P M 리 뷰

Nanocrystalline Materials-an Overview

C. Suryanarayana

*School of Mechanical and Materials Engineering Washington State
University Pullman, WA 99164-2920, U.S.A.*

ABSTRACT Nanocrystalline materials, with a grain size of typically <100 nm, are a new class of materials with properties vastly different from and often superior to those of the conventional coarse-grained materials. These materials can be synthesized by a number of different techniques and the grain size, morphology, and composition can be controlled by controlling the process parameters. In comparison to the coarse-grained materials, nanocrystalline materials show higher strength and hardness, enhanced diffusivity, improved ductility/toughness, reduced, density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher coefficient of thermal expansion, lower thermal conductivity, and superior soft and hard magnetic properties. Limited quantities of these materials are presently produced and marketed in the US, Canada, and elsewhere. Applications for these materials are being actively explored. The present article discusses the synthesis, structure, thermal stability, properties, and potential applications of nanocrystalline materials.

INTRODUCTION

Nanocrystalline materials are single- or multi-phase polycrystalline solids with a grain size of a few nanometers (1 nm=10^{-9} m), typically less than 100 nm. Since the grain sizes are so small, a significant volume of their microstructure is composed of interfaces, mainly grain boundaries, i.e., a large volume fraction of the atoms in Nanocrystalline materials resides in the grain boundaries. In effect, a nanocrystalline material can be considered as a composite made up of crystalline grains and disordered interfaces, and thus the nanocrystalline materials exhibit properties which are significantly different, and often improved, over their conventional coarse-grained polycrystalline counterparts. This article presents an overview of the synthesis, properties, and potential applications of nanocrystalline materials.

The subject of nanocrystalline materials has attracted the attention of materials scientists, physicists, mechanical engineers, chemical engineers,

and chemists. This has led to both an in-depth and broad-brush research activity on different aspects of nanocrystalline materials. A new journal entitled "NanoStructured Materials" was launched in 1992 and a number of dedicated conferences were organized and their proceedings published. The available space for this article does not permit a complete assessment of the whole field of nanocrystalline materials. For more details, the reader is referred to a number of recent reviews and conference proceedings[1-5,8] and also the references at the end of this article.

Nanocrystalline phases were detected in samples of lunar soils. Nanostructures formed chemically under ambient conditions can also be found in natural biological systems from sea shells to bone and teeth in the human body. These materials are notable in that they are simultaneously hard, strong, and tough. Therefore, a number of investigations have been conducted to mimic nature (biomimetics) and also artificially synthesize nanostructured materials and study their chemical,

mechanical, electrical, magnetic, and optical behavior. These investigations have clearly shown that one could engineer (tailor) the properties of nanocrystalline materials through control of grain size.

Nanocrystalline materials can be classified into different categories depending on the number of dimensions in which the material has nanometer modulations. Thus, they can be basically equiaxed in nature (nanostructure crystallites, 3-D) even though filamentary (rod-shaped, 2-D) and lamellar (layered, 1-D) nanocrystalline materials are also investigated. The magnitudes of length and width are much greater than thickness in the layered nanocrystals, and the length is substantially larger than width or diameter in filamentary nanocrystals. The nanophase materials may contain crystalline (nanocrystalline), quasicrystalline (nano-quasicrystalline), amorphous (nanoglasses), or liquid (microemulsions) phases and can be metals, ceramics, or composites. Additionally, Siegel[6] considers atom clusters as zero-dimensional. Gleiter[2] has further classified these materials according to the composition, morphology, and distribution of the nanocrystalline component. Amongst the above, maximum research work is conducted on the synthesis, consolidation, and characterization of the 3-D equiaxed nanocrystals followed by the 1-D layered nanostructures.

An important consequence of the small grain sizes of nanocrystalline materials is that a large volume fraction of the atoms lies in the grain boundaries. Although the actual number varies depending on the shape of the grains and the width of the grain boundary, it is fairly clear that the fraction of atoms in the boundary increases with a decrease in the grain size. Thus, the volume fraction of atoms in the grain boundaries can be as much as 50% for 5 nm grains and decrease to about 30% for 10 nm grains and 3% for 3 nm grains. In contrast, in a conventional coarse-grained material, the volume fraction of grain boundary atoms is <10-~~/o. Recently, it has been noted that instead of only grain boundaries, one should

consider the total interfacial component consisting of both grain boundaries and triple junctions or lines (i.e., intersection lines of three or more grain boundaries)[7]. Even then, the volume fraction of atoms in the interfacial area does not seem to be significantly different from the situation where only grain boundaries are considered.

SYNTHESIS

Nanocrystalline materials can be synthesized either by consolidating small clusters or breaking down the bulk material into smaller and smaller dimensions. They have been synthesized by a wide range of methods including inert gas condensation, mechanical alloying, spray conversion processing, severe plastic deformation, electrodeposition, rapid solidification from the melt, physical vapor deposition, chemical vapor processing, co-precipitation, sol-gel process, sliding wear, spark erosion, plasma processing, auto-ignition, laser ablation, hydrothermal pyrolysis, thermophoretic forced flux system, quenching the melt under high pressure, biological templating, and devitrification of amorphous phases produced by rapid solidification from the melt, mechanical alloying or other techniques[1,5]. Actually, in practice any method capable of producing very fine grain-sized materials can be used to synthesize nanocrystalline materials. Each of these methods has advantages and disadvantages and one should choose the appropriate method depending up on the requirements. If a phase transformation is involved, e.g., liquid to solid or vapor to solid, then steps have to be taken to increase the nucleation rate and decrease the growth rate during formation of the product phase. In fact, it is this strategy that is used during devitrification of metallic glasses to produce nanocrystalline materials[3].

The choice of the method depends up on the ability to control the most important feature of the nanocrystalline materials, viz., the microstructural (grain size or layer spacing) features. Other as-

pects of importance are the chemical composition and surface chemistry or cleanliness of the interfaces. Extremely clean interfaces can be produced and retained during processing and subsequent consolidation by conducting the experiments under ultra high vacuum (UHV) conditions; but, this adds up to the cost of processing. On the other hand, there are also methods which can be very inexpensive; but, the purity of the product may not be high. Inert gas condensation, mechanical alloying, spray conversion processing, electrodeposition, and crystallization of glassy phases are some of the most used techniques to produce nanocrystalline materials.

Inert gas condensation is the technique pioneered by Gleiter[2] to produce nanocrystalline materials. In this method, a metal or a number of metals are evaporated in separate crucibles inside a UHV chamber filled with helium gas. As a result of interatomic collisions with the helium atoms in the chamber, the evaporated metal atoms lose their kinetic energy and condense in the form of small crystals of loose powder which accumulate, because of convective flow, on a vertical liquid nitrogen-filled cold finger. The powder is stripped off the cold finger and directly fed into a compaction unit located below the vacuum chamber. The whole process is done under UHV conditions and so the powder is extremely clean. Oxidation, carburization, or nitridation of the powders can be carried out in-situ to produce oxides, carbides, or nitrides, respectively. Further, it is easy to control the grain size and composition by controlling the process parameters. This process is used commercially to produce nanocrystalline metal and oxide powders by Nanophase Technologies in Darien, IL, USA. A full description of the method and the effect of process variables on the product phase can be found in Refs. 8 and 9.

Mechanical alloying involves repeated welding, fracturing, and rewelding of powder particles in a high energy ball mill. The grain size of the powders decreases with milling time and reaches

nanometer dimensions, usually in a few hours. A recent comprehensive review describes the synthesis and mechanism of formation of nanocrystalline materials by this process[10]. Powder contamination is usually a serious problem with this process, especially when reactive metals and/or long milling times are involved.

Spray conversion processing is another industrial process employed by Nanodyne, Inc. (New Brunswick, NJ, USA) to produce nanocrystalline WC-Co composite powders. This process starts with an aqueous solution precursor which is converted into an aerosol and rapidly spray dried to give extremely fine mixtures of tungsten and cobalt complex compounds. Reduction of this powder with hydrogen and reaction with carbon monoxide in a fluidized bed reactor yields nanophase WC-Co powder[11].

Electrodeposition is a simple and well-established process and can be easily adapted to produce nanocrystalline materials[12,13]. This technique can yield porosity-free finished products which do not require subsequent consolidation processing. Further, the process requires low initial capital investment and provides high production rates with few shape and size limitations. For these reasons, NanoMetals Corporation, London, Ontario, Canada is using this process for industrial applications.

Synthesis of nanocrystalline materials by crystallization of glassy phases (produced by e.g., rapid solidification from the liquid state, mechanical alloying, vapor deposition) involves control of the crystallization kinetics by optimizing the heat treatment conditions (annealing temperature and time, heating rate, etc.). These materials, referred to as FINEMET, were first investigated by Yoshizawa et al.[14] to study the magnetic properties of Fe-base alloys. This simple method produces large quantities of porosity-free material. Further, samples with different grain sizes can be synthesized by controlling the crystallization process, affording a way of comparing the properties of amorphous, nanocrystalline, and coarse-grained materials of

the same composition[3].

Commercial utilization of nanocrystalline materials requires consolidation of the powder into useful shapes and also to establish the structure-property correlations. However, successful consolidation of nanocrystalline powders is a non-trivial problem since fully dense materials should be produced while simultaneously retaining the nanometer-sized grains. Conventional consolidation techniques generally use high pressures and elevated temperatures for an extended period of time to achieve full densification. But, retention of nanostructures requires use of low consolidation temperatures while the achieving of full (theoretical) density requires use of high temperatures. In spite of these opposing requirements, successful consolidation of nanocrystalline powders has been achieved by controlling the process parameters during electrodischarge compaction, plasma activated sintering, shock (explosive) compaction, hot isostatic pressing, and Ceracon processing[1].

STRUCTURE

In nanocrystalline single-phase alloys and pure metals, the most important structural parameter is the grain size. The properties of materials are mostly dependent on the grain size and therefore, an accurate determination of the grain size is important. Both direct (electron microscopic) and indirect (scattering) techniques have been employed to determine the grain sizes. However, for microchemical analysis on the requisite fine scale, further advances in the state-of-the-art of instrumental capabilities will be necessary to obtain the desired lateral scale resolution. Only the atom probe field-ion microscopy (AP-FIM) or scanning tunneling microscopy (STM) seem to offer the required lateral scale resolution for determining the chemistry at present.

Transmission electron microscopic (TEM) techniques (especially, the high-resolution TEM studies) are ideal to directly determine the grain sizes

of nanocrystalline materials using the dark-field technique. The width of a Bragg reflection in an X-ray (large-angle) diffraction pattern can provide grain (or crystal, i.e. the size of the coherently diffracting domain) size information after the appropriate corrections (for instrumental and strain effects) are incorporated. Whereas the TEM techniques can clearly indicate whether there is a distribution of grain sizes and a grain size histogram can be obtained by measuring the grain sizes and counting the number of grains, the X-ray diffraction technique gives only the average crystal size; and, this value depends strongly on which weight function is used when averaging over the size distribution. A number of recent studies discuss the techniques for an accurate measurement of grain sizes and application of X-ray line shape analysis techniques to nanocrystalline materials[1,15].

The structure of the grains (or crystals) in a nanocrystalline material has been normally accepted to be the same as in a coarse-grained material and hence there have not been many investigations into this aspect. However, there are some reports that the crystal structure of the material with an ultra-fine grain size could be different from that of a coarse-grained material. Even if the structure remains the same, the lattice parameter(s) have been found to be slightly different (by about 0.2%), at least in a few cases[3].

The structure of the grain boundaries has received a lot of attention and has been discussed extensively in the literature[1], especially to decide whether it is different in the nanocrystalline and coarse-grained materials of the same composition. The grain boundary structure determines the diffusivity, and consequently the rate of deformation by grain boundary diffusion (Coble creep) and the rates of sintering and grain growth. The conclusions differ and some believe that the structure is fundamentally different in both the types of materials while others believe that it is the same.

Gleiter and co-workers[2,8] studied the structure of nanocrystalline materials using a number of tech-

niques and showed that the grain boundaries in nanocrystalline materials may be random, rather than possessing either the short-range or long-range order normally found in conventional coarse-grained materials. This randomness has been associated with either the local structure of individual boundaries or the structural co-ordination among boundaries[8]. It was also noted that the boundaries in the as-prepared nanocrystalline Pd are in a state with lower atomic short-range order than conventional grain boundaries in polycrystalline materials. The grain boundary free energy of as-prepared nanocrystalline Pd was also computed to be twice that of the relaxed state. EX-AFS (extended x-ray absorption fine structure) studies also indicated a much larger reduction in the atomic co-ordination numbers than that detected by X-ray studies, supporting the concept of wide disordered grain boundaries in nanocrystalline materials. A recent computer simulation study of grain boundaries in nanocrystalline materials[16] reported that (i) long-range periodicity is absent, (ii) grain boundary energy distribution is narrower than in bicrystals, (iii) grain boundaries are wider, but the width distribution is narrower than in bicrystals, and (iv) in the zeroth order, the grain boundaries are an isotropic, cement-like phase, a picture rather dissimilar from the structures found in glasses (which have short-range order) and that derived from bicrystal studies. Based on these results, it has been suggested that the grain boundaries in nanocrystalline materials are fundamentally different from those in conventional coarse-grained materials. All the properties of nanocrystalline materials were thus explained assuming that the material is a mixture of two components-perfect long-range ordered atomic arrangement in the grains and a random interfacial component. But, the details of the atomic structure of the grain boundaries in a given a nanocrystalline material may vary as a function of the time-temperature history of the sample (crystal size and external pressures).

Siegel[17] has recently summarized the literature on the structure of grain boundaries in nanocrystalline materials. Based on the evidence from X-ray diffraction, EXAFS, Mossbauer spectroscopy, Raman spectroscopy, high-resolution TEM images, and computer simulations, he has shown that the grain boundary structure in nanocrystalline materials is similar to that in coarser-grained conventional material. He has also concluded that the atoms that constitute the grain boundary volume in nanocrystalline materials have sufficient mobility during cluster consolidation to accommodate themselves into relatively low-energy configurations. The possible effects of high-resolution TEM specimen surfaces on the grain boundary structure further supported the reliability of such structural observations. He concluded that "indeed, the frequent lack of recognition of significant surface and porosity (and probably adsorbed impurity, as well) contributions to many of the surface-sensitive structural measurements on nanophase materials that have been used to deduce information about their grain boundary structures has undoubtedly exacerbated the problem of elucidating their nature".

From the above, it is apparent that the question of whether the structure of grain boundaries in nanocrystalline materials is basically different from the coarse-grained crystals is not answered clearly. Further and more local investigations are required to get a clearer picture of this aspect.

THERMAL STABILITY

The thermal stability of nanocrystalline materials is of great importance for potential technological applications. Grain growth occurs in polycrystalline materials to decrease the interfacial energy and hence the total energy of the system. Since nanocrystalline materials have a highly disordered large interfacial component (and therefore they are in a high energy state), the driving force for grain growth is expected to be high. This driving force is proportional to the specific grain boun-

dary area, and therefore it varies as the inverse of the grain size. Accurate grain growth studies in nanocrystalline materials are difficult since the grain size cannot be accurately determined. Some studies have been, however, conducted by measuring the grain size using direct electron microscopic techniques or estimated from the X-ray diffraction peak broadening values. Grain growth studies have also been conducted by measuring some macroscopic property as a function of temperature or time which is sensitive to grain size, e.g., electrical resistivity, magnetic susceptibility, coefficient of thermal expansion, etc.

Contrary to the expectations, experimental observations suggest that grain growth in nanocrystalline materials, prepared by almost any method, is very small (and almost negligible) up to a reasonably high temperature. It has been suggested that the resistance to grain growth observed in nanocrystalline materials results primarily from frustration[17]. This has been explained on the basis of structural factors such as narrow grain size distribution, equiaxed grain morphology, low energy grain boundary structures, relatively flat grain boundary configurations, and porosity present in the samples. Additionally, grain boundary Zener drag and triple junction drag have been found to be significant in retarding grain growth[1]. In some instances, however, abnormal grain growth has been observed.

Studies of the isothermal grain growth kinetics can provide information on the microscopic mechanism of growth. Isothermal grain growth kinetics are frequently described by the equation:

$$d - d_o = Kt^{1/n}$$

where d is the grain size at time t and a constant temperature T, d_o is the initial grain size, K is a constant and n is the grain growth exponent. The activation energy for grain growth, Q can also be obtained from the equation:

$$K = K_o \exp(-Q/RT)$$

where K_o is a pre-exponential constant and R is

the gas constant. Both Q and n are important parameters in describing the kinetics and mechanism of grain growth.

The observed grain growth exponent in nanocrystalline materials has been found to vary from low values of 2 to as high a value as 8, different from the value of 2 deduced from the parabolic relationship for grain growth in coarse-grained materials. This suggests that the grain growth behavior in nanocrystalline materials could be complicated and very different from that in the coarse-grained material. Thus, in addition to Zener drag (where a particle interacts with the grain boundary to reduce the energy of the boundary-particle system and restrains the boundary movement), other mechanisms such as pinning of grain boundaries by pores or inclusions also may be operative. In fact, it has been shown that for an initial grain size of 14 nm in TiO_2, when the porosity was about 25%, the grain size after annealing for 20 h at 700℃ was 30 nm. When the porosity was reduced to about 10%, the grain size for a similar annealing treatment was dramatically increased to 500 nm[18]. Grain growth can also occur in nanocrystalline materials during consolidation of the powder, which requires exposure of the powder to high temperatures and pressures for extended periods of time. But, this has not been a serious concern in many cases[19]. Depending on the alloy system under consideration, the activation energy for grain growth in nanocrystalline materials appears to be close to the value for volume diffusion, grain boundary diffusion, or activation energy for crystallization of the amorphous phases[13].

PROPERTIES

Because of the very fine grain sizes and consequent high density of interfaces, nanocrystalline materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained materials. These include increased strength/hard-

ness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher coefficient of thermal expansion, lower thermal conductivity, and superior soft magnetic properties. All of these properties are being extensively investigated to explore possible applications for these materials. The reader is referred to some of the review articles[1-3,6,8,9] and some of the recent conference proceedings[4,5] for detailed results on these properties.

Mechanical Properties

The elastic constants of nanocrystalline materials have been found to be reduced by 30% or less, interpreted as due to the large free volume of the interfacial component and alternatively as due to the level of porosity and state of cracks present in the sample. The 'most significant change resulting from a reduction in the grain size to the nanometer level is a 4-5 times increase in the strength and hardness over the coarse-grained material. This is also the least understood and most controversial area[1]. The Hall-Petch relationship for conventional coarse-grained polycrystalline materials suggests that the yield strength (or hardness) of a material increases with a decreasing grain size according to the equation:

$$\sigma = \sigma_o + Kd^n$$

where d is the mean grain size, σ is the 0.2% yield strength (or hardness), σ_o is the lattice friction stress to move individual dislocations (or the hardness of a single crystal specimen, K is a constant, and n is the grain size exponent (generally -1/2). Even though the above relationship was obeyed by a number of nanocrystalline materials, some instances are also available when, below a critical grain size, the hardness was found to decrease with a decreasing grain size. That is, the slope K has a negative value and this has been termed as the inverse Hall-Petch relationship. Apart from the

sign of K, there are also reports that the grain size exponent n can have very different values, e.g., -1, -1/2, -1/3, and -1/4. Some other investigators have modified the normal Hall-Petch equation by modifying either the grain size exponent and/or the sign and magnitude of the slope K.

The Hall-Petch relationship was derived on the basis of strengthening resulting from dislocation pile-ups at physical obstacles like grain boundaries. Since nanocrystalline materials have extremely small grain sizes, Frank-Read sources may not be operating. Therefore, enough number of dislocations will not generate and migrate to have a pile-up, and so it is doubtful if strengthening could occur by this mechanism; other mechanisms may have to be invoked. While some people accept that the inverse Hall-Petch relationship is real and some theoretical explanations have been offered for its occurrence, others believe that this is an anomaly and caution that when a higher temperature for consolidation or annealing is used to increase the grain size, the size of flaws in the material could decrease or the density and/or the internal stresses in the compact could change. Then, these effects will also have to be considered while discussing the inverse Hall-Petch effect. The reader is referred to Ref. 1 for a detailed discussion on this aspect.

The hardness and strength of nanocrystalline ceramics also is significantly higher than in the conventional coarse-grained materials. Additionally, it has been shown that nanocrystalline ceramics, e. g., TiO_2 and CaF_2, can be plastically deformed at room temperature due to the increased creep rate as a result of grain boundary sliding due to a combination of fine grain size and increased grain boundary diffusivity. Thus, it can be concluded that the inherently brittle ceramics can be made ductile via nanostructure processing. On the other hand, as shown above, the usually soft metals become hard and strong. Thus, the proportions of dislocation activity and grain boundary sliding responsible for the deformation of nanocrystalline metals and ceramics can be quite different de-

pending on the grain size[6]. With a decrease in grain size, the dislocation activity decreases in metals and grain boundary sliding becomes more prominent. But, in ceramics, the opposite behavior is observed. Contrary to the expectations, ductilization of intermetallics has not been realized, even though superplastic-like flow in compression at room temperature was reported in a nanocrystalline Fe-28A1-2Cr (at. %) intermetallic. Instead, superplastic deformation was observed in nanocrystalline titanium aluminides at higher temperatures[20,21].

It has also been recently reported that very high strengths with acceptable levels of ductilities could be obtained in a material if about 20 vol% of a nanocrystalline phase is uniformly dispersed in an amorphous matrix[22]. This appears to be a fruitful area for further investigations.

Chemical Properties

Since majority of the synthesis methods produce nanocrystalline materials in a powder form, the total surface area available can be accurately controlled by controlling the particle size and porosity in the samples. One can consolidate the material to full density for best mechanical properties, or to a highly porous structure to obtain a large surface area, or to an intermediate value of porosity. Beck and Siegel[23] have shown that the chemical reactivity of nanocrystalline TiO_2 which has been only lightly consolidated is significantly higher than that in other commercially available TiO_2 samples. Nanocrystalline samples do not only have the increased activity, but the high activity is retained for a longer time than in commercial coarse-grained samples. This has been attributed to the large surface area of the nanocrystalline material combined with its rutile structure and its oxygen-deficient composition.

The corrosion behavior of nanocrystalline nickel-base alloys has also been reported[24,25]. As expected, the average dissolution rate of Ni was found to be higher than that for the coarse-grained material. However, the nanocrystalline materials exhibited more uniform corrosion morphology in an acidic medium (the coarse-grained material suffered excessive intergranular corrosion) and superior localized corrosion resistance, attributed to the fine grain size and homogeneity of the nanocrystalline material.

Electrical Properties

Because of the increased volume fraction of atoms lying at the grain boundaries, the electrical resistivity of nanocrystalline materials is found to be higher than that in the coarse-grained material or an amorphous material of the same composition. It has also been shown that the electrical resistivity of nanocrystalline materials is sensitive not only to the grain boundaries but also other types of imperfections and/or stresses introduced by the synthesis process[13]. At a constant temperature, the electrical resistivity increases with a decrease in grain size and for a constant grain size, the electrical resistivity increases with temperature, and both these observations are consistent with the theoretical analysis of scattering of electrons by grain boundaries.

The magnitude of the electrical resistivity (and hence conductivity) in nanocomposites can be changed by altering the grain size of the electrically conducting component. For example, by changing the volume fraction of iron particles in a nanocrystalline iron-silica system, the electrical conductivity could be changed by 14 orders of magnitude.

It has been recently reported that pure nanocrystalline ZnO with a 60 nm diameter grain size can exhibit varistor behavior (constant voltage over a wide range of current) with a small, but usable threshold voltage of 0.1 kV/cm[26]. Further, by doping 3-10 nm ZnO with elements like B, Bi, Co, Cu, Sb, and Sn the varistor active range could be extended to 30 kV/cm[27], affording a means of con-

trolling the voltages between 0.1 and 30 kV/cm by choosing the appropriate dopant.

The phenomenon of giant magnetoresistance (GMR)-drastic decrease of electrical resistivity of materials when exposed to a magnetic field-has been reported in a number of nanocrystalline multilayer and equiaxed systems. Whereas the resistance drop is of the order of 1-2% in conventional materials, the drop in nanocrystalline materials could be as much as 50% or more.

Physical Properties

The specific heat, thermal expansion, and optical properties of nanocrystalline materials also seem to be possible to be tailored by controlling the grain size. The specific heat and thermal expansion of nanocrystalline materials are higher than those of the coarse-grained and amorphous materials of the same composition[1,3]. Since the interfacial component contributes quite significantly to the thermal expansion of nanocrystalline materials, the coefficient of thermal expansion can be tailored to any predetermined value by varying the grain size (and hence the interfacial volume).

The optical properties of nanocrystalline materials have been found to be exciting from both the scientific and technological points of view. The band gap of semiconductors and the optical transparency behavior of materials could be changed by controlling the grain and/or pore size in the nanocrystalline state. For example, the band gap in CdSe semiconductor could be changed from 3.0 eV for clusters of 1.2-1.5 nm to 2.3 eV for cluster sizes of 3.0-3.5 nm due to quantum confinement effects; the bulk material has a band gap of 1.8 eV[28]. By controlling the pore size in nanocrystalline Y_2O_3 to be equivalent to the wavelength of light, scattering could be effected and so the material was opaque. On the other hand, when the pore size was much smaller than the wavelength of light, scattering did not take place and so the material was fairly transparent[29]. The optical absorption characteristics can also be modified by allowing interaction to occur between the nanosized CdS clusters[30].

Magnetic Properties

The ferromagnetic properties of materials are influenced by changes in the interatomic distances. Thus, in comparison to the coarse-grained material, the saturation magnetization and Curie temperature are reduced in the nanocrystalline state. This appears to be true whether the material is produced directly in the nanocrystalline state or obtained by crystallization of the amorphous phase. These reductions were attributed to the deviation of interatomic spacing in the interfacial regions as compared with the crystalline component, supported by Mossbauer spectroscopy measurements.

Attractive magnetic properties have been reported for nanocrystalline Fe-based alloys obtained by crystallization of the amorphous ribbon produced by the rapid solidification method[14,31]. These alloys-sometimes referred to as FINEMET-contain nanometer-sized a-Fe grains embedded in the amorphous matrix. The best soft magnetic properties by this route are obtained by the addition of Cu and at least one element selected from the group consisting of Nb, W, Ta, Zr, Hf, Ti, and Mo to an iron-base alloy having an essential composition $Fe_{74.5-x}$ Cu_xNb_3Si 13.5B_9 (Ref. 14). The magnetic properties of these materials depend on the grain size, and hence on the temperature used for the crystallization. By changing the grain size, the coercivity can be changed by several orders of magnitude. The initial permeability also varied in a similar manner, essentially being inversely proportional to coercivity.

While both rapid solidification from the melt and mechanical alloying techniques have been used widely to produce nanocrystalline magnetic alloys, the process parameters can be more easily and accurately controlled in the rapid solidification processing[32,33]. Mechanical alloying seems to be unsuitable for the production of soft magnetic low coercivity alloys, because of the significant in-

troduction of internal strain into the highly magnetostrictive material. Strain removal by annealing leads to undesirable grain growth. Thus, crystallization of amorphous alloys appears to be the best method to synthesize nanocrystalline alloys with attractive soft magnetic properties.

Nanocrystalline materials produced by the crystallization of amorphous alloys (FINEMET alloys) show an excellent combination of magnetic characteristics. They have a low coercivity (5-10 A cm^{-1}), high permeability (100,000), almost zero magnetostriction (0 to 2×10^{-6}), and low core losses (-200 kW m^{-3}) due to the high resistivity (135 μohm-cm) of these alloys. Further, the shape of the hysteresis loop can be altered by magnetic field annealing. All the above characteristics, in combination with good thermal stability, suggest that nanocrystalline Fe-based alloys are very promising candidates for soft-magnetic applications.

A useful magnetic property that nanocomposites offer is called the magnetocaloric effect. When a material containing extremely small magnetic particulates in a non-magnetic or weakly magnetic matrix is placed in a magnetic field, the magnetic spins of the particulates tend to align with the field. This increase in magnetic order lowers the magnetic entropy of the spin system. If this process is performed adiabatically (i.e., no heat is exchanged with the surroundings), the reduction in spin entropy is offset by an increase in lattice entropy, and the specimen temperature will rise. This temperature rise is reversible (the specimen cools down on removal of the magnetic field) and is known as the magnetocaloric effect. Shull and co-workers[34] have extensively investigated this phenomenon and predicted that the magnetocaloric effect may be enhanced at low fields and high temperatures.

APPLICATIONS

Nanocrystalline materials are relatively new and it is only during the last few years that researchers have started exploring the many potential benefits of these materials. Several potential applications have been suggested for these materials, but many of these are either in the laboratory stage or in early experimentation. It is most unlikely that the applications of these materials are decided on the basis of any one single property, but will be based mostly on the combination of a number of desirable properties. Some of the suggested potential applications of nanocrystalline materials can be found in Refs. 1, 35, and 36.

It has been known that the fracture toughness of ceramics can be considerably enhanced by dispersing in them a second phase on a microscopic scale. Since reducing the grain size to nanometer dimensions can provide increased strength and hardness, it is suggested that fabrication of micro/nanohybrids will lead to a new class of superstrong and supertough ceramics. In these hybrids, a nanocomposite matrix is reinforced with submicrometer-sized particles-whiskers, platelets, or long fibers-and these hybrids show enhanced fracture toughness and strength up to very high temperatures; the properties of coarse-grained composites normally degrade at these temperatures. Further, nanoreinforcements increase the creep resistance by suppressing grain boundary sliding. Nanocrystalline WC-Co composites have been shown to have higher hardness and toughness, four times better wear resistance and more than double lifetime in cutting tools than conventional coarse-grained composites. Applications for such powders include fine drill bits for drilling holes in printed circuit boards and rotary cutting tools (because of the fine grain size, sharp edges, and smooth surface finish).

Since ceramics and conventionally brittle intermetallics can be rendered ductile by nanostructure processing, these materials can be formed to near-net shapes by means of deformation processing methods previously applicable only to produce ductile metal parts. In fact, one report suggests that nanocrystalline silicon nitride can be fabricated like chewing gum!

The improved hardness coupled with better corrosion and wear resistance of nanocrystalline electrodeposits makes them strong contenders for protective coating applications[36]. These materials can be used as hard facing on softer, less wear-resistant substrates to improve the life-time resulting in cost savings. A nanocrystalline nickel coating on Nd-Fe-B hard magnets provided the required wear and corrosion resistance. Ontario Hydro Technologies developed the Electrosleeve™ steam generator tube repair technology based on bulk nanostructured electrodeposits. The technology produces a nanostructured nickel microalloy sleeve (several hundred microns thick) having a continuous high strength metallurgical bond to the steam generator tube, superior strength and ductility, and resistance to wear, fatigue, and corrosion.

Nanocrystalline coatings deposited by laser plasma discharge increased the life of ZnS samples more than five times against abrasion/erosion/rain water corrosion/impact damage. A double layer coating has been found to be a suitable method to improve the mechanical properties and recording characteristics of amorphous-ultrafine films; controlling the thickness of the polymer coating is still a problem. Multilayered nanoscale structures also have superior sliding wear resistance at low loads compared to their coarse-grained counterparts.

The increased diffusion rates in nanocrystalline materials considerably reduce the temperatures at which sintering can occur in these materials. The enhanced diffusivity can be used to make oxygen sensors and fuel cells capable of operating at much lower temperatures than systems currently in use. Nanocrystalline ceramics may also be a good candidate material for joining ceramic parts. The enhanced diffusion rates may also make it possible to subject the nanocrystalline materials (both metals and ceramics) to near-net shape forming. When required to be used at high temperatures, the creep resistance may be improved by annealing at high temperatures to achieve grain growth.

The large surface area of nanocrystalline materials can be used for catalysis purposes. Nanocrystalline Ni-Mo alloys produced by mechanical alloying have been found to be more electro-active than conventional polycrystalline alloys. It was determined that the overpotential of the cathodic hydrogen evolution reaction (HER) in high temperature caustic media was reduced considerably. Thus, nanoprocessed HER electrodes of superior elctrocatalytic properties could be produced.

The electrical and magnetic properties of nanocrystalline materials will probably form the basis for their widespread and industrial applications. A new class of electrically conducting, diamond-like nanocomposites with conductivity varying over 18 orders of magnitude have been synthesized. Extremely stable metal-dielectric multilayer structures without interfacial structural boundaries have also been fabricated. The unique combination of diamond-like chemical and mechanical properties with high electrical conductivity could lead to applications in the semiconductor and microelectronics industries as well as in battery technology. The phenomenon of giant magnetoresistance (GMR) can be used for the recording heads of the next generation of information storage systems. The excellent combination of soft magnetic properties of nanocrystalline materials could be useful in producing tape-wound cores for common mode chokes, saturable reactors, high frequency transformers, and magnetic heads. The phenomenon of magnetocaloric effect can be used for magnetic refrigeration, avoiding the use of harmful chlorofluorocarbons.

Nanocrystalline high melting point compounds have been recommended for use in catalysis, manufacture of filters, tools, ductile ceramics and electrical and magnetic appliances. Of these, applications to cutting tools seem to be the most promising. Nanocrystalline ceramics have also been suggested for use in diesel engines[37]

CONCLUDING REMARKS

Nanocrystalline materials are novel materials

which are not only scientifically interesting but also hold great potential for a number of applications. Their properties are different from and often superior to those of conventional coarse-grained polycrystalline materials and also amorphous alloys of the same composition.

Widespread use and search for technological applications of nanocrystalline materials requires the availability of large (tonnage) quantities of well-characterized material with reproducible properties; and this needs to be done economically. Even though nanocrystalline powders are now more expensive than the more commercially available coarse-grained powders, greater usage and tonnage production will bring down the cost. In this respect, one can recall the case of metallic glass tapes produced by the rapid solidification processing, now being used commercially for transformer core laminations. While the tapes costed US $300 per Kg in late 1978 when they were first produced they now cost only about $2[38]. A solution to the barriers for commercial utilization of nanocrystalline materials can be identification of well-defined applications for these materials and this can be a driver for accelerated research. In this context, development of novel synthesis methods to produce these materials in commercially viable quantities is an urgent necessity. Simultaneously, the properties of the existing materials need to be significantly improved. Further studies on nanoglasses, nano-quasicrystalline alloys, and nanocomposites are required to evaluate the properties and compare these with the nanocrystalline alloys.

ACKNOWLEDGMENTS

REFERENCES

1. C. Suryanarayana, Internat. Mater. Rev., **40**, (1995) 41.
2. H. Gleiter, NanoStructured Mater., **6**, (1995) 3.
3. K. Lu, Mater. Sci. Eng. Reports, **R16**, (1996) 161.
4. G. C. Hadjipanayis and R. W. Siegel (eds.), *Nanophase Materials: Synthesis, Properties, Applications*, Kluwer, Dordrecht, The Netherlands (1994).
5. C. Suryanarayana et al. (eds.), *Processing and Properties of Nanocrystalline Materials*, TMS, Warrendale, PA (1996).
6. R. W. Siegel, NanoStructured Mater., **4**, (1994) 121.
7. K. T. Aust, U. Erb, and G. Palumbo, in Ref. 5, p. 11.
8. H. Gleiter, Prog. Mater. Sci., **33**, (1989) 223.
9. R. W. Siegel, in *Processing of Metals and Alloys* (ed. R.W. Cahn), VCH, Weinheim, Germany (1991) 583.
10. C. C. Koch, NanoStructured Mater., **2**, (1993) 109.
11. B. H. Kear and L. E. McCandlish, NanoStructured Mater., **3**, (1993) 19.
12. U. Erb, NanoStructured Mater., **6**, (1995) 533.
13. I. Bakonyi, E. Toth-Kadar, J. Toth, T. Tarnoczi, and A. Cziraki, in Ref. 5, 465.
14. Y. Yoshizawa, S. Oguma, and K. J. Yamauchi, J. Appl. Phys., **64**, (1988) 6044.
15. J. Weismuller, J. Lofler, C. Krill, R. Birringer, and H. Gleiter, in preparation; quoted by J. Weismuller, in *Synthesis and Processing of Nanocrystalline Powder* (ed. D.L. Bourell), TMS, Warrendale, PA (1996) 3.
16. S. R. Phillpot, D. Wolf, and H. Gleiter, J. Appl. Phys., **78**, (1995) 847.
17. R. W. Siegel, in Materials Interfaces: *Atomic Level Structure and Properties* (eds. D. Wolf and S. Yip), p. 431, Chapman & Hall, London (1992).
18. H. Hahn, J. Logas, and R.S. Averback, J. Mater. Res., **5**, (1990) 609.
19. C. Suryanarayana, G. E. Korth, and F. H. Froes, Metall. Mater. Trans. A, (1997) (in press). 20. R. Bohn, M. Oehring, Th. Pfullmann, F. Appel, and R. Bormann, in Ref. 5, 355.
21. R. S. Mishra, A. K. Mukherjee, D. K. Mukhopadhyay, C. Suryanarayana, and F. H. Froes, Scripta Mater., **34**, (1996) 1765.
22. A. Inoue, Y. Horio, Y. H. Kim, and T. Masumoto, Mater. Trans. JIM, **33**, (1992) 669.
23. D. D. Beck and R. W. Siegel, J. Mater. Res., **7**, (1992) 2480.
24. S. J. Thorpe, B. Ramaswami, and K. T. Aust, J. Electrochem. Soc., **135**, (1988) 2162.
25. R. Rofagha, U. Erb, D. Ostrander, G. Palumbo, and K.T. Aust, NanoStructured Mater., **2**, (1993) 1.
26. J. T. Lee, J. H. Hwang, J. J. Mashek, T. O. Mason, A. E. Miller, and R. W. Siegel, J. Mater. Res., **10**, (1995) 2295.

27. R. N. Viswanath, S. Ramasamy, R. Ramamoorthy, P. Jayavel, and T. Nagarajan, NanoStructured Mater., **6**, (1995) 993.

28. M. L. Steigerwald and L. E. Brus, Ann. Rev. Mater. Sci., **19**, (1989) 471.

29. G. Skandan, H. Hahn, and J. C. Parker, Scripta Metall. Mater., **25**, (1991) 2389.

30. G. D. Stucky and J. E. Mac Dougall, Science, **27**, (1990) 669.

31. Y. Yoshizawa and K. Yamauchi, Mater. Trans. JIM, **31**, (1990) 307.

32. K. H. Muller, P.A.P. Wendhausen, N. M. Dempsey,. V. Neu, W. Grunberger, and L. Schultz, in Ref. 5, 429.

33. H. A. Davies, I. Ahmad, and R. A. Buckley, in Ref. 5, 441.

34. R. D. Shull, R. D. McMichael, and J. J. Ritter, NanoStructured Mater., **2**, (1993) 205.

35. H. Hahn and K. A. Padmanabhan, NanoStructured Mater., **6**, (1995) 191.

36. C. Cheung, D. Wood, and U. Erb, in Ref. 5, 479.

37. R. A. Andrievski, J. Mater. Sci., **29**, (1994) 614.

38. C. H. Smith, in *Rapidly Solidified Alloys: Processes, Structures, Properties, Applications* (ed. H.H.Liebermann), Marcel Dekker, Inc., New York (1993) 617.