Part One Introduction and Overview

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1.1 Introduction

Since the title of this book is "Bulk Nanostructured Materials" it seems appropriate to first discuss what we mean by "bulk" and "nanostructured" and to consider where the topics covered in this book fit into the general large and diverse field of nanoscience and nanotechnology. Nanostructured materials have been defined as materials that have at least one dimension in the "nanoscale" (typically 1 to 100 nm). Thus, depending on the dimensions in which the length scale is nanoscale, they can be classified into a) nanoparticles, b) layered or lamellar structures, c) filamentary structures, and d) bulk nanostructured materials [1]. The nanoparticles can be considered to be of "zero" dimensionality and examples include a large range of nanoscale powders of interest for diverse applications such as dispersions in cosmetics and pharmaceuticals. Quantum dots for optoelectronic applications may also fall into this category. A layered or lamellar structure is a one-dimensional nanostructure in which the magnitudes of length and width are much greater than the thickness that is nanoscale. Thin films for electronic device applications are examples of this category. Two-dimensional nanostructures have the length much larger than the width or diameter and nanowires or nanotubes may fit this division. The nanostructures that contain the "bulk" definition relevant to this book are three-dimensional and consist of crystallites, or in certain cases quasicrystals and/or amorphous material that are nanoscale in dimension. While it has been the convention to classify "nanocrystalline" bulk crystalline materials as those with a grain size <100 nm, this arbitrary classification may not always be the most appropriate. Perhaps a definition based on the specific size-dependent property that exhibits a critical dimension in the nanoscale regime would be more fitting. An example of this dimensionality of certain properties is the ferromagnetic coercive force, $H_{\rm c}$. It has been found that the dependence of $H_{\rm c}$ on grain size (D) changes dramatically from a 1/D dependence for larger grains to a D^6 for grain sizes less than about 100 nm as shown in Fig. 1.1 [2]. This occurs when the grain size becomes smaller than the ferromagnetic domain (Bloch) wall thickness such that

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Fig. 1.1 Coercive force, H_c , as a function of grain size. (reproduced with permission from Ref. [2], page 415).

the domain wall now samples several, or many, grains and fluctuations in magnetic anisotropy on the grain size length scale that are then irrelevant to domain-wall pinning and therefore to H_c. Another example of size dependent properties is the critical current density in type-II superconductors. The size scale property of interest in this case is the superconducting coherence length that is approximately the distance over which there are strong correlations between superconducting electrons [3]. For high-field type-II superconductors this distance is of the order of 5-10 nm. This, in turn, determines the geometry of the fluxoid lattice that occurs in an applied magnetic field and must be pinned to obtain high values of critical current density (I_c) . In fact, it is found that grain boundaries are very effective pinning sites that result in high values of J_c . The J_c of the commercial superconducting Nb₃Sn is controlled by grain size and is inversely proportional to grain size, with grain sizes of 50-80 nm providing high values [4]. The situation for mechanical strength is less clear since there is an essentially continuous increase in strength or hardness as the grain size is reduced to the nanoscale. This is reflected in the empirical Hall-Petch behavior that has been modeled by the interaction of dislocations with grain boundaries [5]. Pile-up of dislocations at grain boundaries is considered to be the mechanistic process responsible for the resistance to plastic flow from grain refinement. Several authors [6-8] have suggested divisions of the grain size scale into regions wherein dislocation-based plasticity is dominant (typically from about 10 nm grain sizes and larger) versus the regime below about 10 nm ("nano-1" [6]), where grain-boundary deformation processes are likely. The scheme according to Cheng et al. [6] is shown in Fig. 1.2. The dislocation regime is further divided [6] into the "traditional" regime (typically greater than 1 µm grain size) where both grain boundary and intragranular dislocation sources are operative, from the regime (from about 10 nm up to nearly 1 µm)



Fig. 1.2 Deformation mechanism map for fcc metals. Strength curve is based upon copper. (reproduced with permission from Ref. [6], Fig. 1).

where only grain-boundary dislocation sources exist, and even further subdivision into an "ultrafine" regime (from about 30 nm to 1 µm) where unit dislocations are dominant and a "nano-2" regime where partial dislocations are responsible for the deformation. These divisions were based upon both experimental results and computer simulations. However, recent *in-situ* straining experiments in the electron microscope [9–11] suggest dislocation activity, including pile-ups, may occur at grain sizes down to at least about 20 nm. While more experimental studies, along with modeling and simulations, are needed to better clarify this topic, it seems clear that an arbitrary cutoff of 100 nm below which we define "nanocrystalline" may not be realistic and indeed many interesting mechanical properties are found at grain sizes from 100 nm to 500 nm ("ultrafine grains"), a regime more accessible for many of the processing methods. However, hardness and strength typically reach maximum values at grain sizes below about 50 nm so this regime would appear to be of most interest from a scientific point of view. So we can leave the "nanostructured materials" definition somewhat cloudy, and move to the definition of "bulk". This presumably refers to samples that are not particulates, thin films, or nanoscale wires, but to materials containing many nanoscale grains being of potential usefulness for applications requiring their geometry. If thick enough, perhaps coatings should fall into this category.

In 1997 the author was part of a panel sponsored by the US National Science Foundation and other agencies through the World Technology (WTEC) Division of the International Technology Research Institute that assessed the R & D status and trends in nanoparticles, nanostructured materials, and nanodevices. The present author was responsible for the area of "consolidated materials", that

is, bulk nanostructured materials and wrote the chapter in the book that summarized the panel's findings [12]. This chapter, like the present book, emphasized mechanical behavior, with some discussion of ferromagnetic materials as well as hydrogen storage and corrosion behavior. Thus, the topics of this book are part of the large field of nanoscience and nanotechnology. However, bulk nanostructured materials are often "left out" of topical conferences and journals specific to nanoscience and technology. In many cases, "nano" refers to the size of a component - particle, thin film, or wire - and not to the microstructure of a bulk sample. It is the author's perception that most of the papers published in the topics of this book are found in the conventional materials science and engineering and physics journals rather than in specialized "nano" journals. For example, looking at a recent issue of the Virtual Journal of Nanoscale Science & Technology (a weekly multijournal compilation of the latest research on nanoscale systems) not a single paper of the 110 papers in the issue were in the area covered by this book. This is typical of many other new journals devoted to nanoscience and technology, and to many topical conferences in the field. Of course, the topics of this book are well covered in numerous symposia that are parts of materials science meetings such as TMS or MRS, or in topical meetings devoted to the subject. It is well known that the impetus for the interest in this now large subfield of materials science came from the research of H. Gleiter and coworkers in the early 1980s when materials with nanoscale grain sizes were prepared by the inert gas condensation method and their properties were found in many cases to be dramatically different from those of conventional grain-size materials [13]. The explosion of research in this field that has occurred since these initial discoveries has been influenced by the advances in three important technological areas [14]:

- 1. new and improved processing methods to provide nanocrystalline materials
- 2. new and improved characterization of materials at the nanoscale in terms of spatial resolution and chemical sensitivity
- 3. new and improved understanding of the relationships between nanostructure and properties.

The remainder of this overview chapter will be devoted to a description of the state-of-the-art of these three technological streams and their influence on bulk nanostructured materials.

1.2 Processing

Processing of bulk nanostructured materials can in principle be accomplished by either the "bottom-up" assembly of atoms or molecules into nanoscale clusters that require subsequent consolidation into bulk material, or the "top-down" methods that start with a bulk solid and obtain a nanostructure by structural decomposition. The bottom-up methods include the inert gas condensation and compaction technique that stimulated the field. This technique consists of evaporating a metal inside a chamber containing a partial pressure (typically a few hundred Pascals) of an inert gas, e.g. He, such that the evaporated atoms collide with the gas atoms inside the chamber, lose their energy, and condense in the form of small discrete crystals of loose powder. The condensed fine powders collect on a liquid-nitrogen-cooled cold finger and are stripped off by an annular Teflon ring into a compaction device. The details of this process and improvements to the original design have been published [15]. While this method has provided the materials for the seminal early studies of the properties of nanocrystalline materials, it suffers from both the limited size of samples that can be prepared and from the common problem of two-step methods in that the compaction step may not provide completely dense or bonded material in spite of improvements to the process.

Chemistry is based upon the reactions and manipulations of atoms and molecules and the synthesis of nanocrystalline materials by chemical reactions predates the recent development of this field. Chemical synthesis of nanoscale materials has been reviewed by Chow and Kurihara [16]. In terms of bulk nanostructured materials these methods are two-step in that the particulates formed by the chemical reactions require consolidation. Of course, historically and in the present, the resultant nanoscale particulates can be used as such in applications ranging from catalysts to cosmetic powders. An example of a structural bulk material prepared by chemical reactions is WC-Co. Kear and coworkers [17] have developed a process in which fine and uniform precursor powders are obtained by spray-drying (solvent removal) of homogeneous aqueous solutions of soluble salts of W and Co. This precursor powder is reduced with hydrogen and reacted with CO in a fluidized-bed reactor to yield nanophase WC/Co powder. After consolidation by sintering, the grain size was on the order of 200 nm. These materials provided superior mechanical properties in terms of hardness and toughness compared to larger grain size conventional WC-Co.

Electrodeposition can be classified as a "bottom-up" method of preparation of nanocrystalline materials and also as "one-step" since no consolidation step is needed. Thick electrodeposits may be considered to be bulk materials. Since the late 1980s electrodeposition has been studied as a method to produce nanocrystalline materials and it has moved into the commercial production of such materials. Much of the work was pioneered by Erb and coworkers and this subject has been reviewed by Erb et al. [18]. Using special processing methods, a large number of metals, alloys, composites, and ceramics have been electrodeposited with nanocrystalline microstructures. Electrodeposition occurs by the nucleation of crystallites on the substrate surface and their subsequent growth along with nucleation of new crystallites. In order to obtain a nanocrystalline grain size, nucleation events should be favored over growth. The variables in electrodeposition include bath composition, bath pH, temperature, overpotential, bath additives, and direct current vs. pulse electrodeposition. It has been stated [18] that the two most important mechanisms that are rate-determining steps for formation of nanoscale grains in electrodeposition are charge transfer at the electrode

surface and surface diffusion of adions on the crystal surface. One method to inhibit growth of nucleated crystallites is by reducing the surface diffusion of adions by adsorption of foreign species (which may be referred to as "grain refiners" or "additives") on the growing surface. Most such additives are organic materials and may become trapped at the grain boundaries and are presumably responsible for the brittle mechanical behavior observed in nanocrystalline materials processed by electrodeposition with additives. Since high overpotential favors extensive nucleation, pulse plating, as a powerful method to achieve high overpotentials is a technique to synthesize a nanocrystalline structure without the use of additives. In the codeposition of alloys, the solute ion can act like an organic additive but without the deleterious embrittlement effects. Therefore, there are several processing strategies that can be used to provide artifact-free bulk nanocrystalline materials by electrodeposition. Some of the examples of bulk nanocrystalline materials that exhibit optimized combinations of strength and ductility, to be discussed in the section on properties, were made by electrodepositon.

The ball milling of powders - mechanical attrition - has been a popular method to produce materials with a nanocrystalline grain size [19]. The ball milling of powders can be divided into two categories: 1. the milling of elemental or compound powders - "mechanical milling", and 2. the milling of dissimilar powders - "mechanical alloying", in which material transfer occurs. This subject has been reviewed by a number of authors [20, 21]. Besides being discussed in the examples of general reviews of ball milling, this specific topic has also been reviewed [19]. Mechanical attrition has been found to refine the grain size to the nanoscale of all solid elements studied. The minimum grain size achieved is dependent upon a number of process and material variables [19]. The minimum grain size obtainable by milling has been attributed to a balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes [22]. The minimum grain size is plotted against the melting temperature of the element in Fig. 1.3. At least for the lower melting metals, there appears to be an inverse dependence of minimum grain size on melting temperature that is consistent with the competition between defect creation and removal. It is clear that mechanical attrition can produce nanocrystalline materials with fine grain sizes such that for higher melting point metals, grain sizes below 10 nm can be achieved. However, in order to attain bulk material, the powders need to be consolidated. The ability to maintain the very small grain sizes in as-milled material and obtain artifact-free bulk samples with minimal grain growth remains a challenge.

For all the "two-step" processes for formation of nanostructured materials the first step provides a nanoscale particulate, or as in mechanical attrition, a powder particle with a nanoscale microstructure. These particulates must then be consolidated into bulk form. The consolidation problem remains an active area for more research and development and has not been adequately resolved to date. The problem is to form good atomic bonding between the particulates by a combination of pressure and temperature such that theoretical densities are



Fig. 1.3 Minimum nanocrystalline grain size for ball-milled elements versus their melting temperature (data given in Ref. [19]).

reached along with the complete interparticle bonding. This should be done without significant coarsening of the nanoscale microstructure or by introduction of any structural defects or unwanted phases. This topic has been reviewed, for example, by Groza [23] and Mayo [24]. Most consolidation methods have used pressure-assisted sintering approaches. Shear stresses are most effective in collapsing pores and also disrupt surface oxide layers. Since deformation processes that have significant shear stress components are desired we can list the processes in order of decreasing effectiveness as follows: extrusion – sinterforging – uniaxial hot pressing – hot isostatic pressing (HIP). Nonconventional consolidation methods for densification of nanocrystalline particulates include microwave sintering, field-assisted sintering methods, and shockwave consolidation.

The possibility of producing very fine grain structures by severe plastic deformation was suggested by research using conventional deformation methods taken to very high degrees of strain. It has been known for many decades, going back to the 1950s, that the structure of deformed metals can change with increasing plastic deformation such that random dislocation arrays can lower the energy of the system by "self-assembly" into "cells" or "subgrains" such that there is a high dislocation density in the cell walls and a lower dislocation density within the cells. The cells are typically the result of plastic deformation, the cell boundaries are somewhat diffuse. Subgrains, like cells, show small misorientations with their neighbors, but have sharper boundaries, and are formed by plastic deformation and thermal recovery processes. In most cases, the early studies of microstructures produced by severe plastic deformation gave cell or

subgrain sizes in the micrometer down to submicrometer size scale, but not into the nanoscale. One exception to these results is from the work of Rack and Cohen [25], who reported the cell structure developed in a series of Fe-Ti alloys deformed by wire drawing to large values of true strain up to about 7. The size of the cells decreased with increasing deformation, and reached values of about 50 nm at the highest strains. However, these were all cells with very low angle misorientations. In recent years special methods of mechanical deformation have been developed for producing submicrometer and even nanoscale grains with high-angle grain boundaries. These methods, the microstructure developed, and the properties of the materials with the refined grains so produced have been reviewed by Valiev et al. [26] and form much of the content of this book. The major methods of severe plastic deformation, in addition to mechanical attrition, are severe plastic torsion straining under high pressure (HPT) and equal-channel angular pressing (ECAP). In the case of HPT a disk-shaped sample is compressed to pressures of about 2 to 6 GPa and then one of the dies is moved with respect to the other. With enough rotation very large values of strain can be achieved, well into the 100s. This method has been used to achieve submicrometer grain sizes and in some cases even nanocrystalline grain sizes. The ECAP method that allows for the deformation of bulk samples by pure shear was first developed by Segal et al. [27]. In this method a billet is pressed through a die with two channels at angles of intersection typically 90 to 120°. The billet is subjected to severe deformations without changing its dimensions. Multiple passes through the die provide accumulative strain. The grain sizes developed by this method are typically in the submicrometer, 200 to 300 nm, range. A large body of experimental research and modeling studies has been reported for this technique. There are examples of submicrometer-size grain structures induced by the severe strain of ECAP in several metals that provide an excellent combination of both increased strength along with good ductility [28]. Other severe plastic deformation methods that will be described in more detail in the book include accumulative roll bonding [29] and friction stir welding [30]. It appears that the total strain provided by a given deformation process is in large part responsible for the final grain size that can be obtained. This must be a function of the dislocation density that can be obtained and its subsequent rearrangement by thermal processes. The processes that can provide the highest practical strain levels would be HPT and mechanical attrition of powders. The former has typically been limited to rather small disk samples although recent work is directed to scaling this to larger cylinders [31]. Mechanical attrition typically results in a powder product that then requires consolidation. Recent results on in-situ consolidation during ball milling of several ductile metals and alloys have been reported. The processing challenge is to produce nanocrystalline materials with the finest grain sizes to maximize strength, but without artifacts that might compromise ductility, and in sufficient size for mechanical testing and applications.

1.3 Characterization

An important aspect of the ability to study and develop nanocrystalline materials is the improvement of techniques to probe the spatial and chemical nature of nanoscale regions such as grains, precipitates, and grain-boundary chemistry. X-ray diffraction line-broadening analysis has been used to estimate the grain size and lattice strain of nanocrystalline materials. These techniques for the most part are not new and have been reviewed and discussed in a number of papers. There are several factors that can cause broadening of X-ray diffraction peaks and care must be taken in the separation of these effects. Instrumental broadening (quality of the alignment, receiving slit, etc.) must be corrected for. The problems with such corrections and the use of reference standards have been discussed [32]. A number of different analyses can be performed to deduce the crystalline size and the internal strain present in the sample. The most used of these methods are the Scherrer [33], the Williamson-Hall [34], and the Warren-Averbach [35] methods. While the simple Scherrer method only provides an average unit cell column length, the Williamson-Hall and Warren-Averbach techniques also give estimates of the lattice strain. If the grain-size distributions are narrow, then the X-ray technique can give good values for the average grain sizes [36]. Ungar and coworkers [37, 38] further modified the peak profile analysis methods of Williamson-Hall and Warren-Averbach to estimate grain-size distributions as well as dislocation density and dislocation arrangements. Generally, grain-size determination by the use of X-ray diffraction line-broadening analysis is only advised if the average grain size does not exceed 100 nm and the grain-size distribution is narrow. Correction for instrumental broadening becomes critical for grain sizes greater than about 30 nm. In cases where an inhomogeneous grain-size distribution exists, with some grains >100 nm, other methods, in particular, transmission electron microscopy, must be used.

Transmission electron microscopy, TEM, is one of the most direct methods for the determination of the grain size. High-resolution TEM can reveal grains at the smallest sizes as well as information on the nature of the grain boundaries. More sophisticated Z-contrast imaging can provide chemical information regarding grain-boundary segregation [39]. The advantages of TEM are obvious in terms of providing direct images of the grain size, shape, and size distribution. The analysis of the micrographs involves the application of straightforward stereological relationships, which provide various possibilities to characterize the grains. In order to get accurate statistical information on nanocrystalline grain size by TEM, dark-field TEM must be carried out on many fields of view in many samples.

Other methods that can be used in certain cases to measure nanocrystalline grain size are high-resolution scanning electron microscopy [40], atomic force and scanning tunneling microscopy [41] and Raman spectroscopy [42].

1.4 Properties

1.4.1 Mechanical Properties

One of the areas of research on nanocrystalline materials that has received extensive study is their mechanical behavior. The great interest in the mechanical behavior of nanocrystalline materials originates from the unique mechanical properties first observed and/or predicted by the pioneers of this field, Gleiter and coworkers [13]. Among these early observations or predictions were:

- Lower elastic moduli than for conventional grain size materials by as much as 30–50%,
- Very high hardness and strength hardness values for nanocrystalline pure metals (~10 nm grain size) that are 2 to 10 or more times higher than those of larger grained (>1 μ m) metals,
- Increased ductility perhaps even superplastic behavior at low homologous temperatures in even normally brittle ceramics or intermetallics with nanoscale grain sizes, believed to be due to grain boundary, diffusional deformation mechanisms.

While some of these early observations and predictions have been verified by subsequent studies, in particular the high hardness and strength values, some have been found to be due to high porosity in the early bulk samples (for example the low elastic moduli observed) or to other processing artifacts, and not inherent properties of the nanocrystalline materials. The ductility issue remains a subject of present research, and while most nanocrystalline materials do not exhibit the high predicted ductilities, and in fact show little ductility in tension [43], there are recent examples of good ductility along with high strength in a limited number of cases [44–46].

Three major limitations to ductility for nanocrystalline materials can be identified. These are: 1. artifacts from processing; 2. force instability in tension; 3. crack nucleation or propagation instability. Porosity was a major artifact, especially for earlier studies of metals made by the inert gas condensation method. Even when theoretical density is attained, complete particle bonding may be lacking. Nanocrystalline materials made by ball milling of powders also can suffer from lack of complete bonding after power consolidation. The surfactant that is sometimes used to prevent excessive cold welding during milling can prevent complete bonding during consolidation and therefore limit ductility. Another popular method for producing nanocrystalline materials is electrodeposition. While this method is "one-step" in that it does not require consolidation of particulates and the problems associated with this, most of the nanocrystalline materials made by electrodeposition have also exhibited very poor ductility, presumably due to the additives often used to attain a nanocrystalline microstructure, as discussed in Section 1.2. However, as will be described below, several examples of high strength and good ductility are observed with electrodeposited nanocrystalline materials produced without the use of organic additives.

Necking generally begins at maximum load during tensile testing. The amount of uniform elongation depends upon the strain hardening such that true uniform strain $\varepsilon_u = n$ in a cylindrical specimen (or $\varepsilon_u = 2n$ for a sheet) where *n* is the strain hardening coefficient. For an ideally plastic material (such as amorphous alloys) where n=0, the necking instability would begin just as soon as yielding occurred. This criterion implies that the sample is mechanically stable until the rate of strain hardening falls to a level determined by the flow stress (and prior strain) at that time. Materials with a high capacity for strain hardening are therefore stable, while those with little capacity for strain hardening are potentially unstable.

Elongation to failure in tension is plotted vs. grain size in Fig. 1.4 for a variety of metals and alloys. It is clear that for most metals with grain sizes below about 30 nm the elongation to failure values are very low, typically less than 2–3%. Since this graph was originally published [43] several new datum points have been added that show significant ductility for grain sizes of \leq 30 nm. These more recent breakthroughs in ductility will be described below.

As described above, strain hardening is needed in order to minimize mechanical instabilities that lead to local deformation (necking) and failure. The ability to strain harden therefore becomes an important criterion for ductility in nanostructured materials. An approach that has been used to provide strain hardening in nanostructured materials is to introduce a bimodal grain-size distribution by appropriate processing methods. The supposition was that the larger grains should deform by the usual dislocation mechanisms and provide strain harden-



Fig. 1.4 Elongation to failure in tension versus grain size for a variety of metals and alloys. (reproduced with permission from Ref. [43], Fig. 1).

ing, while the smaller nanoscale grains would provide the strength and hardness.

Results of Ma and coworkers [46] have provided a dramatic example of combinations of high strength and high tensile ductility. Copper was rolled at liquidnitrogen temperature to high strains of 93% to create a high dislocation density that does not dynamically recover. The as-rolled microstructure showed the high dislocation density along with some resolvable nanoscale grains with dimensions less than 200 nm. Annealing for short times at temperatures up to 200 °C provided for the development of grains with high-angle boundaries that were in the nanoscale or submicrometer size range. Some abnormal recrystallization was observed such that for annealing at 200°C for 3 min, about 25% volume fraction of the samples consisted of grains 1-3 µm in diameter. Rolling the Cu at room temperature did not provide sufficient dislocation density to accomplish the subsequent nanoscale/submicrometer grain sizes on annealing. This work on Cu gave stress-strain curves for annealed coarse-grained Cu, Cu rolled to 95% at room temperature, Cu rolled to 93% at liquid-nitrogen temperature, and these samples annealed for 3 minutes at either 180 or 200°C. The optimum properties were obtained for the mixed grain size material with the $1-3 \,\mu m$ grains embedded in the matrix of nanoscale and submicrometer-size grains. This material had a high yield stress of about 340 MPa, a total elongation to failure of 65% and uniform elongation of about 30%. The ductility was thus comparable to that of annealed conventional grain size Cu, but the yield strength was almost 7 times higher.

Lavernia and coworkers have prepared a commercial Al alloy, 5083 [47] and an Al-7.5% Mg alloy [48] by cryomilling followed by powder compaction by hot isostatic pressing and extrusion. The cryomilling of Al alloy 5083 [48] resulted in a nanoscale microstructure with average grain size about 30 nm. After hipping and extrusion the grain size remained mostly nanoscale at an average value of about 35 nm. However, some larger grains were also observed in the TEM analysis. The stability of the nanoscale grain size during the elevated temperature compaction steps was attributed to the large number of various precipitates including several intermetallic compounds such as Mg₂Si and Al₃Mg₂ as well as compounds formed from interstitial impurity atoms, namely AlN and Al₂O₃, which presumably retard grain growth by Zener pinning of the grain boundaries. A few larger micrometer-size grains were formed by secondary recrystallization. These large grains were believed to be responsible for the good ductility observed in these materials along with large increases in strength. Guided by these results, an Al-7.5% Mg alloy was cryomilled to nanostructured grain sizes [49]. The cryomilled powder was then combined with either 15 or 30% by volume of unmilled alloy powder, which was made by powder atomization and had micrometer-scale grain sizes. The powders were then consolidated by hipping and extrusion to bulk samples for tensile testing. The additions of larger grains to the nanocrystalline matrix increased the tensile ductility from about 1.4% to 5.4% elongation, with some decrease in strength values but still about four times the yield strength of conventional Al 5083.

While nanoscale grain boundaries have been the focus for increasing strength in studies of nanocrystalline materials, twin boundaries can also be an effective obstacle to dislocation motion and a potent strengthener. Lu and coworkers [49] have reported the synthesis of nanoscale growth twins in electrodeposited Cu. The Cu grain sizes were of the order of 400–500 nm and the twin lamellae thicknesses ranged from averages of about 100 nm down to <20 nm. The yield strength of the Cu followed Hall–Petch behavior with increased strength as twin lamellae spacing decreased. Increased ductility also was observed with decreasing twin lamellae spacing. The Cu with the finest twin lamellae spacing shows both high strength and ductility. Higher strain hardening than conventional grain size Cu is also noted.

While some strategies for optimization of strength and ductility, such as bimodal grain-size distributions, compromise some strength for ductility, there are several recent results on nanostructured materials where strength levels are high and good ductility can still be achieved. These results are for nanocrystalline materials with small grain sizes (<30 nm) and with relatively narrow grainsize distributions such that no grains >50 nm are present.

Electrodeposited Co metal has been prepared with a small average grain size of about 12 nm and with a fairly narrow grain-size distribution of ±7 nm [44]. This material had the hcp structure with no trace of the fcc phase, that is, it had the equilibrium structure for room temperature. The hardness, yield strength, and ultimate tensile strength for this nanostructured Co were 2-3 times higher than for conventional grain size Co. The nanocrystalline Co exhibited elongation to fracture values of 6 to 9%, which are comparable to those for the conventional grain size Co. Of great interest is the dependence of the mechanical behavior of the nanostructured Co on the strain rate of the tensile tests. Applying lower strain rates resulted in higher flow stress and tensile strength at relatively constant yield strength. This behavior is in contrast to the usual response of a material in which dislocation slip is the dominant mechanism. In such materials higher strain rates result in higher tensile strength. The authors suggest this response of nanocrystalline Co to changes in strain rate are typical of materials that deform predominantly by deformation twinning. That is, higher strain rates result in lower flow stress and tensile strength. They therefore suggest that the dominant deformation mechanism in their nanocrystalline Co is twinning. More studies, in particular high-resolution TEM or in-situ TEM under stress, are needed to confirm these ideas about twinning deformation.

Li and Ebrahimi [45] have prepared nanocrystalline Ni and Ni-Fe alloys by electrodeposition without the use of any additives that might induce embrittlement. Their samples exhibited excellent strength values along with good ductility. The Ni sample had a grain size of 44 nm and the Ni–15% Fe sample had a 9 nm grain size. The fracture behavior of the alloys was very different even though both exhibited good values of elongation. The Ni sample had an elongation of about 9% and also showed significant reduction of area and ductile fracture behavior consistent with that for other ductile fcc metals and deformation

by dislocation motion. While the Ni–15% Fe sample also showed reasonable 6% elongation, the reduction in area was negligible and fracture appeared to be brittle. TEM revealed grain-boundary cracking. The authors suggest that the Ni–15% Fe alloy with the average grain size of 9 nm was below the "crossover" grain size from dislocation dominated deformation processes to grain-boundary deformation processes such as grain boundary sliding. In spite of this apparent brittle fracture behavior good ductility along with high strength were observed, suggesting processing artifacts did not affect the mechanical properties.

The *in-situ* consolidation of ball milled powders in several metals has allowed for the production of artifact-free samples for tensile testing. Bulk nanocrystalline Cu spheres were synthesized using a combination of liquid-nitrogen temperature and room-temperature milling [9]. Spheres with diameters up to about 8 mm were obtained that could be pressed into disks from which samples for mechanical testing could be machined. TEM results shown in Fig. 1.5 A indicate



Fig. 1.5 TEM observations of the typical microstructure in the *in-situ* consolidated nanocrystalline Cu. The bright-field TEM micrograph (A) and the SADP [the upper left inset in A] show roughly equiaxed grains with ran-

dom orientations. The statistical distribution of grain size (B) was obtained from multiple dark-field TEM images of the same sample (reproduced with permission from Ref. [9], Fig. 1).

that the consolidated Cu consists of equiaxed nanograins oriented randomly, as can be seen from the corresponding selected area diffraction pattern, the upper left inset in Fig. 1.5 A. Statistical analysis of multiple dark-field images reveals a monotonic lognormal grain-size distribution with an average grain size of 23 nm (Fig. 1.5 B). Density measurements, scanning electron microscopy of the sample surfaces, and TEM analysis show that no porosity is introduced during the *in-situ* consolidation of nanocrystalline Cu. The chemical analysis of the consolidated nanocrystalline Cu indicated that the oxygen content increased from 0.10 at.% in the starting powder to 0.29 at.% in the final product. The measured Fe contamination was less than 0.1 at.%. Therefore, it may be concluded that the nanocrystalline Cu made by the above procedure is free of artifacts in that there is no porosity, no debonding, and minimal impurity contamination.

Tensile test data for the *in-situ* consolidated nanocrystalline Cu is compared with the stress–strain curve for conventional grain size Cu in Fig. 1.6 [9]. In the case of the nanocrystalline Cu, the 0.2% offset yield strength (σ_y) and the ultimate tensile strength (σ_u) reach values of 971±12 MPa and 1120±29 MPa, respectively. This σ_y value is at least one order of magnitude higher than that of coarse-grained pure Cu samples, and σ_u of the nanocrystalline Cu is about five times higher than that of the coarse-grained Cu sample. The hardness value of this nanocrystalline Cu is 2.3 GPa, which is consistent with the Hall–Petch behavior of Cu. Therefore, it is concluded that the high values of hardness and yield strength are due to the small grain size (23 nm). These strength values are



Fig. 1.6 True stress versus true strain for bulk *in-situ* consolidated Cu in comparison with that for coarse-grained Cu and nanocrystalline Cu made by the inert gas condensation and compaction technique. (reproduced with permission from Ref. [9], Fig. 2).

comparable to the highest values observed for nanocrystalline Cu but more significant is the good tensile ductility observed with 14% uniform elongation and 15% elongation to failure. This ductility is much greater than previously reported for nanocrystalline materials of this grain size and even somewhat greater than the ductility of the nanotwinned Cu [49]. Another important feature of the stress–strain curve (Fig. 1.6) is the large strain hardening observed in the plastic region that suggests a high lattice dislocation accumulation during the plastic deformation up to failure. Strain hardening is often limited in nanocrystalline materials at grain sizes where dislocation activity is believed to be difficult. *In-situ* dynamic straining transmission electron microscope observations of the nanocrystalline Cu were also carried out, which showed individual dislocation motion and dislocation pile-ups. This suggests a dislocation-controlled deformation mechanism that allows for the high strain hardening observed. Trapped dislocations were also seen in individual nanograins.

An artifact-free bulk nanocrystalline Al-5% Mg alloy was also prepared using *in-situ* consolidation during ball milling at liquid nitrogen and room temperatures [50]. The average grain size, determined by TEM, was 26 nm with a relatively narrow grain-size distribution. The nanocrystalline structure produced was a supersaturated solid solution of Mg in Al. The tensile behavior of the nanocrystalline alloy showed an extremely high strength. The tensile yield strength reached 620 MPa (four times that of the coarse-grained Al-5083 alloy), and the ultimate tensile strength was 740 MPa. A significant tensile ductility was obtained with an elongation to failure value of 8.5%. Strain hardening was also observed, which is suggested to originate from dislocation accumulation during plastic deformation.

1.4.2

Magnetic and Other Properties

Nanocrystalline materials have been studied for possible use in applications of soft magnetic materials, hard magnetic materials, and magnetic storage media [51]. The first two topics may be classed with bulk nanostructured materials. Soft ferromagnetic materials for potential use in transformer cores, inductive devices, *etc.* have been mainly developed by the partial crystallization of amorphous precursors to precipitate the nanocrystalline phase which may be *a* FeSi (FINEMET), *a* Fe (NANOPERM), *a* FeCo, (bcc), *a'* FeCo (B2) (HITPERM) [52]. The small single-domain nanocrystalline ferromagnetic precipitates in the amorphous matrix give these alloys their unique magnetic behavior. The averaging of the magnetocrystalline anisotropy over many grains coupled within an exchange length gives the very low coercive force and low energy losses (narrow *B/H* hysteresis loop).

Hard ferromagnetic nanocomposites have been found to exhibit a variety of interesting properties [53]. For example, exchange coupling in magnetically hard and soft phases can increase magnetic induction by the phenomenon of "remanence enhancement". In the Fe₉₀Nd₇B₃ composition, a nanoscale mixture of the

hard $Fe_{14}Nd_2B$ phase and the soft *a* Fe phase exhibit high coercivity along with high values of remanent magnetization. This is associated with exchange coupling between the hard and soft phases which forces the magnetization vector of the soft phase to be rotated to that of the hard phase. The requirements for this behavior are a nanocrystalline grain size and a degree of coherence across the interphase boundaries sufficient to enable adjacent phases to be exchange coupled.

Other properties of bulk nanocrystalline materials that are important and will be addressed in the book are hydrogen-storage materials and surface properties such as corrosion resistance.

The following chapters written by authors with expertise in their fields will expand on the brief overview given here as well as related areas not covered in this short introduction. The result should definitely show that bulk nanostructured materials are an important part of the "nanocrystalline revolution".

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