Nanocomposite Materials from Theory to Application

H. R. Rezaie, A. Shokuhfar and F. Arianpour

Abstract The idea of the limiting size scale of a miniaturized technology is fundamentally interesting, appealing for several reasons. As sizes are limited to the atomic scale, the relevant physical laws change from the classical to the quantum-mechanical laws of nanophysics. A clear distinction between nanostructures and microstructures is given here arbitrarily using length measurements. Nanostructures are defined according to their geometrical dimensions. This definition addresses technical dimensions, induced by external shaping processes; with the key feature of shaping process, the orientation and the positioning are known in accordance to an external reference system, such as the geometry of a substrate. A narrow definition of nanostructures is that they include structures with at least two dimensions below 100 nm. An extended definition also suggests structures with one dimension below 100 nm and a second dimension below 1 μm. Following this definition, ultrathin layers with lateral submicrometer structure sizes are also considered as nanostructures

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1 Introduction and Definitions

The idea of the limiting size scale of a miniaturized technology is fundamentally interesting appealing for several reasons. As sizes are limited to the atomic scale, the relevant physical laws change from the classical to the quantum-mechanical laws of nano physics [1].

A clear distinction between nanostructures and microstructures is given here arbitrarily using length measurements. Nanostructures are defined according to their geometrical dimensions. This definition addresses technical dimensions, induced by external shaping processes; with the key feature of shaping process, the orientation and the positioning is known in accordance an external reference system, such as the geometry of a substrate. This is of less importance, whether this process uses geometrical tools, media or other instruments [2].

A narrow definition of nanostructures is that they include structures with at least two dimensions below 100 nm. An extended definition also suggests structures with one dimension below 100 nm and a second dimension below 1 μm. Following this definition, ultra thin layers with lateral sub-micrometer structure sizes are also considered as nanostructures [2].

Interactions between atoms, groups of atoms, ions and molecules can vary widely with respect to their intrinsic character and their strength. In order to differentiate these interactions, they were divided into classes known as bond types. These classes are well suited for a description of bonds. In contrast to classical synthetic chemistry where strong bonds are important, often the medium and weak bonds are of particular importance in nanotechnology [2].

There are two ways of approaching the properties of nanoscale objects: the bottom-up approach and the top-down approach. According to the bottom-up approach, it consists of assembling of atoms and molecules into objects whose properties vary discretely with the number of constituent entities, and then increases the size of the object until this discretisation gives way in the limit to continuous variation. The relevant parameter becomes the size rather than the exact number of atoms contained in the object [3].

In the latter case, it considers the evolution of the properties of a sample as its size is whittled down from macroscopic toward nanometric lengths. We will examine this approach here, whilst mentioning zones of overlap and exclusion between the two approaches [3].

Considering a homogeneous solid material of compact shape and macroscopic dimensions, most of its properties will be related to its chemical composition and crystal structure. This is the case that is studied in the physics and chemistry of solids. For an object in this size, the surface atoms comprise a negligible proportion of the total number of atoms and will therefore play a negligible role in the bulk properties of the materials. Note that, however, the surface atoms will nevertheless play a predominant role in properties involving exchanges at the interface between the object and the surrounding medium [3].

The specific surface energy γ (J/m^2) could be presented as the energy produced by cleaving a crystal which causes division of the surface area thereby created. More generally, the specific surface energy can be defined as follows. In order to increase the surface area of an object by the amount "dA", e.g. through changing the shape of the object, the amount of work required to do this will be measured by: $dW = \gamma dA$. Here γ is the specific surface energy. In this case, the area of the object is increased by displacing atoms from the bulk to the surface. However, one could also increase the area by stretching it, i.e., keeping constant the number of surface atoms [3].

The physical properties of conventional materials may change with the size of the grains as their constituent units even becoming totally different from what is observed in the bulk solid system. Now, in case of grain size dependence, this dependence can be categorized into two related effects:

- Size effect or confinement effects:

The nanograin behaves like a kind of box, within which a specific property may or may not exist. Below a certain critical size, characteristics of the property directly and strictly depend on the grain size. This is called the size or confinement effect. The way these characteristics vary as a function of size, is often non-monotonic.

- A surface or interface effect:

Through nanograin, the contribution of layers close to the surface occupies a more considerable and substantial role in the overall behavior of the material as the grain size decreases. The surface energy gradually becomes the dominating contributor to the total energy of the material. Such a property will evolve monotonically with size and can be treated within the framework of thermodynamics [3].

There are many examples of phase transitions occurring while the characteristic dimensions of a material go beyond a certain critical value. More interestingly, such transitions are not restricted to any particular type of material.

The grain size dependence of a phase transition in a ceramic can be normally illustrated by the monoclinic–tetragonal transition occurring in zirconia. This property has been known and exploited for a long period of time. At standard atmospheric pressure and room temperature, zirconia crystallizes in a monoclinic (low temperature) structure, whereas at high temperature, above 1100–1150 °C, its crystal structure tends to be tetragonal. If ZrO_2 crystallizes in the form of 'crystals' with order of 10 nm, it is a tetragonal form that is stable at room temperature. The transition temperature, somewhere between 1100 and 1150 °C for micrometric crystals becomes lower as the dimensions of the nanocrystals decrease [3].

Another situation where the grain size dependence has been established is in the case of the Verwey transition, first observed in 1939 by the discontinuous change in conductivity it causes. This transition occurs in magnetite Fe_3O_4, with the so-called spinel crystal structure. Experiments have also demonstrated a remarkable difference between the temperature predicted for large grains and that

observed for nanometric grains (a difference of more than 70 K). It would thus reveal that the Verwey transition proves another example of grain-size-dependent phase transitions [3].

An example of a grain-size-dependent phase transition in metals is evident in case of Nickel. In the bulk solid, the structure of the element is face centered cubic (FCC). However, recent experiments have brought about to prove a grain size dependent phase transition of small Ni nanoparticles, chemically synthesized in solution. Indeed for diameters less than 4 nm, the structure still remains crystalline, but it becomes hexagonal close packed (HCP) rather than FCC. In the bulk materials, an HCP structure is metastable, although it can be obtained in thin films in certain conditions. It should also be noted that the melting temperature of various metals are known to be dependent on the grain size [3].

2 Nanomaterials

2.1 Introduction

During the last decades, not only nanotechnology has evolved from an imaginary concept into a promising and fast-growing field of science, but has found its way into our everyday life [4]. You have undoubtedly heard of sunscreens or refrigerators featuring some tiny particles which though can't be seen, but are supposed to improve your state of health or the quality of the product. That is true; at the heart of nanotechnology, lie so vast and versatile, nanomaterials. These are no new class of materials, but the same ones used for so many years by humans, manipulated at the finest levels by means of nanotechnology. Today, we can engineer the finest building blocks of materials, i.e., to move single atoms and molecules and place them in the desired locations, to achieve an improved quality in one or more characteristic properties of that material and create the so called "Nanostructured materials" [5]. Nanostructured materials include atomic clusters, layered (lamellar) films, filamentary structures, and bulk nanostructured materials.

More precisely, nanostructured materials are materials with at least one dimension in range of 1–100 nm. They consist of atoms of elements or clusters of mixed elements, all packed together to form a nanoparticle or at a larger scale, a bulk nanostructured material with nanosized crystallites [4].

The type of atoms and their arrangement, i.e., composition and structure, are the key elements which determine the properties of a material. However, when the dimensions become smaller than a certain size, then the size effects also influence the material properties. As discussed above, here, the size of nanoparticle or the crystallite size is equal or smaller than a characteristic length concerning a certain property. The other reason for extraordinary properties of nanostructured materials is the high surface to volume ratio (A/V); that is, the presence of a large fraction of atoms at surfaces or interfaces. This factor indicates that the inter-atomic forces

and chemical bonds play an important role in the behavior of material. In polycrystalline nanostructures, for example, more than half of the atoms could be located in grain boundaries [5].

2.2 Metals

There are many routes and techniques introduced, developed and applied for fabricating and synthesizing nanostructured metals, elemental or alloying systems. Metals, as their solid physics interestingly proves, due to their special bodings, exhibit specific attributes such as high thermal and electrical conductivity. So most of the daily affairs are directly connected with application of metallic and alloying materials, hence myriads of attempts have been always dedicated to improve and develop the properties of them. For this goal, nanostructured metals and alloys and, metal matrix nanocomposites, nanofilms, nanolayers, nanorods and nanotubes of metals have been synthesized. Here, two methods for fabrication and synthesizing nanostructured and nanoparticle metallic materials are introduced [5].

2.2.1 Photo Lithography

Typical photolithographic process consists of producing a mask carrying the requisite pattern information and subsequently transferring that pattern, using some optical technique into a photoactive polymer or photo resist (or simply resist). There are two basic photolithographic approaches: (i) shadow printing, which can be rather divided into contact printing (or contact-mode printing), and proximity printing, and (ii) projection printing. The terms “printing” and “photolithography” are used interchangeably in the literature. Figure 1 outlines the basic steps of the photolithographic process, in which the resist material is applied as a thin coating over some base and subsequently exposed in an image-wise fashion through a mask, such that light strikes selected areas of the resist material. The exposed resist is then subjected to a development step. Depending on the chemical nature of the resist material, the exposed areas may be rendered more soluble in some developing solvent than the unexposed areas, thereby producing a positive tone image of the mask. Conversely, the exposed areas may be rendered less soluble, producing a negative tone image of the mask. The effect of this process is to produce a three-dimensional relief image in the resist material that is a replication of the opaque and transparent areas of the mask. The areas of resist that remain following the imaging and developing processes are used to mask the underlying substrate for subsequent etching or other image transfer steps. The resist material resists the etchant and prevents it from attacking the underlying substrate in those areas where it remains in place after development. Following the etching process, the resist is removed by stripping to produce a positive or negative tone relief image in the underlying substrate. Diffraction sets the limit of the

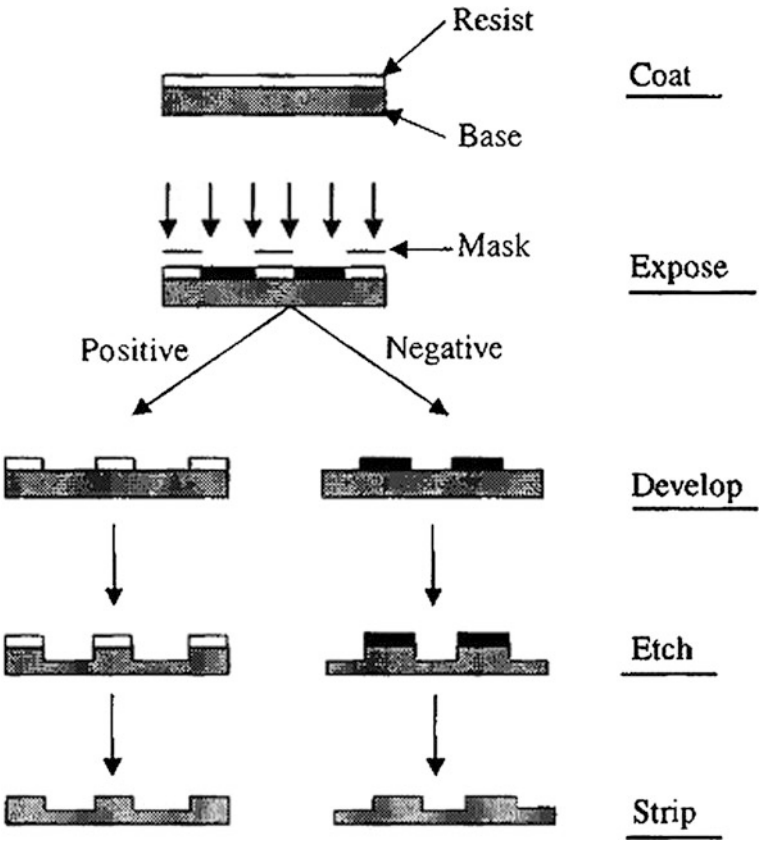

Fig. 1 Schematic representation of the photolithographic process sequences, in which images in the mask are transferred to the underlying substrate surface [6]

maximum resolution or the minimum size of the individual elements by photolithography, which can be obtained [6].

2.2.2 Synthesis of Metallic Nanoparticles

Reduction of metal complexes in dilute solutions is the general method in the synthesis of metal colloidal dispersions, and a variety of methods have been developed to initiate and control the reduction reactions. The formation of mono-sized metallic nanoparticles is achieved in most cases by a combination of a low concentration of solute and polymeric monolayer adhered onto the growth surfaces. Both a low concentration and a polymeric monolayer would hinder the diffusion of growth species from the surrounding solution to the growth surfaces, so that the diffusion process is likely to be the rate limiting step of subsequent growth of initial nuclei, resulting in the formation of uniformly sized nanoparticles. In the synthesis

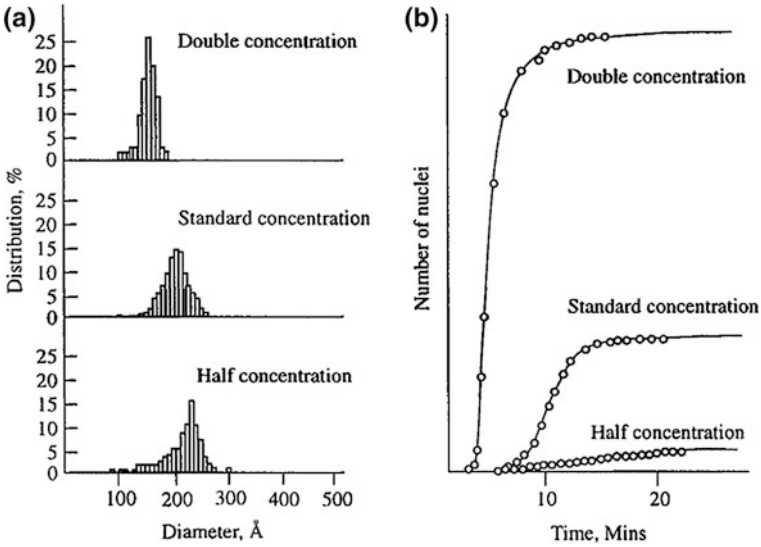

Fig. 2 **a** Particle size distribution curves of gold sol prepared at different concentrations. **b** Nucleation rate curves for gold sols prepared at different concentrations [6]

of metallic nanoparticles, or more specifically speaking, metallic colloidal dispersion, various types of precursors, reduction Reagents, other chemicals, and methods were used to promote or control the reduction reactions, the initial nucleation and the subsequent growth of initial nuclei. The precursors include: elemental metals, inorganic salts and metal complexes, such as, Ni, Co, $HAuCl_4$, H, PtCl, RhCl and $PdCI_2$. Reduction reagents includes: sodium citrate, hydrogen peroxide, hydroxylamine hydrochloride, citric acid, carbon monoxide, phosphorus, hydrogen, formaldehyde, aqueous methanol, sodium carbonate and sodium hydroxide. Examples of polymeric stabilizers include polyvinyl alcohol (PVA) and sodium polyacrylate. Colloidal gold has been studied extensively for a long time. In 1857 Faraday published a comprehensive study on the preparation and properties of colloidal gold. A variety of methods have been developed for the synthesis of gold nanoparticles, and among them, sodium citrate reduction of chlorauric acid at 100 °C was developed more than 50 years ago and remains the most commonly used method. The classical (or standard) experimental conditions are as follows. Chlorauric acid dissolves into water to make 20 ml very dilute solution of $\sim 2.5 \times 10^4$ M. Then 1 ml 0.5 % sodium citrate is added into the boiling solution. The mixture is kept at 100 °C till color changes, while maintaining the overall volume of the solution by adding water. Such prepared colloidal sol has excellent stability and uniform particle size of 20 nm in diameter. It has been demonstrated that a large number of initial nuclei formed in the nucleation stage would result in a larger number of nanoparticles with smaller size and narrower size distribution. Figure 2 compares the size and size distribution of gold nanoparticles and the nucleation rates when the colloidal gold was prepared at different concentrations [6].

2.3 Ceramics

Currently considerable interest in nanocrystalline oxide materials exists owing to their unusual properties. Decreasing particle size results in some remarkable phenomenon. It has been found as particle becomes smaller it leads to:

- Higher catalytic activity (Pt/Al_2O_3).
- Higher mechanical reinforcement (carbon black in rubber).
- Higher electrical conductivity of ceramics (CeO_2).
- Lower the electrical conductivity of metals (not in general but: Cu, Ni, Fe, Co, and Cu alloys).
- Higher photocatalytic activity (TiO_2).
- Higher luminescence of semiconductors.
- Higher blue-shift of optical spectra of quantum dots.
- Higher hardness and strength of metals and alloys.
- Superparamagnetic behavior of magnetic oxides.

Unusual optical and electrical properties in nanostructured materials take place due to a phenomenon known as quantum confinement. The large surface area to volume ratio of nanomaterials leads to their use as catalysts. Excellent sintering characteristics of these fine powders are also useful in ceramics and composites. Dispersion of minute amounts of ceramic particles in various fluids causes the production of corrosion resistant coatings and thin films [7].

The impetus and the ultimate goal in processing of ceramic and oxide materials is to control physical and chemical variability by the assemblage of uniquely homogeneous structures, nanosized second phases, controlled surface compositional gradients, and unique combinations of dissimilar materials to achieve desired properties. Significant improvements in environmental stability and performance should be obtained from such nanoscale or molecular design of materials.

Oxide materials are usually prepared by solid-state reactions, i.e., either by the high temperature method or by precipitation from solution and subsequent decomposition. A variety of metal oxides, with simple or complex compositions are prepared by the conventional ceramic methods. This involves the mixing of constituent metal oxides, carbonates and etc., and their repeated heating and grinding. These methods are used in both laboratory and industrial scale. However, there is an increasing demand for alternate routes of the synthesis of oxide materials that give superior properties when compared with those available from conventional methods. It should not be construed that conventional methods are substandard in any way; they are still used in the industrial production of several oxide materials [7].

Nonuniform powder compositions make reproducible component fabrication difficult because of chemical inhomogeneity and voids in microstructure. Greater purity and homogeneity from novel methods can lead to improved physical properties. Soft chemical routes are now increasingly becoming important to prepare a variety of oxides including nanocrystalline oxide materials. These approaches make it possible the use of simple chemical reactions like co-precipitation, sol–gel, ion

exchange, hydrolysis, acid leaching, and so on, at considerably low temperatures compared to the conventional ceramic methods. Use of precursors, intercalation reactions, electrochemical methods, hydrothermal process, and self-propagating high temperature synthesis (SHS) are some of the other contemporary methods. Although SHS has been successfully used to make non-oxide materials, its application for synthesis of oxide materials was delayed due to economic reasons. Furthermore, it is being a solid-state method, phase purity and particle size control is not possible. Combustion process is different from pyrolysis since once ignited it does not require external heating. In the synthesis of nanomaterials by soft routes there are two approaches: (i) breaking-down and (ii) building-up processes. Solution combustion synthesis of nanocrystalline oxide materials while appearing to be a breaking-down process is in fact an integrated approach, as the desired oxide products nucleate and grow from the combustion residue [7].

2.4 Semiconductors

Semiconductors as most important materials for MEMs and NEMs are being used vastly in electronic devices, as these devices are becoming smaller. The crucial role of nanotechnology in fabricating nanosemiconductors becomes clear. Here, there are some approaches to manufacture nanosemicondutors, but the most applicable one is nanolithography which is developing fast nowadays.

Some examples of this methodology are described below. Very narrow structures have been fabricated through a combination of electron beam lithography with reactive ion etching and ion beam etching or lift-off techniques, yielding, for example, GaAs lines of 10 nm. Silicon structures with high aspect ratios (up to 7) were fabricated by masking Si surfaces with gold nanoparticles and subsequent reactive ion etching in SiC, and plasma. Using 15 nm diameter particles, Si column with a height of up to 100 nm could be achieved. Particles as small as 2 nm were still efficient etching masks [2].

Si needles with extremely high aspect ratios and very small tip diameters were fabricated by a combination of the so-called vapor liquid solid (VU) techniques with ion beam etching. Initially, silicon needles several micrometers in length but only a few micrometers in diameter were created by catalytic deposition on Si from a $SiCl/H_2$ gas mixture. In a second step, these needles were sharpened using Ar or N ions at 30 keV, resulting in tip radii as low as 2 nm. Comparable values were realized by deposition of gold particles on single silicon crystals prior to silicon wafer growth.

Silicon has been subjected to a variety of scanning probe nanolithography experiments. The preferred approach was the oxidation of Si–H surfaces or the direct oxidation of Si into the oxide for local structure fabrication. Another approach applies the direct extraction or deposition of silicon atoms. The width of STM-based, anodically oxidizedlines in silicon increases with voltage, tip current or exposure time. Similar to metals, nanostructured semiconductor materials are of

great interest for the fabrication of single electron tunneling devices. Thus free-standing nanobars of highly-doped silicon with a length of 800 nm and a cross-section of 24 × 80 nm have been fabricated. These dimensions are of great interest to single electron memory devices at room temperature [2].

2.5 Carbon

Carbon is a unique material, and can be a good metallic conductor in the form of graphite, a wide band gap semiconductor in the form of diamond, or a polymer when reacted with hydrogen. Carbon provides examples of materials showing the entire range of intrinsic nanometer scaled structures from fullerenes, which are zero-dimensional nanoparticles, to carbon nanotubes, one-dimensional nanowires to graphite, a two-dimensional layered anisotropic material, to fullerene solids, three-dimensional bulk materials with the fullerene molecules as the fundamental building block of the crystalline phase. In this section, we will briefly discuss the synthesis and some properties of fullerenes, fullerene crystals and carbon nanotubes. For more general research information about carbon science or detailed information on carbon fullerenes and carbon nanotubes, the readers are referred to excellent review articles and books, such as that by Dresselhaus and references therein [8].

Nano-objects of carbon are of particular interest in nanotechnology. They include Buckminster-fullerenes and carbon nanotubes. While the regular, spherical Buckminster fullerenes (e.g., CbOe) exhibit properties of individual single molecules with dimensions in the lower nanometer range, the carbon nanotubes represent a class of nanoobjects that combine properties of molecules with those of solid substrates, and cover a range of dimensions from several micrometers (length) down to a few nanometers (diameter). Therefore, carbon nanotubes exhibit properties of both the mesoscopic world, such as controlled single electron transport, with access to manipulations typical for micro objects. The fabrication of larger quantities of carbon nanotubes has been demonstrated [2, 9].

Carbon nanotubes are often complex structures. Multi-walled tubes reach diameters above 100 nm with hierarchies of several orders of helical structures. Beside continuous walls, spiral cross-sections are also observed. Such tubes with a certain rigidity and length are interesting objects for nanomechanics. One application is their use as ultra thin tips for scanning force microscopy that can be enhanced by subsequent chemical modification for chemical affinity scanning force microscopy. Fullerenes are not only interesting as individual nanoobjects, but also as material for structures in the medium nanometer range. Regular structures in this dimension can be realized by a self-organization process during the thermal activation of fullerene crystals. Single crystals of CG0 exhibit a photon-induced surface reconstruction that leads to periodic structures with dimensions of 30–40 nm [2, 10].

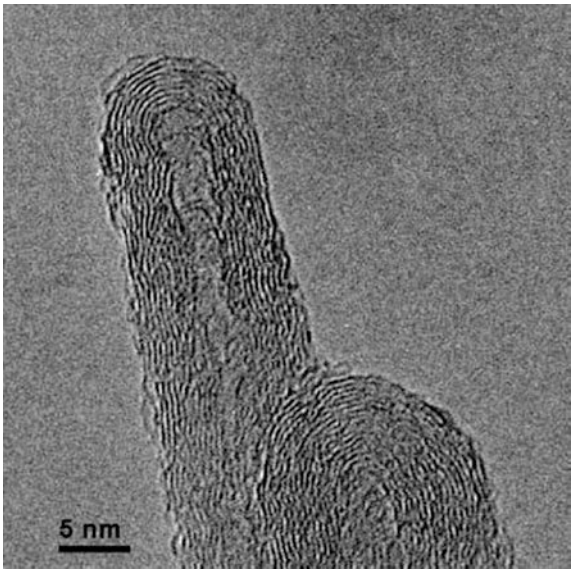

Fig. 3 Carbon nanotubes [11]

Carbon nanotubes, long thin cylinders of carbon, were discovered in 1991. These are large macromolecules that are unique for their size, shape, and remarkable physical properties. They can be thought of as a sheet of graphene (a hexagonal lattice of carbon) rolled into a cylinder. These intriguing structures have sparked much excitement in recent years and a large amount of research has been dedicated to their properties. Currently, the physical properties are still being discovered and disputed. Carbon nanotubes, (Figs. 3, 4) exist as a macromolecule of carbon, analogous to a sheet of graphite (the pure, brittle form of carbon in your pencil lead) rolled into a cylinder. Graphite looks like a sheet of chicken wire, a tessellation of hexagonal rings of carbon. Sheets of graphite in your pencil lay stacked on top on one another, but they slide past each other and can be separated easily, which is how the graphite is used for writing [11].

However, when coiled, the carbon arrangement becomes special and bonding becomes very strong. In fact, nanotubes have been known to be up to 100 times as strong as steel. These nanotubes have a hemispherical "cap" at each end of the cylinder. They are light, flexible, thermally stable, and are chemically inert. They have the ability to be either metallic or semi-conducting depending on the "twist" of the tube. Carbon nanotubes can be found in both single-walled (SWCNT) and multiwalled forms (MWCNT). Determining the elastic properties of SWNTs has been one of the most hotly disputed areas of nanotube study in recent years. On the whole, SWNTs are stronger than metallic glasses and have a much larger elastic limit than steels, and are resistant to damage from physical forces. Pressing on the tip of the nanotube will cause it to bend without damage to the tip or the whole CNT. When the force is removed, the tip of the nanotube will recover to its original state. Quantizing these effects, however, is rather difficult

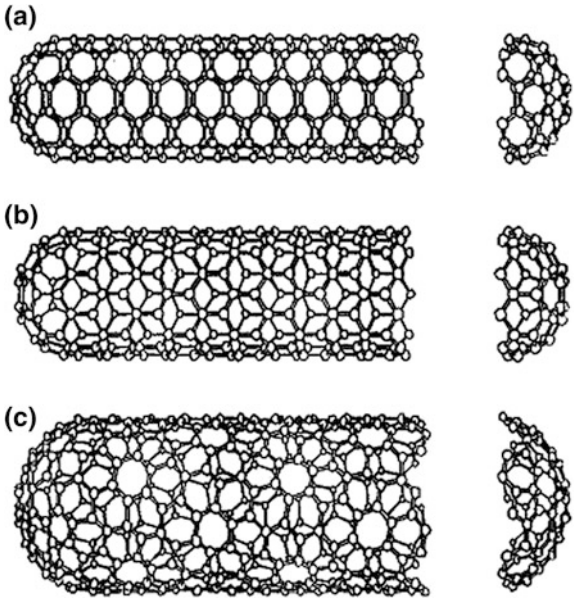

Fig. 4 Schematic models for single-wall carbon nanotubes **a** an armchair nanotube; **b** a zigzag nanotube; and **c** a chiral nanotube [8]

and an exact numerical value cannot be agreed upon. The value of Young's modulus (elastic modulus) for SWNTs lies close to 1 TPa. The maximum tensile strength is close to 30 GPa [11].

2.6 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 keeping the bulk properties of the material unchanged. A typical example is nitriding and carbonitriding of steel parts for engines and other surface applications at relatively low temperatures of about 500 °C in order to increase the hardness of the surface and reduce the wear rate [11].

Modern nanostructured coatings and thin films for structural and functional applications, which were developed during the past decades, are used mainly for wear protection of machining tools and for the reduction of friction in sliding parts and matting surfaces. 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-(Ti1 − xAl_x)N/a-Si_3N_4 (nc- and a- stand for nano-crystalline and X-ray amorphous, respectively), show superior cutting performance as compared with conventional, state-of-the art hard coatings (Ti1 − xAl_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. Also, the heterostructures and multilayer coatings are successfully applied on industrial scale. 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), $MoSi_2$, WS_2 and others that combines with a high hardness and low friction. 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 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, in a similar way as for hard transition-metal nitrides (e.g. 100 GPa for TiAlVN and 80 GPa for TiN). However, this hardness enhancement is of a little use because, upon annealing to ≥500 °C, these coatings soften. Unfortunately, these nanocomposites were often confused with the thermally highly stable superhard nanocomposites prepared according to the generic design principle [11].

2.7 Mesoporous Materials

According to the classification made by IUPAC, porous solids can be grouped into three categories, depending on their pore diameter: microporous ($d < 2$ nm), mesoporous ($2\ nm < d < 50$ nm), and macroporous ($d > 50$ nm) materials. Almost all of zeolites and their derivatives are microporous, whereas surfactant template mesoporous materials and most xerogels and aerogels are mesoporous materials. In this section, we will briefly introduce these mesoporous materials and their respective synthesis techniques. This field has been extensively covered with excellent review articles [12, 13].

Though periodic mesoporous silica had been discovered in 1990, or even much earlier, this type of materials did not attract much attention until 1992, upon the publication of two groundbreaking papers by a group of Mobil's scientists describing the so-called M41S family of mesoporous silicas. Since then, research in this topic has grown so dramatically that it has developed into a separate field. Well over 3000 papers dealing with such materials have been published and a number of international meetings were also devoted to mesoporous materials [14].

Currently, periodic mesoporous silicas may bereadily prepared under an extremely wide range of conditions. Figure 5 shows schematically, the structural parameters that have been explored in the design and synthesis of periodic mesoporous materials. In addition to cationic alkyltrimethylammonium surfactants, a large variety of amphiphile molecules including cationic, anionic, neutral,

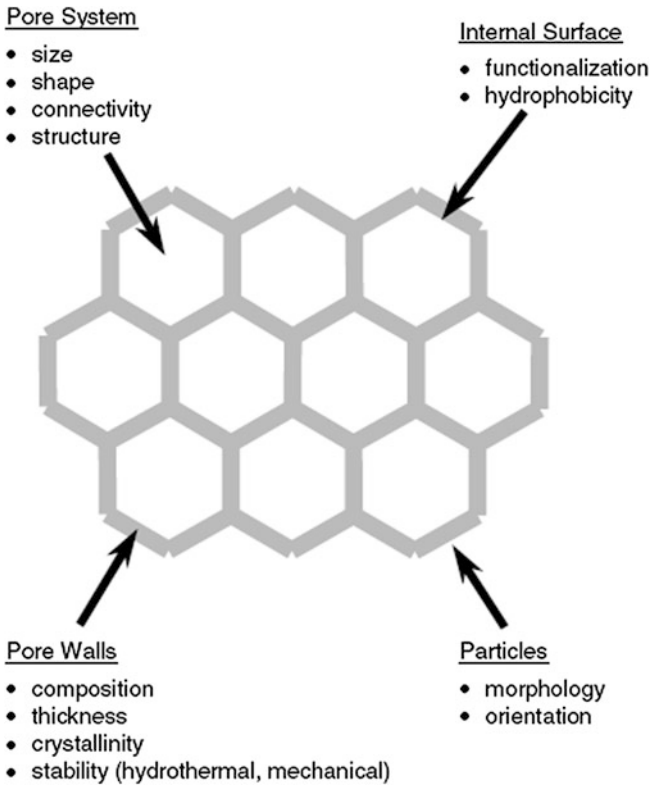

Fig. 5 Structural parameters for the design of mesostructured materials [14]

zwitterionic, bolaamphiphile, gemini anddivalent surfactants as well as many commercially available oligomers and triblockcopolymers and appropriate mixtures were found to be suitable for the preparation of periodic mesoporous silicas. The pH and temperature conditions ranged from extremely acidic to highly basic and from sub ambient to ca. 170 °C, respectively [14].

Furthermore, silica mesophases were in turn used as templates for the synthesis of a variety of other materials such as nanoporous carbons and polymers, as well as metallic and semiconductor nanowires. This extensive effort in the area of synthesis was paralleled by the development of innovative applications not only inconventional fields such as adsorption, separation and catalysis, but also in the area of advanced materials based on their often unique electronic, magnetic and optical properties, or as hosts for quantum dots and sensing species [14].

Since the discovery of the M41S family of silica mesophases, the supramolecular templating technique became a powerful method for the synthesis of mesostructured materials with narrow pore size distributions. Figure 5 lists the main experimental parameters that have been explored in the design and synthesis of such materials [14].

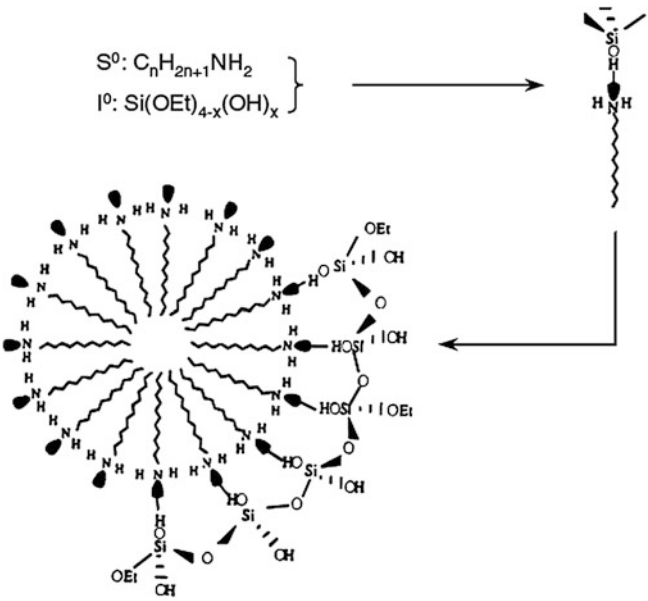

Fig. 6 Neutral templating mechanism [14]

On average, every 2 years since 1992, a new and exciting development in this field occurs. As far as the synthesis of mesostructured materials is concerned, the most important milestones are (i) generalization of synthesis strategies, (ii) framework and surface modified silicas, (iii) non-silica mesostructured materials, (iv) mesoporous organosilicates, and (v) assembly of zeolite seeds into mesoporous structures [14].

Parallel to this remarkable progress in synthesis, a wide variety of potential applications were also investigated. Surface and framework modified mesoporous silicates were tested in a wide range of catalytic processes. The recent discovery that zeolite seeds can be assembled in the presence of amphiphilic molecules into hydrothermally stable mesoporous structures will undoubtedly provide a new impetus to research in acid, redox and photo-catalytic applications using such materials. Moreover, mesoporous silicates were used as molds or nanoreactores for the synthesis of other advanced materials such as metallic or semiconducting nanowires and nanoparticles, as well as nanoporous carbons, metals and polymers [14].

Many mesostructured non-silica oxides and transition metal chalcogenides showed promising applications based on their unique electronic, magnetic or optical properties. The area of synthesis having reached a high level of maturity, it is anticipated that in the future, more attention will be focused on developing innovative applications using mesostructured materials. Figure 6 illustrates neutral templating mechanism [14].

2.8 Nano Crystalline Alloys and Magnetic Materials

A wide variety of nanocrystalline metallic alloys have been developed in recent years, manufactured by rapid solidification from the liquid, condensation from the vapor, electrodeposition and heat treatment of an amorphous precursor. These nanocrystalline alloys have produced considerable scientific interest in understanding the relationships between processing methods and circumstances, structure and properties, and considerable technological interest in use of the resulting products with a wide variety of novel mechanical, magnetic and other properties [15].

High resolution electron microscopy (HREM) has been applied to the understand structure of amorphous alloys, which are strongly dependent on their quenching history in forming the amorphous structure. Atomic medium range order (MRO) in which atomic correlation extends more than several atomic distances often exists in amorphous alloys formed by rapid-quenching and sputter-deposition. The structures of these medium range order regions can be estimated by high-resolution electron microscopy and image simulation when the medium range order sizes are as large as 1–2 nm on the basis of local lattice-fringe spacing and cross-angles of fringes. In amorphous Fe84B16 body centered cubic medium range ordered structures were identified, while in amorphous Pd77:5Cu6Si16:5 and Pd82Si18 face centered cubic medium range ordered structures were identified in the as-formed states by high-resolution electron microscopy. The high-resolution electron microscopy identification of the structure, however, becomes uncertain when the atomic arrangements of medium range order become complex. In such cases, a nanoelectron probe with a probe size of 0.5–2 nm in a field-emission transmission electron microscope (FE-TEM) helps to produce electron diffraction structure analysis of the medium range order [15].

High-strength Al- and Mg-based bulk alloys consisting of novel nanoscale non-equilibrium phases have been produced by rapid solidification and powder metallurgy techniques in Al-Ln-LTM, Al-ETM-LTM and Al-(V,Cr,Mn)-LTM (Ln¼lanthanide metal, LTM¼VII and VIII group transition metals, ETM¼IV to VI group transition metals) alloys with high Al contents of 92–95 % as well as in Mg-Zn-Y alloys with high Mg contents of 96–97 %. Excellent mechanical properties have been obtained by controlling the composition, clustered atomic configuration and stability of the super cooled liquid. The non-equilibrium structures are composed of amorphous, icosahedral quasicrystalline or long periodic hexagonal phases [15].

2.9 Quantum Dots

Nanotechnology is providing an ever increasing number of devices and structures having one, or more than one, dimension less than or equal to about 100 angstroms. The question naturally arises as to the effect of dimensional confinement on the

properties on the phonons in such nanostructures as well as the properties of the phonon interactions in nanostructures. Phonon interactions are altered unavoidably by the effects of dimensional confinement of the phonon modes in nanostructures. These effects exhibit some similarities to those for an electron confined in a quantum dot [16].

Nanoscale materials frequently show behavior which is intermediate between that of a macroscopic solid and that of an atomic or molecular system. Consider, for instance, the case of an inorganic crystal composed of few atoms. Its properties will be different from those of a single atom, but we cannot imagine that they will be the same as those of a bulk solid. The number of atoms on the surface of crystal, for instance, is a significant fraction of the total number of atoms (as discussed above), and therefore will have a large influence on the overall properties of the crystal. We can easily imagine that this crystal might have a higher chemical reactivity than the corresponding bulk solid and that it will probably melt at lower temperatures. A fundamental aspect of quantum mechanics is the particle-wave duality, introduced by De Broglie, according to which any particle can be associated with a matter wave whose wavelength is inversely proportional to the particle's linear momentum. Whenever the size of a physical system becomes comparable to the wavelength of the particles that interact with such a system, the behavior of the particles is best described by the rules of quantum mechanics. The solutions of the Schrodinger equation in such case are standing waves confined in the potential well, and the energies associated with two distinct wave functions are, in general, different and discontinuous. This means that the particle energies cannot take on any arbitrary value, and the system exhibits a discrete energy level spectrum. Transitions between any two levels are seen as discrete peaks in the optical spectra, for instance. The system is then also referred to as "quantum confined". If all the dimensions of a semiconductor crystal shrink down to a few nanometers, the resulting system is called a "quantum dot" [17].

Quantum dots are the ultimate example of a solid in which all dimensions shrink down to a few nanometers. Moreover, semiconductor quantum dots are probably the most studied nanoscale systems. When charge carriers and excitations are confined in all three dimensions, the system is called a "quantum dot". The division is somewhat arbitrary, since, for instance, clusters made of very few atoms are not necessarily considered as quantum dots. Although clusters are smaller than the De Broglie wavelength, their properties depend critically on their exact number of atoms. Large clusters have a well-defined lattice and their properties no longer depend critically on their exact number of atoms. The ultimate technique for the fabrication of quantum dots should be able to produce significant amounts of sample, with such a high control of quantum dot size, shape and monodispersity that single-particle properties are not averaged by sample inhomogeneity. So far, ensembles of quantum dots produced by the best available techniques still show behavior deriving from a distribution of sizes, but this field is evolving very rapidly. Various techniques lead to different typologies of quantum dots. The confinement can be obtained in several different ways, and in addition the quantum dot itself can have a peculiar arrangement with respect to its

surrounding: it can be embedded into a matrix or grown onto a substrate, or it can be a "free" nanoparticle. Each of these cases is strictly related to the preparative approach chosen [17].

2.10 Nanostructured Biological Materials

Several billion years of evolution have led to the generation of an astonishing variety of biological organisms. These organisms vary in many ways, but their fundamental building blocks remain the chemical structures of nucleic acids, proteins, and lipids that make life possible. The hierarchical assembly of these fundamental building blocks into working biochemical machinery is the foundation of cellular function. Many of these assembly processes, however, occur at a size regime in which visualization and characterization are difficult. Detailed structural characterization is an essential goal, not only for understanding these processes, but also for harnessing this technology for later technological application [18].

Each of the biological materials mentioned (nucleic acids, proteins, and lipids) is nanostructured in different ways. Nucleic acids, through base stacking and specific hydrogen bond base pairing, are the informational media for the genetic code. Furthermore, nucleic acids can fold into complex structures that are chemically active. The structure of biological materials is a result of both their chemical composition and their environment. Chemical composition, such as the polypeptide sequence of a protein or the sequence of bases in a nucleic acid strand, is a key determinant of structure. Environment affects the structure of these materials in much more subtle and deterministic ways than most man-made materials. The components found in an aqueous solution, as well as their concentrations, will determine the detailed structure of a bimolecular system. The behavior of these biomaterials varies and often goes beyond a simple assessment of their function. For example, although an enzyme's duty may be converting a substrate into a product, its behavior in a given system may involve not only that catalytic process, but also such processes as diffusive motions, regulatory controls, conformational changes, and environmental factors. These behaviors are important, for they dictate what is actually occurring with the enzyme in the broadest sense; they are not limited, for example, to a simple chemical transformation. As biological systems are utilized more and more for technological applications, their behavior in particular, nonphysiological environments becomes more critical.

Manipulation of these biomolecular assemblies and the nanomaterials they are used in involves engineering and control at the nanometer-scale. This often means ordering a material by crystallization or confining it to nanometer scale regions through the use of patterning or lithography. The ability to change a system at the nanometer scale to construct new, scientifically interesting systems or to suit new design requirements is one of the most exciting aspects of this field and is broadly termed nanostructured materials research [18].

3 Nanocomposites

3.1 Introduction

The field of nanocomposite materials has been under close attention, imagination, and close scrutiny of scientists and engineers in recent years. This scrutiny results from the simple premise that using building blocks with dimensions in the nanosize range makes it possible to design and create new materials with unprecedented flexibility and improvements in their physical properties.

Nanocomposites and nanograined materials have been studied extensively mainly for improved physical properties [19] Nanocomposites refer to materials consisting of at least two phases with one dispersed in another that is called matrix and forms a three-dimensional network, whereas nanograined materials are generally multi-grained single phase polycrystalline materials. A reduced particle size would definitely promote the densification of composites and polycrystalline materials, due to the large surface area and short diffusion distance [6].

The ability to tailor composites by using nanosize building blocks of heterogeneous chemical species has been demonstrated in several interdisciplinary fields. The most convincing examples of such designs are naturally occurring structures such as bone, which a hierarchical nanocomposite is built from ceramic tablets and organic binders. Because the constituents of a nanocomposite have different structures and compositions and hence properties, they serve various functions. Thus, the materials built from them can be multifunctional. Taking some clues from nature and based on the demands that emerging technologies put on building new materials that can satisfy several functions at the same time for many applications, which scientists have been devising synthetic strategies for producing nanocomposites. These strategies have clear advantages over those used to produce homogeneous large-grained materials. Behind the push for nanocomposites is the fact that they offer useful new properties compared to conventional materials [20].

Nanocomposites can be considered solid structures with nanometer-scale dimensional repeat distances between the different phases that constitute the structure. These materials typically consist of an inorganic (host) solid containing an organic component or vice versa. Or they can consist of two or more inorganic/organic phases in some combinatorial form with the constraint that at least one of the phases or features is in the nanosize [20].

Many efforts are under way to develop high-performance ceramics that have promising properties for engineering applications such as highly efficient gas turbines, aerospace materials, automobiles, etc. Even the best processed ceramic materials used in applications pose many unsolved problems; among them, relatively low fracture toughness and strength, degradation of mechanical properties at high temperatures, and poor resistance to creep, fatigue, and thermal shock. Attempts to solve these problems have involved incorporating second phases such as particulates, platelets, whiskers, and fibers in the micron-size range at the matrix

grain boundaries. However, results have been generally disappointing when micron-size fillers are used to achieve these goals. Recently the concept of nanocomposites has been considered, which is based on passive control of the microstructures by incorporating nanometer-size second-phase dispersions into ceramic matrices [20]. Dispersing metallic second-phase particles into ceramics improves their mechanical properties (e.g., fracture toughness). A wide variety of properties, including magnetic, electric, and optical properties, can also be, tailored in the composites due to the size effect of nanosized metal dispersions. Conventional powder metallurgical methods and solution chemical processes like sol–gel and co-precipitation methods have been used to prepare composite powders for ceramic/metal nanocomposites such as Al_2O_3/W, Mo, Ni, Cu, Co, Fe, ZrO_2/Ni, Mo, MgO/Fe, Co, Ni; and so on [20].

Nanocomposite technology is also applicable to functional ceramics such as ferroelectric, piezoelectric, varistor, and ion-conducting materials. Incorporating a small amount of ceramic or metallic nanoparticles into $BaTiO_3$, ZnO, or cubic ZrO_2 can significantly improve their mechanical strength, hardness, and toughness, which are very important in creating highly reliable electric devices operating in severe environmental conditions [20].

Advanced bulk ceramic materials that can withstand high temperatures (>1500 °C) without degradation or oxidation are needed for applications such as structural parts of motor engines, gas turbines, catalytic heat exchangers, and combustion systems. Such hard, high-temperature stable, oxidation-resistant ceramic composites and coatings are also in demand for aircraft and spacecraft applications [20].

Considerable attention has been devoted to "functionally graded nanocomposite materials", for which gradually varying the dispersion (nanoparticles) to matrix ratio in chosen directions continuously changes the material. An example of such a material is SiC dispersions in a C (pyrolytic graphite) matrix, which has served well as thermal barriers on the space shuttle due to its excellent resistance to oxidation and thermal shock [20].

Thin-film nanocomposites are films consisting of more than one phase, in which the dimensions of at least one of the phases are in the nanometer range. These nanocomposite films can be categorized as multilayer films, in which the phases are separated along the thickness of the film, or granular films, in which the different phases are distributed within each plane of the film. Multilayered thin-film nanocomposites consist of alternating layers of different phases and have a characteristic thickness on the order of nanometers. These films are usually used for their enhanced hardness, elastic moduli, and wear properties [20].

Improved wear resistance, good high-temperature stability, and improved friction properties are important characteristics of good coatings for use in applications such as cutting tools. Most widely used coatings are made from TiN, TiC, TiAlN, CrN, diamond-like carbon (DLC), WC/C, MoS_2, Al_2O_3, etc. For improved coatings in which lower friction, increased life time, increased toughness, higher thermal stability, and in some cases, environmental (biomedical, for

example) compatibility are needed, new types of materials are being considered, including nanocomposite materials.

The mechanical behavior of carbon nanotubes is exciting, since nanotubes are seen as the ultimate carbon fiber ever made. The most important application of nanotubes, based on their mechanical properties, will be as reinforcements in composite materials. The nanotube reinforcements promise to increase the fracture toughness of the composites by absorbing energy through their highly flexible elastic behavior during deformation, which will be especially important for nanotube-based ceramic matrix composites. Possible applications are in light-weight armor or conductive durable ceramic coatings [20].

Polymer composites are important commercial materials with applications that include filled elastomers for damping, electrical insulators, thermal conductors, and high-performance composites for use in aircraft. Materials with synergistic properties are chosen to create composites with tailored properties; for example, high-modulus but brittle carbon fibers are added to low-modulus polymers to create a stiff, lightweight composite with some degree of toughness. Recently, a large window of opportunity has opened to overcome the limitations of traditional micrometer-scale polymer composites–nanoscale filled polymer composites in which the filler is <100 nm in at least one dimension. Although some nanofilled composites (carbon black and fumed silica filled polymers) have been used for more than a century, research and development of nanofilled polymers has greatly increased in recent years, for several reasons. The small size of nanofillers can also lead to unique properties of the particles themselves [20].

For example, single-walled nanotubes are essentially molecules, free from defects, and have a modulus as high as 1 TPa and strengths that may be as high as 500 GPa. In addition to the effect of size on particle properties, the small size of the fillers leads to an exceptionally large interfacial area in the composites. The interface controls the degree of interaction between the filler and the polymer and thus controls the properties. Therefore, the greatest challenge in developing polymer nanocomposites may be learning to control the interface. Thus, it seems relevant to define the interfacial region and discuss its properties [20].

Nanocomposites and nanograined materials are not necessarily limited to the bulk materials made by sintering nanosized powders. Deposition of a solid inside a porous substrate, by vapor chemical reactions, is one established technique, referred to as chemical vapor infiltration, for the synthesis of composite [21]. Nanocomposites of polymers and metals or polymers and semiconductors are reviewed by Caseri [22]. Extensive research on various carbon nanotube composites were reviewed by others. A variety of nanostructured materials that have been discussed in previous chapters including this one can be perfectly grouped as nanocomposites or nanograined materials. For example, class I organic–inorganic hybrids can be considered as an organic–inorganic nanocomposite, anodic alumina membrane filled with metal nanowires is metal-ceramic composite.

3.2 Ceramic Nanocomposites

In the past few years, considerable attention has been paid to the development of nanocrystalline ceramics with improved mechanical strength and stiffness, and enhanced wear resistance. Decreasing the grain size of ceramics to the submicrometer/nanometer scale leads to a marked increase in hardness and fracture strength. However, nanocrystalline ceramics generally display worse fracture toughness than their microcrystalline counterparts. The toughness of nanoceramics can be enhanced by adding second phase reinforcements. Grain size refinement in ceramics and their composites can yield superplasticity at high strain rates. Superplasticity is a flow process in which crystalline materials exhibit very high tensile ductility or elongation prior to final failure at high temperatures. Superplastic deformation is of great technological interest because it leads to lower processing temperature and time, and enables near net shape forming of ceramic products. The ability to prevent premature failure of ceramics at high strain rates can have a large impact on the production processes. The development of advanced technologies in the aeronautics, space and energy sectors requires high performance materials with excellent mechanical properties, high thermal conductivity and good wear resistance. Metallic composites can meet these requirements but they suffer from corrosion and oxidation upon exposure to severe aggressive environments [23].

Ceramic-based materials such as zirconia (ZrO_2), alumina (Al_2O_3), silicon carbide (SiC), silicon nitride (Si_3N_4) and titanium carbide (TiC) have been used in industrial sectors at high temperatures due to their intrinsic thermal stability, good corrosion resistance, high temperature mechanical strength and low density. However, ceramics are known to exhibit low fracture toughness since plastic deformation in ceramics is very limited. Several approaches have been adopted to improve the fracture toughness of ceramics. Transformation toughening involves the occurrence of phase transformation in zirconia-based ceramics to arrest the propagation of cracks. Pure zirconia exhibits three different crystalline structures: monoclinic (room temperature to 1170 °C), tetragonal (1170–2370 °C) and cubic (>2370 °C). Several stabilizers or dopants are known to stabilize the tetragonal and cubic phases at room temperature in the metastable state. Partial stabilization enables retention of the metastable tetragonal phase of zirconia at ambient temperature by adding appropriate dopants such as MgO, CaO and Y_2O_3 [23].

Fracture toughness of ceramics can also be improved by the addition of ceramic reinforcements in the forms of particulates, whiskers, and fibers to form ceramic matrix composites (CMCs). The reinforcing effect of fibers is much higher that of particulates and whiskers. Continuous silicon carbide and carbon fibers have been widely used to reinforce ceramics. The toughening mechanisms of fiber-reinforced CMCs are mainly attributed to the crack deflection at the fiber-matrix interface, crack bridging and fiber pull-out. It has been demonstrated that weak fiber-matrix interfacial bonding facilitates the fiber pull-out toughening mechanism to operate.

This is due to strong interfacial bonding which allows the crack to propagate straight through the fibers, resulting in low fracture toughness [23].

3.3 Carbon Nanotube Reinforced Ceramic Nanocomposites

Carbon nanotubes (CNTs) with high aspect ratio, extraordinary mechanical strength and stiffness, excellent thermal and electrical conductivity (as briefly discussed above in previous sections) are attractive nanofillers which produce high-performance ceramic composites with multifunctional properties. The reinforcing effect of CNTs with high aspect ratio is considered to be analogous to that of continuous or short-fiber-reinforcement. The superior flexibility of CNTs is very effective in improving the fracture toughness of brittle ceramics. This is accomplished by means of crack deflection at the CNT-matrix interface, crack-bridging and CNT pull-out mechanisms. Recently, Huang et al. reported that SWNTs exhibit super plastic deformation with an apparent elongation of 280 % at high temperatures. This finding shows the potential application of CNTs as reinforcing fillers for CMCs with improved ductility. Thus, such ceramic-CNT nanocomposite could possess superplastic deformability. Peigney et al. investigated the extruding characteristics of metal oxide-CNT nanocomposites at high temperatures. They indicated that superplastic forming of nanocomposites will become easier through addition of CNTs. All these attractive and unique properties of CNTs enable materials scientists to create novel strong and tough ceramic and metallic nanocomposites. Moreover, the electrical and thermal conductivities of ceramics can be improved markedly by adding nanotubes. The electrical conductivity of alumina-CNT composites can reach up to twelve orders of magnitude higher than their monolithic counterpart. Recent study has shown that the thermal conductivity of alumina-CNT nanocomposites exhibits anisotropic behavior. The nanocomposites conduct heat in one direction, along the alignment of the nanotube axial direction, but reflect heat at right angles to the nanotubes. This anisotropic thermal behavior makes alumina-CNT nanocomposites potential materials for application as thermal barrier layers in microelectronic devices, microwave devices, solid fuel cells, chemical sensors, and so on [23].

3.4 Preparation of Carbon Nanotube Reinforced Ceramic Nanocomposites

Despite the fact that the CNTs exhibit remarkable mechanical properties, the reinforcing effect of CNTs in ceramics is far below our expectation. The problems arise from inhomogeneous dispersion of CNTs within the ceramic matrix, inadequate densification of the composites and poor wetting behavior between CNTs and the matrix. All these issues are closely related to the fabrication processes for

making ceramic-CNT nanocomposites. As recognized, CNTs are hard to disperse in ceramics. They tend to form clusters caused by van der Waals force interactions. Such clustering produces a negative effect on the physical and mechanical properties of the resulting composites. Individual nanotubes within clusters may slide against each other during mechanical deformation, thereby decreasing the load transfer efficiency. Furthermore, toughening of the ceramic matrix is difficult to achieve if the CNTs agglomerate into clusters. Carbon nanotube clusters minimize crack bridging and pull-out effects greatly. Therefore, homogeneous dispersion of CNTs in the ceramic matrix is a prerequisite of achieving the desired mechanical properties [23].

Spark plasma sintering (SPS) is recognized as an effective process for achieving higher densification of ceramics at a relatively lower temperature with short holding time. Accordingly, several researchers have used the SPS method to consolidate ceramic-CNT nanocomposites. For instance, Balazsi et al. compared the effects of HIP and SPS treatments on the microstructural and mechanical properties of Si_3N_4/MWNT nanocomposites. Large differences in the properties of composites prepared by these two sintering techniques have been found. Fully dense nanocomposites with improved mechanical properties can be achieved using the SPS method. In contrast, HIP-treated composites exhibit a partially dense structure with coarse grains [23].

One possible approach to improve the wettability between CNTs and inorganic ceramic host is to coat CNT surfaces with proper surfactants. However, surfactants may introduce undesirable impurities that can affect the sintering process and resulting ceramic-CNT composite properties. It has been reported that molecular level mixing, aqueous colloid and polymer-derived ceramics processes can yield homogeneous dispersion of CNTs and strong interfacial strength in the ceramic-CNT nanocomposites. For example, Fan et al. reported that the fracture toughness of the alumina/SWNT nanocomposites is twice that of monolithic alumina. They attributed this to the strong interfacial CNT-alumina bonding obtained by heterocoagulation [23].

3.5 Oxide-Based Ceramic Nanocomposites

For most Al_2O_3/CNT nanocomposites, CNTs were synthesized independently, and then introduced into micro- or nano alumina powders under sonication to form nanocomposites. This may lead to poor dispersion of nanotubes in the alumina matrix. A growing interest has been directed toward the synthesis of Al_2O_3/CNT nanocomposites by the in situ reaction method. This can be achieved by exposing transition metal/metal oxide catalysts to reactive gases at high temperatures. The advantage of this technique is that the CNTs formed in situ are directly incorporated into the alumina matrix during the synthetic process. For instance, Peigney et al. used a catalysis method for the in situ production of composite powders [23].

Silica-based ceramics are attractive materials for use in optical devices but their brittleness limits their applications. The incorporation of CNTs into silica can improve its mechanical performance markedly. Since CNTs have unique linear and nonlinear optical properties, silica-CNT nanocomposites show promise for photonic applications including optical switching, optical waveguides, and optical limiting devices and so on. The nanocomposites also exhibit excellent low dielectric constant and electromagnetic shielding characteristics. Silica-CNT nanocomposites can be produced by direct powder mixing, sol–gel and electrophoretic deposition (EPD) processes. Among them, sol–gel is often used to make silica-CNT nanocomposites with better dispersion of CNTs in silica [23].

Titania (TiO_2) is a semiconducting oxide with high photocatalytic ability. It finds application in many technological areas such as microelectronics, photocatalysis and sensors. Titania is also an important bioceramic coating material for metal implants due to its excellent biocompatibility. Incorporating CNTs into titania can lead to the development of novel composite materials with advanced functional properties for photocatalytic, microelectronic and biomedical applications. The techniques used for forming titania-CNT nanocomposites include heterocoagulation, sol–gel and hydrothermal treatment [23].

Zirconia-based ceramics are well recognized for their excellent mechanical, electrical, thermal and optical properties. They find a broad range of industrial applications including oxygen sensors, solid oxide fuel cells and ceramic membranes. The physical and mechanical properties of zirconia can be further enhanced by adding low loading level of CNTs. Zirconia-CNT nanocomposites can be fabricated by hot-pressing, heterocoagulation and hydrothermal crystallization [23].

3.6 Non Oxide-Based Ceramic Nanocomposites

Non-oxide ceramics such as silicon carbide, boron carbide and silicon nitride are attractive structural materials for high temperature applications because of their low density, super hardness, and excellent thermal and chemical stability. Despite these advantages they are susceptible to fast fracture during mechanical loading due to their inherently brittle nature. The incorporation of metal nanoparticles into such ceramics can mitigate the problems associated with brittleness. Carbon nanotubes with high aspect ratios are excellent reinforcing and toughening materials for improving the toughness of non-oxide ceramics. Silicon carbide exhibits different crystalline structures from hexagonal (α-SiC), cubic (β-SiC) to rhombohedral. The cubic β-SiC is particularly important due to its higher bending strength, hardness, stiffness and fracture toughness when compared with α-SiC. Because of the high melting point of silicon carbide, the M-method becomes the primary processing technique for making ceramic products. Further, silicon carbide exhibits poor sinterability due to its strong covalent bonding and high melting point. Thus, sintering aids must be added to obtain dense ceramic specimens. SiC-CNT

nanocomposites have been fabricated by spray pyrolysis, conventional powder mixing followed by hot pressing or by SPS, microwave synthesis and preceramic polymer precursor methods. Spark plasma sintering with very short processing time is an alternative consolidation route for SiC-CNT nanocomposites. However, SPS of SiC-based materials must be carried out at 1800 °C due to the strong covalent bonding of ceramics. Hirota et al. studied the effect of SPS temperature on the microstructure of monolithic SiC and its composites reinforced with carbon nanofibers. Monolithic SiC and its composites were prepared by direct mixing of powder constituents in methyl alcohol followed by ball milling and SPS [23].

It is recognized that silicon nitride is difficult to sinter and consolidate into a dense material using conventional sintering processes. The incorporation of CNTs into silicon nitride would further impair its sinterability. Balazsi et al. fabricated the Si_3N_4/1 % MWNT nanocomposite using hot isostatic pressing and SPS. For the hipping process, ball-milled composite powder mixtures were sintered at 1700 °C under a pressure of 20 MPa for 3 h, and under 2 MPa for 1 h, respectively. In the case of SPS, ball-milled composite powder mixtures were consolidated at 1500 °C under 100 MPa for 3 min, and at 1650 °C under 50 MPa for 3 min, respectively [23].

4 Properties

When interpreting the experimental results, obtained for bulk nanomaterials, it is important to be able to distinguish grain boundary (associated with interfaces) from volume (associated with small grain size) effects. This problem is far beyond being solved because till now, investigations of bulk nanomaterials are in the stage of collecting experimental results. For this reason, the level of understanding of the structure and properties of the bulk nanocrystalline materials is considerably lower in comparison with isolated nanoparticles. The properties of bulk nanomaterials are significantly related to the particle size and the state of the grain boundaries [24].

4.1 Magnetic Properties

Three main phenomena that characterize magnetism in matter are:

- The formation of the magnetic moment on the atomic scale,
- The occurrence of magnetic order, resulting from the strong interactions existing between atomic moments,
- The alignment of moments along some favored crystallographic axis, leading to the phenomenon of magnetic anisotropy.

Iron, cobalt and nickel belong to the first series of magnetic elements, the 3rd series, whilst the second series comprises the 14 rare earth elements. A moving

electric charge is the source of a magnetic field and a magnetic moment can be associated with it. On the atomic scale, magnetism results from electron motion [3].

The main interactions between electrons in matter are due to electrostatic repulsion. In quantum mechanics, the Hamiltonian describing them contains the so-called exchange term, resulting from the in distinguish ability of electrons. As Heisenberg showed, magnetism then arises naturally as soon as the Pauli Exclusion Principle is taken into account. This states that two electrons cannot occupy the same quantum state defined by the space and spin variables, and thus requires the wave function for the electron ensemble to be antisymmetric in those variables. This in turn means that the interaction energy between electrons depends on their spin states. As mentioned above, it is the exchange interactions that cause the atomic magnetic moment. Then, insofar as the electrons in different atomic sites affect one another by exchange interactions, a magnetic coupling exists between the atomic moments of different atoms, and this is the source of magnetic order in a material [3].

Ferromagnetic particles become unstable when the particle size reduces below a certain size, since the surface energy provides a sufficient energy for domains to spontaneously switch polarization directions. As a result, ferromagnetics become paramagnetics. However, nanometer sized Ferro-magnetic turned to paramagnetic behaves differently from the conventional paramagnetic and is referred to as superparamagnetics. Nanometer sized ferromagnetic particles of up to $N = 10^5$ atoms ferro- magnetically coupled by exchange forces, form a single domain [25], with a large single magnetic moment p with up to l05 Bohr magnetons, μB. Beam and Livingston demonstrated that these clusters or particles at elevated temperatures can be analogously described as paramagnetic atoms or molecules, however with much larger magnetic moments [6]. The magnetization behavior of single domain particles in thermodynamic equilibrium at all fields is identical with that of atomic paramagnetism, except that an extremely large moment is involved, and thus large susceptibilities are involved. An operational definition of super paramagnetism would include at least two requirements. First, the magnetization curve must show no hysteresis, since that is not a thermal equilibrium property. Second, the magnetization curve for an isotropic sample must be temperature dependent to the extent that curves taken at different temperatures must approximately superimpose when plotted against *H*/*T* after correction for the temperature dependence of the spontaneous magnetization. Superparamagnetism was first predicted to exist in small ferromagnetic particles below a critical size by Frankel and Dorfman [26]. This critical size was estimated to be 15 nm in radius for a spherical sample of the common ferromagnetic materials [27]. The first example of superparamagnetic property was reported in the literature as early as 1954 on nickel particles dispersed in silica matrix [28]. Figure 7 shows the typical magnetization. Below some real experiments are described in measuring the magnetization potential of materials [29].

In nanoparticles of transition metal oxides, measurements reveal a reduction in the average magnetization. This happens for maghemite nanoparticles (γ-Fe_2O_3), a collinear ferrimagnetic material in the bulk. For an insulating system, such a

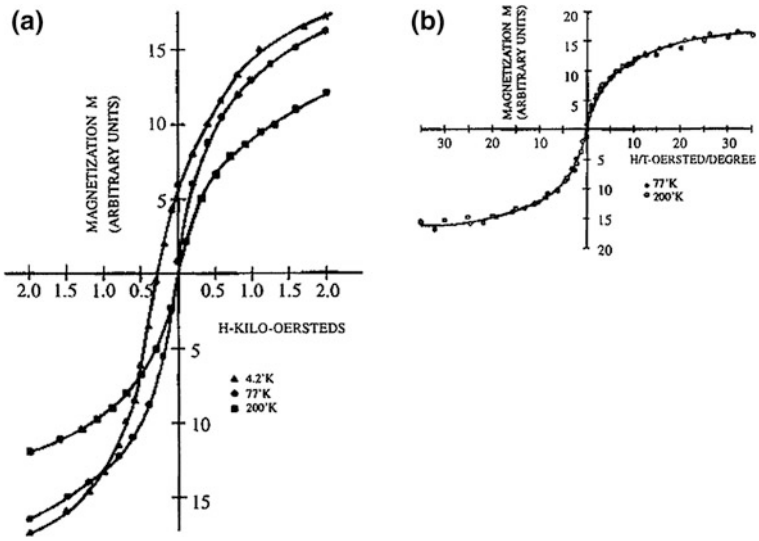

Fig. 7 Typical magnetization curves of 2.2 nm iron particles suspended in mercury at various temperatures and the approximate H/T superposition observed for their 77 and 200 K data [29]

reduction in magnetization cannot be attributed to a lower iron moment, since the latter does not depend on the size of the system. In fact, Mossbauer spectroscopy on the Fe57 nucleus reveals non-collinear arrangements of the moments. Such arrangements are characteristic of atoms located in a low-symmetry environment and subject to magnetic interactions of various signs. Numerical simulation confirms the highly non-collinear nature of the calculated arrangements whenever the reduced symmetry of the environment of surface atoms is taken into account [3]. Non-collinear arrangements of the same origin also occur in nanoparticles of systems that are antiferromagnetic in the bulk state, such as NiO. There is no reason why the moments should cancel one another exactly. The result is that antiferromagnetic nanoparticles carry a small magnetic moment.

4.2 Electrical Properties

The ability to transport charge (electric current), spin (magnetic current), and energy (heat, sound) through nanostructures is of great importance in both scientific studies and technological applications. The quantum nature of matter on the nanometer scale leads to new transport phenomena and necessitates the development of new theoretical descriptions. The electrons that flow through the nanostructure are supplied from macroscopic metal contacts. The energy and electron number of the large reservoirs are not affected by the presence of the nanostructure. It is thus natural to denote the metal contacts as electron reservoirs

[30]. To become more specific on nanomaterials electrical conductivity, there is some explanation as follow:

The effects of size on electrical conductivity of nanostructures and nanomaterials are complex, since they are based on distinct mechanisms. These mechanisms can be generally grouped into four categories: surface scattering including grain boundary scattering, quantized conduction including ballistic conduction, Coulomb charging and tunneling, and widening and discrete of band gap, and change of microstructures. In addition, increased perfection, such as reduced impurity, structural defects and dislocations, would affect the electrical conductivity of nanostructures and nanomaterials [6]. Below a critical size, properties become more likely to change in the bulk itself, thereby affecting the cluster as a whole. On the structural level, the icosahedral transition is well known. Size-dependent transitions also occur for the electronic structure. This can be exemplified by the metal–insulator transition in clusters of divalent metals, induced by the separation of the "s" and "p" energy bands at small sizes. When the number of atoms or constituents is decreased further, one ends up in a regime where properties are reconstructed at each new size. At this point, a discrete form of behavior is superposed on the laws of scaling. This is the size range characterized by finite size effects. These are partially due to the discrete nature of the atomic structure, which must now be taken into account explicitly and partly to the quantum nature of the electrons participating in the chemical binding. In covalent systems, binding is ensured by electron delocalization among several atoms. This delocalization may sometimes be more extensive, as in the π systems, even extending to the whole cluster, as in the case of delocalized electrons in metals. At small sizes, electronic and geometrical properties can become highly interdependent. Ionization or addition of an electron is likely to have repercussions for the structure. An external perturbation in the form of an electric or magnetic field, or some specific type of environment, e.g., solvent, matrix, can also strongly perturb or even determine the properties of such a system. Another feature here is that classical concepts as simple as volume or area can no longer be clearly defined, owing to the spatial extension of the electron wave function in quantum mechanics. This spatial extension also leads to the tunneling effect, which is significantly in near-field microscopy and manipulation techniques which have underscored the rise of nanoscience. In addition to all this, the energy levels, which are grouped into bands in periodic solids, become discrete in confined systems. Hence, small metallic clusters always exhibit a finite gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [3].

Stability of clusters involving certain well defined numbers of electrons indicates a structuring of the electron shells and establishes an analogy with the properties of super atoms or the shell structure of atomic nuclei. In this context, electronic properties are determined by the quantum nature of a system of fermions confined within a spherical potential well. This novel electronic structure plays a key role in the stability, fragmentation, optical properties, or reactivity of metallic particles [3].

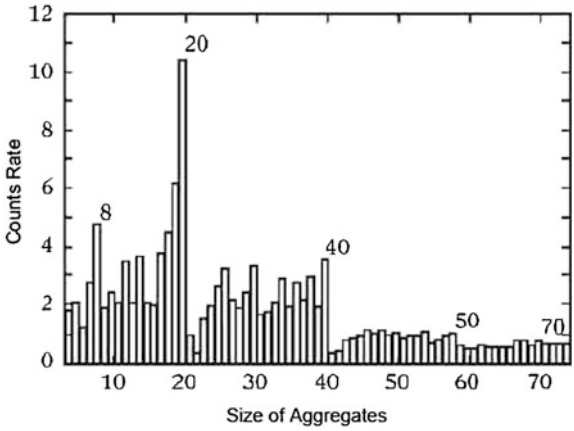

Fig. 8 Mass spectrum of sodium clusters in a molecular beam [3]

Theory and simulation are of the utmost importance, especially when it comes to electronic structure. Joint progress in computing, theory and calculation techniques mean that electronic structure can be determined ab initio (from the beginning), i.e., from first principles, for an ever wider range of increasingly complex systems, by directly solving the equations of quantum mechanics without introducing empirical parameters. This approach has been the source of many computational codes for electronic structure, developed by solid-state physicists and quantum chemists. Although not specifically designed to deal with nanoparticles, certain codes can now be used to tackle non-periodic systems containing more than a hundred atoms (at least for calculating the electronic structure in a given geometric configuration). Certain versions are also integrated into dynamical codes. The advantage with "ab initio" calculations is not only quantitative. When it used to analyze data concerning small or periodic systems, they often provide a way of building appropriate approximate models which make calculation and simulation possible in size ranges that cannot be tackled directly. In the field of electronic structure and molecular simulation, numerical experimentation has become an indispensable complement to laboratory experimentation using real systems [3].

As shown in Fig. 8, a reduction in characteristic dimension below a critical size, i.e. the electron de Broglie wavelength, would result in a change of electronic structure, leading to widening and discrete band gap. Effects of such a change of band gap on the optical properties has been extensively studied and discussed in the previous section. Such a change generally would also result in a reduced electrical conductivity. Some metal nanowires may undergo a transition to become semi-conducting as their diameters are reduced below certain values, and semiconductor nanowires may become insulators. Such a change can be partially attributed to the quantum size effects, i.e. increased electronic energy levels when the dimensions of materials are below a certain size as discussed in the previous section. For example, single crystalline Bi nanowires undergo a metal-to-semiconductor transition at a diameter of ~ 52 nm [31] and the electrical resistance of Bi nanowires of ~ 40 nm

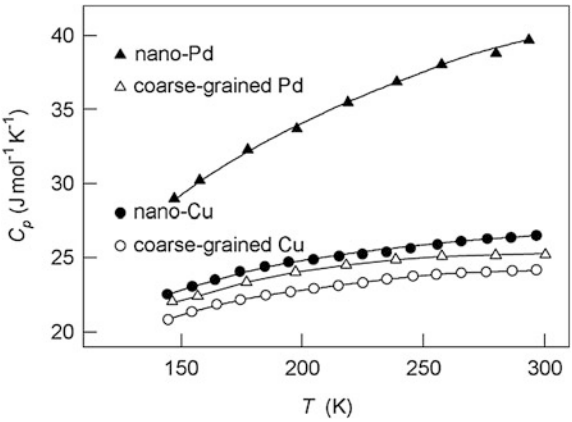

Fig. 9 Effect of the nanostructured state on the temperature dependence of heat capacity Cp(T) of copper and palladium [24]

was reported to decrease with decreasing temperature. GaN nanowires of 17.6 nm in diameter were found to be still semiconducting, however, Si nanowires of $\sim$15 nm became insulating [32].

4.3 Thermal Properties

The theoretical analysis and calorimetric investigations show that in the temperature range 10 K $\leq T \leq \theta_D$ the heat capacity of nanopowders is from 1.2 to 2 times higher than that of the coarse-grained bulk materials. The increased heat capacity of the nanopowders is determined both by the size effect and by the very large surface area, which introduces an additional contribution to heat capacity. In contrast to the nanoparticles, investigations of the heat capacity of nanocrystalline bulk materials are limited to several studies [24].

The heat capacity C_p of nanocrystalline compacted specimens of nc-Pd ($D = 60$ nm) and nc-Cu ($D = 8$ nm), prepared by compacting nanoclusters, was measured in the temperature range from 150 to 300 K. The relative density of the nc-Pd specimens was equal to 80 % and that of the nc-Cu specimens was equal to 90 % of the density of pore-free polycrystalline coarse-grained palladium Pd and copper Cu. Measurements revealed that the Cp of nc-Pd and nc-Cu specimens are 29–53 % and 9–11 % higher than the heat capacity of conventional polycrystalline Pd and Cu, respectively (Fig. 9). When nc-Pd was heated at $T = 350$ K, an exothermic effect was observed but the grain size remained constant or increased up to 10 nm. The heat capacity of nc-Pd heated to 350 K, was found to exceed the heat capacity of coarse-grained palladium by 5 %. It is assumed that the observed elevated heat capacity is caused by the 'looser' structure of the interfaces. This explanation is not plausible because it has been established on the structure of the grain boundaries in the compacted nanomaterials containing free volumes with the

size of monovacancy or deviancy. It though the effect of this frees volumes is not large enough in order to explain excess of heat capacity. One of the explanations of excess could be about the impurities in palladium [24].

4.4 Optical Properties

Novel optical properties arise in nanoparticles, due to resonance in the absorption spectrum of the nanoparticles, the surface plasmon resonance. Its characteristics, such as spectral width and position, and sensitivity to light polarization, depend not only on the intrinsic properties of the nano-objects (composition, structure, size, shape), but also on their environment. In the case of noble metals, it occurs in the visible region of the spectrum, in the blue somewhere near 400 nm and in the green around 520 nm for small silver and gold spheres, respectively, and it produces yellow and red coloring, respectively, of the material in which they are included [3].

Apart from such decorative applications, this possibility of modifying the optical properties of nanomaterials and may be even controlling them in such a way as to achieve specific functions, by adjusting their characteristics or those of their surroundings, has generated a good deal of interest recently. The impact of these novel materials in the field of photonics has already made itself felt, and it is only in its early stages, extending to a wide range of different areas, e.g., linear and nonlinear optics, polarisers, solar cells, chemical and biosensors, nano-optical devices, optical switches, local electromagnetic field enhancement, and molecular labeling in biology. In addition, their optical response provides a way of studying the characteristics of nano-objects and hence constitutes a powerful tool for analyzing their fundamental properties [3].

In contrast to semiconducting nanoparticles or quantum dots, the optical properties arising with size reduction in metallic media are due to a classical enhancement effect on the electric field, often called dielectric confinement. The discretisation of electronic states (quantum confinement) which underlies the optical properties of quantum dots only leads to small corrections to the observed responses down to nanometric sizes. Actually, this difference results from the very high electron density in metals (5×1022 cm^{-3}) compared with typical values in semiconductors (1018 cm^{-3}). In metallic media of nanometric size, electronic properties stem from high energy quantized states, close to the Fermi level. The separations between these energy levels are very small compared with their widths and the thermal energy (at room temperature).

For the nanoparticle sizes considered here, greater than one nanometer, these states can therefore be modeled to a first approximation by a quasi-continuum of states similar to what is observed in the bulk metal [3].

4.5 Mechanical Properties

The growing interest in nanomaterials over the past decade or so can be put down to their unique structure, characterized by grains with nanometric dimensions and by a rather high density of crystal defects, which will undoubtedly lead to quite exceptional properties. In particular, extrapolating the constitutive laws of large-grained materials down to the nanoscale leads one to expect interesting mechanical behavior for nanomaterials. Materials can be produced with high levels of hardness, ductility, and sometimes superplasticity at relatively low temperatures. These characteristics lead to remarkable mechanical performance and machining possibilities, by virtue of which such nanomaterials have immediate scope for technological innovation.

The elastic limit of a material (the stress beyond which a permanent plastic strain is observed) is intimately related to its elastic constants. Indeed, a plastic strain only occurs in order to reduce the energy associated with the elastic strain of the material. The elastic constants reflect the nature and density of atomic bonds. In nanomaterials, the high densities of structural defects and grain boundaries have an effect on the elastic constants [3].

The first measurements of Young's modulus revealed a significant difference between nanostructured materials and the corresponding large-grained materials. In some cases the modulus was much higher, as for superlattices, and in others much lower, as for materials produced by sintering. However, it was subsequently demonstrated that these early results were due to experimental artifacts and often to the presence of defects, such as fractures and high porosity, introduced during fabrication and not properly taken into account when interpreting the observations. More recent results obtained on dense materials have finally shown that the Young's modulus gradually falls off only for grain sizes below 10 nm, i.e., when the fraction of atoms associated with grain boundary and triple junctions becomes very high [3].

The nanoindentation technique is a mechanical test derived from the standard hardness test. The idea is to sink a hard tip of known geometry into the material under investigation and monitor the depth of penetration as a function of the applied load. By carrying out a loading–unloading cycle, a characteristic force-penetration curve is obtained. By analyzing the unloading curve and modeling the material as an elastic and isotropic continuous medium, one can deduce the relevant parameter here, which is the true contact area between the indenter and the material under maximal load. One can then deduce not only the hardness, but also the Young's modulus of the material. The applied forces range from a few tenths to several hundred millinewtons, and the depths of penetration from a few nanometers to several microns [3].

Extrapolating this law to grains of around ten nanometers, very high values of the hardness are predicted, the only limit being the theoretical limiting stress of a perfect crystal, generally taken as $G/10$, where G is the transverse shear modulus. However, although the hardness does indeed increase at small grain sizes, the

observed effects are generally much smaller than would be predicted in this way, and at very small grain sizes, or for very small periods in the case of multilayer films, the opposite trend to the Hall–Petch relation is sometimes observed, i.e., a reduction in hardness with reduced grain size (or period). This 'negative' Hall–Petch effect has nevertheless been explained for nanocrystalline materials that have undergone thermal treatment, by invoking densification or phase transformation phenomena [3, 24].

4.6 Superplasticity

The fabrication of dense fine-grained materials is certainly the most delicate stage in the lead-up to a forming process based on superplasticity. In order to develop new alloys with grain sizes of a few tens of nanometers, metallurgists have turned to cold working processes by severe plastic deformation, torsion straining (TS), and forced shear obtained by extrusion through a channel bent through an angle of as much as 90° (equal channel angular extrusion ECAE). These processes have led to a certain degree of success, especially for light alloys, and are able to obtain submicron grain sizes. However, they cannot produce large solid items. Today, aluminum, zinc and titanium alloys (e.g., Al–Mg, Al–Zn and Ti–Al) are the main metal alloys used in superplastic forming processes [3].

Superplasticity provides a rapid way of obtaining items with complex geometry in a single forming operation and with relatively low flow stresses. It is thus easy to understand the growing interest shown by the world of industry for this property and the superplastic forming (SPF) and diffusion bonding (DB) processes it makes possible, which reduce the required quantities of matter and fabrication costs. However, industrial applications are still restricted mainly to the aeronautic industry and on the whole concern light aluminum and titanium alloys. Titanium alloys are the most widely used today because these were the superplastic alloys first developed industrially, with TA6 V being the main representative. Superplastic forming can be used to obtain in a single operation an element that would otherwise have required the assembly of several parts by riveting. Assembly times are thereby greatly reduced and, by avoiding extra thickness due to assembly, superplastic forming can also make lighter elements. Although superplasticity has been demonstrated in fine-grained ceramics, and in particular in stabilized tetragonal phase zirconia (Y-TZP), the fabrication of ceramic items using this property remains a laboratory curiosity that has barely entered the research and development stage. There are nevertheless several remarkable examples: the fabrication of missile nozzles and axially symmetric elements by the US group Lockheed, and the forming of parabolic sheaths to protect the leading edges of helicopter rotor blades at the National Industrial Research Institute of Nagoya (NIRIN, Japan) [3].

4.7 Thermodynamics of Nanocrystalline Materials

Materials termed nanocrystalline may display very different structures. A first type is entirely made of small crystals produced by techniques for atom condensation and eventual compaction. A second type consists of ensembles of particles deposited on top of a substrate to form a film or a coating. The material may be nanostructured due to the thickness of the film and/or because the film contains fine particles. A third type is represented by bulk solids processed by thermal and/or mechanical means so that crystal sizes are in the nanometer range. There is no unique thermodynamic description for all categories. It is usually stated that materials composed fully or partially of nanocrystals are not in stable equilibrium since they retain a large amount of excess free energy [15].

Nanocrystalline substances are prepared by means of various techniques such as vapor condensation, ball milling and electro deposition. The particles constituting these materials are usually of sizes as small as a few nanometers; therefore it is legitimate to question whether they possess special thermodynamic properties. However, it can be clearly stated that nanocrystals of the elements display bulk properties in many respects. It was shown in the early 1980s that clusters of some 100–150 atoms exhibit photoelectron spectra characteristic of the bulk metals so their internal energies should have corresponding values. However, materials prepared by means of the techniques mentioned above are unstable in the as-prepared state mostly because their interfaces are not equilibrated and need to relax to structural states of lower energy. As an example consider high purity elements processed by heavy deformation. Careful thermal analysis shows that recovery may occur even at room temperature, whereas recrystallization takes place at higher temperature. Therefore the material is unstable at room temperature with respect to defect recovery [15].

In order to evaluate the free energy trend, consider pure elements: nanocrystalline Cu obtained by deformation or deposition. The free energy will be easily taken, neglecting second order contributions due to specific heat differences. As for the enthalpy difference, high purity Cu, heavily deformed by rolling, gives a single DSC peak of 55 J/mol due to recrystallization at 500 K when heated at 30 K/min. If transition elements (e.g. Mn) are added in amounts of parts per million, the recrystallization peak is shifted to higher temperatures (above 673 K) and anew peak appears, due to recovery, at temperatures below 473 K. Extrapolating this behavior to pure Cu, it can be envisaged that recovery of defects should occur dynamically during both deformation and the storage of samples. Therefore, deformed Cu is unstable at room temperature with respect to defect concentration. Once recovery occurs, it will remain in a metastable state up to the temperature of start of recrystallization [15].

Nanocrystalline Cu, prepared as a powder by vapor deposition and compacted, behaves similarly. It releases 300 J/mol around 430 K when analyzed immediately after compaction and 53 J/mol around 450 K when analyzed 5 days after preparation. Such values of enthalpy release have been confirmed by a study on

nanocrystalline Cu prepared by electro deposition and cold rolled to variable amounts. On the other hand, nanocrystalline Cu films obtained by sputtering release 1200–1700 J/mol starting at 450 K and powders prepared by ball milling release 5 kJ/mol. The enthalpy release occurs over a broad temperature range. From these values it was deduced that the interfacial enthalpy may exceed 1 J/m^2. Comparison of all data shows that these materials are far from equilibrium soon after preparation, not only because they contain a large amount of interfaces but also because these interfaces are not equilibrated. Their thermodynamic state is defined and a series of metastable states may be attained after suitable annealing [15].

5 Synthesis

5.1 Gas Phase Synthesis

Isolated nanoparticles are usually produced by evaporation of metal, alloy or semiconductor at a controlled temperature in the atmosphere of a low-pressure inert gas with subsequent condensation of the vapor in the vicinity or on the cold surface. This is the simplest method of producing nanocrystalline powders. In contrast to vacuum evaporation, the atoms of the substance, evaporated in a rarefied inert atmosphere, lose their kinetic energy more rapidly as a result of collisions with gas atoms and form segregations. The nanocrystalline particles with a size of $\leq$20 nm, produced by evaporation and condensation, are spherical, and large particles may be faceted [24].

The systems using the principle of evaporation and condensation, differ in the method of input of evaporated material; the method of supplying energy for evaporation; the working medium; setup of the condensation process; the system for collecting the produced powder [24].

5.2 Plasma Chemical Technique

One of the most widely used chemical methods of producing highly dispersed powders of nitride, carbides, borides and oxides is plasma chemical synthesis. The main conditions of producing highly dispersed powders by this method is the occurrence of a reaction away from equilibrium and the higher rate of formation of nuclei of a new phase at a low growth rate of this phase. In the real conditions of plasma chemical synthesis, the formation of nanoparticles can be carried efficiently [24].

By increasing the cooling rate of the plasma flow in which condensation from the gas phase takes place; this decreases the size of particles and also suppresses the growth of particles by their coalescence during collisions. Plasma chemical synthesis is carried out with the use of low temperature (4000–8000 K) nitrogen,

ammonia, hydrocarbon plasma, argon plasma of arc, glow, high frequency or microwave discharges. Starting materials are represented by elements, halides and other compounds. The characteristics of the produced powders depend on the starting materials used, synthesis technology and the type of reactor. The particles of plasma chemical powders are single crystals and their size varies from 10 to 100–200 nm or larger [24].

5.3 Thermal Spraying

Thermal spraying is a coating process used to produce metallic, non-metallic and ceramic coatings in which a spray of molten or semi-molten solid particles generated from a thermal source are deposited onto substrate by mechanical bonding. The microstructure of the coating results from rapid solidification of the particulates. In principle, powders, rods, and wires which do not sublimate or decompose at temperatures close to their melting points can be used as spraying materials. Metals and alloys in the form of rods or wires are commonly used in arc spraying (AS) and flame spraying (FS). Powders of metals, alloys, ceramic oxides, cermets, and carbides are often used in thermal spraying to produce a homogeneous microstructure in the resulting coating. In most cases, the sprayed surface should be degreased, masked, and roughened prior to spraying to maximize the bonding strength between the coating and the sprayed material. Today, flame spraying (FS), atmospheric plasma spraying (APS), arc spraying (AS), detonation gun (D-gun) spraying, high-velocity oxy-fuel spraying (HVOF), vacuum plasma spraying (VPS), and controlled atmosphere plasma spraying (CAPS) are widely used to produce various coatings for various industrial applications. In general, the heat source for thermal spraying processes may be generated by an electrical or a chemical (combustion) source [33].

5.4 Precipitation from Colloidal Solution

Precipitation from colloid solutions is evidently the first method of producing nanoparticles. The conventional method of producing nanoparticles from colloid solutions is based on a chemical reaction between the components of the solution and interrupting the reaction at a specific moment in time. Subsequently, the dispersed system is transferred from the liquid colloidal state to the nanocrystalline solid state. Nanoparticles can also be produced by means of ultrasound treatment of colloid solutions, containing large particles. Precipitation from colloid solutions makes it possible to synthesize nanoparticles of a mixed composition, i.e. nanocrystalline heterostructures [24].

In the group of all the methods of producing isolated nanoparticles and other powders, the method of precipitation from colloid solutions is characterized

by high selectivity and makes it possible to produce stabilized nanoclusters with a narrow size distribution which is very important for the application of nanoparticles as catalysts or in nanoelectronic devices. The main problem of precipitation from colloid solutions is how to avoid coalescence of the produced nanoparticles [24].

5.5 Thermal Decomposition and Reduction

Thermal decomposition is usually carried out using complex element-organic and organometallic compounds, hydroxides, carbonyls, formiates, nitrates, oxalates, amides and imides of metals which at a specific temperature decompose with the formation of a synthesized substance and generation of the gas phase. A combination of thermal decomposition and condensation is the supersonic discharge of gases from a chamber, in which increased constant pressure and temperature is maintained, through a nozzle into vacuum. In this case, the thermal energy of gas molecules is transformed into the kinetic energy of the supersonic flow [24].

The highly dispersed powders of silicon carbide and nitride are produced by pyrolysis of polycarbosilanes, polycarbosiloxanes and polysilazanes. Initial heating is carried out by a means of low temperature plasma or laser radiation and the products of pyrolysis are subsequently annealed at a temperature of ~ 1600 K to stabilize the structure and composition [24].

5.6 Milling and Mechanical Alloying

The basis of mechanical alloying is the mechanical treatment of solid mixtures leading to refining and plastic deformation of substances, acceleration of mass transfer and mixing of the components of the mixture on the atomic level, together with the activation of chemical reaction of the solid reagent A stress field forms in the near-contact regions of the solid substance as a result of the mechanical treatment. A relaxation of the stress field may take place by the generation of heat, formation of a new surface, formation of different defects in crystals, excitation of chemical reactions in the solid phase [15].

Non-equilibrium processing of materials has attracted the attention of a number of scientists and engineers due to the possibility of producing better and improved materials than is possible by conventional methods [34]. Rapid solidification processing (RSP) and mechanical alloying (MA) are two such processing methods with somewhat similar capabilities. RSP has started as an academic curiosity in 1960 and matured into an industrially accepted technology with its use for the production of amorphous ferromagnetic sheets for transformer core applications by Allied Signal. On the other hand, MA started as an industrial necessity in 1966 to produce oxide dispersion strengthened (ODS) nickel- and iron-based super alloys for applications

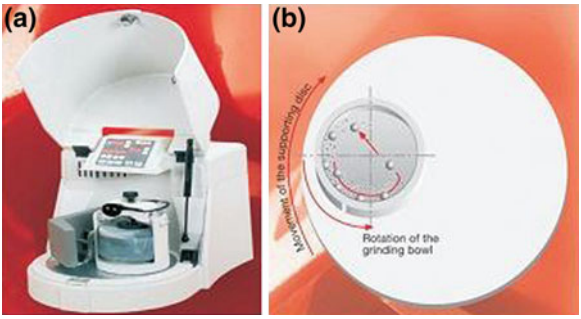

Fig. 10 **a** A High Energy Ball mill machine **b** A schematic representation of the movements of grinding medium in the container [4]

in the aerospace industry and it is only recently that the science of this "apparently" simple processing technology has begun to be investigated. While the scientific basis underlying RSP was investigated in detail from the beginning, applications for the products of RSP were slow to come about mostly because of the limitations on the size and shape of the RSP materials. Thus, invention of the melt spinning technique to produce long and continuous ribbons and of the planar flow casting method to produce wide ribbons accelerated the applications of RSP alloys. Even today use in transformer core laminations remains the major (and most voluminous) application of the RSP alloys. The developments in the science of RSP and the applications of RSP products can be found in several monographs and proceedings of the RQ conferences (see, e.g., [34]). In contrast, the technique of MA was used for industrial applications from the beginning and the basic understanding and mechanism of the process is beginning to be understood only now. There have been several reviews and conference proceedings on this technique too, but the present status of MA has been most recently reviewed by Suryanarayana [35]. The MA literature available up to 1994 has been collected together in an annotated bibliography [35].

Mechanical milling is the most productive method of producing large quantities of nanocrystalline powders of different materials: metals, alloys, intermetallics, ceramics, and composites. Mechanical milling and mechanical alloying may lead to the complete solubility in the solid state of elements characterized by very low mutual solubility in the equilibrium condition [15].

In recent years, nanostructures of brittle ceramics, polymer blends and metal-ceramic nanocomposites have been investigated, which demonstrates the high flexibility of this process.

Figure 10a shows a high energy ball mill machine and Fig. 10b a schematic representation of the movements of grinding medium in the container [4]. The process starts by mixing powders of different elements with the desired proportion and particle size of 1–200 μm. Then, the mixture along with the grinding medium is loaded into a sealed container which, depending upon the type of milling equipment employed, the container is moved or agitated. Collision of the charge and the balls, delivers a high energy to the powder, and the material undergoes a severe plastic deformation. The powder deforms plastically and the rest of energy

is converted into heat and stored in the metal, raising its internal energy. Plastic deformation at high strain rates within particles refines the grain size to nanoscale after prolonged milling. The grain refinement mechanism by the ball milling process has been proposed by Fecht [4], and includes three basic stages:

- Initially, the deformation is localized in shear bands consisting of an array of dislocations with high density.
- At a certain strain level, these dislocations annihilate and recombine to small angle grain boundaries separating the individual grains. The subgrains formed via this route are already in the nanometer size range (about 20–30 nm).
- The orientations of the single-crystalline grains with respect to their neighboring grains become completely random, and the high-angle grain boundaries replace low-angle grain boundaries.

Basically, there are two types of this process. The first one is mechanical milling in which a high energy ball mill is used to crush and refine powders.

The second type is reaction milling which involves in situ solid state chemical reactions between different powders during mixing and milling. Like any other method, mechanical alloying has its own advantages and drawbacks. Advantages include simplicity, relatively inexpensive equipment, versatility in production of a wide range of materials and possibility of producing large quantities, that can be scaled up to several tons. A serious problem, concerning mechanical alloying is the surface contamination from the milling media (balls and vial) and/or atmosphere. Though it is not possible to completely overcome this problem, evacuating the container or using inert gas atmospheres, may help. It should be noted that the degree of contamination depends on a number of factors like mechanical properties of the powder and its chemical affinity for milling media. Other drawbacks of mechanical alloying include rough structures of produced powder, non-homogeneity in particle size and inhomogeneous chemical composition. In order to improve the roughness of the final structure, Cryomilling, in which the milling operation is carried out at cryogenic (very low) temperatures and/or milling of materials is done in cryogenic media such as liquid nitrogen, can be employed to modify the deformation behavior of materials, i.e., increasing the brittleness. This could also help in reducing the degree of contamination. By adjusting the energy received by the powder through a number of variables like ball-powder ratio (BPR), and the milling time, homogeneity of particle size and chemical composition should be improved. As already indicated, this method can be used to produce amorphous or nanocrystalline structures, whether in pure elements or equilibrium and nonequilibrium alloys. Nanocrystalline structure of a large number of elements has been investigated, and crystallite size of the final nanostructure has been determined by standard X-ray analysis methods. The minimum grain size achieved is, however, dependent upon a number of variables as well as the properties of the element, alloy, or compound being milled. The minimum grain size obtainable by milling, $d_{\min}$, has been attributed to a balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes. It has been found that the minimum grain size induced by milling scales inversely with the

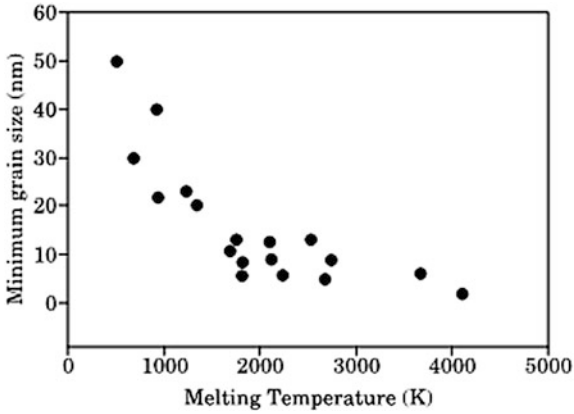

Fig. 11 Minimum grain size versus melting temperature [4]

melting temperature of a group of face-centered cubic (FCC) structure metals studied [36]. These data are plotted in Fig. 11 along with data for other metallic elements and carbon (graphite) [37]. For these data, only the lower-melting-point metals show a clear inverse dependence of minimum grain size on melting temperature. Recent progress in chemical engineering for elements with higher melting temperatures ($>T_m$ for Ni), exhibit essentially constant values with melting temperature for given crystal structure classes. For these elements it appears that d_{min} is in the order: FCC < BCC < HCP [4]. Equilibrium and nonequilibrium solid solutions with nanocrystalline structures are in Ti, Al, Cu and Fe [4].

Systems along with many others have been successfully produced via mechanical alloying and the solid solution formation mechanisms, structure–property relationship and many other facts have been investigated.

Figure 11 shows minimum grain size vs. melting temperature. The metal powders (Ti, Fe, V, Zr, W, Hf, Mo, etc.) transform to a nanocrystalline nitride by high-energy ball milling under nitrogen gas flow. Nanostructured materials in the solid-state interdiffusion reaction during reactive ball milling is triggered by fragmentation of the starting powder, thus creating new surfaces. These freshly created surfaces react with the flowing nitrogen gas to form a nitride surface layer over the unreacted core particle. With further milling, this reaction continues and a homogeneous nitride phase is formed and the unreacted core of metal disappears resulting in a nanostructured (often metastable) metal-nitride with a typical grain size of 5 nm. Mechanical alloying is a complex process and hence involves optimization of a number of variables to achieve the desired product phase and/or microstructure [4]. Some of the important parameters that have an effect on the final constitution of the powder are:

- Type of mill,
- Milling container,
- Milling speed,
- Milling time,

- Type, size, and size distribution of the grinding medium,
- Ball-to-powder weight ratio,
- Extent of filling the vial,
- Milling atmosphere,
- Process control agent, and
- Temperature of milling.

All these process variables are not completely independent. For example, the optimum milling time depends on the type of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio, etc. [4].

Reviewing a number of investigations by our research teams, some examples of different applications, underlying mechanisms in formation of nanocrystalline structures and the effects of a number of process variables are studied [4].

5.7 Self-Propagation High-Temperature Synthesis

The self-propagating high-temperature synthesis (SHS) represents a rapid process of solid combustion of reagents (a metal and carbon for carbides or a metal in nitrogen for nitrides) at a temperature from 2500 to 3000 K. Usually carbides are synthesized in a vacuum or an inert atmosphere (argon). The mean size of grains in carbides produced by the SHS method is 10–20 mm, while the size of nitride grains usually is smaller and they are in the range of 5–10 mm. SHS synthesized carbides and nitrides of group IV and V transition metals have, as a rule, an inhomogeneous composition and require additional grinding and annealing for homogenization. To decrease the grain size in synthesized carbides or nitrides, the starting mixture is diluted with the final product (for example, up to 20 mass% TiC is added to the Ti + C mixture). For the same purpose, some carbon in the mixture is replaced by polymers (polystyrene, polyvinylchloride) during synthesis of carbides. As a result, carbides and nitrides with grains 1–5 mm in size on the mean can be synthesized [24].

5.8 Sol Gel Synthesis

The top-down approach corresponds essentially to the research of miniaturization process in electronics. Clearly, chemistry is not really involved in this approach. In contrast, the bottom up approach which aims to prepare materials with well defined optical, magnetic, mechanical, chemical, etc. corresponds perfectly to the chemists, know-how. In this approach, chemistry is needed on the one hand for the synthesis of the nano-objects, and on the other hand, for the assembling and organizing of these nano-objects into nanomaterials [38, 39].

A very active area of research especially in the ceramics field involves using the sol gel route to fabricate crystalline and amorphous products which may be dense or porous bulk solids, fibers, thin films, or powders. The term of sol gel includes products made from both inorganic colloidal particles suspended in aqueous solutions (particulate systems) and via alkoxides which can be partially hydrolyzed and then polymerized into a gel (polymeric systems) where a classical sol never existed [40, 41].

A colloid is a suspension in which the dispersed phase is so small (1–1000 nm) that gravitational forces are negligible and interactions are dominated by short range forces, such as van der Waals attraction and surface charge. The inertia of the dispersed phase is small enough that is exhibit Brownian motion, a random walk driven by momentum imparted by collision with molecules of the suspension medium. A sol is colloidal suspension of solid particles in liquid [42].

The resultant force on molecules varies with time because of the movement of the molecules; the molecules at the surface will be pointed downward into the bulk phase. The nearer the molecule is to the surface, the greater the magnitude of the force due to asymmetry. The region of asymmetry plays a very important role. Thus, when the surface area of a liquid is increased, some molecules must move from the interior of the continuous phase to the interface. The surface of a liquid can thus be regarded as the plane of potential energy. Colloids are an important class of materials, intermediate between bulk and molecularly dispersed systems. The colloid particles may be spherical, but in some cases one dimension can be much larger than the other two (as in a needle shape). The size of particles also determines whether they can be seen by the naked eye [43].

The development of sol–gel technology has at very early step put forward a request on development of precursor compounds-chemical substances that have high solubility in organic solvents, are easily transformed into chemically reactive forms of hydrated oxides on hydrolysis. They should display considerable stability in solution to guarantee the reproducibility of the materials preparation and, last but not the least, be easy to be purified to provide sufficient chemical quality of the final products. Metal alkoxides, are derivatives of alcohols, ROH, which are usually easily accessible and inexpensive organic compounds, and are extremely weak as acids, easily removable via hydrolysis and thermal treatment, leaving high purity hydrated oxides. This circumstance made metal alkoxides the most common candidates for the role of molecular precursors [44].

The works in this field during the last 20 years, including both the studies of the molecular and crystal structure and the reactivity of these compounds, have considerably changed their image in the eyes of both chemists and the materials scientists. It turned out that sometimes the compounds that are the most stable products in the reactions of synthesis of metal alkoxides and that were earlier considered to be M(OR)n are in fact oxo alkoxides [44].

In many cases, especially for the preparation of complex solutions, including derivatives of several metals, it turned out impossible to use only the derivatives of aliphatic alcohols, because of their poor solubility, stability or reactivity. This gave rise to development of two new types of alkoxide precursors—derivatives of

functional alcohols (alkoxyalcohols and aminoalkohols), on one hand, and heteroleptic alkoxides including other ligands (such as carboxylate and amino-alkoxide ones) in addition to common aliphatic alkoxide groups, on the other. The complexity of situation has been increased even more by the rise of a still quite small but quickly growing family of alkoholates highly soluble complexes of metal carboxylates or with functional alcohols. The latter do not contain formally the alkoxide ligands but are related to metal alkoxides in many of their properties and find the increasing application in sol–gel technology [44].

The sol–gel dip process is almost exclusively applied for the fabrication of transparent layers, primarily for the deposition of oxide films on float glass as a transparent substrate with a high degree of planarity and surface quality. Other substrates are possible, provided they can withstand the required curing temperature of about 500 °C. Film thicknesses up to 1 μm can be deposited, preferred are well defined thicknesses within the wavelength range of visible light. Several additive layers can be superimposed. The chemical reaction involved is based on metal compounds in alcoholic solutions which can be readily hydrolyzed. The oxides are formed through polycondensation at about 500 °C [45].

In the sol–gel technique, fibrous gels are drawn from the sols around room temperature, and then are converted to glass or ceramic fibers by heating at several hundred to one thousand degrees centigrade. Recently, various kinds of glassy fibers, such as silica, alumina-silica and zirconia-silica fibers, and ceramic fibers, such as SiC, zirconia, alumina and titania fibers, have been prepared by this type of sol gel technique, that is, the method based on the conversions sol to gel fiber and then to glass or ceramic fiber [45].

By a careful control of sol preparation and processing, monodispersed nano-particles of various oxides, including complex oxides,organic- inorganic hybrids, and biomaterials, can be synthesized. The key issue is to promote temporal nucleation followed by diffusion-controlled subsequent growth. The particle size can be varied by changing the concentration and aging time. In a typical sol, nanoclusters formed by hydrolysis and condensation reactions commonly have a size ranging from 1 to 100 nm [6]. Sol–gel and other techniques can be used for preparation of different nanomaterials and nano composites.

5.8.1 Sol Gel Synthesis and Characterization of Al_2O_3–SiC Nanocomposite

α-alumina is the harder and more dense the other forms of alumina, which is commonly formed by heating of other forms of alumina to high temperature in the range of 1100–1200 °C or even higher. One of the main purposes of introducing the second phase particles into alumina was to enhance the inherent mechanical properties by deflecting the cracks on the grain boundaries into the matrix grains. In addition, the properties of the composites can be tailored by controlling parameters such as reinforcement particle distribution, size, volume fraction, orientation, and matrix microstructure. Silicon carbide (SiC) powder is an excellent reinforcement for ceramic composites because of its high hardness, high strength, chemical

inertness and oxidation resistance. Since the coefficient of thermal expansion of alumina is much higher than that of silicon carbide, the residual stress states in alumina–silicon carbide composites are such that the second phase particles are in approximately hydrostatic compression, and there are tensile hoop stresses in the surrounding matrix. The tensile stresses in the alumina matrix can promote crack propagating and so reduce its toughness. Simultaneously, the counter forces (compressive stresses of the second phase particles) can be passed to the grain boundaries and consequently resulting in toughening. The change of grain and grain boundary toughness can dramatically change the fracture behavior of the composites. There are several common synthesizing methods of ceramic nanopowders such as mechanical synthesis, vapor phase reaction, precipitation, combustion and sol–gel methods. But among them sol–gel method because of homogeneous mixing condition in liquid phase is the most promising one. Homogeneous mixing cause accelerating reaction rate and lower reaction temperature and consequently producing finer powders. Nanocomposites usually have been densified by using hot pressing. But hot pressing is costly, and also puts restrictions on the sample geometry. Pressureless sintering generally gives rise to lower density nanocomposites because the driving force for grain boundary movement is lower. As result work has been done by using sintering aids [46].

In this research the fabrication process for high dense pressureless sintered Al_2O_3-5 vol% SiC nanocomposites were investigated. The precursor solutions for Al_2O_3 nano powder were prepared by sol–gel method using $AlCl_3$ anhydrous, distilled water and NH_4OH. At first, the aluminum chloride was mixed with distilled water. The solution was stirred using a magnetic stirrer at 25 °C for 1 h to obtain a transparent solution. Then NH_4OH was gradually added to the solution. The amount of base in the mixture must be precisely controlled. The obtained gel was dried at 80 °C for 24 h. The dried gel was then ground and calcined in a furnace at 1000, 1100 and 1200 °C with the heating rate and soaking time of 10 °C/min and 2 h correspondingly [46].

The chemical reagents used for preparing saccharose-SiO_2 gel as β-SiC precursors were tetraethoxysilicate (TEOS, $(C_2H_5)_4SiO_4$) and saccharose ($C_{12}H_{22}O_{11}$) as silicon and carbon source respectively. Ethanol and distilled water were solvents and also oxalic acid and ammonia were catalysts. Firstly, tetraethylorthosilicate and ethanol were added into saccharose solution with the molar ratio of C:Si = 4:1. During the process of stirring for homogeneity, the pH value of the mixture was kept at 2–3 by using oxalic acid. After 4 h of stirring at room temperature ammonia was added and raised the pH up to 4.

The prepared dark brown gel was placed in drying oven at 100 °C for 24 h. The xerogel was ground and poured into a graphite crucible inside a sintering furnace and then fired at 1500 °C for 1 h in 0.1 MPa argon atmosphere for carbothermal reduction reactions with the heating rate of 10 °C/min. Because of the existence of some residual carbon in obtained powders and probability of no desirable effect on final product the prepared powders were fired at 700 °C in air atmosphere for 1 h to remove the extra carbon [46].

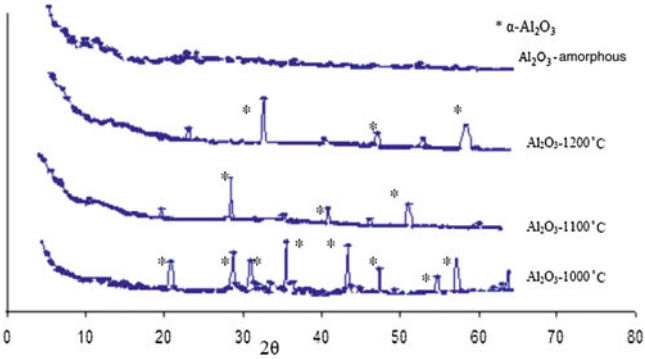

Fig. 12 The XRD pattern of alumina xerogel and powders heat treated at various temperatures for 2 h [46]

A powder mixture of nano α-Al_2O_3 and 4.1 wt% nano SiC was prepared by agate. Doped samples were also prepared by adding TiO_2 (0.5–2 %wt with respect to the Al_2O_3 content). The TiO_2 powder, which is a standard material in the field of photocatalytic reactions, contains anatase and rutile phases in a ratio of about 3:1. To help green pallets formation 2 wt% polyvinyl alcohol (PVA) was added. The mixed powders were uniaxially hand pressed at 137 MPa by using a small mold ($r = 1$ cm, $h = 1$ cm). The green pallets were placed in an Al_2O_3 protective powder bed in an alumina crucible and pressureless sintered in nitrogen atmosphere with a flow rate of 5 l/min at 1600 and 1630 °C. The heating rate of the furnace was 10 °C/min and cooling at the same rate. The densities of the sintered samples were determined by using a technique based on Archimedes principle with distilled water [46].

Aluminum chloride anhydrous was hydrolyzed in distilled water to produce the sol. The initial pH of the sol should be fixed at 3–3.5. The hydroxides groups that were produced in this step finally linked together to form the gel at pH = 9. The appearance of sol would be opaque or translucent when the ratio of NH_4OH/H_2O was lower than 0.2. Adding more base than this ratio would result in a decrease of the gelation time which may be attributed to the catalytic effect. Generally the gelation time decreases by increasing aluminum chloride powder due to increasing the rate of hydrolysis and condensation reactions. However, increasing the amount of aluminum content in the sol decreases transparency due to inadequate solubility of aluminum chloride in the sol. It seems that 2 is an optimum ratio of NH_4OH/H_2O. As can be seen in Fig. 12 the first peaks of α-Al_2O_3 phase are detected in the gel heat treated at 1000 °C. By raising the temperature to 1100 °C, the intensity of their corresponding peaks increases. Usually transformation of the metastable phases of alumina to the final stable α-alumina start at about 1100 °C but in this investigation α-Al_2O_3 was appeared at 1000 °C and completely crystallizes at 1200 °C [46].

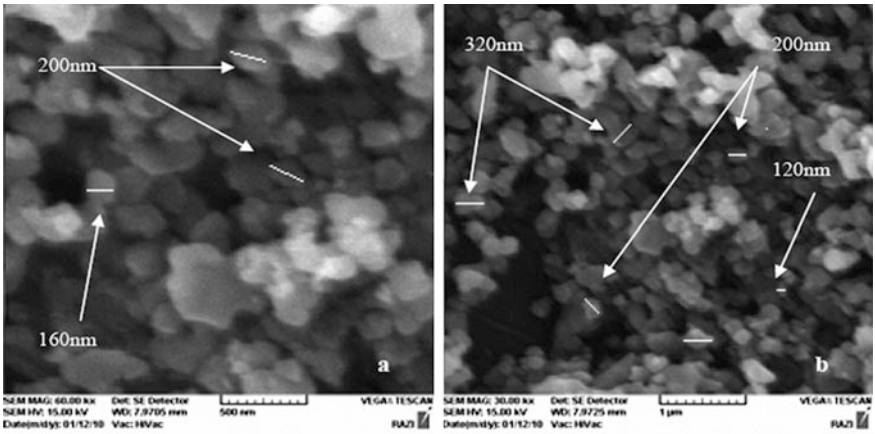

Fig. 13 SEM images of α-Al_2O_3 in two magnitudes **a** 6000, **b** 3000 [46]

As shown in Fig. 13 most of the particles heat treated at 1200 °C are in the range of 100–200 nm and spherical in shape. The crystallite size calculations were done by using Scherrer's equation resulted in 30–90 nm [46].

In the gel formation from TEOS, at first hydrolysis of Si-OC_2H_5 groups produced Si–OH groups. Then condensation between two Si–OH groups or between a Si–OH group and a Si-OC_2H_5 formed Si–O-Si chains. At the end the chains cross-link and/or entangle with each other in the whole liquid to form the gel. It is proved that hydrolysis and condensation rates of TEOS were greatly dependent upon the catalyst and the pH value. Typically when pH was below 7 hydrolysis rate increased with decreasing pH, but condensation rate decreased and reached its lowest point at pH = 2, the isoelectric point of silica. The dark brown dried gel should be reduced to form the SiC powder. The gas–solid reactions of SiC formation proceed in these two steps (Eqs. 1, 2):

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \tag{1}$$

$$C_{(s)} + SiO_{(g)} \rightarrow SiC_{(s)} + CO_{(g)} \tag{2}$$

But there are some intermediate reactions between these two steps. The first step begins with the reduction of SiO_2 by carbon to form SiO gas according to reaction Eq. (1). Once carbon monoxide (CO) is formed, SiO can also be produced according to this reaction:

$$SiO_{2(s)} + CO_{(g)} \rightarrow SiO_{(g)} + CO_{2(g)} \tag{3}$$

Any CO_2 produced will be consumed shortly by the surrounding carbon particles to form CO gas (Eq. 4):

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \tag{4}$$

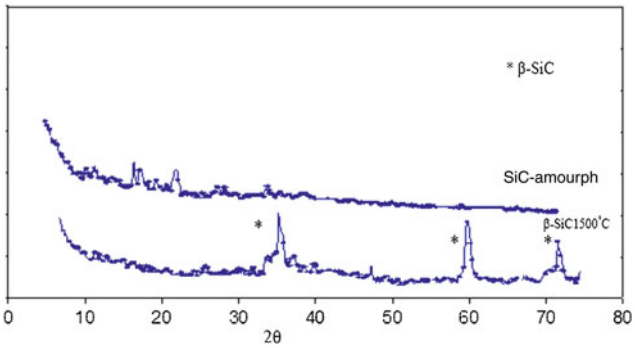

Fig. 14 The XRD patterns of SiO_2-saccharose xerogel and β-SiC powder heat treated at 1500 °C for 1 h [46]

The gaseous silicon monoxide (SiO) following reacts with C and CO according to reactions Eqs. (5) and (6):

$$SiO_{(g)} + C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)} \tag{5}$$

$$SiO_{(g)} + CO_{(g)} \rightarrow SiO_{(g)} + CO_{2(g)} \tag{6}$$

The reaction Eq. (6) is followed by reaction Eq. (4) to synthesize CO, which in turn reacts with SiO according to reaction Eq. (3) and SiO according to reaction Eq. (6), and to continue the cycle. Silicon carbide can be formed by continuing the cycle. Silicon carbide can be formed by heterogeneous nucleation according to reaction Eq. (5) [46].

XRD analysis in Fig. 14 shows that β-SiC is formed, and no other crystalline phases such as silica, carbon or other impurities are detected. This SiC has a well crystalline structure. The widths and intensities of the diffraction peaks in the XRD patterns are related to the average crystallite size, and they are often used to estimate the particle size. According to Scherer's equation it was calculated that the crystallite size were mainly between 30–70 nm. There was an interesting effect of small TiO_2 additions on densification at 1600 °C and 1630 °C (Table 1) [46].

Sample 2 that doped with TiO_2 reached 93.9 and 94.2 % of full density at 1600 °C and 1630 °C respectively, while the undopped material (sample 1) reached almost the same result at the same temperature. By increasing the percentage of TiO_2 densities were raised but these intensifies are not as high as the desired result. Effect of TiO_2 additions on density was more pronounced at the higher sintering temperature 1630 °C. The smallest grain size is belonged to sample 4. Its grain boundaries and triple grain junctions were shown in Fig. 15. In this sample the highest density and hardness were achieved [46].

Comparing samples 4 and 5 resulted that there is an optimum amount of sintering aid and adding more TiO_2 at high temperature had a converse result. This is because more TiO_2 than optimum value with attendant of SiC at higher

Table 1 Experimental samples [46]

Samples name	TiO_2 (%wt)	Sintering temperature (°C)	Density (%)	Hardness (GPa)	Grain size (μm)
1	–	1600/1630	93.9–94.1	14.1–13.3	0.7
2	0.5	1600/1630	93.9–94.2	14.8	1.5
3	1	1600/1630	95.1–6	15.2	1.9
4	1.5	1600/1630	97–97.3	16.5	2
5	2	1600/1630	96.5–97	16.3	2.3

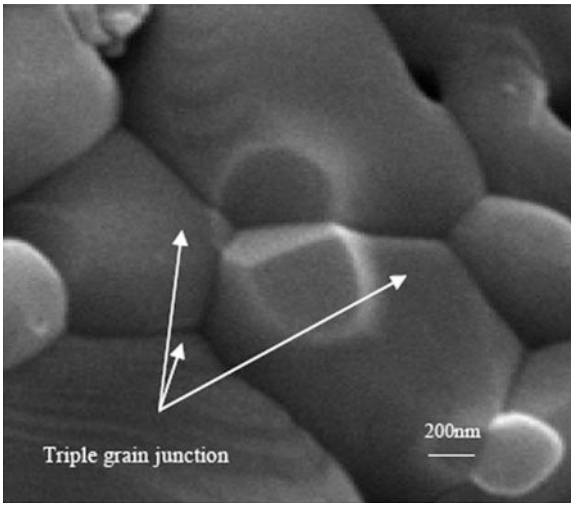

Fig. 15 Triple grain junctions in sample 4 [46]

temperature would prepare the situation for oxidation of more SiC and producing of more SiO_2 and this causes more grain growth and lower density.

Vickers hardness of the doped materials increased with density (Table 1). The material without the addition of TiO_2 had the lowest hardness of 14.1 GPa and 13.3 GPa respectively at 1600 and 1630 °C and the addition of 1.5 %wt TiO_2 resulted in a hardness of 16.5 GPa. The samples hardness that sintered at 1630 °C varied between 14.8 and 16.5 GPa (Table 1) [46].

It is well substantiated that a small addition (a few hundred ppm) of MgO is an effective densification aid during sintering of Al_2O_3 ceramics at temperatures in the range of 1600–1900 °C. In this work for the first time the effect of TiO_2 was investigated. Small additions of TiO_2 have controlled the Al_2O_3 grain size by repressing excessive grain growth according to Zener pinning. Zener pinning is the influence of a dispersion of fine particles on the movement of low and high angle grain boundaries through a polycrystalline material. Small particles act to prevent the motion of such boundaries by exerting a pinning pressure which counteracts the driving force pushing the boundaries. Zener pinning is very important in materials processing as it has a strong influence on recovery, recrystallization and grain growth. The small additions of TiO_2 in the samples in the present

investigation did not have any obvious effect on matrix grain size during sintering at a particular temperature (Table 1) and only a limited number of larger matrix grain section areas were present. This exhibits that local abnormal grain growth did occur under the applied sintering conditions and it didn't related to the existence of TiO_2. Also TiO_2 may promote a more homogeneous grain size distribution by solute pinning of grain boundaries. Other mechanisms that may operate in the presence of a glassy/liquid phase include modification of liquid–solid interfacial energies and glass viscosity. Also by adding these sintering aids to this nanocomposite the significant segregation of Si and Ti in the grain boundaries would be occurred. Whether this causes a glassy grain boundary layer and in continues the segregation simply forms a boundary with a high diffusivity grain boundary layer. The much increased segregation in this material is apparently related to some interaction between SiC and TiO_2. Such an interaction has previously been reported by Ding et al. They found a much greater rate of oxidation of SiC in the presence of MgO and Al_2O_3 than they did when just Al_2O_3 was present. They associated this with the lower eutectic temperature of SiO_2–Al_2O_3–MgO glass compared to SiO_2–Al_2O_3 glass. With the same words by adding TiO_2 the glassy phases of Al_2O_3–TiO_2–SiO_2 with the eutectic temperature of 1470 °C, would be formed. This phenomenon would be affected on process in two different ways. First is that by reaching this temperature with different percentage of components the sintering temperature would be decreased. And the second is the greater oxidation of SiC will release more SiO_2 which can contribute to the grain boundary glass or segregated layer, either of which may allow faster grain boundary diffusion [46].

5.8.2 Synthesis of Biodegradable Nanocomposite Scaffold for Bone Tissue Engineering

Over the past decade, tissue engineering has been widely inspected as a promising approach towards regeneration of bone tissue. Biomaterials are necessary in tissue engineering strategies for the manufacture of scaffolds where pertinent cells attach, grow, proliferate and differentiate. Thus, as the main target, bone tissue engineering has applied developed biodegradable materials as bone graft substitutes for filling large bone defects. In bone tissue engineering, scaffold serves as the matrices of tissue formation and plays a pivotal role. Thus, the choice of the most appreciated material to produce a scaffold is an indispensably important step in the construction of a tissue-engineered product, since its characteristics will identify the properties of the scaffold Polyhydroxyalkanoates (PHAs) are a class of biodegradable polyesters that have been used in combination or alone for biomedical applications such as sutures, repair devices, repair patches, slings, cardiovascular patches, orthopedic pins, adhesion barriers, stents, guided tissue repair/regeneration devices,

articular cartilage repair devices, nerve guides, tendon repair devices, bone marrow scaffolds, and wound dressings. Poly (3-hydroxybutyrate), as a member of the polyhydroxyalkanoates family, known as PHB, has attracted much attention for a variety of medical applications because of its biodegradation which exhibits a much longer degradation time than polymers of the poly (a-hydroxyacid) group (e.g. PLA or PLGA) and its excellent biocompatibility which has a good degree with various cell lines Several composites of PHB and bioactive inorganic phases, like hydroxyapatite, wollastonite and bioglass, have been produced to give strength and bioactivity to the composites. Inorganic phases can be augmented to the polymer matrix in their micro or nanosize. However, for PHB composites, mainly microparticles have been investigated. Recently, nanotechnology and its production have been utilized in a wide variety of medical engineering applications. Nanoscience is particularly useful in tissue engineering since the interactions between cells and biomaterials occur in nanoscale and the components of biological tissues are nanomaterials. Nanoscales of hydroxyapatite, tricalcium phosphate, bioactive glass, titanium oxide, carbon nanotubes and diamonds, for example, have been prepared and used as reinforcement materials in biopolymer matrix composites. The greater specific surface area of the nanoparticles should lead to higher interface effects and also cause improved bioactivity and mechanical properties when compared to micro size particles. In addition, their utilization in a polymeric matrix closely mimics the structure of a natural bone. PHB/bioglass nanocomposite scaffold was prepared using a combination of published salt-leaching techniques. Briefly, 2 g PHB and 0.2 g nano bioglass were dissolved in chloroform with 6 %w/v and refluxed at 60 °C for 6 h. Then, they were sonicated for 30 min using a sonicating probe, and subsequently, the solution was poured into a bed of sieved sodium chloride particles 250–300 nm and the sodium chloride: polymer weight ratio was 90:10. The scaffold was placed under vacuum in a desiccator for 24 h for the solvent to evaporate completely. Then it was rinsed with distilled water for leaching the salt. After the salt leaching process, the microporous polymer scaffold was obtained and then vacuum dried. The microstructure of nanocomposite scaffold containing 10 wt% nano bioglass particles is shown in Fig. 16a–c. The SEM images demonstrated uniform porosities of 250–300 nm pore size that is suitable for osteoblast migration [47].

Also there have been many other experiences by the author in the fields of nanomaterials and nano technology in order to develop new methods for synthesis of advanced nano materials, new characterization techniques, phase and microstructural evolution. Some of these works including synthesis and characterization of ceramic nano composites [48–50], nano ceramic synthesis [51–53], nano biomaterials [54–58], nano coatings [59], sol–gel synthesis [60], mechanochemical synthesis [61–65], nano structured metallic alloys [66–68], nano polymer-silicate composites [69].

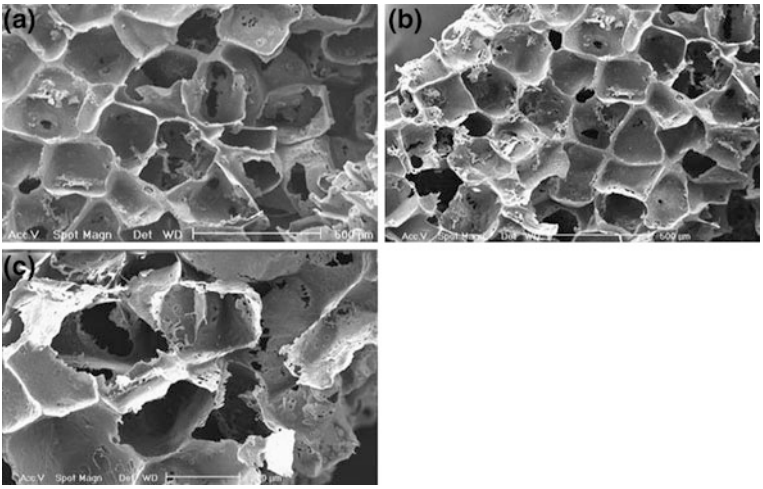

Fig. 16 **a** The SEM of nanocomposite scaffold's surface with 50× magnification. **b** The SEM of nanocomposite scaffold's cross section with 50× magnification. **c** The SEM of nanocomposite scaffold's cross section with 90× magnification [47]

6 Applications

6.1 Introduction

The early application of nanomaterials and nanocompositesare utilized in systems that nanopowders are used in their free form, without consolidation or blending. For a simple example, nanoscale titanium dioxide and zinc oxide powders are now commonly used by cosmetics manufacturers for facial base creams and sunscreen lotions for UV protection. Nanoscale iron oxide powder is now being used as a base material for rouge and lipstick. Paints with reflective properties are also being manufactured using nanoscale titanium dioxide particles. Nanostructured wear-resistant coatings for cutting tools and engineering components have used for several years. Nanostructured cemented carbide coatings are used on some Navy ships for their increased durability. Recently, more sophisticated applications of nanoscale materials have been realized. Nanostructured materials are in wide use in the area of information technology, integrated into complex products such as the hard disk drives that provide faster communication in today's world [11].

Many uses of nanoscale particles have already appeared in specialty markets, such as defense applications, and in markets for scientific and technical equipments. Producers of optical materials and electronics substrates such as silicon and gallium arsenide have embraced the use of nanosize particles for chemomechanical polishing of these substrates for chip manufacturing. Nanosize particles of silicon carbide, diamond, and boron carbide are used as lapping compounds to reduce the waviness of finished surfaces from corner to corner and produce surface

finishes to 1–2 nm smoothness. The ability to produce such high-quality components is significant for scientific applications and could become even more important as electronic devices and optical communications systems become a larger part of the nation's communications infrastructure [11].

6.2 Ceramic Nanocomposites for Load-Bearing Applications

Researchers have observed unusual behavior, in the form of high contact-damage resistance with no corresponding improvement in toughness, in Al_2O_3/nanotube composites. Researchers from the University of Connecticut and the National Institute for Materials Science in Tsukuba, Japan, used the spark-plasma sintering (SPS) method to produce the Al_2O_3/single-walled nanotube (SWNT) composites and observed their behavior under Vickers (sharp) and Hertzian (blunt) indentation tests. These composites are not tough in the classical sense, but are resistant to indentation (contact) damage. Such a combination is uncommon in ceramics. The researchers observed similar behavior in Al_2O_3/graphite composites. The reason for this is the unique way in which SWNTs go to the grain boundaries in alumina and provide shear weakness under indentation [11].

6.3 Nanotechnology in Automotive Applications

Diesel particulate-based filters for cars are being developed using a nanotechnology approach. Nano Pt-CeOx particles are improved to optimize the contact between the particle and diesel soot. Because of the lower particle size a relatively lower filter regeneration temperature is achieved (less than 450 °C). Nanocomposites are currently used in Toyota or GM cars instead of regular plastic. In addition to being stronger and longer-lasting than conventional plastics, nanocomposites also have a significant advantage: they are lighter. It is important for a car to be as light as possible. Lighter cars use less fuel, which means that they are less expensive for people to own [11].

6.4 Nanoclay-Polymer Composites for Structural Applications

Emerging nanotechnologies offer the potential for revolutionary new polymer materials with enhanced physical features: reduced thermal-expansion coefficients, increased stiffness and strength, barrier properties, and heat resistance, without loss of impact strength. Nanocomposites, which contain nanometer-scale particles that are homogeneously dispersed throughout traditional polymers, can provide stiffness and strength approaching that of metals, but with significant reductions in

weight. While the most cost-effective nanosized reinforcing particles are clays, they require surface modification with surfactants to achieve homogeneous dispersion at the nanoscale. Even at a cost of $3–7/lb, commercially available nanoclays are only truly compatible with polar polymers like nylon. The proper design of surfactant coatings used to make nanoclays remains a critical technical/economic obstacle to the commercial production of engineered plastics for high-volume applications like automobile body panels [11].

Researchers at Argonne National Laboratory have focused on the improvement of an integrated approach to achieve good exfoliation of nanosized clays in a broad range of polymers, including polyolefins. The Argonne approach begins with a patented clay purification process that selectively separates and recovers exfoliated nanoclays. The surface modification of the mineral surface begins during the early stages of the purification process and uses a range of unique surface chemistries with enhanced thermal stability and unusually high affinity for nonpolar polymers like polypropylene [11].

6.5 Metal Matrix Nanocomposites for Structural Applications

Metal matrix composites (MMCs) such as continuous carbon or boron fiber reinforced aluminum and magnesium, and silicon carbide reinforced aluminum, have been used for aerospace applications owing to their lightweight and tailorable properties. There is much interest in producing metal matrix nanocomposites that incorporate nanoparticles and nanotubes for structural applications, as these materials show even greater improvements in their physical, mechanical and tribological properties as compared to composites with micron-sized reinforcements. The incorporation of carbon nanotubes in particular, which have much higher strength, stiffness, and electrical conductivity compared with metals, can improve these properties of metal matrix composites. Currently metal matrix nanocomposites are being explored for structural applications in the defense, aerospace and automotive sectors [11].

Concurrent with the interest in producing novel nanocomposite materials is the need to develop low-cost means to produce these materials. Most of the previous work in synthesizing nanocomposites involved the use of powder metallurgy techniques, which are not only high cost, but also result in the presence of porosity and contamination. Solidification processing methods, such as stir mixing, squeeze casting, and pressure infiltration are advantageous over other processes in rapidly and inexpensively producing large and complex near-net-shape components; however, this area remains relatively unexplored in the synthesis of nanocomposites. Stir mixing techniques, widely utilized to mix micron-size particles in metallic melts, have recently been modified for dispersing small volume percentages of nanosized reinforcement particles in metallic matrices. Although there are some difficulties in mixing nanosize particles in metallic melts resulting from their tendency to agglomerate. A research team in Japan worked on

dispersing nanosize particles in aluminum alloys using a stir mixing technique and other researchers at the Polish Academy of Science has recently demonstrated the incorporation of greater than 80 Vol% nanoparticles in metals by high-pressure infiltration with pressures in the GPa range. Composites produced by this method possess the unique properties of nanosized metallic grains and are certainly useful in structural nanocomposites [11].

6.6 Application of Ferrofluids with Magnetic Nanoparticles

A ferrofluid is a simple liquid medium containing a colloidal suspension of ferromagnetic nanoparticles. Ferrofluids show remarkable properties in the presence of a magnetic field. Typical ferrofluids consist of 10 nm particles of magnetite suspended within an appropriate solvent. Most commercial ferrofluids utilize an oil-based liquid solvent. The nanoparticles in the ferrofluids are special permanent magnets; when placed in suspension, the net magnetization of the ferrofluid is zero until a magnetic field is applied. What distinguishes ferrofluids from other fluids are the body and surface forces and torques that arise in the ferrofluids when magnetic fields are applied to them, which in turn give rise to unusual fluid-mechanical response [11].

6.7 Nanocomposite Coatings

The industrialization of the "Ti–Al–Si–N" coatings with Si dissolved in the (Ti1–xAlx)N metastable solid solution was pioneered by Tanaka et al. (2001), whereas Jilek and Holubarwere developing industrial applications of the nc-(Ti1–x Alx)N/a-Si_3N_4 nanocomposites. Already the "Ti–Al–Si–N" metastable solution coatings showed an enhanced hardness, improved oxidation resistance and a better cutting performance as compared to the state-of-the art (Ti1–xAl_x)N ones (Tanaka et al. 2001). However, as pointed out by Tanaka later, the nc-(Ti1–xAl_x)N/a-Si_3N_4 nanocomposites exhibited an even better cutting performance (Tanaka et al., 2004). The "Ti–Si–N"solid-solution coatings with the FCC structure of TiN were recently studied in detail by Flink et al. (2005). These researchers have shown that, in this solid solution, the hardness increases almost linearly with silicon content and reaches about 45 GPa for Si content of 14 %. Upon annealing, the hardness remains nearly constant up to about 900 °C and decreases afterward reaching about 26 GPa after annealing at 1100 °C. Compared with the results, it is clear that the nanocomposites possess a higher thermal stability [11].

6.8 Electrodeposited Nanostructures

Electrodeposition is a one-step process for production of nanostructured materials. It is based on the old technology, but with refinements such as pulse plating much work has been done in recent years to develop nanocrystalline materials by electrodeposition. Electrodeposited nanocrystalline metals can exhibit both high strength and good ductility. Electrodeposited nanocrystalline materials can be in the form of thick coatings, and free-standing foils, plates, or tubes, so may be considered to be bulk structural materials. Palumbo et al. have reviewed the applications for electrodeposited nanostructures. These researchers listed a wide variety of applications, some already in commercial use, some potential. One example of a large-scale structural application of a bulk nanostructured material was the use of an electrodeposited nickel microalloy as an in situ repair technique for nuclear steam generator tubing [11].

6.9 Military Applications

Nanocrystalline materials can be tough, due to the possible combination of high strength and good ductility. Zhong et al. found that Ni–Fe armor plating can be twice as tough as the required specifications for military vehicles when made in nanocrystalline form [11].

Electromagnetic launchers, rail guns, utilize electrical-magnetic energy to propel penetrators/projectiles at velocities up to 2.5 km/s. This improvement in velocity over conventional explosives can deliver projectiles with an impact velocity of Mach 5 to targets at ranges of 250 miles. Since a rail gun operates on electrical energy, the rails need to be very good conductors of electricity. They also need to be strong, tough and rigid so that the rail gun does not sag while firing and buckle under its own weight. While a good electrical conductor like Cu might be the choice for the rails, Cu is too weak and does not have sufficient wear resistance or high temperature strength. Therefore, nanocomposites of tungsten, copper, and titanium diboride are being studied which may provide the combination of good electrical conductivity and strength required [11].

6.10 Nanoelectronic

These are mainly silicon based microelectronic devices which have invaded our life. Integrated circuits are now found everywhere not only in personal computers but also in a lot of equipment we use each minute as cars, telephones, etc. We always need more memory as well as faster and cheaper processors. If the reduction in size of electronic devices continues at its present exponential pace, the

size of entire devices will approach that of molecules within few decades. However, major limitations will occur well before this happens. For example, whereas in current devices electrons behave classically, at the scale of molecules, they behave as quantum mechanical objects. Also, due to the increasing cost of microelectronic factories, there is an important need for much less expensive manufacturing process. Thus, an important area of research in nanotechnology and nanoscience is molecular electronics, in which molecules with electronics functionality are designed, synthesized and then assembled into circuits through the processes of self-organization and self-alignment. This could lead to new electronics with a very high density of integration and with a lower cost than present technologies [70].

7 Environmental Implications

7.1 Introduction

Nanotechnology is concerned with the world of invisible miniscule particles that are dominated by force of physics and chemistry that cannot be applied at the macro or human scale level. These particles have come to be defined as nanomaterials, and these materials posses unusual properties not presenting traditional and/or ordinary materials.

It is important to note that the environmental health and hazard risks associated with both the nano particles and the application of nanotechnology in industry is at present not fully known. Some early studies indicate that nanoparticles can serves as environmental poisons that accumulate in organs. Although these risks may prove to be either minor, avoidable, or both, the engineer and scientist is duty bound to investigate if there are in fact any health, safety, and environmental impacts associated with nano technology [71].

Some examples of nanotechnology in commercial use under series investigation include as follow:

- Semiconductor chips and other microelectronic applications.
- High surface-to-volume catalysts which promote chemical reactions more efficiently and selectively.
- Ceramic, lighter weight alloys, metal oxides and other metallic compounds,
- Coatings, paints, plastic, fillers, and food packaging applications.
- Polymer-composite materials, including tires with improved mechanical properties.
- Transparent composite materials such as sunscreen containing nanosize titanium dioxide and zinc oxide particles.
- Use in fuel cells, battery electrodes, communications applications, photographic film developing and gas sensors.
- Nano barcodes.

- Tips for scanning probe microscopes.
- Purification of pharmaceuticals and enzymes.

7.2 Classifications and Sources of Pollutants

It is relatively reasonable to say that there will be two classifications of nano emissions: particulates and gases. Additional details cannot be provided at this time since many of new processes and their corresponding emissions have yet to be formulated. It seems reasonable to conclude that many of these emissions will be similar in classifications to what presently exists. The classification and sources of pollutants of necessity have to be emitted to traditional contaminants. Recently the nation's natural resources were exploited indiscriminately. Water ways served as industrial pollution sinks, skies dispersed smoke from factories and power plants, and the land provided to be a cheap and convenient place to dump industrial and urban wastes. However, society is now more aware of the environmental and the need to protect it. While economic growth and prosperity are still important goals, opinion polls exhibit overwhelming public support for pollution controls and a pronounced willingness to pay for them [71].

7.2.1 Air Pollutant

Major air pollutants termed criteria pollutants under the act, include: ozone, carbon, air born particulates, sulfur dioxide, lead and nitrogen oxide. Although the Environmental Protection Agency (EPA) has made considerable progress in controlling air pollution, all of the six criteria except lead and nitrogen oxide are currently a major concern in a number of areas in the countries.

Generally, the main air pollutant can be classified to ozone and carbon monoxide, air born particulates, air born toxics, sulfur dioxide, acid deposition, indoor air pollutant, radon, environmental tobacco smoke, asbestos, formaldehyde and other volatile organic compounds and pesticides [71].

7.2.2 Water Pollutants

The EPA in partnership with governments is responsible for developing and maintaining water quality. These efforts are organized around three themes. The first is maintaining the quality of drinking water this is addressed by monitoring and treating drinking water prior to consumption and by minimizing the contamination of the surface water protecting against contamination of ground water needed for human consumption. The second is preventing the degradation and destruction of critical aquatic habitats, including wet lands, near shore coastal waters, oceans and lakes. The third is reducing the pollution of free flowing surface waters and protecting their uses [71].

7.2.3 Land Pollutants

Historically land has been used as the dumping ground for wastes, including those removed from the air and water. Early environmental protection efforts focused on cleaning up air and water pollution. It was not until the 1970s that there was much public concern about pollution of the land. There are five different forms of land pollutant. These include:

1. Industrial hazardous wastes
2. Municipal wastes
3. Mining wastes
4. Radioactive wastes
5. Underground storage tanks.

7.3 Health and Safety Issues

As for the potential environmental, health and safety risks associated with nanotechnology, critics not that since the plethora of nanosized materials (such as metal and metal oxides, polymers, ceramics and carbon derivatives) are not biodegradable, rigorous ongoing investigation is required to determine what their behavior will be in various ecosystems, in term of absorption or desorption, biotic uptake, and accumulation in plants and animals, similarly, questions remain about the potential toxicity of nano scaled materials to human, in terms of all potential modes of exposure to such ultra fine particles. Short term and long term mode of exposure, such as skin absorption, ingestion, and inhalation among others, must be systematically studied to determine any potential for organ or tissue damage, inflammation, a triggering of autoimmune diseases, and other health related consequences.

Recently it is reported that exposure to fullerenes, or bucky balls, (C-60 molecules) can cause extensive brain damage and alter the behavior of genes in the liver cells of juvenile large mouth bass. Meanwhile in an unrelated 2003 study, researchers found that carbon nanotubes can damage the lungs if inhaled. The animal studies show that the nanotubes are so small that the cells that normally resist other air contaminant are not equipped to handle them.

These reports are among several studies that raise questions about the potential health and environmental effects of nanoscaled materials, and while the initial toxicological data are preliminary, they underscore the need to learn more about how bucky balls and other nanoscaled materials are absorbed, how they might damage living organism, and what level of exposure create unacceptable hazards [71].

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