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## *Synthesis, Processing, and Application of Nanostructures*

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### **1.1 Introduction to Nanotechnology**

During the past years scientists have achieved significant successes in nano science and technology. Nanotechnology is a branch of sciences that deals with fine structures and materials with very small dimensions—less than 100 nm. The measurement unit of “nano” has been extracted from the *nano-* prefix, which is a Greek word meaning “extremely fine.” One nano ( $10^{-9}$  m) is the length equivalent to 5 silicon atoms or 10 hydrogen atoms aligned side by side. To introduce a perspective note the following examples: A hydrogen atom is about 0.1 nm; a virus is about 100 nm; the diameter of a red blood cell is 7000 nm; and the diameter of a human hair is 10000 nm.<sup>1-3</sup>

Nanotechnology is a field of applied sciences focused on design, production, detection, and employing the nanosize materials, pieces, and equipment. Advances in nanotechnology lead to improvement of tools and equipment as well as their application in human life. *Nanoscience* is the study of the phenomena emerged by atomic or molecular materials with the size of several nanometers to less than 100 nm. In chemistry this size involves a range of colloids, micelles, polymer molecules, and structures such as very large molecules or dense accumulation of the molecules. In the physics of electrical engineering, nanoscience is strongly related to quantum behavior or electron behavior in structures with nano sizes. In biology and biochemistry, also, interesting cellular components and molecular structures such as DNA, RNA, and intercellular components are considered as nanostructures.<sup>4-7</sup>

*Nanotechnology* is applying the sciences in control of the phenomena with molecular dimensions. In this range, materials properties are significantly different than those of its mass state. These differences are related to design, properties’ detection analysis, structures application, as well as tools and

systems for nano shape and size control. In other words, nanoscience and technology is a study field including

1. Advances in the methods for producing the materials and surface analysis equipment for producing the materials and structures
2. Understanding the changes in physical and chemical properties in order to materials fining
3. Using these properties for the development of new highly used materials in the equipment

Alive cells are the best examples of machines working at the nano level. The study field of the nanotechnology major is interconnected to physics, chemistry, materials science, microbiology, biochemistry, and molecular biology. Integration of nanotechnology, biotechnology, and medical engineering is demonstrated in the use of nano-size structures for disease prognosis, defining the gene sequence, and medicine transport.<sup>8,9</sup>

The main applications of nanotechnology are

- Medicine: drug delivery and tissue engineering
- Chemistry and environmental studies: catalysts, filtration
- Energy: decrease in energy uses, increasing of the efficiency of the products yielding batteries recycling energy, use of environmentally friendly energy systems
- Information and communications: new semiconductors, new electrical pieces, display monitors with low energy use, quantum computers
- Consumer goods: food production, safety, and packaging, self-cleaner system, fibers and textiles, optical equipment, sport facilities

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## 1.2 History of Nanotechnology

Use of nanotechnology by humans, contrary to the dominant belief, has a long history. There is evidence implying the nanostructured nature of the blue color used by the Mayans. Since then, Romans used these materials for fabrication of cups with live colors; they applied gold for dyeing these cups. One of these cups was the Lycurgus cup that was made in 4 BC. This cup involves gold and silver particles and reveals various colors once exposed to light. This method was also used in the Middle Ages for making church windows.<sup>10,11</sup>

Among various scientific fields, biology was the first that entered this realm. The basic mechanism of biological machines was nanodimensional reactions. Mosquitoes, ants, and flies can be named as examples of natural nanomachines. However, the scientific account of nanotechnology varies

from that explained above. Early investigations on nanoparticles stem from Faraday. In 1811 working on the red colloid of Ag, he found that the red colloid color depends on metallic particles sizes, and the gold and silver found 2000 years ago were actually nanoparticles.

The use of nanostructured catalysts began 70 years ago. In the early 1940s the evaporated and deposited nanoparticles of silicon were fabricated and used as an alternative for tiny particles of black carbon for rubber reinforcement in the United States and Germany. These products have a wide range of applications, from dry milk used with coffee to car tires and optical fibers. In the 1960s and 1970s, metallic nanopowders were made for information storing on film. In 1976, nanocrystals were invented by some researchers using the complete gas evaporation method.

The first breakthrough in the history of nanotechnology originates from the speech of Richard Feynman in a conference in 1959. In this conference, he discussed materials manipulation in nano dimensions in his paper entitled "There Are Plenty of Rooms in the Bottom." Today this paper is used as part of a nanotechnology committee's regulation. He extracted his notion from biological mechanisms, which are very tiny on one hand, and very active on the other. He stated that "There is nothing that I can see in the physical laws that says the computer elements cannot be made enormously smaller than they are now."<sup>16</sup>

The first impetus for materials and structures' fining arose from the electronics industry. Their goal was to industrialize their equipment to produce tinier electronic tools on silicon chips with sizes of 40 to 70 nm. Nowadays, nanoengineering is rapidly developing and introduces mechanical, catalyzer, electrical, magnetic, optical, and electronic potentials.<sup>12-17</sup>

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### 1.3 What Is a Nanomaterial?

A nanomaterial belongs to a group of substances that have exterior dimensions or constituent phases (at least in one dimension) less than 100 nm; however, most of their unique properties occur in dimensions less than 50 nm. With respect to this definition, nanomaterials are divided into the following groups:<sup>18</sup>

1. Atomic clusters or nanoparticles
2. Nanolayers
3. Nanotubes and nanorods
4. Nanocrystals
5. Nanocomposites

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\* "There's Plenty of Room at the Bottom, An Invitation to Enter a New Field of Physics," Richard P. Feynman, transcript of the classic talk that Richard Feynman gave on December 29th 1959 at the annual meeting of the American Physical Society.

Dimensionality classification of nanostructures ( $L < 100 - 500 \text{ nm}$ )



Designation: dimensionality of NS  $\rightarrow$   $kDlmn..$   $\leftarrow$  Dimensionality of elementary units

$$k \geq l, m, n \quad \{k, l, m, n\} = \{0, 1, 2, 3\}$$






Elementary building units:

1. 0D  Molecules, clusters, fullerenes, rings, metcarbs, thoroids, domens, particles, powders, grains, schwartzons	2. 1D  nanotubes, fibers, filaments, whiskers, spirals, belts, springs, horns, columns, needles, pillars, helicoids, wires, ribbons	3. 2D  layers
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


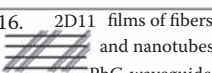


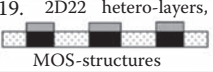

0D-nanostructures:

4. 0D0  uniform particles arrays	5. 0D00  heterogeneous particles arrays, "core-shell" dendrimers, onions
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














1D-nanostructures:

6. 1D0  molecular chains, polymers	7. 1D00  heteropolymers	8. 1D1  bundles, ropes, cables, corals	9. 1D11  heterochains, heterocables, saws, hair, heterobundles, junctions, combs, bows	10. 1D10  beads, pea-pods, fullereno-fibers
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2D-nanostructures:

11. 2D0  fullerene films	12. 2D1  nanostraw, PhC, fibers films	13. 2D2  tiling, mosaic, layered films	14. 2D00  heterofilms of heteroparticles, fullereno-powders	15. 2D10  films of pods, fullereno-fibers	16. 2D11  films of fibers and nanotubes, PhC-waveguides
17. 2D20  fullereno-plate films	18. 2D21  bridges, fiber-layer films	19. 2D22  hetero-layers, MOS-structures	20. 2D210  fullerene-fiber-layer films		

3D-nanostructures:

21. 3D0  Fullerites, clathrates, powder skeletons, fog	22. 3D1  skeletons of fibers, nanotubes	23. 3D2  layer skeletons, buildings, honeycombs, foams	24. 3D00  sols, colloids, smogs, heteroparticles composites
25. 3D10  skeletons of fibers-powders	26. 3D11  skeletons of heterofibers nanotubes	27. 3D20  intercalates, skeletons of layers and powders	28. 3D21  Cross-bar-layers, layer-fiber skeletons
29. 3D22  heterolayers	30. 3D30  opals, dispersions, particles, pores, fullerenes in matrix	31. 3D31  membranes, PhC, fiber compositers, waveguides	32. 3D32  friction pairs, contacts, interfaces, cavities, grain boundaries
33. 3D210  composites of layers, fibers and particles in matrix	34. 3D310  membranes + impurities, powder-fiber composites	35. 3D320  powder-layers composites	36. 3D321  layers-fibers-composites in matrix, VCSEL

Notices:

1. Interfaces between building units not regarded as additional 2D-NSs
2. Inverse NSs with cavity building units not regarded as separate ones
3. The classification may be extended with account of fourfold combinations

FIGURE 1.1

Dimensionality classification of nanostructures. (Reprinted from Pokropivny, V. V., and Skorokhod, V. V., Classification of nanostructures by dimensionality and concept of surface forms engineering in nanomaterial science, *Materials Science and Engineering C* 27 (5-8 SPEC. ISS.), 990-993, Copyright 2007, with permission from Elsevier.)

Categorization of nanomaterials by their nanometric dimensions is shown in Figure 1.1. Atomic clusters are known as nondimensional nanomaterials, while bulk nanocrystals and nanocomposites are called three-dimensional (3D) nanomaterials. Within the nanocrystals, the grains (crystallites) are co-axis and their size is in the nano range. The structure of nanocomposites is made of two or more phases, where one of the phases is presented in zero, one-, two-, or three-dimensional states. Nanocrystals and nanocomposites are generally known as nanostructured materials.

All nanomaterials share this feature that a significant portion of their atoms is located in interfaces such as free surfaces, grains boundaries, and interphase faces. Most nanomaterial properties come from this fact. There are several physical, chemical, and mechanical methods invented for production of nanomaterials. Nanomaterial is made of structural units that are laid side by side. In some methods for production of nanomaterials, first the structural units are made from atoms or molecules and then combining these structural units the given nanostructure is achieved. These methods are known as “bottom-up.” However, there are some other methods known as “top-down,” in which the large structural units of a material are gradually divided into smaller parts until we reach nano dimensions.<sup>19–22</sup>

The first point in production of nanomaterials can be started from a gas, liquid (or melted), and even solid phase. Table 1.1 shows some of the main processes in each group. Figure 1.2 presents an example for a method that has been used in order to fabricate reduced graphene oxide.

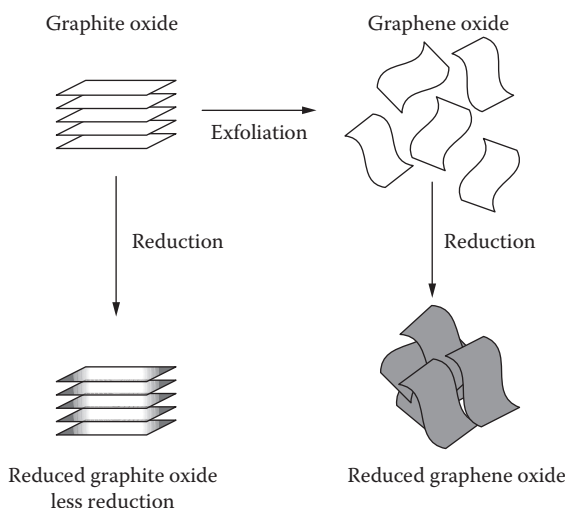
In each of these processes, it is possible to change the dimension, morphology, and texture of nanostructured material by controlling the involved parameters and achieving favorable characteristics. Nevertheless, it must be noted that in processes that involve a change of phase (e.g., changing the vapor phase into a solid or changing the liquid phase into a solid), creating the structure requires an increase in nucleating rate and a decrease of growth rate during the production process. Each of these processes involves advantages as well as disadvantages. Choosing a production method depends on multiple factors such as characteristics of the final structure (grain size, phase morphology, etc.) and purity of the final product.

Processes for producing nanomaterials in solid phases involve low production costs. The operation is performed in low temperatures (generally

**TABLE 1.1**

Classification of Nanomaterials Production Processes

Production from vapor phase	Physical and chemical deposition of the vapor
Production from liquid (or melted) phase	Sol-gel, electrochemical deposition, sudden freezing
Production from solid phase	Mechanical alloying, severe plastic deformation, mechanochemical process, crystallization of the amorphous phase

**FIGURE 1.2**

Representative scheme of a degree of reduction of graphite/graphene oxides. (Reprinted from Park, S., An, J., Potts, J. R., Velamakanni, A., Murali, S., and Ruoff, R. S., Hydrazine-reduction of graphite- and graphene oxide, *Carbon* 49 (9), 3019–3023, Copyright 2011, with permission from Elsevier.)

in room temperature). In addition, these processes can be applied for a variety of materials including pure metals, metallic alloys, intermetallic components, ceramics, and polymers. Moreover, it is possible to easily control production conditions to create ideal fine structures. This feature has caused wide use of solid-state production processes for creating 3D nanomaterials, particularly once the high rate of purity is not our objective. In the following sections of this chapter, the techniques applied for production of nanostructured materials will be discussed briefly.<sup>24–27</sup>

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## 1.4 Properties of Nanostructured Materials

In general, a material's properties depend on atom arrangement and atom alignment in its structure. For instance, steel's properties differ from those of copper, because their atoms are different. Furthermore, properties of face-centered cubic (FCC) crystalline steel are different from body-centered cubic (BCC) crystalline steel because their atom arrangement in the crystal structure is not the same.

One distinct property of nanomaterials is their different behavior in macro- or microstructural states. All materials, irrespective of their composition, reveal new features (such as improvement of their optical features,

decrease of melt point, increase of tensional strength, enhancement in catalytic properties, increase of semiconductors' band gap, increase of magnetic properties, and decrease of electrical resistance) once their size drops lower than 100 nm. As well as composition and structure of a substance, its dimension, once it goes below a specific limit, is another critical factor that has an effect on its properties. The following items can be mentioned as reasons for these behaviors of the materials:

1. Material size approaching molecular and atomic ranges
2. The high surface-to-volume ratio in nanomaterials; this means that the atom's distance from the surface is very short, so the interatomic forces and chemical bounds are of great importance and have a determining role
3. Increase in the volume of grains' boundaries with decrease of grains' sizes which, in turn, affects the material's physical features

It must be noted that with an increase in the surface ratio, the free energy of the material rises; this causes changes in the material's features. This can be explored in another way: According to the above-mentioned points, materials' characteristics also depend on their atoms arrangement, so as the grains sections increase, the larger number of atoms would be present in its exterior surface, implying that the material's atoms are in an environment different than that of atoms in conventional materials; hence, atoms placed at the surface experience a different environment than that of interior atoms.<sup>28-30</sup>

Materials properties considerably rely on their internal structures' dimensions. As the size of grains or constituent phases of a material decreases up to the nano range, common mechanisms of the mechanical and physical properties cannot be considered, and the material's properties dramatically change. For instance, pure microcrystalline metals indicate a low yield strength, which results from ease of dislocation movements and development across their grains. However, once grain size of pure metal drops to the nanometric range, the dislocations mechanism would not be active, and yield strength of the material will be significantly enhanced.

Properties of nanostructured materials depend on three main factors:

- Size of constituent phases or grains of the material
- Structure or nature of the existing interfaces such as grain contacts and interphase faces
- Chemical of the substance

In some cases it is possible that just one of the above-mentioned factors plays a main role in defining properties of the nanostructured material.

In different control methods, it may be possible to partially control these three factors and achieve the objective properties through control of process parameters. But the efficacy of controlling all these three factors is not equal in all methods.

One of the most important characteristics of nanostructured materials is their having an extensive interface surface with each other.<sup>31–36</sup> So, a considerable ratio of their atoms is located in their interfaces. For example, once we have a nanocrystalline material with spherical or cubic grains with a diameter of  $d$ , the surface-to-volume ratio will be  $6/d$  taking the grain boundary's thickness ( $\delta$ ) into account and regarding this fact that each grain boundary is shared with two adjacent grains, the ratio of atoms located in grain boundaries ( $X_b$ ) is defined by the following equation:

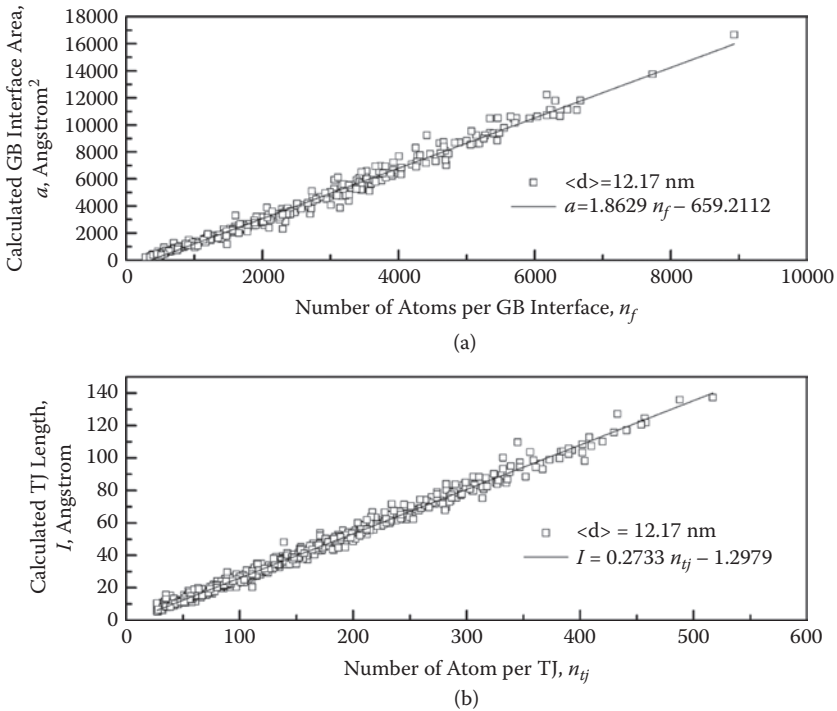
$$X_b = 3\delta/d \times 100 \quad (1.1)$$

Usually as the grain size drops, the number of atoms in grain boundaries greatly increases (e.g., when the grain size is 5 nm the atom number in the grain boundary of 0.5 nm will be 50%). If the grain boundary thickness is 1 nm, 80% of the atoms will be located in grain boundaries. Thus, it is predicted that in this condition the nanocrystalline material's properties is strongly influenced by grain boundaries' properties. The relation between the number of atoms per grain boundary (GB) interface and the calculated grain boundary interface area is calculated in Figure 1.3.

Although several studies have been performed to identify grain boundaries in nanocrystalline materials, it is not clear that weather atoms arrangement in grain boundaries of nanocrystalline and microcrystalline materials is the same, and weather structure and nature of grain sizes in nanocrystalline materials are influenced by their production technique. In any event, the average distance between atoms in grain boundaries is the maximum, and the number of closest neighbors for each atom is the minimum. In addition, interatomic bonds in grain boundaries are the weakest. In addition to an extensive interface surface, the presence of voids created by production steps and crystalline defects such as atomic vacancies, or residual dislocations, has a significant effect on the properties of nanostructured materials. Therefore, it is expected that nanostructured materials properties, even in grain size and chemical composition, be varied according to their production method.<sup>38–43</sup>

As previously mentioned, there is an extensive interface surface in nanostructured materials, where a considerable ratio of atoms can be accommodated. Such a structure results in different and superior chemical, physical, and mechanical properties of nanostructured materials compared with traditional substances (microcrystals). There is also a possibility to change different characteristics in a definite range by controlling the grain size and phases. Some of these changes are shown in Figure 1.4.




**FIGURE 1.3**

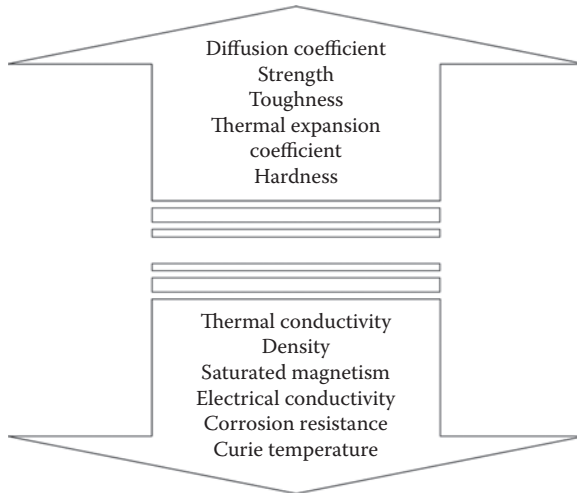
(a) The linear relation between the number of atoms per grain boundary (GB) interface,  $n_f$ , and the calculated GB interface area; (b) the linear relation between the number of atoms per triple junction (TJ),  $n_{ij}$ , and the calculated TJ length. The number of grains in the nanocrystalline Cu sample is 50, and the mean grain size is 12.17 nm. (Reprinted from Li, M., and Xu, T., Topological and atomic scale characterization of grain boundary networks in polycrystalline and nanocrystalline materials, *Progress in Materials Science* 56 (6), 864–899, Copyright 2011, with permission from Elsevier.)

## 1.4.1 Physical Properties

### 1.4.1.1 Diffusion Coefficient

For their wider atomic arrangement, grain boundaries and interphase faces are considered as quicker diffusion paths in polycrystalline materials, as activation energy of atoms' diffusion through grains boundary is about half of their activation energy for diffusion across the grains. The difference between the diffusion rate in a grain's boundary and the diffusion rate across the grains themselves is of a great importance in low temperatures.<sup>44–56</sup> Diffusion coefficient and temperature are correlated by the following exponential Arrhenius function:

$$D = D_0 \exp \frac{-Q}{RT} \quad (1.2)$$

**FIGURE 1.4**

Usual mechanical and physical trends of changes for nanostructured materials.

where  $D$  is the diffusion coefficient,  $D_0$  is the constant coefficient,  $Q$  is the diffusion activation energy,  $T$  is the temperature (K), and  $R$  is the universal gas constant. Table 1.2 presents grain boundary and lattice diffusion coefficients for self-diffusion of Au at two different temperatures.

In any case, in microcrystalline materials, the grain boundary share in whole diffusion is negligible, but for nanocrystalline materials, where there is an extensive grain boundary, it is predicted that the diffusion rate would be considerably high, in comparison with microcrystalline materials. Table 1.3 shows diffusion coefficients of silver atoms in copper at three different temperatures, which reveals that the diffusion coefficient for a nanocrystalline sample is higher than that of grain boundaries.

An increase in diffusion of nanostructures is also observed in some other metals. Here, it must be noted that the diffusion coefficient in a nanocrystalline sample ( $D_n$ ) is even more than that of grain boundary ( $D_b$ ) diffusion, suggesting that the structure of the grain boundary for nanocrystals might

**TABLE 1.2**

Diffusion Coefficient across the Grain Boundary ( $D_b$ ) and Lattice ( $D_L$ ) for Self-Diffusion of Au

Material	Temperature	$\alpha^{-5/3}t^{-1/2} \times 10^{-9}$	$D_L$ (cm <sup>2</sup> /sec)	$\delta D_b$ (cm <sup>3</sup> /sec)
	(°C ± 0.2°C)			
(A) Bulk	444.1	1.23	$1.85 \times 10^{-14}$	$2.11 \times 10^{-16}$
	367.2	1.37	$5.54 \times 10^{-16}$	$4.19 \times 10^{-17}$
(B) Films (Au-Mo-SiO <sub>2</sub> )	177.0	0.58	$5.41 \times 10^{-22}$	$1.78 \times 10^{-20}$
	117.0	0.33	$4.17 \times 10^{-25}$	$2.81 \times 10^{-22}$

**TABLE 1.3**

Diffusion Coefficients of Silver Atoms in Nanocrystalline Copper, in Copper Grain Boundaries, in the Lattice of Copper, and on Copper Surfaces

$T$ (°K)	Nanocrystalline $D_i$ (m <sup>2</sup> /s)	Grain boundaries <sup>(a)</sup> $D_b$ (m <sup>2</sup> /s)	Lattice $D_L$ (m <sup>2</sup> /s)	Surface <sup>(b)</sup> $D_s$ (m <sup>2</sup> /s)
373	$1.2 \times 10^{-17}$	$22.5 \times 10^{-20}$	$8.1 \times 10^{-33}$	$9 \times 10^{-14}$
353	$3.1 \times 10^{-18}$	$6.9 \times 10^{-21}$	$1.4 \times 10^{-34}$	$5.3 \times 10^{-14}$
303	$0.3 \times 10^{-18}$	$1.3 \times 10^{-22}$	$2.6 \times 10^{-38}$	$1 \times 10^{-14}$

<sup>a</sup> Assuming a grain boundary thickness of 1 nm.

<sup>b</sup> Silver diffusion on Cu (110) and (331) surfaces.

Source: Reprinted from Schumacher et al., Diffusion of silver in nanocrystalline copper between 303 and 373k, *Acta Metallurgica* 37(9), 2485–2488, Copyright 1989, with permission from Elsevier.

be wider in microcrystalline materials though an increase of the diffusion coefficient can originate from the presence of fine voids in nanocrystalline samples. An effective diffusion coefficient in a polycrystalline material can be obtained by the following equation:

$$D_{eff} = (1 - F)D_L + FD_b \quad (1.3)$$

where  $F$  is the grain boundary fraction. Once  $\delta$  is the grain boundary thickness and  $d$  is the grain size, one can say

$$F \approx \frac{2\delta}{d} \quad (1.4)$$

Assuming that the thickness of the grain boundary is 7 nm, Equation (1.3) shows that decreasing grain size from 100 to 50 nm caused the effective diffusion coefficient to increase from  $1 \times 10^{-18}$  (m<sup>2</sup>/sec) to  $5.7 \times 10^{-15}$  (m<sup>2</sup>/sec).

Equation (1.3) also shows that supposing that diffusions are mainly performed through grain boundaries, the following condition must be achieved:

$$FD_b \gg (1 - F)D \quad (1.5)$$

or

$$\frac{\delta}{d} D_b \gg 1 - \frac{\delta}{d} D_L \quad (1.6)$$

These conditions will be achieved once the grain size is very fine.

An increase of the diffusion rate in nanostructures is followed by acceleration of solid-state alloying and a considerable change in creep and

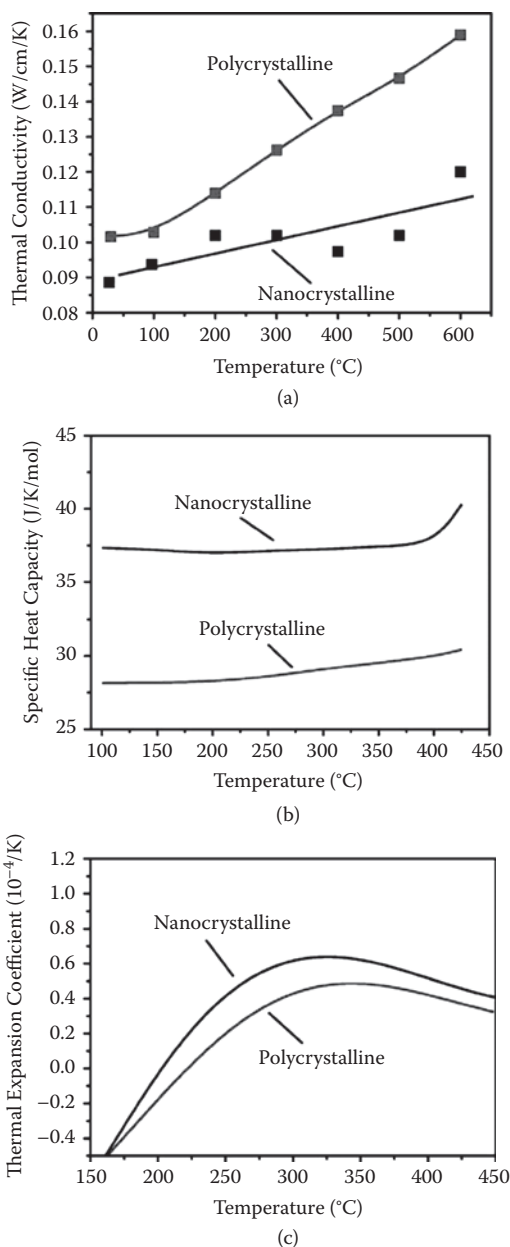
superplastic behavior of the material. This also causes acceleration of the sintering process during preparation of pieces from nanostructured powders. This means that the sintering process of the powder metallurgy pieces can be performed in much lower temperatures. For instance, it was reported that the required temperature for sintering titanium dioxide powder ( $\text{TiO}_2$ ) with grain sizes around 12 nm is about  $400^\circ\text{C}$  to  $600^\circ\text{C}$  lower than that of the same powder with grain size of 1.3  $\mu\text{m}$ .

#### 1.4.1.2 Thermal Expansion Coefficient

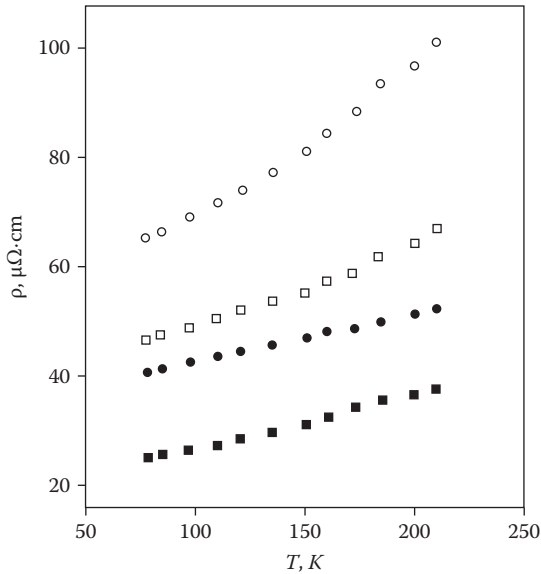
Metallic nanoparticles and semiconductors are of lower melt or phase transition temperature in contrast to their mass state. The lower melting temperature of the particles emerges once the particle size is less than 100 nm, which is due to a decrease of surface energy with grain size. A drop in phase transition temperature can be described with changes in surface energy to volume energy as a function of grain size.

It is supposed that the optimum diffusion in the grain boundaries of the nanomaterials is due to changes in their thermal features. In the metals, melt point and thermal conductivity decrease through use of nanotechnology (e.g., melt temperature of the nano-gold is  $27^\circ\text{C}$  less than that of conventional gold). Besides, the thermal expansion coefficient has been decreased in the nano-gold. Decrease in thermal conductivity of the nanostructured ceramics can develop their application as a thermal shield. Another application of these materials is in the coating blades of airplanes' turbines, which multiplies their life up to six times more than the common ones.<sup>46,59-69</sup>

Contradictory results were reported about the effect of grain size drop on the thermal coefficient of the materials. Basically, because a high fraction of atoms are located in grain boundaries, it is expected that the thermal expansion coefficient of nanostructures is a large figure. Some measurements on several metals and nanocrystalline alloys prove this prediction. For example, it was reported that the thermal expansion coefficient of copper with a grain size of 8 nm in the range of  $110^\circ\text{K}$  to  $293^\circ\text{K}$  is twice as much as that of a single crystal copper sample. On the other hand, some other results imply no change in the thermal expansion coefficient of nickel in the nanocrystalline state, in comparison with the microcrystalline state. In addition, some results have shown that the thermal expansion coefficient of nanocrystalline samples, which are made by consolidation of the initial powder, decreases with an increase of applied pressure. Based on these findings, one can conclude that there is basically no significant difference between the thermal expansion coefficient of common nanocrystalline and microcrystalline materials. An increase of the thermal expansion coefficient of some nanocrystalline materials, presented in some experiments, can be interpreted as a result of voids, fractures, and other structural defects in the final structure of the prepared samples. Figure 1.5 compares the thermal conductivity, the specific

**FIGURE 1.5**

(a) The thermal conductivity, (b) the specific heat capacity, and (c) the thermal expansion coefficient of the prepared ultrafine nanocrystalline Gd bulk as a function of the temperature, together with a comparison with those of the polycrystalline Gd bulk. (Reprinted from Lu, N., Song, X., and Zhang, J., *Microstructure and fundamental properties of nanostructured gadolinium (Gd)*, *Materials Letters* 63 (12), 1089–1092, Copyright 2009, with permission from Elsevier.)



**FIGURE 1.6**

Dependence of electrical resistivity on temperature for nanocrystalline Fe-Cu-Si-B alloys with grain sizes of (○) 30 nm, (□) 40 nm, (●) 50 nm, and (■) 90 nm. (Reprinted from Wang, Y. Z., Qiao, G. W., Liu, X. D., Ding, B. Z., and Hu, Z. Q., Electrical resistivity of nanocrystalline Fe-Cu-Si-B alloys obtained by crystallization of the amorphous alloy, *Materials Letters* 17 (3–4), 152–154, Copyright 1993, with permission from Elsevier.)

heat capacity, and the thermal expansion coefficient of ultrafine nanocrystalline Gd bulk as a function of the temperature with those of the polycrystalline bulk Gd.

### 1.4.1.3 Electrical Resistance

Figure 1.6 indicates changes of specific electrical resistance with temperature for some nanocrystalline alloys of Fe-Cu-Si-B with different grain sizes.

For nanocrystalline materials, like microcrystals, specific electrical resistance increases with temperature. However, once the grain size rises, this increase grows with higher rates. Also, at a constant temperature, specific electrical resistance considerably intensifies with grain size increase.

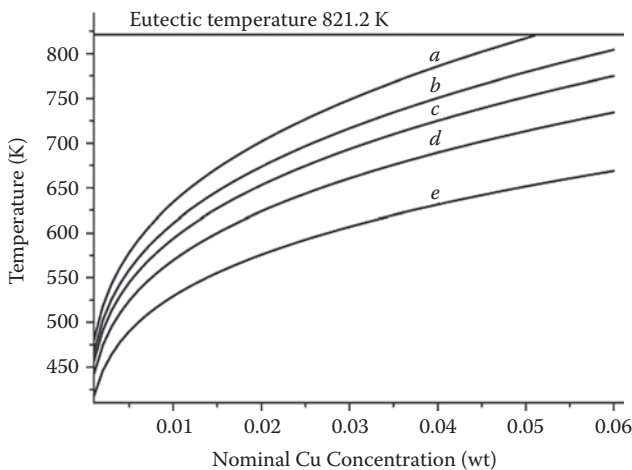
Due to entropies in atoms' arrangement in grains' boundary, electrons are scattered during passing from the boundaries; this, in turn leads to enlargement of specific electrical resistance of the material. It is obvious that as grain size decreases, or in other words area of grain boundaries increases, electron dispersion and consequently electrical resistance, increases. Then, by controlling the grain size, it is possible to change the specific electrical resistance.<sup>66,72–80</sup>

#### 1.4.1.4 Solubility of Alloy Elements

Solubility of elements in nanocrystalline materials is notably higher than common polycrystalline materials. Due to the presence of an expanded grain boundary in nanocrystalline materials and low concentration of atoms in grain boundaries, a large amount of alloy elements can be dissolved in nanocrystalline materials. For instance, solubility of mercury in polycrystalline copper is less than 1 atomic percent, while it is 17 atomic percent for mercury dissolved in nanocrystalline copper. This phenomenon even exists in alloy systems in which there is a solubility defect area (like alloy systems such as Ag-Fe, Ti-Mg, and Cu-Fe). For example, the solubility of Mg in Ti in the solid phase is less than 0.2 atomic percent, but decreasing the titanium grain size up to the nanometric range brings the number up to 30 times.<sup>81–87</sup> Thus, it is possible to produce new alloys with new properties via increasing solubility of alloy elements. Figure 1.7 indicates that lower temperatures are needed for nominal copper solubility in Al-Cu alloys with lower nanometric grain sizes.

#### 1.4.1.5 Magnetic Properties

Because the magnetic properties increase with the increase of the surface-to-volume ratio, magnetic nanomaterials demonstrate unusual behaviors, which is due to particle size and their charge transmission properties. Magnetic properties in nanostructured materials vary with those in a mass



**FIGURE 1.7**

The nominal copper solubility (solvus) in Al-Cu alloys with different grain sizes. Grain size (a)  $d = \infty$ , (b)  $d = 100$  nm, (c)  $d = 50$  nm, (d)  $d = 25$  nm, and (e)  $d = 10$  nm. (Reprinted from Meng, Q. P., Rong, Y. H., and Hsu, T. Y., Distribution of solute atoms in nanocrystalline materials, *Materials Science and Engineering A* 471 (1–2), 22–27, Copyright 2007, with permission from Elsevier.)

state of the materials, because an increase of surface energy leads to development of enough energy for spontaneous changes of the magnetic fields in polar directions, which changes the material into a paramagnetic state. As the behavior of these modified paramagnetic differs from that of prevalent paramagnetic, it is called supermagnetic. In other words, due to high levels of the energy paramagnetic properties of the mass, materials are removed in nanodimensions and the material turns into a supermagnetic state.

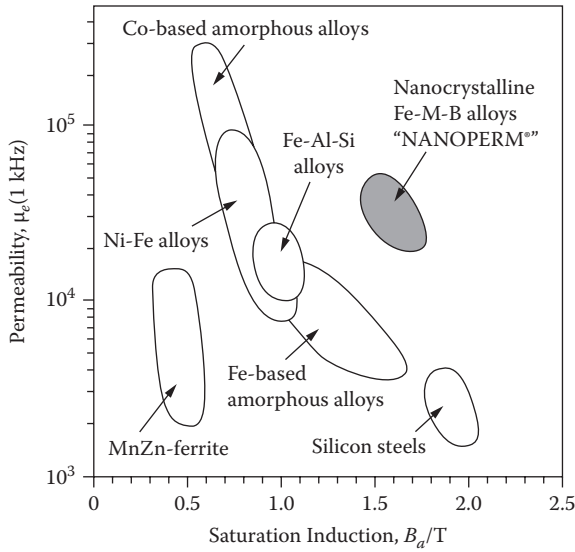
Materials' ferromagnetic properties are controlled by their interatomic distances, grain size, and constituent phases. For this reason, saturated magnetic properties ( $M_s$ ) and Curie temperature ( $T_C$ ) in nanocrystalline materials are considerably low compared with microcrystalline materials. For instance, magnetism of microcrystalline Fe is 220 emu/g, while this declines to 130 emu/g once Fe grains size goes down to 6 nm. Or it is reported that Curie temperature of nanocrystalline Gadolinium (Gd) with grain size of 10 nm is about 10°C less than that of microcrystalline Gd. These changes all come from decreasing the grain size to the nanometric range, as each grain can act like an independent unit. In addition, a considerable fraction of the atoms in nanocrystalline structures are located in the grain boundary, where average atomic distances are more than those in grains.

Alloys of nanostructural Fe, such as  $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$  (commercially known as Finement) and  $Fe_{91}Zr_7B_2$  (commercially known as Nanoperm) manifest an efficient complex of magnetic properties. These materials involve a low inhibition of 5 to 10 A/cm, high permeability of  $10^5$ , and a low energy waste, as well as magnetic properties of about zero (less than  $2 \times 10^{-6}$ ). Furthermore, due to a high electrical resistance, nanostructured materials display a low core waste of 200 KW/m<sup>3</sup>. These characteristics all together have made nanocrystalline Fe alloys among the best magnetic materials and an alternative for matrix amorphous alloys of cobalt. Figure 1.8 presents a comparison of magnetic properties of nanocrystalline magnetic Fe alloy (Nanoperm) and conventional soft magnetic materials.<sup>89-96</sup>

Creating nanostructures in permanent magnets such as  $Fe_{90}Nd_7B_3$  has significantly improved their magnetic properties. The magnetic properties of these alloys are induced from the  $Nd_2Fe_{14}B$  phase, which has hard magnetic properties. This phase with the Fe phase (ferrite), which involves soft magnetic properties, is present in the structure of Fe-Nd-B alloy. Once this biphasic structure is created in nanodimensions, the residual magnetism ( $M_r$ ) increases, and then  $M_r$  will be considerably larger than  $1/2 M_s$ .

Development of nanostructures causes improvement of the high magnetic resistance phenomenon. This feature is defined as dramatic reduction of electrical resistance due to applying a magnetic field. This reduction is about 1% to 2% for microcrystalline materials, while for nanocrystalline materials this has been reported to be 50% or even more. The creation of nanostructures in magnetic coolers improves their performance and output.





**FIGURE 1.8**

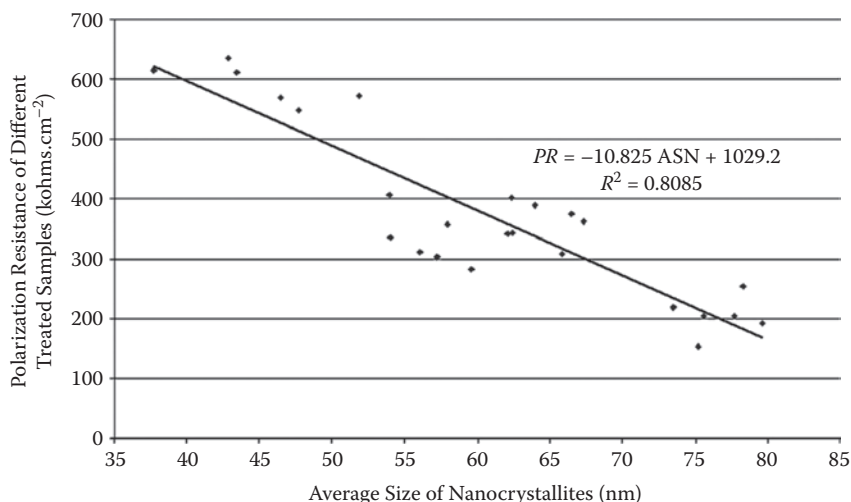
A comparison between magnetic properties of Nanoperm and conventional soft magnetic materials. (Reprinted from Makino, A., Inoue, A., and Masumoto, T., Nanocrystalline soft magnetic Fe-M-B (M = Zr, Hf, Nb), Fe-M-O (M = Zr, Hf, rare earth) alloys and their applications, *Nanostructured Materials* 12 (5), 825–828, Copyright 1999, with permission from Elsevier.)

#### 1.4.1.6 Corrosion Resistance

A number of researchers have investigated corrosion resistance of nanocrystalline materials. A study on corrosion of Ni-P alloy shows that the corrosion rate of nanocrystalline alloys is higher than that of common microcrystalline alloys; however, corrosion is more general.

Higher rates of corrosion in nanocrystalline materials are due to their extensive grain boundary, where atoms are in balance and then have higher energy levels that make them able to participate in chemical corrosive reactions. More regular corrosion of nanostructured materials is due to their more homogenous structures. Experiments performed on nanocrystalline 304 stainless steel in HCl reveal that nanostructures have higher local resistance against corrosion than traditional structures.<sup>98–103</sup>

Decreasing the average size of nanocrystallites usually can increase the corrosion resistance, while some other factors such as the nature of the material and its porosity can affect this trend. Figure 1.9 shows the close relationship between corrosion resistance and average nanocrystallite size for a kind of hard coating fabricated by plasma electrolysis.



**FIGURE 1.9**

Polarization resistances of different coatings versus the average size of their nanocrystallites. (Reprinted from Aliofkhazraei, M., Sabour Rouhaghdam, A., and Heydarzadeh, A., Strong relation between corrosion resistance and nanostructure of compound layer of treated 316 austenitic stainless steel, *Materials Characterization* 60 (2), 83–89, Copyright 2009, with permission from Elsevier.)

#### 1.4.1.7 Hydrogen Capacitance Properties

Hydrogen is among the best alternatives for fossil fuels such as oil and gas. Hydrogen combustion produces no pollution and is available from renewable energy resources. However, industrial use of hydrogen as a fuel requires the development of safe and economic capacitance systems. One of the best techniques to store the hydrogen is to use metallic hydrides. Compounds such as  $\text{LaNi}_5$ ,  $\text{ZrV}_2$ ,  $\text{Mg}_2\text{Ni}$ , and  $\text{FeTi}$  can store a considerable amount of hydrogen (about 8 weight percent) by the development of metallic hydrides and release it once there is a favorable condition of temperature and pressure. In this regard, required rate, temperature, and pressure for absorption or release of hydrogen by the material are of great importance in industry. These characteristics can be surprisingly improved by creating nanostructures.<sup>105–113</sup>

#### 1.4.2 Mechanical Properties

Mechanical properties of the nanomaterials are improved as their size decrease. Most studies conducted in this area are focused on mechanical properties in one-dimensional structures such as nanowires. Enhanced mechanical strength in nanowires or nanorods is attributed to the high rate of internal defects in the nanowires. In general, defects, such as impurities,

dislocations, and microtorsions, in crystals contain high energy content and must be removed from the completely crystalline structures. As the section area of the nanowires decreases, their defect rate drops because nanodimensions allow for removal of such defects.

Also, as the grain size increases, the volumetric ratio of the grain's size would increase in a single cell, as for the grains with a size of 5 nm about 50% of the volume would be empty space. One can explain the decrease of material strength due to the decrease of grain size as follows: The grain sizes start to slip because of high density of the defects in the stress field, so the atoms and dislocations would be widely expanded in the stress field.

During recent years, various studies have been conducted on mechanical properties of nanostructures. The results show that once the grain size is fine enough (up to nanometric range), many mechanical properties of materials—compared with common materials—dramatically change.

Mechanical properties of the nanostructured materials are mainly due to their extensive interfaces and the presence of a considerable fraction of atoms in these faces. Some factors including phase shape, distribution, size, impurities, and also density of crystalline defects influence mechanical behavior of the nanostructured materials. It must be noticed that the presence of voids or cracks in their structures, which mainly occur during the production processes, can also change their many other characteristics. Some discrepancy between results obtained by different researchers might be the result of these factors. Unfortunately, there is no comprehensive study about the role of voids, second-phase particles, alloy elements or impurities, and the nature of interfaces on mechanical properties of nanostructured materials. Hence, offering a complete summation is rather difficult.<sup>114–123</sup>

Table 1.4 shows mechanical properties of Ni in three different grain sizes. Some of these properties such as yield strength, final strength, hardness, and abrasive strength in the nanostructural state are several times higher than those in the microcrystalline state. But on the other hand, some other features such as Young elastic modulus ( $E$ ) show no noticeable change and some, like flexibility, even show a reduction.

#### 1.4.2.1 Elastic Properties

Initial measurements to determine elastic constants of nanocrystalline materials were done on samples produced with the powder metallurgy method. These research studies indicate that elastic properties such as  $E$  in nanocrystalline materials are greatly (up to 30%) more than traditional microcrystalline materials. However, laboratory test results and the following models clearly suggest that the presence of voids and cracks in samples can have a considerable effect on elastic modulus reduction of nanocrystalline materials, as it can decrease up to 80% regarding size, percentage, and shape of the voids.<sup>36,121,125–130</sup> The presented results in Table 1.4 show that for a nanocrystalline sample with insubstantial porosity, Young modulus basically does not change with

**TABLE 1.4**

Mechanical Properties of Ni in Nanocrystalline and Microcrystalline States in Ambient Temperature

Property	Grain Size		
	10 $\mu\text{m}$	100 nm	10 nm
Yield strength (MPa, 25°C)	103	690	>900
Ultimate tensile strength (MPa, 25°C)	403	1100	>2000
Tensile elongation (% , 25°C)	50	>15	1
Elongation in bending (% , 25°C)	—	>40	---
Modulus of elasticity (Gpa, 25°C)	207	214	204
Vickers hardness (kg/mm <sup>2</sup> )	140	300	650
Work hardening coefficient	0.4	0.15	0.0
Fatigue strength (MPa, 10 <sup>8</sup> ) cycles/air/25°C)	241	275	—
Wear rate (dry air pin on disc, $\mu\text{m}^3/\mu\text{m}$ )	1330	—	7.9
Coefficient of friction (dry air pin on disc)	0.9	—	0.5

Source: Reprinted from Robertson, A., Erb, U., and Palumbo, G., Practical applications for electrode-positied nanocrystalline materials, *Nanostructured Materials* 12(5), 1035–1040, Copyright 1999, with permission from Elsevier.

grain size decrease. It is predicted that this trend is true up to a grain size of 5 nm. But, once grain size is smaller than 5 nm the number of atoms located in the grain boundary will be significant<sup>131</sup> and can dramatically change the elastic properties of the material. Thus, most of the time nanocrystalline materials with a grain size of 10 nm have the similar elastic constants with common microcrystalline materials. The changes of different related properties for an ultrananocrystalline diamond can be seen in Figure 1.10.

#### 1.4.2.2 Plastic Properties

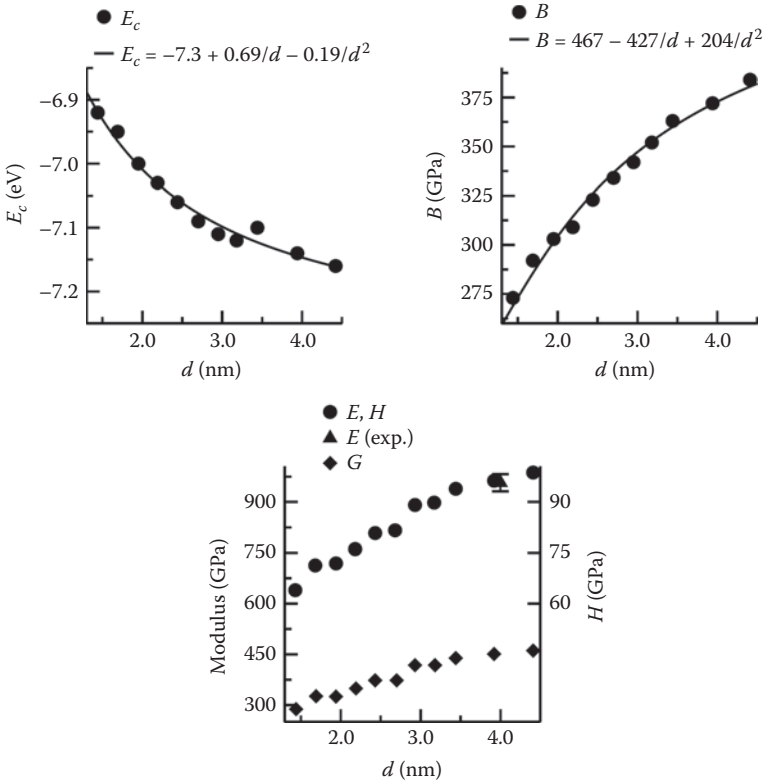
Yield strength and hardness of common polycrystalline materials depend on their grain size. For polycrystalline materials the empirical Hall–Petch equation states the relationship between yield strength and grain size as follows:

$$\sigma_y = \sigma_0 + kd^{-1/2} \quad (1.7)$$

where  $\sigma_y$  is the yield stress,  $\sigma_0$  is the innate yield stress for starting a single dislocation,  $d$  is the grain diameter, and  $k$  is a constant related to the grain boundaries' effect on dislocations. In the same way, Equation (1.8) shows the effect of grain size on the hardness of polycrystalline materials:

$$H = H_0 + k'd^{-1/2} \quad (1.8)$$

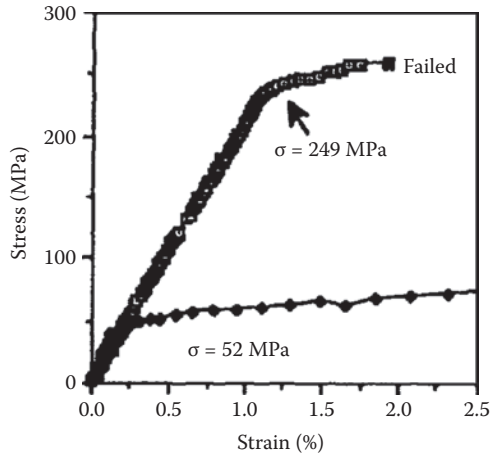
where  $H$  and  $H_0$  are, respectively, hardness and innate hardness (hardness of a single crystal).



**FIGURE 1.10**

Cohesive energy (left panel), bulk modulus (central panel), Young’s and shear moduli, and estimated hardness (right) of ultrananocrystalline diamond (UNCD) versus the average grain size. The solid lines in the left and central panels are fits to the data. The function used assumes different compressibilities for atoms in the bulk, grain boundaries, or edges. In the right panel, the experimental value from Espinosa and colleagues is also shown. (Reprinted from Remediakis, I. N., Kopidakis, G., and Kelires, P. C., Softening of ultra-nanocrystalline diamond at low grain sizes, *Acta Materialia* 56 (18), 5340–5344, Copyright 2008, with permission from Elsevier; also reprinted from Espinosa, H. D., Peng, B., Moldovan, N., Friedmann, T. A., Xiao, X., Mancini, D. C., Auciello, O., Carlisle, J., Zorman, C. A., and Merhegany, M., Elasticity, strength, and toughness of single crystal silicon carbide, ultrananocrystalline diamond, and hydrogen-free tetrahedral amorphous carbon, *Applied Physics Letters* 89 (7), Copyright 2006, with permission from the American Institute of Physics.)

Equations (1.7) and (1.8) show that drawing the  $\sigma_y$  (or  $H$ ) in terms of  $d^{-1/2}$  leads us to a line with gradient of  $k$  (or  $k'$ ). To describe these empirical equations, several models have been suggested that are mainly based on production, movement, and concentration of dislocations behind the grains. If the Hall–Petch equation is true for nanocrystalline materials without changing the  $k$  (or  $k'$ ) coefficient, these materials’ strength and hardness should increase up to 10 times.<sup>134–136</sup> For instance, if grain size reduces from 10  $\mu\text{m}$  to 10 nm,



**FIGURE 1.11**

Stress–strain curve for nanocrystalline (grain size of 7 nm) and microcrystalline (grain size of 100 μm) Pd. (Reprinted from Nieman, G. W., Weertman, J. R., and Siegel, R. W., Tensile strength and creep properties of nanocrystalline palladium, *Scripta Metallurgica et Materiala* 24 (1), 145–150, Copyright 1990, with permission from Elsevier.)

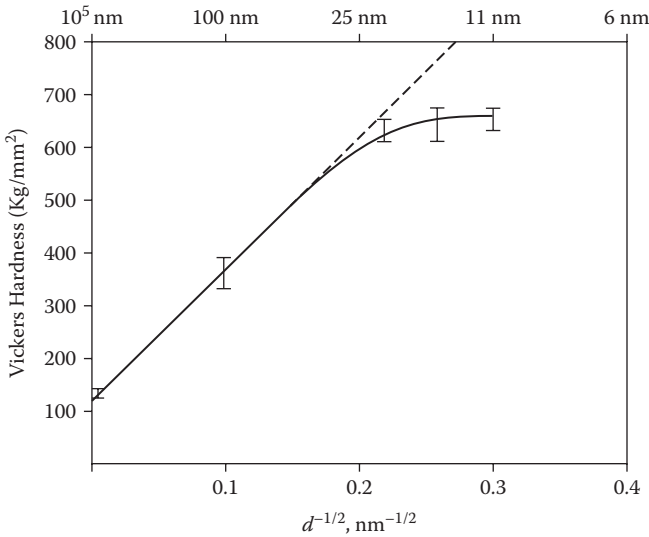
the strength must increase up to 30 times, though laboratory results do not support this claim (Table 1.4).

Due to limitations in making laboratory samples with large scales, the performed studies (particularly mechanical properties of nanostructured materials) are limited for measuring fine hardness. However, some results about tensional test will also be available. Figure 1.11 shows the result of the tension test on Palladium (Pd) in both microcrystalline and nanocrystalline states. This obviously reveals that in nanostructured Pd there would be a dramatic rise in yield strength with a decrease of grain size.

In total, for nanocrystalline materials with a grain size of 10 nm, hardness and yield strength are about two to seven times more than common materials with grain sizes of more than 1 μm. As previously mentioned, the effect of grain size on hardness and yield strength of a material is typically described by the Hall–Petch equation. In Figures 1.12 and 1.13, some examples of this equation for nanocrystalline materials are presented.

Evaluating these results implies that in all cases, disregarding the production method, hardness and strength increase according to the Hall–Petch equation, but once the grain size is lower than a critical range (15 to 25 nm) it does not rise by the previous gradient. In other words, in grain sizes lower than a critical size  $k'$  (or  $k$ ), the coefficient in the Hall–Petch equation will be reduced. In grain sizes lower than the critical size, nanocrystalline materials display three different behaviors.

In most of the cases, the Hall–Petch equation continues but its gradient declines. In a few cases Hall–Petch curve's gradient limits to zero. This occurs

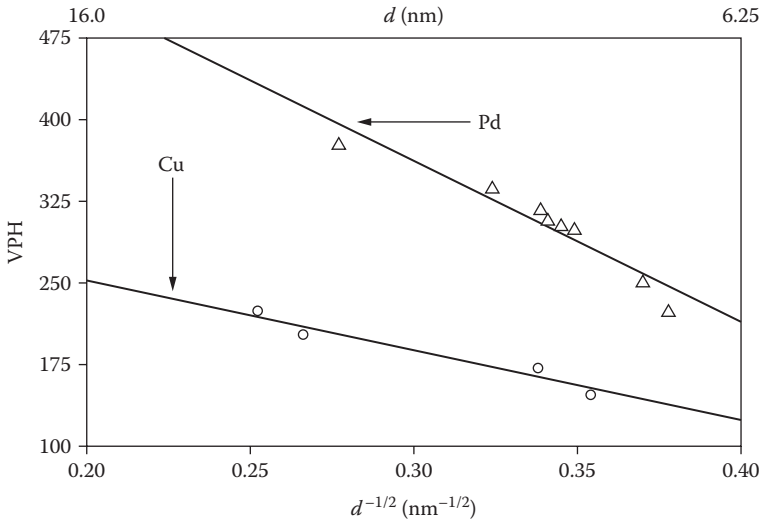


**FIGURE 1.12**

Hall–Petch diagram for nanocrystalline nickel (Ni). (Reprinted from El-Sherik, A. M., Erb, U., Palumbo, G., and Aust, K. T., Deviations from Hall–Petch behaviour in as-prepared nanocrystalline nickel, *Scripta Metallurgica et Materiala* 27 (9), 1185–1188, Copyright 1992, with permission from Elsevier.)

in a small group of materials in grain sizes lower than critical size where the curve's gradient is negative. This means that the smaller the grain size, the lower is the hardness. In this situation, we are faced with an inverse Hall–Petch equation, so instead of work hardening there will be work softening. Figure 1.13 shows these behaviors for Cu and Pd and alloys of  $\gamma$ -TiAl, respectively.

Why an inverse Hall–Petch curve behaves in this way is not yet fully answered. However, it is mainly believed that common mechanisms, about creation and movement of dislocations, offered for plastic deformation are not at play in nano ranges. Principally, in grain sizes less than 50 nm dislocations cannot be presented. The absence of dislocations in limited spaces such as whiskers was proven a long time ago. The required stress for activation of dislocations sources, such as the Frank–Read ones, are inversely correlated with distance between two dislocations' interlocking. Therefore, due to close grain boundaries in nanocrystalline materials, the distance between dislocations locking is negligible and the required stress for activation of dislocation sources can amount to theoretical shear stress in a sample with no dislocations. So, it is expected that in very small grain sizes some other phenomena control the plastic behavior of the materials. For example, it is suggested that processes such as grain boundary slips or grain disorientation (diffusive creep) are the main mechanism for plastic deformation of the nanocrystalline materials with critical grain sizes.



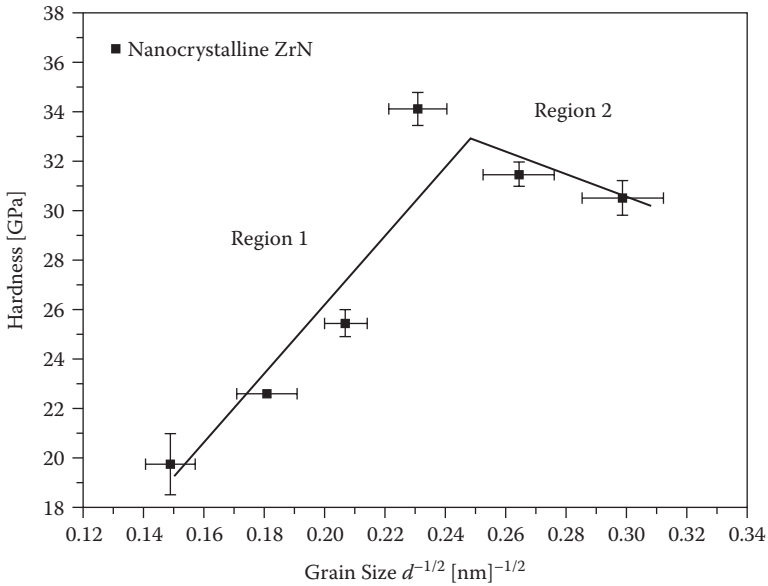
**FIGURE 1.13**

Inverse Hall–Petch curve for hardness of nanocrystalline Cu and Pd. (Reprinted from Chokshi, A. H., Rosen, A., Karch, J., and Gleiter, H., On the validity of the Hall–Petch relationship in nanocrystalline materials, *Scripta Metallurgica* 23 (10), 1679–1683, Copyright 1989, with permission from Elsevier.)

Although the results above are mainly for pure metals, the reported results for nanocrystalline intermetallic components or alloys bearing ceramic nanoparticles (oxides, carbides, etc.) are qualitatively similar to the results mentioned above. Observing inverse Hall–Petch behavior in ceramics and composites promises production of these materials in lower temperatures. Figure 1.14 schematically displays Hall–Petch behavior in two grain sizes for ZrN coating.

Like hardness and strength, it is predicted that flexibility of a substance would rise with the drop of grain sizes down to the nano range. This prediction is based on empirical experimental results on common microcrystalline materials, suggesting that smaller grain sizes lead to higher flexibility and fracture toughness. As a matter of fact, in these materials as the grain size decreases fracture strength intensifies more than yield strength, and the substance shows a soft behavior. Nevertheless, the empirical results do not prove this. As previously mentioned, nanostructured materials have lower flexibility (particularly in tension test) than the common materials. Polycrystalline Ni with a grain size of 10  $\mu\text{m}$  would have a linear strain of up to 50%, while once the grain size is 100 nm this strain is 15% of its original length. If the grain size is higher than 100 nm, Ni displays an insignificant flexibility (about 1%). In this way, nanocrystalline Ni will basically behave like a brittle substance.



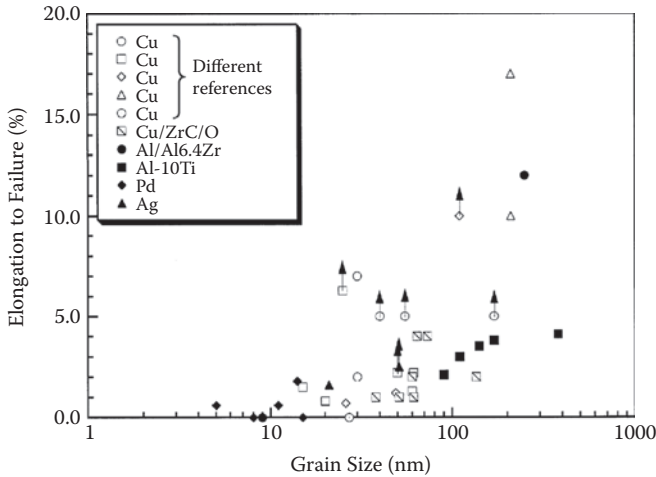


**FIGURE 1.14**

Hall–Petch plot of hardness of nanocrystalline ZrN coatings against the inverse square-root of grain size. (Reprinted from Qi, Z. B., Sun, P., Zhu, F. P., Wang, Z. C., Peng, D. L., and Wu, C. H., The inverse Hall–Petch effect in nanocrystalline ZrN coatings, *Surface and Coatings Technology* 205 (12), 3692–3697, Copyright 2011, with permission from Elsevier.)

It is worth mentioning that most of the tests for measuring mechanical properties of the nanostructured materials were performed on samples prepared by the powder metallurgy method. Under this condition, the samples will generally have a considerable amount of voids, and the measured flexibility will be influenced by the presence of voids and lack of complete consistency between particles of the powder. In addition, sample surface quality intensely affects the results of flexibility tests. To examine the role of these factors, samples with no porosity or cracks were prepared using some other production methods such as precipitation from the vapor phase or electrochemical deposition. Mechanical tests on these samples also prove this limited flexibility in the nanocrystalline state. Figure 1.15 shows flexibility of some metals and alloys in terms of grain size. Although the data are highly distributed, they all show that once the grain size decreases the flexibility also reduces, and if grain size is less than 25 nm the flexibility will be negligible. However, all these materials demonstrate a significant flexibility of 40% to 60% in the microcrystalline state. Figure 1.16 compares true stress–true strain curves for electrodeposited nanocrystalline nickel and coarse grained nickel.

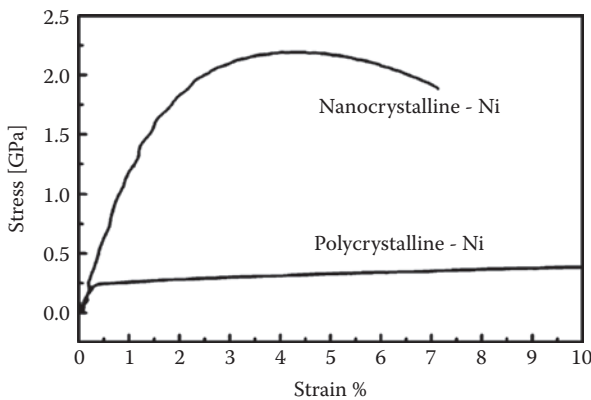
The reported flexibility for nanostructured materials in a tensional test is less than a compressive test. For example, nanocrystalline copper samples (with a



**FIGURE 1.15**

Flexibility (in tensional test) in terms of grain size for some alloys and metals. (Reprinted from Malow, T. R., and Koch, C. C., Mechanical properties in tension of mechanically attrited nanocrystalline iron by the use of the miniaturized disk bend test, *Acta Materialia* 46 (18), 6459–6473, Copyright 1998, with permission from Elsevier.)

grain size of 20 nm) show 12% to 18% of flexibility in a compressive test, while this sample's flexibility in a tensional test is about 2%. This difference is partially due to lack of sensitivity to the presence of voids and cracks of the sample in the compressive test, but in the tensional test these defects lead to stress concentration and drop of flexibility. One factor limiting the use of intermetallic



**FIGURE 1.16**

True stress–true strain curves for electrodeposited nanocrystalline nickel and coarse grained nickel. The coarse grained nickel reached a total elongation of 20%. (Reprinted from Van Swygenhoven, H., Footprints of plastic deformation in nanocrystalline metals, *Materials Science and Engineering A* 483–484 (1–2 C), 33–39, Copyright 2008, with permission from Elsevier.)

compounds and ceramics is their brittle behavior. It is expected that in the process of creating nanostructures, intermetallic compounds and ceramics show soft behavior in temperatures lower than half of their melting point ( $^{\circ}\text{K}$ ). This prediction is based on the fact that in common materials a grain size decrease leads to a quicker increase of fracture stress compared with yield stress, so brittle fracture changes into a soft fracture occur in lower temperatures.

On the other hand, based on creep theories, we have

$$R \approx D_b/d^3T \quad (1.9)$$

where  $r$  is the creep rate,  $D_b$  is the diffusion rate in grain boundary,  $d$  is the grain size, and  $T$  is temperature (in Kelvin).

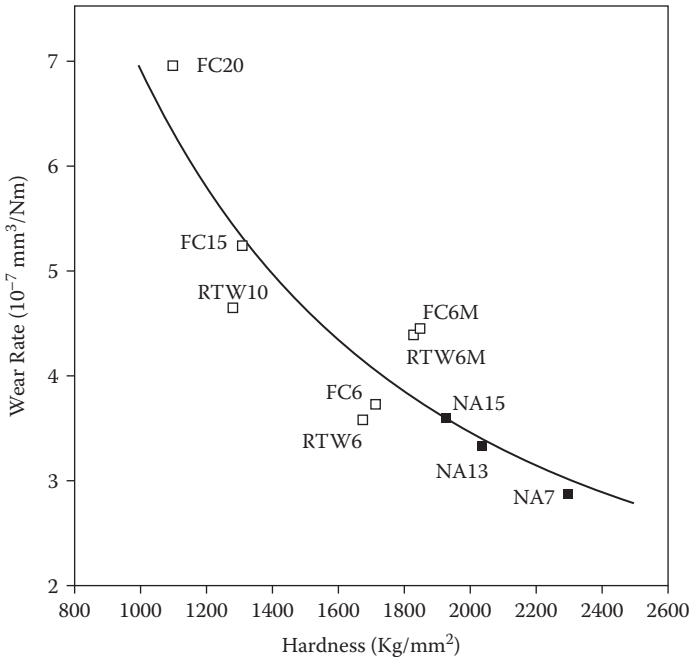
According to Equation (1.9), if the grain size decreases from  $10\ \mu\text{m}$  to  $10\ \text{nm}$  (which is 1000 times) the creep rate will increase  $10^9$  times. In addition, the higher diffusion rate in the grain boundary for nanocrystalline materials leads to more growth in creep rate. It is expected that an increase in creep rate for nanostructured materials makes it possible to perform plastic deformation of ceramics and intermetallic compounds in lower temperatures. Although plastic behavior of ceramics and intermetallic compounds was observed in lower temperatures in some cases (including  $\text{TiO}_2$ ,  $\text{CaF}_2$ , and  $\text{NiAl}$ ), test repeatability has not yet been proved. Hence, it is not possible to offer a conclusion at this point.

Fatigue strength is another important mechanical characteristic of materials. To date, there have been few studies on fatigue behavior of nanostructured materials. The early results suggest that most nanocrystalline metals have a longer fatigue life in high stress cycles and vice versa. These results might originate from the fact that fatigue life in high stress cycles is closely related to strength of the materials, whereas short fatigue life in low stress cycles relates to flexibility of the material. Also, it was reported that surface hardening treatments, such as shot peening, have no effect on improvement of nanocrystalline materials' fatigue properties.

Because nanostructured materials have higher strength and hardness than common materials, it can be assumed that their abrasive strength is considerably higher than the customary materials (e.g., hardness of cobalt-tungsten carbide [WC-Co] nanocomposites is twice as much as their hardness in the microcrystalline state). Figure 1.17 illustrates the wear rate of WC-Co composites (summarized in Table 1.5) in both nanostructured and traditional states. This increase in wear rate can enhance the life span of cutting tools and piece exposed to abrasion up to five times. The variation of wear coefficient with the carbide grain size can also be seen in Figure 1.18.

#### 1.4.2.3 Superplasticity

Some polycrystalline substances at a given temperature and strain rate demonstrate a high plastic deformation (100 to 1000 percent or even more)



**FIGURE 1.17**

Comparison between hardness and wear rate in WC-Co composite in both nanostructured and conventional states. (Reprinted from Jia, K., and Fischer, T. E., Sliding wear of conventional and nanostructured cemented carbides, *Wear* 203–204, 310–318, Copyright 1997, with permission from Elsevier.)

without any fracture or necking phenomenon. This phenomenon is known as superplasticity that typically occurs in materials with fine grains (less than  $10\ \mu\text{m}$ ) and temperatures higher than  $T_m/2$  (where  $T_m$  is the melting point in Kelvin). As superplasticity behavior allows us to produce pieces with very complicated shapes from materials such as metallic matrix composites and intermetallic compounds (which cannot be machined), it is vital and useful in industrial issues.

To the moment, industrial application of superplastic deformation is limited due to its requirement for a low rate of deformation (about  $10^{-3}\text{s}^{-1}$ ), which causes a longer deformation period (20 to 30 minutes). Still, the needed deformation rate for the occurrence of the superplasticity behavior is inversely related with square of grain sizes. Hence, one can claim that if grain size decreases up to 10 times, the optimum rate of plastic deformation for achieving superplastic behavior increases up to 100 times. To simplify, a decrease of grain size from  $2\ \mu\text{m}$  to  $200\ \text{nm}$  cut the superplasticity time from 20 to 30 minutes to 20 to 30 seconds. Moreover, with the decrease of grain size the temperature range necessary for superplasticity will shrink. Then, it is

**TABLE 1.5**

Nominal Composition and Structural Characteristics of WC-Co Composites in Figure 1.17

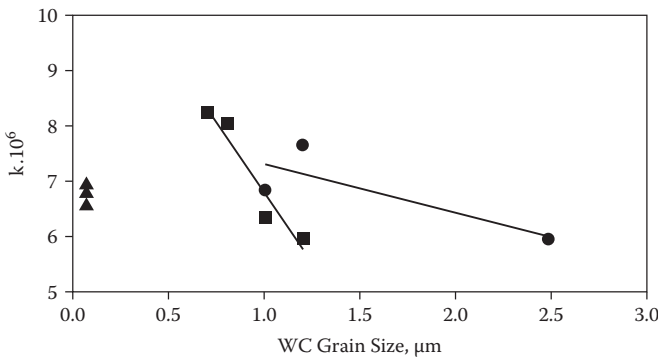
Sample	Structural Characteristics			Hardness and Toughness	
	WC Grain Size ( $\mu\text{m}$ )	Cobalt Content (vol%)	Measured Mean Free Path ( $\mu\text{m}$ )	Vickers Hardness (GPa)	$K_{IC}$ ( $\text{MPa}\cdot\text{m}^{1/2}$ )
FC20	1.2	30.5	1.06	11	NA
FC15	1.0	23.6	0.61	13	NA
FC6	1.0	10.1	0.39	17	9
FC6M	0.7	10.1	0.25	18.6	8.2
RTW10	2.5	16.3	1.0	12.8	16.4
RTW6	1.2	10.1	0.43	16.8	10
RTW6M	0.8	10.1	0.14	18.4	8.4
NA15	0.07	23.6	0.068	19.4	8
NA13	0.07	20.8	0.068	20.5	8.3
NA7	0.07	11.7	0.039	23.0	8.4

Note: The number in the sample identification indicates the cobalt content in wt%. For example, NA15 contains 15 wt% and 23.6 vol% Co. Hardness indicated in GPa.  $1000 \text{ kg}\cdot\text{mm}^{-2} = 9.81 \text{ GPa}$ .

Source: Reprinted from Jia, K. and Fischer, T. E., Sliding wear of conventional and nanocrystalline cemented carbides, *Wear* 203–204, 310–318, Copyright 1997, with permission from Elsevier.

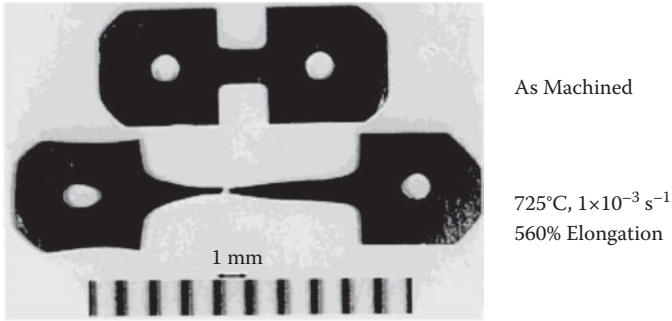
predicted that industrial applications of superplastic shaping with nanostructures would have a huge development.<sup>144,145</sup>

Superplastic behaviors in low temperatures have been reported in some nanostructured metals or even intermetallic compounds. For example, nanocrystalline nickel in a temperature of  $0.36 T_m$  shows a superplastic behavior.



**FIGURE 1.18**

The variation of wear coefficient with the carbide grain size in WC-Co composites: Triangles, nanocomposites; squares, cermets with 6% Co; circles, RTW10, FC15, and FC20 from Table 1.5. (Reprinted from Jia, K., and Fischer, T. E., Sliding wear of conventional and nanostructured cemented carbides, *Wear* 203–204, 310–318, Copyright 1997, with permission from Elsevier.)



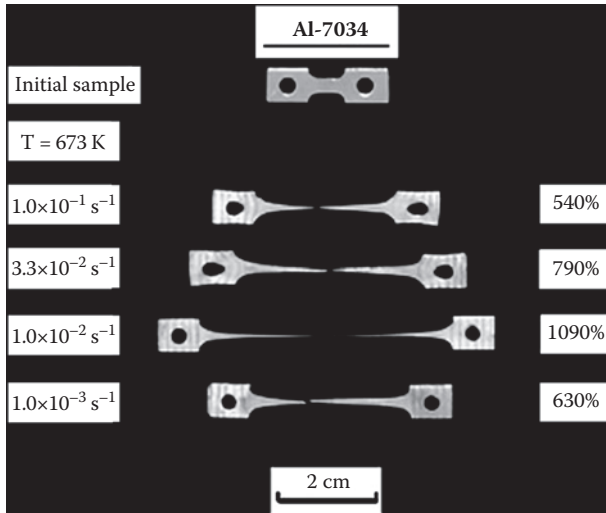
**FIGURE 1.19**

Nanocrystalline samples of  $\text{Ni}_3\text{Al}$  before and after tension test in  $725^\circ\text{C}$  and strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$ . (Reprinted from Mishra, R. S., Valiev, R. Z., McFadden, S. X., and Mukherjee, A. K., Tensile superplasticity in a nanocrystalline nickel aluminide, *Materials Science and Engineering A* 252 (2), 174–178, Copyright 1998, with permission from Elsevier.)

This temperature is about  $450^\circ\text{C}$  less than the superplastic temperature of microcrystalline Ni. Pure nanocrystalline copper shows a linear strain of 5000% without any hardening, whereas microcrystalline copper samples can have a linear strain of only 800%. A fascinating example on this issue is superplastic behavior of an intermetallic compound of  $\text{Ni}_3\text{Al}$  (Figure 1.19). These materials (with grain size of 50 nm) manifest a superplastic behavior in temperature more than  $650^\circ\text{C}$ , while the tensional sample of  $\text{Ni}_3\text{Al}$  has a linear strain of 560% in a temperature of  $725^\circ\text{C}$ . Figure 1.20 exhibits superplastic behavior in 7034 aluminum alloy under a tension test. It must be mentioned that thermal stability of nanostructures and lack of grain growth should be considered for use of their superplastic behavior. This thermal stability will be discussed in the next section.

Mechanical properties of nanostructures can be summed as follows:

1. Elastic modulus of nanocrystalline materials almost equals that of microcrystalline materials. However, in very fine grain size (less than 50 nm) elastic properties have not fully been studied.
2. Once grain size decreases to 15 to 25 nm, hardness and yield strength of nanostructured materials rise according to the Hall-Petch equation. In some cases, in grain sizes less than 15 to 25 nm, the curves gradient is zero, whereas in some others it is negative.
3. Creation of nanostructures in metals leads to a substantial rate of flexibility. Also, it results in high flexibility for brittle materials (such as ceramics and intermetallic compounds) in low temperatures.
4. Superplastic deformation of nanostructured materials takes place in lower temperatures and with higher rates.

**FIGURE 1.20**

Appearance of the specimens after equal-channel angular pressing (ECAP) through six passes at  $473\text{ K}$  and then pulling to failure at different initial strain rates at  $673\text{ K}$ : the upper specimen is untested. (Reprinted from Xu, C., Furukawa, M., Horita, Z., and Langdon, T. G., Using ECAP to achieve grain refinement, precipitate fragmentation and high strain rate superplasticity in a spray-cast aluminum alloy, *Acta Materialia* 51 (20), 6139–6149, Copyright 2003, with permission from Elsevier.)

## 1.5 Thermal Stability of Nanostructures

Due to having extensive interfaces, nanostructured materials have more freedom than the common materials (microcrystals). As a result, nanostructured materials, disregarding their production method, are more stable in terms of thermodynamic aspects. Nanostructured materials lose their free energies by decreasing their interfaces, which result in growth of grains and phase particles.

The study of thermal stability and growth of grains and phases of nanostructures has two main aspects:

1. If the objective is production of a structure with the least grain size, we must stop grain and phase growth during the production processes (such as sintering), because enlarging the structure eliminates so many desirable properties of the nanostructures.
2. Through grain size and phase change through the growth process, it is feasible to obtain a wide range of mechanical and physical properties. In this way, through the control of growth process, one can create a fine structure in favorable dimension and size and given properties.

According to the Gibbs–Thomson equation, the thermodynamic motive force for grain growth in polycrystalline materials can be stated as follows:

$$= \frac{2\gamma V}{d} \quad (1.10)$$

where  $\Delta\mu$  is the chemical potential difference in both sides of the grain boundary caused by their face curve,  $\gamma$  is the grain boundary energy in the surface unit,  $V$  is the atomic volume, and  $d$  is the grain size.

Equation (1.10) shows that once the grain size is smaller, the thermodynamic motive force ( $\Delta\mu$ ) for their growth would be higher. This means that the growth rate of the grains is inversely correlated with their size. On the other hand, grain growth is a diffusive process, so an increase in temperature leads to its increase. Then, one might say,

$$\frac{\delta d}{\delta t} = \frac{K}{d} \quad (1.11)$$

where  $K$  is a quantity that depends on energy and structure of grain boundary and varied with temperature according to the following equation:

$$K = K_0 \exp(-Q/RT) \quad (1.12)$$

where  $Q$  is the activation energy of the grain growth,  $T$  is the temperature (in Kelvin),  $R$  is the gas constant, and  $K_0$  is a constant value.

If  $d$  is the grain size in the moment in which grains start to grow, integrating from Equation (1.11), we have

$$d^2 - d_0^2 = 2Kt \quad (1.13)$$

If we consider that the  $d_0$  is small enough, then

$$d^2 = 2Kt \quad (1.14)$$

Equation (1.14) is a parabola that presents grain growth in ideal conditions. This shows that passing the time, grain growth rate (curve's gradient) shrinks. However, due to the presence of alloy elements, impurities, second-phase particles, voids, and so forth, on grain boundaries, Equation (1.14) does not match data obtained in the laboratory, so the grain growth equation is presented as

$$d^n = Kt \quad (1.15)$$

For standard polycrystalline materials,  $n$  is greater than two. Once the materials purity increases and temperature goes up,  $n$  approaches 2. The growth



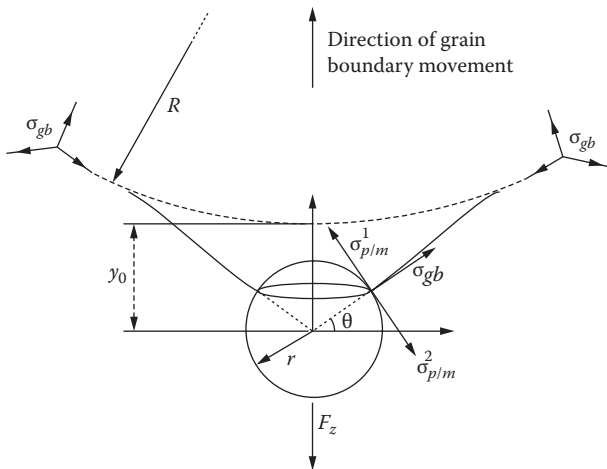
mechanism of the grains can be explained by two parameters of  $n$  and  $Q$ . In common polycrystalline materials activation energy of grain growth is rather equal to activation energy through grain boundary diffusion. This implies that grain growth is performed by their movement and transition through the grain boundary.

The presence of second-phase particles or impurities on the grain boundary causes a decrease of the grain growth rate. The presence of second-phase particles on the grain boundary leads to a decrease of its surface area. Consequently, grain boundary movement and its separation from second-phase particles requires a new grain boundary. To simplify, second-phase particles inhibit grain boundary movements by inserting a force against thermodynamic motive force. This is known as Zener force. When grain boundary energy in the surface unit and radius of second-phase particles are, respectively,  $\gamma$  and  $r$ , it can be inferred from Figure 1.21 that the magnitude of Zener force in a length unit of the grain boundary equals  $\gamma \sin\theta$ . If we multiply this by distance between intersection of the grain boundary with a second-phase particle ( $2\pi r \cos\theta$ ), the total value of Zener force would be

$$F = 2\pi r \gamma \sin\theta \cos\theta \tag{1.16}$$

The maximum amount of this force ( $F_m$ ) is when  $\theta = 45^\circ$ , so

$$F_m = \pi r \gamma \tag{1.17}$$



**FIGURE 1.21** Effect of second-phase particles on movement of grain boundary. (Reprinted from Moelans, N., Blanpain, B., and Wollants, P., A phase field model for the simulation of grain growth in materials containing finely dispersed incoherent second-phase particles, *Acta Materialia* 53 (6), 1771–1781, Copyright 2005, with permission from Elsevier.)

If  $f$  is the volume fraction of the second phase, the average number of particles in volumetric unit of second phase ( $N$ ) is

$$N = \frac{f}{\frac{4}{3}\pi r^3} \quad (1.18)$$

Because it is only possible for particles with a distance of  $\pm r$  to touch the grain boundary, the number of particles in the second phase in the surface unit of a grain boundary would be

$$N = 2rN = \frac{3f}{2\pi r^2} \quad (1.19)$$

Then, the total Zener force inserted on a surface unit of the grain boundary can be obtained from the following equation:

$$P = F_m \times N = \frac{3f\gamma}{2r} \quad (1.20)$$

Because the grain size is small enough, the prohibiting force against grain growth ( $P$ ) is very unsubstantial in comparison with the thermodynamic motive force for grain growth, so grain starts to be enlarged. But, once the grain size goes up thermodynamic motive force decreases, and whenever it is equal to the  $P$  grain growth would be stopped. Hence, the maximum grain diameter ( $d_m$ ) achieved in the growth process in the presence of second-phase particles is as follows:

$$\frac{2\gamma}{d_m} = \frac{3f\gamma}{2r} \quad (1.21)$$

$$d_m = \frac{4r}{3f} \quad (1.22)$$

The most important result obtained from Equation (1.21) is that the finer particle size of second phase and their higher volumetric fraction leads to their greater influence on grain growth rate.

With respect to discussions above, it is expected that grain growth in nanocrystalline materials can be done even in low temperatures, though data and results of laboratory tests do not support this. In fact, many nanocrystalline materials including metals, ceramics, and intermetallic compounds produced in different methods are stable even in fairly high temperatures. Thermal stability of nanomaterials has been reported even

at 40% to 50% of their melting point, which is equal to that for common polycrystalline materials.

The results show that activation energy for grain growth ( $Q$ ) in nanocrystalline materials is in agreement with activation energy of grain boundary diffusion ( $Q_b$ ), though different values have been reported for  $n$  (2 to 10). Some other outcomes imply that for nanocrystalline materials, activation energy of grain growth in high temperatures is in agreement with activation energy of lattice diffusion; however, in low temperatures it is close to the activation energy of grain boundary diffusion.

Thermal stability of nanocrystalline materials and lack of grain growth can originate from several factors such as the presence of coaxial grains with a flat surface, the presence of impurities and their separation in the grain boundary, and the occurrence of voids in their structure. For example, it was reported that grain size of nanocrystalline titanium oxide ( $\text{TiO}_2$ ) with a porosity of 25%, after thermal operation in a temperature of 700°C for 20 hours, shifts from 14 to 30 nm. However, once the porosity drops to 10%, after performing the same thermal operation the grain growth exceeds 500 nm. This high thermal stability of the nanocrystals was assessed with several models. These models show that in grain sizes lower than a critical value ( $d_c$ ), grain growth has a linear relationship with time, but in grain sizes larger than  $d_c$ , grain growth relationship with the time, like common polycrystalline materials, is a parabolic equation. Because  $d < d_c$  grain growth is not controlled by thermodynamic motive force caused by grain boundaries curve, it might be possible that some other mechanisms, such as elimination of vacancies in grain boundaries, are responsible for grain growth. Because grain growth leads to a decrease of total area of grain boundary surface, then vacancies in grain boundaries must be located in other places or transferred to sample surfaces. Computational models indicate that during the growth process, these vacancies are mainly removed in areas close to grain boundaries and in the form of atomic vacancies. As a result, this leads to creation of an unbalanced concentration in atomic vacancies of the sample and an increase of free energy, which can compensate for the decrease of energy caused by grain growth. Based on this model, once the grain growth is controlled by redistribution of the vacancies, activation energy of the grain must be a larger number (close to activation energy of lattice diffusion). The obtained results from this model fairly match laboratory data. It is worth mentioning that the presence of second-phase particles, impurities, and voids created by production operations is a source of contradictions between the results of different researchers and laboratory data with mathematical models. In the presence of the above-mentioned agents, grain growth can mainly occur by atomic lattice diffusion.

Nanocomposites contribute to growth of reinforced phase particles, as well as grain growth. Similarly, grain growth is due to thermodynamic motive force of the second-phase particles and the extensive interface

between second-phase particles and the matrix. Hence, the particles of nanophases gradually start to grow, and their number in a volumetric unit drops and the free energy of the system drops. This process leads to removal of favorable features of a nanocomposite-like decrease of its hardness and strength. Moreover, according to Equation (1.20), once the particles of the second phase expand in size, their effect on stopping grain growth will be less significant.

Like growth process of the grains, second-phase particles are controlled by atomic diffusion and then they will grow with an increase in the temperature. Atomic diffusion can occur across the grains, from grain boundary, or through the interface of second-phase particles and the matrix. Assuming that the diffusion only occurs across the grains, growth rate of second-phase particles ( $dr/dt$ ) is offered as

$$dr/dt = K/r^2 \quad (1.23)$$

where  $r$  is the average size of second-phase particles in each moment,  $t$  is time, and  $K$  is a value related to the diffusion coefficient ( $D$ ) and interface contact energy ( $\gamma$ ).

If the particles' initial size is  $r_0$ , integrating from Equation (1.23) gives

$$r^3 - r_0^3 = 3Kt \quad (1.24)$$

From Equation (1.23) it can be found that finer grains have a higher growth rate. Because  $K$  increases with a increase of  $\gamma$  and  $D$ , then the growth rate of the second-phase particles will be low in the cases of small  $\gamma$  and  $D$ . Decrease of  $\gamma$  demands using a second phase that can create a shared interface with the interface. In addition, if particles of the second phase have elements with low solubility in the matrix, the diffusion coefficient ( $D$ ) will be extremely small which, in turn, leads to thermal stability of the second phase.<sup>149–154</sup>

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## 1.6 Nanotechnology and Future Perspectives

Nanotechnology mainly involves four key aspects including

1. Miniaturizing systems
2. Obtaining new materials with nanodimensions
3. Enhancing the efficiency and automation of the systems and equipment
4. Increasing informatics storage capability

Nanotechnology is used in several aspects ranging from electronic, visual communication, and biological systems to new intelligent materials. The reasons for the wide use of nanostructures and nanomaterials are listed below:

1. Unusual physical properties of the nanostructured materials, such as Au nanoparticles as an inorganic color used for glass dyeing
2. Expanded surfaces, like Au nanoparticles that are placed on the metallic oxides and used as low temperature catalyzers or nanoparticles for several types of the sensors
3. Extremely fine dimension, which is of great importance

Table 1.6 introduces some current and future applications of the produced materials by the nanotechnology using the new technologies in this field. In this text, some nanostructures and nanomaterials' applications as well as capabilities and potentials of the nanomaterials will be discussed in detail.<sup>155-160</sup>

**TABLE 1.6**

Some Current and Future Applications of the Produced Materials by the Nanotechnology

Technology	Current Impacts	Future Impacts
Distribution and coating	Heat-resistant coatings	Optimum heat resistance coatings
	Enhancing images' quality	Multiuse nanometric coatings
	Antiabrasive coatings	Fine-grain structures
	Information storing layers	Information storing layers with higher storage capacity
High contact surface	Molecular sifter	Specific molecules sensor
	Medicine carrier in the human body	Stimulated spotter particles
	Providing appropriate catalyzers	Energy storage (fuel cells)
	Absorptive and repellent materials	Gas sensors
Reinforced materials	Soft magnetic materials	Superplastic ceramics shaping
	Ductile and hard cutting tools	Ductile materials with high strength
	Nanocomposite cements	Composites filled with nanostructured fillers
Biological-medical aspects	Activated nanoparticles	Cellular marking
		Local heating
Nanotools	Reading heads made of giant magnetic resistance (GMR)	Memories and microprocessors with capacity of several thousands of Gigabites
		Biological sensors
		Nanotubes, highly bright monitors

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## 1.7 Some Applications of Nanostructures

Applying the nanomaterials, it is possible to achieve the following in the nanomaterials and nanosystems:

1. Ability to control the systems' size
2. Ability to determine the accurate needed composition (not approximate one) without any structural defects such as voids
3. Possibility to control frequency dimension
4. During the assemblage of the constituting pieces, control of the mutual effect level between the pieces as well as materials designs

### 1.7.1 Nanoelectronic and Molecular Electronic

Many advances in the molecular electronic and nanoelectronic field have been made. In the molecular electronic, single molecules are designed for control of electron transfer. The control on the surface of common metals and semiconductors is conducted by surface arrangement and solid materials molecules via designing an electrical circuit. Once the molecules are biologically active the bioelectronics pieces would be obtained.

Many nanoelectronic pieces, such as adjustable connections, electronic switches, carbon nanotube transistors, single-molecular transistors, and so on, were fabricated until now. Au nanoparticles are widely used in nanoelectronics and molecular electronics, due to their surface characteristics and unified sizes. For instance, Au nanoparticles can serve as carriers through several types of applied organic molecules or biological components. Au nanoparticles can be used as connectors in many practical connections in the structure of the electronic nanoparticles for employing in the sensors and detectors.<sup>161–165</sup>

### 1.7.2 Nanorobots

Future applications of nanotechnology in medical sciences, mainly in nanodrugs, will be very broad. One interesting application of nanomedicine is creating nanotools for promotion of curing and recognition level. These types of nanoparticles are known as nanorobots. These nanorobots can be used as transportation tools for carrying therapeutic factors and early detectors of the diseases and maybe metabolic or genetic defect treatments.<sup>166–168</sup>

### 1.7.3 Biological Applications

Among the most important applications of the colloid biological nanocrystals, one can name molecules detection. Some biomolecules are able to

detect one another with high precision and selectivity and can connect one to another. Antibodies as receptors have several applications in molecular detection applications. For instance, if a virus enters a live creature's body, antibodies detect it as an invader and attach to it, so the other sections of the immune system would be able to kill the virus.

Nanocrystals attached to a molecular receptor are directly connected to the position of ligand molecules. In this way, molecular labeling would be possible and completed by the receptor. For instance, in the very sensitive chromatic analysis method of DNA, color change of the Au nanoparticles from the rubious to the blue is used (because of its accumulation).

Other biological capabilities of the nanostructures and nanomaterials include employing semiconductor nanocrystalline colloids as a fluorescence sensor in cellular and chemical detection and use of nanostructured materials as artificial bone.<sup>169–172</sup>

### 1.7.4 Catalytic Applications

Each material with high catalytic absorption activity certainly includes a high contact surface. Because a decrease in nanomaterials size leads to an increase of the surface area, these materials are vastly used in catalysts. For instance, in a nanocrystal with a diameter of 10 nm, 15% of the atoms are placed on its surface, while in a nanocrystal with a diameter of 1 nm, 100% of the atoms are placed on the surface. Thus, a tiny nanocrystal with a vast surface would show further catalytic activities.

Metallic nanoparticles have fairly high catalytic potential and selective reduction potential of the materials. For example, the smooth surface of gold has no catalytic properties at the temperature of 473°K in the reaction of H<sub>2</sub> and O<sub>2</sub>, but gold nanoparticles (>10 nm) deposited on the oxide surface show very high catalyst activity in the hydrogenation and oxidation reaction of the carbon monoxide. This potential is up to an extent in which oxidation reaction of the carbon monoxide is even possible at a temperature of -70°C.<sup>173–177</sup>

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