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978-0-521-85565-5 — Structural Nanocrystalline Materials
Carl C. Koch , Ilya A. Ovid'ko , Sudipta Seal , Stan Veprek
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1 Introduction

With the explosion of research interest in nanocrystalline materials in recent years, one sub-area that has received significant attention is the mechanical behavior of materials with grain sizes less than 100 nm. The great interest in the mechanical behavior of nanocrystalline materials originates from the unique mechanical properties first observed and/or predicted by the pioneers of this field, Gleiter and co-workers, in materials prepared by the gas condensation method (Gleiter, 1989). Among these early observations or predictions were:

- 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) that are 2–10 or more times higher than those of larger grained (>1 μm) metals;
- increased ductility – perhaps even superplastic behavior – at low homologous temperatures in even normally brittle ceramics or intermetallics with nanoscale grain sizes, believed to be caused by grain boundary, diffusional deformation mechanisms.

While some of these early observations and predictions have been verified by subsequent studies, in particular the high hardness and strength values, some have been found to be caused by high porosity in the early bulk samples (for example, elastic constant behavior) or to other artifacts introduced by the processing procedures. The ductility issue remains a subject of present research and while most nanocrystalline materials don't exhibit the high predicted ductilities (Koch *et al.*, 1999), there are recent examples of good ductility along with high strength in a limited number of cases (Karimpoor *et al.*, 2003; Li and Ebrahimi, 2004; Youssef *et al.*, 2004). Similarly, while nanocrystalline ceramics or intermetallics have not been found to be ductile at ambient temperature, ductility, and in some cases even superplasticity (McFadden *et al.*, 1999), has been found at lower homologous temperature than for the conventional grain size counterparts.

An important question in this field is "what are the needs for structural nanocrystalline materials?" Are there applications for which the superior properties and/or the grain size are required for feasible performance? Are there cases in conventional structural applications where nanostructured materials could be substituted in a cost effective way? This chapter will attempt to address these questions for structural nanomaterials in the form of coatings and thin films as well as bulk parts.

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1.1 Coatings and thin films

Coatings and thin films are applied to structural bulk materials in order to improve the desired properties of the surface, such as wear resistance, friction, corrosion resistance and others, yet keeping the bulk properties of the material unchanged. A typical example is nitriding and carbonitriding of steel parts for engines and other machines at relatively low temperatures of about 500 °C in order to increase the hardness of the surface and reduce wear.

Modern nanostructured coatings and thin films for structural and functional applications, which were developed during the past 10–15 years, are used mainly for wear protection of machining tools and for the reduction of friction in sliding parts. One distinguishes between nanolayered coatings, where a few nanometers thin layers of two different materials are deposited subsequently, and nanocomposites, which are, in the optimum case, isotropic. The superhard nanocomposites, such as nc-$(Ti_{1-x}Al_x)N$/a-Si_3N_4 (nc- and a- stand for nanocrystalline and X-ray amorphous, respectively), show superior cutting performance as compared with conventional, state-of-the art hard coatings $(Ti_{1-x}Al_x)N$ that presently dominate the applications for dry machining. The costs of their large-scale industrial production are comparable with those of the conventional coatings (Jilek *et al.*, 2004). Also, the heterostructures and multilayer coatings are successfully applied on industrial scale (Münz *et al.*, 2001; Münz, 2003). Low-friction nanostructured coatings consisting of a hard transition-metal carbide or nitride in combination with a solid lubricant, such as diamond-like carbon (DLC), MoS_2, WS_2 and others that combine with a high hardness and low friction (Voevodin *et al.*, 1996a; 1996b; 1997a; 1997b; Voevodin and Zabinski, 1998; 2000; Voevodin *et al.*, 2002). They are applied in a variety of bearings and sliding parts operating without liquid lubricants, which is an important advantage particularly in a hostile environment, and when the movable parts have to stop and go very frequently, e.g. in the textile industry.

The recent development of nanocomposites consisting of a hard transition-metal nitride or carbide in combination with soft and ductile metal (Baker *et al.*, 2005) is likely to find numerous applications in a variety of machine parts. The hardness of these coatings varies between about 13 and 30 GPa depending on the composition. When deposited under energetic ion bombardment and temperatures below about 350 °C, an enhancement of the hardness up to about 50 GPa was found (Zeman *et al.*, 2000), in a similar way as for hard transition-metal nitrides (e.g. 100 GPa for TiAlVN and 80 GPa for TiN) (Musil *et al.*, 1988; for further examples see Veprek *et al.*, 2005). However, this hardness enhancement is of a little use because, upon annealing to ≥ 500 °C, these coatings soften (Karvankova *et al.*, 2001). Unfortunately, these nanocomposites were often confused (see Musil 2000; and personal communication) with the thermally highly stable superhard nanocomposites prepared according to the generic design principle (Veprek and Reiprich, 1995).

The nanolayered coatings should be subdivided into multilayers and superlattices. When a 3–4 μm thick monolytic layer of a hard ceramic material, such as TiN, is replaced by a stack of 20–100 nm thin multilayers of TiN and another hard nitride, boride or carbide (see Holleck *et al.*, 1990; Zhitomirsky *et al.*, 1999; Soe and Yamamoto, 1999), the resistance against brittle failure strongly increases because the crack cannot propagate through the

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whole layer. Usually, also an increase of the hardness above that of the rule-of-mixtures is found. Similar enhancement was found also in metallic multilayers, for example Fe/Cu and Ni/Cu (Bunshah *et al.*, 1980) and Ni_3Al/Ni (Tixier *et al.*, 1999), and in metal/nitride multilayers, for example Ti/TiN (Kusano *et al.*, 1998). The majority of hard protecting coatings applied to machining tools nowadays are such multilayers.

The concept of superlattices goes back to a theoretical paper of Koehler who suggested depositing alternate epitaxial crystal layers of two different materials A and B with similar lattice parameters but with elastic moduli as different as possible (Koehler, 1970). The thickness of the layer should be small so that dislocation multiplication sources cannot operate. If, under an applied stress, a dislocation moves within the layer with the smaller modulus, it will be hindered in crossing the interface A/B owing to the repelling image force induced within the stronger layer by elastic deformation, when the dislocation approaches that interface. Koehler's concept was experimentally confirmed by Lehocky, who prepared heterostructures consisting of different metals (Lehocky, 1978a; 1978b). Later, several research groups applied this concept to hard transition-metal nitrides and obtained superhard heterostructures with hardnesses of 50–56 GPa for TiN/NbN and TiN/VN systems (Shinn *et al.*, 1992). In a note added in proof, Koehler stated that the ideas described in his paper are also valid if one of the materials is amorphous (Koehler, 1970). Indeed, later work by a number of researchers confirmed that the hardness enhancement can also be achieved in polycrystalline heterostructures and in laminates consisting of amorphous and crystalline materials. For further information the reader should consult some of the numerous reviews (see, for example, Barnett, 1993; Veprek, 1999; Chung and Sproul, 2003; Barnett *et al.*, 2003; Münz *et al.*, 2001; Münz, 2003).

Examples of nanostructured, low-friction hard coatings are nanocomposites consisting of a hard transition-metal carbide (MeC) in combination with amorphous, "diamond-like" carbon (DLC) (Voevodin *et al.*, 1997a), which were originally developed in order to reduce the high-compressive stress in DLC that causes delamination. Alternatively, coatings consisting of multilayers and combination of multilayers with nanocomposites (Voevodin *et al.*, 1996a; Voevodin *et al.*, 1997b) or functionally gradient nanolayered nanocomposites (Voevodin and Zabinski, 1998) can be used. The high degree of hardness of these coatings (exceeding 30 GPa) allows their use under the conditions of a high contact load, and the high toughness provides them with a long lifetime also under impact load. The low friction of these coatings is the result of the formation of a thin hydrated, graphitic surface layer. Such coatings find many applications in sliding gears operating either under a high contact load or in a dusty environment, where liquid lubricants cannot be used. Another advantage of such a "solid lubricant" is the low friction when starting a machine, because when two surfaces lubricated by oil are at rest, the lubricant is pressed out of the surface asperities and, therefore, upon starting, the friction is high. The disadvantage of the DLC-based nanocomposites is the fact that the low coefficient of friction is achieved only in humid atmosphere. In order to solve this problem, Voevodin and co-workers included into the nc-MeC/DLC nanocomposites a second lubricant phase, such as MoS_2 or WS_2, that provides a low coefficient of friction in a dry environment. These coatings show an excellent adaptation of surface properties upon changing the environment (Voevodin and Zabinski, 2000; Voevodin *et al.*, 2002).

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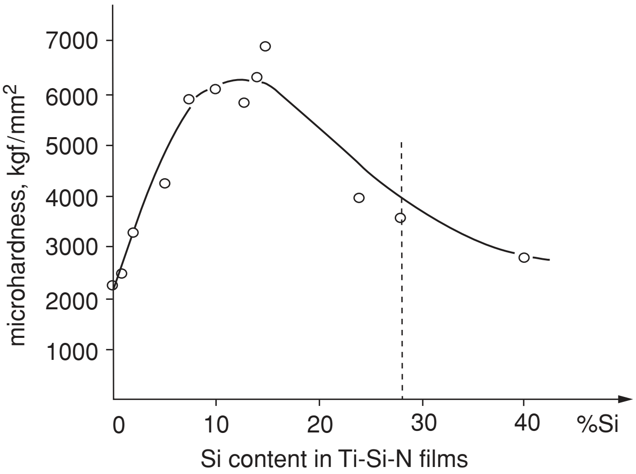

Figure 1.1. Hardness of Ti-Si-N films as a function of Si content (from Li *et al.*, 1992, with permission).

Superhard nanocomposites, such as nc-TiN/a-Si_3N_4 (here a- stands for X-ray amorphous) were pioneered by Li and co-workers who used plasma CVD in order to deposit ≥5 μm thick "Ti–Si–N" coatings at a temperature of 560 °C. A strong hardness enhancement up to ≥60 GPa (Figure 1.1) was found at a silicon content of about 12 at.% (Li *et al.*, 1992). Originally, the researchers attributed the large increase in the hardness to dispersion hardening. However, when, later on, these coating were studied in more detail and the two-phase nature of immiscible stoichiometric nitrides consisting of 3.0–3.5 nm TiN nanocrystals imbedded in X-ray-amorphous Si_3N_4 was found (Veprek *et al.*, 1995a), it became clear that the dispersion hardening cannot operate in such systems. Therefore, a generic design concept for the preparation of such nanocomposites was elaborated (Veprek and Reiprich, 1995) and its validity was verified on several nc-(Me_nN)a-Si_3N_4 (Me = W, V, . . .) systems in which superhardnesses in excess of 40–50 GPa were achieved (Veprek *et al.*, 1995b; Veprek *et al.*, 1996). Compared with conventional hard nitride and carbide coatings the advantage of the superhard nanocomposites is the significantly higher hardness which strongly decreases abrasive wear.

Li and co-workers had noticed that, when the hardness reaches its maximum value, the columnar structure, which is typical for refractory ceramic coatings deposited at a relatively low homologous temperature, vanishes (Li *et al.*, 1992). This was further confirmed for nc-TiN/a-Si_3N_4 (Veprek *et al.*, 1995a) and extended to other systems (Veprek *et al.*, 1995b; Veprek *et al.*, 1996). Furthermore, it was found, that the Si_3N_4 layer provides the nanocomposites with a much higher oxidation resistance than TiN (Veprek *et al.*, 1995a; Veprek and Reiprich, 1995; Veprek *et al.*, 1996). This is because of the formation of a dense interfacial Si_3N_4 layer, the thickness of which was estimated to be about 0.3–0.5 nm (Veprek and Reiprich, 1995). We shall see later in this book that the thickness of the interfacial layer of about one monolayer of Si_3N_4, BN and possibly other covalent nitrides, is crucial for the optimum properties of these materials. More-recent work has suggested that the formation

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of the stable nanostructure probably occurs during the deposition by spinodal mechanism (Zhang and Veprek, 2006). The high immiscibility of the stoichiometric TiN and Si_3N_4 (Rogl and Schuster, 1992) provides the nanocomposites with a high thermal stability up to $\geq 1100\ ^\circ C$. In the case of the nc-$(Ti_{1-x}Al_x)N$/a-Si_3N_4 nanocomposites, the decomposition and softening, which for the conventional $(Ti_{1-x}Al_x)N$ coatings occurs at 800–900 °C, is suppressed up to about 1250 °C (Veprek *et al.*, 2004). Let us emphasize that the high thermal stability and oxidation resistance of the nanocomposites is a very important advantage for their application in dry machining when the temperature of the tool and coatings reaches $\geq 800\ ^\circ C$. For these reasons, the superhard nanocomposites prepared according to the design principle represent a new class of advanced nanocrystalline materials that are already used in large-scale industrial applications.

1.2 Bulk parts

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 for nanostructured matrices the relatively recent focus is the result of new discoveries of unique properties of some nanoscale materials.

Early in the twentieth 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 (Mehl and Cahn, 1983). The phenomenon, discovered by Alfred Wilm (1906) was essentially explained by Merica *et al.* (1919) and the microstructural features responsible were first inferred by the X-ray studies of Guinier (1938) and Preston (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, for example, are clusters of Cu atoms (Guinier–Preston (GP) zones) and the metastable partially coherent θ' precipitate (Porter and Easterling, 1983). 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. Carbide precipitates in certain steels can be nanoscale and affect the mechanical behavior in advantageous ways. A recently developed cast stainless steel with nanoscale alloy carbides has been found to have exceptional strength and creep resistance at operating temperatures up to 800 °C (Maziasz and Pollard, 2003). The many examples of nanoscale second phases on the strength of structural materials are confined to matrices wherein the grain size is "conventional," that is typically tens of microns. The focus of recent work, and of this book, is on structural materials where the matrix has a nanoscale grain size.

If nanocrystalline bulk structural materials could be processed in a cost-effective manner and on a scale sufficient for some present structural applications, it is clear that with

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their special, often superior, properties they might supplant existing conventional grain-size materials. However, at this stage of development this is not possible. Most methods for preparing truly nanocrystalline materials (grain sizes <100 nm) do not allow for significant quantities or sizes of artifact-free bulk materials at the present time. Major breakthroughs in processing will be needed to accomplish this. However, some processing methods, to be discussed in more depth in Chapter 2, are capable of producing limited sizes of artifact-free nanostructured materials. What are the potential uses for such small sample sizes? One potential structural application for nanostructured materials comes from the requirements for miniaturization of components for engineering components for biotechnology, sensors, electro-optics, and micro-nanoscale integration. Material grain sizes must be a factor of 50–100 times smaller than component/feature sizes. Otherwise, mechanical properties will be highly variable and unsuitable for fabrication or end-use. Miniaturization scales <5–10 μm thus require grain sizes <100 nm, that is, nanocrystalline materials. Grain sizes in conventional engineering metals and alloys are typically in the range of 5–50 μm, which would mean that essentially single-crystal behavior would be operative in components of this size. This would lead to large variations in elastic and plastic properties owing to the inherent crystallographic differences in behavior. In conventional parts the grain anisotropies are averaged over millions of grains and such variation is not observed. A general guideline for obtaining uniform and predictable properties using polycrystalline materials is that there should be at least 50 grains on the span of a component or feature cross-section (Ehmann *et al.*, 2000). When this is the case, the resultant mechanical properties will be the uniform polycrystalline averages expected by the manufacturing engineer.

Once the force components, deflections, and other functional requirements are specified for miniaturized components, and material properties are available, the design protocols follow well-established rules. For structural integrity, yield stresses determine the maximum stresses and deflections that are allowed before the onset of plastic yielding failures. Fracture toughness determines the onset of fracture failure, either in static loading or cyclic fatigue loading. Fracture toughness and fatigue-crack growth correlations are used to determine fatigue life. Miniaturization can affect failure modes through changes in the properties owing to grain size reduction or through reduction in component cross-section sizes. With all else constant, this would increase the resistance to fracture and fatigue failures for nanostructured materials. However, fatigue life depends on the number of cycles needed for an initial crack to grow to a critical size. For higher-toughness materials, this length can typically be in the range of centimeters. Consequently, with all else constant, miniaturized components with cross-section sizes on the order of 1 mm or less would have reduced fatigue life because sub-critical cracks grow completely through the cross-section causing premature failure. The existing limited studies on fatigue of nanostructured materials will be discussed in Chapter 4.

Miniaturized parts can be made in relatively high-volume production using the so-called Swiss machining techniques developed decades ago for precision mechanical watch movements. For the current state-of-the-art, multi-axis precision machine tools are commercially available that incorporate high-speed spindles and very small tooling. Figure 1.2 (Scattergood and Koch, 2003) shows an example of miniaturized parts made using these techniques. Figure 1.3 (Scattergood and Koch, 2003) shows a machining tool with

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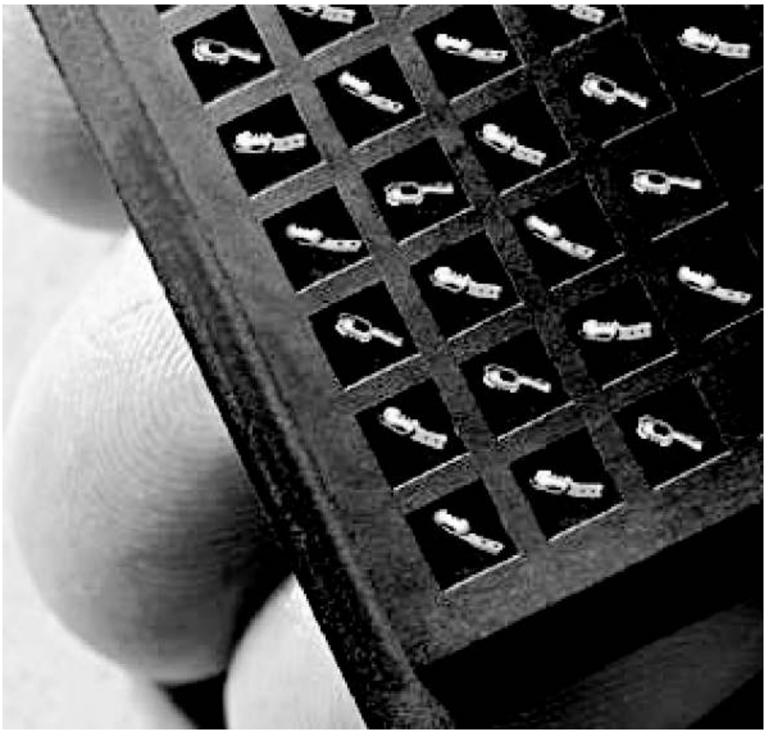

Figure 1.2. Miniaturized parts produced by micromachining. (www.remmele.com)

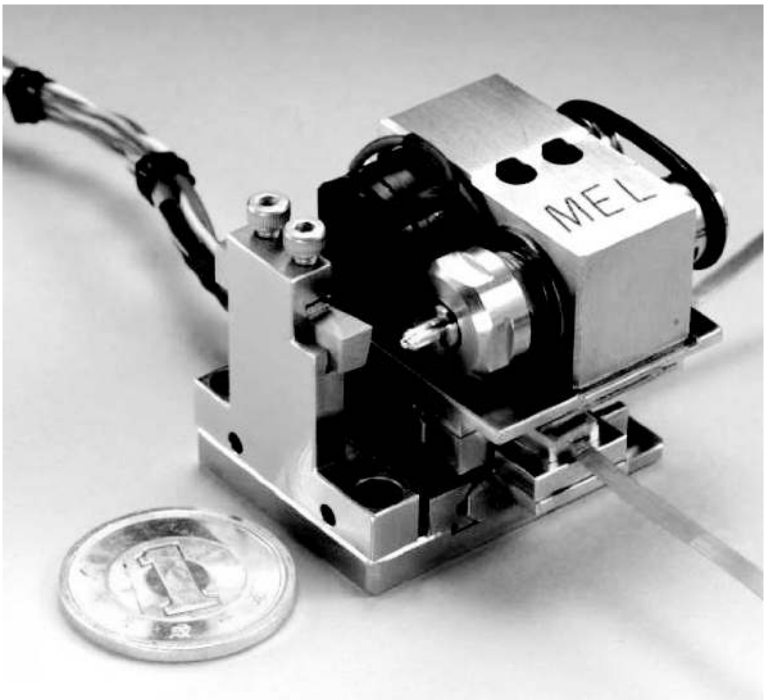

Figure 1.3. Miniature machine tool. Reprinted from Y. Okazaki, N. Mishima, and K. Ashida "Microfactory-Concept, History, and Developments" in *Journal of Manufacturing Science and Engineering*, Nov 2004, vol 126, with permission.

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dimensions of the order of a few centimeters. These advances will undoubtedly change the protocols for designing, manufacturing, and handling very small components for high-volume production applications. The mechanical properties of the nanostructured materials that will be used for such miniaturized parts will have a critical effect on the machining parameters. Delicate tooling requires low tool forces, therefore machining feed rates must be reduced. However, very-high-speed machining appears to be a necessary requirement for volume production using these materials. Burr formation is another important consideration for machining miniaturized parts. Even small burrs become unacceptable when feature sizes are reduced. Depending on the application, removing burrs after machining can be difficult and costly. Since burr formation involves complex deformation paths with a final fracture process to separate the chip from the work-piece, the interplay of the material properties that control burring is not easily identified. Experience shows that high-strength materials, with lower ductility, perform better in this regard. This may be an advantage for nanostructured materials.

1.3 Other nanostructured materials for structural applications

As discussed earlier, nanocrystalline materials have an average grain size less than 100 nm. The small grain size results in positioning the atoms in grain boundaries that are not part of the original crystalline lattice (Sun and Murray, 1999). This structure leads to new material properties and it is possible to utilize this phenomenon to create new structural materials with hardness comparable to that of diamond (Berger, 1996). To obtain materials with combinations of properties, multiphase structures are used. The nanocomposites can be used as hard surfaces with excellent properties and great corrosion resistance. There is a current need for high-performance magnetic composites for a wide variety of structural applications. It is possible to fabricate nanocomposites with new magnetic properties leading to the development of large structural magnets.

1.3.1 Magnetic nanomaterials and composites

Magnetism in small scales has created a lot of interest in potential technological applications (Heinrich and Bland, 1994). Magnetic nanomaterials are the most popular basis for data storage in modern computers, but they are also used in many other fields of science and technology including engineering, medicine, and biotechnology. In magnetic nanoparticles, the magnetization direction often fluctuates and is not necessarily fixed as in larger crystals. Furthermore, if nanoparticles are in close proximity, the magnetic properties are often dominated by phenomena that take place at the interface (Berger, 1996). Magnetic nanoparticles based on transition metals show a variety of unusual magnetic behaviors when compared with the bulk materials. This is mostly because of the surface and the interface effects of symmetry breaking, electronic environment, charge transfer, and magnetic interactions. Reducing the size or dimensions of the magnetic systems changes drastically the electronic properties by reducing the symmetry of the system. This further introduces a quantum limitation in the material; this is often an intriguing aspect of nanoscale magnets.

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These magnets are regarded as molecularly complex with a net magnetic moment considered as a single domain (Slonczewski, 1996). However, in many technological applications such molecular magnets may suffer from poor magnetic densities, but research efforts are on-going to develop magnetic network materials where magnetic centers are combined with organic linker molecules in three-dimensional nanoporous structures. These materials have great structural flexibility due to the variable coordination chemistry of the transition-metal centers. Through changes in the ligands it is possible to control the magnetic properties of the material.

Through the use of appropriate interstitial material, the assembly of these magnetic building blocks into ordered two-dimensional arrays would allow for tunable and externally controllable inter-particle interactions that modify the macroscopic material properties for future application as superior performance magnetic memory, sensors, and ultra-high-speed large-scale device architectures (Urazhdin *et al.*, 2003). The control of structure on the nanoscale has been used to improve the performance of magnetic materials, and this progress in turn will contribute to improvements in performance of electric motors and generators; this is a key component in many structural applications.

The past ten years have seen great interest in the magnetism of reduced dimensionality structures. Researchers around the world have recently started to study one-dimensional and zero-dimensional magnets by laterally structuring thin magnetic films into magnetic quantum wires and dots. As well as being an excellent experimental means of studying fundamental magnetic phenomena, these low-dimensionality magnets may in the future form the basis of new data storage and computing technologies.

One of the biggest challenges of these nanomagnets lies in the complex characterization mode. This is why a new type of nanomagnetic probe uses the Magneto Optical Kerr Effect (MOKE), a phenomenon by which the polarization of light is rotated when it is reflected from the surface of a magnetic material. The NanoMOKE probe can determine quantitative hysteresis loops from small to large arrays of nanomagnets or from individual nanomagnets (Krivorotov *et al.*, 2005). A hybrid magneto-optical magnetometer has been designed and constructed for probing the magnetic properties of submicron nanomagnets. For example, 10 nm-thick square nanomagnets have been fabricated individually and in small arrays from $Ni_{80}Fe_{14}Mo_5$ (“supermalloy”) by electron-beam lithography. Hysteresis loops with a good signal-to-noise ratio have been obtained from individual nanomagnets as small as 400 nm and from arrays of nanomagnets ranging in size from 500 nm to 75 nm (Cowburn *et al.*, 1998).

The strength of a magnet used in structural applications is measured in terms of coercivity and saturation magnetisation values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume) of the grains. It has been shown that magnets made of nanocrystalline yttrium–samarium–cobalt grains possess very unusual magnetic properties owing to their extremely large surface area (Cowburn *et al.*, 1998). Typical applications for these high-power rare-earth nanocrystalline magnets include quieter submarines, automobile alternators, land-based power generators, motors for ships, ultra-sensitive analytical instruments, linear motors using Hallback arrays, and in magnetic resonance imaging (MRI) in medical diagnostics (Buschow, 1988).

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One can also create nanocomposites with soft and hard magnetic attributes via exchange reaction. The system has excellent hard-magnetic properties: the hard-magnetic phase gives rise to a high anisotropy and coercivity, whereas the soft magnetic phase enhances the saturation magnetization (Jianu *et al.*, 2004). Because of their unusual high remanence, large energy product and low cost, the exchange spring magnets provide attractive potential applications as permanent magnets. Micromagnetic calculations (Kneller and Hawing, 1991) and experimental results have shown that the exchange coupling is achieved in nanocomposite materials in which the hard-magnetic ($RE_2Fe_{14}B$, where RE = rare earth) and additional soft (a-Fe or Fe_3B) nanophases are crystallographic coherent. Nanocomposite exchange spring magnets may be obtained from amorphous ribbons with RE–Fe–B defined composition, using suitable annealing treatments. By reducing the rare-earth content we alter the crystallization process. For example, in nanocomposite $Nd_2Fe_{14}B/Fe_3B$ or a-Fe the magnetic properties are strongly related to the microstructure. The optimum structure consists of uniformly distributed soft- and hard-magnetic nanophases.

1.3.2 *Tougher and harder cutting tools*

Large-scale cutting tools made of nanocrystalline materials, such as cemented tungsten carbide, tantalum carbide, and titanium carbide, are much harder, much more wear- and erosion-resistant, and last longer than their conventional (large-grained) counterparts. They also enable the manufacturer to machine various materials much faster, thereby increasing productivity and significantly reducing manufacturing costs. Also, for the miniaturization of microelectronic circuits, the industry needs microdrills, drill bits with diameters much less than the thickness of an average human hair, with enhanced edge retention and far better wear resistance. Since nanocrystalline carbides, nitrides and silicides are much stronger, harder, and wear-resistant, they are currently being used in these microdrills (Singh *et al.*, 2003, Mohanan *et al.*, 2005).

1.3.3 *Better insulation materials*

New insulation materials have been created by utilizing the nanoscale properties of materials. A new foam-like structure called “aerogels” are in fact nanocrystalline oxide materials synthesized by the sol–gel technique discussed later in Chapter 2. These aerogels are porous and extremely lightweight and they can withstand a load equivalent to 100 times their weight. Aerogels are composed of three-dimensional, continuous networks of nano/microcrevices with air or gases trapped at their interstices. Since they are porous and air is trapped at the interstices, aerogels are currently being used for insulation in offices, homes, etc. By using aerogels for insulation, heating and cooling bills are drastically reduced, thereby saving power and reducing the attendant environmental pollution. They are also being used as materials for “smart” windows, which darken when the Sun is too bright, just as in changeable lenses in prescription and sunglasses. They lighten themselves when the Sun is not shining too brightly.

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