

## Elastic properties of nano-structured materials

The early measurements of the elastic constants on nanocrystalline materials prepared by the inert-gas-condensation method gave values, for example for Young's modulus,  $E$ , which were significantly lower than values for conventional grain size materials. The presence of extrinsic defects, e.g. pores and cracks, was responsible for the low values of  $E$  in nanocrystalline materials compacted from powders.

This conclusion was based upon the observation that nanocrystalline NiP produced by electroplating with negligible porosity levels had an  $E$  value comparable to fully dense conventional grain size Ni.

The change in  $E$  and  $G$  (the shear modulus) of nanocrystalline materials, which are porosity free, with a grain size larger than about 5 nm, should be very limited and the moduli consist of contributions from the grain interior, grain boundary, and grain triple junctions; the grain-boundary thicknesses of 0.5 nm and 1.0 nm was assumed. The data for nanocrystalline Fe closely fit the curve for 0.5 nm grain-boundary thickness. It is concluded that the intrinsic moduli of nanocrystalline 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.

The presence of porosity and cracks present in the consolidated material can be significantly affected by the presence of porosity and cracks present in the consolidated material. If the pore size is  $R$  and the flaw size emanating from the surface of the pore is  $S$ , then  $E$  of the compacted material is given by

$$E = E_0 / (1 + 4V(1 - \nu^2)\phi/\pi)$$

where  $E_0$  is the Young's modulus of the material without any porosity,  $V$  is the pore volume fraction,  $\nu$  is the Poisson's ratio, and  $\phi$  is a function of  $S$  and  $R$ .

## Anelastic properties

Anelasticity is defined as the dependence of elastic strain on both stress and time. This can result in a lag of strain behind stress. In materials subjected to cyclic stress, the anelastic effect causes internal damping. Internal friction or mechanical damping has been a valuable research tool for the study of the properties of lattice imperfections in crystalline solids. There are a number of mechanisms by which vibrational energy can be dissipated internally by a material. These include the thermoelastic effect, stress-induced ordering of interstitial and substitutional solute atoms, grain-boundary relaxation, motion of dislocations, and certain phase transformations. Studies on the anelastic behavior of nanocrystalline Fe and Ni in the quasistatic and low-frequency anelastic regime has shown a significant change in the magnitude of  $Q^{-1}$  was observed after annealing for 30 min. at 200 °C even though no grain growth occurred. The activation energies determined for these processes were comparable to those of grain-boundary diffusion for the respective metals. It was suggested that the mechanical response may originate from a viscous behaviour at the grain boundaries mediated by atomic diffusion in the grain-boundary disordered regions. In the nanocrystalline Fe the samples with initial grain size of 40 nm showed lower damping values than samples with smaller, 15 nm grain sizes. However, no difference in damping was observed between 40 nm and 20 nm grain size Ni.

## Specific heat

A comparison of the specific heats of different nanocrystalline, coarse-grained polycrystalline, and amorphous materials suggests that, at room temperature, the specific heat in the nanocrystalline state is much higher than that in the coarse-grained material and of even the amorphous material. Variation of specific heat with temperature may be nonlinear (parabolic), or linear. The specific heat increase linearly with the reciprocal crystal size at a constant temperature. The large enhancement of the specific heat at room temperature and above is interpreted as the Einstein oscillator contribution due to weakly bound atoms at the interfaces of the nanocrystals. When the specific heat of 40 nm iron samples was measured at low temperatures (1.8–26 K), a quadratic temperature-dependent contribution to the heat capacity associated with surface modes was clearly observed. The electronic specific heat coefficient decreased by about 50%, suggesting the effect of increasing electron energy level spacing. A small increase (2.5%) in specific heat was observed for porosity free nanocrystalline Ni obtained by electrodeposition. The specific heat of a material is closely related to its vibrational and configurational entropy, which is significantly affected by the nearest-neighbor configurations. Thus, the increase in specific heat of nanocrystalline materials has been attributed to the small crystal size (and consequent large interfacial component). If this is so, grain growth should reduce the specific heat of the nanocrystalline material.

## Optical properties

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. 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. The optical absorption characteristics can also be modified by allowing interaction to occur between the nanosized CdS clusters.

## Strength and hardness

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. 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:

$$\sigma = \sigma_0 + kd^{-n}$$

where  $d$  is the mean grain size,  $\sigma$  is the 0.2% yield strength (or hardness),  $\sigma_0$  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 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. When a high 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 and this could be the reason for the observed inverse Hall–Petch effect.

## Ductility and toughness

It is well known that grain size has a strong effect on 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  $40^\circ\text{C}$  by reducing the grain size by a factor of 5. Grain size refinement can make crack propagation more difficult and therefore increase the apparent fracture toughness in conventional grain size materials. However, the large increases in yield stress (hardness) observed in nanocrystalline materials suggests that fracture stress can be lower than yield stress and therefore result in reduced ductility. The results of ductility measurements on nanocrystalline metals are mixed and are sensitive to flaws and porosity, surface finish, and method of testing (e.g., tension vs. compression). The elongation to failure has been found to decrease with a decrease in the grain size. Further, the ductility of nanocrystalline materials that exhibit ductile behavior with conventional grain sizes typically show reduced ductility – sometimes brittle behaviour – at the smallest nanometer grain sizes. This is presumably due to the inability of usual dislocation generation and motion to occur at It was shown that nanocrystalline ceramics, e.g.,  $\text{TiO}_2$  and  $\text{CaF}_2$ , could 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. An intriguing suggestion based on these early observations (not reproduced till date) is that the inherently brittle ceramics or intermetallics can be made ductile via nanostructure processing

since the strain (creep) rate is given by: 
$$\frac{d\varepsilon}{dt} = \frac{B\sigma\Omega\Delta D_b}{d^3kT}$$

where  $\sigma$  is the applied stress,  $\Omega$  the atomic volume,  $\Delta$  the grain boundary width,  $d$  the grain size,  $k$  the Boltzmann constant,  $T$  the temperature,  $B$  a constant and  $D_b$  the grain boundary diffusion coefficient. Decreasing the grain size from  $1\ \mu\text{m}$  to  $10\ \text{nm}$  should increase  $d\varepsilon=dt$  by  $10^6$  or more if  $D_b$  is significantly larger for nanocrystalline materials. However, recent creep measurements of nanocrystalline Cu, Pd, and Al–Zr at moderate temperatures find creep rates comparable to or lower than corresponding coarse-grain rates. However, there have not been reports for brittle ceramics or intermetallics of the dramatic increases in ductility predicted by the equation at temperatures significantly  $< 0.5T_m$ .

Very high strengths with acceptable levels of ductility could be obtained in a material if about 20 vol% of a nanocrystalline phase is uniformly dispersed in an amorphous matrix. This appears to be a fruitful area for further investigations. As grain size is decreased it is found that the temperature at which superplasticity occurs is lowered, and the strain rate for its occurrence is increased. The creep rates could be enhanced by many orders of magnitude and superplastic behavior might be observed in nanocrystalline materials at temperatures much lower than  $0.5T_m$ . Tensile superplasticity in nanocrystalline nickel obtained by electrodeposition and nickel aluminide obtained by severe plastic deformation. They reported that nickel exhibited superplasticity at  $350^\circ\text{C}$ , which is only  $0.38T_m$  and  $470^\circ\text{C}$  below the previous example of superplasticity in nickel. The initial grain size was of nanometer dimensions with a few larger ( $0.3\mu\text{m}$  size) grains and grain growth occurred during the tensile test at  $350^\circ\text{C}$  up to about a micron. Strain hardening was also observed which was not reported for nanocrystalline materials at ambient temperature.

### **Deformation mechanisms**

While there is still limited data on the mechanical behavior – especially tensile properties – of nanocrystalline 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  $<0.5T_m$ .

As grain size decreases, dislocation activity apparently decreases. The essential lack of dislocations is presumably the result of the image forces that act on dislocations near surfaces or interfaces. The creation of new dislocations is also made difficult as the grain size reaches the lower end of the nanoscale (610 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.

The existing data on mechanical properties provide the following tentative conclusions, although much work remains to be done to clarify the detailed deformation mechanisms. Except for very small grain nanocrystalline samples (65 nm) the elastic properties are essentially identical to those of coarse-grained material.

- \_ High hardnesses and yield strength values are observed for nanocrystalline materials.
  - \_ Ductile coarse-grained materials are less ductile, perhaps brittle as nanocrystalline materials.
  - \_ Brittle coarse-grained materials may exhibit slight ductility when nanocrystalline. Not enough evidence to verify this.
  - \_ Superplasticity has been observed at low temperatures ( $0.38T_m$ ) for nanocrystalline nickel and nickel aluminide samples.
- Shear banding and perfectly plastic behavior have been seen in some nanocrystalline materials analogous to plastic deformation in amorphous materials.
- \_ Mechanical twinning may be an alternate deformation mechanism in nanocrystalline materials.

### **Electrical properties**

Because of the increased volume fraction of atoms lying at the grain boundaries, the electrical resistivity of nanocrystalline materials, as affected by grain boundary scattering, is found to be higher than that in the coarse-grained material of the same chemical 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. 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 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. 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, affording a means of controlling 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. Nanostructured materials should be important in magnetic recording applications as new materials are developed with a stable, large GMR effect at room temperature that can operate at magnetic fields as low as a few mT.

## **Magnetic properties**

Changes in the magnetic properties of nanoscale ferromagnetic materials can be attributed to their small volume, which means that they are typically single domain, and to the large fraction of atoms associated with the grain boundaries/interfaces. If the grain sizes are small enough, the structural distortions associated with the surfaces or interfaces can lower the Curie temperature,  $T_c$ , and reduce the magnitude of the saturation magnetization  $M_s$ . For example, the  $M_s$  of 6 nm Fe was reported to be 130 emu/g compared to 220 emu/g for normal polycrystalline Fe. The Curie temperature of 10 nm Gd was decreased about 10 K from that of coarse-grained Gd, and the transition was broader. These reductions were attributed to the deviation of interatomic spacings in the interfacial regions as compared with the crystalline component, supported by Mössbauer spectroscopy measurements. Such reductions were, however, not observed in fully dense electrodeposited nanocrystalline Ni suggesting that the earlier results were influenced by the presence of porosity in the samples.

Attractive magnetic properties have been reported for nanocrystalline Fe-based alloys obtained by devitrification (at temperatures between 500 and 600°C) of the amorphous ribbon produced by the rapid solidification method. The best soft magnetic properties by this route were 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  $\text{Fe}_{74.5-x}\text{Cu}_x\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ . These FINEMET alloys contain 10–15 nm-sized bcc Fe–Si grains embedded in the amorphous matrix. Small Cu-enriched particles have been found in the intergranular regions.

Nanocrystalline materials produced by the crystallization of amorphous alloys (FINEMET alloys) show an excellent combination of magnetic characteristics. They have a low

coercivity ( $5\text{--}10\text{ A cm}^{-1}$ ), high permeability (100, 000), almost zero magnetostriction ( $0\text{--}2 \times 10^{-6}$ ), and low core losses ( $\sim 200\text{ kWm}^{-3}$ ) due to the high resistivity ( $135\text{ }\mu\Omega\text{-cm}$ ) 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. 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.

Due to the relatively low Fe content, the FINEMET alloys have a  $B_s$  less than 1.4 T. It is desirable to have soft magnetic materials with  $B_s > 1.5\text{ T}$  and  $\mu_e$  above  $10^5$  at 1 kHz for various kinds of power transformers. Higher Fe content amorphous alloys of type Fe–M–B (M = Zr, Hf, or Nb) were subsequently studied and mixed phase nanocrystalline/amorphous structures were found to exhibit excellent soft magnetic properties. The addition of Cu aids (in Fe<sub>86</sub>Zr<sub>7</sub>B<sub>6</sub>Cu<sub>1</sub> alloy) increased nucleation while Zr acts to inhibit growth (as well as allowing for amorphization). The mechanism proposed for the good soft magnetic properties for the nanoscale bcc Fe–M–B alloys is believed to be due to the following factors:

- a high  $B_s$  resulting from the increased Fe content and the magnetic coupling between the nanoscale bcc particles via the ferromagnetic amorphous phase,
- the reversible magnetization due to magnetic homogeneity from the nanocrystalline bcc Fe phase being smaller than the width of magnetic domain walls,
- the stability of the nanocrystalline structure enhanced by the enrichment of solute elements in the amorphous phase,
- the reduction of the saturated magnetostriction,  $\lambda_s$ , resulting from the redistribution of the solute elements between the nanocrystalline bcc and amorphous phases.

The addition of Co to these alloys can enhance the values of  $B_s$  and  $\mu_e$  and balancing additions of Zr and Nb can achieve nearly zero  $\lambda_s$ . The first attempts to produce nanoscale microstructures to enhance the magnetic properties of the Nd–Fe–B permanent magnetic materials used mechanical alloying of blended elemental powders followed by heat treatment. 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 needed to provide the crystallographic anisotropy. While the coercivities of these nanocrystalline alloys are high, the remanent magnetization is decreased.

Studies to increase the magnetic induction have utilized exchange coupling in magnetically hard and soft phases. The Fe-rich compositions (e.g., Fe<sub>90</sub>Nd<sub>7</sub>B<sub>3</sub>) result in a mixture of the hard Fe<sub>14</sub>Nd<sub>2</sub>B phase and soft  $\alpha$ Fe 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  $0.5M_s$ . 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.

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. Mechanical alloying seems to be unsuitable for the production of soft magnetic low coercivity alloys, because of the significant introduction 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.

A useful magnetic property that nanocomposites offer is called the magnetocaloric effect. When a material containing extremely small magnetic particulates in a nonmagnetic 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. The nanocomposite  $\text{Gd}_3\text{Ga}_{5-x}\text{Fe}_x\text{O}_{12}$  gives superior magnetocaloric effects which increase with  $x$  up to  $x = 2.5$  and can be extended to higher temperatures than existing paramagnetic refrigerants. It was predicted that the magnetocaloric effect may be enhanced at low fields and high temperatures.

## **Chemical properties**

The corrosion behavior of nanocrystalline nickel-base alloys has been reported. 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 and superior localized corrosion resistance, attributed to the fine grain size and homogeneity of the nanocrystalline material while the coarse-grained material suffered excessive intergranular corrosion.

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. Example, the chemical reactivity of nanocrystalline  $\text{TiO}_2$  that has been only lightly consolidated is significantly higher than that in other commercially available  $\text{TiO}_2$  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 class of Pd-Fe alloy, showing continuous solid solubility at all compositions, was shown to have a high degree of  $\text{H}_2$  permeation through the membrane material, without experiencing poisoning by CO,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{O}$ , which is commonly encountered in membrane materials that are used for  $\text{H}_2$  separation. Hydrogen absorbing alloys (FeTi,  $\text{LaNi}_5$ ,  $\text{Mg}_2\text{Ni}$ , and other Mg-based materials) in the nanocrystalline form show much better hydrogen adsorption properties than their polycrystalline counterparts. Further improvement was accomplished by modifying the metal powders with a small amount ( $<1$  wt.%) of a catalyst, such as Pd, present in the form of small clusters or particles dispersed on the surface of the absorbing material. There appears to be a lot of potential in developing improved catalytic materials for the industry. By controlling the processing parameters during the synthesis/production of

nanocrystalline materials, one can fine-tune various crystalline structural parameters such as lattice parameters, defect concentration, surface chemistry, and compositional variation. Further, one can control the structure of not only the catalytic material, but also their support. The nanoporous support design could further enhance the overall catalytic processes through increased activity, better selectivity, improved stability, and greater poisoning resistance.