

Chapter 6

Bulk Behavior of Nanostructured Materials

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INTRODUCTION

Bulk nanostructured materials are defined as bulk solids with nanoscale or partly nanoscale microstructures. This category of nanostructured materials has historical roots going back many decades but has a relatively recent focus due to new discoveries of unique properties of some nanoscale materials.

Early in the century, when “microstructures” were revealed primarily with the optical microscope, it was recognized that refined microstructures, for example, small grain sizes, often provided attractive properties such as increased strength and toughness in structural materials. A classic example of property enhancement due to a refined microstructure—with features too small to resolve with the optical microscope—was age hardening of aluminum alloys. The phenomenon, discovered by Alfred Wilm in 1906, was essentially explained by Merica, Waltenberg, and Scott in 1919 (Mehl and Cahn 1983, 18), and the microstructural features responsible were first inferred by the X-ray studies of Guinier and Preston in 1938. With the advent of transmission electron microscopy (TEM) and sophisticated X-ray diffraction methods it is now known that the fine precipitates responsible for age hardening, in Al-4% Cu alloys, for example, are clusters of Cu atoms—Guinier-Preston (GP) zones—and the metastable partially coherent θ' precipitate (Silcock et al. 1953-54; Cohen 1992). Maximum hardness is observed with a mixture of GPII (or θ'') (coarsened GP zones) and θ' with the dimensions of the θ' plates, typically about 10 nm in thickness by 100 nm in diameter. Therefore, the important microstructural feature of age-

hardened aluminum alloys is nanoscale. There are a number of other examples of nanoscale microstructures providing optimized properties. The critical current density J_C of commercial superconducting Nb_3Sn is controlled by grain size and is inversely proportional to grain size, with grain sizes of 50-80 nm providing high values of J_C (Scanlan et al. 1975).

The field of nanocrystalline (or nanostructured, or nanophase) materials as a major identifiable activity in modern materials science results to a large degree from the work in the 1980s of Gleiter and coworkers (Gleiter 1990), who synthesized ultrafine-grained materials by the in situ consolidation of nanoscale atomic clusters. The ultrasmall size (< 100 nm) of the grains in these nanocrystalline materials can result in dramatically improved—or different—properties from conventional grain-size ($> 1 \mu m$) polycrystalline or single crystal materials of the same chemical composition. This is the stimulus for the tremendous appeal of these materials.

While there are a number of bulk properties that may be dramatically changed when the microstructure is nanoscale, this chapter focuses on those for which the recent work with nanostructured materials has been most extensive. These are (1) the mechanical properties of nanostructured materials for a variety of potential structural applications, and (2) ferromagnetic materials with nanoscale microstructures for potential applications as soft magnetic materials and permanent magnet materials, and for other special applications such as information storage, magnetoresistance spin valves, and magnetic nanocomposite refrigerants. Other bulk applications such as hydrogen storage are discussed briefly.

MECHANICAL BEHAVIOR: STRUCTURAL NANOSTRUCTURED MATERIALS

The great interest in the mechanical behavior of nanostructured materials originates from the unique mechanical properties first observed and/or predicted for the materials prepared by the gas condensation method. Among these early observations/predictions were the following:

- lower elastic moduli than for conventional grain size materials—by as much as 30 - 50%
- very high hardness and strength—hardness values for nanocrystalline pure metals (~ 10 nm grain size) are 2 to 7 times higher than those of larger grained ($> 1 \mu m$) metals
- a negative Hall-Petch slope, i.e., decreasing hardness with decreasing grain size in the nanoscale grain size regime
- ductility—perhaps superplastic behavior—at low homologous temperatures in brittle ceramics or intermetallics with nanoscale grain sizes, believed due to diffusional deformation mechanisms

While some of these early observations have been verified by subsequent studies, some have been found to be due to high porosity in the early bulk samples or to other artifacts introduced by the processing procedures. The following summarizes the author's understanding of the state of the art of the mechanical behavior of nanostructured materials, as determined from the literature, presentations at the U.S. workshop (Siegel et al. 1998), and the WTEC panel's site visits in Japan and Europe.

Elastic Properties

Early measurements of the elastic constants on nanocrystalline (nc) materials prepared by the inert gas condensation method gave values, for example for Young's Modulus, E , that were significantly lower than values for conventional grain size materials. While various reasons were given for the lower values of E , it was suggested by Krstic and coworkers (1993) that the presence of extrinsic defects—pores and cracks, for example—was responsible for the low values of E in nc materials compacted from powders. This conclusion was based on the observation that nc NiP produced by electroplating with negligible porosity levels had an E value comparable to fully dense conventional grain size Ni (Wong et al. 1994, 85). Subsequent work on porosity-free materials has supported these conclusions, and it is now believed that the intrinsic elastic moduli of nanostructured materials are essentially the same as those for conventional grain size materials until the grain size becomes very small, e.g., < 5 nm, such that the number of atoms associated with the grain boundaries and triple junctions becomes very large. This is illustrated in Figure 6.1 for nanocrystalline Fe prepared by mechanical attrition and measured by a nano-indentation technique. Thus, for most nanostructured materials (grain size > 10 nm), the elastic moduli are not unique properties and not a “negative.”

Hardness and Strength

Hardness and strength of conventional grain size materials (grain diameter, $d > 1 \mu\text{m}$) is a function of grain size. For ductile polycrystalline materials the empirical Hall-Petch equation has been found to express the grain-size dependence of flow stress at any plastic strain out to ductile fracture. In terms of yield stress, this expression is $\sigma_o = \sigma_i + kd^{-1/2}$, where σ_o = yield stress, σ_i = friction stress opposing dislocation motion, k = constant, and d = grain diameter. Similar results are obtained for hardness, with $H_o = H_i + kd^{-1/2}$. To explain these empirical observations, several models have been proposed, which involve either dislocation pileups at grain boundaries or grain boundary dislocation networks as dislocation sources. In

all cases the Hall-Petch effect is due to dislocation motion/generation in materials that exhibit plastic deformation.

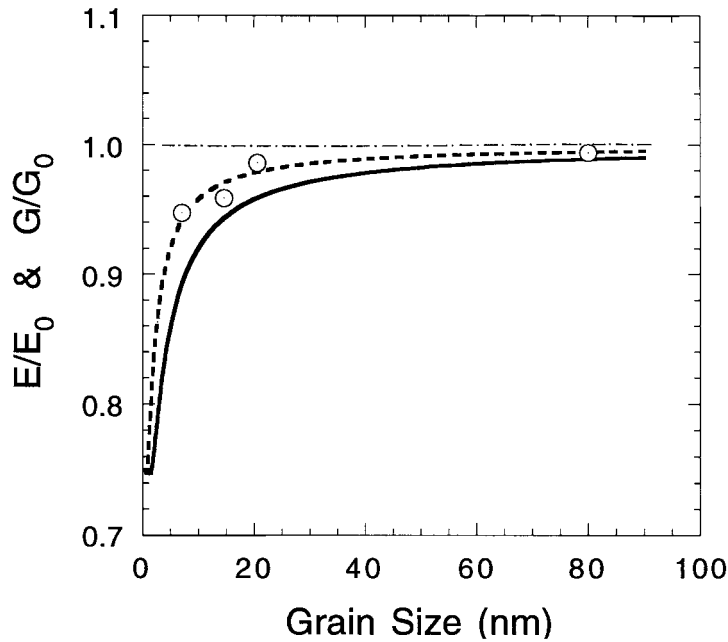


Figure 6.1. Ratio of the Young's (E) and shear (G) moduli of nanocrystalline materials to those of conventional grain size materials as a function of grain size. The dashed and solid curves correspond to a grain boundary thickness of 0.5 and 1 nm, respectively (Shen et al. 1995).

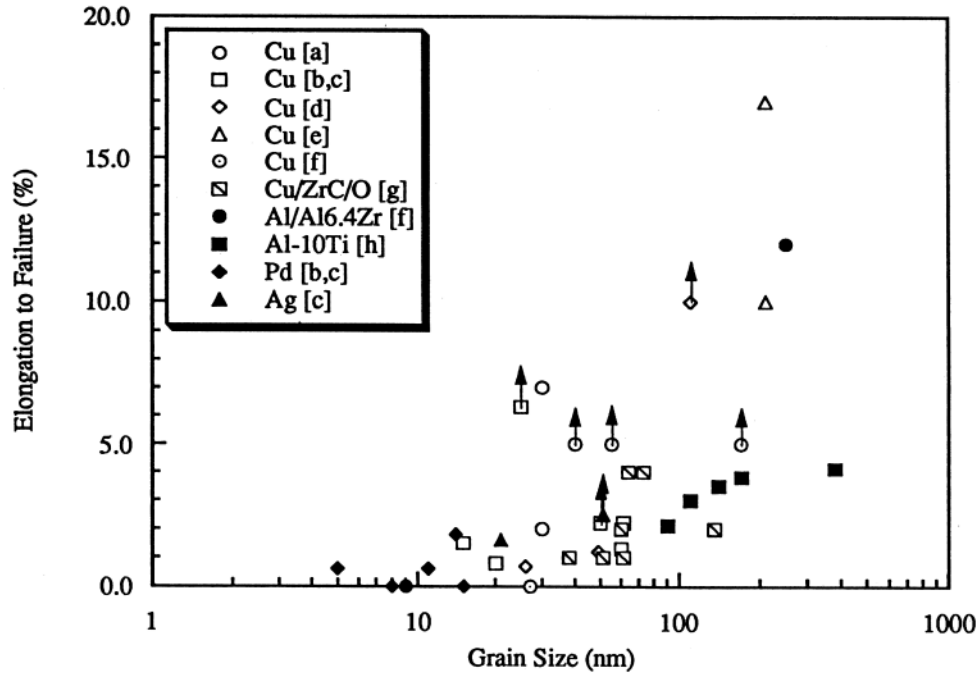
Most of the mechanical property data on nc materials have pertained to hardness, although some tensile test data are becoming available. Several recent reviews have summarized the mechanical behavior of these materials (Siegel and Fougere 1994, 233–261; Siegel 1997; Morris and Morris 1997; Weertman and Averback 1996, 323–345). It is clear that as grain size is reduced through the nanoscale regime (< 100 nm), hardness typically increases with decreasing grain size and can be factors of 2 to 7 times harder for pure nc metals (10 nm grain size) than for large-grained (> 1 μm) metals.

The experimental results of hardness measurements, summarized previously, show different behavior for dependence on grain size at the smallest nc grains (< 20 nm), including (a) a positive slope (“normal” Hall-Petch behavior), (b) essentially no dependence (\sim zero slope), and (c) in some cases, a negative slope (Siegel and Fougere 1994, 233–261; Siegel 1997; Morris and Morris 1997; Weertman and Averback 1996, 323–345). Most data that exhibit the negative Hall-Petch effect at the smallest grain sizes have resulted from nc samples that have been annealed to increase their

grain size. It is suggested that thermally treating nanophase samples in the as-produced condition may result in such changes in structure as densification, stress relief, phase transformations, or grain boundary structure, all of which may lead to the observed negative Hall-Petch behavior (Siegel and Fougere 1994, 233–261). Only a few cases of negative Hall-Petch behavior have been reported for as-produced nanocrystalline samples with a range of grain sizes. These include electrodeposited nc alloys and devitrified nc alloys (Erb et al 1996, 93-110; Alves et al. 1996). Nanocrystalline thin films with grain sizes ≤ 6 nm are also observed to exhibit a negative Hall-Petch effect (Veprék 1998). While it seems likely that in many cases the observed negative Hall-Petch slopes are due to artifacts of the specimen preparation methods, it is also likely that conventional dislocation-based deformation is not operable in nanocrystalline materials at the smallest grain sizes ($< \sim 30$ nm). At these grain sizes, theoretically, mobile dislocations are unlikely to occur; nor have they been observed in *in situ* TEM deformation experiments (Siegel and Fougere 1994, 233–261; Milligan et al 1993; Ke et al. 1995). Thus, the hardness, strength, and deformation behavior of nanocrystalline materials is unique and not yet well understood.

Ductility and Toughness

It is well known that grain size has a strong effect on the ductility and toughness of conventional grain size ($> 1 \mu\text{m}$) materials. For example, the ductile/brittle transition temperature in mild steel can be lowered about 40°C by reducing the grain size by a factor of 5. On a very basic level, mechanical failure, which limits ductility, is an interplay or competition between dislocations and cracks (Thomson 1996, 2208–2291). Nucleation and propagation of cracks can be used as the explanation for the fracture stress dependence on grain size (Nagpal and Baker 1990). Grain size refinement can make crack propagation more difficult and therefore, in conventional grain size materials, increase the apparent fracture toughness. However, the large increases in yield stress (hardness) observed in nc materials suggest that fracture stress can be lower than yield stress and therefore result in reduced ductility. The results of ductility measurements on nc metals are mixed and are sensitive to flaws and porosity, surface finish, and method of testing (e.g., tension or compression testing). In tension, for grain sizes < 30 nm, essentially brittle behavior has been observed for pure nanocrystalline metals that exhibit significant ductility when the grain size is conventional. This is illustrated in Figure 6.2.



Key to Sources

a. Gunther et al. 1990	e. Gertsman et al. 1994
b. Nieman et al. 1991a	f. Eastman et al. 1997, 173-182
c. Nieman et al. 1991b	g. Morris and Morris 1991
d. Sanders et al. 1996, 379-386	h. Liang et al. 1996

Figure 6.2. Elongation to failure in tension vs. grain size for some nanocrystalline metals and alloys.

In some metals, Cu for example, ductile behavior is observed in compression, along with yield strengths about twice those observed in tension. While it is likely that the flaws and porosity present in many nc samples seriously affect the results of mechanical tests and may be partly responsible for the asymmetry of results in compression compared to tension tests, the nature of the deformation process in terms of shear banding (see below) may also be important. The above behavior is presumably due to the inability of usual dislocation generation and motion to occur at these smallest nc grain sizes.

An intriguing suggestion based on early observations of ductile behavior of brittle nc ceramics at low temperatures is that brittle ceramics or intermetallics might exhibit ductility with nc grain structures (Karch et al. 1987; Bohn et al. 1991). Karch and colleagues (1987) observed apparent

plastic behavior in compression in nc CaF₂ at 80°C and nc TiO₂ at 180°C. These observations were attributed to enhanced diffusional creep providing the plasticity at these temperatures, where conventional grain-size materials would fail in the elastic regime. It was assumed that diffusional creep was responsible for the plasticity; observations were rationalized, with boundary diffusion dominating the behavior such that the strain (creep) rate is defined as

$$\frac{d\varepsilon}{dt} = \frac{B\sigma\Omega\Delta D_b}{d^3kT} \quad (\text{Equation 1})$$

where σ is the applied stress, Ω the atomic volume, d the grain size, k the Boltzmann constant, T the temperature, B a constant, and D_b the grain boundary diffusion coefficients. Going from a grain size of 1 μm to 10 nm should increase $d\varepsilon/dt$ by 10^6 or more if D_b is significantly larger for nc materials. However, these results on nc CaF₂ and nc TiO₂ have not been reproduced, and it is believed that the porous nature of these samples was responsible for the apparent ductile behavior. In addition, the idea of unusually high creep rates at low temperatures has been refuted. Recent creep measurements of nc Cu, Pd, and Al-Zr at moderate temperatures by Sanders et al. (1997) find creep rates comparable to or lower than corresponding coarse-grain rates. The creep curves at low and moderate homologous temperatures (.24 – .48 T_M) could be fit by the equation for exhaustion (logarithmic) creep. One explanation is that the observed low creep rates are caused by the high fraction of low energy grain boundaries in conjunction with the limitation on dislocation activity by the small grain sizes.

In sum, the predicted ductility due to diffusional creep in nc brittle ceramics or intermetallics at temperatures significantly less than 0.5 T_M has not been realized.

Superplastic Behavior

Superplasticity is the capability of some polycrystalline materials to exhibit very large tensile deformations without necking or fracture. Typically, elongations of 100% to > 1000% are considered the defining features of this phenomenon. As grain size is decreased it is found that the temperature is lowered at which superplasticity occurs, and the strain rate for its occurrence is increased. As discussed previously, Equation 1 suggests that creep rates might be enhanced by many orders of magnitude and superplastic behavior might be observed in nc materials at temperatures much lower than 0.5 T_M . As mentioned above, actual creep experiments have not borne out this prediction, but instead have shown creep rates

comparable to or lower than those in coarse-grained samples of the same material. This is presumably why little enhancement in ductility or superplastic behavior has been observed for nc materials at temperatures $< 0.5 T_M$. However, there is evidence of enhancement of superplastic behavior in nc materials at temperatures $> 0.5 T_M$. Superplasticity has been observed at somewhat lower temperatures and at higher strain rates in nc materials. The evidence for tensile superplasticity is limited and observed typically at temperatures greater than $0.5 T_M$ and in materials that exhibit superplasticity in coarser grain sizes (1–10 μm). For example, Mishra et al. (1997) observed superplastic behavior in nc Pb-62%Sn at $0.64 T_M$ and nc Zn-22%Al at 0.52 to $0.60 T_M$. However, Salishekev et al (1994) observed superplastic behavior in submicron—200 nm—Ti and several Ti and Ni base alloys. Here, superplasticity (190% elongation, $m = 0.32$) was observed in Ti at $0.42 T_M$. This was at a temperature 50°C lower than for 10 μm grain size Ti. The flow stress for the 200 nm Ti at 550°C was 90 MPa, compared to 120 MPa for 10 μm Ti at 600°C .

Very recently, Mishra and Mukherjee (1997) have observed superplastic behavior in Ni_3Al with a 50 nm grain size at temperatures of 0.56 to $0.60 T_M$ to strains of 300 - 600%, but with unusual stress-strain behavior and significant apparent strain-hardening. These new results suggest very different mechanisms may be causing superplastic behavior in these nc materials.

Unique Mechanical Properties of Nanocrystalline Materials

While there are still only limited data on the mechanical behavior—especially tensile properties—of nc materials, some generalizations may be made regarding the deformation mechanisms. It is likely that for the larger end of the nanoscale grain sizes, about 50 - 100 nm, dislocation activity dominates for test temperatures $< 0.5 T_M$. As grain size decreases, dislocation activity apparently decreases. The essential lack of dislocations at grain sizes below 50 nm is presumably the result of the image forces that act on dislocations near surfaces or interfaces. The lack of dislocations in small, confined spaces such as single-crystal whiskers has been known for many years (Darken 1961). Creation of new dislocations is also made difficult as the grain size reaches the lower end of the nanoscale (< 10 nm). Stresses needed to activate dislocation sources, such as the Frank-Read source, are inversely proportional to the distance between dislocation pinning points. Since nanoscale grains will limit the distance between such pinning points, the stresses to activate dislocation sources can reach the theoretical shear stress of a dislocation-free crystal at the smallest grain sizes (~ 2 nm). Thus, at the smallest grain sizes we may have new phenomena controlling deformation behavior. It has been suggested that such

phenomena may involve grain boundary sliding and/or grain rotation accompanied by short-range diffusion-assisted healing events (Siegel 1997).

Several examples of deformation by shear banding have been reported for nc materials. Carsley et al (1997, 183-192) have studied nc Fe–10% Cu alloys with grain sizes ranging from 45 to 1,680 nm. In all cases, deformation in compression proceeds by intense localized shear banding. The stress-strain curves exhibited essentially elastic, perfectly plastic behavior; that is, no measurable strain hardening was observed. Shear banding is also the deformation mode observed in amorphous metallic alloys and amorphous polymers. The deformation shear banding in nc Fe–10% Cu was compared to that for metallic glasses, amorphous polymers, and coarse-grained polycrystalline metals after significant plasticity and work hardening had taken place. While this suggests a close similarity between deformation in nc materials and amorphous materials, not all tensile data on nc materials exhibit a lack of strain hardening. The Fe–10% Cu samples of Carsley et al. (1997, 183-192) showed shear bands even in their larger grained specimens (i.e., about 1,000 nm).

Theoretical Needs

Central to all of the above discussion is the lack of understanding of the microscopic deformation and fracture mechanisms in nc materials. Clearly, a stronger theoretical effort is needed to guide critical experiments and point the direction for optimizing properties. There has been limited work in this area, especially in Russia, in applying disclination theory to grain rotation (Romanov and Vladimirov 1992, 191), for example. However, a much larger theoretical effort is required. Another alternate deformation mechanism that may be important in nc materials is mechanical twinning (Huang et al. 1996). Little theoretical work has been carried out to address this possibility. Another important potential approach to understanding the deformation mechanisms in nc materials is to explore the rich older literature on shear banding—mechanical instabilities that have been observed in, for example, mild steels as grain size decreases; the approach to very low strain hardening (perfectly plastic behavior) is observed. Amorphous materials exhibit many of the phenomenological characteristics of deformation in nc materials, that is, shear banding, asymmetry between tensile and compressive behavior, and perfectly plastic behavior. However, deformation mechanisms are not well understood in amorphous materials either. Recent work on bulk metallic glasses may help clarify this.

Applications

Of the present or near-term applications for nc materials, the hard material WC/Co is an example of several important trends. Nanostructured WC/Co composites have been prepared that can have the following characteristics:

- nanoscale grain sizes after consolidation of powder
- hardness values about twice that of conventional micrograined WC/Co
- enhanced wear resistance and cutting performance

While this material has increased hardness and strength, preliminary reports from Stevens Institute of Technology in Hoboken, NJ, and the Royal Institute of Technology in Stockholm, Sweden, point to similar or increased fracture toughness values for nanostructured WC/Co. As noted earlier, single-phase nanostructured materials studied to date have exhibited high strength and hardness but brittle behavior at low homologous temperatures ($< 0.5 T_M$). The results of these studies of WC/Co two-phase nanostructured materials suggest that the combination of high hardness/strength and toughness/ductility may be possible in multiphase nanostructured materials.

Other examples that point to this possibility come from the work of Professor A. Inoue at Tohoku University in Japan, whose lab the WTEC panel visited (see Appendix D). Inoue and coworkers have synthesized a variety of multiphase Al, Mg, and Ni-base alloys with nanoscale microstructures. Many of these alloys consist of nanocrystallites in an amorphous matrix. Some Al-rich alloys contain nanoscale quasi-crystalline particles surrounded by crystalline face-centered cubic Al. The fascinating properties of these multiphase nanostructured alloys include extremely high strength coupled with some ductility. Ductility is high in compression, but uniform elongation in tension is limited. Again, this behavior is analogous to that exhibited by ductile amorphous alloys. These results again suggest the possibility for development of nanostructured multiphase composites that combine extremely high hardness and strength with toughness and ductility. Such materials could have many applications as unique structural materials.

Multiphase ceramic nanocomposites are the focus of several efforts. One significant effort is underway at the Research Center for Intermaterials of the Institute of Scientific and Industrial Research at Osaka University in Japan (see site report, Appendix D). Professor Koichi Niihara has a large effort studying micro-nano composites such as Al_2O_3/SiC that have enhanced toughness and also a variety of hard matrix/soft dispersion or soft matrix/hard dispersion nanocomposites. The enhanced toughness in some ceramic nanocomposites observed by Prof. Niihara has been verified by parallel studies of Dr. Steve Roberts at University of Oxford in England (see site report, Appendix B).

While “low temperature” superplasticity has not been realized in nanostructured materials, enhanced superplastic behavior has been observed at elevated temperatures in terms of a somewhat lower temperature range for superplasticity and, perhaps more significant, a higher strain rate regime. While much needs to be understood about superplastic behavior of nanostructured materials, the possibility for using more conventional strain rates for forming has major industrial implications. This is of particular interest for near net shape forming of ceramics.

Outstanding Issues: Opportunities and Challenges

Perhaps the overriding issue for defining the mechanical behavior of nanostructured materials is the lack of understanding of the mechanisms for plastic deformation and fracture in these materials. An extensive experimental and theoretical research effort should be applied to solve these questions. Only with such understanding can the intelligent design of nanostructured materials with optimum mechanical properties be realized.

Since many of the synthesis routes for nanostructured materials involve using powder or particulate products, compaction of such powders is needed to form bulk parts without coarsening the nanoscale microstructure. While there has been ongoing work on compaction and the thermal stability of nanocrystalline microstructures, more basic work is needed in this critical area. If some unique properties are limited to the finest grain sizes, methods must be found to stabilize the grain size while attaining theoretical density and complete particulate bonding. Furthermore, conventional processing methods are desirable if realistic scaleup and economy are to be realized.

Near-term opportunities for structural applications of nanostructured materials are in the form of coatings prepared by, for example, thermal spray deposition or electrodeposition. There is a significant effort in the United States on thermal spray deposition of nc materials. Several groups in Canada lead in deposition of nc materials by electrodeposition methods. A spin-off company, Nanometals, formed under the auspices of Parteq Research and Development Innovations, has adopted a commercial electrodeposition method to produce nanostructured metals.

Structural applications of nanostructured materials may be viewed as a focused approach to a long standing, well known design of materials with optimum mechanical properties. Use of nanoscale precipitates or dispersoids has been known for decades to improve mechanical behavior. The “new” emphasis on using nanostructured materials comes from 2 significant factors:

1. the special processing methods to push microstructures to the limits of the nanoscale
2. the unique properties and phenomena—as yet not well understood—when this limit is approached

FERROMAGNETIC NANOSTRUCTURED MATERIALS

Soft Magnetic Nanocrystalline Alloys

The discovery of nanocrystalline Fe-based soft magnetic materials is less than ten years old. The first class of such materials was the melt-spun Fe-Si-B alloys containing small amounts of Nb and Cu (Yoshizawa et al. 1988). The Fe-Si-B-Nb-Cu amorphous phase transforms to a body-centered cubic (bcc) Fe-Si solid solution with grain sizes of about 10 nm during annealing at temperatures above the crystallization temperature. The presence of small amounts of Cu helps increase the nucleation rate of the bcc phase while Nb retards the grain growth. These “Finemet” alloys provide low core losses (even lower than amorphous soft magnetic alloys such as Co-Fe-Si-B), exhibit saturation induction of about 1.2 T, and exhibit very good properties at high frequencies, comparable to the best Co-based amorphous alloys. These were first developed in Japan and have stimulated a large amount of research and development worldwide to optimize the magnetic properties. There has been relatively little work in the United States in this area, however.

While many of the soft magnetic properties of Finemet-type nanocrystalline alloys are superior, they exhibit lower saturation inductions than Fe-metalloid amorphous alloys, mainly because of the lower Fe content to attain amorphization and because of the addition of Nb and Cu (or other elements to control the nucleation and growth kinetics). In order to remedy this problem, another class of Fe-based nanocrystalline alloys was developed by Inoue and coworkers at Tohoku University (Makino et al. 1997), which is commercialized by Alps Electric Co., Ltd., of Nagaoka, Japan (see also the Tohoku University site report, Appendix D). These “Nanoperm” alloys are based on the Fe-Zr-B system; they contain larger concentrations of Fe (83-89 at.%) compared to the Finemet alloys (~ 74 at.% Fe) and have higher values of saturation induction (~ 1.6-1.7 T). The Nanoperm nc alloys have very low energy losses at power frequencies (60 Hz), making them potentially interesting for electrical power distribution transformers. The issues of composition modification, processing, and the brittle mechanical behavior of these nanocrystalline/amorphous alloys are discussed by V.R. Ramanan in the first volume of this WTEC study, the proceedings of the May 8-9, 1997 panel workshop on the status of nanostructure science and technology in the United States (Ramanan 1998, 113-116). Figure 6.3 compares the soft magnetic properties of Finemet, Nanoperm, and other materials.

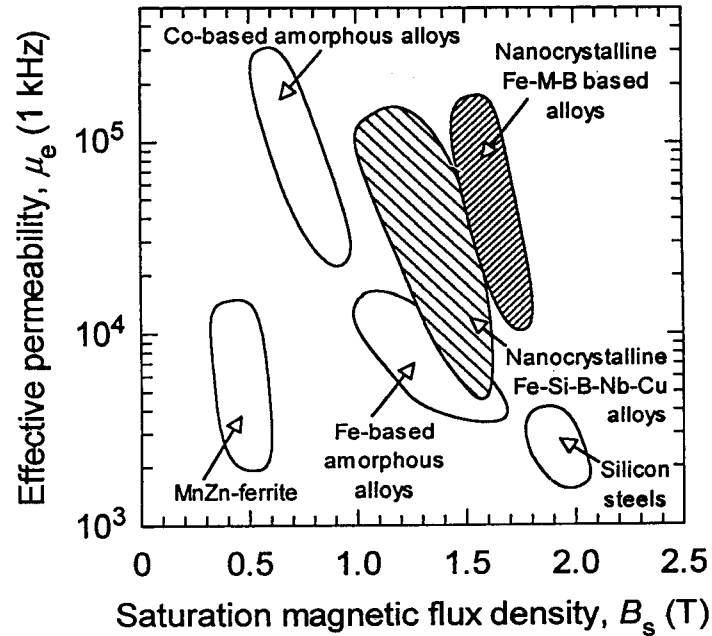


Figure 6.3. Effective permeability, μ_e , vs. saturation magnetic flux density, B_s , for soft ferromagnetic materials (after A. Inoue 1997).

While there has been extensive research on these alloys, particularly in Japan and Europe, most of the development has been carried out in Japan. The Finemet family of alloys is marketed by Hitachi Special Metals. Vacuumschmelze GmbH (Germany) and Impky (France) also market similar alloys. The Nanoperm alloys are being commercialized by Alps Electric Co. (Japan). No extensive research nor any commercialization of these materials has been carried out in the United States.

The small single-domain nanocrystalline Fe particles in the amorphous matrix gives these alloys their unique magnetic behavior, the most dramatic being the lowest energy losses (narrowest B/H hysteresis loop) of any known materials, along with very high permeabilities. These alloys can also exhibit nearly or exactly zero magnetostriction. To date, these materials have been made by crystallization of rapidly solidified amorphous ribbons. Other methods that might provide geometrically desirable products should be explored or developed. Electrodeposition is one such method that requires further work. Electrodeposited nc Fe-Ni soft magnetic alloys are being developed in Canada.

The brittle nature of these materials is a problem for scaleup and transformer manufacture. The brittleness problem must be solved by finding less brittle materials or applying the handling and processing knowledge that exists for embrittled (after annealing) metallic glasses.

Permanent Magnet Materials

The first attempts to produce nanoscale microstructures to enhance the magnetic properties of the Nb-Fe-B permanent magnetic materials used mechanical alloying of blended elemental powders followed by heat treatment (Schultz et al. 1987). Since the grain structure so obtained does not exhibit any crystallographic texture—and limits the energy product—special processing methods such as die-upsetting were used by Schultz and coworkers (1989) to provide the crystallographic anisotropy. While the coercivities of these nanocrystalline alloys are high, the remanent magnetization is decreased.

Recent approaches to increasing the magnetic induction have utilized exchange coupling in magnetically hard and soft phases. The Fe-rich compositions (e.g., $\text{Fe}_{90}\text{Nd}_7\text{B}_3$) result in a mixture of the hard $\text{Fe}_{14}\text{Nd}_2\text{B}$ phase and soft αFe phase. The nanoscale two-phase mixtures of a hard magnetic phase and a soft magnetic phase can exhibit values of remanent magnetization, M_r , significantly greater than the isotropic value of $0.5 M_s$. This “remanence enhancement” is associated with exchange coupling between the hard and soft phases, which forces the magnetization vector of the soft phase to be rotated to that of the hard phase (Smith et al. 1996). Two important requirements for alloys to exhibit remanence enhancement are a nanocrystalline grain size and a degree of coherence across interphase boundaries sufficient to enable adjacent phases to be exchange-coupled. The significant feature of the exchange coupling is that it allows crystallographically isotropic materials to exhibit remanence values approaching those achieved after full alignment. Such two-phase nanoscale ferromagnetic alloys have been prepared by nonequilibrium methods such as melt-spinning, mechanical alloying, and sputter deposition. Besides the high reduced remanence, the material cost is reduced by reduction in the content of the expensive hard rare earth-containing magnetic phase.

The theoretical understanding of remanence enhancement appears to be developed to a degree enabling prediction of magnet performance; however, this performance, while a significant improvement over single-phase isotropic magnets, does not reach predicted values. Work is required on optimizing the orientation relationships between the hard and soft phases and the interphase properties (coherency) between them.

Research on nanocrystalline hard magnetic alloys has received attention worldwide. The U.S. efforts are summarized in the article by G.C. Hadjipanayis (1998, 107-112). While less research seems to be carried out in the world on these materials compared to the nanocrystalline soft magnetic alloys, some efforts exist in most countries. Notable programs are those of L. Schultz and coworkers at the Institut für Festkörper und Werkstofforschung (IFW) in Dresden (see site report in Appendix B) and P.G. McCormick and coworkers at the University of Western Australia.

While the very low losses of the nc soft magnetic materials (Finemet or Nanoperm) are dependent on grain size for their properties, the hard magnetic nc alloys with remanence enhancement provide flexibility in processing, especially with powder materials. These remanence-enhanced nc hard magnetic alloys may find many applications as permanent magnet components.

Giant Magnetoresistance (GMR)

The phenomenon of giant magnetoresistance (GMR)—the decrease of electrical resistance of materials when exposed to a magnetic field—was first reported in a number of multilayer ferromagnetic/nonferromagnetic thin film systems (Baibich et al. 1988). More recently, GMR was observed in equiaxed granular nanocrystalline materials (Berkowitz et al. 1992). In particular, GMR systems with low saturation fields offer a wide area for application in magnetoresistive devices. GMR sensors have a higher output than conventional anisotropic magnetoresistive sensors or Hall effect sensors. They can operate at higher magnetic fields than conventional magnetoresistive sensors. In multilayer systems the antiferromagnetic alignment of the ferromagnetic layers in zero field becomes ferromagnetic as the field is applied and causes a decrease in resistance. Granular materials that show GMR consist of small ferromagnetic single-domain particles with randomly oriented magnetic axes in a nonmagnetic matrix. An external field rotates the magnetic axes of all magnetic particles. The rotation towards complete alignment of all magnetic axes again reduces the resistance in a similar way as for multilayers. The GMR in granular systems is isotropic. The explanation for the GMR is spin-dependent scattering of the conduction electrons at the ferromagnetic/nonmagnetic interfaces and, to a lesser extent, within the magnetic grains. The GMR scales inversely with the average particle diameter.

There is worldwide research on the GMR effect. U.S. programs are reviewed by R. Shull and G.C. Hadjipanayis in the proceedings of the WTEC U.S. nanotechnologies workshop (Shull 1998, 43-58; Hadjipanayis 1998, 107-112). The NIST work described by Shull has provided material with the largest GMR values for the smallest switching fields. Japanese research on GMR includes studies in Prof. Fujimori's group at Tohoku University (see site report in Appendix D).

While the theory for GMR of spin-dependent scattering referred to above has been used as an explanation, other explanations taking into account interaction between magnetic regions have been proposed (El-Hilo et al. 1994). Combined theoretical and experimental studies should help to clarify the mechanism for this effect.

Other Ferromagnetic Nanocrystalline Materials

Magnetic nanocomposite refrigerants, which have four times the magnetocaloric effects of the best low temperature magnetic refrigerant, were developed by NIST and described by R. Shull (1998, 43-58). The entropy change at a given (low) temperature for a system of magnetic spins is enhanced when the isolated spins are clustered. Shull et al. (1993) have shown that the nanocomposite $Gd_3Ga_{5-x}Fe_xO_{12}$ gives superior magnetocaloric effects, which increase with x up to $x = 2.5$ and can be extended to higher temperatures than conventional materials.

Magnetostrictive materials such as Terfonol-D ($Tb_{0.3}Dy_{0.7}Fe_2$) have been of scientific and technological interest in recent years. It is suggested by G.C. Hadjipanayis (1998, 107-112) that nanostructured magnetostrictive materials can have improved properties, such as lower saturation fields, with reduced anisotropy and in multilayers with alternate layers of magnetostrictive and soft magnetic materials that are exchange-coupled. Hadjipanayis states that most of the research in this area is carried out in Japan and Europe.

Opportunities and Challenges

Nanocrystalline magnetic materials offer perhaps the nearest-term prospect of significant applications of bulk nanostructured materials. The remanence enhancement in two-phase hard/soft magnetic materials can result in excellent energy products—comparable to those from rapid solidification processing routes—in powder composites. The flexibility in manufacturing this allows should provide many possible permanent magnet applications.

Nanocrystalline soft magnetic materials have the lowest energy losses of any material. While problems such as mechanical brittleness remain, these materials promise to replace existing transformer core materials for power applications. The U.S. research and industrial effort in these materials lags the efforts in Japan.

OTHER BULK APPLICATIONS OF NANOSTRUCTURED MATERIALS

Nanocrystalline Hydrogen Storage Materials

R.B. Schwarz (1998, 93-95) has pointed out that nanostructured materials offer several potential advantages for hydrogen storage materials. Rapid kinetics of absorption/desorption can be aided by refining the microstructure

to the nanoscale. For example, nanoscale inclusions of Mg₂Ni in Mg catalyze the decomposition of the molecular hydrogen, increasing the hydrogen absorption/desorption kinetics. Another advantage of the nanoscale microstructure is that the alloy powder does not comminute on repeated charging/discharging with hydrogen. This is not strictly a bulk material, since powder agglomerates or green compacts can be used, thus obviating the need for compaction to theoretical density.

Nanocrystalline Corrosion-Resistant Materials

The limited work to date on corrosion resistance of nanocrystalline materials indicates that no generalizations can be made. Superior localized corrosion resistance in HCl was observed for nanocrystalline 304 stainless steel (Fe–18%Cr–8%Ni) prepared by sputter deposition (Inturi and Szklavska-Smialowska 1991 and 1992). This was attributed to the fine grain size and homogeneity of the nc material. However, the average dissolution rate of nc Ni was found to be higher than that for coarse-grained material (Rofagha et al. 1991).

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