constraints* must be satisfied?

For example, a dental implant (function) needs to be fully biocompatible with human body (objective) for a specified strength and cost (constraints). Other constraints on the design can include machinability and fatigue life. As we see, material performance for a specific application is very rarely governed by one individual property, which can be easily found in handbooks or manufacturers datasheets, but by combinations of two or more of these properties. So modern engineering requires materials with a set of multifunctional properties. Disparate material properties need to be engineered and optimized simultaneously.

However, now we face a problem which is based on the fact that the disparate material properties can often be very conflicting. This can be easily illustrated by materials selection charts, which are also referred to as Ashby plots [35], where one property is plotted against another one for further analysis. Every material in these charts is represented as a point or as an ellipse showing the range of its possible values. These charts provide a quick, visual indication of the relative position for all of the materials being considered. This is sufficient to focus on likely candidates and also helps to develop an intuitive feel for the relative performance of materials. Another advantage of these charts is that they provide a graphical environment to make trade-offs between conflicting properties. Let us have a look at a simple example: Electrical engineering needs conductors having enhanced mechanical

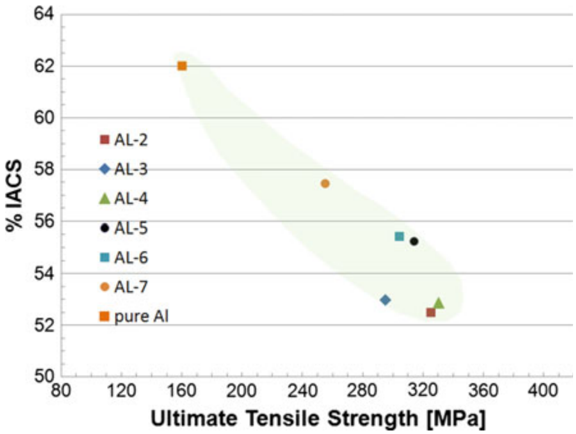


Fig. 1.6 Electrical conductivity versus ultimate tensile strength in some Al-based conductors [36]

properties (enhanced strength) combined with improved physical properties (electrical conductivity). Figure 1.6 shows electrical conductivity (in IACS[1]) plotted versus ultimate tensile strength for a range of the commercial Al–Mg–Si alloys, which have been widely used in electrical engineering for overhead power transmission lines [36]. It is clearly seen that electrical conductivity of these alloys decreases with increasing mechanical strength. A material with the satisfying strength and conductivity can be selected from the chart for a given application.

So far, we have been focused on multifunctional properties of conventional coarse-grained metallic materials. What about bulk nanostructured materials? The research activities carried out by the authors and recent achievements in several laboratories around the world have clearly demonstrated that nanostructuring in metallic materials can open new avenues for solving the conflicting objectives in materials design, so one property can be enhanced without any sacrifice of another property or even both, or several conflicting properties can be enhanced simultaneously. The main objective of the present work is to analyze the multifunctional properties of bulk nanostructured metallic materials with respect to their potential applications in various sectors of engineering. As the multifunctional properties of nanomaterials are controlled by microstructure, the next chapter of this book is devoted to the nanostructural design in metallic materials.

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Chapter 2

Nanostructures in Materials Subjected to Severe Plastic Deformation

As was already noted above, the first observations of the production of Ultrafine-grained materials (UFG) microstructures in bulk materials using the ‘top-down’ approach appeared in the scientific literature in the early 1990s in several publications by Valiev et al. dealing with pure metals and alloys [1, 2]. It is important to note that these early publications provided a direct demonstration of the ability to employ heavy plastic straining in the production of bulk materials having fairly homogenous and equiaxed microstructures with grain sizes in the submicrometer or nanometer ranges and with a high fraction of high-angle grain boundaries. By now, the formation of UFG structure by Severe plastic deformation (SPD) processing is shown in many metals and alloys. Furthermore, recently a number of other nanostructural features (twins, particles, and so on) have been revealed in SPD-processed materials. The type and the morphology of such nanostructured elements and their density determine the mechanical, chemical, and physical properties of bulk nanomaterials. Over the last few years, the studies of bulk nanostructured materials tend to be more and more oriented to the development of their advanced and superior properties, and in this case, the conception of nanostructural design plays a far more important role. For example, the critical parameter for bulk nanostructured metals and alloys produced by SPD together with the grain refinement to the nanosized range is the grain boundary structure because the boundaries can be formed as low- and high-angle, special and random, and equilibrium and non-equilibrium boundaries depending on the SPD processing regimes [3, 4]. Furthermore, boundaries having different structures exhibit different transport mechanisms (deformation, diffusion, etc.) including grain boundary sliding, which in turn leads to differences in the properties. In such a manner, this opens a new way for advancing the properties of UFG materials by appropriately tuning their grain boundary structures.

The concept of nanostructural design of materials is schematically illustrated in Fig. 2.1—the scheme modifies and further develops a well-known concept of contemporary creation of novel materials through the integration of theory and modeling, structure characterization, processing and synthesis, as well as the properties of studies. In addition, nanostructuring of bulk materials deals with a far larger number of structural parameters related to the grain size and shape, lattice defects in the grain interior, as well as with the grain boundary structure, and also

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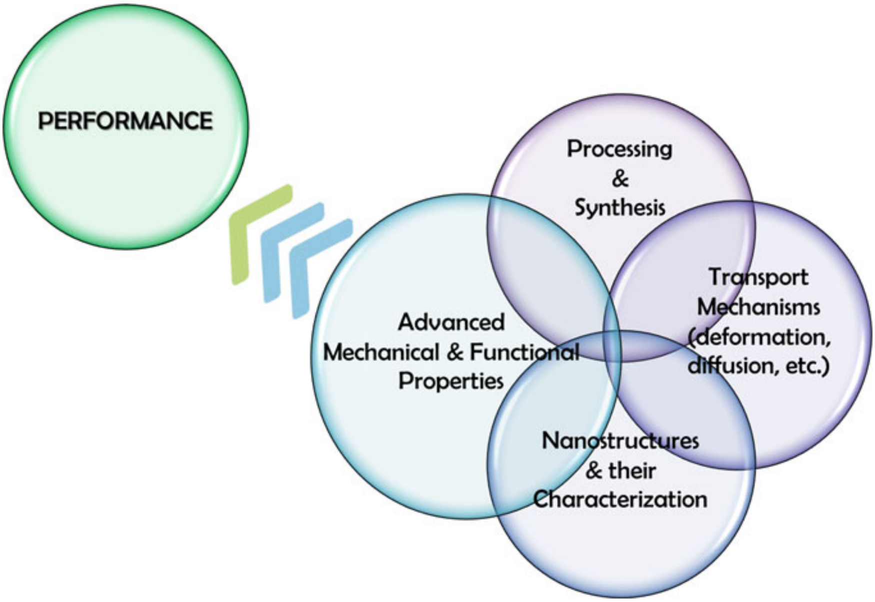

Fig. 2.1 Principles of nanostructural design of bulk nanostructured materials. The figure is reproduced from [5] with permission from the publisher

the presence of segregations and second-phase nanoparticles. This provides an opportunity to vary the transport mechanisms and therefore can drastically increase the properties. For example, nanostructuring of bulk materials by SPD processing not only permits a considerable enhancement of many mechanical and physical properties but also contributes to the appearance of multifunctional materials [6–10]. In this respect, one can anticipate that already in the near future, nanostructuring of materials by various processing and synthesis techniques may provide many new examples in the development of materials with superior properties for advanced structural and functional applications.

This book is devoted specifically to bulk nanostructured metallic materials produced by SPD. In recent years, a breakthrough has developed in studies of nanostructured metals and alloys as advanced structural and functional materials, associated both with the development of new routes for the fabrication of bulk nanostuctured materials using SPD and with investigations of the fundamental mechanisms that lead to the new properties of these materials.

The main nanostructural elements produced in the materials subjected to SPD processing, we consider in more detail below. In general, it is possible to identify four types of nanostructured elements in metals and alloys subjected to SPD that can be observed through the application of modern techniques of structural analysis such as high-resolution transmission electron microscopy (HRTEM) and 3D-atom probe [4, 11–14].

2.1 Grain Refinement via Severe Plastic Deformation

As it was mentioned above, SPD techniques have been used mostly because of their ability to produce UFG metallic materials through microstructure refinement in initially coarse-grained materials. The final grain size produced depends strongly on both processing regimes and the type of material. For pure metals, the mean grain size is typically about 100–200 nm after processing by HPT and about 200–300 nm after processing by ECAP or other techniques. For alloys and intermetallics, the grain size is usually smaller, and in some cases, it is in the range of 50–100 nm.

For the formation of UFG structures with primarily high-angle grain boundaries through SPD processing, five basic rules for grain refinement have been defined [15], four of which are related to the requirements for SPD processing regimes and routes, while the fifth is related to the intrinsic nature of the material under study. These rules are briefly considered below. A detailed description of SPD processing regimes and routes may be found in recent overviews on the subject [12, 16–18].

SPD processing at low temperatures (as a rule, less than 0.4 T_m) is referred to as a rather important requirement for its realization. Only under these conditions is it possible to achieve dislocation densities of 10^{14} m^{-2} or higher, up to the limiting values of 10^{16}–10^{17} m^{-2} [16, 19], which is necessary for the formation of the UFG structure. Higher processing temperatures result in a lower accumulated dislocation density and an increase in grain size above 1 μm.

The degree of strain during processing (true strain) should exceed 6–8. Although a considerable refinement of the microstructure and the attainment of dislocation densities exceeding 10^{14} m^{-2} occur at a strain of 1–2 [16], the formation of UFG structures with a majority of high-angle grain boundaries requires further straining.

High hydrostatic pressures, usually >1 GPa, are important for efficient SPD processing. High pressure contributes to the enhancement of deformability of the processed material and, therefore, provides solidity of the billets even under high strain [12, 20]. Furthermore, the pressure affects the diffusion and thus suppresses the annihilation of deformation-induced lattice defects [21].

The formation of equiaxed ultrafine grains depends on the vorticity of the metal flow. At the macrolevel, the vorticity is related to the non-monotonous character of deformation. For example, the ECAP with route B_C, in which the billet is rotated by 90° between each pass, is considerably more effective for grain refinement by comparison with route C, in which the billet position does not change [12]. At the microlevel, the vorticity is associated with grain rotations and displacements [22].

Grain refinement is also related to the atomic structure of the material processed. The ordering of alloys or low stacking fault energy (SFE), all other conditions being equal, contributes to the enhancement of an accumulated dislocation density and considerably reduces the grain size produced [16]. For example, for Pd–20 % Ag alloy with SFE = 125 mJ m^{-2}, in comparison with pure Pd with SFE = 190 mJ m^{-2}, during HPT (5 rotations under $P = 6$ GPa), the grain size produced equals 150 nm for Pd–20 % Ag and 240 nm for Pd, respectively [23].

These five rules are required and typically sufficient conditions for effective grain refinement by SPD processing.

2.2 Grain Boundaries in Nanostructured Materials

With grain sizes in a submicron (100–1000 nm) or nanocrystalline (<100 nm) range, UFG materials contain in their microstructure a very high density of grain boundaries, which can play a significant role in the development and exhibition of novel properties. For this reason, UFG materials can be typically considered as interface-controlled materials [24].

Already in first works on nanocrystalline materials pioneered by Gleiter and colleagues, it was suggested that grain boundaries can possess a number of peculiar features in terms of their atomic structure in contrast to grain boundaries in conventional polycrystalline materials [24, 25]. This is of particular importance for UFG materials produced by SPD methods.

Depending on the regimes of SPD processing, different types of grain boundaries can be formed in the UFG materials (high- and low-angle, special and random, and equilibrium and so-called non-equilibrium grain boundaries containing extrinsic dislocations) [16, 26], which paves the way to grain boundary engineering of UFG materials, i.e., to the control of their properties by means of varying the grain boundary structure.

The notions on non-equilibrium grain boundaries were first introduced in the scientific literature in the 1980s [27, 28] reasoning from investigations of interactions of lattice dislocations with grain boundaries. According to [28], the formation of a non-equilibrium grain boundary state is characterized by three main features, namely excess grain boundary energy (at the specified crystallographic parameters of the boundary), the presence of long-range elastic stresses (Fig. 2.2), and enhanced free volume. Discontinuous distortions of crystallographically ordered structures, which may come about by accommodation problems of differently oriented crystallites of finite sizes or by high densities of lattice dislocations and their interaction with grain boundaries, can be considered as sources of elastic stress fields that modify the atomic structure of high-angle grain boundaries so that their excess free energy becomes enhanced. These ‘unusual’ grain boundaries have been termed ‘non-equilibrium’ grain boundaries although in a strict sense, each grain boundary is a non-equilibrium defect if segregation effects (see Sect. 2.4) are not to be considered. Since, however, the term has been accepted and utilized by the entire community who works on severe plastic deformation, we also use it here, describing as ‘grain boundaries’ with strain distorted structures.

A model for these non-equilibrium grain boundaries has been developed by Nazarov, Romanov, and Valiev in a series of papers [29, 30] processing on their formation and behavior. Lattice dislocations that are created during the plastic straining move toward high-angle grain boundaries on their respective glide planes during continued straining and then, when reaching a high-angle grain boundary, transform into so-called extrinsic grain boundary dislocations, i.e., dislocations that do not contribute toward the misorientation of the two adjacent grains. As a net effect, high-angle grain boundaries with high densities of such extrinsic grain

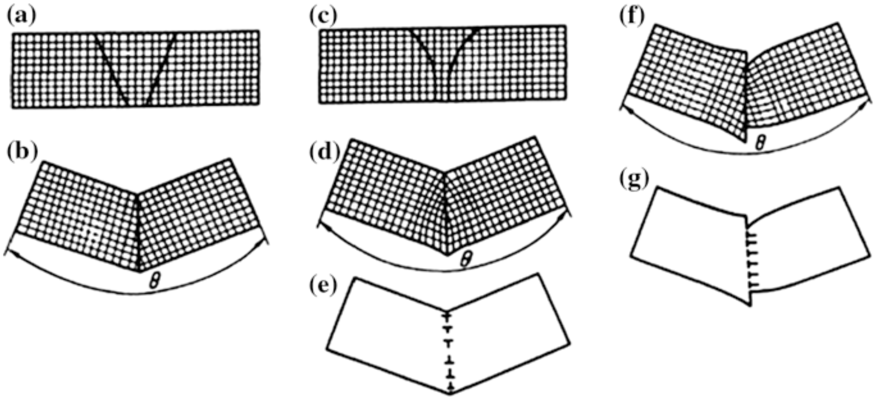

Fig. 2.2 Phenomenological engineering of grain boundaries via thought cuts: **a**→**b** equilibrium grain boundary (bunches of deformation are connected without mesoscopic strain); **c**→**d** and **a**→**f** non-equilibrium grain boundaries (deformation is required for crystal joint–bending and tension–compression, respectively); **e** and **g** schemes of grain boundary dislocation (GBD) complexes initiating the same character of mesoscopic elastic distortions as in (**d**) and (**f**). The figure is reproduced from [28] with permission from the publisher

boundary dislocations would also contain increased energy and free volume and considerable microstrain associated with the grain boundary region [29].

In earlier studies of grain boundaries in UFG materials processed by SPD techniques, there have been already used various, often mutually complementary, structural methods: transmission electron microscopy (TEM), X-ray diffraction, Mössbauer spectroscopy, dilatometry, differential calorimetry, and others (see, e.g., [16]). They clearly evidenced that mostly high-angle grain boundaries leading to grain refinement can be formed after optimization of SPD processing routes and these grain boundaries possess specific non-equilibrium structures. Later, structure-sensitive probes have been applied that are sensitive to modifications of the atomic structure, such as grain boundary diffusion measurements or HRTEM analyses, in order to identify and characterize transformations of the grain boundary structure due to the severe deformation processing.

For example, as illustrated in Fig. 2.3 [31], an excessively high density of dislocations, facets, and steps are observed at grain boundaries of the UFG alloy Al–3 % Mg after HPT that leads to a non-equilibrium state of boundaries with a crystal lattice distortion zone of ~5–7 nm in width [32, 33] and which considerably influences the properties of the alloy. Non-equilibrium grain boundaries are typical for different materials after SPD processing, and their role in the mechanical behavior of UFG materials is observed in a number of reports [33, 34].

Horita et al. [31] and Valiev et al. [16] noticed also serrated contrast features in bright field TEM images and also in HRTEM analyses, respectively, that were interpreted as evidence for a high local density of dislocation structures associated with the apparent non-equilibrium grain boundary. However, due to the possible Moiré effect occurring in the projection of sample regions near interfaces and due to

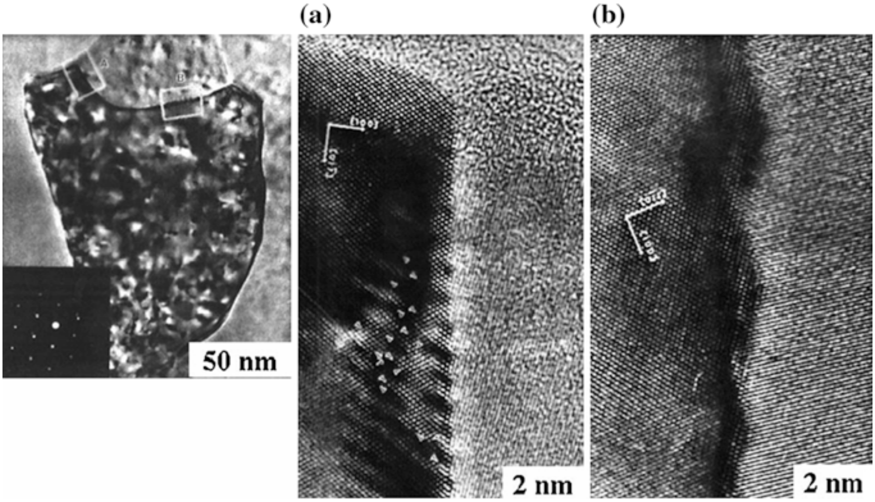

Fig. 2.3 TEM images of non-equilibrium grain boundaries in the UFG Al–3 % Mg alloy with a grain size of ~100 nm illustrating high-resolution photographs of regions *A* and *B*. The images are reproduced from [31] with permission from the publisher

the delocalization of information in HRTEM analyses by aberrations of the electromagnetic lenses, unambiguous interpretations of grain boundary structures require more sophisticated analyses, which today can be provided by the use of so-called Cs-corrected TEMs that are corrected for spherical aberration. Figure 2.4a shows the HRTEM image of a grain boundary with both adjacent grains oriented with their <110> zone axis parallel to the electron beam in a Pd90Ag10 alloy that had been severely deformed by repeated rolling and folding. The details of the synthesis process are similar to the procedure described earlier [35, 36]. The image was taken with a FEI-Titan TEM equipped with a field emission cathode and a Cs-corrector. The non-equilibrium character of this grain boundary in term of the interpretations given earlier by Valiev et al. is manifested in the non-uniform faceted form (Fig. 2.4a) of the two joining <110>-oriented grains. Grain boundaries with similar features are commonly observed for materials after SPD processing [37]. Yet, it should be noted that not all grain boundaries in severely deformed materials present morphologies as in Fig. 2.4a. In fact, only a minority of grain boundaries with an average spacing of a few grain diameters display non-uniform faceting, implying that also during SPD processing, the localization of deformation controls the evolution of the microstructure.

In order to analyze whether the non-uniformly faceted grain boundaries might correspond to non-equilibrium grain boundaries, the residual microstrain present at the grain boundary shown in Fig. 2.4a was analyzed by the method of geometric phase analysis (GPA) that allows calculating relative magnitudes of the in-plane components of the strain tensor and of the tensor of rigid body rotation with respect to a reference lattice, based on the intensity distribution in high-resolution electron

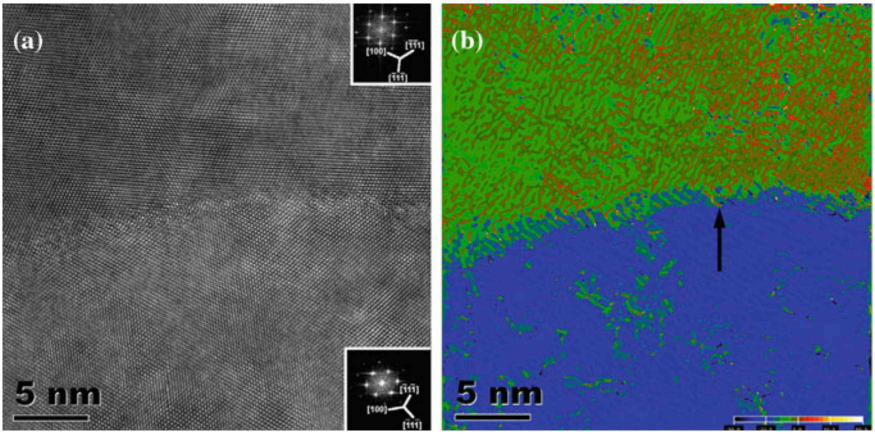

Fig. 2.4 **a** HRTEM micrograph showing two adjacent grains of Ag10Pd90 (after 110 cycles) both oriented along the <110> direction. The grains are rotated by an angle of 23.7° with respect to each other. The grain boundary appears here in a wavy faceted form. The Fourier transforms of the images of both grains are given as inserts. **b** Strain map showing the in-plane rigid body rotation xy [rotations on a scale from −50○ (*dark blue*) to +60○ (*yellow-white*) (anticlockwise positive) are displayed]. Hot spots (see *arrow* pointing on one example) in *bright yellow color* (where the phase of the electron wave changed discontinuously), which are discernible at high density along the GB if examined at higher magnification, refer to dislocation cores. The *greenish color* of the upper grain represents the zero rotation taken as a reference. The images are reproduced from [40] with permission from the publisher

micrographs [38, 39]. Details concerning the analysis and concerning the conditions under which the HRTEM micrograph was taken can be found in [40]. One result of this analysis is displayed in Fig. 2.4b as the rigid body rotation. In addition to the misorientation between the two neighboring grains, a clear and significant variation of the color representing the variation of the relative rotations of the lattice is observed in the near-boundary region. It should be noted that the bright spots (‘hot spots’) in Fig. 2.4b represent regions where a discontinuity in the transmitted phase of the electron wave occurs, i.e., these spots mark the positions of the core region of full or partial dislocations. Additionally, local structures within the distorted grain boundary region that show an abrupt change in the local orientation of the crystal lattice with respect to the orientation of the lattice of the parent grain could also contribute such bright features in the strain maps, since the linear density of the hot spots that is estimated to be about 10^9 m^{-1} is obviously much too high to be associated with the extrinsic GB dislocations only.

Thus, with respect to the grain boundary structure in SPD-processed materials with ultrafine grain size, recent studies enable to conclude that

- Non-equilibrium grain boundaries with strain distorted structure exist in UFG materials, and these specific grain boundaries possess an increased free-energy density, increased width, high density of dislocations (full or partial) associated with the near-boundary region, and correspondingly large residual microstrain.

- The structural width of non-equilibrium grain boundaries is about several nanometers, and it seems significantly larger than the width of relaxed high-angle grain boundaries in annealed coarse-grained materials.

2.3 Nanotwins in Metallic Materials After Severe Plastic Deformation

It is well known that contrary to coarse-grained metals, which become more difficult to twin with decreasing grain size, nanocrystalline face-centered-cubic (fcc) metals become easier to twin with decreasing grain size, reaching a maximum twinning probability, and then become more difficult to twin when the grain size decreases further, i.e., exhibiting an inverse grain-size effect on twinning. Molecular dynamics simulations and experimental observations have revealed that the mechanisms of deformation twinning in nanocrystalline metals are different from those in their coarse-grained counterparts. Consequently, there are several types of deformation twins that are observed in nanocrystalline materials, but not in coarse-grained metals [41]. It has also been reported that deformation twinning can be utilized to enhance the strength and ductility of nanocrystalline materials.

In particular, nanotwins are typical of the materials after ECAP at lower temperatures and/or those subjected to additional cold rolling (CR), extrusion, or drawing. Figure 2.5 shows a TEM image of atom resolution of UFG Cu after ECAP and CR at liquid nitrogen temperature with clearly observed twins of 10–20 nm in size [42]. Such nanostructured defects also have a considerable effect on material strength by, for example, increasing the yield stress (YS) in UFG Cu from ~380 to ~510 MPa [42, 43].

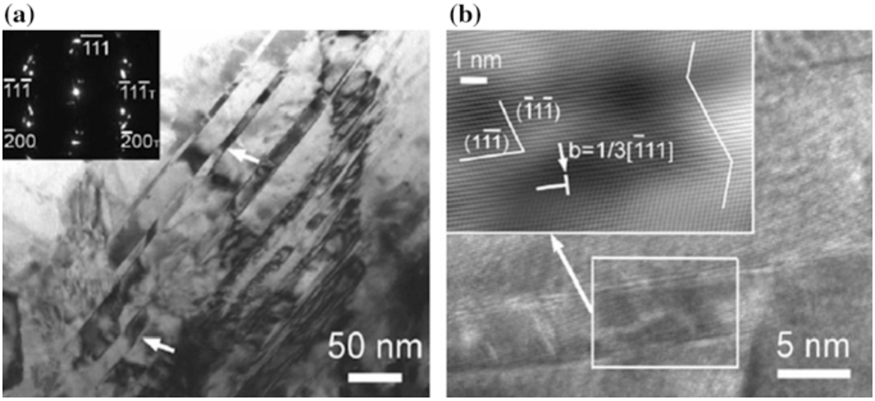

Fig. 2.5 TEM images at **a** low and **b** high magnifications of a typical grain with a high density of deformation twins in UFG Cu processed by ECAP with subsequent cold rolling. The images are reproduced from [42] with permission from the publisher

2.4 Segregations in Nanostructured Alloys Processed by Severe Plastic Deformation

Indirect evidence of grain boundary segregation in UFG materials processed by SPD has been reported in a few cases where the thermal stability has been investigated as a function of the impurity level in Ni [44] or as a function of the concentration of Sb in Cu [45]. However, only recently, reports providing direct evidence of grain boundary segregation in UFG materials processed by SPD have appeared. Most of them rely on atomic scale characterization thanks to atom probe tomography (APT). This technique provides only very limited crystallographic information, and the grain boundary misorientation is usually unknown. Moreover, only small grain boundary areas can be analyzed making any statistics almost impossible. Anyway, it was demonstrated that grain boundary segregation in SPD-processed materials is not a marginal feature but could be observed in various kinds of alloys.

Grain boundary segregations were reported in an AA6061 processed by HPT [46] or ECAP [47] where Mg, Cu, and Si segregations along planar defects attributed to grain boundaries were observed. The solute element-enriched layer is about 2 nm, and the local enrichment does not exceed 2 at.%. Grain boundary segregations were also reported for an Al–Mg–Cu–Zn alloy processed by ECAP (Fig. 2.6) [14], an AA7075 processed by HPT [48], and an Al–6.8 % Mg processed by HPT [49]. In the HPT processed AA7075 (20 turns), a mean grain size of about 100 nm is achieved, with a large fraction of high-angle grain boundaries. Using APT, very strong Mg local enrichments up to 25 at.% in a much thicker layer (6–8 nm) were observed (Fig. 2.7). This thickness is much larger than the grain boundary width measured on HRTEM images thanks to GPA (about 2 nm), where this parameter was defined as a zone where the averaged rotational component of

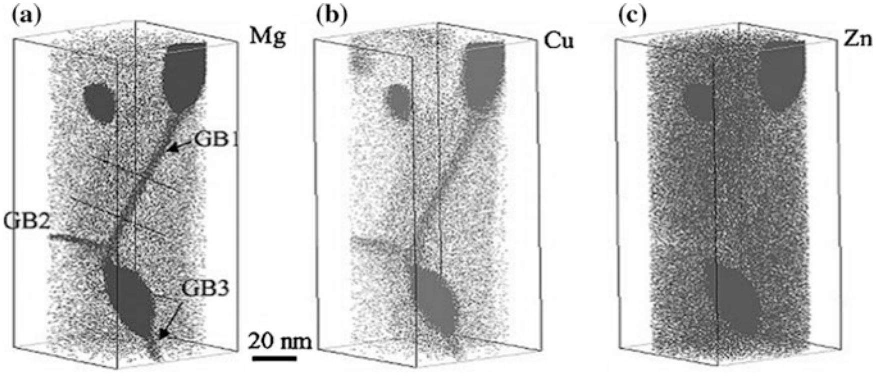

Fig. 2.6 Elemental maps of polycrystalline region of an Al–Zn–Mg–Cu alloy after 8 passes of ECAP. **a** Mg, **b** Cu, and **c** Zn maps. The figure is reproduced from [14] with permission from the publisher

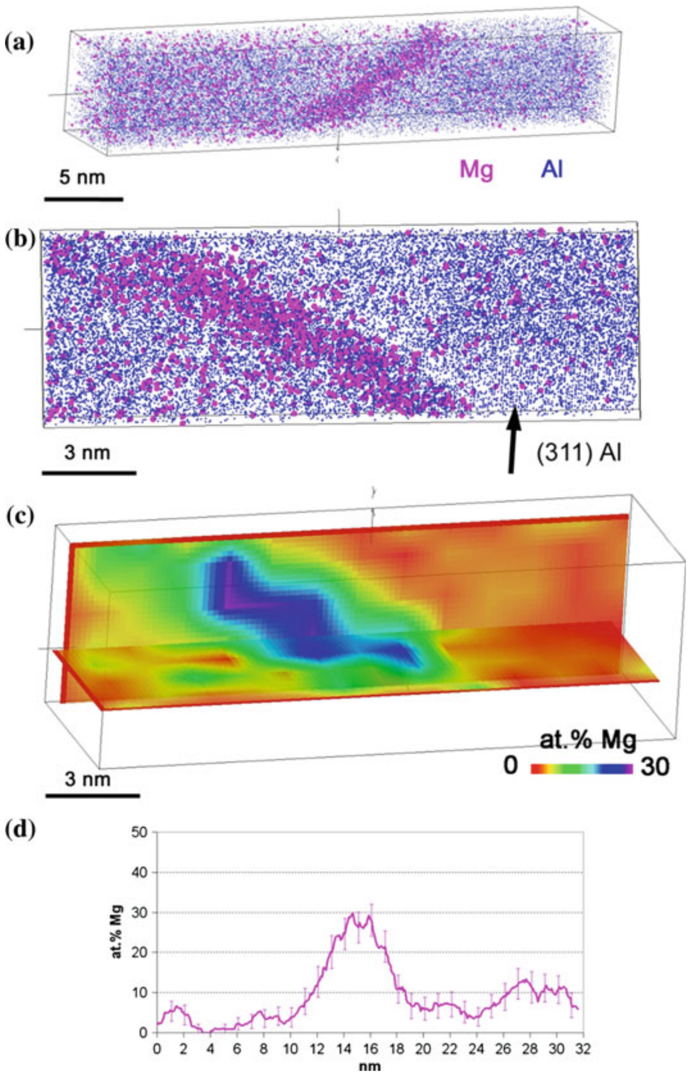

Fig. 2.7 3D reconstruction of an analyzed volume in the UFG 1570 alloy: **a** full data set showing a planar segregation of Mg (Al atoms are displayed as dots and Mg atoms as bubbles); **b** selected part orientated to display (311)Al atomic planes on the right of the planar segregation; **c** 2D chemical map showing the Mg concentration fluctuations within the volume; **d** concentration profile computed across the segregation (sampling volume thickness 1 nm). The figure is reproduced from [49] with permission from the publisher

the strain field is changed from the value in one grain to that in its neighbor. It seems a non-equilibrium grain boundary may incorporate a larger amount of segregating atoms with respect to relaxed interfaces (as a result of the increased free volume), but the thickness of the segregated layer might not only be determined by the distorted layer near the non-equilibrium GB (as it is defined by GPA). APT data also revealed that grain boundaries are not homogeneously covered and that the Mg concentration in solid solution may strongly vary from one grain to another [49]. Such features might indicate that the local configuration of the GB and especially dislocations lying in the vicinity of the boundaries may affect the distribution of solute elements. It is also interesting to note that this material exhibits a very high YS after HPT processing, much higher than a prediction based on the Hall–Petch law. Thus, it seems that GB segregations could significantly affect the deformation mechanisms (dislocation nucleation and glide) in nanostructured metallic materials processed by SPD.

2.5 Precipitation of Second Phases in Alloys During and/or After Severe Plastic Deformation

The formation of particles has been observed in many alloys subjected to SPD after solution quenching [11, 12]. Figure 2.8 illustrates an example of such nanoparticles ~10–20 nm in size precipitated in the UFG AA6061 after ECAP-PC processing [50]. The presence of nanoparticles is related to dynamic aging and provides additional precipitation hardening of the alloys [12, 50]. However, the size and morphology of precipitates are usually closely related to the SPD processing parameters. Recently, this approach has been used for the development of a new strategy for nanostructural design in the Al alloys for the new generation conductors [52]. This strategy is based on intelligent manipulation with the strengthening mechanisms and mechanisms of electrical resistivity by grain refinement down to submicrometer scale, using SPD processing at room temperature, followed by

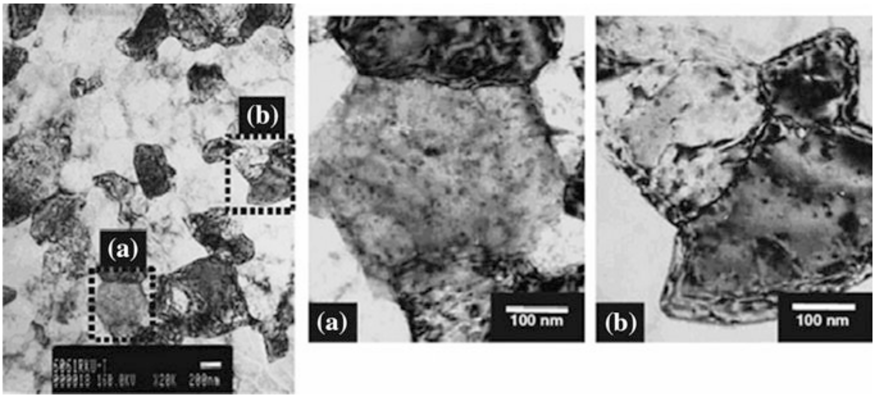

Fig. 2.8 UFG structure of an AA6061 after ECAP with parallel channels (four passes): The formation of nanosized precipitations is clearly visible inside the grain after processing in areas *A* and *B*

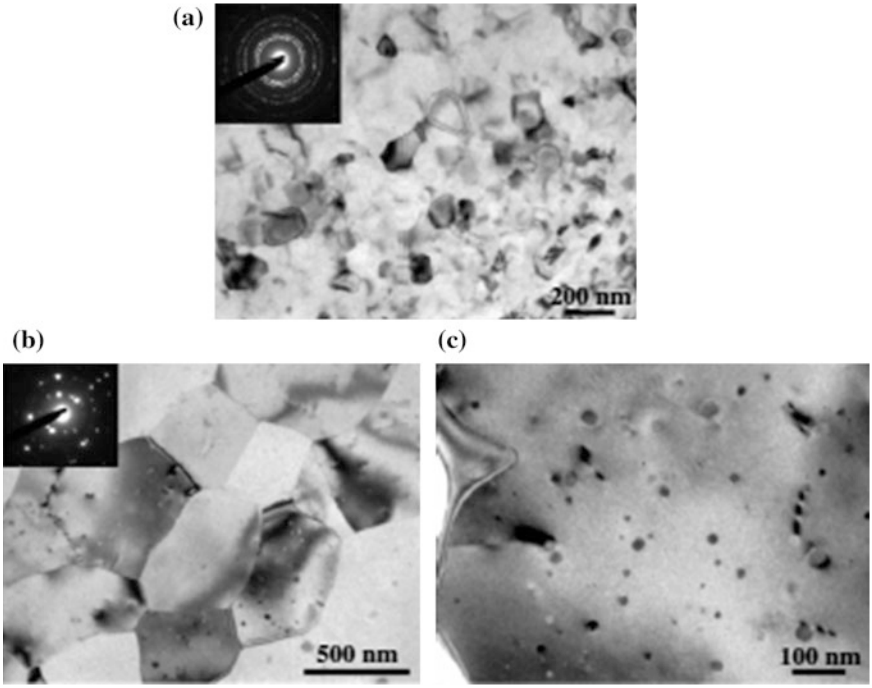

Fig. 2.9 TEM images of the AA6201 subjected to HPT processing at: **a** RT; **b**, **c** 180 °C. **a**, **b** General view of UFG structures, and **c** morphology of precipitates

decomposition of supersaturated solid solution and formation of nanosized second-phase precipitates via dynamic aging during SPD processing at elevated temperatures. These ultrafine-grained (UFG) microstructures with second-phase nanoprecipitates can show superior mechanical strength owing to grain boundary strengthening and precipitation hardening. At the same time, the very low content of solute atoms and the absence of GP zones in the Al matrix result in significantly enhanced electrical conductivity. For experiment, an AA6201 was chosen, which has been widely used as a material for electroconductors [52]. Disks with diameter 20 mm and thickness 1.5 mm were solution treated at 530 °C for 2 h and quenched in water. Then, the disks were subjected to SPD processing by high-pressure torsion (HPT) using unconstrained anvils [17]. Several processing parameters were selected: room temperature (RT) and further straining at 130, 180, and 230 °C. The disks were subjected to one HPT turn at room temperature followed by 20 HPT turns at elevated temperatures.

Careful TEM studies have shown that the alloy processed at RT exhibits a very homogeneous UFG microstructure with a mean grain size of ~130 nm (Fig. 2.9a). The grain interior is characterized by a low density of lattice dislocations. Meanwhile, spreading of spots on selected area electron diffraction patterns and extinction lines inside grains point to the high residual stresses present as a result of the non-equilibrium character of grain boundaries containing extrinsic dislocations [4, 31].

Further HPT straining at elevated temperatures significantly affects the UFG microstructure (Fig. 2.9b). The results of microstructural characterization of the HPT processed AA6201 alloy are presented in Table 2.1. The mean grain size in the alloy increases to 280, 440, and 960 nm after HPT processing at 130, 180, and 230 °C, respectively (Table 2.1). A very important feature of these microstructures is the presence of spherical second-phase nanoprecipitates (Fig. 2.9c). The average size of the second-phase precipitates increases with increasing HPT processing temperature from 10 nm (at 130 °C) to 50 nm (230 °C) (Table 2.1). These nanoprecipitates have been identified as β-Mg_2Si, and they are typically formed as a result of dynamic aging, which occurs during SPD processing of the Al–Mg–Si alloys at elevated temperatures [51, 53, 54]. It should be noted that these nanoprecipitates have a different morphology compared with the nanoprecipitates formed in the material during static aging, which have a needle shape. This was attributed to the strong dislocation activity during SPD processing and the resulting shear of precipitates [52, 53]. The X-ray measurements clearly show that HPT processing leads to a significant decrease in the lattice parameter of the Al matrix (Table 2.1) illustrating a strong decomposition of the supersaturated solid solution. This is in a good accordance with the results of the recent investigations using the 3D APT technique [4]. The lattice parameter in the alloys processed at 230 °C becomes nearly equal to that of the pure Al (4.0494 Å), which indicates near-complete purification of the matrix from the solute atoms as a result of dynamic aging (Table 2.1). The appearance of typical banded diffraction contrast at grain boundaries indicates significant recovery of non-equilibrium grain boundaries during HPT at elevated temperatures (Fig. 2.9b) [32].

From this Chapter, it is seen that manipulation with the SPD processing parameters provides a powerful tool for nanostructural design in the metallic materials. Basically, all microstructural parameters (grain size, grain boundary state, dislocations density, nanosegregations of solute atoms, etc.) can be controlled in the SPD-processed materials in order to tailor their mechanical and functional properties. The effect of microstructure on the properties of the nanostructured metallic materials via SPD is considered in the next chapter.

Table 2.1 Microstructure and mechanical properties of the AA6201 alloy in the studied conditions

Processing	Microstructure	α [Å]
Solid solution treated	CG; $d = 65$ μm	4.0526
T81	CG; $d = 65$ μm	4.0512
HPT at room temperature	UFG; $d = 130$ nm	4.0521
HPT at room temperature + HPT at 130 °C	UFG; $d = 130$ nm, $d_p = 10$ nm	4.0509
HPT at room temperature + HPT at 180 °C	UFG; $d = 130$ nm, $d_p = 30$ nm	4.0505
HPT at room temperature + HPT at 230°C	UFG; $d = 130$ nm, $d_p = 50$ nm	4.0500

d grain size; d_p size of second-phase precipitates; α lattice parameter

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Chapter 3
Multifunctional Properties of Bulk Nanostructured Metallic Materials

This chapter focuses on multifunctional properties of bulk nanostructured metallic materials and structure–properties relationship therein. The most important structural factors affecting mechanical, physical, and chemical properties of the nanomaterials are discussed, and the strategies to their further improvement are outlined. Special attention is paid to nanostructural design for simultaneous improvement of mutually exclusive properties.

3.1 Superstrength and Enhanced Mechanical Properties

Although the mechanical and functional properties of all polycrystalline metallic materials are determined by several factors, the grain size of the material generally plays the most significant and often a dominant role. Thus, the strength of different 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

$$\sigma_y = \sigma_o + k_y d^{-1/2}, \tag{3.1}$$

where σ_o is termed the friction stress and k_y the Hall–Petch constant [1, 2]. It follows from Eq. 3.1 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.

The fabrication of bulk samples and billets using equal channel angular pressing (ECAP), high pressure torsion (HPT), and other severe plastic deformation (SPD) techniques was a crucial first step in initiating investigations into the properties of bulk nanomaterials because the use of SPD processing permitted, and subsequently fully supported, a series of systematic studies using various nanostructured metallic materials including commercial alloys [3–8]. The research

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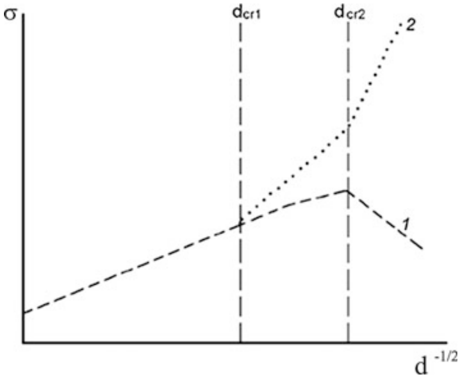
works include strength and strengthening mechanisms, ductility, and ways to its enhancement, fatigue, and wear resistance. The main achievements of these studies are discussed in the section below.

3.1.1 Superstrength and Ductility

During the last two decades, the influence of grain size reduction to nanometer range on the materials strength has been explored in multiple works (see, e.g., [5, 9–11]. The enhancement of strength with grain size reduction in compliance with Eq. 3.1 was observed in many studies (Fig. 3.1), but for nanosized grains (20–50 nm), this relations reported to be typically violated so that the Hall–Petch plot deviates from linear dependence at lower stress values and its slope k_y often becomes negative (the curve 1 in Fig. 3.1). In recent years, this problem has been widely analyzed in both experimental and theoretical studies [5, 10]. At the same time, Hall–Petch relationship breakdown is not observed in ultrafine-grained materials with a mean grain size of 100–1000 nm produced by SPD processing. Moreover, recently it was shown that UFG alloys can exhibit a considerably higher strength than the Hall–Petch relationship predicts for the range of ultrafine grains [12–15]. The nature of such superstrength may be associated with another nanostructural features (dislocation substructures, nanophase particles and segregations, nanotwins, etc.) which could be observed in the SPD-processed metals and alloys (see Chap. 2).

For example, this was shown in studies of the mechanical behavior of Ni subjected to ECAP and subsequent rolling [16]. Figure 3.2 shows the difference in strength between the states of Ni where the grains contain dislocation substructures within the grains and where the grains contain no substructure [17–19]. An attempt was made to describe quantitatively the deviation from the Hall–Petch rule by taking into account the influence of two types of boundaries, high-angle boundaries between grains and low-angle cell boundaries, on the yield stress of the material. Following an earlier analysis [20], it was assumed that each of these types of

Fig. 3.1 The two types of the Hall–Petch slopes within different characteristic length scales



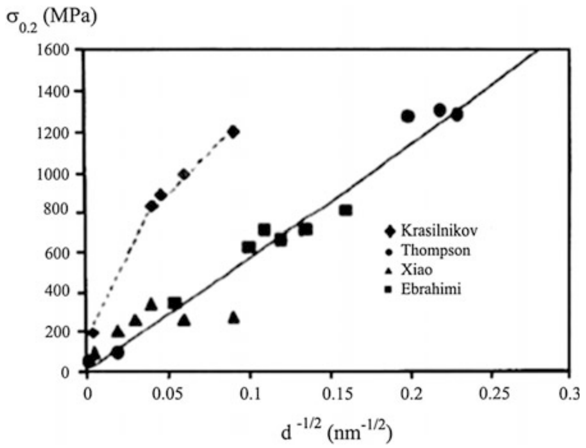


Fig. 3.2 Yield stress as a function of $d^{-1/2}$ for Ni: the continuous line is for material states with grains without substructure, and the dashed line is for nanostructured Ni containing a dislocation substructure [16–19]

boundaries, and also the non-equilibrium state of grain boundaries, contributes in an independent way to the yield stress:

$$\sigma_y = \sigma_o + \sigma_{LAB} + \sigma_{HAB} + \sigma_{NGBs} \tag{3.2}$$

and

$$\sigma_y = \sigma_o + M\alpha Gb\left((1.5S_v\theta/b)_{LAB}\right) + k_y d^{-1/2} + M\alpha Gb(\rho_{GBDs})^{1/2} \tag{3.3}$$

where σ_o is the threshold stress, M the Taylor factor, α a constant ($\alpha = 0.24$), G the shear modulus, b the Burgers vector, θ the misorientation angle of the low-angle grain boundaries, d the average grain size, ρ_{GBDs} the density of extrinsic grain boundary dislocations, k_y the Hall–Petch constant and the term S_v associated with the cell size. The numerical values for the constants were taken from the earlier report [20].

The contributions of these different components for SPD-processed Ni correspond well to the experimentally obtained data as shown in Table 3.1. After HPT, a homogeneous UFG structure was formed with mainly high-angle misorientations. Therefore, for the HPT sample, it is reasonable to neglect the contribution of low-angle grain boundaries. The analysis of mechanical test data shows that the presence of substructure and the non-equilibrium state of grain boundaries contributes more strongly to the yield stress of SPD-processed Ni than the strength calculated according to the Hall–Petch rule for a material with the given grain size.

In addition to the dislocation substructure and non-equilibrium grain boundaries, other nanostructured elements formed in the UFG materials processed by SPD may contribute to the change of yield stress and flow stress. This issue was recently studied in detail for the case of superstrong UFG Al alloys, namely AA1570 and AA7475 [12, 13].

Table 3.1 Contribution to flow stress for SPD-processed pure Ni

Processing of Ni	YS_{exp} (MPa)	YS_{calc} (MPa)	σ_{LAB} (MPa)	σ_{HAB} (MPa)	σ_{GBDs} (MPa)
ECAP + rolling	990	980	510	280	170
HPT	1200	1190	–	460	710

YS_{exp}—experimental data, YS_{calc}—calculated by means of Eq. 3.3

The transmission electron microscopy (TEM) analysis demonstrated that HPT leads to a complete transformation of the initial coarse-grained structure of the alloys into the UFG structure. In the alloys 1570 and 7475, homogeneous UFG structures with a grain size of about 100 nm were formed after HPT as shown in Fig. 3.3. It was also determined that HPT processing has a visible effect on the value of the crystal lattice parameter α of Al alloys. For example, in the AA1570, its value after straining was reduced considerably in comparison with the initial state, from 4.0765 ± 0.0001 Å to 4.0692 ± 0.0003 Å, which results from the formation of Mg segregations at grain boundaries [12, 13].

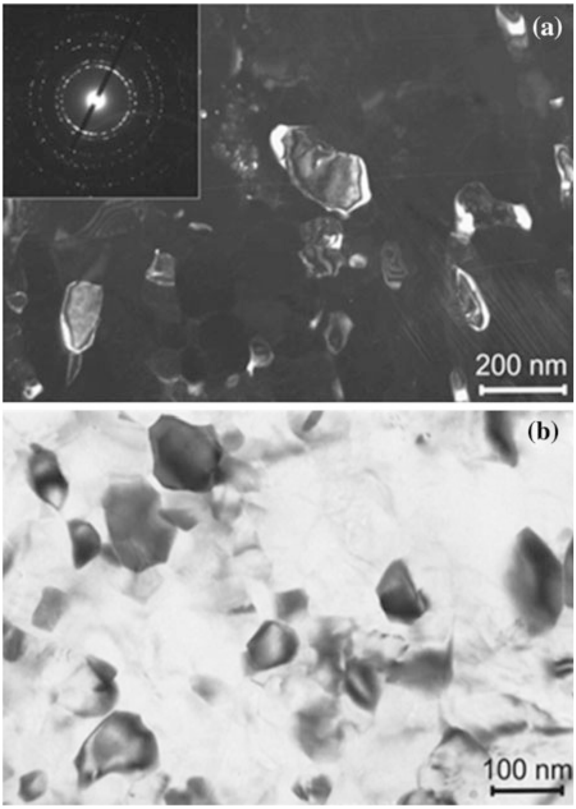


Fig. 3.3 A typical TEM dark-field image of the UFG 1570 alloy with a corresponding SAED (**a**), a bright-field image (**b**). The images are reproduced from [12] with the permission from the publisher

Figure 3.4 shows the results of mechanical testing of the 1570 and 7475 alloys. It can be seen that the UFG alloys processed by HPT at room temperature demonstrate record strength that more than twice exceeds the level of strength of the material subjected to standard hardening.

Figure 3.5 illustrates the data for a number of Al alloys presented in the form of the Hall–Petch relation in which the yield stress ($\sigma_{0.2}$) is plotted against the inverse square root of the grain size ($d^{-1/2}$) for a UFG AA1100 produced by accumulative roll bonding (ARB)-rolling and consequent heat treatment [21] as well as for an ECAP-processed Al–3 % Mg alloy [22]. For the Hall–Petch relation in the AA1100 [21], the following parameters were set: $\sigma_o = 6.0$ MPa and $k_y = 105$ (for the grain sizes in μm); for the ECAP-processed Al–3 % Mg alloy [22], $\sigma_o = 62$ MPa and $k_y = 149$. Figure 3.5 also shows the data obtained for the coarse-grained and UFG AA1570 and AA7475.

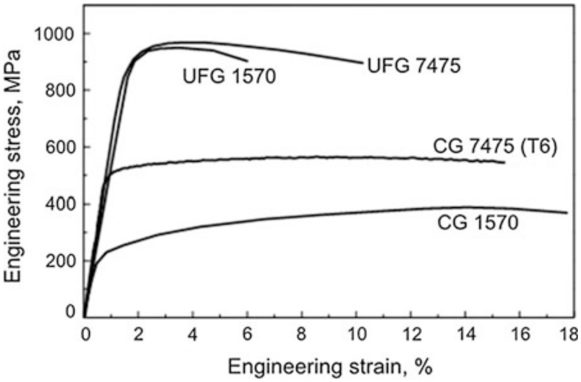


Fig. 3.4 Engineering stress–strain curves for AA1570 and AA7475 in UFG and coarse-grained states. The curves are reproduced from [12] with the permission from the publisher

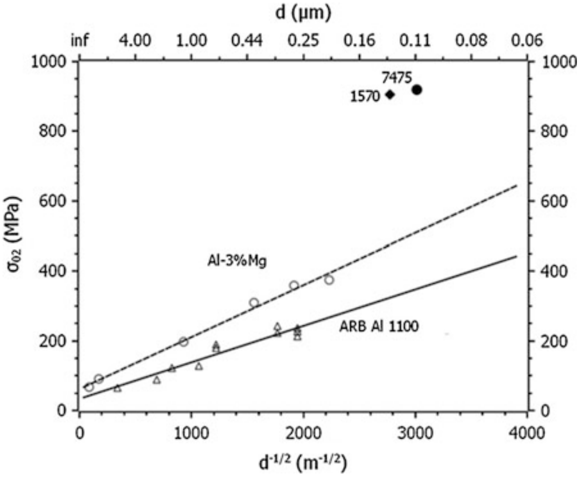


Fig. 3.5 The Hall–Petch relation for the Al alloys 1100 [21] and Al–3 % Mg [22] and data on the yield stresses of the UFG alloys 1570 and 7475

From the available data, it is seen that the σ_y values for the coarse-grained solution-treated alloys are close to the results for the Al–3 % Mg alloy. However, for the UFG states in the 1570 and 7475 alloys with a grain size of 100–130 nm, the value σ_y is considerably higher than that calculated from the Hall–Petch relation.

The Hall–Petch plot for commercially pure (CP) Ti (A-70, similar to Grade 4) and Armco-Fe is given in Figs. 3.6 and 3.7, respectively [23–26]. Here, one can also see experimental data for several UFG materials produced by SPD. In the case of CP Ti, the data are presented for HPT-processed UFG Ti–6 % Al–4 % V [27] and also for UFG Ti (Grade 4) processed by ECAP and further thermo-mechanical treatment (TMT) [28]. For the UFG CP Ti, the σ_y values are higher than those could be predicted by the Hall–Petch relation for the given grain sizes. For UFG Fe, the data on tensile mechanical tests are presented only in [29], but there is evidence on microhardness H_v that is demonstrated in Fig. 3.7 using the ratio $\sigma_y = H_v/3$. The data for HPT-processed UFG steel 20 with 0.2 % C content are also presented here [30]. Similar to CP Ti, there is a considerable excess of experimental σ_y values (for steel 20) over the values predicted from the Hall–Petch relation.

Thus, the new phenomena of 'superstrength' of nanostructured metals and alloys produced by SPD can be observed for various materials reflecting the 'positive' slope of the Hall–Petch relation as demonstrated in Fig. 3.1 (curve 2). 'Superstrength' in bulk nanostructured materials can be of different origin. First, it can result from additional—already known—strengthening mechanisms, i.e., solid solution strengthening, precipitation strengthening, and dislocation strengthening [5, 31]. However, the influence of new strengthening mechanisms is also possible—these arise from the change in grain boundary structure and lead to further strength enhancement [15, 32].

Recently, based on experimental studies of materials obtained by vacuum deposition [33], Firstov et al. [34] reported a 'positive' slope of the Hall–Petch relation, where for the grain size range $d_{cr2} < d < d_{cr1}$, the exponent of d in Eq. 3.1

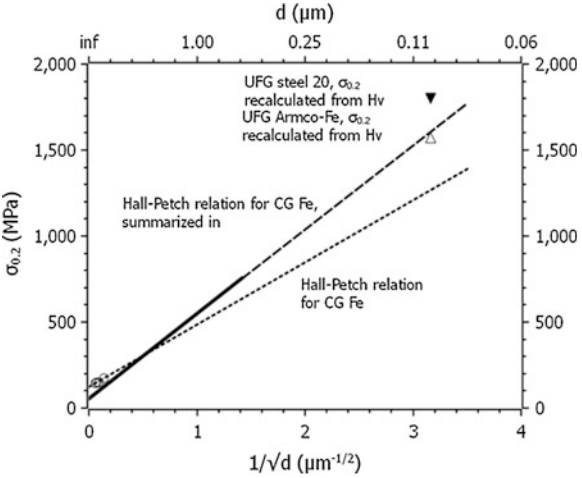


Fig. 3.6 The Hall-Petch relation for Armco-Fe [25] and iron [26] and data on the yield stresses of UFG Fe [23, 29] and steel 20 [30]

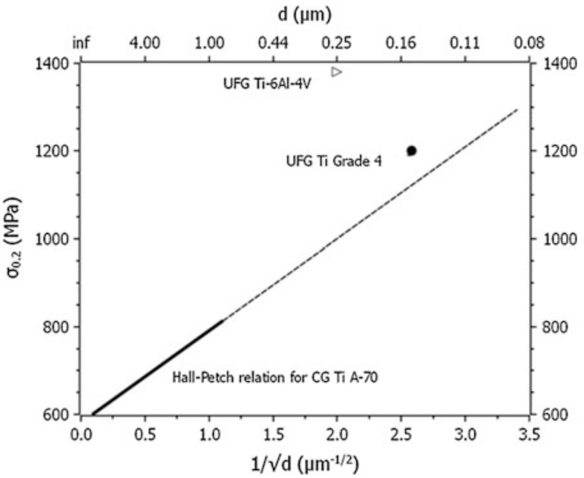


Fig. 3.7 The Hall–Petch relation for Ti and A-70 [24] and data on the yield stresses of UFG Ti [28] and T–6 % Al–4 % V alloy [27]

varied from −1/2 to −1, and for $d < d_{cr1}$, the exponent of d was equal to −3 with the presence of grain boundary segregations.

For SPD-processed metals, it is difficult yet to speak in terms of definite values for the exponent of d in Eq. 3.1 due to low statistics of experimental data presently available. However, it is possible that the presence of two characteristic grain size values is also valid for nanostructured SPD materials. Indeed, as it has been already pointed out, the presence of non-equilibrium grain boundaries is typical for the majority of SPD-processed materials, but their influence on mechanical properties becomes considerable when the grain size is below 500–1000 nm [35]. When the grain size decreases down to 100 nm and less, grain boundary segregations provide a significant contribution to the overall strength. Recently, this topic was addressed in [12], where it was shown that high strength of the UFG Al alloys was directly related to the formation of Mg segregations at grain boundaries revealed in the alloys by 3D APT technique [12, 36, 37]. Because in UFG materials deformation takes place by dislocations generated at grain boundaries and moving through a grain to be captured by an opposite grain boundary, the rate-controlling mechanism is the 'dislocation–grain boundary' interaction. In this case, the elevated concentration of solutes in grain boundaries can suppress emission of dislocations from such boundaries due to solute drag, and as a result, the stress needed to emit a dislocation increases.

Recently, this finding was confirmed for the case of UFG stainless steel 316 produced by HPT at different temperatures [38]. Earlier, it was found that the HPT 316 steel processed at room and elevated temperatures demonstrates similar strength despite the difference in grain size and dislocation density [39, 40]. In [38], it was shown that the steel, SPD processed at room temperature, exhibits no pronounced grain boundary segregations and fits well the Hall–Petch relation extrapolated to the corresponding grain size. However, the steel processed at 400 °C was found to contain complex Si–Cr–Mo grain boundary segregations, and its strength considerably exceeded the value predicted by the Hall–Petch law. Similar idea was used to explain enormous increase (from 1360 MPa to 2230 MPa) in yield stress of a 316 steel subjected to HPT at room temperature followed by subsequent annealing at 500 °C for 1 h [41]. The authors suggested that it can be explained by the fact that thermal treatment leaded to formation of grain boundary segregations which became precursors for G-phase observed in grain boundaries after further long-term annealing.

These findings on the role of SPD-induced GB segregations open a way for a new direction in nanostructural design of SPD-processed materials and also may be used in grain boundary segregation engineering of the other types of nanomaterials [42, 43].

This point is in good agreement with the experimental data and also makes it possible to explain considerably higher strength values observed in the UFG alloys in comparison with pure metals. At the same time, the task of oncoming research is to explore the segregations and determine which elements, and the level of their concentrations, produce the most influence on strength enhancement in bulk nanostructured materials. This point is also important in answering the question of the precise origin of very high strength in nanostructured multiphase alloys that possess the most strength among metallic nanomaterials, which was recently discussed in [44].

High ductility in metallic materials is another very important property for their structural use. It is essential for metal-forming operations as well as to avoid catastrophic failure in load-bearing applications during their service life. The ductility of materials is defined as the extent to which a material can be plastically deformed. Two measures of ductility will be considered below. First, uniform elongation is the maximum strain where homogeneous plastic flow (uniform reduction of cross-sectional area) is still observed and beyond which a diffuse necking begins. The uniform elongation is determined by competition between plastic flow and materials resistivity to macro-localization of plastic flow. It can be important in stretch-metal-forming operations. The second measure, elongation to failure (often referred to as total elongation to fracture or engineering strain at fracture), is a sum of uniform elongation and necking elongation. The latter is controlled by competition between localized plastic flow and fracture processes.

It has been a long-standing goal for materials scientists to synthesize structural materials with balanced combinations of high strength and high ductility. However, during the last decade, it has been widely demonstrated that a major grain refinement, down to the nanometer range, may lead to a very high hardness and strength in various metals and alloys, but nevertheless, these materials invariably exhibit low ductility under tensile testing [6, 45, 46]. A similar tendency is well known for metals subjected to heavy straining by other processes such as rolling, extrusion, or drawing. Strength and ductility are the key mechanical properties of any material, but these properties typically have opposing characteristics. Thus, materials may be strong or ductile, but they are rarely both. The reason for this dichotomy is of a fundamental nature. Indeed, the plastic deformation mechanisms associated with the generation and movement of dislocations may not be effective in ultrafine grains. This is generally equally true for SPD-processed materials. Thus, most of these materials have a relatively low ductility, but they usually demonstrate significantly higher strength than their coarse-grained counterparts. It is important to note that SPD processing leads to a reduction in the ductility which is generally less than in more conventional deformation processing techniques such as rolling, drawing and extrusion. For example, experiments were conducted to compare the strength and ductility of the AA3004 processed by ECAP and cold-rolling (CR) [47]. As illustrated by the data plotted in Fig. 3.8, the yield strength increased monotonically with the increasing equivalent strain imparted into the alloy by either CR or ECAP [48]. However, it is apparent also that the overall ductility exhibits different trends for these two processing methods. After one ECAP pass, equivalent to a strain of ~1, the elongation to failure decreases from ~32 to ~14 %. At the same time, there is no additional reduction in the ductility with additional ECAP passes. By contrast, CR decreases the ductility by a similar magnitude initially, but thereafter, the ductility continues to decrease with increasing rolling strain although at a slower rate. Consequently, ECAP processing of the alloy leads ultimately to a greater retention of ductility than conventional CR.

Typically, in the nanostructured metallic materials, plastic deformation localizes at the very early stage of plastic deformation (1–3 %) resulting in necking, followed by a specimen failure. Various strategies to improve low ductility of the nanostructured metals and alloys have been proposed [31, 49, 50]. These strategies could be divided into two groups which we would define as (1) 'mechanical' strategies and (2) 'microstructural' strategies. The 'mechanical' strategies employ the mechanical characteristics of the UFG materials such as their work hardening ability and/or strain rate sensitivity. These mechanical characteristics can be varied by changing the testing parameters such as temperature and/or strain rate. The 'microstructural' strategies are based on the idea of intelligent microstructural design.

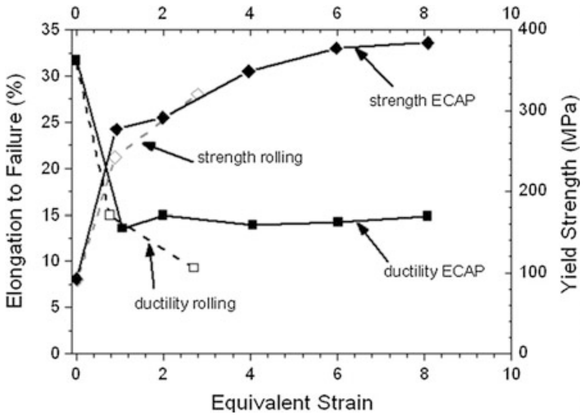


Fig. 3.8 A comparison of yield strength and ductility for an Al-3004 alloy processed by cold-rolling or ECAP. The figure is reproduced from [48] with the permission from the publisher

For tensile behavior, the uniform strain is usually in good agreement with the well-known Considère criterion [51],

$$(\mathrm{d}\sigma/\mathrm{d}\varepsilon) = \sigma \tag{3.4}$$

which is a geometric criterion stating that when the work hardening rate, ($\mathrm{d}\sigma/\mathrm{d}\varepsilon$), decrease to the level of the flow stress, σ, macro-localization of plastic deformation (necking) should occur resulting in a specimen failure. The nanostructured metallic materials are usually characterized by increased strain rate sensitivity even at low temperatures compared to their coarse-grained counterparts [49, 50]. Therefore, the Hart criterion [52] is more appropriate to predict the uniform elongation of the nanostructured metals and alloys:

$$(\mathrm{d}\sigma/\mathrm{d}\varepsilon) = (1 - m)\sigma \tag{3.5}$$

where m is the strain rate sensitivity index. It follows from Eq. 3.5 that the uniform elongation can be enhanced by (1) increasing the work hardening rate $\mathrm{d}\sigma/\mathrm{d}\varepsilon$ and/or (2) the strain rate sensitivity m.

Meanwhile, since the mechanical characteristics of the materials are also determined by their microstructure, it can be outlined that manipulation with the microstructure is the major tool to enhance the ductility of the nanostructured alloys.

In this connection, findings of extraordinarily high strength and good ductility in several bulk UFG metals produced by SPD are of special interest [53–57]. It is important to consider in detail the three different approaches that were used in the earlier investigations.

In the first study, high-purity (99.996 %) Cu was processed at room temperature using ECAP with a 90° clockwise rotation around the billet axis between consecutive passes in route $\mathrm{B_C}$ [54]. The strength and ductility were measured by uniaxial tensile tests, and the resulting engineering stress–strain curves are shown in Fig. 3.9 for the Cu samples tested at room temperature in the initial coarse-grained condition and in three processed states [54]. It is apparent that the initial coarse-grained Cu with a grain size of about 30 μm has a very low yield stress with significant strain hardening and a large elongation to failure. CR of the Cu with reduction ratio of 60 % significantly increases the strength (curve 2 in Fig. 3.9), but dramatically decreases the elongation to failure. This result is consistent with the classical mechanical behavior of metals that are plastically deformed. The same tendency is true also for Cu subjected to two passes of ECAP. However, further straining of Cu to 16 passes of ECAP (curve 4 in Fig. 3.9) simultaneously increases both the strength and ductility. Furthermore, the increase in ductility is much more significant than the relatively minor increase in strength. Thus, the data shown in Fig. 3.9 for ECAP-processed Cu clearly demonstrate an enhancement of strength as well as ductility with accumulated deformation due to an increase in the number of passes from 2 to 16 [54]. This is a very remarkable result that for the first time was observed in metals processed by plastic deformation. Accordingly, this effect was

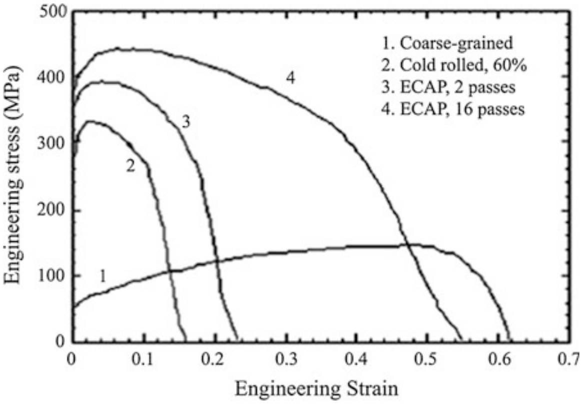
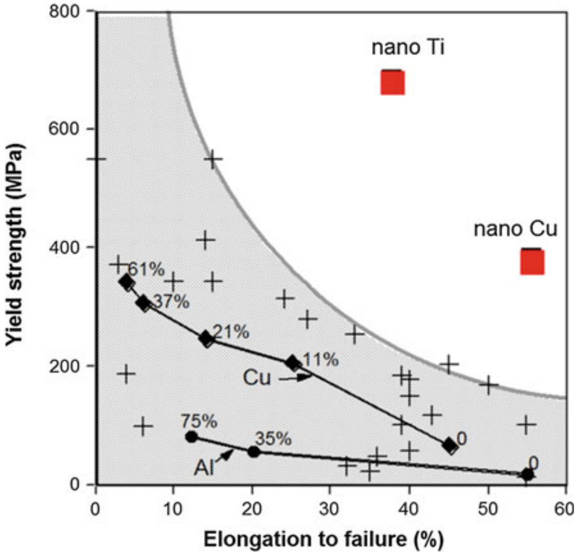


Fig. 3.9 Tensile engineering stress–strain curves for Cu tested at 22 °C with a strain rate of $10^{-3}\ s^{-1}$: The processing conditions for each curve are indicated. The curves are reproduced from [54] with the permission from the publisher

termed the 'paradox of strength and ductility in SPD-processed metals,' and the principles of this paradox are illustrated in Fig. 3.10, where it is apparent that conventional metals lie within the lower shaded quadrant [54]. As shown in Fig. 3.10, for Cu and Al, CR (the reduction in thickness is marked by each datum point) increases the yield strength but decreases the elongation to failure [58, 59]. The extraordinary combination of high strength and high ductility shown in Fig. 3.10 for the nanostructured Cu and Ti after SPD processing clearly sets them apart from the other coarse-grained metals.

Fig. 3.10 The paradox of strength and ductility in metals subjected to SPD: the extraordinary combination of high strength and high ductility in nanostructured Cu and Ti processed by SPD (*two upper points*) clearly sets them apart from conventional coarse-grained metals (*lower points* relating to metals of 99.5–99.9 % purity) [54]



In recent years, similar tendencies have been reported in a number of metals, including Al [60, 61], Cu [62], Ni [16], and Ti [54, 57], after SPD processing via ECAP, HPT, and ARB. Concerning the origin of this phenomenon, it has been suggested that it is associated with an increase in the fraction of high-angle grain boundaries with increasing straining and with a consequent change in the dominant deformation mechanisms due to the increasing tendency for the occurrence of grain boundary sliding and grain rotation [53, 54].

Another approach to enhance ductility is based on introduction of a bimodal distribution of grain sizes [56, 64]. In [56], nanostructured Cu was produced through a combination of ECAP and subsequent rolling at the liquid nitrogen temperature prior to heating to a temperature of ~450 K. This processing route resulted in the formation of a bimodal structure of micrometer-sized grains, with a volume fraction of around 25 %, embedded in a matrix of nanocrystalline grains. The material exhibited an extraordinarily high ductility but also retained a very high strength. The reason for this behavior is that while the nanocrystalline grains provide strength, the embedded larger grains stabilize the tensile deformation of the material. Other evidences for the importance of grain size distribution come from investigations on Zn [63], Cu [64], and Al alloys [65]. Furthermore, the investigation of Cu [64] showed that bimodal structures may increase the ductility not only during tensile testing but also during cyclic deformation. This observation is also important in improving the fatigue properties of materials, as discussed in Sect. 3.1.2.

Some microstructural modification may not only increase the strength at expense of ductility (or to increase ductility sacrificing strength), but also improve both ductility and strength [68]. Given that the low ability for strain hardening in nanostructured materials is caused by the limitations for accumulating dislocations and other defects in nanostructured materials, these strategies are based on modifying the nanostructural features to promote accumulation of dislocations [46]. This idea was successfully realized in a commercial Al–Zn–Mg–Cu–Zr alloy [66] and an Al–10.8 % Ag alloy [55] subjected to ECAP and subsequent artificial aging. The principle of this approach is illustrated in Fig. 3.11 for the Al–Ag alloy, where the Vickers microhardness is plotted against the aging time at 373 K for samples in a solution-treated (ST) condition and after CR and ECAP [55]. For the ST condition, the hardness is initially low but increases with aging time to a peak value after 100 h (3.6×10^5 s). For the CR condition, the hardness is higher, but there is only a minor increase with aging. The hardness is even higher after ECAP and further increases with aging to a peak value after 100 h. The relatively lower values of hardness recorded after CR in comparison with ECAP are due to the lowerequivalent strain imposed on the sample: These strains were ~1.4 in CR and ~8 in ECAP, so the microstructure after CR consisted of subgrains and cell boundaries having low misorientation angles. It was shown, using scanning TEM, that the peak hardness achieved after ECAP and aging for 100 h is due to precipitation within the grains of spherical particles with diameters of ~10 nm and elongated precipitates with lengths of ~20 nm. The spherical particles were identified as η-zones consisting of arrays of solute atoms lying parallel to the (001) planes, and the elongated precipitates were identified as the platelike γ' particles. It was shown also that additional

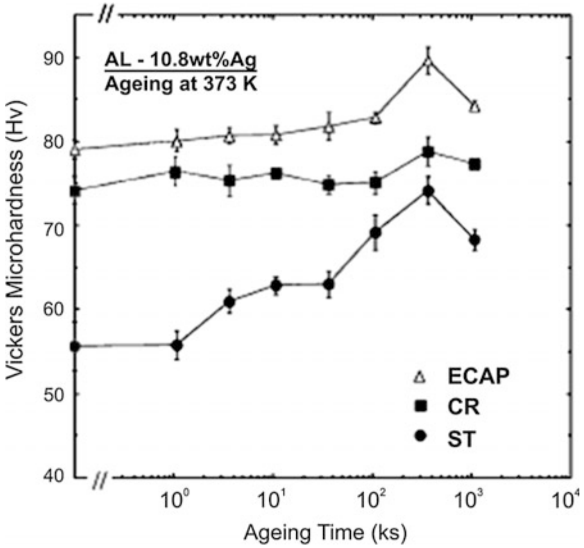
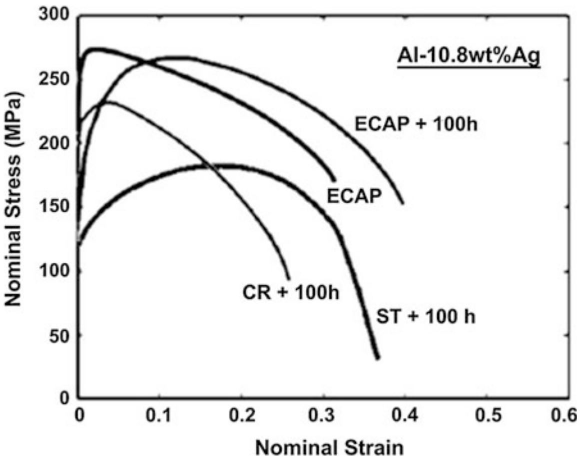


Fig. 3.11 Variation of the Vickers microhardness with aging time for the Al–10.8 % Ag alloy after solution treatment (ST), cold-rolling (CR), and ECAP [55]

aging up to 300 h led to a growth in the γ' particles and a very significant reduction in the density of the fine η-zones, thereby giving a consequent loss in hardening at the longest aging time recorded in Fig. 3.11. Introduction of artificial aging after ECAP has an important influence on the stress–strain behavior at room temperature, as demonstrated in Fig. 3.12, where the tensile stress–strain curves are shown after ECAP and after ST, CR, and ECAP with additional aging for 100 h at 373 K: Each sample in Fig. 3.12 was tested at room temperature at an initial strain rate of 10^{-3} s^{-1} [55]. Thus, ST and artificial aging give a reasonable tensile strength, an extensive region of uniform strain and good ductility, whereas CR and aging give an increased strength but very limited uniform strain and a marked reduction in the total ductility. For the ECAP condition, the strength is high in the absence of aging, but there is a negligible region of uniform strain and no significant strain hardening. By contrast, the sample processed by ECAP and aged for 100 h shows a similar high strength, a region of strain hardening and good ductility. In practice, the uniform strain of ~0.14 achieved in this specimen is similar to the uniform strain of ~0.17 in the sample after ST and aging, and the elongation to failure of ~0.40 is comparable to, and even slightly exceeds, the elongation of ~0.37 recorded in the ST and aged condition. These results demonstrate, therefore, the potential for producing high strength and good ductility in precipitation-hardened alloys. Furthermore, although the results documented in Figs. 3.11 and 3.12 relate to a model Al–Ag alloy, it is reasonable to anticipate that it should be possible to achieve similar results in commercial engineering alloys where the aging treatments are generally well documented. Indeed, this approach was successfully realized also on AA7075 [68] and AA2024 [69].

The next strategy in nanostructural design to improve strength and ductility relies on introduction of high density of twins, which could also assist effective

Fig. 3.12 Tensile plots of stress versus strain at room temperature for the Al–10.8 % Ag alloy after solution treatment (ST) or cold-rolling (CR) with aging at 373 K for 100 h or ECAP without subsequent aging and ECAP with aging at 373 K for 100 h [55]



dislocation accumulation inside grains. This was demonstrated on pulsed electrodeposited Cu where the extraordinary strength (about 1 GPa) with reasonable ductility was observed [70]. In SPD-processed materials, nanotwins can be introduced via low-temperature processing and/or deformation at high strain rate. The first way was realized on the example of nanostructured Cu with twins produced by ECAP followed by cryogenic drawing and cryogenic rolling [71]. Dynamic plastic deformation (deformation at high strain rate) in combination with liquid nitrogen temperature allowed to increase dramatically the strength of Cu retaining ductility in [72]. The other approaches involve lowering stacking fault energy (SFE) to promote partial dislocation slip [73], the abovementioned low dislocation density and high-angle grain boundaries formation and multiple phases and phase transformations [74].

It is worth also noting that in the nanostructured metals processed by SPD, both strength and ductility can be improved by performing mechanical tests at lower temperature and/or high strain rate [68, 75]. As an example, Fig. 3.13 displays the tensile engineering stress–strain curves of UFG Ti with a grain size of 260 nm tested at room temperature and 77 K [67, 75]. At room temperature, the Ti has some ductility and a small uniform elongation, as shown by curve A obtained at a strain rate of 10^{-3} s^{-1}. However, at 77 K, the strength of the material is drastically elevated to ~1.4 GPa. There is also a simultaneous increase in the elongation to failure, and this increases with strain rate up to a maximum close to ~20 %, as shown in Fig. 3.13 where curves B–D are for strain rates of 10^{-3} s^{-1}, 10^{-2} s^{-1}, and 10^{-1} s^{-1}, respectively. These results for strength and ductility are better than, or at least comparable to, those of Ti alloys with a high percentage of alloying elements. Here, pronounced necking is delayed even for this very strong metal, resulting in a large area under the stress–strain curve and a generally tough behavior of the material. For comparison, curve E shows the initial 18 % of strain for a conventional coarse-grained Ti sample tested at 77 K [67].

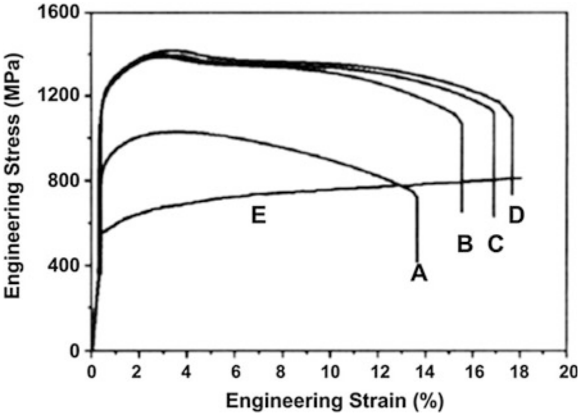


Fig. 3.13 Engineering stress–strain curves for nanostructured Ti where *curve A* is for testing at room temperature at a strain rate of 1 × 10^{-3} s^{-1} and *curves B–D* for the same Ti tested at 77 K for strain rates of 1 × 10^{-3} s^{-1}, 1 × 10^{-2} s^{-1} and 1 × 10^{-1} s^{-1}, respectively; for comparison, curve E shows the behavior of coarse-grained Ti over the initial 18 % of strain when testing at 77 K [67]. The curves are reproduced from [75] with the permission from the publisher

Another fundamental concept to control ductility is based on manipulation with strain rate sensitivity of material (Eq. 3.5). The UFG Cu with high ductility was found to have higher strain rate sensitivity, *m*, which is defined as $\{d\ln\sigma/d\ln\dot{\varepsilon}\}$ where σ is the applied stress and $\dot{\varepsilon}$ is the strain rate [54]. Indeed, nanostructured materials as a rule have small strain hardening rate that means a limited capability to store dislocations inside grains. The increased strain rate sensitivity would mean that a mixture of grain boundary sliding and dislocation slip operate the plastic flow, thus providing plastic deformation.

The value of *m* was equal to ~0.14 for ECAP-processed Cu taken through 16 passes compared with a value of *m* of ~0.06 for ECAP-processed Cu taken through only 2 passes. A high value for the strain rate sensitivity indicates viscous flow and renders the material more resistant to necking and, therefore, more ductile. Increased strain rate sensitivity was also revealed in a number of other studies [61, 76]. It was recently demonstrated that the *m*-value in the UFG Al alloys at room temperature can be increased up to 0.24 via manipulation with the chemical composition of grain boundaries [77] that can lead to the extraordinarily high ductility at room temperature. At the same time, there are also some reports illustrating low values of *m* in the SPD-processed materials. It is possible that these apparent differences are due to microstructural features in the samples since the microstructures formed during SPD processing may differ significantly depending upon the processing conditions.

As a rule, the ductility of UFG metallic materials is examined through tensile or compression tests representing uniaxial mechanical load. However, an additional question is peculiarity of deformation behavior of SPD materials under multiaxial loading typical for commercial metal-forming processes. Recent works showed that even at limited elongation to failure values measured by tensile tests, the SPD materials can demonstrate the same technological plasticity as their coarse-grained counterparts [78]. This is attributed to heterogeneity of plastic flow combined with dislocation glide and grain boundary sliding. This makes SPD materials to be not only attractive research objects but also reliable candidates for advanced industrial applications from technological point of view even if their uniaxial ductility is reduced in comparison with their coarse-grained counterparts.

In conclusion, recent results show that grain refinement by SPD can lead to a unique combination of strength and ductility in metallic materials. Such superior mechanical properties are highly desirable in the development of advanced structural materials for the next generation [5, 11, 53]. However, the achievement of these properties is associated with the tailoring of specific microstructures which, in turn, are determined by the precise processing regimes and the nature of any further treatments. This strategy represents the art and science of nanostructuring for advanced properties using SPD techniques [14].

3.1.2 Fatigue Properties of Nanostructured Metallic Materials

Fatigue occurs when a material is subjected to repeated loading and unloading. If the loads are above a certain threshold, microscopic cracks will begin to form at the stress concentrators such as the surface, persistent slip bands (PSBs), and microstructural heterogeneities (second-phase precipitates, particles, pores, etc.). Eventually, a crack will reach a critical size, the crack will propagate suddenly, and the structure will fracture. The nominal maximum stress values that cause such failure may be much lower than the ultimate tensile strength or yield strength of material. Therefore, fatigue considerations are very important in materials engineering. There are three main forms of fatigue: high-cycle fatigue (HCF), low-cycle fatigue (LCF), and thermal–mechanical fatigue (TMF). In this chapter, we focus on HCF and LCF of nanostructured metallic materials. The principal distinction between HCF and LCF is the region of the stress–strain curve, where the repetitive application of load (and resultant deformation or strain) is taking place. HCF is characterized by low-amplitude high-frequency elastic strains, whereas LCF is the mode of material degradation when plastic strains are induced [79].

The fatigue properties of bulk nanostructured metallic materials have been widely studied over the last two decades, and comprehensive overviews of these activities can be found in [80–83].[1] Most of these investigations have clearly shown

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[1] It should be noted that size of specimens is the main limitation for investigation of fatigue behavior of SPD-processed nanostructured metallic materials. Thus, in most of investigations, ECAP-processed objects were studied, which have size sufficient for the preparation of fatigue specimens. However, very recent modifications and/or upscaling of other SPD techniques, such as HPT, allowed fabrication of larger samples. Research on fatigue behavior of nanostructured metallic materials produced by other SPD techniques has just started [84].

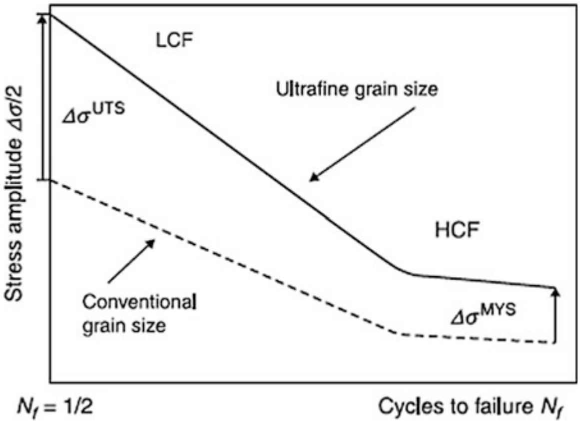

Fig. 3.14 Schematic Woehler (S–N) diagram showing the effect of grain refinement on fatigue life. The diagram is reproduced from [80] with the permission from the publisher

that the nanostructured metallic materials show enhanced fatigue life compared to the coarse-grained materials, which has been related to unique microstructure of nanostructured metallic materials and their enhanced mechanical properties. The outcomes of fatigue studies can be roughly generalized as follows: The higher the increase in fatigue life at a given amplitude, the higher the strength amplitude [80]. As nanostructured metallic materials have much higher enhanced ultimate tensile strength, the sustainable stress level at a given fatigue life is markedly increased in the LCF regime. As the stress amplitude decreases, the plastic strain amplitude decreases and work hardening is reduced. Therefore, in the HCF regime, the sustainable stress levels of nanostructured metallic materials at a given fatigue life are higher compared to those of the coarse-grained counterparts, but the difference is not that significant as in the LCF regime (as shown schematically in Fig. 3.14) [80].

3.1.2.1 High-Cycle Fatigue Behavior of Nanostructured Metallic Materials

Although grain refinement down to ultrafine or nanoscale can dramatically enhance tensile strength of metallic materials (see Sect. 3.1.1), their HCF properties are often not enhanced as significantly as tensile strength. For instance, the ratio of the endurance fatigue limit σ_{fo} to the ultimate tensile strength σ_{UTS} (σ_{fo}/σ_{UTS}) was found to be lower for most of the nanostructured metallic materials compared to their coarse-grained counterparts [80, 81]. This is clearly seen from Table 3.2, where data on mechanical properties of some nanostructured metallic materials produced via SPD are listed. However, a significant increase of this ratio was observed in some cases, for example, in the friction stir-processed AA7075 in [85] or in ECAP-processed Fe–36 % Ni Invar in [86].

Sometimes, standard thermo-mechanical processing might even lead to somewhat better HCF properties in the coarse-grained materials than in their nanostructured counterparts. This was demonstrated in comparison with HCF properties

Table 3.2 Mechanical properties of some nanostructured metallic materials produced via SPD

Material	Processing; grain size	$\sigma_{0.2}$ (MPa)	σ_{UTS} (MPa)	ε_f (%)	σ_{fo} (MPa)	σ_{fo}/σ_{UTS}	References
CP Cu	CG; $d = 35$ μm	140	240	–	65	0.27	[87]
	ECAP 10p; $d = 0.2$ μm	440	480	–	80	0.17	
AA5056	CG T6,	276	310	12	50	0.16	[88]
	ECAP 8p, $d = 0.2$ μm	392	442	7	116	0.26	[89]
AA6106Zr	CG, ST, AA	250	350	23	175	0.5	[90]
	ECAP 4p, $d = 0.2$ μm	570	590	9	225	0.38	
Fe–36 % Ni Invar	CG	275	490	40	137	0.28	[86]
	ECAP 12p, $d = 0.18$ μm	835	912	52	330	0.36	
CP Ti (VT1)	CG; $d = 25$ μm	380	460	26	238	0.52	[91]
	ECAP 8p; $d = 0.3$ μm	650	810	15	380	0.47	[92]
CP Ti (Grade 2)	CG; $d = 105$ μm	248	418	42	210	0.50	[93]
	CR; $d = 15$ μm	380	460	26	238	0.52	[94]
	ECAP 6p; $d = 0.3$ μm	635	669	33	350	0.52	[93]
Ti–6Al–4V	HR; $d = 3$ μm	900	930	20	550	0.59	[95]
	ECAP 4p; $d = 0.16$ μm	1340	1370	14	620	0.45	
SM490 steel	CG; $d = 12.5$ μm	424	691	25	275	0.40	[96]
	TMT; $d = 0.8$ μm	653	796	18	400	0.50	

d—grain size, $\sigma_{0.2}$—yield strength, σ_{UTS}—ultimate tensile strength, ε_f—elongation to failure, σ_{fo}—endurance limit (on the basis of 10^7 cycles and stress ratio $R = -1$), *CR*—cold-rolling, *HR*—hot-rolling, *ST*—solution treatment, *AA*—artificial aging, *TMT*—thermo-mechanical treatment, *CG*—coarse grained

of AA5056 and Al–Mg–Sc alloys in coarse-grained condition and after ECAP processing [97]. Such a little improvement (or no improvement) in fatigue life observed in the nanostructured metallic materials in HCF regime can be related to insignificant increase in resistance against crack nucleation in these materials, since the fatigue life in the HCF is determined by the resistance of material to the crack nucleation. As it is difficult for slip bands to pass through the HAGBs, intergranular cracking by piling up of dislocations at grain boundaries is more likely to occur at HAGBs than in grain interior or at LAGBs, where dislocations can be transported into adjacent grain by shear bands [98].

The HCF response in nanostructured metallic materials is also strongly determined by their chemical composition. For example, it was shown that increasing Mg content in the Al alloys resulted in longer fatigue life for the same stress amplitude [89, 99]. Significantly enhanced fatigue properties in high-cycle regime were also demonstrated by an AA6106 with Zr and Sc additions in [90] and by an Al–6Mg–Sc alloy in [100] that can be attributed to a higher content of Sc [100] or combination of Zr with Sc [90], resulting in a high volume fraction of strengthening

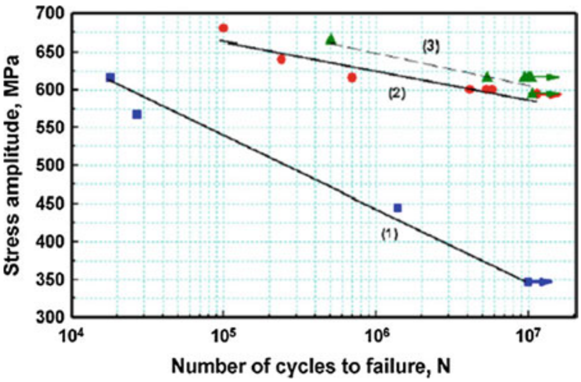

Fig. 3.15 Dependence of the stress amplitude on the number of cycles for smooth samples of coarse-grained CP Ti (*curve 1*), nanostructured CP Ti after ECAP and thermal mechanical treatment (TMT) (*curve 2*), and after ECAP + TMT and additional annealing at 350 °C for 6 h (*curve 3*). The figure is reproduced from [101] with the permission from the publisher

particles when optimum aging treatment is applied. Significant improvement of fatigue performance was reached via nanostructuring also in Ti-based materials. For example, in CP Ti, grain refinement via ECAP led to an increase in the fatigue limit by nearly 50 % [87, 101]. It can also be further enhanced, if the SPD-processed Ti is subjected to additional TMT and annealing, as shown in Fig. 3.15 [101]. Similar effect was also observed in the SPD-processed Ti–6Al–4V ELI alloy [95]. Notable improvement of HCF properties was observed in the ECAP-processed Fe–36 % Ni Invar (Table 3.2), which showed many advantages compared with other commercially available dimensionally stable alloys [86]. In particular, (i) the conventional yield stress increased after ECAP by a factor of 3 depending on the number of ECA passes; (ii) the improvement of HCF life by an order of magnitude was attained; (iii) the ductility of UFG Invar was also notably better than that of its conventional counterparts; (iv) due to this good ductility, the LCF properties were also significantly improved; and finally, (v) the resistance to crack propagation attested by LCF testing was regarded as rather high, supposing good reliability of ECAP-processed Invar in engineering applications.

In the very high-cycle fatigue (VHCF) regime, where the number of cycles to failure is much higher than 10^7, the fatigue life of the nanostructured pure metals remains high compared to the coarse-grained ones, as was observed in pure Cu [102] and pure Al [103]. However, the VHCF behavior of the nanostructured alloys can be influenced by their microstructure, since the strength of the weakest phase or weakest microstructural detail and the area of maximum localized plastic deformation determine the crack initiation sites in the VHCF regime [103].

3.1.2.2 Low-Cycle Fatigue Behavior of Nanostructured Metallic Materials

The LCF behavior of the nanostructured metallic materials is very complex, since ultrafine and nanograins have a low ability to sustain cyclic loads in the LCF regime. This was related to the limited ductility on monotonic and cycling deformation promoting early crack initiation as well as higher fraction of grain boundaries favorable for crack propagation in the nanomaterials [81]. Unlike coarse-grained metals, their nanostructured counterparts usually show no significant increase of stress amplitude (cyclic hardening) (Fig. 3.16) or its decrease (cyclic softening) when they are cyclically deformed under constant strain amplitude [97, 104, 105]. The cyclic softening ratio in this case is nearly zero (Fig. 3.17). This kind of response strongly depends on the chemical composition [97] and microstructure of metals and alloys [104] (Fig. 3.17). The nanostructure in the SPD-processed pure metals is usually unstable, both mechanically and thermally. Microstructural instabilities in the form of dynamic grain coarsening in the nanostructured pure metals (Fig. 3.18a) and/or formation of fatigue shear bands have been proposed (Fig. 3.18b) as possible reasons for softening effect [97, 104, 106].

For instance, UFG pure Al showed cyclic softening [81], whereas an increase of Mg content in the Al alloys suppressed cyclic softening and even increased cyclic hardening effect. Artificial aging of the cryorolled AA2024 introducing nanosized *S* precipitates in the microstructure resulted in little cyclic hardening (negative cyclic softening ratio), whereas naturally aged material showed cyclic softening [107] (Fig. 3.17). The LCF life is mainly controlled by fatigue crack propagation. The fatigue crack growth behavior in the nanostructured Al alloys was also found to be different from that in the coarse-grained ones [108–110]. The standard crack growth rate $\mathrm{d}a/\mathrm{d}N$ versus stress intensity factor range ΔK plots for the nanostructured materials showed the same stages of crack propagation as in the coarse-grained materials. However, the fatigue 'threshold' ΔK_{th} corresponding to

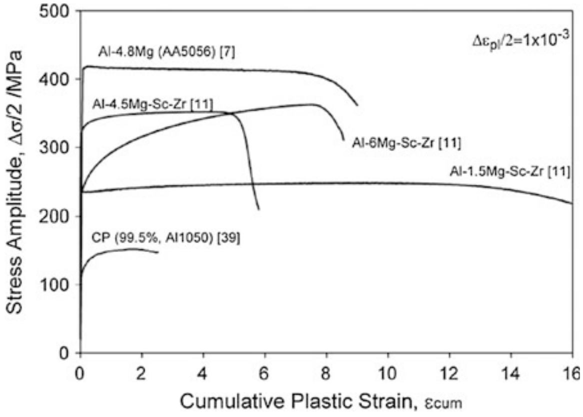

Fig. 3.16 Cyclic response of ECAP-processed Al and various Al–Mg alloys under the same constant plastic strain amplitude. The figure is reproduced from [81] with the permission from the publisher

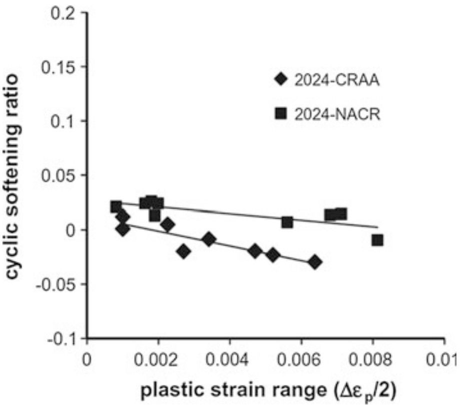

Fig. 3.17 Cyclic softening ratio as a function of strain amplitude for an Al2024 alloy produced via cryorolling followed by natural aging (NACR) or cryorolling followed by artificial aging (CRAA). This image is reproduced from [107] with the permission from the publisher

the low-end limit of the curves decreased after SPD processing in pure Al [109], AA5056 [110], and Al–1.5MgScZr [108].

SPD processing can lead to improvement of the LCF properties also in Mg alloys [111]. For example, ECAP processing (for 1–2 passes) of the AZ31B alloy led to significant improvement of the LCF life due to grain refinement as well as reorientation of grains, though it was reduced with further ECAP pressing. The orientation dependence (anisotropy) of the LCF properties in this material was also demonstrated [111]. The LCF life is mainly controlled by fatigue crack propagation. The fatigue crack growth behavior in the NS metals was found to be different from that in the coarse-grained counterparts [108–110]. The standard crack growth rate da/dN versus stress intensity factor range ΔK plots for the nanostructured materials showed the same stages of crack propagation as in the coarse-grained materials. However, the fatigue ‘threshold’ ΔK_{th} corresponding to the low-end limit of the curves decreased after SPD processing in CP Al and a range of Al alloys [108–110]. Similar results were reported for CP Ti [112], where ECAP processing reduced ΔK_{th} and led to the higher cyclic crack growth rate. A lower crack growth rate and a lower fatigue limit due to texture softening and reduction of crack nucleation resistance were reported for the ECAP-processed AZ31 alloy [113].

3.1.2.3 Strategies to Increase Fatigue Properties of Nanostructured Metallic Materials

Analysis of literature on fatigue performance of nanostructured metallic materials shows that intelligent microstructural design is the main approach to improve their fatigue behavior [80]. Microstructure of these materials can be tuned via optimization of the SPD processing parameters, such as temperature, strain, strain rate,

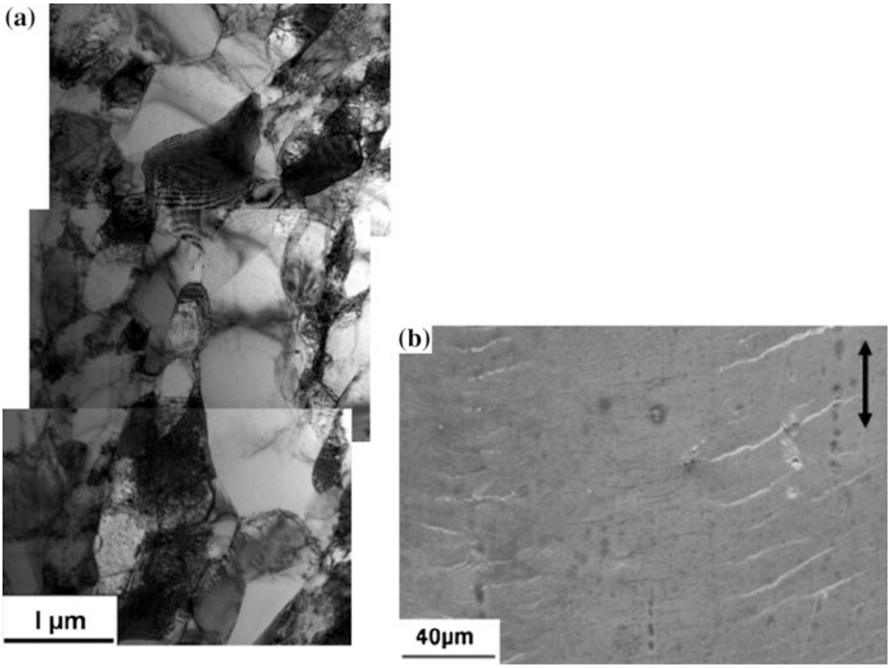

Fig. 3.18 **a** TEM image of the cryorolled CP Al fatigued at a strain amplitude of $\Delta\varepsilon_p = 0.0015$ showing the locally coarsened grains; **b** surface relief of face surface of cryorolled AA2024 tested at strain amplitude of $\Delta\varepsilon_p = 0.0056$ showing shear bands (*double arrow* indicates the stress axis). The images are reproduced from [104, 107] with the permission from the publishers

and strain path. Intelligent microstructural design can improve HCF properties dramatically. For example, a large enhancement in fatigue life by one order of magnitude in HCF regime was achieved in the AA6061 after a single ECAP pass leading to the formation of subgrains [98]. However, this effect disappeared after the alloy was pressed further for 4 passes due to significant increase of HAGB fraction. On the contrary, the AA2124 showed a higher fatigue life after 8 ECAP passes than that after 4 ECAP passes (Fig. 3.19), and complex microstructure consisting of grains/subgrains was observed in both conditions [114]. Microstructure evolution during SPD processing is determined to large extent by chemical composition of the material. Therefore, microstructure and fatigue properties can be also tuned via appropriate selection of kind and amount of alloying elements in the alloys.

Enhancement of ductility of nanomaterials is particularly useful for improvement of properties in the LCF regime, where plastic strain amplitudes dominate the fatigue life. The ductility of nanostructured metallic materials is often enhanced via their heat treatment after SPD which results in decrease of dislocation density in the interior of nanograins, as well as in relaxation of non-equilibrium grain boundaries. For example, this approach was successfully applied to nanostructured CP Ti in

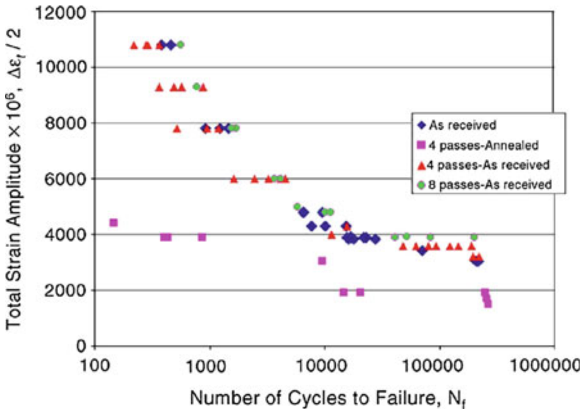

Fig. 3.19 Strain–life fatigue for the AA2124 in the coarse-grained condition and after ECAP for 4 and 8 passes. The image is reproduced from [114] with the permission from the publisher

[101] (Fig. 3.15). Very promising fatigue properties in the LCF and HCF regimes can be achieved by introducing the so-called bimodal grain size distributions, where nanograins having the size of several hundred nanometers are embedded into matrix of coarse grains having the size of several microns [81]. Such bimodal microstructures can be also generated via heat treatments of nanostructured metallic materials, though it cannot be done in every material.

Cyclic stability and fatigue life can be also enhanced via manipulation with shear banding. On the one hand, it was suggested that disposition of macroscopic shear banding should improve fatigue life [80]. This can be done, for example, via stabilization of nanostructures against growth of nanograins during cyclic deformation, as coarse grains can act as sites for the formation of shear bands. On the other hand, higher fatigue ductility and consequently higher fatigue life of cryo-rolled CP Al coincided with a much higher density of shear bands in [115]. It was shown that grain coarsening within the macroscopic shear bands increases the capacity of these shear bands to accommodate strain by eliminating the heavily worked regions from the shear band, allowing additional strain to be accommodated in those regions. These large strain-free grains are softer than their ultrafine-grained surroundings, and this encourages further localization of deformation within the shear bands [116]. However, such effect may not be expected in other nanostructured materials. Special attention should be paid to the as-SPD nanostructures formed in the material, since macroscopic shear bands can grow from shear bands induced into material during SPD processing.

3.1.3 Wear Resistance

Wear resistance is another very important property for metallic materials used in moving structural parts [117]. The wear of a component leads to an increased clearance and to loss of precision. For example, during the service of total joint replacements, there are inevitable sliding contacts between the femoral cup and the tibial of acetabular head during motion of the human body. These contacts generate wear debris, and they produce a dimensional loss for the bioimplants that may cause serious health problems for the patient [118]. Therefore, a high wear resistance of material yields a longer service life of component. As is well known, the higher the strength, the better the wear resistance of metallic materials [117]. So, it could be expected that nanostructuring should improve this property. However, investigations show that there is no consistent effect of nanostructuring on wear properties. The obtained results are often contradictory and can be divided into three groups [119] as shown in Table 3.3.

1. ***Nanostructured metallic materials show increased wear resistance***. In [119], it was demonstrated that the wear resistance of the Al–2, 3, and 5 % Cu improves with increasing number of ECAP passes leading to increased hardness for all alloy compositions (Fig. 3.20a). This effect was found to increase with increasing load applied (Fig. 3.20a). Nanostructuring of the AA2024 via mechanical milling and hot pressing led to a dramatic reduction of the wear rate to 0.012 mg/m (0.079 mg/m for the coarse-grained T6 material) [120]. The friction coefficient was reported to decrease in the nanostructured AA6060 and AA2024 alloys [120, 121]. These effects were related to the increased hardness of the SPD-processed alloys since a clear correlation between the hardness and wear resistance was observed [119, 120]. Similar results were also observed on Zn-based alloys processed by ECAP [122, 123]. Nanostructuring of metallic materials can also affect the wear mechanisms [119, 120]. Analysis of the worn surfaces and wear debris showed that adhesion and delamination were mainly operating in the Al–Cu alloys and contribution of adhesion wear increased with increasing number of ECAP passes [119]. Both mechanisms were also reported for the AA6060 in both coarse-grained and UFG conditions, though less surface damage and smaller laminated debris resulting in a smaller wear mass loss were observed in the as-ECAP samples. Adhesive and abrasive wear mechanisms seen in the coarse-grained T6 AA2024 alloy were replaced by delamination and oxidation in the nanostructured AA2024 [120]. Adhesion as the dominant wear mechanisms was also reported for the HPT-processed Al–Al_2O_3 nanocomposites [124].
2. ***Nanostructuring of metallic materials does not affect their wear resistance***. In [125], the authors were surprised that significant improvement of mechanical strength in pure Ti (Grade 2) due to nanostructuring via ECAP processing did not lead to any improvement of its wear resistance independently on the applied pressure. This finding was mainly attributed to the tribochemical reaction leading to oxidative wear with the abrasive effect in Ti. As is well known, the dominant wear mechanism is the oxidative wear in pure Ti and also Ti alloys, which controls the weight loss during sliding. The studies on wear surface showed that a thick mechanically unstable oxide layer appeared on the sliding surface of the Ti samples in both coarse-grained and nanostructured conditions due to tribochemical reactions and frictional temperature [126] (Fig. 3.21). This

Table 3.3 Effect of SPD nanostructuring on wear properties of various metallic materials

Material	SPD method	Wear rig	Lubrication condition	Effect of SPD nanostructuring on friction coefficient	Effect of SPD nanostructuring on wear resistance	References
Al-1050	ECAP	Reciprocating sliding tester	Unlubricated	No effect	Decreases	[119]
Al–Al_3Ti	ECAP	Block-on-disk	n/a	n/a	No effect	[127]
Al–Cu	ECAP	Pin-on-disk	Unlubricated	n/a	Increases	[132]
Al–12 % Si	ECAP	Pin-on-disk	Unlubricated	n/a	Decreases	[129]
Al-1100	ARB	Pin-on-disk	Unlubricated	n/a	Decreases	[130]
Al-5052	ARB	Pin-on-disk	Unlubricated	n/a	Decreases	[130]
Al-6061	ARB	Pin-on-disk	Unlubricated	n/a	Decreases	[128]
Al–Al_2O_3	HPT	Ball-on-disk	Unlubricated	n/a	Increases	[124]
Cu–10 % Al–4 % Fe	ECAP	Ring-on-block	Unlubricated	Reduced	Increases	[133–135]
AZ61 alloy	ECAP	Pin-on-disk	Unlubricated	n/a	No effect	[128]
Low-carbon steel	SMAT	Reciprocating sliding tester	Unlubricated	Reduced	Increases	[136]
Low-carbon steel	ECAP	Pin-on-disk	Unlubricated	n/a	Decreases	[130]
Pure Ti	ECAP		Unlubricated	Reduced	Increases	[137]
Pure Ti	ECAP	SRV oscillating tester	Unlubricated	No effect	Increases	[138]
Pure Ti	HE	Pin-on-disk	Unlubricated	n/a	No effect	[139]
Pure Ti	HE	Pin-on-disk	Various conditions	n/a	Decreases	[139]
Pure Ti	ECAP	Pin-on-disk	Unlubricated	n/a	No effect	[125]
Pure Ti (Grade 2)	HPT	Microscratch testing	Unlubricated	No effect	Increases	[140]
Pure Ti (Grade 2) + TiN coating	HPT	Microscratch testing	Unlubricated	Reduced	Increases	[141]
TiNi	ECAP	Ring-on-block	Unlubricated	n/a	Increases	[142]
Zn–40 % Al–2 % Cu–2 % Si	ECAP	Pin-on-disk	Unlubricated	Reduced	Increases	[122]
Zn–8 % Al	ECAP	Block-on-ring	Lubricated by oil	n/a	Increases	[123]

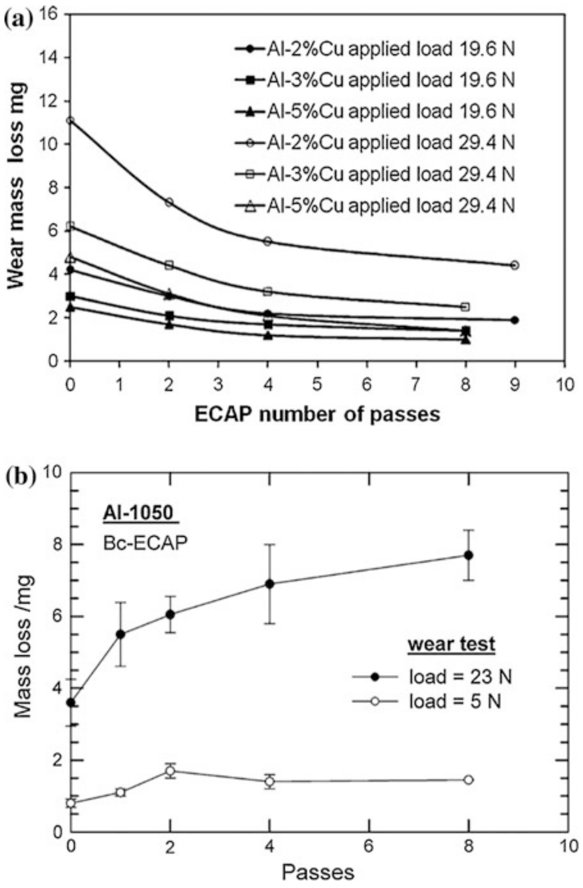

Fig. 3.20 **a** The effect of number of ECAP passes and the copper content on the wear mass loss in Al–2, 3 and 5 % Cu alloys (the sliding distance is 268.6 m under applied load of 29.4 N). The image is reproduced from [132] with the permission from the publisher; **b** the effect of number of ECAP passes on the wear mass loss in AA1050 at loads of 5 and 23 N. The image is reproduced from [119] with the permission from the publisher

Ti oxide layer plays a dominant role in determining the wear resistance of Ti independently of its grain size, so it 'masks' the effect of strengthening of nanostructure on the wear resistance. Wear-induced plastic deformation resulted also in microstructural changes in the subsurface regions (deformed region) due to the local thermal and thermo-mechanical processes. Nanostructuring of pure Ti resulted in thicker deformed region (Fig. 3.21). No significant effect of nanostructuring was seen in the Al–Al_3Ti composite in [127] and AZ61 Mg alloy in [128]. It should be noted that wear behavior of the composite materials is also determined by size and shape of reinforcements which can be affected by SPD processing.

3. ***Nanostructured metallic materials show degraded wear resistance***. Effect of number of ECAP passes on the wear mass loss in the AA1050 alloy is shown in Fig. 3.20b [119]. Wear mass loss gradually increases with increasing number of ECAP passes when a load of 29 N is applied although hardness of the material increases with increasing number of ECAP passes saturating only after 4 passes.

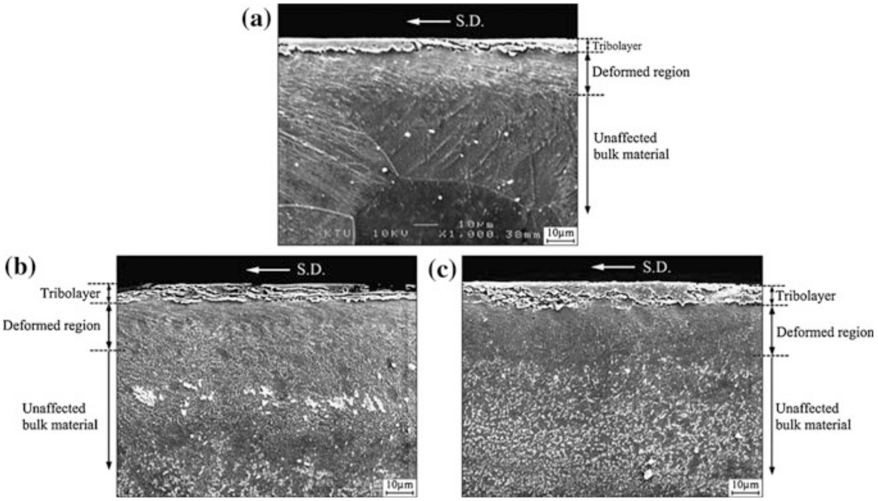

Fig. 3.21 Subsurface regions of **a** coarse-grained Ti and nanostructured Ti processed using ECAP through **b** 8E route and **c** 12E route. The wear tests were performed for a period of 2.63 h corresponding to a sliding distance of 10.40 km under a pressure of 1.5 MPa and at a sliding speed of 1.1 m s^{-1}. The image is reproduced from [125] with the permission from the publisher

At a lower applied load of 5 N, the wear mass loss slightly increases with increasing number of ECAP passes and saturates after 2 passes. No significant effect of ECAP processing on the friction coefficient was found [119]. Similar observations were reported for the Al–12 % Si alloy [129] processed by ECAP, CP Al [130, 131] and AA5052 [130] processed by ARB, and dual-phase steel processed by ECAP [130]. Analysis of the wear mechanisms showed that abrasive wear in the coarse-grained CP Al was replaced by delamination of the deformed surface layer in the ARB-processed material [131]. Higher oxidation rate leading to higher weight loss was reported for the ECAP-processed Al–12 % Si alloy [129]. ARB processing of the AA5052 resulted in significantly smaller wear debris [130], whereas an opposite effect was observed in the ECAP-processed AA1050 tested under load of 23 N [119]. A decrease of wear resistance in the Al alloys after SPD processing was mainly related to the loss of strain hardening capability [119, 130], to non-equilibrium grain boundaries [130, 131], and to intensive cracking at the interface of martensite and ferrite phases [130].

As it is clearly seen, no clear relationship between microstructure and wear properties can be outlined based on the available experimental results. Generally, wear mechanisms and wear properties are significantly affected by testing parameters such as applied load, sliding speed, application of lubricants, and pin material. More systematic studies on a wide range of SPD-processed metallic materials with greater respect to their microstructure are needed to optimize microstructural parameters in order to achieve high properties. Nevertheless, Table 3.3 clearly demonstrates that various nanostructured metallic materials with increased wear resistance can be successfully fabricated by existing SPD techniques.

3.2 Improved Physical Properties

Nanostructuring of metals and alloys by SPD processing allows to improve various functional properties. This section focuses on the effect of nanostructuring on electrical conductivity, magnetic properties, and irradiation resistance of metallic materials.

3.2.1 Electrical Conductivity

Electrical conductivity is another very important functional property of metallic materials. Electrical conductivity in metals is a result of the movement of electrically charged particles. The atoms of metal elements are characterized by the presence of valence electrons—electrons in the outer shell of an atom that are free to move about. These 'free electrons' allow metals to conduct an electric current. Because valence electrons are free to move, they can travel through the lattice that forms the physical structure of a metal. Under an electric field, free electrons move through the metal much like billiard balls knocking against each other, passing an electric charge as they move [143, 144]. The transfer of energy is strongest when there is little resistance. On a billiard table, this occurs when a ball strikes against another single ball, passing most of its energy onto the next ball. If a single ball strikes multiple other balls, each of those will carry only a fraction of the energy. By the same token, the most effective conductors of electricity are metals that have a single valence electron that is free to move and causes a strong repelling reaction in other electrons. This is the case in the most conductive metals, such as Ag, Cu, and Au, which have a single valence electron that moves with little resistance and causes a strong repelling reaction. Al with three valence electrons comes as the fourth most conductive metal. Their properties are compared in Table 3.4. Ag and

Table 3.4 Properties of pure metals with the highest electrical conductivity

Metal	Electrical conductivity (MS/m)	Electrical resistivity[2] (10^{-8}, Ω m)	Density (g/cm^3)	Melting point (°C)
Silver	62.1	1.6	10.5	961
Copper	58.5	1.7	8.9	1083
Gold	44.2	2.3	19.4	1064
Aluminum	36.9	2.7	2.7	660

[2] Resistivity is the opposite of electrical conductivity, evaluating how strongly a metal opposes the flow of electric current

Au are noble metals and do not attract much interest of engineering due to extremely high price. Cu and Al are currently the most widely used metals in electrical engineering and electronics.

Mechanical strength and electrical conductivity are the most important properties of conducting materials. However, high strength and high electrical conductivity are mutually exclusive in metallic materials, and trade-off between strength and conductivity is always encountered in developing conducting materials [157]. Pure Cu and Al having high electrical conductivity show very low mechanical strength (Table 3.5). The alloying of pure metals, strain hardening, or introduction of precipitates dramatically improve their mechanical strength due to suppression of dislocation glide. But all strengthening methods lead to a degradation of electrical conductivity, since the latter is determined by the scattering of conductive electrons due to disturbances in the crystal structure including thermal vibrations, solute atoms, and crystal defects [158]. This is clearly seen from the electrical conductivity–yield strength plot for coarse-grained pure Cu and its alloys presented in Fig. 3.22: The electrical conductivity of most conventional Cu alloys ranges from ~30 to ~85 % of International Annealed Copper Standard (IACS).

The key to making strong but conductive metals is to generate an appropriate microstructure in which dislocation glide is effectively blocked, while the scattering of conducting electrons is minimized. The effective resistivity of a metal ρ, by virtue of Matthiessen's rule, is normally written as

$$\rho = \rho_{\mathrm{T}} + \rho_{\mathrm{R}}, \tag{3.6}$$

where ρ_{R} is called the residual resistivity and is due to the scattering of electrons by lattice defects and impurities [158]. For nearly perfect crystals of high purity, the resistivity is dominated by phonon scattering ρ_{T} which is temperature dependent and nearly linear in absolute temperature. For polycrystalline metallic materials, the temperature-independent residual resistivity ρ_{R} can be split up into several contributions as [152, 156]

$$\rho_{\mathrm{R}} = \rho_{\mathrm{ss}} + \rho_{\mathrm{p}} + \rho_{\mathrm{d}} + \rho_{\mathrm{v}} + \rho_{\mathrm{gb}}, \tag{3.7}$$

where ρ_{ss} is the resistivity due to scattering of solute atoms dissolved in the matrix, ρ_{p} the resistivity added by second-phase particles, ρ_{d} and ρ_{v} resistivity due to dislocations and vacancies, and ρ_{gb} resistivity due to scattering on grain boundaries. It should be noted that the ρ_{p} part in turn can consist of several parts if several types of second-phase precipitates (such as Guinier–Preston zones, non-coherent precipitates, coherent precipitates) are present in the microstructure. In alloys, the ρ_{ss} and ρ_{p} parts provide the highest contribution to its effective resistivity, whereas scattering of electrons at grain boundaries (i.e., ρ_{gb} part) is insignificant. As it was discussed in Sect. 3.1.1, grain size hardening provides the highest contribution to total strength of nanostructured metallic materials. Therefore, pure nanostructured metals should demonstrate much higher strength with slightly lower conductivity compared to their coarse-grained counterparts. This was first demonstrated by Lu

Table 3.5 Mechanical properties of some nanostructured Cu- and Al-based materials produced via SPD

Material	Processing; grain size *d*	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation (%)	Electrical conductivity at RT, IACS (%)	References
99.95Cu	CG	62	172	40	~100	[145]
99.96Cu	ECAP 8p; d = 0.44 μm + coarser grains	360^{*}	375^{*}	–	96	[146]
HP Cu	PED; d = 0.4 μm + nanotwins	900	1068	12	96.9	[70]
HP Cu	DPD at LNT; d = 66 nm + nanotwins	610		8	95	[147]
99.999Cu (powder)	BM at LNT; d = 54 nm	688	770	7*	51	[148]
OF Cu	ARB 8 cycles; $w \approx 400$ nm	360^{*}			96^{*}	[149]
DLP Cu	ARB 8 cycles; w = 190 nm	472			74^{*}	
Cu–1Fe–0.017Pb	CG	160^{*}			90^{*}	
	ARB 8 cycles; $w \approx 250$ nm	405^{*}			85^{*}	
ADS Cu–0.5Al_2O_3	ECAP 4p; d = 0.37 μm	$525^{\#*}$	535^{*}	14.3^{*}	86.7	[150]
ADS Cu–1.1Al_2O_3	ECAP 4p; d = 0.35 μm	$565^{\#*}$	575^{*}	15.8^{*}	81.8	
Cu–0.36Cr	ECAP 8p + AA;	390^{*}	445	23	77	[151]
Cu–0.44Cr–0.21Zr	ECAP 8p + AA;	690^{*}	710	12	76	
Cu–0.8Cr–0.05Zr	ECAP 8p + AA; d = 0.2 μm	580^{*}	595	14	78	
Cu–5 at.%Nb	MA + compaction at 600 °C; d = 17 nm	1090^{*}			25	[152]
	MA + compaction at 600 °C + AA at 900 °C; d = 40 nm	~1000			~50	
Cu–0.5Cr–0.12Ag	CG HT;	295^{*}	430	20^{*}	75	[153]
	HPT at RT; d = 0.2 μm	480^{*}	530*	13^{*}	30^{*}	
	HPT at RT + AA at 450 °C; d = 0.2 μm + nanoprecipitates	820^{*}	840	10	85	
99.5Al	CG	28	76	39	61.3	[145]
AA6201	CG T81	310	331	6	54	
Al–0.60Mg–0.45Si	ECAP-PC 6p + AA; d = 0.5 μm +nanoprecipitates	275	289	14	55.7	[154]
AA6060	CG T6		250	8	53.6	[155]
	HPT at RT; d = 0.18 μm		525	5	51.8	
	HPT at 180 °C; d = 0.35 μm + nanoprecipitates		347	7	58.1	

(continued)

Table 3.5 (continued)

Material	Processing; grain size *d*	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation (%)	Electrical conductivity at RT, IACS (%)	References
AA6063	CG, SST		100	25	52.9	[155]
	Coarse grained, T6		200	14	54.5	
	UFG, ECAP-PC at 100 °C		264	13	51.8	
	UFG, ECAP-PC at 100 °C + aging at 130 °C		308	16	58.6	
AA6201	CG T81; $d = 65$ μm		330	6.1	53.6	[156]
	HPT at RT; $d = 0.13$ μm		510	2.5	47.7	
	HPT at RT + HPT at 130 °C; $d = 0.28$ μm + nanoparticles		412	4.9	55.6	
	HPT at RT + HPT at 180 °C; $d = 0.44$ μm + nanoparticles		365	8.8	58.4	

d—grain size, *w*—mean spacing of high-angle lamellar boundaries, IACS—International Annealed Copper Standard, HP—high purity, AA—artificial aging, TMT—thermo-mechanical treatment, CG—coarse grained, OF—oxygen free, DLP—deoxidized low phosphorous, PED—pulsed electrodeposition, ADS—alumina dispersion strengthened, MA—mechanical alloying, DPD—dynamic plastic deformation, BM—ball milling, RT—room temperature, LNT—liquid nitrogen temperature

Chemical composition of materials is provided in wt%, if not otherwise specified

[*] The value is estimated from experimental curves provided in the given reference

[#] 0.5 % offset strength

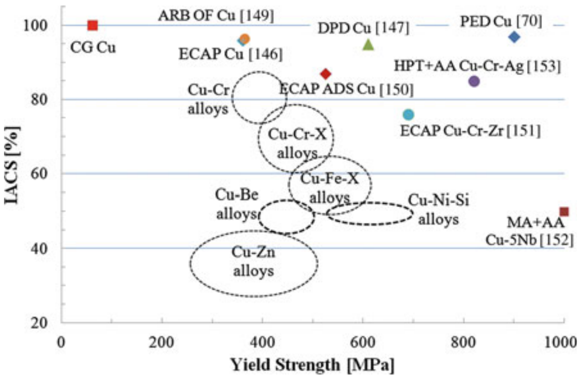

Fig. 3.22 Room temperature electrical conductivity (in IACS) versus yield strength for CG pure Cu and Cu-based alloys and their nanostructured counterparts obtained via SPD processed

et al. [70] on nanostructured Cu foil of high purity synthesized by pulsed electrodeposition technique. Nanograins with an average size of 400 nm had a high density of nanotwins of the {111}/[112] type with perfectly coherent and atomically sharp twin boundaries, which also act as strong barriers to dislocation motion, thus providing additional strengthening effect. This nanocrystalline Cu with the average twin/matrix lamellar thickness of 15 nm demonstrated unique combination of extremely high yield strength of 900 MPa and electrical conductivity of 96.9 % of IACS at room temperature (Table 3.5), which was just a few percent less than the conductivity of oxygen-free (OF) high-conductivity coarse-grained Cu [70]. The slightly elevated resistivity of the nano-Cu was ascribed dominantly to the intrinsic grain boundary scattering [159]. Since the technological applications of foils are very limited, further research activities focused on fabrication of bulk nanostructured Cu with similar properties. In [147], the same research group successfully applied dynamic plastic deformation at liquid nitrogen temperature to Cu cylinders with 18 mm in diameter and 25 mm in height. Such processing conditions ensured effective suppression of dislocation recovery, and the critical stress required for twinning was exceeded. The as-processed bulk Cu samples had nanostructure with an average grain size of 66 nm and nanoscale twins showing yield strength of 610 MPa and electrical conductivity of 95 % of IACS at room temperature (Table 3.5) [147]. Higuera-Cobos and Cabrera [146] subjected bulk CP Cu samples to ECAP processing resulting in the formation of bimodal microstructure with some coarse grains (several micrometers in size) embedded into UFG matrix with an average grain size of 440 nm. Again, a good combination of enhanced yield strength, 360 MPa, and high electrical conductivity, 96 %, of IACS, was found (Table 3.5). UFG sheets of OF Cu and deoxidized low phosphorous (DLP) Cu showing similar level of properties were successfully processed via ARB by Takata et al. [149]. However, high-strength nanocrystalline Cu obtained via two-step ball milling process and in situ consolidation demonstrated very low electrical conductivity of 51 % of IACS in [148]. Such significant degradation of electrical conductivity was related to impurities induced from the balls and jar during milling

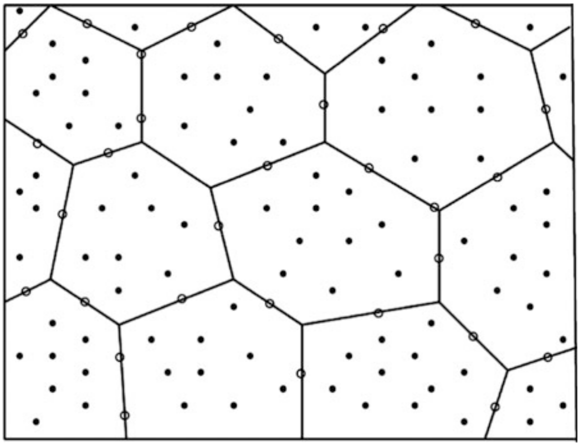

Fig. 3.23 Nanostructure with nanodispersed particles to be achieved to demonstrate a combination of high strength, good electrical conductivity, and enhanced thermal stability in alloys

process as well as to some possible micro- and nanoscale porosity significantly contributing to the resistivity.

In the alloys, nanostructuring provides unique opportunity to improve dramatically both mechanical strength and electrical conductivity. Enhanced mechanical strength can be achieved due to grain size hardening and dispersion hardening (see Sect. 3.1.1). Analysis of Eq. 3.7 shows that matrix should be maximally purified from the solute atoms and the most effectively scattering second-phase precipitates in order to minimize the scattering of conducting electrons in the microstructure and, thus, to further enhance the electrical conductivity [156]. This new approach illustrates the schematic presentation of an ‘ideal nanostructure’ to be achieved in the alloys to demonstrate a combination of increased strength, electrical conductivity, and thermal stability (Fig. 3.23). The nanoprecipitates in such structure should be the least scattering conductive electrons, and their significant amount should be located in the grain boundaries, thus suppressing mobility of grain boundaries and grain growth. Such nanostructures can be generated via SPD processing in two ways:

1. *Nanostructuring of alloy* (*solid solution*) via *SPD processing at ambient temperature followed by artificial aging for precipitation*. SPD processing at room temperature typically can result in significant grain refinement down to nanoscale, whereas the subsequent artificial aging leads to decomposition of solid solution, i.e., reduction of content of solute atoms in the matrix, and formation of nanoprecipitates of the required morphology. For example, in the case of the Al–Mg–Si alloys, one should avoid GP zones and β'' precipitates as conductive electrons are most effectively scattered on these types of precipitates. This approach was successfully applied to the Cu–0.5Cr–0.12Ag alloy in [153]. The solution-treated material was subjected to HPT processing at room temperature which led to grain refinement (Fig. 3.24a), improvement of mechanical strength to 480 MPa, and reduction of electrical conductivity from 75 to 30 % (Table 3.5). The subsequent artificial aging dramatically increased both yield

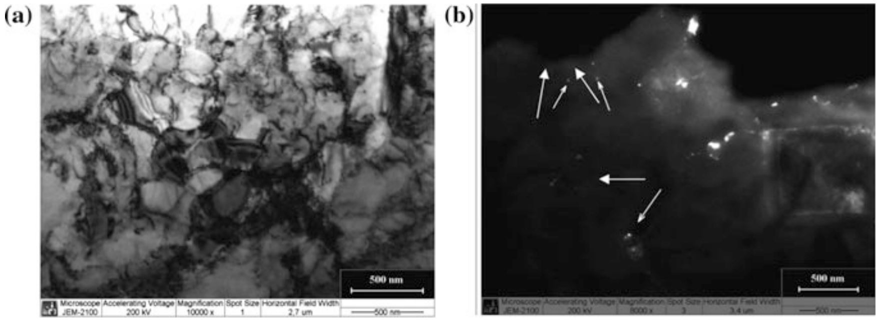

Fig. 3.24 **a** Nanostructure in the Cu–0.5Cr–0.12Ag alloy after HPT processing at RT; **b** formation of Cr nanoparticles (*marked by arrows*) in the nanostructure presented in (**a**) during artificial annealing at 500 °C for 30 min

strength to 820 MPa and electrical conductivity to 85 % due to decomposition of solid solution and formation of Cr nanoparticles (Fig. 3.24b; Table 3.5). It should be noted that precipitation kinetics is accelerated in the SPD-processed alloys due to higher diffusion coefficient because of high density of lattice defects and increased volume fraction of grain boundaries [160–162]. Therefore, a careful study of the effect of artificial aging parameters (temperature and time) on the microstructure and properties needs to be performed in order to determine the optimum aging parameters for given alloy after given SPD processing.

2. *Nanostructuring of alloy* via *SPD processing at elevated temperatures* (*250–500 °C for Cu alloys, 100–200 °C for Al alloys,* etc.) Grain refinement during SPD processing of alloys at elevated temperatures can be accompanied by dynamic aging which manifests itself in decomposition of supersaturated solid solution and formation of nanoprecipitates [153, 154, 156, 163, 164]. This effect has been related to significantly enhanced dislocation density and vacancy concentration leading to a dramatic increase of effective diffusion coefficient during SPD processing of alloys [161, 165]. This results in accelerated precipitation kinetic as the latter is controlled by diffusion of solute atoms [166]. For instance, it was observed on friction stir-processed AA2024 alloy that plastic deformation increases the precipitation kinetics at the temperatures below 300 °C [166]. At higher temperatures, the influence of plasticity on the volume fraction of precipitates was negligible. In [162], evolution of second-phase precipitates during ECAP processing of the AA7136 at 200 °C was found to be 50 times faster than during conventional aging treatments at the same temperature. Similar observations were also reported for the Al–Zn–Mg alloys in [20]. In the presence of deformation during the heat treatment, the precipitate morphology can be profoundly modified. In [167], dynamic aging during ECAP-PC processing of an AA6061 at 100 °C led to the formation of spherical β' nanoprecipitates, although rod-shaped β' precipitates are typically formed in this alloy during conventional artificial aging. This was attributed to the strong dislocation activity during ECAP processing and the resulting shear of precipitates.

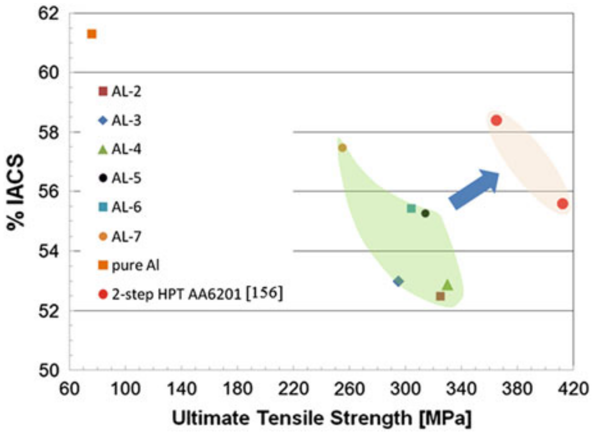

Fig. 3.25 Electrical conductivity (in IACS) of the various Al–Mg–Si alloys (AL-2–AL-7) used in electrical engineering for overhead power lines is plotted versus their ultimate tensile strength [168] and compared with the properties of a nanostructured AA6201 produced by two-step HPT processing [156]

In the recent new strategy [156], SPD processing at room temperature provides grain refinement in alloy, while further SPD processing promotes purification of matrix from solute atoms and second-phase precipitates of undesired morphology (ies). In some cases, just SPD processing at elevated temperatures is sufficient to achieve required nanostructure. In Fig. 3.25, electrical conductivity and strength of some commercial Al–Mg–Si alloys used for overhead power lines [168] are compared with the properties of nanostructured AA6201 alloy after two-step HPT processing (HPT processing at room temperature followed by HPT processing at elevated temperature). It is seen that the latter processing led to dramatic improvement of both electrical conductivity and strength (Table 3.5; Fig. 3.25).

Very recent research activities have focused on the effect of nanostructuring via SPD processing on superconductivity of superconductors [169–171]. It was reported that HPT processing not only improves mechanical strength in Nb (which is a well-known superconducting metal), but also increases the critical temperature for superconductivity due to the quantum confinement effect and size-independent superconductivity (Fig. 3.26), while the critical current density increases after HPT because of the vortex-pinning effect by lattice defects such as dislocations and grain boundaries [169].

However, an opposite behavior was demonstrated by the HPT-processed Nb–47 wt% Ti alloy (material for superconducting magnets) in [171]. The transition temperature in this material initially decreased with increasing shear strain and saturated to a steady-state level at large shear strains ($\gamma > 800$). This observation was rationalized based on dissolution of Ti in Nb during HPT processing. Further annealing of the HPT-processed specimens resulted in the elemental decomposition and enhancement of transition temperature and mechanical strength.

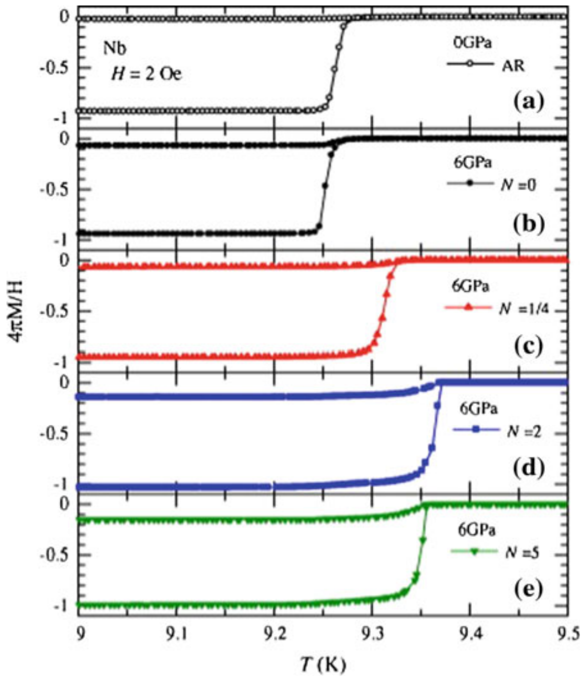

Fig. 3.26 Temperature dependence of the magnetization $M(T)$ of Nb in the magnetic field H = 2 Oe: **a** as-received coarse-grained material. **b–e** HPT-processed samples with different revolution numbers N. The figure is reproduced from [169] with the permission from the publisher

It can be outlined that nanostructuring of conducting materials can provide unique opportunity to dramatically improve mechanical strength without significant degradation of electrical conductivity in pure metals, whereas both strength and conductivity can be significantly enhanced in alloys via intelligent nanostructural design. Nanostructuring also appears as an effective approach to achieve both high strength and enhanced superconductivity in superconductors.

3.2.2 Magnetic Properties

Most of magnetic materials of industrial interests are ferromagnetic materials. Ferromagnetic materials with the demagnetized state do not show magnetization although they have spontaneous magnetization. This is because the ferromagnetic materials are divided into many magnetic domains. Within the magnetic domains, the direction of magnetic moment is aligned. However, the direction of magnetic moments varies at magnetic domain walls so that it can reduce the magnetostatic energy in the total volume. When domain wall can easily migrate, the ferromagnetic material can be easily magnetized at low magnetic field. This type of ferromagnetic materials is referred to as ***soft magnetic material*** and is suitable for applications of magnetic cores or recording heads. When domain wall is difficult to migrate, magnetization of the ferromagnetic material occurs only when high magnetic field is applied. In other words, this type of ferromagnetic materials is difficult to magnetize, but once magnetized, it is difficult to demagnetize. These materials are referred to as ***hard magnetic materials*** and are suitable for applications such as permanent magnets and magnetic recording media [172].

Soft magnetic materials are one of the most investigated classes of functional materials. Their microstructure can be amorphous or crystalline with grain sizes ranging from some nanometers in nanocrystalline soft magnetic materials to several centimeters in transformer steels [172]. Most of them are available as powders, ribbons, and thin films and are used in a huge variety of industrial applications such as motors, generators, transformers, sensors, or microelectronic devices. Earlier investigations showed the strong influence of nanostructuring via SPD on magnetic hysteresis characteristics of soft magnetic metals, such as Ni [173, 174], Co [175], Fe, and Fe–Si [176]. A sharp increase in the coercivity Hc was revealed in pure metals after SPD processing. It was demonstrated that coercivity in nanostructured pure Ni strongly depends on grain size, dislocation structure, and the non-equilibrium state of the grain boundaries [174]. For example, SPD-processed specimens subjected to recovery annealing at 100 and 200 °C had different values of coercivity by $\sim$40 %, though their grain sizes were nearly the same. At the same time, at 200 °C, an intense recovery of non-equilibrium grain boundaries was observed. As the temperature of annealing increased, a further decrease in the value of Hc was correlated with increasing grain size. An analogous regularity was revealed in Co processed via HPT [177]. TEM investigations of the domain structure of nanostructured Co with a grain size of about 100 nm used the Lorentz method. It was established that the magnetic domain sizes were significantly larger than the grain sizes and remagnetization was conditioned by the movement of domain walls, but at the same time, this movement was hampered by non-equilibrium grain boundaries.

In [176], five sets of soft magnetic metals, such as pure Fe, pure Ni, Fe–3 wt% Si, Fe–6.5 wt% Si, and Fe–17 wt% Co, were subjected to HPT processing at different temperatures (−196, 20, and 450 °C) up to strain levels, where a saturation of the microstructural refinement was observed. Depending on the material, the average grain sizes in the steady state varied from 300 nm at 450 °C to 30 nm at −196 °C. The coercivity was characterized in a magnetic closed system by using ring-shaped samples. Magnetic measurements obtained on ring-shaped samples give a much higher accuracy for determining the coercivity. The coercivity of the deformed materials first increased with decrease in grain size (Fig. 3.27). Once the crystallite size was far below 100 nm, the coercivity showed a strong decrease (Fig. 3.27). When the grain size becomes comparable to the magnetic exchange length, coupling over the grain boundaries occurs [178]. For magnetic materials, a maximum in coercivity versus the grain size occurs at the single-domain particle size, which is close to a grain size of about 100 nm, however depending on the material parameters (anisotropy energy, etc.). At this grain size, a pinning of the domain walls at grain boundaries can be expected. For smaller grain sizes, the

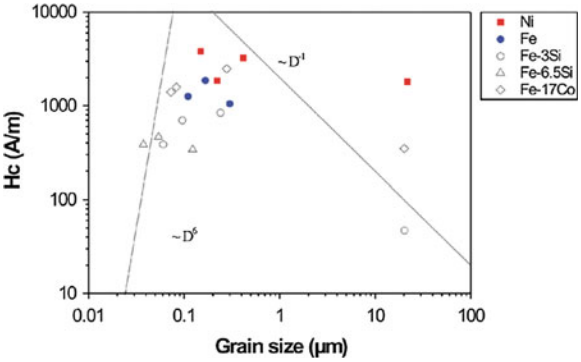

Fig. 3.27 Coercive force H_C as a function of the grain size for five soft magnetic materials. The figure is reproduced from [176] with the permission from the publisher

'effective' anisotropy is reduced due to exchange coupling which causes a dramatic reduction of coercivity with decrease in grain size.

A significant increase in the coercive force was also observed in hard magnetic alloys (such as Fe–Pd [179], RE–Fe–B [180–184], Fe–Cr–Co [185], and Cu–Co [186, 187]) processed by SPD. This is very important for practical applications and manufacturing of permanent magnets. However, the origin of Hc changes in these alloys has a more complex character and it is caused not only by the formation of a nanostructure but also by changes in the phase composition. For example, as in R–Fe–B (RE = Nd, Pr) system alloys which have attracted much research and practical interest in recent years. These alloys are used for fabrication of sintered [188] and hot deformed [189] permanent magnets with record values of magnetic force. The influence of HPT at room temperature and subsequent annealing on magnetic properties and structural changes in the cast $Pr_{20}Fe_{73.5}B_5Cu_{1.5}$ alloy was studied in [184]. In addition to the basic tetragonal $R_2Fe_{14}B$ phase (2:14:1), bcc (α-Fe type) and hcp (Pr rich) phases were present in the initial cast alloy. The basic magnetic phase 2:14:1 was in the form of very coarse dendritic grains and α-Fe additions constituted about 8 vol%, while the non-ferrite hcp phase constituted 25 vol%. At small strains, the alloy was characterized by stable phase composition and formation of a substructure with a mean subgrain size of less than 300 nm and a high density of dislocations. With increasing strain, the amount of the 2:14:1 phase relative to the amount of the bcc phase decreased, and in the alloy with the high strain, an amorphous phase was observed within the whole sample volume, while the 2:14:1 phase and other crystalline phases were not detected. Such microstructural evolution has also significantly affected the magnetic properties of the $Pr_{20}Fe_{73.5}B_5Cu_{1.5}$ alloy. Figure 3.28 shows Hc values of the alloy processed to varying strain (HPT rotation angle). In the initial state, Hc of the alloy was 20 kA/m, whereas after upset straining, Hc increased to 192 kA/m, grew further with increasing rotation angle, and reached the peak value at the angle range of 2–5. Annealing of the deformed samples restored the phase composition of the initial

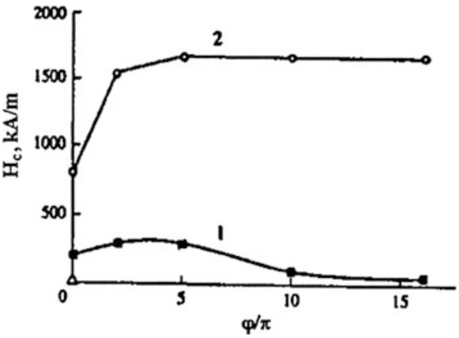

Fig. 3.28 Dependence of the coercitive force Hc of the $Pr_{20}Fe_{73.5}B_5Cu_{1.5}$ alloy in as-deformed (1) and annealed at 600 °C (2) conditions as a function of the HPT rotation angle (shear strain). The figure is reproduced from [184] with the permission from the publisher

alloy, but the grain size of the 2:14:1 phase did not exceed 300 nm and the amount of the α-Fe phase decreased sharply. As a result, annealing leads to a significant increase in the Hc value (Fig. 3.28). Thus, the application of the SPD method at room temperature with subsequent annealing resulted in a record value of Hc > 1600 kA/m for the $Pr_{20}Fe_{73.5}B_5Cu_{1.5}$ alloy. This value exceeded significantly the Hc values in permanent magnets fabricated from the same alloy via sintering or hot deformation.

In [179], a FePd alloy was nanostructured by severe plastic deformation following two different routes: Ordered and disordered states were processed by HPT. A grain size in a range of 50–150 nm was obtained in both cases (Fig. 3.29a, b). HPT induced some significant disordering of the long-range-ordered L10 phase. However, TEM analysis clearly showed that few ordered nanocrystals had remained in the deformed state. The deformed materials were annealed to achieve nanostructured long-range-ordered alloys. The transformation proceeded via a first-order transition characterized by the nucleation of numerous ordered domains along grain boundaries. The influence of the annealing conditions (temperature and time) on the coercivity was studied for both routes (Fig. 3.29d). It was demonstrated that starting with the disorder state prior to HPT and annealing at low temperature (400 °C) leads to the highest coercivity (about 1.8 kOe) (Fig. 3.29d).

There is also a body of research on magnetic properties of nanostructured Cu–Co alloys having a pronounced giant magnetoresistance (GMR) effect. In [186], the as-cast Cu–Co alloys with 2.2 and 4.9 wt% Co were subjected to HPT processing that dramatically refined the microstructure. For the as-cast Cu–2.2 wt% Co alloy, magnetization was only 79 emu/g_{Co} at the vanishing 1/H, which was about 50 % of the saturation magnetization for Co. After HPT, the alloy demonstrated typical superparamagnetic behavior without any tendency to saturation, namely $J = 18$ emu/g_{Co} at $1/H \rightarrow 0$, which was only about 11 % of pure Co. The absence of the saturation and such low J values in the Cu–2.2 wt% Co alloy were due to nanosize of all Co particles in the HPT samples, which was below the ferromagnetic limit for Co (4–10 nm). High fraction of coarser ferromagnetic Co grains in the Cu–2.2 wt%

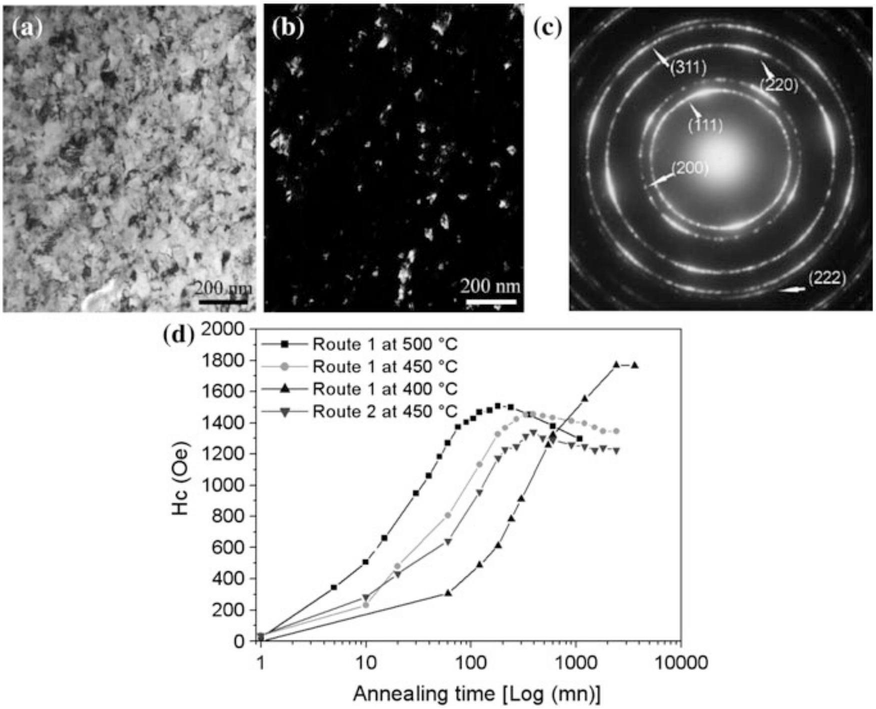

Fig. 3.29 TEM images of the FePd alloy processed by HPT (route 1—HPT of the disordered state); **a** *bright-field image* showing the nanoscaled structure, **b** *dark-field image* obtained by selecting with an aperture a part of the (111) fcc ring and showing few isolated nanoscaled grains, **c** SAED pattern with Debye–Scherrer rings characteristic of a polycrystalline structure with a very small crystallite size, **d** evolution of the coercivity of the FePd alloy processed by routes 1 and 2 as a function of the aging time for different temperatures. The figure is reproduced from [179] with the permission from the publisher

Co alloy resulted in a different behavior of the material. The magnetization of the as-cast alloy reached the saturation at J_s = 135 emu/g_{Co}. It was somewhat lower than the J_s for Co. The magnetization of the HPT-treated alloy did not saturate, although it was about three times higher at 1/H → 0 in comparison with the Cu–2.2 wt% Co alloy. Evolution of magnetic properties of the Cu–6.5 wt% Co alloy during ECAP processing with varying parameters was studied in [187]. The significant increase of the magnetic coercivity after first ECAP pass was related to a pinning effect of lattice defects for the movement of magnetic domain walls. Additional increase in the coercivity after further processing through route A was attributed to the refinement of the ferromagnetic Co particles to 10–30 nm through intense shear by ECAP. The magnetic anisotropy was prominent when the material was processed through route A, but was negligible through routes Bc and C (Fig. 3.30). The anisotropy occured because precipitate particles were successively elongated through route A with increasing number of ECAP passes, but they

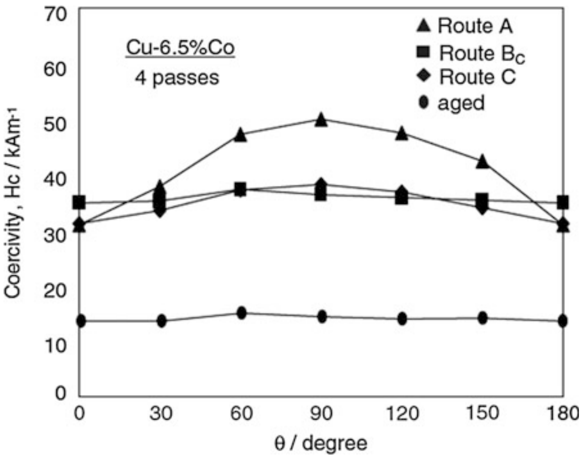

Fig. 3.30 Plots of coercivity with respect to rotation angle after 4 passes of ECAP through *route A*, *route B$_C$*, and *route C*. The figure is reproduced from [187] with the permission from the publisher (in the label, 'aged' stands for coarse-grained material)

reserved the original equiaxed shape while pressing through routes B$_C$ and C after 2 passes.

SPD techniques have been also successfully utilized for compacting nanopowders. Metal–ceramic powder mixtures consisting of Co (ferromagnetic) and NiO (antiferromagnetic) phases were compacted by HPT both with and without a prior ball milling [190]. Enhanced coercivity of the obtained materials was ascribed to the Co particle size refinement, the increase of stacking faults, and the magnetic coupling between Co and NiO phases. Nanostructured Ni with an average grain size of 20 nm obtained via HPT consolidation of ball milled powders in [191] is another example. However, it should be noted that such materials are usually characterized by enhanced contamination and are often not fully dense, which can degrade their magnetic properties [191].

It is seen that intelligent nanostructural design using SPD processing and possibly further annealing treatments can dramatically improve magnetic properties of both soft and hard magnetic materials. The outstanding properties of nanomaterials arise from the fact that the grain size becomes comparable with the magnetic exchange length, which causes the so-called exchange domains resulting in strongly modified magnetic properties compared to the coarse-grained materials.

3.2.3 Irradiation Resistance of Bulk Nanostructured Metallic Materials

Global demand for electric power is being accelerating in present-day world from year to year. In view of the development of new types of reactors and a decrease of the traditional raw energy resources, this share will increase. Controlled nuclear fusion energy development will allow the mankind to generate the energy mainly by fusion reactors in the future. One of the challenges is the task of developing radiation-resistant materials for advanced energy technologies [192, 193]. Indeed, the materials composing, for example, fusion components have to operate reliably in highly radiated environment. The properties of solids are subjected to be significantly modified by different kinds of high-energy particles and radiation fluxes (fast neutrons, γ- and X-radiation). Such irradiation causes changes in materials' microstructure expressed by irregularity in oriented crystal structure, radiation-induced defects (vacancies, clusters, dislocation loops, etc.) leading to degradation of their mechanical properties—bulging, limpness, accelerated creep of the radiation-exposed constructions.

Materials used in fission and fusion reactors are permanently in the conditions of irradiation by high fluxes of fast neutrons. Collisions of neutrons with atoms result in displacement cascades and the formation of non-equilibrium point defects such as vacancies, self-interstitials, and their clusters [193, 194]. At high doses of irradiation, these defects are accumulated that lead to a number of unwanted effects: radiation swelling (volume increase due to vacancies), radiation growth of anisotropic (textured) materials (a directional increase in one dimension), radiation creep, radiation work hardening, and simultaneous embrittlement [193–195]. In addition, nuclear reactions under the effect of neutrons result in the formation of a series of foreign elements with a subsequent accumulation of gaseous impurities and changes of phase composition. The most troublesome problems are the radiation swelling and growth, which change the shape and dimensions of fuel elements and other components of reactor cores, a decrease in thermal conductivity of fuel rod claddings and in the space between them that results in violations of the work regime of reactors and a decrease of the available fuel burn-up. In some materials, significant volume changes (up to several percent) are accumulated after the fluence of the order of 10^{23-26} m^{-2} that for typical values of the flux 10^{17-19} $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$ occurs in a few months [196]. These problems will be even more critical for fusion reactors, in which neutron flux is much higher than that in fast breeder reactors.

Therefore, a safe, reliable, and economical operation of nuclear power reactors critically depends on the radiation resistance of materials used in nuclear engineering. In view of this, fundamental research toward the development of radiation-resistant materials is a very important multidisciplinary task of condensed matter physics, materials science and nuclear engineering.

The rate of accumulation of radiation damages and related property changes to a great extent depend on the chemical composition and structure of materials. Thus, there are two main ways to decrease the harmful effects of irradiation. The first one is the change of main components of steels and alloys and doping by small additions of different elements. This method allows decreasing of one or two of the consequences of irradiation, but can result in a deterioration of other properties. For instance, austenitic steel has high mechanical properties but is largely prone to swelling, while another steel, ferritic–martensitic one, swells not much, but quickly embrittles [197–199]. For an efficient control of radiation resistance properties of materials, this first method is to be combined with the second one.

The second way to increase the irradiation resistance is the modification of microstructure, increase of the density of dislocations, and decrease of the grain size. The reduction of defect accumulation rate in this case is associated with the sink role of dislocations and grain boundaries for vacancies and interstitials. Reduction of the grain size is especially efficient for this purpose. At grain sizes less than 10 μm, a drastic decrease of radiation swelling is observed [200]. Defect-free layers with the thickness of about 10–30 nm in the vicinity of grain boundaries are often observed [201]. In stainless steel, a decrease of the grain size from 3.7 to 0.5 μm results in an order of magnitude reduction in radiation swelling [196].

In this relation, nanostructured materials are currently attracting a considerable interest as potential radiation-resistant materials. Up to date, a few studies focused on the microstructure changes in nanocrystals during ion and proton irradiation have been carried out. In [202], through a measurement of electrical resistivity, it was shown that the accumulation of point defects in nanocrystalline Au with the grain size of 23 nm occurs significantly more slowly than that in a polycrystal with the grain size of 10 μm. In [203], electron microscopic studies of the microstructure of irradiated nanocrystalline Pd and ZrO_2 with varying grain sizes were carried out. The density of point defect clusters decreased by a factor of 3–4 when the grain size is reduced from 100 to 40 nm. For smaller grain sizes, no defects were observed.

In a series of papers [204–206], molecular dynamics simulations of the evolution of displacement cascades have been carried out for Ni nanocrystals with the grain sizes of 5 and 12 nm for primary knock-on atom values in the range from 5 to 30 keV. These studies have revealed significant differences in the formation of primary defects in nanocrystals from that in single crystals. Due to the high mobility of interstitials, these defects sink at grain boundaries and triple junctions and annihilate with the free volumes there. The structure of grain boundaries during this process does not change significantly. In the grains enriched by vacancies, stacking fault tetrahedra are formed similarly to single crystals. But in some cases, in nanocrystals, the vacancies are completely absorbed by grain boundaries. At high energies of primary knock-on atoms, dislocation networks are formed near grain boundaries upon the resolidification of a thermal spike region. These networks annihilate the excess volume associated with vacancies. The preferred sites for the sink of interstitials are grain boundary dislocations and triple junctions. Molecular dynamics simulations conducted in [207] also demonstrate that the grain boundary structure at the nanoscale regime strongly affects the primary radiation damage state, with the grain boundary acting as a sink for interstitials.

Thus, both the experimental data and simulations have demonstrated that grain boundaries and junctions in nanocrystals can efficiently absorb interstitials and hamper the accumulation of point defect clusters, thus resulting in slowing down the volume expansion due to displacement cascades.

However, the scarce data available to date do not allow drawing qualitative conclusions on the structure and mechanical property changes of nanomaterials under irradiation. Moreover, the results cited have been obtained using a model irradiation of thin nanocrystalline films by ions and thus do not allow one to make conclusions on the mechanical property changes of bulk materials under real reactor irradiation. Molecular dynamics simulations can predict the behavior of defects only in a short timescale, and the role of grain boundaries in the evolution of defects during long-term irradiation has not been studied systematically.

In all of the cited works, nanocrystalline metals were prepared by inert gas condensation method which produced small-sized samples that limits the feasibility of studies of mechanical properties and especially of applications. To explore fully the potentials of the use of nanostructured materials in nuclear power engineering, a systematic study of the properties of bulk nanostructured materials under neutron irradiation is needed.

As it was already shown in Chap. 2, bulk nanostructured materials with advanced properties meeting the requirements of particular applications can be tailored by nanostructuring through SPD processing, which imposes extremely large plastic strain on materials without changing their geometry [208–214]. The most developed SPD method, ECAP, is especially attractive from the viewpoint of fabrication of structural nanomaterials for nuclear engineering.

Quite recently, proton irradiation experiments have been carried out on nanocrystalline Ni and Cu–0.5Al_2O_3 synthesized by ED and SPD [215]. In irradiated samples, no defects except for stacking fault tetrahedrons were observed and the density of the latter was much lower than that in coarse-grained polycrystals. Other studies on ion irradiation of nanocrystalline TiNi shape memory alloys [216] and nanostructured 316 stainless steel produced by HPT [217, 218] also testify a great potential of these materials as radiation-resistant ones. For example, X-ray studies of the TiNi alloy with a grain size of 23 nm showed no tendency for radiation-induced disordering of crystal structure (Fig. 3.31) [216]. These data inspire that SPD method will allow the fabrication of nanomaterials efficiently resisting radiation swelling and embrittlement.

The major weakness of most ion irradiation techniques is that the examined region usually is a fraction of a micron from the ion-incident surface which introduces some uncertainty in our ability to correlate the ion results with predicted bulk behavior attained during neutron irradiation. However, the data on the effect of high-dose neutron irradiation on stability of commercial nanostructured materials in the environment of real reactors are poorly presented in the literature. The first publications in this area were focused on the 321 stainless steel produced by ECAP [219] and low-carbon steel produced by ECAP-C [220, 221]. In [219], a study of ECAP 321 steel before and after the neutron irradiation at temperature ~350 °C in the reactor BOR-60 with the maximum damage dose 5.3 dpa was carried out. The ECAP-processed steel demonstrated the thermal stability (up to 650 °C) of irradiation hardening after the neutron irradiation. However, the steel after ECAP was characterized by a rather wide distribution of grain sizes and substructures, so a conclusion of further studies to clarify and explain the observed regularities was drawn. Studies in [220, 221] focused on steel 10 produced by ECAP-C, which was subjected to neutron irradiation with the maximum dose of 1.37 dpa. High number densities of nano-Mn–Si-enriched precipitates were observed in both coarse-grained and UFG steels after irradiation (Fig. 3.32). However, the number density and the radius of the clusters were larger in the case of the UFG steels due to the shorter path that the defects need to diffuse before they reach the grain

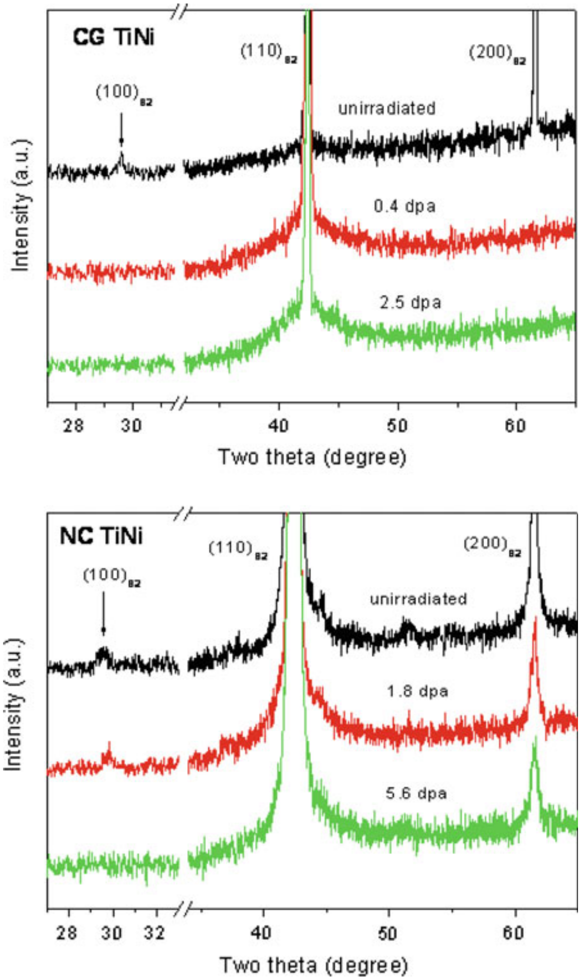

Fig. 3.31 X-ray studies revealed better irradiation resistance of nanostructured TiNi produced by HPT (with an average grain size of about 23 nm) as compared to CG TiNi (80 μm). The figure is reproduced from [216] with the permission from the publisher

boundary and hence less defect recombination probability in the matrix. The fact that these small clusters were not observed before irradiation confirms that their formation was radiation-induced. The hardness and strength of UFG steel showed minor changes after irradiation as compared to CG one indicating less radiation hardening effect (Fig. 3.33). The irradiation hardening in the UFG steel was mainly due to the irradiation-induced clusters. In general, UFG steel revealed better irradiation tolerance; however, the pronounced precipitation effects and stability of these nanoprecipitates should be carefully considered in future studies.

Thus, preliminary studies demonstrate that nanostructuring of metals by the use of SPD methods can be capable of producing new materials, which will have enhanced radiation resistance. To make a fundamental basis for the development of these materials, there is a need to study the processes occurring in nanocrystals

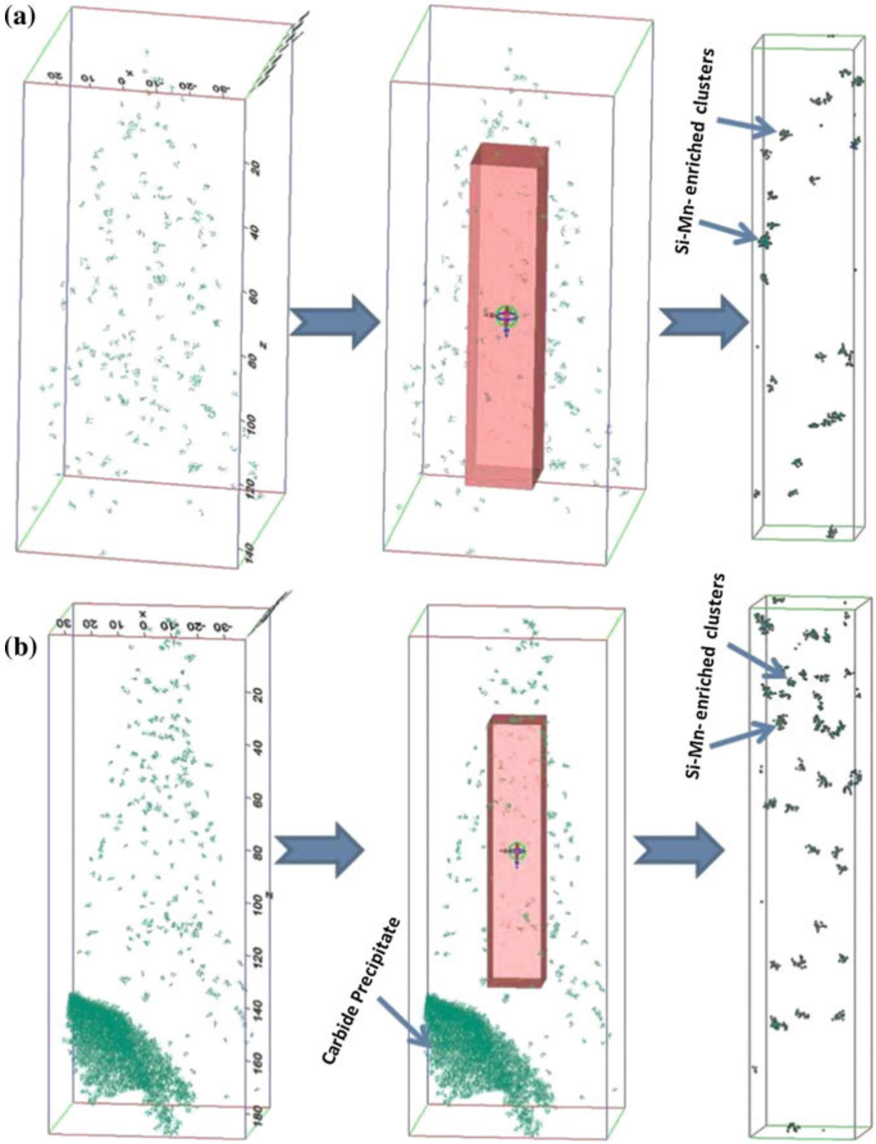

Fig. 3.32 Si–Mn-enriched cluster distribution postneutron irradiation for **a** CG and **b** UFG steels. The dimension of the interior (*colored*) boxes is 20 × 20 × 100 nm. The figure is reproduced from [221] with the permission from the publisher

during irradiation, changes in the structure and mechanical properties of nanocrystals under long-term irradiation.

Up to date, radiation resistance investigations of bulk nanostructured materials have been just started, but have already demonstrated promising results and

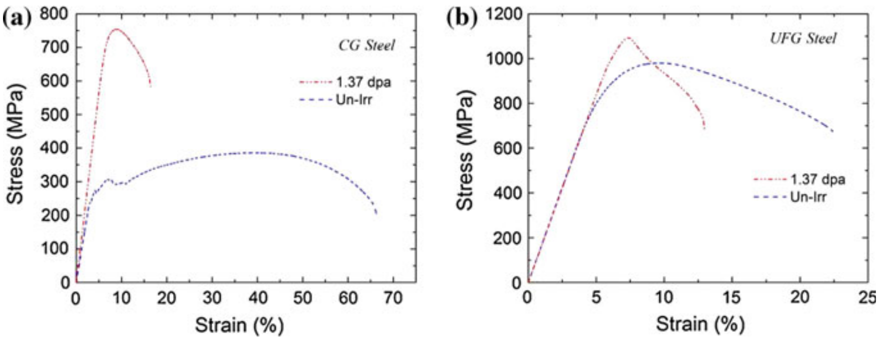

Fig. 3.33 Engineering stress–engineering strain curves for UFG **a** and CG **b** steel before and after irradiation to 1.37 dpa. The figure is reproduced from [221] with the permission from the publisher

important tendency in enhancing a radiation tolerance of metals by their nanostructuring. The origin and physical background of radiation-resistant behavior of bulk nanostructured materials is a primary task to be investigated for establishing a scientific fundament to improve essentially radiation-resistant properties of commercial alloys used in energy industry. The second task is manufacturing of pilot articles from SPD-processed commercial alloys (austenitic steels) and their tests under irradiation. The combination of high mechanical and radiation-resistant properties makes bulk nanostructured metallic materials to be of a high potential being applied to the future energy technologies.

3.3 Enhanced Chemical Properties

This section is about chemical properties of nanostructured metallic materials processed via SPD. We focus on two main functional properties, corrosion resistance and biocompatibility, which are important for applications.

3.3.1 Corrosion Resistance

Corrosion, the property of a material to deteriorate its properties due to interaction with the environment, especially chemically aggressive one, is an old problem for the industry since the very beginning. The embrittlement of a metal, leading to cracking of metallic materials inducing catastrophic failures of constructions, inspired the challenge to modify microstructures to survive hostile conditions. Materials required by different branches of industry are generally described by corresponding standards, but they are not flexible enough to reflect the industry needs. Development of corrosion-resistant metallic materials for advanced applications is a topical task for modern materials science with attention to both effectiveness and security of the cutting-edge technologies and ecological security taking into consideration risks of global warming and industrial disasters. The problem of utmost importance is development of new functional materials with reasonable corrosion resistance to be used in new-generation applications.

Corrosion resistance was shown to be significantly enhanced in several nanocrystalline metals and alloys as compared to their coarse-grained counterparts. A tendency for localized corrosion was observed to be lower for electrodeposited (ED) nanocrystalline Ni [222]. The origin of better corrosion resistance for nanocrystalline metals was a subject of discussion and was attributed to increased breakdown potential and a better resistance to anodic dissolution as a result of lower porosity. Evidence provided to substantiate these hypotheses or cogent reasons for not observing a higher localized corrosion (such as pitting or intergranular attack) even in the presence of such a high volume fraction of grain boundaries has not been conclusive. The discovery of grain boundaries in ED nanocrystalline Ni to be predominantly coherent low-sigma coincidence site lattices ($\Sigma 3$ CSLs) has been attributed to the possible origin of its superior corrosion resistance. Recently, it has been demonstrated [222] that grain refinement, independent of the processing route, leads to the formation of high-angle boundaries and provides corrosion resistance to down-hole alloys. This breakthrough and recent advances in processing technology to engineer high-strength corrosion-resistant metallic nanomaterials will enable the design of nanostructured metallic materials specifically for the oil and gas industry.

However, for the case of bulk nanostructured materials processed via SPD, it is necessary to note that up to now, there is no unified opinion on their corrosion properties. The fundamentals of the effect of grain size on corrosion behavior in different metallic materials were discussed in overview [223]. One can find in the literature a wide diversity in the data obtained on different nanostructured materials subjected to corrosion in different environments. In case of nanostructured CP Ti, it was shown that simultaneous enhancement of both mechanical strength and corrosion properties in aggressive environments, such as HCl and H_2SO_4 solutions, is possible [224–226]. Corrosion resistance of SPD-processed Ti is determined not only by grain size, but also by the crystallographic texture developed during SPD processing [226]. Particularly, basal planes of CP Ti offer higher corrosion resistance independently of grain size. Dislocation density can also significantly affect corrosion properties of this material. Very recently, it was demonstrated that corrosion resistance of the SPD-processed CP Ti can be further improved without any loss of mechanical strength via proper annealing treatments due to reduction of dislocation density and residual stresses (Fig. 3.34) [227]. Very similar results were reported for SPD-processed Mg alloy AZ61 tested in 0.1 M NaCl solution [228].

On the other hand, authors of [229] demonstrated that UFG samples of 321 (08Cr18Ni10) austenitic stainless steel exhibit less corrosion resistance than their coarse-grained counterparts in NaCl environment and higher stability in H_2SO_4 at room temperature, whereas in [230], an enhanced corrosion rate of UFG ferritic steel produced by SPD was observed in H_2SO_4 solution. Besides, the data published in [231] testify that SPD processing of interstitial-free steel does not lead to

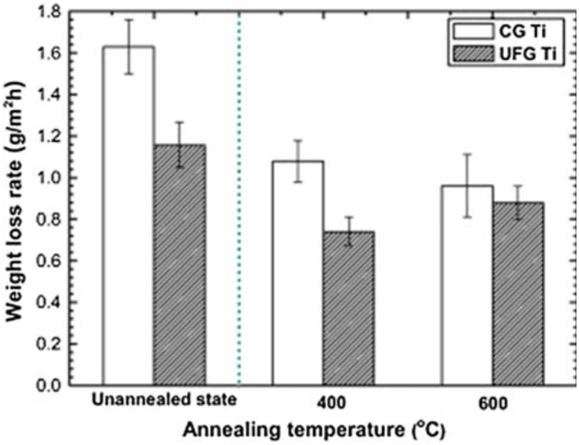

Fig. 3.34 The weight loss measurement test results of the coarse-grained Ti and SPD-processed Ti in a 0.5 M H_2SO_4 solution before and after annealing at different temperatures for 2 h. The figure is reproduced from [227] with the permission from the publisher

considerable change in corrosion properties in NaCl. It should be noted that crystallographic texture of steels can also affect their corrosion resistance. Particularly, it was shown that the pitting corrosion susceptibility of the grains of 316LVM stainless steel is dependent on the crystallographic planes [232]. The planar orientation {111} and {100} parallel to the surface had the highest resistance to pitting corrosion, and a lower pitting resistance was expected for the crystallographic planes with lower atomic density. So pitting susceptibility index (PSI) of the surface can be predicted based on texture measurements, and pitting resistance of steels can be improved by designing the desired crystallographic texture [232]. In [233], corrosion resistance of pure Mg in NaCl solution tended to degrade with increasing ECAP passes. Macroscopic preferential corrosion and grain boundary corrosion were observed in ECAPed pure Mg. The former resulted from the inhomogeneous strain distribution in the ECAPed samples, and the latter correlated with the stored energy around the deformed grain boundaries. Similar results, showing higher corrosion rate of ECAP processed pure AZ91 alloy than the as-cast state, were also reported in [234].

Grain refinement down to nanoscale can significantly affect the local corrosion behavior of metallic materials. In [235], nanostructured Al–Mn alloy subjected to immersion in 3.5 % NaCl artificial seawater for 168 h had fewer and finer pits compared to its coarse-grained counterpart due to the energy equilibration between non-equilibrium grain boundaries and intragranular defects as well as due to the finer Al_6Mn particles. Refinement of β-$Mg_{17}Al_{12}$ phase to nanoscale size via ECAP processing of the AZ61 Mg alloy decreased its susceptibility to microgalvanic corrosion [228]. An increased pit initiation resistance was reported also for Al–Mg alloys and AA5083 subjected to short-term corrosion testing [236], AA5052 [237],

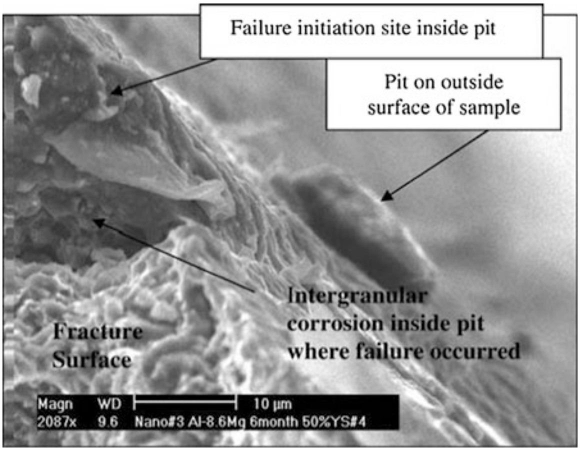

Fig. 3.35 SEM micrograph of the nanostructured Al–8.6 Mg after 6 months of alternate immersion in 3.5 % NaCl in the 50 % YS condition. Inside the pit intergranular corrosion is obvious. The image is reproduced from [236] with the permission from the publisher

AA6082 [238]. However, the long-term pit resistance of the nanostructured Al alloys shows an ambiguous character [236, 239]. The pitting depth in the nanostructured Al–Mg alloys was larger than that in the conventional material and also varied with varying Mg content [239]. This effect was related to susceptibility of the nanostructured Al alloys to intergranular corrosion (Fig. 3.35), whereas their coarse-grained counterparts are non-susceptible [236, 239].

Some nanostructured metallic materials attract significant interest of biomedical engineering (this is considered more in detail in Sects. 3.3.2 and 4.1). The biocorrosion response of nanostructured CP Ti processed by different ECAP routes was also studied in simulated body fluid [240, 241]. The nanostructured CP Ti produced by ECAP showed better corrosion resistance than the CG CP Ti in the Hank's solution due to the formation of highly stable oxide film on metal surface with higher grain boundary fraction. Crystallographic texture also significantly affected the corrosion response of the nanostructured material in the simulated body fluid. In [242], the ECAP and back pressure ECAP-processed AZ31 alloys (tested in the Hank's solution) exhibited corrosion rate similar to that of the as-extruded one, but the corrosion rate slightly increased after 1–2 passes ECAP or backpressure ECAP and further decreased after 4-pass procedure. One possible explanation could be attributed to the accumulative residual strains during deformation leading to more energy restored in the deformed grains and grain boundaries, which results in higher sensitivity of deformed grains and grain boundaries. Another explanation might be related to the gradual transformation of subgrain boundaries from low-angle type to high-angle ones after ECAP by absorbing dislocations generated during processing, and high-angle grain boundaries are more susceptible to chemical attack with higher grain boundary energies. Additionally, severe local corrosion was also observed for the 1–3 passes ECAP or back pressure

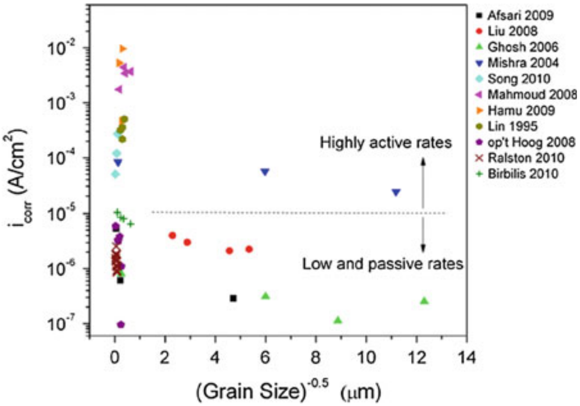

Fig. 3.36 The effect of grain size on corrosion rate (expressed as A cm^{-2}) for different materials and environments. The figure is reproduced from [243] with the permission from the publisher

ECAP-processed AZ31 alloy [242]. Compared to the as-extruded AZ31 alloy, the samples after ECAP or back pressure ECAP procedure showed much smaller sized corrosion pits on the surface after removing the corrosion product.

Generally, it can be outlined that nanostructured metallic materials show complex corrosion behavior depending on the environment. Careful analysis of all data available in the literature was performed in [243], and all the data in the literature were separated into two main classes (Fig. 3.36):

- range of material–environment combinations showing low-to-passive corrosion rates (≤10 μA cm^{-2}),
- range of material–environment combinations exhibiting highly active corrosion rates (≫10 μA cm^{-2}).

It was found that the data belonging to the first class tend to follow the Hall–Petch-type law where corrosion resistance can be presented as [243]

$$i_{\text{corr}} = (A) + (B)d^{-1/2} \tag{3.8}$$

where A is a function of the environment (as the same material with the same microstructure can have a different corrosion rate in different electrolytes) and B is a material constant determined by chemical composition of the material and its purity. This effect was experimentally observed on a wide range of metallic materials exhibiting some level of passivity (which have oxide on the metal surface). Figure 3.37 illustrates this effect for pure Mg, $Ni_{50.5}Ti_{49.5}$, Ni–Cu, and pure Al with different average grain sizes achieved using different processing routes (ECAP, cryorolling, drawing, etc.) [243–248]. This was related to the fact that grain refinement allows different rates of oxide growth on the surface. Since the oxide film conduction rate on surface is governed by grain boundary density, UFG and nanostructures are expected to be more corrosion resistant. In the absence of an oxide film on the surface (at dissolution rates of ≫10 μA cm^{-2}), UFG and nanostructures containing high grain boundary densities will enhance overall surface

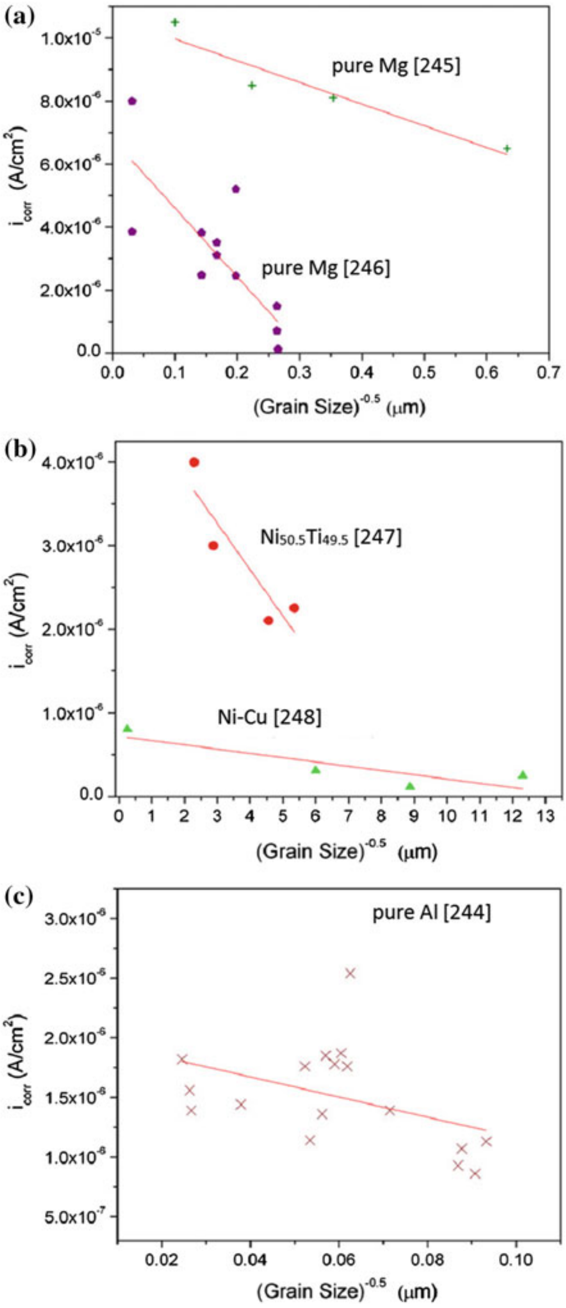

Fig. 3.37 The relationship between corrosion rate and grain size for low-to-passive current densities. The figure is reproduced from [243] with the permission from the publisher

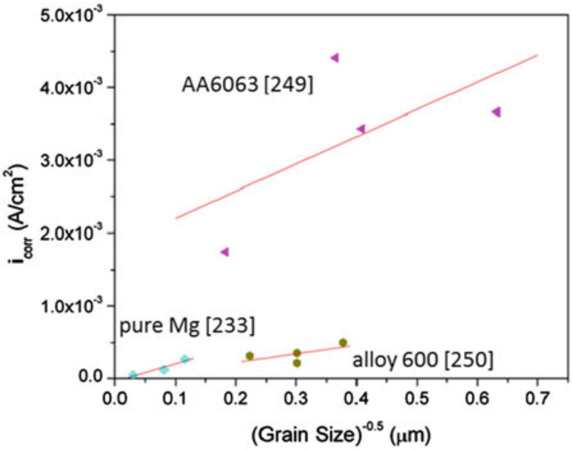

Fig. 3.38 The relationship between corrosion rate and grain size for high current densities in AA6063, pure Mg, and alloy 600. The figure is reproduced from [243] with the permission from the publisher

reactivity and, consequently, the corrosion rate as demonstrated for pure Mg, AA6063, and alloy 600 in Fig. 3.38.

This section clearly shows that there is no a general consensus in the literature as to the effect of nanostructuring on corrosion resistance. The reason for these controversial results is obviously connected with microstructural features of nanostructured metallic materials. Deformation processing imparts significant physical and chemical changes to the material in addition to the grain refinement that, in turn, considerably affects the demonstrated functional properties including corrosion behavior. Thus, systematic investigations of corrosion stability of SPD nanostructured materials and revealing its dependence on nanostructural parameters remain as one of the most challenging tasks in modern materials science.

3.3.2 Biocompatibility

For a long time, metallic biomaterials have been successfully used for fabrication of surgical implants due to their high strength combined with good formability, sufficient fatigue properties, and resistivity to fracture [251]. In addition to mechanical stability under physiological strains and stresses, the implant materials should be able to perform with an appropriate host response in a specific situation, i.e., to be biocompatible. This means that a material has to perform and not simply exist in the tissues, that the response which it evokes has to be appropriate for the application, and that the nature of the response to a specific material and its appropriateness may vary from one situation to another. The key to understand biocompatibility is the determination of which chemical, biochemical, physiological, physical, or other mechanisms become operative, (and why), under the highly specific conditions associated with contact between biomaterials and the tissues of the body and what are the consequences of these interactions [252]. Nowadays, just three metallic systems Co–Cr-based alloys, Fe–Cr–Ni alloys (stainless steels), and pure Ti and Ti-based alloys have been used for implantation, since other systems do not possess required level of mechanical properties and/or biocompatibility [251]. The Co–Cr alloys are sought for medical applications because of their combination of corrosion resistance, wear resistance, and high strength. Increasing amounts of Cr added in solid solution to Co, up to 35 wt%, enhances corrosion resistance through the presence of a passive chromium oxide film. Stainless steels are the most widely used family of alloys for medical applications. They contain 17–21 wt% Cr which imparts good corrosion resistance due to the adherent chromium oxide film that forms and heals in the presence of oxygen. From the viewpoint of corrosion resistance, Ti is superior to other surgical metals due to the formation of a very stable passive layer of TiO_2 on its surface. Also, Ti has the low elastic modulus (twofold lower compared to Co–Cr alloys or stainless steels), which results in less stress shielding and associated bone resorption around Ti implants. Furthermore, Ti has the lower density and produces less artifacts on computer tomography and magnetic resonance imaging [253–255]. Pure Ti has low mechanical strength and fatigue endurance, so it has been alloyed by V and Al for improvement of mechanical properties. Currently, Ti–6Al–4V is the most widely used surgical Ti alloy.

Biocompatibility of biomaterial strongly depends on interrelated responses of both parts of the biomaterial–tissue complex and the interfacial processes. When placed in the tissues of the body, various reactions to a material may be seen over time. Within the host, one can envisage a sequence of events, potentially involving the interaction between proteins and other physiological macromolecules with the biomaterial surface, the initiation of inflammatory and/or immune responses, and then the repair and/or regeneration processes that may lead to stable equilibrium between material and host. The biomaterials are required to optimize the rate and quality of bone apposition to them, to minimize the rate of release of corrosion or degradation products and the tissue response to them, to minimize the rate of wear debris release and the tissue response to this debris, and to optimize the biomechanical environment in order to minimize disturbance to homeostasis in the bone and surrounding soft tissue [252].

In the last decade, there has been a breakthrough in studying the potential applications of bulk nanostructured metallic biomaterials in biomedical engineering, focusing on the effect of nanostructuring on cell/bacteria response. Few comprehensive review articles focused on this topic have been published very recently [251, 256, 257]. In 2004, Webster and Ejiofor [258] provided the first evidence of increased osteoblast adhesion on Ti, Ti–6Al–4V alloy and Co–Cr–Mo compacts with nanometer compared to conventionally sized particles. The increased cell adhesion was related to higher percentage of grain boundaries on the surface of nanomaterials considering that osteoblasts adhere specifically at grain boundaries. In two years, this group demonstrated that nanostructuring of these materials not only enhanced osteoblast adhesion, but also increased osteoblast metabolic activities leading to calcium deposition [259]. However, it should be noted that the studied compacts were not fully dense and had porosity of 5–10 %,

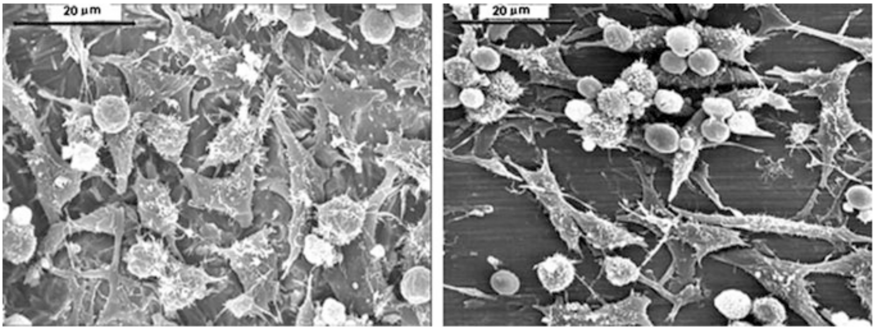

Fig. 3.39 Occupation of the mice fibroblast cells L929 after 24 h on the surface after hydrofluoric acid treatment of the nanostructured (*left*) and coarse-grained (*right*) CP Ti (Grade 4). The image is reproduced from [262] with the permission from the publisher

so, strictly speaking, the reported observations cannot be related only to the grain size effect. Later, research activities were more focused on fully dense bulk nanostructured metallic biomaterials produced via SPD processing [260–270], though nanostructuring of pure Ti via ECAP for application in medical implants was patented already in 2002 [271]. It was demonstrated that apart from ultrahigh strength (see Sect. 4.1), the nanostructured pure Ti has also increased bioreactivity. Preliminary cytocompatibility tests utilizing fibroblast mice cells L929 were carried out with hydrofluoric acid surface etching being performed prior to cell exposure [262]. The cell attachment investigation showed that fibroblast colonization of the CP Ti (Grade 4) surface increases after nanostructuring (Fig. 3.39). Further research focused on interactions of human bone marrow-derived mesenchymal stem cells (hMSCs) during the initial stages of cell attachment and spreading on the surface of nanostructured Ti [267]. The effect of nanostructuring was found to be quite striking: 40 min after seeding the biovolume of the hMSCs was up to 2.5 times greater on the ECAP-processed CP Ti than on the conventional coarse-grained material (Fig. 3.40; Table 3.6). Surface characterization by a range of techniques showed that the main factor responsible for the observed acceleration of hMSC attachment and spreading on CP Ti due to grain refinement in the bulk is the attendant changes in surface topography on the nanoscale [267]. Such acceleration of the initial attachment of hMSCs on Ti surfaces may prevent their apoptosis on the implant surface [272].

The nanostructured stainless steels also provide enhanced cell growth and proliferation [268, 270]. This was demonstrated on a 316L stainless steel processed using the phase reversion concept that allows to obtain grain size from nanograined to coarse-grained structure [270]. Grain refinement from 22 μm to 320 nm resulted in the increase of yield strength from 350 to 768 MPa without any significant reduction in ductility. The higher attachment on the substrate with the smallest grain size was visible within the first hour of culture (Fig. 3.41a), suggesting that the cell attachment to the surface was influenced by the grain structure of the steel substrate

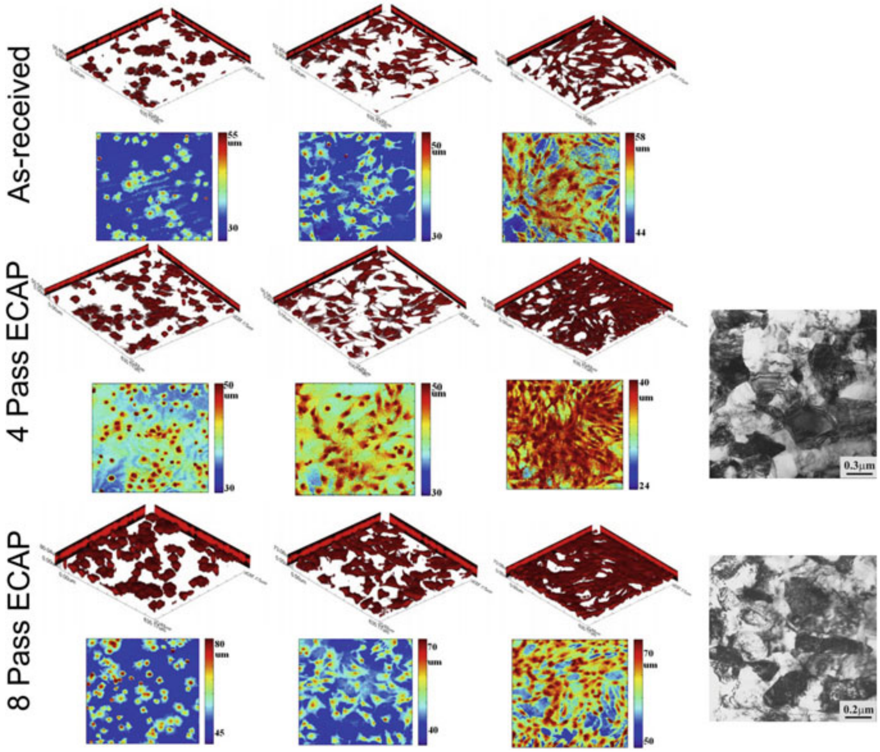

Fig. 3.40 Confocal scanning laser microscopy images of human bone marrow-derived mesenchymal stem cells on the surface of the as-received and ECAP-processed pure Ti (Grade 2) for different cultivation times (40 min, 2 h and 24 h) and corresponding TEM images of the ECAP-processed pure Ti. All images are reproduced from [267] with permission of the publisher

Table 3.6 Biovolume ($\mu m^3\ \mu m^{-2}$) of human bone marrow-derived mesenchymal stem cells on the surfaces of coarse-grained and nanostructured CP Ti (Grade 2)

Titanium, condition	Incubation time		
	40 min	2 h	24 h
Coarse grained	7.5 ± 0.2	22.0 ± 1.2	32.0 ± 5.2
ECAP 4 passes	15.2 ± 2.8	29.9 ± 2.3	37.1 ± 0.8
ECAP 8 passes	19.4 ± 5.3	38.0 ± 0.4	41.2 ± 0.7

The table is reproduced from [267] with the permission from the publisher

and was not a function of cell development or adaptation over time. With increasing time increases, the surface characteristics such as hydrophilicity started having a significant effect on cell attachment and proliferation. Similarly, cell metabolism measured by mitochondrial reduction of MTT was again higher for the nanograined steel and decreased with increasing grain size for tests conducted for 1 h to 7 days, even though the cell density on all surfaces increased over time, indicating cytocompatibility of steels. Examination of individual proteins (fibronectin, actin, and vinculin) also indicated strong interplay between grain size and expression level of proteins. In a manner similar to cell attachment data, the fibronectin expression by preosteoblasts was greater on nanograined steel than on the coarse-grained substrate (Fig. 3.41b, c), as documented by a distinct network with stronger fluorescence intensity of immunostained fibronectin. The expression level of vinculin, a protein that forms focal contacts and actin stress fibers, after 48 h of culture, also showed a higher expression level at the edges and well-defined stress fibers on nanograined steel than on substrates with higher grain size (Fig. 3.41d). The expression level of vinculin from nanograins to coarse grains was lower, and actin was less prominent with increase in grain size (Fig. 3.41d, e). The very strong effect of grain size on osteoblast parameters (cell area, perimeter, Feret's diameter) is clearly demonstrated in Fig. 3.42.

No research on grain refinement in Co–Cr alloys with the aim to improve their biocompatibility can be found in the literature. Partly, it is related to the fact that superalloys are very hard to deform, so their nanostructuring in bulk via SPD processing cannot be performed. Ultrafine grain size can be achieved in Co–Cr alloys via their conventional forging using conditions that induce a novel mechanism of dynamic recrystallization, as described by Yamanaka et al. [273, 274]. It should be noted that conventional Co–Cr alloys have high mechanical strength, so surface nanostructuring can be envisaged as a strategy to improve biocompatibility of the material [275]. One technique of particularly high potential is surface mechanical attrition treatment (SMAT) [276–281]. SMAT induces large deformation in surfaces by recurring impact of hard spheres. Thus, induced surface deformation results in the formation of microstructures containing high densities of strengthening defects, including twins and the intersecting twin systems, dislocation walls, microbands, highly disoriented polygonal submicronic grains, and randomly oriented nanograins below the surface. The SMAT technique has been successfully applied to Co [276] and other difficult to deform metals, such as Ni_3Al [277], Fe_3Al [278], and Fe–30Ni [279]. The hierarchical textured surfaces obtained via SMAT on pure Ti and Ti–6Al–4V alloy showed enhanced cell attachment, spreading, viability, and alkaline phosphatase activity [280]. Biocompatibility improvement was also reported for CP Ti subjected to low-temperature plasma treatment that not only refined the surface grains to nanosize, but also altered the surface roughness and surface chemical composition [281].

There is now an increasing interest to use biodegradable metallic materials in various medical device applications, as discussed in the recent overviews [282, 283]. The biodegradable materials for implants and stents should satisfy a number of requirements toward medical materials, in particular high reliability, bioresorbability, and biodegradability (making the second surgery to remove an implant superfluous), required elastic modulus and strength, drug release option, etc. Nanostructured metals (Mg and Fe) and based on them porous composites have a great potential to satisfy all these requirements, with their biodegradability and bioresorbability (achieved by combining biodegradable magnesium and iron

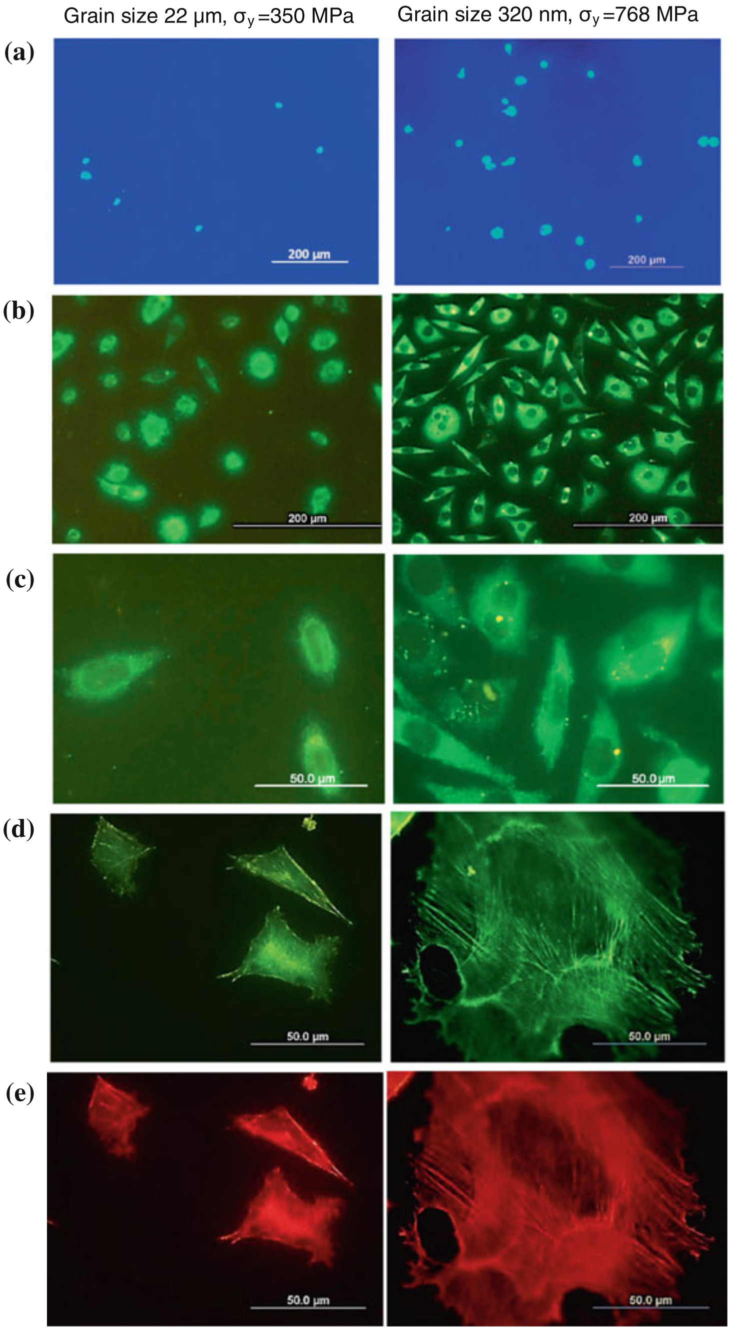

Fig. 3.41 Fluorescence micrographs illustrating the effect of grain size in the 316L stainless steel on **a** preosteoblast cell nuclei stained with Hoechst 33258 after 1-h culture; **b**, **c** immunocytochemistry of fibronectin expressed by preosteoblasts after incubation for 48 h; **d** the organization and assessment of vinculin focal contacts; and **e** actin stress fibers of preosteoblasts cultured for 48 h. The micrographs are reproduced from [270] with the permission from the publisher

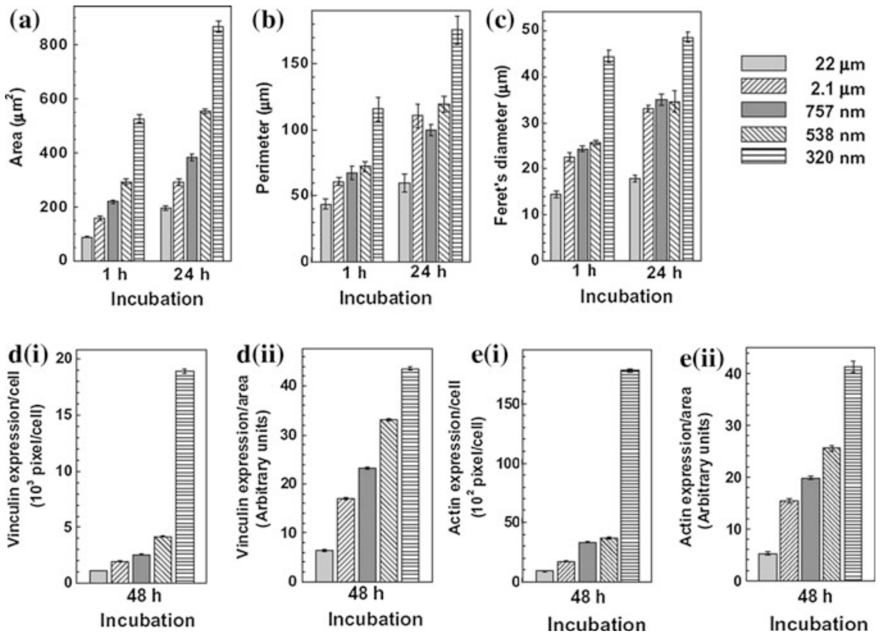

Fig. 3.42 Cytomorphometric evaluation of osteoblast parameters (cell area, perimeter, Feret's diameter). Data are mean ± SD ($n = 3$, $p < 0.05$), indicating a statistical difference from coarse-grained to nanograined 316L stainless steel with various grain sizes (22 μm, 2.1 μm, 757 nm, 538 nm, 320 nm). The figure is reproduced from [270] with the permission from the publisher

components), high strength (achieved by nanostructuring as well as iron reinforcement/skeleton in Mg), controlled corrosion behavior (by choosing the Mg/Fe distributions), required elastic modulus, enhanced possibility of bone adaptation, and controlled drug release option (achieved by macro- and microporosity) [283–287].

First studies of biocompatibility of SPD-processed Mg alloys [242, 288] show promising results of their increased potential as enhanced biodegradable materials encouraging further fast development of research in the field. Particularly, ECAP (also with backpressure) processing of the AZ31 Mg alloy has dramatically improved mechanical strength and reduced corrosion rate of the material without any degradation of its biocompatibility. The multipass ECAP (and also back pressure)-processed AZ31 alloy exhibited acceptable toxicity to MG63 cells with grade I toxicity (according to ISO 10993-5), which is comparable as other conventional Mg alloys, such as Mg–Ca [289] and Mg–Zn [290], showing good biocompatibility from the in vivo studies. However, 3-pass backpressure ECAP processed alloy indicated grade II toxicity, which may be attributed to the higher Mg and Al concentration leading to the osmolarity shock to the cells [242]. Thus, the optimum processing parameters should be carefully chosen for fabrication of

Mg alloys with set of required multifunctional properties for biomedical applications. Again, attention should be paid to the crystallographic texture developed during SPD processing, since the control of texture in Mg and Mg-based implants could be used to tailor the mechanical properties and the resorption rates without compromising cytocompatibility [291]. Surface modifications can be also utilized for further improvement of its biological properties [292, 293].

It is clearly seen that grain size and surface features of metallic biomaterials have significant effect on absorption of proteins that mediate cell adhesion and control and enhance subsequent cell functions and tissue growth. Relative increase in surface area and enhanced reactivity are the distinctive intrinsic aspects of nanostructured metallic biomaterials giving them the potential to manipulate their interaction with cells, and there are certain grain size thresholds that stimulate the mechanoreceptive responses in specific cells. Although there are numerous reports indicating that grain refinement can promote cell adhesion and subsequent activities, still more systematic studies are required to address the fundamental gaps in determining the mechanisms governing the specific cell response to nanograins. Most studies have focused on evaluating short-term response of cells to nanostructure, and supplementary in vivo studies are needed to validate their functionality in mediating the bone response.

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Chapter 4
Bulk Nanostructured Metals for Innovative Applications

As seen from Chap. 3 of this book, nanostructuring of various metallic materials is a key for obtaining extraordinary multifunctional properties that are very attractive for different structural and functional applications. Materials experts have asserted that materials breakthroughs in the twentieth century required about 20 years from the time of invention to gain widespread market acceptance [1].[1] Bulk nanostructured metallic materials also have been following this track. Despite a wide research started at the beginning of 1990, very significant progress in their commercialization has been made just in recent years, which is evident by the first production of advanced pilot articles from nanostructured metals and alloys with new functionality. These aspects of innovations of bulk nanostructured metallic materials processed by SPD are discussed in this chapter.

Application and commercialization of bulk nanostructured metallic materials are associated with three primary points: their superior properties, their efficient fabrication, and the possibility to produce cutting-edge products from these materials. Analytical reports documented more than 100 specific market areas for nanostructured metals [2, 3], and it is evident that many of these new structural and functional applications involve extreme environments where exceptional strength and improved functional properties are needed. Below are the examples of nanomaterials developments for their innovation applications in engineering and medicine.

4.1 Nanostructured Ti and Ti Alloys for Biomedical Engineering

Pure Ti possesses the highest biocompatibility with living organisms, but it has limited use in medicine due to its low strength. High-strength nanostructured pure Ti processed via SPD opens new avenues and concepts in medical device

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[1] Some applications, such as the use of aluminum in automobile bodies, have taken much longer, despite clear advantages in materials properties. This lag can be caused by many factors, ranging from poor market education to technical obstacles to financial infeasibility.

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Table 4.1 Mechanical properties of conventional coarse-grained and nanostructured CP Ti (Grade 4). TMT stands for thermo-mechanical treatment

Processing/treatment conditions	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation (%)	Reduction area (%)	Fatigue strength at 10^6 cycles
Conventional coarse-grained Ti	530	700	25	52	340
Nanostructured Ti via ECAP-C + TMT	1200	1240	12	42	620
Annealed Ti–6Al–4V ELI alloy	840	940	16	45	530

technology [4, 5]. First, expensive and toxic alloying elements are absent in the material. Thus, the implants made therefrom have better biocompatibility (see Sect. 3.3.2). Second, implant size can be noticeably reduced decreasing the level of surgical intervention into human body. Third, the material demonstrates improvement of biological reaction on its surface. A new SPD-based technology has been recently developed for the fabrication of nanostructured Ti for dental implants. The processing route consists of ECAP-C leading to grain refinement and secondary processing (swaging/drawing) providing shaping and additional strengthening [4, 5]. Long rods having lengths up to 3 m, diameters of 4–8 mm, and accuracy grade h8 suitable for automation of implant machining can be produced using this method. The effect of this SPD processing on mechanical properties of Ti is demonstrated in Table 4.1. It is seen that nanostructuring increases both yield strength and fatigue strength by a factor of nearly 2.

Mechanical properties of this nanostructured Ti are even higher compared to those of conventional high-strength Ti alloys (such as Ti–6Al–4V) used in biomedical engineering. Nanostructuring of Ti also positively affects its biomedical properties, as was already demonstrated in Sect. 3.3.2.

The company ‘Timplant’ (Ostrava, Czech Republic) has been manufacturing dental implants from nanostructured Ti under the trademark Nanoimplant® since 2006 [www.timplant.cz]. To date, these dental implants have been certified according to the European standard EN ISO 13485:2003. The new generation implants have a smaller diameter (2.0 mm) compared to the standard ones (3.5 mm). Therefore, they can be successfully inserted into thin jawbones where larger implants cannot be used. Another advantage of smaller dental implants is less damage induced into jawbone during surgery intervention. Figure 4.1a illustrates the Nanoimplant®. It is installed into the body of 18-year-old patient with thin jawbones between teeth 11 and 13. Another implant with the diameter of 2.4 mm was inserted to the right-side position 12 (Fig. 4.1b, c). The patient left the dental office with two nanoimplants and with two provisional crowns made in the same day as implants were inserted. After 6 weeks, final metal–ceramic crowns were fixed on the implants. One of the next nanostructured Ti products, also a dental implant, was manufactured and marketed by BASIC Dental Implant Systems under

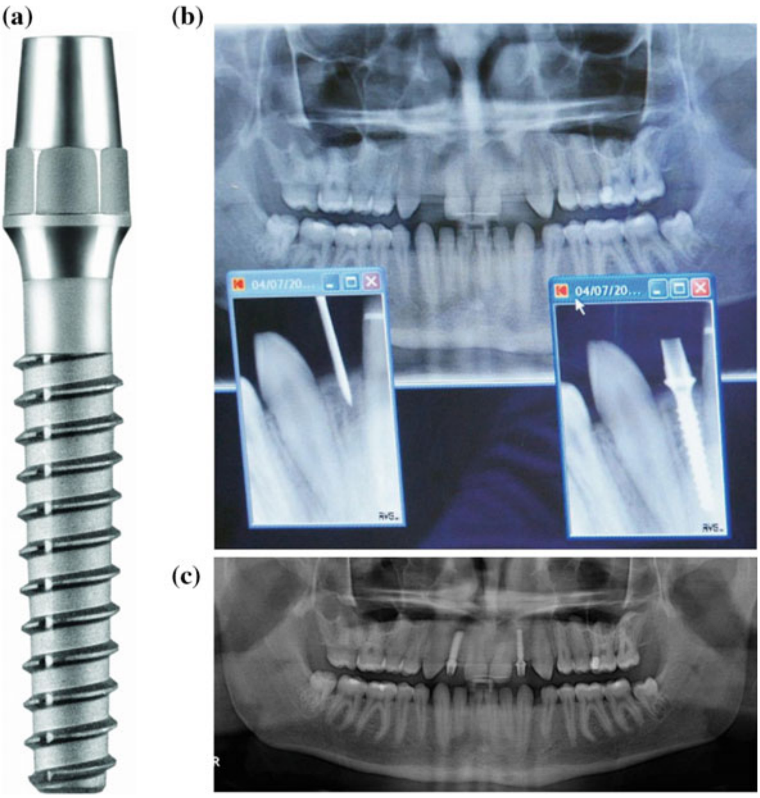

Fig. 4.1 **a** Dental implant from nanostructured Ti; **b**, **c** X-ray photographs after surgery and control photograph after incorporation of dental implants into human jaw. The image is reproduced from [5] with permission of the publisher

the trademark Biotanium in the USA beginning in 2011. The nanostructured Ti for both these products was fabricated by NanoMet LLC (Ufa, Russia).

Another very promising group of materials for the medical applications are nanostructured Ti-based alloys with shape memory and superelasticity effects, such as TiNi (nitinol). Nitinol is a biocompatible nickel–titanium alloy with low elastic modulus closer to that of bone than the modulus of any other surgical metal. The low stiffness makes nitinol especially attractive as a bone replacement material since it prevents stress shielding of the ingrown and peri-implant bone. During recent years, significant advances have been made in nanostructuring of TiNi alloys using HPT and ECAP techniques and in increasing essentially mechanical and functional properties of nanostructured TiNi alloys [6–8]. TiNi alloys have been already used in biomedical industry for stents, vena caval filters, and orthodontic devices. Numerous research groups around the world have been working on the development of implantable artificial sphincters made from TiNi alloys. Nanostructured high-strength TiNi alloys are promising for further miniaturization of those medical devices.

It should be noted that for medical applications, the use of SPD processing methods is favored by the fact that the cost of the constituent metal is typically a very small fraction of the total cost of most medical devices. For example, the value of commercial purity titanium that is typically used in a dental implant is on the order of $0.30 USD. Yet, a single dental implant may be sold to oral surgeons for prices ranging from $50 to $400 USD [9].

Magnesium and its alloys have been receiving much interest as promising material candidates in the field of biodegradable devices such as stents and several orthopedic applications in recent years [10]. It was proven that the daily intake of Mg for a normal adult exceeds 300 mg and excessive magnesium cations possibly produce by degradation could be safely excreted in the urine. However, the greatest limitation of Mg consists of its fast corrosion rate, especially in human body fluid containing chloride, giving rise to immature drop in mechanical integrity of the device before accomplishing its defined mission. A further challenging issue concerns mechanical properties. Generally, Mg alloys have lower mechanical properties than commonly used inert biomaterials. Considering stent applications, fracture of the stent strut during expansion also has to be avoided by enhancing alloy ductility. Therefore, controlling the corrosion rate to achieve a prolonged and uniform degradation of the device made by alloys with reasonable strength and ductility is the key factor in the development of Mg implants and stents. Nanostructuring via SPD processing appears as a very promising technique to solve these problems. First studies of corrosion behavior of high-strength ECAP-processed Mg alloys [11, 12] show promising results of their increased potential as enhanced biodegradable materials encouraging further fast development of research in the field. In [11], UFG size billets of the ZM21 alloy were obtained by two-stage ECAP aimed at achieving an initial refining of the structure at 200 °C and then reaching the submicrometer grain size range by lowering the processing temperature down to 150 °C. The 0.2 % yield strength increased from 180 to 340 MPa after 150 °C ECAP processing, while maintaining a fairly high tensile ductility. The ultrafine ZM21 alloy billets were then used for the extrusion of stent precursors having the form of small-size tubes. It was demonstrated that processing of biodegradable Mg stent having an ultrafine-grained microstructure by ECAP and low-temperature extrusion is feasible and that the obtained products feature promising properties. In [12], ECAP was performed on ZK60 alloy and pure Mg in the temperature range 150–250 °C. A significant grain refinement was detected after ECAP, leading to an ultrafine grain size (UFG) and enhanced formability during extrusion process. Comparing to conventional coarse-grained samples, fracture elongation of pure Mg and ZK60 alloy was significantly improved by 130 and 100 %, respectively, while the tensile strength remained at high level. Extrusion was performed on ECAP-processed billets to produce small tubes (with outer/inner diameter of 4/2.5 mm) as precursors for biodegradable stents. Pure Mg tubes showed an additional improvement in terms of grain refining and mechanical properties after extrusion. Electrochemical analyses and microstructural assessments after corrosion tests demonstrated two major influential factors in corrosion behavior of the investigated materials. The presence of Zn and Zr as alloying elements simultaneously increased the nobility by formation of a protective film and increased the local corrosion damage by amplifying the pitting development. ECAP treatment decreased the size of the second phase particles thus improving microstructure homogeneity, thereby decreasing the localized corrosion effects.

4.2 Nanostructured Cu and Al Alloys for Perspective Electro-Conductors

In Sect. 3.2.1, it was demonstrated that nanostructuring of Cu, Al, and their alloys can significantly increase their mechanical properties with no reduction of their electrical conductivity or even with its further improvement. Development of metallic conductors with such attractive electrical conductivity is one of the most topical subjects in the modern electrical engineering. Given that the global consumer market of just Al–Mg–Si alloy for overhead power transmission lines [13] accounts for about 450.000 tons/year and continues to grow, the R&D activities focused on the improvement of their properties are of keen interest. The largest aluminum producer in the world, RUSAL, is currently developing a new manufacturing line for mass production of nanostructured Al–Mg–Si alloys with improved mechanical strength and electrical conductivity for the overhead power lines [14, 15]. An experimental extruder will be built in the casthouse of IrkAZ that will utilize intensive plastic deformation to produce nanostructured alloys.

Current research activities also focus on development of novel Al alloys for the applications in electrical engineering. For example, Horita et al. [16] have utilized HPT technique for fabrication of Al–Fe thin wires having diameter of 80 μm (Fig. 4.2). Fe is an ideal alloying element for electrical conductivity of Al because of its low solubility in the matrix, and simultaneously, Fe can provide some strength and creep resistance if intermetallic particles are finely dispersed. Processing by HPT enabled the formation of mostly equiaxed ultrafine grains with high dislocation densities and fine dispersions of eutectic phases, of which microstructures were ideal to increase not only the strength but also the formability to allow further wire drawing with 25:1 area reduction. The HPT-processed Al–Fe alloy after wire drawing showed very good surface (Fig. 4.2). The electrical conductivity of the drawn wires ranged from 49 to 51 % of IACS and increased to 52–54 % of IACS after aging at 200 °C for 1 h. There is a large potential to further improve the electrical conductivity of the Al–Fe alloys with an optimized aging treatment. Such thin wires can be useful for applications in microelectromechanical systems (MEMS), which are discussed in more detail in Sect. 4.5 below.

Nanostructured pure copper would be an innovative solution for electrotechnical systems and connections (e.g., electric engine and voltage current converter). In the field of microelectronics materials, and more precisely in copper interconnections, electrical performances have to coexist with resistance to creep and electro-voiding when reducing the channel and via size of the system. In

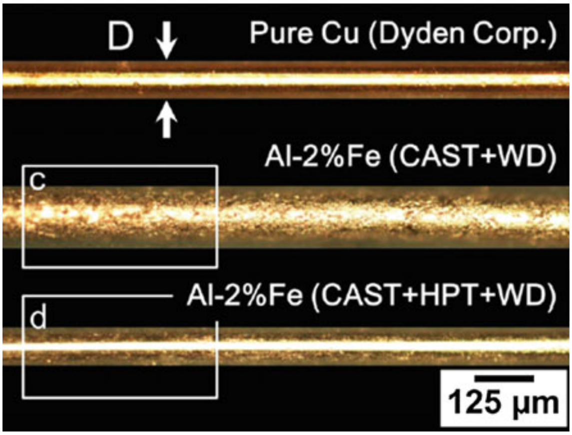

Fig. 4.2 Wires and surface condition of pure Cu and Al–2 % Fe as-drawn wires. The figure is reproduced from [16] with permission of the publisher Springer

particular, mechanical properties become size dependant when the dimensions are below few tens of micrometers, for two reasons: (1) because the microstructural scale (grain size) is size dependant and (2) because the confinement of plasticity in small dimensions leads to new phenomena which make mechanical properties "sample size dependant" [17]. Champion and Brechet highlighted the potential application of high nanostructured Cu with improved wear resistance as a material for reversible electrical contacts in [17], where an optimal design for reversible electric contacts was also proposed.

4.3 Nanostructured Mg Alloys for Hydrogen Storage

The term hydrogen storage relates to methods for use H_2 as energy carrier for mobile applications. The methods to store hydrogen cover many approaches, including high pressures, cryogenics, and chemical compounds that reversibly release hydrogen upon heating. Storing hydrogen in the solid state still remains a significant technological challenge. Mg and its alloys have been considered as one of the most attractive hydrogen storage materials, mainly because of the high-storage capacity (7.6 wt%), lightweight, and low cost. Nevertheless, high thermodynamic stability ($\Delta H = -75$ kJ/mol), high hydrogen desorption temperature (≥ 400 °C), and relatively poor hydrogen absorption–desorption kinetics at temperatures ≤ 350 °C impede the use of Mg in industrial applications.

Grain refinement can be used to improve the hydrogen storage properties of Mg. Nanosized Mg powders have been produced by mechanical alloying. Ball milling (BM) of Mg/MgH_2 results in fine nanopowder with grain size in the range of 10–30 nm [18]. By reducing the grain size to nanocrystalline dimensions, the H-sorption kinetics are accelerated substantially due to the increased volume fraction of grain boundaries, and the hydrogen desorption temperature is decreased by about

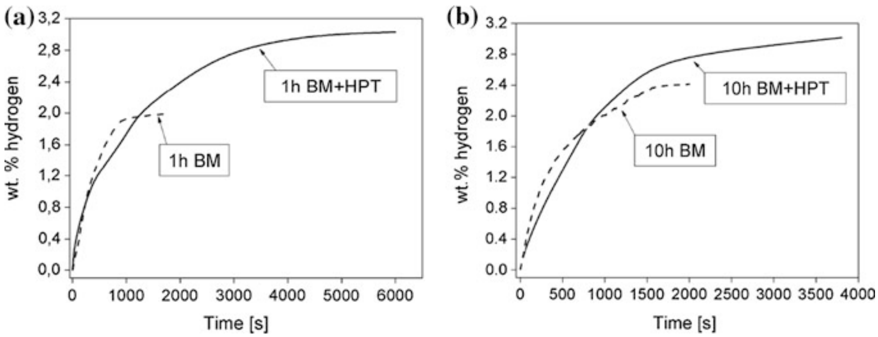

Fig. 4.3 Hydrogen kinetic absorption curves of Mg70Ni30 powder: **a** milled for 1 h and consolidated by HPT; **b** milled for 10 h and consolidated by HPT. The curves are reproduced from [22] with permission of the publisher Elsevier

100 °C [19]. Improved hydrogen storage capacity and kinetics can be also achieved in bulk Mg-based samples via ECAP [20] and HPT [21, 22]. Figure 4.3 illustrates hydrating kinetic data for the nanocrystalline $Mg_{70}Ni_{30}$ powders milled for 1 and 10 h, as well as for the HPT consolidated disk [22]. The as-milled powders and the HPT samples absorb hydrogen without activation, as the maximum capacity is reached after the first couple of absorption–desorption cycles. The maximum capacity of the powders increases with increasing milling time due to the finer microstructure and enhanced density of defects. Noticeable improvement in the H-uptake (3 wt%) is observed in the HPT consolidated disk. The obtained capacity of 3 wt% corresponds to the composition of $Mg_2NiH_{3.3}$ and means nearly complete hydrating.

Despite the major progress on using metal hybrids as hydrogen carriers, SPD may offer new technological solutions in this area. ECAP may be a cheap process for processing the nanocrystalline elements for hydrogen batteries in shape of cylindrical rods, and high pressure torsion could be used for the process of metal hybrid tablets.

4.4 Large-Size Tools Made from Bulk Nanostructured Metallic Materials

A relatively small size of SPD-processed samples is one of the main obstacles for a wide commercialization of the nanostructured metallic materials for various applications. Recent activities of the research community have nicely demonstrated the ability of robust up- and downscaling of the SPD-forming facilities [23]. The feasibility of upscaling ECAP and HPT process for the fabrication of samples of industry-scale dimensions has been consistently confirmed [24–26]. For example, Honeywell Electronic Materials has successfully scaled up the ECAP technique and is capable of ECAP processing of Al and Cu plates having a mass up to 32.7 kg,

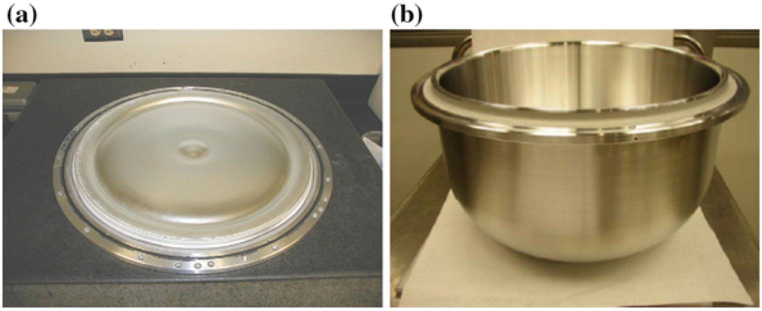

Fig. 4.4 **a** Flat 300-mm monolithic ECAE $Al_{0.5}Cu$ target with dimensions diameter 523.8 mm × 25.4 mm thickness sputtered up to 2738 kWh (+52 % life increase); **b** non-flat and non-sputtered 300 mm monolithic ECAP 6N Cu with overall dimensions diameter 393.7 mm × 25.4 mm thickness × 381 mm height. The figure is reproduced from [27] with permission of the publisher Elsevier

whereas the typical mass of samples processed at laboratory scale is of a few hundred grams [27]. Monolithic sputtering targets for physical vapor deposition were produced from these billets (Fig. 4.4) [27]. They are used for metallization of silicon wafers in the production of semiconductor devices. This is a unique design compared to that of traditional targets, which consists of a target material bonded or soldered to a backing plate made from strong materials such as AA6061 or CuCr. Tests of monolithic target processed by ECAP from Al–05 % Cu alloy showed a drastic improvement in target lifetime over 41 % (because sputtering is no longer limited by the diffusion bond line) and wafer processing by 23 %, and a better kit utilization. ECAP-processed targets reduced significantly the cost-of-ownership of PVD tools and the total cost of manufacturing [28].

4.5 Micro- and Mini-devices from Bulk Nanostructured Materials

In conventional coarse-grained metallic materials, the decreasing sample size may significantly affect the fundamental mechanisms of plasticity. While the plasticity of macroscopic samples appears as a smooth process, in the plastic deformation of microscopic samples specific dislocation avalanches are formed leading to an uncontrolled deformation process including also the possibility of catastrophic failure. Therefore, fabrication of miniaturized parts or tools, particularly components for biomedical devices or MEMS having geometrical features of a few micrometers, requires very careful scaling of their internal structures. The average grain size in the microparts should be smaller than the smallest dimension of the geometrical features in order to ensure their reliable property control.

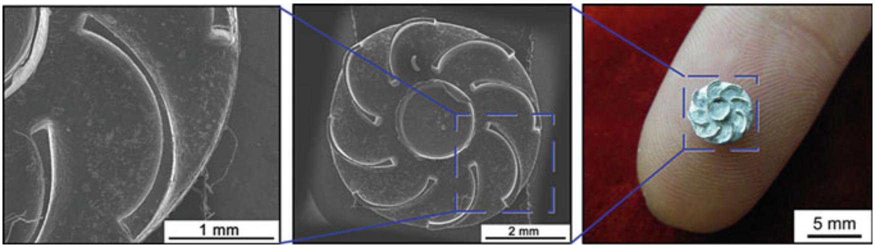

Fig. 4.5 Microturbine of UFG pure aluminum formed at ambient temperature. The image is reproduced from [30] with permission of the publisher Wiley

Nanostructured materials lead to new directions in the fabrication of complex shape microparts for microdevices. For instance, it was demonstrated that hot embossing on UFG AA1050 processed via ECAP shows a good potential for application in fabrication of microheat exchangers with geometrical features smaller than 10 μm and high thermal conductivity [29]. Hot embossing on this material provided a very smooth embossed surface with fully transferred pattern and low failure rate of the mold, while hot embossing on the coarse-grained AA1050 resulted in a much rougher surface with shear bands [29]. In [30], a microforming process was successfully used to fabricate a microturbine from ECAP-processed UFG pure Al at ambient temperature (Fig. 4.5). Subsequent examination demonstrated that UFG pure aluminum gives much higher strength and more uniform mechanical properties by comparison with conventional coarse-grained pure aluminum. Downscaling of the SPD processing techniques along with combination with another processing method can dramatically ease fabrication of microparts for microdevices. A nice example was presented in [31], where a miniaturized ECAP die with a millimeter-scale channel was developed to produce Al wires with grain size of 1–2 μm in a single ECAP step showing enhanced strength. This ECAP preprocessing can be combined with a final extrusion step where a desired axisymmetric profile can be easily imparted to the final product. An example of a possible product is a long bar with a cogwheel profile that can be chopped easily into MEMS gears [2].

4.6 Nanostructured Magnets

In Sect. 3.2.2, it was demonstrated that SPD nanostructuring can dramatically improve magnetic properties of soft- and hard-magnetic materials. Nanostructured $RE_2Fe_{14}B$ (RE = Nd, Pr)-based alloys with high coercivity H_C up to 2240 kA/m were produced via HPT followed by annealing at 600 °C [32]. Similar results were reported for melt-spun $Nd_9Fe_{85}B_6$ alloy [33]. Metal–ceramic powder mixtures consisting of Co (ferromagnetic) and NiO (antiferromagnetic) phases were compacted by HPT both with and without a prior BM [34]. Enhanced coercivity of the obtained materials was ascribed to the Co particle size refinement, the increase of stacking faults, and the magnetic coupling between Co and NiO phases [34].

Novel high-speed electrical machines require high-strength magnetic materials with ultimate rupture strength ≥900 MPa. However, the maximum ultimate rupture strength in conventional magnets processed via rolling or high-temperature forging does not exceed 700 MPa. Recently, it was demonstrated that nanostructured Fe–25Cr–15Co and Fe–30Cr–8Co alloys with good magnetic properties and excellent mechanical properties (compression stress of 1400 MPa) can be fabricated via complex two-stage upsetting torsion under isothermal conditions [35, 36]. These nanostructured magnetic materials could be used in developing high-speed electric machines for lower power consumption. These machines include the following:

- turbo-generators and turbo-compressors;
- turbo-molecular pumps;
- inertial energy-storage devices;
- technological and medical centrifuges; and
- electric spindles and electric drivers.

Another future application of nanostructured magnets is a generation of new material exhibiting energy waves, referred to as magnons, that coalesce into a common ground state in the manner of a Bose–Einstein condensate.

4.7 Bulk Nanostructured Materials for Sport Industry

There have been attempts to commercialize nanostructured materials in sport industry. Producers of sport devices/equipment could benefit from nanostructured materials in the cases where high strength and low weight are required. Bulk nanostructured metallic materials could find applications in golf, tennis, hockey, high-performance bicycles, sailing equipment, mountaineering equipment, etc. One example is NanoDynamics (USA) high-performance (NDMX) golf balls, which have a hollow nanostructured titanium core [37]. The core material is manufactured using the UFG chip machining technology licensed from Purdue University. Another example of using UFG metals in sporting goods is the commercial activity of PowerMetal Technologies (USA), a company with an exclusive license to use Integran's electrodeposition technology in consumer products. They cooperate with HEAD in the production of their new Metallix and airflow racquets, which use a composite of carbon fibers and nanostructured metals [37]. The Institute for Metals Superplasticity Problems (Russia) has developed a technology for the fabrication of golf club components from nanostructured Ti–6Al–4V alloy (Fig. 4.6). This technology allowed a reduction in weight of a golf club along with increase of ball's flight distance due to increased restitution factor. The experts noted the kick became smoother, while the kickback lesser [38].

Fig. 4.6 Components of golf club made from nanostructured Ti–6Al–4V alloy. The figure is reproduced from [38] with permission of the publisher Institute of Problems of Mechanical Engineering RAMS

4.8 Bulk Nanostructured Materials for Fabrication of Fasteners and Fixings

Superior high-strength and enhanced fatigue properties of nanostructured metallic materials can be especially attractive for manufacturers of fasteners and fixings. For example, lightweight high-strength bolts were manufactured from ECAP-processed Ti alloys processed by ECAP in [39]. Microbolts using the UFG carbon steel processed by ECAP at room temperature were also successfully fabricated as shown in Fig. 4.7 [40].

Thus, the superior properties achieved in nanostructured materials have enabled the identification of many new applications whereby nanomaterials are capable of providing a performance previously unattainable with other materials. More innovative applications of bulk nanomaterials have been also discussed in several recent reviews [41, 42]. The true potential of multifunctional nanomaterials is now starting to emerge from many new innovations. With further development and testing, nanostructured metals and alloys will evolve, leading to significant advances in light-weight structures for engineering and medicine.

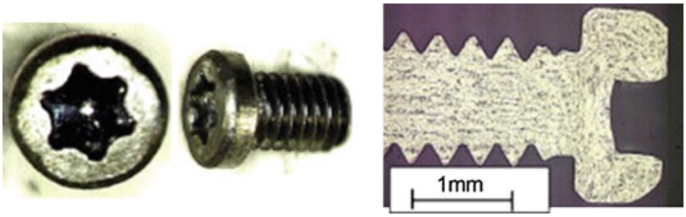

Fig. 4.7 Overview and cross section of microbolts manufactured UFG carbon steel processed by cold ECAP. The image is reproduced from [40] with permission of the publisher Elsevier

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