The Structure and Properties of Nanocrystalline Materials: Issues and Concerns

C. Suryanarayana

In this article, issues and concerns arising from the present research into nanocrystalline materials are highlighted.

INTRODUCTION

Due to their novel properties and varied potential applications, nanocrystalline materials, with typical grain sizes <100 nm, are attracting increasing attention from researchers all over the world.[1-6] These materials are traditionally classified as one-dimensional (1-D), or layered structures, two-dimensional (2-D), or rod- or wire-like, and three-dimensional (3-D), or equiaxed, with the 1-D layered and 2-D wire-like structures being extensively investigated for coating and electronic applications and the 3-D equiaxed structures exploited for potential structural or bulk applications. Because of the small grain size of these materials, and consequently the large volume fraction of atoms in or near the grain boundaries, these materials exhibit properties that are often superior, and sometimes completely new, in comparison to those of conventional coarse-grained materials. Figure 1 shows a summary of the properties of nanocrystalline materials in comparison to their coarse-grained counterparts. In this figure, an upward arrow indicates an improvement in the property, while a downward arrow indicates a decrease in the property. However, it should be realized that a full understanding of the structure, thermal stability, and properties of these novel materials is not yet available. A number of issues and concerns still need to be solved.

SYNTHESIS/PROCESSING

Nanocrystalline materials can be synthesized by a number of techniques with the starting material existing either in the vapor, liquid, or solid state. Inert-gas condensation, in which the evaporated material is quenched onto a cold substrate, was the first technique used to synthesize nanocrystalline metals and alloys. Subsequently, plasma processing and other physical and chemical vapor deposition techniques have also been used. Electrodeposition and rapid solidification processing use the liquid state as the starting material. Mechanical alloying, friction stir welding, severe plastic deformation, spark erosion, sliding wear, and repeated cold rolling produce nanocrystalline materials in the solid state. While some of these techniques are commercially in use for large-scale production purposes (e.g., inert-gas condensation, electrodeposition, and mechanical alloying), many of the other techniques are essentially used for laboratory investigations.

The choice of technique for the synthesis of nanocrystalline materials is determined by the ease of the process, its economic viability, its scalability, and the purity of the end product desired. Most of the techniques referred to previously produce the nanocrystalline material in the form of powder. The application of nanocrystalline materials requires that these powders are consolidated to full density with minimal or no porosity, and this is not a trivial matter. Full densification with complete interparticle bonding requires exposure of the powder to high temperatures and pressures for extended periods of time, which is likely to coarsen the microstructural features. Retention of the material in the nanocrystalline state, however, warrants that the powder is not taken to high temperatures for long periods of time; this may not result in complete densification. Thus, successful consolidation to full density requires innovative methods of consolidation. However, since nanocrystalline materials have a large fraction of the atoms in the grain boundaries, the (effective) diffusivity of nanocrystalline materials is much higher than that of a coarse-grained material of the same composition. This will facilitate achieving full consolidation of nanocrystalline materials at temperatures 300°C to 400°C lower than those required for the coarse-grained materials. Successful consolidation of nanocrystalline powders has been achieved by electrodischarge compaction, plasma-activated sintering, shock (explosive) consolidation, hot isostatic pressing (HIP), Ceracon processing, hydrostatic extrusion, strained powder rolling, and sinter forging.[7] Consolidation is not required if the powder could be used as-is (e.g., in slurries, as catalysts, or for coating purposes).

Figure 1. The properties of nanocrystalline materials in comparison to their coarse-grained counterparts. An upward arrow indicates an improvement in the property, while a downward arrow indicates a decrease.
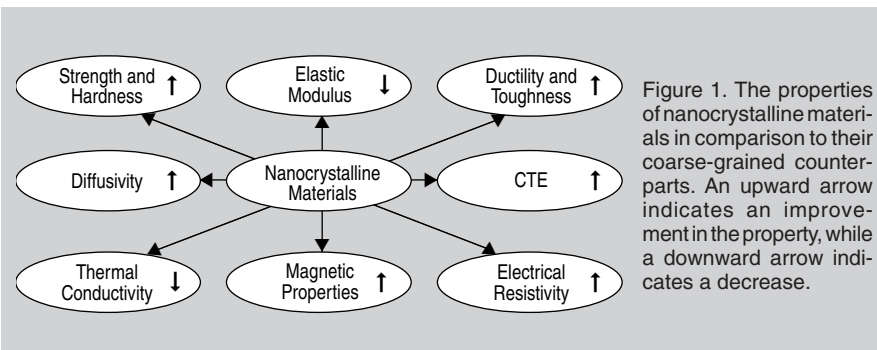
Figure 2 shows a transmission electron micrograph of a mechanically alloyed Ti-24Al-11Nb (at.%) alloy powder HIPed at 900°C.[8] The microstructure exhibits a bimodal distribution of grain sizes. The smaller grains measuring about 100 nm are devoid of any internal structure (under any operating diffraction conditions in the transmission electron microscope [TEM]) and have been identified as belonging to the B2 phase. On the other hand, the larger grains, measuring about 200 nm, contain a high density of internal (lamellar) structure and have been identified as a mixture of the B2 and the orthorhombic "O" phases. A similar bimodal structure was observed in this alloy at other consolidation temperatures. The only difference was that the proportion of the orthorhombic "O" to the B2 phases increased with increasing consolidation temperature, suggesting that equilibration is occurring at higher consolidation temperatures. The grain size also increased with increasing consolidation temperature. Full densification could be achieved in this alloy at a low temperature of 725°C.

STRUCTURE

The volume fraction of atoms residing in or near the grain boundaries increases as grain size decreases. Consequently, in materials with a small grain size of a few nanometers, the fraction of atoms in the grain boundaries is comparable to that in the grains. Therefore, nanocrystalline materials can be considered to consist of two structural components—the small crystallites with long-range order and different crystallographic orientations constituting the "crystalline component," and a network of intercrystalline regions (grain boundaries, triple junctions, etc.), the structure of which differs from region to region and is referred to as the interfacial component. A number of studies have been devoted to understanding the structure of the crystallites and the interfaces. It has been noted that the structure of the crystallites is essentially the same as that of the coarse-grained materials, with the difference that the lattice parameters in the nanocrystalline condition are slightly larger (0.2% to 0.8%).[9,10] Even though this has been reported in nanocrystalline materials obtained by crystallization of the

Figure 2. A transmission electron micrograph of a Ti-24Al-11Nb (at.%) alloy powder mechanically alloyed and hot isostatically pressed at 900°C, 207 MPa pressure for 2 h. The smaller grains (without any internal structure) are the B2 phase and the larger grains (with a lamellar structure) represent a mixture of the B2 and orthorhombic "O" phases.

amorphous phase, this has not been reported in nanocrystalline materials prepared by other techniques. The structure of the grain boundaries, however, was investigated in great detail using high-resolution TEM techniques; the results are still inconclusive. There are two schools of thought regarding the grain boundary structures—one suggesting a gas-like disorder at the grain boundaries[11] and the other suggesting that the structure of the grain boundaries is the same in both nanocrystalline and coarse-grained materials.[12] The latter suggestion has gained widespread acceptance in recent years.[13]

THERMAL STABILITY

Because of their small grain size, and, consequently, large surface area, nanocrystalline materials exhibit a strong driving force for grain growth. Knowledge of the thermal stability of nanocrystalline materials is important for both scientific and technological reasons. From a technological point of view, the thermal stability is important for consolidation of nanocrystalline powders without coarsening the microstructure. From a scientific point of view, it would be instructive to check whether the grain growth behavior in nanocrystalline materials is different from that in coarse-grained materials. Grain growth in conventional materials is described

by the equation:

$$D^n - D_0^n = K_0 \exp\left(-\frac{Q}{RT}\right)t$$

where D is the grain size on annealing the sample at temperature T for time t, D_0 is the initial grain size, n is the grain-growth exponent, K_o is a pre-exponential constant, Q is the activation energy for grain growth, and R is the gas constant. Both Q and n are important parameters in describing the kinetics and mechanism of grain growth. Ideally, n is expected to be 2, suggesting a parabolic relationship for grain growth; but the observed values in nanocrystalline materials were found to vary from as low as 2 to as high as 10.[14] Further, it has been noted that the value of n decreases toward 2 only when annealing is conducted at relatively high homologous temperatures (T/T_m, where T_m is the melting or liquidus temperature of the material). Coarse-grained materials also exhibit a similar trend. In fact, the ideal value of n = 2 has only been observed in high-purity elements such as cadmium, iron, and tin and at high values of T/T_m.[15] Among the factors that may be responsible for the higher values of n are pinning of grain boundaries and solute segregation to grain boundaries.

The activation energy for grain growth in nanocrystalline materials has normally been compared to the activation energy for either lattice (Q_l) or grain boundary (Q_{gb}) diffusion in coarse-grained materials. It has been clearly noted that the activation energy for grain growth in nanocrystalline materials compares more favorably with Q_{gb} than with Q_l, although a few exceptions have been reported. It has also been reported that Q for grain growth at higher temperatures (e.g., > 500°C for nanocrystalline iron) compares favorably with Q_l, while at lower temperatures, it compares favorably with Q_{gb}, suggesting that the mechanism of grain growth in nanocrystalline materials at low temperatures is different from that in coarse-grained materials.[16] Contrary to expectations, grain growth in nanocrystalline materials, prepared by any method, is very small up to a reasonably high temperature. This resistance to grain growth has been attributed to factors such as narrow grain size distribution, equiaxed grain morphology, low-energy grain boundary

structures, relatively flat grain boundary configurations, and porosity of the consolidated samples. In some instances, however, abnormal grain growth has been observed.[17]

PROPERTIES

Because of the very small grain size and consequent high density of interfaces, nanocrystalline materials exhibit a variety of properties that are different and often superior to those of conventional coarse-grained materials. These include increased strength/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 magnetic properties. It is becoming increasingly clear, however, that the early results on the properties of nanocrystalline materials are not very reliable, mainly due to the significant amount of porosity present in those samples. Thus, for example, the room-temperature ductility in ceramic samples has not been reproduced. Even though some researchers have confirmed that the coefficient of thermal expansion increased with a decrease in grain size,[18] others reported that it was approximately the same for both the nanocrystalline and coarse-grained materials.[19] Similarly, the decrease in the modulus of elasticity could be related to the porosity and cracks present in the consolidated material.[20] Thus, it is important to evaluate the properties only in materials that are fully dense and have no porosity, cracks, or discontinuities.

Even though the different properties of nanocrystalline materials have been evaluated, the mechanical properties are the most important for commercial applications and, perhaps, the least

understood. This has been mostly due to the non-availability of sufficiently large and defect-free samples for meaningful and reliable tensile testing. Thus, hardness has been the most common measure to evaluate the mechanical properties of nanocrystalline materials.

It has been well documented in the literature that a decrease in grain size will result in an increase in the hardness and yield strength according to the Hall-Petch equation:

$$\sigma \text{ (or } H) = \sigma_o \text{ (or } H_o) + K\, d^{-n}$$

where σ is the 0.2% yield strength of the material, σ_o is the lattice friction stress to move individual dislocations, K is a constant, d is the grain size, and n is the grain size exponent. n usually has a value of 1/2, although very different values (e.g., 1, 1/3, and 1/4) have also been reported. In this equation, H represents the hardness and H_o represents the hardness of a single crystal. Such a relation has also been shown to follow down to nanometer dimensions and, in comparison to a coarse-grained material, a 4–5 times increase in hardness has been reported for most nanocrystalline materials. However, some people have also reported softening with a decrease in grain size;[21] this has come to be known as the inverse Hall-Petch behavior. Since the Hall-Petch equation was developed based on the dislocation activity in coarse-grained materials and because nanocrystalline materials with very small grain sizes cannot support dislocations, it is reasonable to expect that dislocation activity will be minimal and consequently, hardening is not expected. By equating the repulsive force between dislocations and the applied force, one could calculate the critical grain size below which grain size softening would be observed. This value is calculated to be about 10–30 nm for most materials.

Figure 3 shows the variations of hardness plotted against the reciprocal of the square root of the grain size for γ-TiAl samples. The data includes results from consolidated samples of mechanically alloyed powders, inert-gas condensed powders, ingot-processed material, and thermomechanically processed material.[22] It may be seen that the hardness values obey the Hall-Petch relationship for grain sizes larger than about 30 nm. At smaller grain sizes, the hardness decreased with decreasing grain size. A similar relationship is noted for other materials, also. Since the size and number of flaws in the material could decrease and the internal stresses in the sample could change as a result of annealing to change the grain size, some people believe that the inverse Hall-Petch relation is an anomaly.[23] But, the inverse Hall-Petch relationship is being reported in a number of materials; there has been much discussion in the scientific literature recently about this aspect.[24,25]

The strength of nanocrystalline materials is much higher than that of a coarse-grained material. However, another approach to synthesize high-strength materials appears to be to produce a nanocrystalline composite with a nano-sized phase dispersed in an amorphous matrix. This could be achieved by producing a fully amorphous phase by techniques such as rapid solidification from the melt or mechanical alloying and allowing low-temperature primary crystallization to effect the formation of a nanocrystalline phase. Alternately, an appropriate alloy composition could be chosen to directly produce the nanocomposite. Such nanocomposites have been shown to have strength values much higher than their fully amorphous counterparts. For example, an $Al_{85}Ni_5Y_8Co_2$ (at.%) alloy was gas atomized to produce the amorphous phase, which had a compressive strength of 370 MPa at 483 K. On crystallizing this alloy at 533 K, pure aluminum particles of 10 nm to 30 nm precipitated and were uniformly dispersed in the amorphous matrix. This nanocomposite had a compressive strength of 1,130 MPa. The alloy was fully crystalline on annealing at a higher temperature of 693 K, when it contained pure aluminum, Al_3Y, and an Al-Ni-Y-Co intermetallic, with a compressive
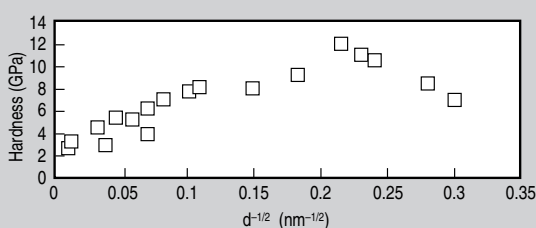

Figure 3. A plot of hardness vs. reciprocal of the square root of grain size for γ-TiAl alloys processed by different methods. Note that the hardness increases with a decrease in grain size up to about 30 nm following the normal Hall-Petch behavior. Below this value, the hardness decreases with a decrease in grain size (negative Hall-Petch behavior).

strength of 1,420 MPa and a plastic strain of 1%.[26] Similar results have been reported in other alloy systems.[27]

The major driver for research in nanostructured intermetallics and ceramic materials has been the promised improvement in ductility. It is well established that a decrease in grain size lowers the ductile-brittle transition temperature (DBTT) and, therefore, nanocrystalline materials should exhibit a lower DBTT than their coarse-grained counterparts. Further, the Coble creep equation suggests that the strain (creep) rate is given by:

$$\frac{d\varepsilon}{dt} = \frac{B\sigma\Omega\Delta D_b}{d^3 kT}$$

where $d\varepsilon/dt$ is the creep rate, σ is the applied stress, Ω is the atomic volume, Δ is the grain boundary width, D_b is the grain boundary diffusivity, d is the grain size, k is the Boltzmann constant, T is the temperature, and B is a constant. Accordingly, if the grain size is decreased from 10 μm to 10 nm (by three orders of magnitude), the creep rate should increase by nine orders of magnitude. Additionally, the grain boundary diffusivity is higher in nanocrystalline materials. The combination of these effects is expected to significantly increase the creep rate of nanocrystalline materials, allowing the ceramics and intermetallics to be deformed plastically even at room temperature.

The results of ductility measurements on nanocrystalline materials are mixed and are sensitive to flaws and porosity, surface finish, and method of testing (e.g., tension vs. compression). Available results show that the elongation to failure is lower with a decrease in grain size. Further, conventional materials that exhibit high ductility show reduced ductility in the nanocrystalline state and improvements in ductility have been observed in the nanocrystalline state, when the coarse-grained counterparts show very limited ductility. This has been attributed to the different degrees of dislocation activity in the conventional materials; significant dislocation occurs in ductile materials, whereas it is limited in ceramic materials. Also, dislocation generation and movement are difficult in nanocrystalline materials.

Recent results, however, indicate increased ductility in nanocrystalline high-strength materials. Lu et al.[28] have recently prepared fully dense nanocrystalline copper with a grain size of 27 nm by electrodeposition. They reported that this material had a tensile ductility of 30% even though the tensile strength was as high as 202 MPa. Coarse-grained copper exhibits this large elongation only when the tensile strength is about 120 MPa. Extensibilities of over 5,000% without any cracking were also reported when the copper specimen with a grain size of 20 nm was rolled at room temperature.[29]

The promised room-temperature superplasticity has not been observed in any nanocrystalline material so far, although the temperature at which superplasticity was observed is more than 400°C less than that required for coarse-grained materials. For example, superplasticity has been reported in nanocrystalline nickel (20 nm),[30] Ni$_3$Al (50 nm),[30] and Ti$_3$Al (100 nm) at 350°C, 650°C, and 600°C, respectively, whereas the temperatures required for observance of superplasticity in the coarse-grained materials were 820°C, 1,100°C, and 1,100°C, respectively. More work needs to be done to elucidate this important aspect of nanocrystalline materials.

CONCLUSION

Widespread use and the search for technological applications require the economical production of well-characterized nanocrystalline materials in tonnage quantities and with reproducible properties. This calls for new and innovative methods for the synthesis and consolidation of nanocrystalline powders. The identification of well-defined applications for these materials can be a driver for accelerated R&D in this area. The use of nanocrystalline materials for hydrogen storage (and recovery), as catalysts, coatings, and for use in slurries and paints are the upcoming applications. Applications of nanostructured materials are in their infancy, but the explosion of interest and infusion of funding in this area is expected to provide an early maturation.

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C. Suryanarayana is with the Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida.

For more information, contact C. Suryanarayana, Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, Fl 32816-2450; (407) 823-6662; fax (407) 823-0208; e-mail: csuryana@mail.ucf.edu.