2 Nanostructured Materials: Basic Concepts, Microstructure and Properties

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1. INTRODUCTION

Nanostructured Materials (NsM) are materials with a microstructure the characteristic length scale of which is on the order of a few (typically 1-10) nanometers. NsM may be in or far away from thermodynamic equilibrium. NsM synthesized by supramolecular chemistry are examples of NsM in thermodynamic equilibrium. NsM consisting of nanometer-sized crystallites (e.g. of Au or NaCI) with different crystallographic orientations and/or chemical compositions are far away from thermodynamic equilibrium. The properties of NsM deviate from those of single crystals (or coarse-grained polycrystals) and/or glasses with the same average chemical composition. This deviation results from the reduced size and/or dimensionality of the nanometer-sized crystallites as well as from the numerous interfaces between adjacent crystallites. An attempt is made to summarize the basic physical concepts and the microstructural features of equilibrium and non-equilibrium NsM. Concerning the properties of NsM three examples (the diffusivity, the plasticity and the ferromagnetic properties) will be considered. In fact, the properties of NsM will be shown to deviate significantly from those of the corresponding coarse-grained polycrystals if a characteristic length and/or energy scale of the microstructure of NsM (e.g. the grain size, the excess boundary energy, etc.) is comparable to a characteristic length and/or an energy scale controlling a property of a NsM (e.g. the thickness of a ferromagnetic domain wall or an activation energy).

2. BASIC CONCEPTS

One of the very basic results of the physics and chemistry of solids in the insight that most properties of solids depend on the microstructure, i.e. the chemical composition, the arrangement of the atoms (the atomic structure) and the size of a solid in one, two or three dimensions. In other words, if one changes one or several of these parameters, the properties of a solid vary. The most well-known example of the correlation between the atomic structure and the properties of a bulk material is probably the spectacular variation in the hardness of carbon when it transforms from diamond to graphite or vice versa.

The synthesis of materials and/or devices with new properties by means of the controlled manipulation of their microstructure on the atomic level has become an emerging interdisciplinary field based on solid state physics, chemistry, biology and material science. The materials and/or devices involved may be divided into the following three categories Gleiter (1995).

The first category comprises materials and/or devices with reduced dimensions and/or dimensionality in the form of (isolated, substrate-support or embedded) nanometer-sized particles, thin wires or thin films. The second category comprises materials and/or devices in which the nanometer-sized microstructure is limited to a thin (nanometer-sized) surface region of a bulk material. PVD, CVD, ion implantation and laser beam treatments are the most widely applied procedures to modify the chemical composition and/or atomic structure of solid surfaces on a nanometer scale. Surfaces with enhanced corrosion resistance, hardness, wear resistance or protective coatings (e.g. by diamond) are examples taken from today's technology.

In this paper we shall focus attention on the third category of bulk solids with a nanometer-scale microstructure. In fact, we shall focus on bulk solids in which the chemical composition, the atomic arrangement and/or the size of the building blocks (e.g. crystallites or atomic/molecular groups) forming the solid vary on a length scale of a few nanometers throughout the bulk. Two classes of such solids may be distinguished. In the first class, the atomic structure and/or the chemical composition varies in space *continuously* throughout the solid on an atomic scale. Glasses, gels, supersaturated solid solutions or some of the implanted materials are examples of this type.

In the last two decades a second class of materials with a nanometer-sized microstructure has been synthesized and studied. These materials are *assembled of nanometer-sized buildings blocks* – mostly crystallites – as displayed in Fig. 1. These building blocks may differ in their atomic structure, their crystallographic orientation and/or their chemical composition (Fig. 2). In other words, materials assembled of nanometer-sized building blocks are microstructurally *heterogeneous* consisting of the building blocks (e.g. crystallites) and the regions between adjacent building blocks (e.g. grain boundaries). It is this inherently heterogeneous structure on a nanometer scale that is crucial for many of their properties and distinguishes them from glasses, gels, etc. that are microstructurally homogeneous. Materials with this kind of a nanometer-sized microstructure are called "Nanostructured Materials" or – synonymously – nanophase materials, nanocrystalline materials or supramolecular solids. In this paper we shall focus on these "Nanostructured Materials" (NsM).

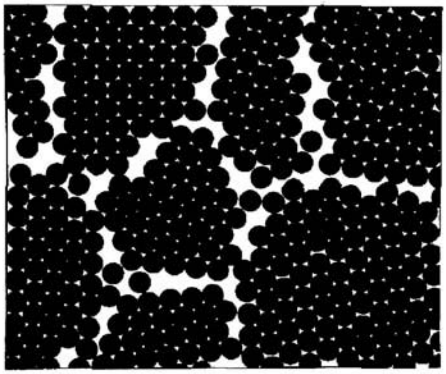

Figure 1 Schematic, two dimensional model of one kind of nanocrystalline material.

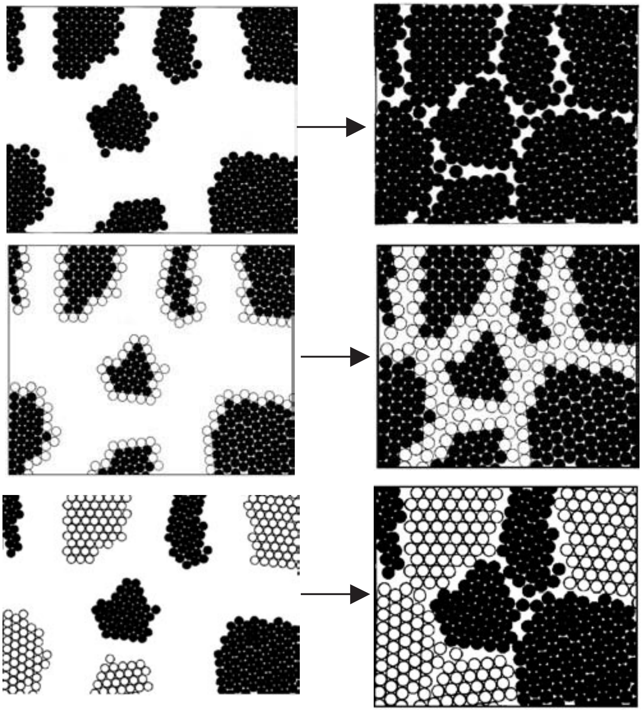

Figure 2 Synthesis of nanomaterials with different chemical microstructures by the consolidation of small, pre-fabricated, isolated nm-sized crystal. (a) All atoms have idendical, chemical composition. (b) The free surfaces of the nm-sized crystals are coated with atoms that differ chemically from the core resulting in a NsM with boundaries that are chemically different from the crystalline regions open and full circles. (c) Nm-sized crystals with different chemical compositions resulting in a nanocomposit.

3. SYNTHESIS OF NANOSTRUCTURED MATERIALS (NSM)

The methods deviced for the synthesis of NsM may be divided in the following two groups.

- Top-down synthesis routes. This approach involves the assembly of NsM from pre-fabricated or pre-existing structural elements (e.g. pre-fabricated nm-sized crystals, supramolecular units, etc.). These elements or building blocks are assembled into a bulk solid with a nm-scale microstructure.
- The bottom-up synthesis starts from individual atoms/molecules and assembles them into a bulk piece of material. Evaporation onto a cold substrate or crystallization from the glassy state are examples of this route of synthesis.

3.1 Top-down Synthesis of NsM

One frequently used top-down route for the synthesis of nanocrystalline materials involves a two-step procedure. In the first step, isolated nanometer-sized crystallites are generated which are subsequently consolidated into solid materials. PVD, CVD, electrochemical, hydrothermal, thermolytic, pyrolytic decomposition and precipitation from solution have been used so far. The most widely applied PVD method involves inert gas condensation. Here, the material is evaporated in an inert gas atmosphere (most frequently helium at a pressure of about 1 kPa) is used. The evaporated atoms transfer their thermal energy to the (cold) helium and hence, condense in the form of small crystals in the region above the vapor source. These crystals are collected and consolidated into a bulk NsM. Instead of evaporating the material into an inert gas atmosphere, bulk nanocrystalline materials may also be obtained by depositing the material in the form of a nanometer-sized polycrystalline layer onto a suitable substrate. The methods for generating small crystallites by precipitation reactions may be divided into processes involving precipitation in nanoporous host materials and host-free precipitation. In both cases a wide range of solvents (e.g. water, alcohol, etc.) as well as different reactions (e.g. addition of complex forming ions, photochemical processes, hydrolytic reaction, etc.) have been utilized. A widely applied method for generating nanometer-sized composites is based on the sol-gel process. An interesting subgroup of sol-gel generated nanocomposits are organic-inorganic nanoscale ceramics, so called ceramers, polycerms of ormocers (Schmidt, 1992). Following the ideas of Mark and Wilkes (Garrido et al., 1990), these materials are prepared by dissolving pre-formed polymers in sol-gel precursor solutions, and then allowing the tetraalkyl orthosilicates to hydrolyze and condense to form glassy SiO_2 phases of different morphological structures. Alternatively, both the organic and inorganic phases can be simultaneously generated through the synchronous polymerization of the organic monomer and the sol-gel precursors.

The main advantages of producing nanocrystalline materials by a two-step procedure (involving the generation of isolated nanometer-sized crystals followed by a consolidation process) are as follows (Fig. 2): (i) Crystals with different chemical compositions can be co-generated, leading to "alloying" on a nanometer-scale. (ii) The free surfaces of the small crystals may be coated prior to the compaction process by evaporation, sputtering, chemical reaction (e.g. by surface oxidation) or in suspension. (iii) The interior of the crystallites may be modified by ion implantation before consolidation. Due to the small crystal size, the implantation results in materials that have the same chemical composition throughout the volume. In bulk materials, ion implantation is limited to surface regions.

3.2 Bottom-up Synthesis of NsM

3.2.1 Synthesis of NsM from glasses or sols

In principle the following two routes have been used so far to generate nano-crystalline materials by means of bottom-up synthesis method. The first method to be discussed here starts from a noncrystalline structure, e.g. a glass. The nanocrystalline materials are obtained by nucleating numerous crystallites in the glass e.g. by annealing. These nuclei subsequently grow together and result in a nano-crystalline material (Fig. 3). The various modifications of this approach differ primarily in the starting material used. So far metallic glasses (e.g. produced by melt spinning, Lu et al., 1991) and (Chakravorty, 1992) have been successfully applied. The most important advantages of this approach are as follows. Low-cost mass production is possible and the material obtained exhibits little or no porosity. Obviously this approach is limited to chemical compositions which permit the generation of glasses or sols.

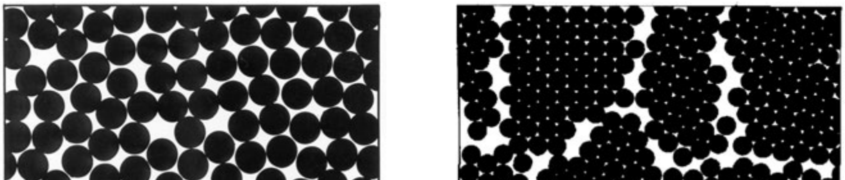

Figure 3 Synthesis of a nanocrystalline material (right figure) by crystallization from the glass (left).

3.2.2 Self-organized[1] nanostructured arrays

A modified Stranski-Krastanov growth mechanism has been noticed to result in self-organized (periodic) arrays of nanometer-sized crystallites. If a thin InGaAs layer is grown on a AlGaAs substrate, the InGaAs layer disintegrates into small islands once it is thicker than a critical value (Nötzel et al., 1995). These islands are spontaneously overgrown by a AlGaAs layer so that nanometer-sized InGaAs crystals buried in AlGaAs result. The observations reported indicate that the size, morphology and the periodic arrangement of the buried islands are driven by a reduction in the total free energy of the system (Pohl et al., 1999).

3.2.3 Polymeric nanostructured materials

So far, the considerations have been limited to elemental or low molecular weight NsM, i.e. NsM formed by atoms/molecules that are more or less spherical in shape. A different situation arises if NsM are synthesized from high molecular weight polymers, i.e. long, flexible molecular chains.

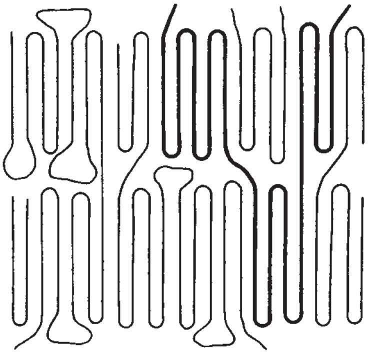

Figure 4 Molecular folding in semicrystalline polymers resulting in stacks of lamellar crystals with a thickness of about 10-20 nm separated by “amorphous” regions.

It is one of the remarkable features of semicrystalline polymers that a nanostructured morphology is always formed (Fig. 4) if these polymers are crystallized from the melt or from solution, unless crystallization occurs under high pressure or if high pressure annealing is applied subsequent to crystallization. The disordered interfacial regions between neighboring crystals (Fig. 4) consist of macromolecules folding back into the same crystal and/or of tie molecules that meander between neighboring crystals. The typical thickness of the crystal lamellae are of the order of 10-20 nm. These relatively small crystal

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[1] In this paper the term self-organization is used for dynamic multistable systems generating, spontaneously, a well-defined functional microstructure. It covers systems exhibiting spontaneous emergence of order in either space and/or time and also includes dissipative structures such as non-linear chemical processes, energy flow, etc. Systems are called self-assembled in the spontaneously created structure is in equilibrium (Landauer, 1987; Haken, 1978 and 1994; Nocolis and Prigogine, 1977).

thickness have been interpreted in terms of a higher nucleation rate of chain-folded crystals relative to extended-chain crystals or in terms of a frozen-in equilibrium structure: at the crystallization temperature, the excess entropy associated with the chain folds may reduce the Gibbs free energy of the chain-folded crystal below that of the extended-chain crystal.

Chain folding may lead to rather complex nanometer-sized microstructures, depending on the crystallization conditions. Spherulites consisting of radially arranged twisted lamellae are preferred in unstrained melts. However, if the melt is strained during solidification, different morphologies may result, depending on the strain rate and the crystallization temperature (i.e. the undercooling). High crystallization temperatures and small strain rates favor a stacked lamellae morphology (Fig. 5a), high temperatures combined with high strain rates result in needle-like arrangements (Fig. 5b). Low temperatures and high strain rates lead to oriented micellar structures (Fig. 5c). The transition between these morphologies is continuous and mixtures of them may also be obtained under suitable conditions (Fig. 5d). The way to an additional variety of nanostructured morphologies was opened when multicomponent polymer systems, so-called **polymer blends**, were prepared. Polymer blends usually do not form specially homogeneous solid solutions but separate on length scales ranging from a few nanometers to many micrometers. The following types of nanostructured morphologies of polymer blends are formed in blends made up of one crystallizable and one amorphous (non-crystallizable) component: (I) The spherulites of the crystallizable component grow in a matrix consisting mainly of the non-crystallizable polymer. (II) The non-crystallizable component may be incorporated into the interlamellar regions of the spherulites of the crystallizable polymer. (III) The non-crystallizable component may be included within the spherulites of the crystallizable polymer forming domains having dimensions larger than the interlamellar spacing. For blends of two crystallizable components, the four most common morphologies are: (I) Crystals of the two components are dispersed in an amorphous matrix. (II) One component crystallizes in a spherulitic morphology while the other crystallizes in a simpler mode, e.g. in the form of stacked crystals. (III) Both components exhibit a separate spherulitic structure. (IV) The two components crystallize simultaneously resulting in so-called mixed spherulites, which contain lammelae of both polymers. **Block copolymers** constitute a class of self-organized nanostructured materials. The macromolecules of a block copolymer consist of two or more chemically different sections that may be periodically or randomly arranged along the central backbone of the macromolecules and/or in the form of side branches. As an example of the various self-organized nanostructured morphologies possible in such systems, Fig. 6 displays the morphologies formed in the system polystyrene/polybutadiene as a function of the relative polystyrene fraction. The large variety of nanostructured morphologies that may be obtained in polymers depending on the crystallization conditions and the chemical structure of the macromolecules causes the properties of polymers to vary dramatically depending on the processing conditions. NsM formed by block copolymers seem to represent (metastable) equilibrium structures despite the high excess energy stored in the interfaces between the structural constituents. The formation of these interfaces results from the local accumulation of the compatible segments of the macromolecules.

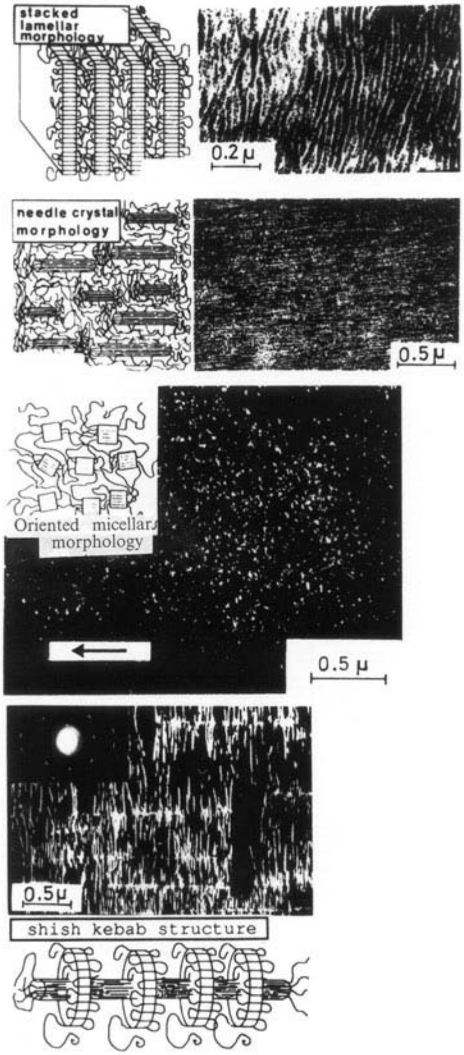

Figure 5 a) Stacked lamellar morphology in polyethylene (TEM bright field). b) Needle-like morphology in polybutene-1 (TEM bright field). c) Oriented micellar morphology in polyethylene terephthalate (TEM dark field) phology in polyethylene terephthalate (TEM dark field micrograph). d) Shish-kebab morphology in isotactic polystyrene (TEM dark field micrograph) (Petermann, 1991).

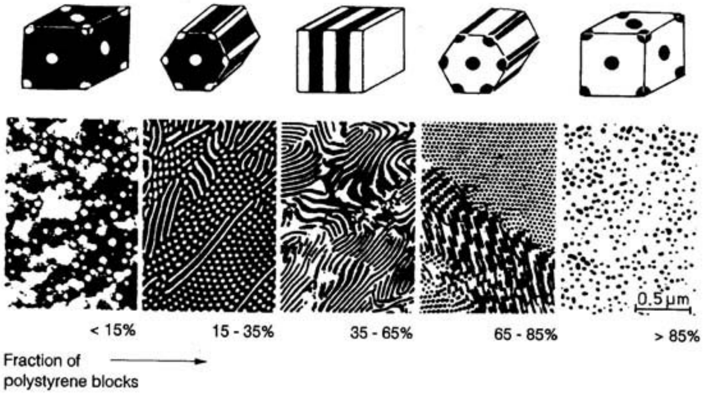

Figure 6 Electron micrographs of the morphologies of a copolymer consisting of polystyrene and polybutadiene blocks, as a function of the fraction of polystrene blocks. The spacial arrangements of the polystyrene and polybutadiene in the solidified polymer are indicated in the drawings above the micrographs (Petermann, 1991).

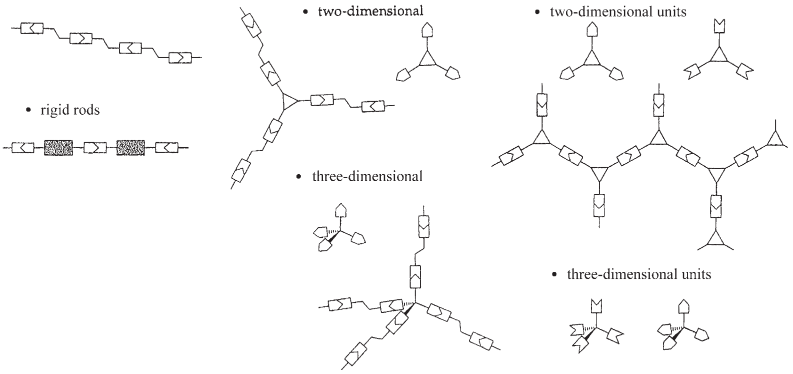

Figure 7 Schematic diagram indicating some of the (many) possible nanometer-sized molecular structures to be synthesized by supramolecular polymer chemistry (Lehn, 1993).

3.2.4 Supramolecular self-assembled structures

Supramolecules are oligomolecular species that result from the intermolecular association of a few components (receptors and substrates) following an inherent assembling pattern based on the principles of molecular recognition.

Supramolecular self-assembly[2] concerns the spontaneous association of either a few or a large number of components resulting in the generation of either discrete oligomolecular supermolecules or of extended polymolecular assemblies or of extended polymolecular assemblies such as molecular layers, films, membranes, etc.

Self-assembly seems to open the way to nanostructures, organized and functional species of nanometer-sized dimensions that bridge the gap between molecular events and macroscopic features of bulk materials. For a detailed discussion of this development and of future perspectives, we refer to the review by Lehn (1995). This paper will be limited to outline only those aspects of the field (Lehn, 1993, 1995 and 1997) that are directly related to the synthesis of NsM.

3.2.5 Self-assembled organic architectures

Self-assembly of organic architectures utilizes the following types of interaction between the components involved: electrostatic interaction, hydrogen bonding, Van der Waals or donor-acceptor effects. Self-assembly by hydrogen bonding leads to two- or three-dimensional molecular architectures which often have a typical length scale of a few nanometers. The self-assembly of structures of this type requires the presence of hydrogen-bonding subunits, the disposition of which determines the topology of the architecture. Ribbon, tape, rosette, cage-like and tubular morphologies have been synthesized.

Supramolecular interactions play a crucial role in the formation of liquid crystals and in supramolecular polymer chemistry. The latter involves the designed manipulation of molecular interactions (e.g. hydrogen bonding, etc.) and recognition processes (receptor-substrate interaction) to generate main-chain or side-chain supramolecular polymers by self-assembly of complementary monomeric components.

Figure 7 displays several different types of polymeric superstructures that represent supramolecular versions of various species and procedures of supramolecular polymer chemistry leading to materials with nanometer-sized microstructures. The controlled manipulation of the intermolecular interaction opens the way to the supramolecular engineering of NsM.

3.2.6 Template-assisted nanostructured materials and self-replication

The basic idea of templating is to position the components into pre-determined configurations so that subsequent reactions, deliberately performed on the pre-assembled species or occurring spontaneously within them, will lead to the generation of the desired nanoscale structure. The templating process may become self-replicating if spontaneous reproduction of one of the initial species takes place by binding, positioning and condensation (Dhal and Arnold, 1991; Philips and Stoddart, 1991; Benniston and Harriman, 1993).

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[2] Self-assembly should be distinguished from templating. Templating involves the use of a suitable substrate that causes the stepwise assembly of molecular or supramolecular structures. These structures would not assemble in the same way without the template.

Inorganic and organic templating has been used for the generation of nanometer-sized polymer arrangements displaying molecular recognition through imprinting, i.e. a specific shape and size-selective mark on the surface or in the bulk of the polymer (Wulff, 1986 and 1993).

Mesophase templating represents a special case that appears to be of considerable significance for the development of this area. Silica precursors when mixed with surfactants result in polymerized silica "casts" or "templates" of commonly observed surfactant-water liquid crystals. Three different mesoporous geometries have been reported (Kresge et al., 1992; Beck et al., 1992; McGehee et al., 1994; Monnier et al., 1993), each mirroring an underlying surfactant-water mesophase. These mesoporous materials are constructed of walls of amorphous silica, only about 1 nm thick, organized about a repetitive arrangement of pores up to 10 nm in diameter. The resulting materials are locally amorphous (on atomic length scales) and periodic on larger length scales.

The availability of highly controlled pores on the 1-10 nm scale offers opportunities for creating unusual composites, with structures and properties unlike any that have been made to date. However, the effective use of mesoporous silicates requires two critical achievements: (i) controlling the mesophase pore structure; and (ii) synthesizing large monolithic and mesoporous "building blocks" for the construction of larger, viable composite materials.

A special case is the reproduction of the template itself by self-replication. Reactions occurring in organized media (e.g. molecular layers, mesophases, vesicles) (Hub et al., 1980; Gros et al., 1981; Ringsdorf et al., 1988; Wegner, 1982; Paelos, 1985; Rees et al., 1993; Vlatakis et al., 1993; Morradian et al., 1989; Sellergren et al., 1989) offer an entry into this field.

Supramolecular templating processes seem to provide an efficient route for the synthesis of nanoporous materials used as molecular sieves, catalysts, sensors, etc. In fact, mesoporous bulk (Kresge et al., 1992; Beck et al., 1992; Beck, 1994; Davis, 1993) and thin-film (Yang et al., 1991; Aksay, 1996) silicates with pore sizes of 2-10 nm have been synthesized by using micellar aggregates of long-chain organic surfactant molecules as templates to direct the structure of the silicate network. Potential applications of these molecular-sieve materials are catalysts, separation membranes and components of sensors.

3.2.7 Synthesis by an highly enhanced free energy

An important approach for synthesizing an organic or metallic NsM by the bottom-up route is based on increasing the free energy of a (initially coarse-grained) polycrystal. The various modifications of this synthesis route differ by the procedures that are applied to increase the free energy. Ball-milling (Fig. 8), high-strain-rate deformation (Fig. 9) sliding wear, irradiation with high-energy particles, spark erosion and detonation of solid explosives have been used so far. All of these techniques are based on introducing a high density of lattice defects by means of plastic deformations or local atomic displacements. The crystal size of the final product can be varied by controlling the milling, the deformation, the irradiation or the wear conditions (e.g. the milling speed, temperature, type of mill used, etc.). This group of methods have been scaled up successfully. For example,

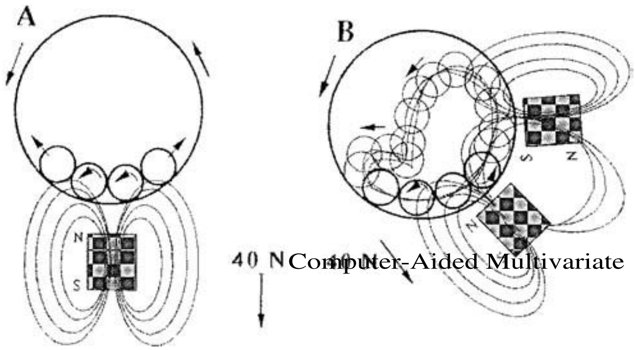

Figure 8 Low temperature magnete ball milling. The trajectories of the balls are controlled by the external magnetic field resulting in shearing (A) or inpaet milling conditions (B). (Calka and Nikolov, 1995).

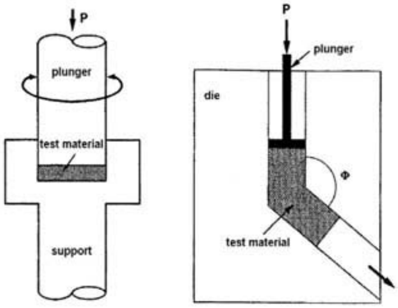

Figure 9 Generation of nanostructured materials by severe plastic deformation. Left side: Severe plastic trosion under pressure. Right side: Equal channel angular extrusion (Valiev, 2000).

cryomilling has been applied to produce commercial quantities of nanocrystalline Al/Al_2O_3 alloys.

4. STRUCTURE-CONTROLLED PROPERTIES OF NANOSTRUCTURED MATERIALS

The properties of solids depends on size, atomic structure and the local chemical composition. Hence NsM may exhibit new properties as all three parameters are modified in a NsM in comparison to a single crystal with the same (average) chemical composition (cf. Fig. 2). In fact, it turns out that the most significant property variations are observed, if a characteristic length, energy, etc. scale of the NsM (e.g. the crystal size, the boundary thickness, the interfacial energy, etc.) becomes comparable to a characteristic length, energy, etc. scale (e.g. a magnetic exchange length, a coherency length, an activation energy, etc.) controlling the properties (e.g. the diffusional, the magnetic etc. properties) of solids. The enhanced diffusivity, the remarkable mechanical and magnetic properties of NsM are used in this paper as examples for the modification of properties by a nanometer-sized microstructure.

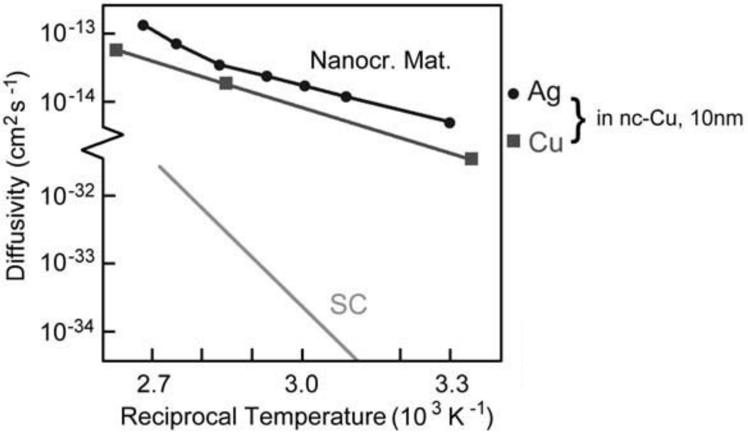

Figure 10 Enhanced diffusivity of Ag and Cu in nanocrystalline Cu. The line labelled SC displays the lattice self diffusion in Cu (Würschum, 1996).

Figure 10 displays, the **diffusivity** of Ag and Cu in nanocrystalline Cu in comparison to the diffusivity in a Cu single crystal. A most remarkable enhancement of the diffusivity of as much as about 10^{18} was noticed[3]. This enhancement results from the high atomic mobility in the grain boundaries between the nanometer-sized Cu crystallites (Horvath et al., 1997; Schumacher et al., 1989). The experimental observations suggest that the enhancement is primarily due to a reduced activation energy of diffusion in the boundaries relative to lattice diffusion. For a comprehensive review we refer to the paper by Würschum (1996).

The high density of grain boundary in nanocrystalline materials has been demonstrated to affect the **mechanical properties** significantly. If the plastic deformation of polycrystals occurs at elevated temperature, deformation processes based on grain boundaries sliding and diffusional processes become increasingly important. In other words, nanocrystalline materials are expected (due to their reduced crystal size) to become more ductile at elevated temperatures than coarse-grained polycrystals with the same chemical composition. The expected enhanced

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[3] For comparison, if the rate of growth of trees is compared with the speed of light in vacuum, one finds an enhancement by a comparable factor.

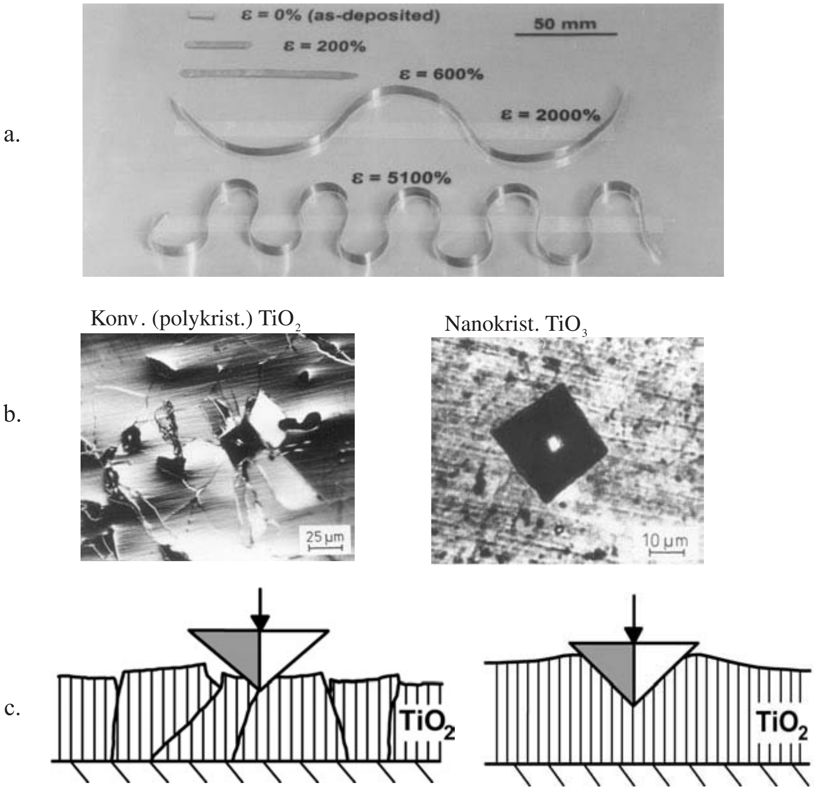

Figure 11 (a) Plastic deformation of nanocrystalline Cu at ambient temperature (Lu et al., 2000). (b) Comparison of the plasticity (diamond indentation) of polycrystalline and nanocrystalline TiO_2 at 20°C. (c) Schematic diagram showing schematically the response of polycrystalline and nanocrystalline TiO_2 if a diamond pyramid penetrates into the material (Karch et al., 1987).

ductility has been experimentally confirmed (Fig. 11) for both metallic (Lu et al., 2000; McFadden et al., 2001), as well as ceramic nanocrystalline materials (Karch et al., 1987). Figure 11 displays the plasticity of nanocrystalline Cu as well as of nanocrystalline TiO_2. At low temperatures, grain boundaries may act as slip barriers during plastic deformation of polycrystals. Hence, nanocrystalline materials are expected to be harder than a single crystal with the same chemical composition. Indeed at low temperatures, nanocrystalline materials were noted to become harder when the crystal size is reduced. A spectacular example of this kind has been reported for nanocomposits of Si_3N_4 and TiN or W_2N, respectively. If the crystal size was reduced to 3 nm, the hardness became comparable to diamond (Veprek et al., 1996).

High performance **hard magnetic materials** are based on the optimization of the intrinsic magnetic properties, the microstructure and the alloy composition. Nanocrystalline microstructures permit the tuning of the exchange and dipolar coupling between adjacent ferromagnetic grains, and, moreover the reduction of the grain size into the ferromagnetic single domain regime (Mc Henry, Laughlin, 2000). Modern developments of computational micromagnetism (Kronmüller et al., 1996) indicate that magnets with maximum coercitivity are obtained if single domain grains are magnetically decoupled by non-ferromagnetic boundary regions. Maximum remanence requires a mixture of magnetically hard and soft nanocrystals. The grain size of the magnetically soft grains (low crystal anisotropy energy) is shown to be optimized if it is about twice the wall width of the hard phase (Fig. 12).

Approaches to improving intrinsic and extrinsic **soft ferromagnetic properties** involve (a) tailoring chemistry and (b) optimizing the microstructure. Significant in microstructural control has been the recognition that a measure of the magnetic hardness (the coercivity, H_c) is roughly inversely proportional to the grain size (D_g) for grain sizes exceeding ~0.1-1 μm where D_g exceeds the domain (Bloch) wall thickness, δ_w. Here grain boundaries act as impediments to domain wall motion, and thus fine-grained materials are usually magnetically harder than large grain materials. Significant recent development in the understanding of magnetic coercivity mechanisms has led to the realization that for very small grain sizes D_g <~100 nm (Herzer, 1997), H_c decreases rapidly with decreasing grain size (Fig. 13). This can be understood by the fact that the domain wall, whose thickness, δ_w, exceeds the grain size, now samples several (or many) grains and fluctuations in magnetic anisotropy on the grain size length scale which are irrelevant to domain wall pinning. This important concept of random anisotropy suggests that nanocrystalline and amorphous alloys have significant potential as soft magnetic materials. Soft magnetic properties require that nanocrystalline grains be exchange coupled.

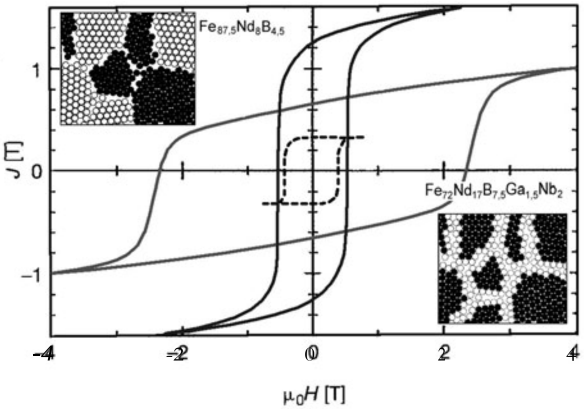

Figure 12 Magnetization curves of high remanence and high coercivity nanocrystalline magnets. The microstructure of the high coercivity material consists of single domain crystallites that are magnetically decoupled by a boundary layer (cf. insert on lower right side). High remanence magnets are composits of a magnetically hard and soft component (cf. insert on upper left side). The magnetization in both components is exchange coupled (Kronmüller et al., 1997).

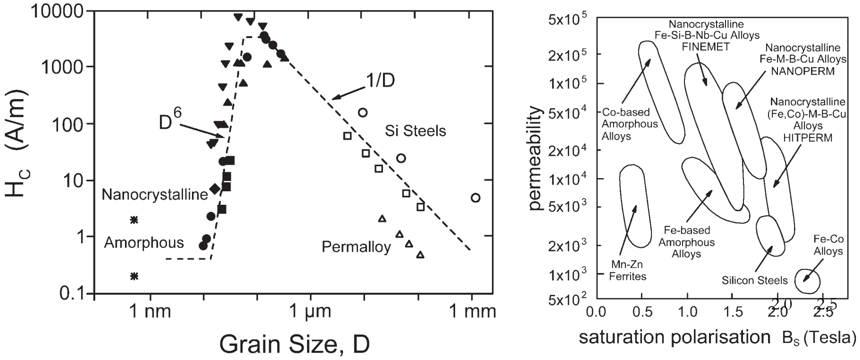

Figure 13 (a) Herzer diagram (Herzer, 1997) illustrating the dependence of the coercivity, H_C, with grain size in magnetic alloys and (b) the relationship between permeability, μ_C (at 1 kHz) and saturation polarization for soft magnetic materials (Makino et al., 1991).

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