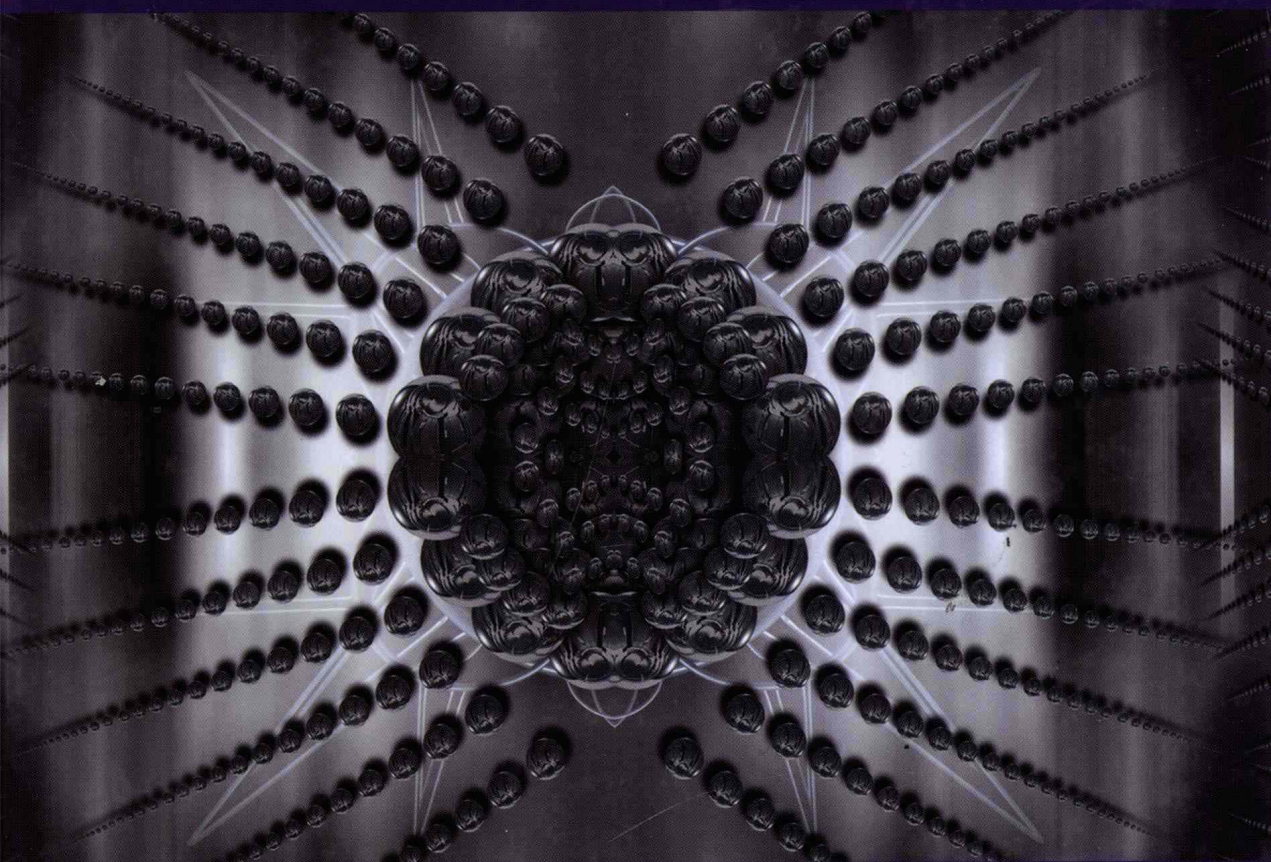


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Nanostructured Materials



Edited by
Gerhard Wilde

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Functional Nanostructured Materials – Microstructure, Thermodynamic Stability and Atomic Mobility

S. Divinski, H. Rösner and G. Wilde

SCOPE OF THE BOOK

One way to distinguish nanostructured materials is based on their dimensionality, i.e. according to the number of spatial dimensions in which the materials are *not* nanoscaled. In recent years, much attention has been devoted to zero-, one- and two-dimensional nanostructures, e.g. nanoparticles (0-D), nanotubes and nanowires (1-D) or thin films and multilayer systems (2-D) with a fair number of overview and review volumes published in these areas. However, hierarchical structures as analysed in Chapter 7 or porous nanocrystalline films (Chapter 5) do not fit well into such a classification scheme, since the respective functional property depends sensitively on both the size confinement and interface contributions due to the nanoscale building blocks and also on the structure and structuring on the micrometre level. It is believed that both dependencies are crucial and necessarily need to be regarded for any functional nanosystem that should be transferred into a device application. Thus, this book focuses on functional aspects of nanostructured materials that have a high relevance to immediate applications, such as catalysis (Chapter 4), energy harvesting (Chapter 5), energy storage (Chapter 6), optical properties (Chapter 7) and surface functionalization via self-assembly (Chapter 8). Additionally, Chapters 1–3 are devoted to massive nanostructured materials and composites and deal with basic properties and requirements of this new class of engineering materials. In particular the issues concerning stability and reliability and those concerning mechanical performance are mandatory aspects that need to be regarded carefully for any nanostructured engineering material.

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1. INTRODUCTION

The technological progress of recent decades has mostly been driven by the scientific and technological developments in the area of information technology. The ever-faster progress is to a large extent a result of achieving and controlling smaller and smaller feature sizes of the functional and structural components, thus allowing for higher integration densities, higher speed or lower energy consumption and lower costs. At the same time, the term 'nanotechnology' has found its way to the funding organizations and, in recent years, also to the media, thus reaching the general public. In many cases, the research trends in the nanosciences and in nanotechnology have been mapped directly onto expectations and projections from the information technology sphere, for example the famous Moore's 'law', since the developments proceeded roughly at the same time and since many aspects concerning the progress in information technology are directly related to, or are rather dependent on, the advances made in nanotechnological research.

However, if nanotechnology as a whole is addressed, then a broader range of scientific aspects needs to be considered, with additional research areas such as nanoparticle research that have already entered everyday life, e.g. nanosized particulates for scratch protection on eye glasses, for UV light absorption in sun protection lotions or for viscosity adjustment and wear minimization in the rubber of car tyres. With these applications, it is the reduced size alone that serves the purpose. Yet, there are vast areas of research on nanoscale systems that have just begun to surface, with prominent examples such as an atomic-scale electrical switch [1], inorganic/organic composite structures for bio-mimicked structural applications [2], nano-biological transporter systems for targeted drug delivery [3] or the bio-functionalization of surfaces for advancing new nano-lithography techniques [4], to mention just a few. With most of the future applications that are in the background of today's basic research, not only the functional units need to be nanosized; but also the material used for interfacing the micro- or even the macro-world to the nanosized systems such as substrates, supports or leads will have to be structured on the nanoscale. Thus, the respective material property or the combination of properties that makes the material suitable and desirable for the specific application needs to be analysed in terms of the specific size dependence [5].

Properties of materials are often modified for spatially confined or finite-size systems [5,6]. Depending on the type of property, this behaviour is explained by the crossing of length scales when characteristic interaction lengths or wavelengths become comparable with the system size. This type of argument is usually invoked for explaining the well-known size dependence of electronic properties, e.g. optical or magnetic properties, of nanostructured materials. In these cases, the size of the nanoscale structural unit (the nanoparticle or the nanocrystalline grain) becomes equal to or smaller than a characteristic correlation length. Concerning, e.g., ferromagnetism, the ferromagnetic correlation length $L_0 = \sqrt{A/K_1}$, with the exchange interaction constant, A , and the local magnetocrystalline anisotropy, K_1 [7] becomes comparable with or even smaller than the

average diameter of the particles or grains if size effects become significant. Within this volume, Chapter 7 on optical applications of nanomaterials with hierarchical structures by E. Kumacheva et al., Chapter 5 on porous nanocrystalline films for advanced solar cells by G. Hodes and A. Zaban and Chapter 8 on interfacial self-assembly by L. Chi and X. Chen are strongly concerned with this first type of *finite-size effect*. A second type of argument concerning the size dependence of properties is related to the presence of interfaces or, more specifically, the presence of a large fraction of the atoms of the system at or near a surface or an internal interface. In addition, and as will be shown here, the atomistic details of these interfaces matter[6].

Traditionally, the impact of the internal or external interfaces has been implemented into the description of interface-controlled property modifications by describing the interface and the core of the particles or grains as two separate phases with intrinsically different properties. One aspect of such 'two-phase' models considers that the atoms situated at or near such an interface are energetically in a different state compared with the atoms in the core of the crystallite or the nanoparticle. Transport properties or parameters that describe the gas-solid interactions, e.g. in the context of hydrogen storage in interstitial sites [8], are current examples for property modifications that are discussed by two-phase descriptions. Similar approaches also apply for describing reversible phase transformations between thermodynamically stable phases, which are often modified for spatially confined or finite-size systems [9]. Within this volume, specifically, Chapter 4 on catalysis and fuel cells by J.-S. Yu et al., Chapter 6 on energy storage by M. Fichtner, Chapter 3 on the mechanical properties of nanocomposites by A. Mukherjee et al. and Chapter 2 on stability and reliability issues of nanomaterials by K.A. Padmanabhan and S. Balasivanandha Prabu are addressing topics within this area of interface controlled properties.

2. NANOSTRUCTURED AND NANOCRYSTALLINE MATERIALS

In addition to materials that are to be structured by means that control the shape and feature size on the nanometre scale, an entire range of promising property modifications, such as mechanical or magnetic properties of *nanocrystalline materials* [5], generate the desire to synthesize and stabilize *massive nanocrystalline materials*, i.e. polycrystalline materials with bulk shape consisting of a dense array of crystallites in the size range well below 100nm. It was Herbert Gleiter who proposed at the Risø conference in 1981 the basic idea of such a new class of materials in which 50% or more of the atoms are situated at grain boundaries. In distinction to nanostructured materials, the details of the nanocrystal assembly concerning the position and orientation of individual nanocrystals are not controlled, but irreversible processes and non-equilibrium processing steps generate an ensemble of nanosized crystals with properties that are defined for the average of the thermodynamic ensemble. Yet, however different nanostructured and nanocrystalline materials are, with respect to the respective synthesis routes, two issues need to be addressed for both situations that are crucial for any

application: first, the size dependence of the properties must be understood for any meaningful materials design or property prediction. Secondly, the material needs to be stabilized against detrimental coarsening such that the nano-scaled microstructure is at least kinetically stabilized. This is a basic precondition for obtaining properties that are independent of time within the lifetime of the respective product or device application. In view of the similar requirements concerning the materials aspects for both nanostructured and nanocrystalline materials, both types of material are considered interchangeably in the following.

3. BULK NANOCRYSTALLINE MATERIALS

Nanostructured materials and composites can be produced by a variety of different methods. Besides the fabrication of clusters, thin films and coatings from the gas or liquid phase, chemical methods such as sol-gel processes and electro-deposition are common methods of processing. As a versatile alternative, however, mechanical methods have been developed which allow fabricating nanostructured or nanocrystalline materials in large quantities with a broad range of chemical compositions and atomic structures and even in bulk shape. These methods, which are schematically shown in Figure 1.1, can be applied to powder samples, to thin foils and to the surface of bulk samples and are characterized by the application of extremely large plastic strain levels.

While some of the methods such as equal channel angular pressing [10] mostly yield material with submicron grain sizes in the range of a few hundred nanometers – so-called *ultrafine grained material* – and other methods such as high pressure torsion straining [11] are inherently limited to small amounts of material, some techniques, such as repeated cold-rolling [12,13], have been shown to allow the production of bulk quantities of truly nanocrystalline material. In fact,

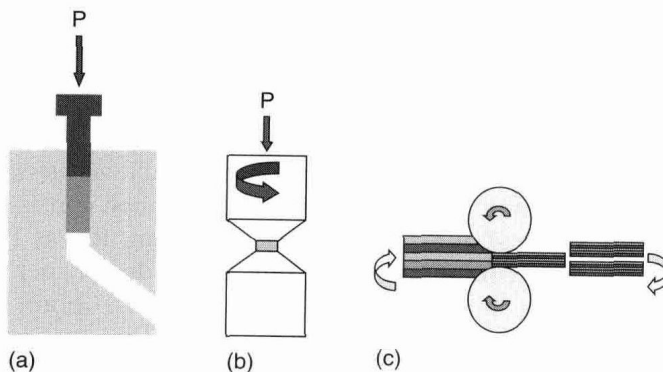


FIGURE 1.1 Schematic representation of three important methods for performing severe plastic deformation. (a) Equal channel angular pressing (ECAP), where a massive cylindrical sample is pressed repeatedly through a knee; (b) high pressure torsion (HPT) straining, where a disc-shaped specimen is torsion strained under very high pressure; and (c) repeated cold-rolling (RCR) with intermediate folding, where sheet metal is repeatedly rolled and folded.

one recent example showed that massive samples of pure Ni with an average grain size as small as 10 nm diameter could be obtained by repeated cold-rolling (Figure 1.2a) [13]. Yet, although important with respect to the exceptional mechanical properties of these materials [14], synthesizing kinetically stabilized two-phase composite nanostructures by plastic deformation processing does not seem

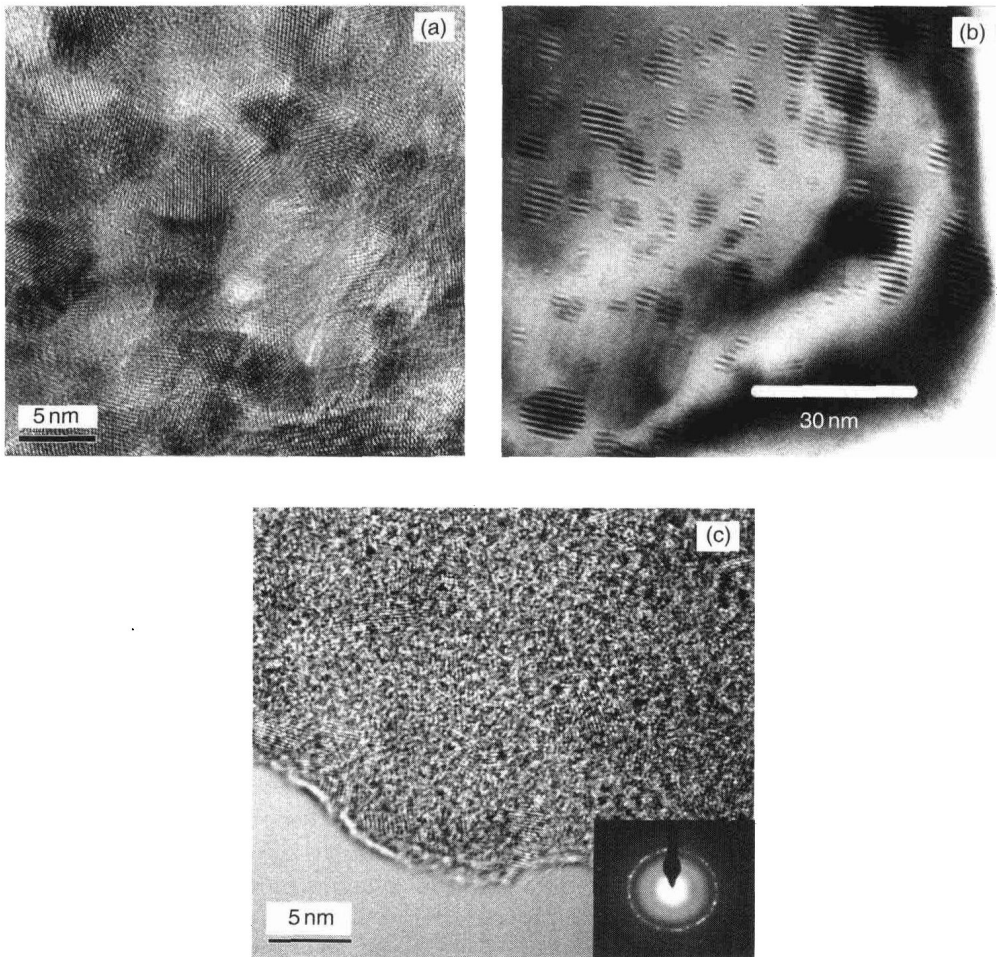


FIGURE 1.2 Bulk nanocrystalline materials synthesized by severe plastic deformation treatments. (a) Nanocrystalline Ni with an average grain size of 10 nm diameter synthesized by repeated cold-rolling. (b) Immiscible Al-Pb nanocomposite obtained by ball milling. (c) Ni-Ti nanocomposite obtained by repeated cold-rolling. The average grain size amounts to only 3–4 nm. Yet, alloying or phase formation during plastic deformation is not observed. The inset of (c) shows a selected area electron diffraction pattern of the Ni-Ti specimen. The broad intensity distribution near the centre indicates the presence either of an amorphous phase or of crystallites with grain sizes in the range of a few nanometres.

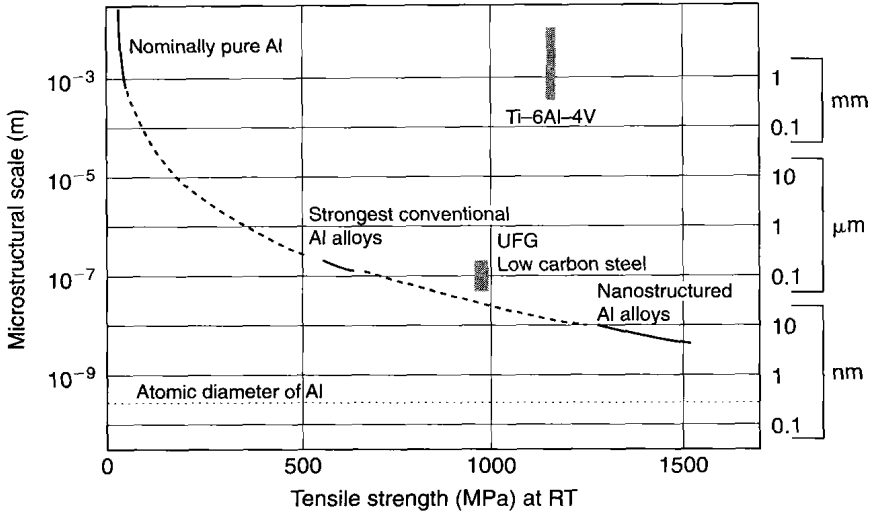


FIGURE 1.3 Relationship between the characteristic scale of the microstructure and the tensile strength at room temperature for Al-based alloys. Strength values for a Ti alloy and for an ultrafine grained (UFG) steel are shown for comparison. The results indicate the enormous benefits that can be entailed with nanostructuring. They also indicate the importance of retaining the size of the microstructure on the nanoscale.

to be straightforward, although nanocomposites of two immiscible components [15] or of two components that require large activation energies for mixing [16] have been obtained, as indicated in Figure 1.2b,c.

An alternative non-equilibrium synthesis route utilizes an initial rapid quenching step for synthesizing a vitreous precursor structure that forms parent phase and matrix for creating *in-situ* nanocomposites within a bulk material, which avoids issues related to contamination and powder compaction. For so-called marginal glass formers – a class of alloys based on Al, Mg or Fe that show the formation of extremely large number densities of primary-phase nanocrystals [17,18] – the unusually high nanocrystal number densities offer improved performance in magnetic and structural applications and exceptional property combinations. Fe-based alloys that transform via a similar mechanism are already applied as nanostructured soft or hard material depending on the specific alloy chemistry, with extremely low or high coercivity values at high saturation magnetization [19,20]. Al-based systems show a combination of high tensile strength of up to 1500MPa, a high hardness and a low mass density of about 3g/cm³ as long as the microstructure scale is of the order of 10nm or below (Figure 1.3, after [21]).

In addition, the composite nanostructure is self-stabilizing due to overlapping diffusion fields surrounding the nanocrystals [22,23]. Thus, the key strategy in enhancing the nanocrystal number density, and thus to improve both property performance *and* microstructure stability, is to promote the nucleation density of nanocrystals while minimizing the change of the amorphous matrix phase. One new opportunity for enhancing the number density of nanocrystals is presented

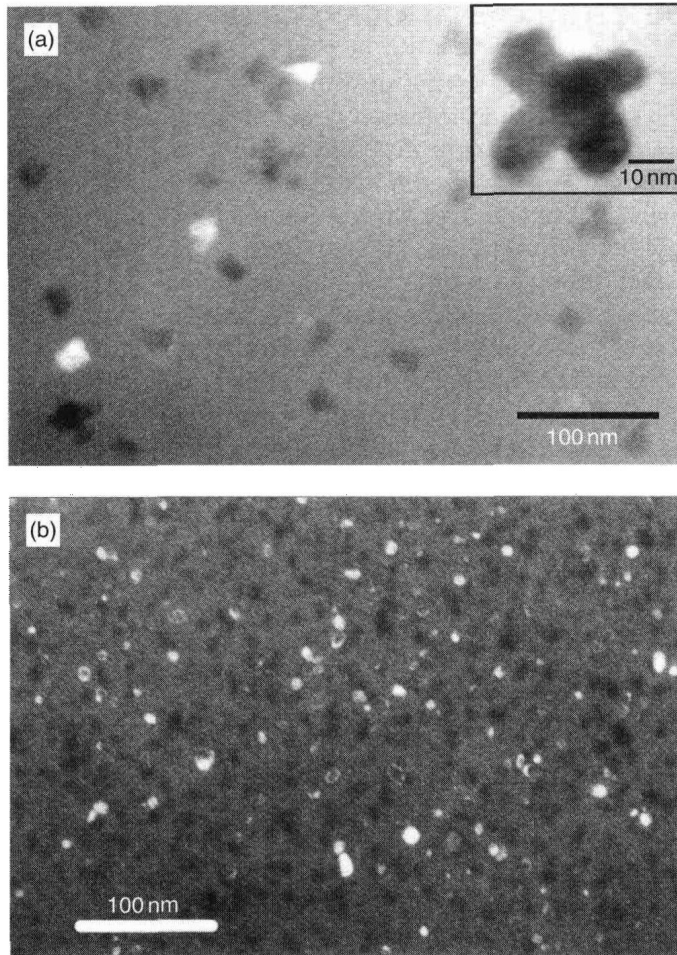


FIGURE 1.4 $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ *in-situ* composites consisting of almost pure fcc-Al nanocrystals embedded in a residual amorphous matrix. Nanocrystallization can be induced by thermal annealing (a) or with a much higher number density by plastic deformation (b). The inset of (a) shows a dendritic nanocrystal at higher magnification.

by severe plastic deformation of rapidly quenched marginally glass-forming alloys [24,25]. In addition to nanostructure formation, the deformation treatment serves as a consolidation step, which is important for producing bulk shapes. Figure 1.4 shows representative examples of partially nanocrystallized $\text{Al}_{88}\text{Y}_7\text{Fe}_5$ samples after (a) thermally induced and (b) deformation-induced nanocrystallization. The comparison indicates clearly the enhanced nanocrystal number density that can be obtained by combining different non-equilibrium processing pathways sequentially. These initial results together with results from combining different plastic deformation treatments indicate an entire range of advanced processing routes for obtaining bulk nanostructured materials or bulk nanocomposites that yet waits to be explored.

4. MICROSTRUCTURE OF NANOCRYSTALLINE MATERIALS

Nanocrystalline materials are single- or multiphase polycrystals with typical grain diameter significantly less than 100 nm. Owing to decreasing dimensions, the fraction of surface atoms located at grain boundaries or interfaces increases for nanocrystalline materials. A simple geometrical estimation, where the grains are assumed as spheres or cubes, yields for the volume fraction of the interfaces the following values: 50% for 5 nm grains, 30% for 10 nm grains and about 3% for 100 nm grains [26]. In fact, many properties of nanocrystalline samples (as for instance strength/hardness ductility, elastic moduli, diffusivity, specific heat, thermal expansion coefficient or soft magnetic properties) are found to be fundamentally different compared with their conventional coarse-grained counterparts. In order to predict these unique properties, it is essential to understand how the structures vary with decreasing crystallite sizes, since for all these new superior properties the grain size is the dominant structural parameter governing a material's properties. Therefore, microstructural investigations are essential to elucidate the underlying mechanisms.

An appropriate way to investigate the microstructures of nanocrystalline materials is to image them in a transmission electron microscope (TEM). In the following, the advantages and disadvantages of TEM as an appropriate tool for the characterization of nanocrystalline materials are described.

4.1 Transmission Electron Microscopy (TEM) – Conventional TEM

Conventional TEM is based on amplitude or scattering contrast owing to the fact that the electron beam is scattered in crystalline material. Two modes are usually used for imaging: bright-field (BF) where deflected electrons are blocked away from the optical axis of the microscope by placing the objective aperture to allow the unscattered electrons only to pass through, and dark-field (DF) using diffracted electrons to form the image. Both imaging modes are illustrated by Figures 1.5 and 1.6.

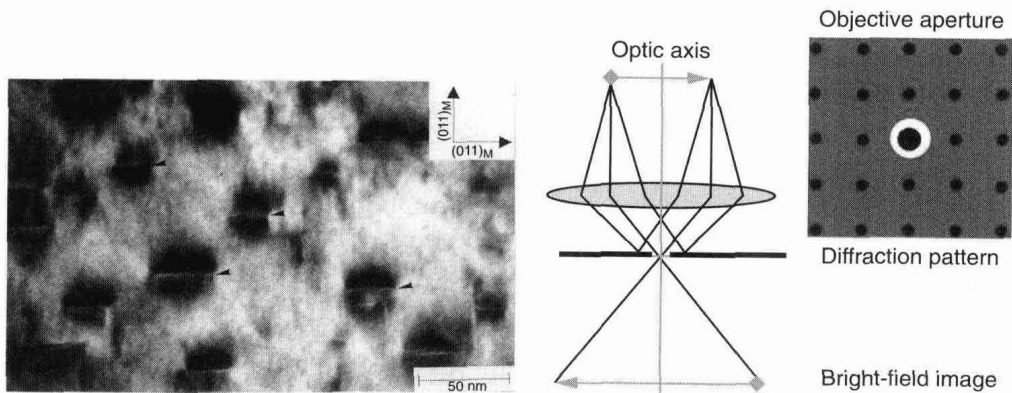


FIGURE 1.5 Left: bright-field image displaying coffee bean contrast due to misfit strains around plate-like precipitates in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ (taken from reference [27]). Right: schematic sketch showing the principle of bright-field imaging.

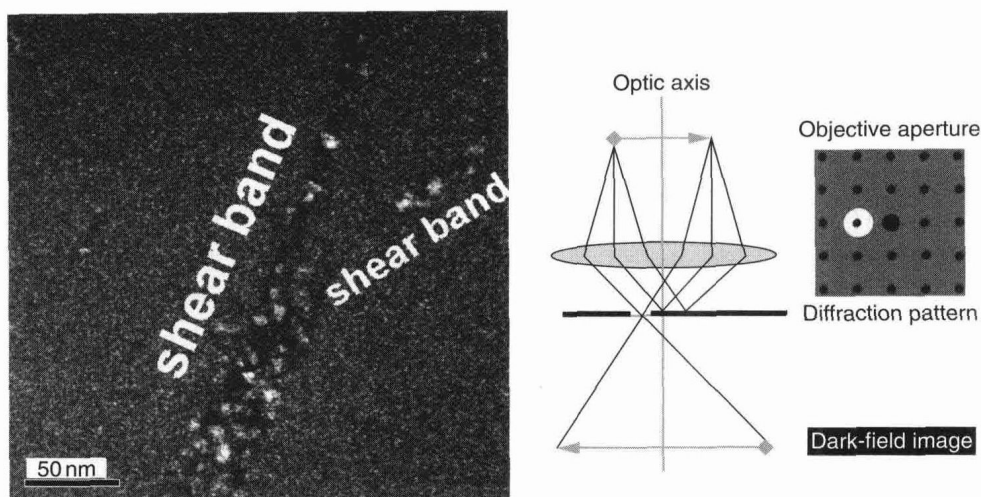


FIGURE 1.6 Left: dark-field image displaying shear bands with nanocrystals (taken from reference [28]). Right: schematic sketch showing the principle of dark-field imaging.

In particular, hollow-cone DF imaging is a rather useful technique for nanocrystalline materials where the tilted beam is rotating over the whole diffraction ring in order to image all grains meeting the Bragg condition. Furthermore, diffraction patterns, which yield information from the k -space, can be obtained simultaneously by selected area electron diffraction (SAED). These techniques are sufficient with respect to panoramic views and statistical analysis of grain size distribution. Due to the small grain sizes of nanocrystalline materials, it is difficult to image dislocations or other defects by conventional TEM since the dislocation contrast is based on its strain field which overlaps with the usual strain contrast of the nanometre-sized grains. Accordingly, and due to the fact that interfaces are dominating the material's behaviour, there is a need for investigations with better resolution to elucidate the operating processes in more detail.

4.2 Transmission Electron Microscopy (TEM) – High-Resolution TEM

High-resolution TEM is a technique developed since the 1970s to image the atomic structure of materials. A decade ago, the technique was restricted to a few research laboratories with highly specialized equipment and staff. Due to the continued development of TEMs, especially the introduction of digital controllers and the improvement of microscope stability, state-of-the-art microscopes with a resolution of 0.2 nm and below are commercially available. High-resolution TEM uses the phase contrast, which is based on the coherent interference of many electron beams, to show lattice fringes and atomic structures. Figure 1.7 shows the principle of high-resolution imaging.

The contrast arises from the difference in the phase of the electron waves scattered through a thin specimen. Phase contrast images are in most cases difficult to interpret because they are very sensitive to many factors such as thickness, orientation,

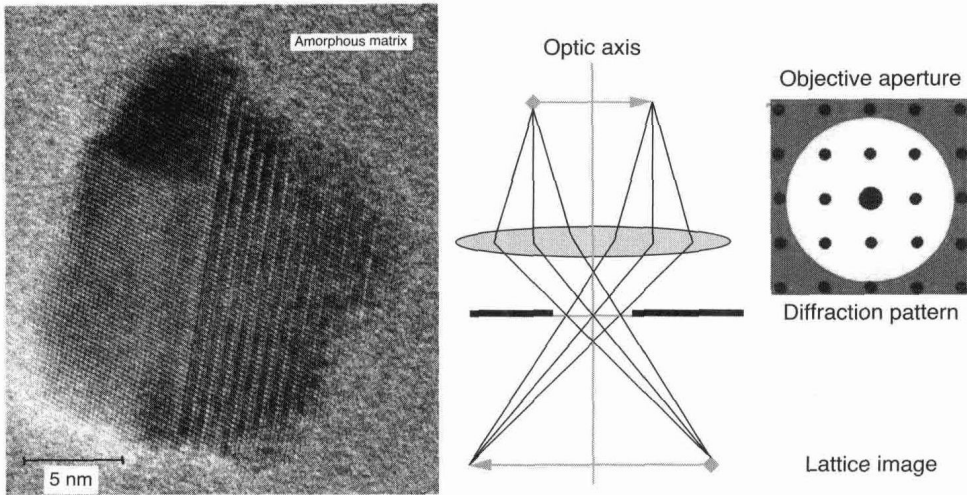


FIGURE 1.7 Left: experimental lattice image using many beams of a $[110]$ zone axis. A nanocrystal (Al dendrite) embedded in an amorphous matrix is imaged with atomic resolution. Note the defects (twins) appearing as stairs on the right side of the Al dendrite. Right: schematic sketch showing the principle of high-resolution imaging.

scattering factor of the specimen and focus and astigmatism of the objective lens. Hence, for the correct interpretation of high-resolution images, numerical simulations, matching the experimental images with computer simulated ones, are required taking the aberrations of the microscope as well as the actual specimen conditions into account. To overcome these difficulties, the following approaches are suggested:

1. imaging of simple well-known structures (for instance metals) having lattice spacings near the point resolution of the TEM using Scherzer focus conditions;
2. reconstruction of the exit wave from a through-focus series (e.g. 20 images) with different defocus values when a microscope equipped with a field-emission gun is used;
3. using an aberration-corrected TEM since the spherical aberration of the objective lens leads to a delocalization of the information. The compensation of the spherical aberration improves the image quality and enhances the reliability for determining the atomic positions in high-resolution TEM [29,30].

In the following, conventional and high-resolution TEM are applied to practical problems in nanocrystalline materials in order to demonstrate the relevance for materials characterization.

5. PLASTICITY IN NANOCRYSTALLINE MATERIALS

The mechanisms of deformation in nanocrystalline materials differ from those of conventional, coarse-grained materials. Molecular dynamic (MD) simulations have

delivered new insight into structure and deformation processes in nanocrystalline materials [31–34]. A transition in the mechanical behaviour from dislocation-based deformation mechanisms to grain boundary (GB)-mediated ones [35], which manifests in change of slope or even a change of the sign of the slope of the Hall–Petch relationship [36], has been found for decreasing grain sizes. A recent review on the results of MD simulations of nanocrystalline materials is given by Wolf et al. [37]. Observations of an ‘inverse Hall–Petch’ behaviour were explained in terms of diffusion creep by fast transport along the numerous disordered grain boundaries [38–40]. For lower strain rates, a mechanism based on grain-boundary sliding and on coplanar alignment of grain boundaries to form so-called ‘mesoscopic glide planes’ has been suggested by Hahn and Padmanabhan [41]; this provides explanations for the occurrence of the ‘inverse Hall–Petch’ behaviour and for a moderate work hardening, respectively. Markmann et al. [42] have shown that, similar to what is known for conventional materials, the dominant deformation mechanism in nanocrystalline materials is a function of the strain rate. Diffusion creep is dominant in the limit of very low strain rate and, in nanocrystalline materials, it becomes noticeable at much lower temperatures than in coarse-grained materials. The following chapter by Padmanabhan elucidates this important point in greater detail. At higher strain rates, partial dislocations must be active as evidenced by the creation of stacking faults. In addition, the absence of a deformation texture indicates that grain-boundary sliding and grain rotation take place along with the dislocation-based plasticity. The experimental findings at large strain rate in nanocrystalline materials agree with predictions from MD simulations, where even higher strain rates are imposed: dislocation activity, i.e. the emission of partial dislocations from grain boundaries, as well as grain-boundary sliding were predicted based on these studies [34,43–49].

Defect structures of plastically deformed nanocrystalline Pd investigated by high-resolution transmission electron microscopy (HRTEM) are presented in this section. Material with an average grain size of about 15 nm was prepared by inert gas condensation and this was plastically deformed by cold-rolling up to a true strain of 0.32 at a strain rate of about 0.3 s^{-1} . Abundant deformation twinning on [111] planes was found and Shockley partial dislocations were identified [50]. Remarkably, in each grain, twinning occurs only on a single set of parallel planes, as shown in Figure 1.8.

This implies that only one out of the five independent slip systems required for the general deformation of a grain is active, a finding which suggests that rigid-body grain rotation and grain boundary sliding must be active along with twinning.

5.1 Transmission Electron Microscopy (TEM) – *in-situ* TEM

In-situ tensile tests performed in a transmission electron microscope (TEM) in combination with high-resolution TEM are feasible. Furthermore, this method is appropriate to elucidate the deformation processes in nanocrystalline materials directly. Until now, only hints of the mechanisms at play have been obtained through changes in contrast, which indicate that dislocations [51–53] as well as