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INNER EYE OF NANOSCIENCE FOCUSSES THE OUTREACH OF MILESTONE

[1]*Dr. Sampa Dhabal, [2]Dr. Dhrubo Jyoti Sen and [3]Dr. Dhananjoy Saha

[1]Forensic Scientist, Kolkata, West Bengal, India.
[2]Department of Pharmaceutical Chemistry, School of Pharmacy, Techno India University, Salt–Lake City, Sector–V, EM–4/1, Kolkata–700091, West Bengal, India.
[3]Directorate of Technical Education, Bikash Bhavan, Salt Lake City, Kolkata– 700091, West Bengal, India.

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***Corresponding Author**
Dr. Sampa Dhabal
Forensic Scientist, Kolkata,
West Bengal, India.

ABSTRACT

The term 'nanomaterials' has a particular meaning. 'Nanomaterials' are materials at the nanoscale whose properties (such as conductivity, colour and mechanical hardness) change due to their nanoscale dimensions. 'Nanomaterials' encompass all nanoscale materials or materials that contain at least one nanoscale structure, either on their surfaces or internally. They can be inorganic, organic or biological. Nanomaterials such as nanoplates, nanoparticles, nanowires and nanotubes can be engineered in labs. Nanomaterials can also occur in nature—naturally occurring nanoparticles include smoke, sea spray and volcanic ash, as well as minerals, soils, salt particles and biogenic particles. Nanoparticles, nanowires, nanotubes and nanoplates are all types of nanomaterials, distinguished by their individual shapes and dimensions. What these materials have in common is that they have one or more dimension at the nanoscale.

- *Nanoparticles have all three dimensions within the nanoscale.*
- *Nanowires/tubes have diameters in the nanoscale, but can be several hundred nanometres long—or even longer.*
- *Nanoplates' thickness is at the nanoscale, but their other two dimensions can be quite large. An example of a nanoplate is graphene, a sheet of carbon one atom thick.*

Decades of research and development in nanoscience and nanotechnology have delivered both expected and unexpected benefits for our society. Nanotechnology is helping to improve products across a range of areas, including food safety, medicine and health care, energy, transportation, communications, environmental protection and manufacturing. It is being

used in the automotive, electronics and computing industries, and in household products, textiles, cosmetics—the list goes on. Already there are over 800 products on the market that are enhanced with nanotechnology. The ability to tailor the core structures of materials at the nanoscale to achieve specific properties is at the heart of nanotechnology. A few examples of current nanotechnology include the following.

FOOD SECURITY: Nanosensors in packaging can detect salmonella and other contaminants in food.

MEDICINE: Some of the most exciting breakthroughs in nanotechnology are occurring in the medical field, allowing medicine to become more personalised, cheaper, safer and easier to deliver. The potential for nanotechnology to improve drug-delivery systems for a range of diseases including cancer, heart disease, diabetes and other age-related illnesses is an area of intense research for scientists. For example, a 2014 breakthrough saw the development of nano cages, which can theoretically deliver cancer-killing drugs directly at the molecular level. This drug delivery method would reduce the dosage amount needed, target cancer cells rather than healthy cells, and reduce side effects. The technology is still being tested and undergoing approvals, but may see some real-world applications as early as 2016. Other exciting developments include the possibility of using nanotechnology to increase the growth of nerve cells (for example in a damaged brain or spinal cord), and using nanofibres to help regenerate damaged spinal nerves (currently being tested on mice).

ENERGY: Nanotechnology is being used in a range of energy areas—to improve the efficiency and cost-effectiveness of solar panels, create new kinds of batteries, improve the efficiency of fuel production using better catalysis, and create better lighting systems.

AUTOMOTIVE: Nanoengineered materials are in a range of products including high-power rechargeable batteries, fuel additives, fuel cells and improved catalytic converters, which produce cleaner exhaust for longer periods.

ENVIRONMENT: Researchers are developing nanostructured filters that can remove virus cells and other impurities from water, which may ultimately help create clean, affordable and abundant drinking water. A nanofabric paper towel, which can absorb 20 times its weight in oil, can be used for oil-spill clean-up operations.

Each development teaches us something about the technology, what it is capable of, and how we can refine it further. These developments are just the beginning.

ELECTRONICS: Many new screen-based appliances (TVs, phones, iPads and so on) incorporate nanostructured polymer films known as organic light-emitting diodes (OLEDs). These screens are brighter, lighter and have a better picture quality, among other things.

TEXTILES: Nanoscale additives in fabrics help resist staining, wrinkling and bacteria growth.

COSMETICS: Nanoscale materials in a range of cosmetics provide functions such as improved coverage, absorption or cleansing. As with the spread of any powerful new technology, there are likely to be a range of negative as well as positive outcomes associated with nanotechnology. As investment in nanoscience and nanotechnology continues, some people are voicing ethical, environmental and economic concerns. While science-fiction theories of 'grey goo' (millions of self-replicating nanomachines) with the potential to destroy the world are far-fetched, there are valid concerns about other areas of nanoscience. For example, how do manufactured nanoparticles interact with biological systems of the human body and what health effects may this have? In laboratory tests some nanomaterials have been shown to affect the formation of fibrous protein tangles, which are similar to those seen in some brain diseases. There is some evidence that nanoparticles could lead to genetic damage. Nanoparticles have also been examined for their impact on the heart and blood vessels. Long-term exposure to nanoparticles, particularly as they become more common in everyday items, is something that needs to be monitored. The way that nanomaterials interact with the environment also needs further study. How a particle behaves in the lab may be very different to how it behaves in water, air or soil, and how it interacts with organic matter. Indeed, the way nanoparticles behave in the environment depends not only on their individual physical and chemical characters, but also on the character of the receiving environment (whether it is hot, wet, acidic and so on). When exposed to an environment, nanoparticles may remain intact, or undergo one of the following processes: dissolution, speciation (association with other ionic or molecular dissolved chemical substances), settling, agglomeration/deagglomeration, biological or chemical transformation in to other chemicals.

Further research is needed in these areas and appropriate controls set up in relation to risk assessment. There is also the possibility that nanomaterials may move from organism to organism, or through food chains. The fact that there are many different types of nanomaterials means there is the potential for a wide range of effects. Some experiments have shown that they could have harmful effects on invertebrates and fish, including changes to their behaviour, development and reproduction. Risk assessment and testing needs to keep pace with the technology, especially as the use of nanomaterials expands into the production of ever more consumer goods. Testing needs to include methods for estimating exposure and

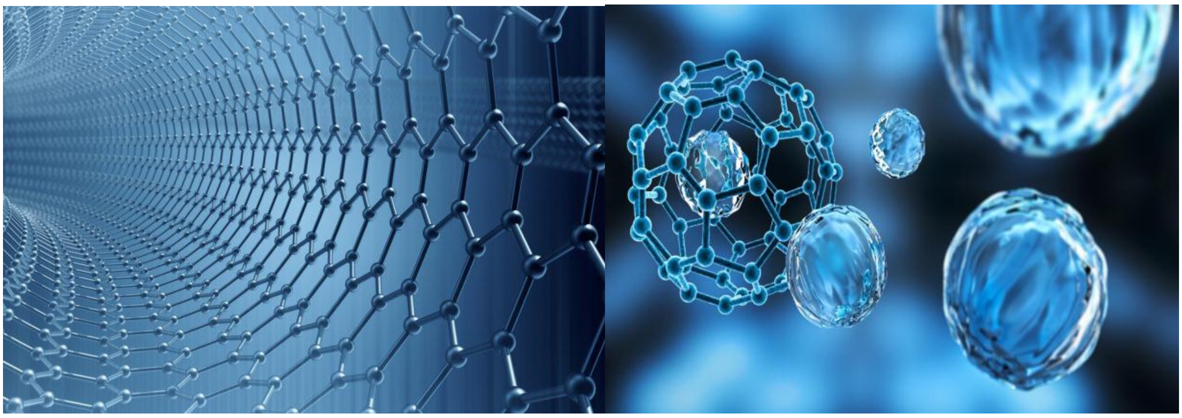
identifying hazards. At present, the nanoparticles that possess the highest potential risk are free, insoluble nanoparticles, such as those dispersed in a dust or liquid.

As we have seen, the unique physical and chemical properties of nanomaterials also often differ from those of bulk materials and require special assessment. Despite these concerns, most scientists believe that nanoscience will lead to huge advances in medicine, biotechnology, manufacturing, information technology and other equally diverse areas.

KEYWORDS: Nanoparticles, Nanowires, Nanotubes, Nanoplates, Nanopowders, Nanocrystals, Buckminsterfullerene.

BACKGROUND

Physical properties of the polycrystals suffer a noticeable change when the size of the crystallite is very small (of the order of nanometers). Usually such polycrystals are called nanocrystals. Small crystallite embedded in a matrix (may be of same chemical composition or of different) following certain pattern is called nanostructured material. Multilayer thin films with thicknesses in nanometer range are also defined as nanodimensional solids. These materials possess a unique complex physical and mechanical properties.[1,2] During the last decade, materials of this kind have attracted world wide attention when it became recognized that the atomic structures and, hence, their properties deviate from those of the states of condensed matter (e.g. crystals or glasses) with the same chemical compositions. These deviations result primarily from the following two factors: firstly, due to small crystallite sizes, upto 50% of the atoms are located within the cores of the incoherent boundaries between the crystallites, and secondly, the size and dimensionality effects are known to become important if the size of the crystallite regions in solids is reduced to a few interatomic spacing. The synthesis, characterization and processing of such nanodimensional solids are part of an emerging and rapidly growing field referred to as nanotechnology. Although development in this field of research is interdisciplinary in nature, correlation between the properties of solids and their structure is the fundamental concern for the Solid-State Physicists and Material Scientists’. The techniques available today for preparing and characterizing nanoscaled materials have been broadened, as far as chemical composition, crystallite size, porosity, homogeneity etc. are concerned. These developments appear crucial for an improved physical understanding of the atomic structure and the properties of these materials. In fact, there are evidences that by the preparation technique and an appropriate time temperature treatment, the atomic structure and the properties of these materials can be modified. An improved understanding would open the door to numerous new developments and hence, appears to be an attractive research goal for the near future. Number of research articles published, review papers appeared, new journals started (Nanostructured Materials- Pergamon Press, Nano Letters- American Chemical Society publications), series of conferences and symposia held could be an index of the importance of the subject under discussion.[3-6]



Nanoscience & Buckminsterfullerene

This chapter presents a broad overview of the structure and properties of nanocrystalline solids in general. Brief introductory remarks are made on the classification and various synthesis routes, followed by latest developments on structure property correlations of nanocrystalline metallic and oxide systems. Special mentions are being made on the latest developments in the studies of nanopowders of TiO_2, Al_2O_3, SiO_2.

Classifications and preparation of nanocrystalline materials

Classification of nanocrystalline materials: Nanocrystalline materials are classified according to morphologies, chemical compositions and structures. According to Gleiter, these materials are broadly divided in three different categories.[5] The first one comprises of materials with reduced dimensions in the form of (isolated, substrate- supported or embedded) nanometer-sized particles, thin wires or thin films. CVD, PVD, inert gas condensation, various aerosol techniques, precipitation from the vapor from supersaturated liquids or solids (both crystalline and amorphous) appear to be the techniques most frequently used to generate this type of microstructure. Depending on the details of the production process, the nm-sized crystallites obtained may be chemically identical, chemically different or they may be coated at their free surfaces. The second category comprises of materials in which the nanometer–sized microstructure is limited to a thin (nm–sized) surface region of a bulk material. PVD, CVD, ion implantation and laser beam treatments are the most widely applied procedures to modify the chemical composition and atomic structure of solid surfaces on a nanometer scale. This approach involves the introduction of high density of crystal defects (dislocation, grain boundaries etc) into a former perfect (or nearly perfect) single crystal by heavy deformation (e.g. by ball milling, extrusion, shear, wear, or high energy irradiation). The third category is the bulk solid with a nanometer-scale microstructure. The chemical composition, the atomic arrangement and the size of the building blocks (e.g. crystallites or atomic /molecular groups) forming the solid vary on a length scale of a few nanometers throughout the bulk. In other words, materials assembled of nanometer sized building blocks are microstructurally heterogeneous consisting of the building blocks and the regions between adjacent building blocks. Inoue describes nanocrystalline metallic systems as made of three structurally distinct phases like amorphous phase, nano quasicrystalline phase and nanocrystalline phase.[6] Depending on the process of formation of nonequilibrium phases nanocrystalline materials may be consisting only of nanocrystalline phases or may be combinations of nano crystalline plus amorphous phases, nanoscale crystalline plus quasicrystalline phases and nanoscale quasicrystalline plus amorphous phases.

Methods of preparation: The first effort towards synthesizing nanostructured materials, investigating their properties and those of nanopowders from which they were obtained, was made in the mid-seventies, which have given a new impetus by the invention of the technique allowing synthesis and consolidation of nanopowders in the same chamber.[7,8] Increased activities on the synthesis of nanocrystalline materials in recent years have been due to the pioneering work of Gletier.[5] Gletier synthesized ultra-fine nanometer sized metallic particles using an inert gas condensation technique and consolidated the powders in situ into small discs under ultrahigh vacuum conditions. Since then a number of techniques have been developed in which the starting material can be either in the solid, liquid, or gaseous states and could be grouped according the scheme shown in Table-1.

Table-1: Techniques of synthesis of nanocrystalline materials.

Starting phase	**Techniques**
Vapour	Inert gas condensation
	Sputtering
	Plasma processing
	Vapor deposition (physical and chemical)
Liquid	Electrodeposition
	Rapid solidification
Solid	Mechanical alloying/ milling
	Sliding wear
	Spark erosion

In principle, any method capable of producing very fine-grained polycrystalline powders could be used to produce nanocrystalline materials.[3] If a phase transformation is involved, e.g. liquid to solid or vapor to solid, then steps have to be taken to increase the nucleation rate and decrease the growth rate during formation of the product phase. The methods which have commonly been employed to synthesize these materials include inert gas condensation, mechanical alloying, spray conversion processing, sputtering, physical vapor deposition (PVD), chemical vapor processing, electrodeposition, co-precipitation, plasma processing, laser ablation, hydrothermal pyrolysis, thermophoretic forced flux system, and quenching the melt under high pressure.[9-24] The grain size (physical dimension), morphology, and texture can be varied by suitably modifying and controlling the process variables in each of these methods.

Controlled crystallization of the amorphous phases produced by any of the above methods (e.g. mechanical alloying, vapor deposition, electrodeposition) or by rapid solidification from the liquid state can also be used to produce nanocrystalline materials. There have also been several basic investigations during the past 2 to 3 years to define the conditions under which ultrafine powders could be obtained from the amorphous phases.[25-27]

Above mentioned methods have been used with different degrees of success to produce nanocrystalline phases in a variety of materials. Methods like gas condensation, mechanical alloying, and crystallization of amorphous alloys, chemical precipitation, and spray conversion processing have, widely, been used to produce 3D equiaxed nanocrystallites and also materials in the highly dispersed state depending the post preparation techniques. Vapor deposition, sputtering, and electrodeposition techniques have been used to synthesize the 1D–

layered nanocrystals while the sol-gel process is generally used to produce clusters. Following paragraphs describe briefly some of the fundamental techniques.

(i) Gas condensation technique: In this method, a metal or a mixture of metals is evaporated inside an ultrahigh vacuum (UHV) chamber filled with helium.[9,10] Due to interatomic collisions with helium atoms in the chamber, the evaporated metal atoms lose their kinetic energy and condense in the form of small crystals. These crystal powders are accumulated on vertical liquid nitrogen filled cold finger. The powder is stripped off the cold finger by moving an annular Teflon ring down the length of the tube into a compaction device. The scraping and compaction process also are carried out under UHV conditions. This done to minimize the amount of any trapped gases at the interfaces.[28] The densities of as compacted samples are found to be within 75-90% of corresponding bulk densities.

(ii) Mechanical alloying: Mechanical alloying (MA) is a solid-state powder processing technique that allows production of homogenous materials starting from blended elemental powder mixtures. The first report of the formation of nanostructured material synthesized by mechanical alloying is by Thompson and Politis in 1987, though the specific mention of formation of “nanocrystalline structures produced by mechanical alloying” was by Shingu et al in 1988.[29,30] Unlike many of the other methods, mechanical alloying produces low dimensional structures not by cluster assembly but by the structural decomposition of coarser-grained structures as a result of severe plastic deformation. This process consists of repeated welding, fracturing and rewelding of powder particles in dry high energy ball charge.[31,32] In mechanical alloying process, mixtures of elemental or prealloyed powders are subjected to grinding under a protective atmosphere in equipment capable of energy compressive impact forces such as attrition mills (Figure-1), vibrating ball mills, and shaker mills. A very recent comprehensive review described the process of mechanical alloying and the properties of the nanocrystalline materials obtained thereby.[11]

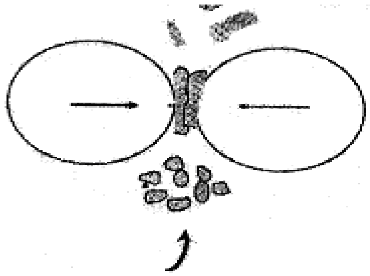


Figure-1

It has been shown that nanometer sized grains can be obtained in almost any material after sufficient milling time down to a minimum value which seems to vary with the melting temperature.[11]

(iii) Spray conversion processing: The process involves the atomization of a precursor solution into droplets, which are then directed through a heated region, usually a reaction furnace, by a carrier gas. Inside the furnace the solvent evaporates and intra-particle reactions occur that form the product material. The main advantage is the high purity of the product powder.[33] Other advantages are that the particles are more uniform in size and composition compared to the particles produced by other techniques. Experimental layout of this process is shown in Figure-2. Particle size is found to be a function of the furnace temperature with the average diameter decreasing as the furnace temperature increases. The process parameters are being further optimized and since the process is fully integrated, online control is also being planned.

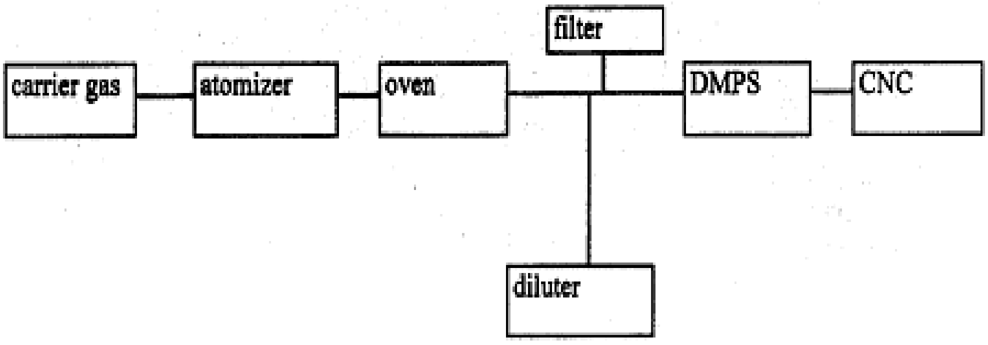


Figure-2

(iv) Physical vapor deposition: The use of physical vapor deposition (PVD) techniques is the most preferred method among all the synthesis methods used to produce sub-nanometric layers.[34] Even for the tool industry, the use of chemical vapor deposition to produce nitride and carbide coatings may gradually give way to PVD technologies. Amongst the many PVD methods used to produce nanoscaled multilayers, as electron beam evaporation, ion beam sputtering, molecular beam epitaxy, magnetron sputtering, the method used most frequently is thermal evaporation. Vacuum evaporation by electrical resistance heated sources inside a tungsten filament or boat (wire baskets, crucibles, multi-strand filaments) is often a preferred entrance level technique for the deposition of the thin films. The material vapor finally condenses in form of thin film on the cold substrate surface and on the vacuum chamber walls. Usually low pressures in the range 10^{-6} to 10^{-5} torr are used, to avoid reaction between the vapor and atmosphere. Vapor deposition is the heart of ongoing efforts to shrink microelectronic circuitry into the nanoscale regime to create functional thin films (e.g. exhibiting high temperature superconductivity, nonlinear optical behavior), and to synthesize materials with high thermoelectric figures of merit. It is widely used to grow nanoscaled particles as well.[34]

(v) Chemical Vapor Deposition: The CF-CVD process is based upon pyrolysis of chemical precursors in the narrow hot zone of a flat flame that is stable at pressure (<66 mbar).[35] The CF-CVD system, shown in Figure-3, consists of a water cooled vacuum chamber continuously pumped with a roughing pump.

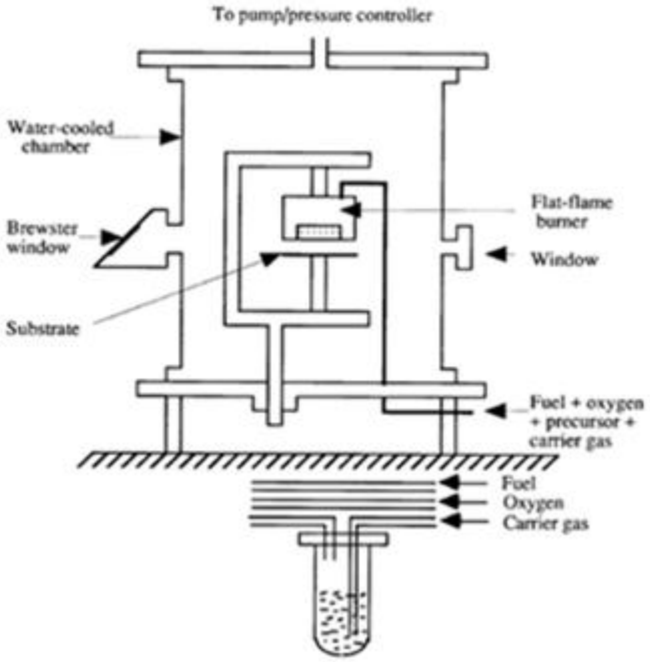


Figure-3

A constant dynamic pressure is maintained with a closed-loop pressure controller. Inside the chamber, a 2.5" diameter burner and a substrate are fixed rigidly to a mount such that the burner to substrate distance can be varied as desired. Metalorganic precursors are typically used in the Chemical Vapor process. In the configuration shown in Figure-3, the flow is highly one-dimensional, and the temperature and chemical species concentrations vary only in the axial direction (i.e. perpendicular to the face). The flow rate used for production of the different kinds of powders are presented in Table-1.[36]

Flow Parameters for Powder Production

	SiO_2	TiO_2	Al_2O_3
Fuel used	Methane	Hydrogen	Acetylene
Optimized fuel flow rate (cm^3/sq. cm of burner area)	27.64	44.23	37.91
Oxygen flow rate (cm^3/sq. cm of burner area)	78.98	31.59	108.32

The precursor pyrolyzes in the preheat zone of the flame, and particles condense as the flame gases cool upon approach to the substrate. The high degree of uniformity in these flames ensures that the particle size distribution in the deposit will be narrow since all the particles experience a similar time/temperature history. Widespread application of nanocrystalline materials requires production of the powder in tonnage and also efficient methods of consolidating the powders into bulk shapes.[33] Since the gas condensation process is carried out completely under UHV conditions, the cost of production is high. However, the powder produced is very clean and the cleanness between the particles can be maintained even after compaction. Mechanical alloying, on the other hand is a proven commercial process to produce oxide dispersion strengthened. But, contamination of the powder during milling (because of the fine size of the powder, atmosphere, and addition of process control agents to prevent excessive welding of powder particles among themselves and to the container walls) could prove a serious limitation of the process. Plasma processing can be another viable commercial process for making nanocrystalline powders. Limitations and advantages exist for each synthesis method when compared with others.

Review of recent work done on structure- property correlations of nanocrystalline materials: In nanocrystalline materials two types of atoms can be distinguished; crystal atoms with nearest neighbor configuration corresponding to the lattice and boundary atoms with a variety of interatomic spacings, differing from boundary to boundary. A nanocrystalline metal sample, for example, contains typically a high number of interfaces (~ $6\times10^{25}m^{-3}$ for a 10 nm grain size) with random orientation relationships, and consequently, a substantial fraction of atoms lies in the interfaces. Assuming that grains have the shape of spheres or cubes, the volume fraction of nanocrystalline materials associated with the boundaries has been calculated.[37] It has been shown that the volume fraction of atoms in the grain boundaries could be as much as 50% for a grain size of the order of 5 nm and decreases with increase in size. Thus, nanocrystalline materials in general, may be considered as consisting of two basic structural components – the numerous, small crystallites with long range order and different crystallographic orientations constituting the 'crystalline component' and a network of inter-crystalline regions, the structure of which differs from region to region, called interfacial component.[3] The situation is similar in case of multilayer thin films except for epitaxially grown films. The complex nature of the structure thus attribute to the observed unique physical and mechanical properties of these materials.[1,2] These materials have a wide range of possible applications with significant technological importance. For example, among the outstanding properties of metallic nanocrystals very high level of yield and fracture stress may be mentioned.[1,38] On the other hand nanophase ceramics are more ductile than conventional ceramics.[2,38] Multicomponent nanophase films are the main materials in modern electronic devices. The stability of devices is directly determined by the mechanical stability of the films and their mechanical properties.[39] Thus, in order to understand the interrelationship between structure and properties, nanocrystalline materials need to be characterized on both atomic and nanometer scales. The microstructural features of importance include (a) crystal size (grain size), distribution, and morphology, (b) the nature and morphology of grain boundaries and interphase interfaces (c) the perfection and nature of crystal defects. In the case of layered nanostructures, the features of importance are (a) the thickness and coherency of interfaces (b) composition profile across the interfaces to understand the nature of interdiffusion. Following sections review the recent developments in correlating structure dependent physical properties of nanocrystalline materials in general, separate sections on ceramic oxides and multilayer thin films are also discussed. Important microstructural parameters influencing the physical properties may, broadly, be grouped as: (i) Size effects influencing primarily mechanical strength, phase transitions, grain growth, electrical, magnetic and optical properties and, (ii) Diffusion dominates formation of intermetallic phases at grain boundaries and also sinterability.

(i) Size effect and its influence on physical and mechanical properties: When the dimensions of solids are comparable with the correlation length of some physical phenomenon (e.g., the Cooper-pair length, an exciton size, dislocation pileup length, etc), a detailed revision of all physical properties of solids become necessary and are usually referred to as size effects.[40] Size effect may also occur for structural elements of massive solids (crystallites, pores, etc). When the size of crystallites is very small (of the order of nm), most physical properties of the polycrystals suffer a noticeable change.[4] Mechanical properties of solids are, in most cases, structure sensitive, so an influence of size effect on the behavior of lattice defects in crystals ought to drastically change their physicomechanical characteristics. One of the most important crystal defects determining mechanical properties is lattice dislocation. Decreasing the grain size leads to increased hardness. It is thus clear that there must be a maximum in hardness at an optimal grain size.[3,40] For individual small crystals, lattice dislocation tend to leave the crystals, when the crystal size is less than the characteristic length.[40] Dislocation instability explains low deformability of small particles.[41] Theoretical results concerning the behavior of dislocations in small particles and nanocrystals has been reported, for the first time in where the problem of stability of defects in nanovolumes have been considered and the existence of critical size of dislocation stability in nanoparticles or nanograins has been predicted.[40,42] Below this critical size, material parameters such as elastic (shear) modulus (G) and lattice resistance (σ_{p}) to the dislocation motion, gliding dislocations are unstable in nanovolume interior. The reason for such instability are due to “image” forces F_i of elastic nature which strongly depend on nanocrystalline size.[41] Two kinds of forces act on dislocations in solids, one is continuum forces caused by the presence of interfaces and surfaces or by external stresses etc, second is the elastic friction forces depending on the position of the dislocation in a crystals.[42] Dislocations are non-equilibrium defects but in unloaded real nanocrystals they may exist for infinitely long time periods, since the continuum forces are too weak to overcome lattice friction. The elementary scheme of defect interaction will include one defect (dislocation, disclination etc) and interface of different geometry: plane interface, spherical interface, junction interfaces and so on.[41] In nanoscaled materials the elastic properties are strongly modified by the interaction of defects with interfaces.[38] The elastic constants of nanocrystalline materials have been found to be reduced by 30% or less. These results were interpreted as a result of the large free volume of the interfacial component resulting from the increased average interatomic spacings in the boundary regions.[1] The most significant change resulting from a reduction in the grain size to the nanometer level is a 4-5 times increase in the strength and hardness over the coarse-grained material. This is also the least understood and most controversial area.[3] Nanocrystalline materials are expected to show much higher yield strength than the coarse-grained materials of the same composition. However, it should be realized that the Hall-Petch relationship, which explains the increase in yield strength with decreasing grain size has certain limitations.[43,44] First, the strength value cannot increase indefinitely to beyond the theoretical strength limit. Second, any relaxation process taking place at the grain boundaries could lead to a decrease in strength. Third, the Hall-Petch relationship has been derived on the basis of strengthening resulting from dislocation pile-ups at physical obstacles. Recently, there has been an active debate in the literature on the origin of the high strengths of nanocrystalline materials, and attempts have been made to modify the Hall-Petch relationship to explain the observed results. At extremely fine grain sizes, e.g. the nanometer regime, the individual grains cannot support more than one dislocation and thus the Hall-Petch relationship may not be valid.[3] However, since in very fine-grained materials, e.g. nanocrystalline materials, pile-ups cannot form when the grain size is less than a critical value (d_c), weakening mechanisms (e.g. viscous type flow) operate and lead to a decrease in hardness with decreasing the grain size.[45,46] Assuming that the dislocation pile-up model is valid even in nanocrystalline materials, Pande et al considered the effect of a smaller number of dislocations in the pile-up and also the effect of anisotropy and suggested that the grain size exponent could be modified from the traditional value of (–1/2). Other investigations have modified the grain size exponent and /or the slope of the plot.[47-51] According to Palumbo et al, the transition from a positive to a negative slope occurs when the triple junctions in the microstructure begin to comprise a significant volume fraction of the bulk specimen value.[52] Fougere et al and Liu et al observed that the hardening or softening of nanocrystalline materials could depend on the method used to vary the grain size.[53-55] Annealing a sample to produce grain growth resulted in hardness values greater than those of as prepared samples with similar grain sizes. Lu and Sui, on the other hand felt that thermal annealing of the as prepared sample will relax the interfacial structure leading to a reduction in interfacial excess energy and this could explain the abnormal Hall-Petch behavior.[56]

(ii) Size effect on diffusion and sinterability: Since nanocrystalline materials contain a very large fraction of atoms at the grain boundaries, the numerous interfaces provide a high density of short circuit diffusion paths. Cosequently, they are expected to exhibit an enhanced diffusivity in comparison with the same chemical composition.[57-63] This enhanced diffusivity can have a significant effect on mechanical properties such as creep and super plasticity, ability to drop efficiently nanocrystalline materials with impurities at relatively low temperatures, and synthesis of alloy phases in immiscible metals and at temperatures much lower than those usually required in other systems.[3] The measured diffusivities in nanocrystalline Cu are about 14-20 orders of magnitude higher than lattice diffusion and about 2-4 orders of magnitude larger than grain boundary diffusion.[61] Similarly enhanced diffusivities have been also observed for solute diffusion in other metals. Diffusion coefficient strongly depends on the concentration and hence on the time-temperature history of the material. The nature of the diffusion profiles is found to change with time and also with annealing owing to the formation of the intermetallic phases. The enhanced self and impurity diffusivities in nanocrystalline materials appear to be strongly linked to the porosity present in the samples. Averback et al showed that diffusion coefficients could be reduced to conventional values by sintering the samples to full density.[64] The increased diffusivity (and consequently the reactivity) leads to increased solid solubility limits, formation of intermetallic phases (at temperatures much lower than those required for coarse grained materials and sometimes new phases), and increased sinterability of nanocrystalline powders. Solid solubility limits are usually enhanced when the material is in the nanocrystalline state. In extreme cases, solid solutions can also form in alloy systems which exhibit miscibility gaps both in the liquid and solid states. Typical examples of this phenomenon are the Ag-Fe, Ti-Mg and Cu-Fe systems.[65-68] The enhanced solid solubility limits in these systems have been[explained on the basis of elastic strains at the interfaces for various alloys. The nanostructure processing appears to be a novel way of forming solid solution alloys in systems in which alloying has not been possible by any other technique. The high diffusivity of nanocrystalline materials results in alloying by diffusion along the grain boundaries resulting in the formation of stable and metastable phases at relatively low temperatures. For example, formation of the Pd_3Bi intermetallic has been found to occur at 120^0C, a temperature much lower than normally observed.[69] Similarly, nanocrystalline mixtures of Cu and Er crystallites formed the equilibrium CuEr compound by compound by compaction.[69]

Another important consequence of the increased diffusivity is that sintering of nanocrystalline powders can occur at temperatures lower than those required for sintering coarse-grained polycrystalline powders. Significant improvements in the sinterability and mechanical properties have been obtained in nanocrystalline TiO_2 (rutile) in comparison with conventionally synthesized coarse-grained rutile.[70-72] Additionally, the fracture characteristics of sintered nanocrystalline TiO_2 appear to be significantly different from those of sintered commercial powder. It is not surprising that nanocrystalline materials, with their ultrafine grain sizes (and possibly clean particle surfaces and high grain boundary purity), will sinter at much lower temperatures than conventional coarse-grained materials.

Dislocation, growth and strength properties of nanocrystalline ceramic powders: Nanophase ceramic powders offer a host of attractive properties that are different from those associated with coarse particles.[35] Nanocrystalline ceramics may also be a good candidate material for joining ceramic parts. The usual problems in joining conventional ceramics is the requirement of high pressures and temperatures for diffusion bonding and non-retention of strength at elevated temperatures for reactive braze metals and molten glass – can be overcome with nanocrystalline ceramics because of their high diffusivity and super-plastic forming characteristics.[3] Also in the area of mechanical behavior, it has been observed that nanophase ceramics are easily formed and nano indenter measurements on nanophase TiO_2 have recently demonstrated that there is a dramatic increase in strain rate sensitivity with decreasing grain size.[72-76] Application areas for oxide ceramic nano powders include Chemical Mechanical Polishing (CMP), opacity in the ultra violet region of the light spectrum, heat transfer fluids, chemical gas sensors, catalysts and catalyst supports, conducting inks, biological filters and solar cells. All of these applications are driven by the need for a high surface area powder. Strong grain-size dependence is found for sets of samples in which the porosity change very little, it appears that this increased tendency toward ductility is an intrinsic crystal-size dependent property of these ultrafine crystalline ceramics.[3] The enhanced strain rate sensitivity at room temperature found in the nanophase ceramics (TiO_2, Al_2O_3) appears to result from increased grain boundary sliding in this material, aided by the presence of porosity, ultrafine crystal size, although the mechanism is yet to be demonstrated. In many ceramic systems such as TiO_2, Al_2O_3 and SiO_2 various kinds of metastable phases (polymorphs) are frequently observed in the ultrafine powders. Nanocrystal TiO_2 have important applications in photovoltaic devices due to its large specific surface area which can act as the light receiving surfaces for the efficient solar cell.[77] Moreover, TiO_2 is used in many applications such as integrated wave-guides, gas and humidity sensors, inorganic membranes, catalyst supports and electrochemical displays as well as in ecology for wastewater treatment.[78] Alumina (Al_2O_3) has been extensively investigated because of its wide-ranging industrial applications. This includes applications as a refractory material both of high-hardness and stability up to high temperatures, as a support-matrix in catalysis, as well as a variety of fundamental interests.[79-81] Silicon based advanced ceramics are being studied in great details for mechanical and opto-electronic applications.[82] SiO_2 is widely used in the ceramic and glass industries and has an enormous application potential in optical fibers, in microelectronics and in catalysis. On the other hand, silica is one of the most difficult materials to study. The origin of this difficulty is in the enormous structural complexity.[83] It is important to understand the grain growth processes of the nano powders during annealing, in order to be able to achieve the fabrication of ceramics with controlled microstructure.

Recent studies on nanocrystalline TiO_2: Anatase is a TiO_2 polymorph which is less stable than rutile, but more efficient than rutile for several applications like catalysis, photocatalysis, and solar cells.[84-86] Moreover, significant improvements in the sinterability and mechanical properties have been obtained in nanocrystalline TiO_2 powders in comparison with conventionally synthesized coarse-grained powders.[72,87,88] In all the applications, surface properties are of important considerations. However, while the surfaces of rutile have been extensively investigated, due to the limited availability of sufficiently large anatase single crystals the fundamental surface properties of this polymorph are still largely unexplored.[85,89] Only recently, some experimental studies of well-defined anatase surfaces have been undertaken.[90,91] From detailed surface energy calculations of the different crystallographic planes, it has been shown that anatase phase is the most probable phase during synthesis if the grain sizes are within 10 nm.[92] Experimental and theoretical models based on surface energy calculations on phase stability of TiO_2 are contradictory.[92-94] However, this has been attributed due to the small difference in the surface energies of the component phases.[92]

Strength properties of the nano-powders are found to be grain size dependent. Recently there has been an active debate in the literature on the origin of high strength of nanocrystalline materials (mostly in metals and alloys) and attempts have been made to explain strength related properties on the basis of dislocation movements.[3,95] It has been reported that hardness decreases if the grain sizes are bellow a critical size.[50] Dislocation-grain boundary interactions have been attributed for the grain growth in nanomaterials.[96] Database both theoretical and experimental available in regard to growth and strength properties of nanocrystalline TiO_2 powders is limited and findings, in general, are in contradictions.[87,92-96] The behavior of dislocations when the grain size becomes so small that predictions based on dislocation theory may be wrong because the fundamental assumptions in the theory are no longer valid. However, as the database for nanocrystalline metals and alloys is extremely thin, both in the variety of materials studied and the type of tests carried out, it is extremely difficult to arrive at such conclusions. Nevertheless, dislocation-grain boundary interaction plays an important role in controlling the grain growth, phase change and strength properties of the nanocrystalline materials. Hence models based on such dislocation interactions need careful examination. Again, strength related physical parameters like Young's moduli and shear moduli could be measured from X-ray diffraction analysis. Determination of such physical quantities from X-ray data may therefore be used to test the applicability of the X-ray diffraction technique for nanocrystalline materials.

Williamson and Smallman derived the basic equations for deducing the dislocation density in powdered materials from crystallite size and strain breadth measured from the X-ray Debye-Scherrer spectrum.[97] It has been shown that with cold working and annealing the nature of dislocation distribution changes. With proper modeling it is possible to get both a narrow bracket for dislocation density and considerable information on the dislocation arrangement. In this work an attempt has been made to explain the size dependent phase transformation observed in nanocrystalline powders of TiO_2. Dislocation model proposed by Williamson and Smallman has been used to explain the transformation.[97]

Recent studies on nanopowder Al_2O_3: Crystallites in nanometer dimensions have become highly important and are widely investigated, which is also the case in the alumina (Al_2O_3) system of compounds.[98,99] The large surface to volume ratio in these materials affects the physical and chemical properties. For possible applications stability of specific structural phases of alumina under high pressure and at high temperatures is of great interest.[100-103] Nanocrystalline γ-Al_2O_3 produced by high-pressure compaction has revealed very interesting properties; viz, that it plays an important role in improving the performance of composite or compacted materials.[3] The addition of nanophase alumina into conventional coarse-grained alumina may enhance the elastic modulus and thermal shock resistance.[102]

Zhao et al studied the high-pressure behavior of nanophase γ-Al_2O_3 and α-Al_2O_3 using synchrotron X-ray diffractometric technique.[104] It has been suggested that if the grain-size of alumina is below a critical value of several nanometers, a substantial change may be expected in the isothermal bulk modulus compared with that of bulk value. Kruger observed that the bulk modulus of nanophase γ-Al_2O_3 is independent of the crystallite size in the range 21-67 nm.[105] Mechanical properties of solids, are, in most cases, structure sensitive, so an influence of size effects on the behavior of lattice defects in crystal ought to change drastically their physio mechanical characteristics. One of the most important crystal defects determining mechanical properties is lattice dislocation. Gryaznov et al have shown that if the nano-crystallite size becomes less than the characteristic length Λ ($\sim Gb/\sigma_p^2 \sim 10 – 100$ nm, where G is the Shear Modulus, b is the Burger's vector and σ_p is friction stress), substantial dislocation redistribution in the nanocrystals may occur and may drastically change dislocation density.[40,42] This effect can occur even for homogeneous nanocrystals having mobile boundary structures (slipping boundaries).

Keeping in view of the limitations in measuring directly the strength properties of nanodimensional solids in general, present study aims to understand the nature of dislocation distributions and their interactions in nano powder of Al_2O_3 prepared by CF-CVC technique.[35] Using the existing relation between the elastic constants and dislocation density developed by Williamson and Smallman attempts have been made to infer about the values of the elastic constants in nano Al_2O_3 powder.[97]

Recent studies on nanophase SiO_2: Silica has been widely studied because of its importance to both physics and materials science and also because it has relatively simple crystal structures but a rich phase behavior.[106] Stability and the mechanical properties of nanocrystalline and amorphous SiO_2 at high temperatures have become highly important and are extensively investigated for the comparison with silica glass.[107-113] A comparison is also made with the results from chemical analysis. The large surface to volume ratio of these nanostructured materials affects the physical and chemical properties. Recently, Wolf et al reported thermodynamic properties of nanocrystalline materials and glasses, implying that the excess specific heat depends on the grain size.[114] Experimental measurements of heat capacity at constant pressure C_p indicate that C_p values of nanostructured materials are frequently higher that those for the coarse–grained materials.[115-117] Glass transition temperature (T_g) for the two same grain sizes with different specific surface of nano SiO_2 sample and one coarse grained amorphous SiO_2 sample has been determined at higher temperatures.[118] It is possible to control the crystallinity by proper selection of annealing temperature.[82] The kinetics of these phase transitions can be extremely sluggish, and there are several other metastable crystalline phases of lower symmetry derived from appropriate selection of annealing temperature. David A. Keen et al give the detailed quantitative analysis of the relationship between the structures of the amorphous and crystalline silica phases obtained from neutron total scattering measurements.[119] These measurements give information about both long-range crystallographic order and short- range atomic arrangements. In the high temperature crystalline phases, the structure over short length scales may differ significantly from that corresponding to the 'average' structure given by the long-range order. The observed surface features are generated due to a change in crystallographic order where the defects exist. Petra Feichtinger et al studied the misfit dislocation interaction characteristics of silica.[120] A misfit dislocation generates a strain field around its path and thus reduces the unstrained channel on top of the interface, an orthogonal misfit segment may encounter resistance as it glides across the pre-existing misfit segment. Individual dislocations have also been observed during subsequent high temperature anneal steps. They also studied the differences in interaction behavior during subsequent annealing cycles. Grain growth and also phase transition in nanophase SiO_2 is a topic of interest because of the various polymorphic forms of SiO_2.[83] In this work attempt has been made to explain this physical basis of growth of nanophase SiO_2.

Microstructure from X-ray Diffraction Analysis: Diffraction peaks broaden either when the crystallites become small or when the crystals contain lattice defects. The two effects usually occur concomitantly. They can be separated on the basis of the different order dependence of broadening. Two classical methods have evolved during the last five decades: the Williamson-Hall and the Warren-Averbach procedures.[163-165] The first is based on the full width at half maximum (FWHM) and the integral breadths while the second on the Fourier coefficients of the profiles. Both methods provide apparent size parameters of crystallites or coherently diffracting domains and values of mean square strain. The evolutions become, however, complicated if either the crystallite shape or strain are anisotropic.[166,167] The mean square strain is most often attempted to be given as a single valued quantity.[164,165,168] A vast amount of experimental work has shown, however, that the mean square strain ($\overline{S}^{2}{}_{L, g}$) is almost never constant, neither as a function of L or as g, where L and g are the Fourier length and the diffraction vector respectively.[164,165,169-178] The g dependence is further complicated by strain anisotropy, which means that neither the breadth nor the Fourier coefficients of the diffraction profiles are monotonous functions of the diffraction angle or g.[167,174-176,179-181] Peak profile analysis can only be successful if the strain effect is separated correctly. Two different models have been developed so far for strain anisotropy: (i) a phenomenological model based on the mean square strain of dislocated crystals.[170,172,183] The dislocation model of ($\overline{S}^{2}{}_{L,g}$) takes into account that the contribution of a dislocation to strain broadening of a diffraction profile depends on the relative orientations of dislocation line and the Burgers vectors of the dislocations and the diffraction vector. This has the similarity as the contrast effect of dislocations in electron microscopy. Anisotropic contrast factors, C, which can be calculated numerically on the basis of the crystallography of dislocations and the elastic constants of the crystals.[172,175,176,184-186] By appropriate determination of the type of dislocations and the Burgers vectors present in the crystal, the average contrast factors, <C>, for the different Bragg reflections can be determined. Using the average contrast factors in the modified Williamson-Hall plot and in the modified Warren-Averbach procedure, the different averages of crystallite sizes, the density and the effective outer cut off radius of dislocations can be obtained.[174,185] On the other hand, strain anisotropy enables the determination of the Burgers vector population, the type of dislocations in terms of edge or screw dislocations and, especially in more complicated crystal systems like hexagonal crystals, active slip systems or Burgers vectors.[176,187,188]

It can be shown that, once the strain contribution has been separated, diffraction peak profiles depend on the shape, the mean size and the size-distributions of crystallites or coherently diffracting domains.[189-192] If the shape of the crystallites can be assumed to be uniform, the area and the volume-weighted mean crystallite sizes can be determined from the Fourier coefficients and the integral breadths of the X-ray diffraction profiles.[187,188,192-195] These two mean sizes of crystallites can be used for the determination of a crystallite size distribution function. There is a large amount of experimental evidence that the crystallite size distribution is usually log-normal.[24,193,194] Langford and coworkers have elaborated a whole powder pattern fitting procedure to determine the crystallite size distribution in absence of strain.[192]

Rietveld refinement is a technique by which a crystal structure model can be refined from an experimental powder diffraction pattern using the least squares.[196] The modified Warren-Averbach and modified Williamson-Hall analysis have been used in the past few years both in individual profile analysis as well as whole pattern fitting algorithms by Rieltveld method.[174,197,187, 198]

Due to several the presence of several polymorphic phases in the nano crystalline ceramic powders selected for the present studies (also the different phases present in multilayer metal thin films), most of the X-ray diffraction profiles of individual phase in the X-ray diffraction pattern are completely or partially overlapped. As a result, without a reliable profile fitting method it is almost impossible to extract the information regarding FWHM, integrated intensity, Gaussianity etc., of individual profile by any conventional X-ray method for particle size and strain analyses by the Scherrer formula, integral breadth, Warren-Averbach's Fourier method. Furthermore, the X-ray line-broadening due to small crystallite size and rms strain, can be modeled by Lorentzian and Gaussian type profile fitting functions, respectively. The pseudo-Voigt (pV) profile is a combination of these two functions. A crystal structural model for polycrystalline material based on these considerations namely, the Rietveld method would be the best for microstructure characterization as well as for quantitative estimations of these types of multiphase materials. The advantages of this method are many folds: (i) it does not require a pure standard for quantitative analysis, (ii) completely as well as partially overlapped reflections can be analyzed with sufficient accuracy; (iii) particle size and strain analyses are based on whole profile fitting methodology; (iv) structural parameters can be refined by this method and so on. To overcome difficulties and limitations of other methods of microstructure analysis and considering all the benefits of the whole profile fitting methodology, Rietveld's powder structure refinement procedure based on pV profile fitting function has been adopted in the present course of studies.[199]

AIMS AND OBJECTIVES

In nanocrystalline materials structure-modulated properties are exploited for possible technological applications; however, much remains to be understood as regards to the interplay between the process parameters and the microstructural characteristics of these materials. It is worthwhile to mention a few examples. In case of polycrystalline materials, the yield strength (or hardness) increases with decreasing grain size and is described by Hall-Petch relationship connecting grain size and yield strength or hardness. Accordingly, nanocrystalline materials are expected to show much higher yield strength than the coarse-grained materials of same composition. In some metallic nanocrystals very high level of yield strength and fracture stress is observed. On the other hand, nanophase ceramics are more ductile than conventional ceramics. Recently there is an active debate to modify the Hall-Petch relation to explain the strength properties of nanograined materials. Attempts are being made to explain the observed experimental results in terms of dislocation movements and their arrangements. Consolidation of the fine powders and the thermal stability of the nanometer-sized grains is another concern of materials scientists. It has been realized that the interfaces for nanophase materials are softer than the bulk crystal, and the interaction of individual defects with the interfaces and junctions of interfaces should be considered as the main event, which is responsible for the mechanical properties of the nanoscale materials. It is gratifying to note that optimization of process parameters to consolidate these materials to full density has just begun and models based on cooperative effects of an ensemble of interacting defects and interfaces are being developed. Although the mechanisms, till date, are not clear, the grain growth appears to be minimal and this augurs well for future of nanocrystalline materials. The physical basis of enhanced diffusivity observed in these materials is the other area, which need to be addressed as the process of diffusion is exploited to produce non-conventional alloy phases.

Conventional physical models for crystal plasticity and traditional approaches of solid mechanics need to be revised and modified to include size effects due to the presence of a large density of grain and phase boundaries in these materials. From physical point of view the influence of boundaries and interfaces is twofold. Interfaces and junctions present the obstacles to deformation process and contribute to the strengthening of the material. On the other hand, plastic deformation in nanophase materials takes place mainly at interfaces, which are softer than the bulk crystal. Therefore, it is clear that the interaction of individual defects with interfaces and junctions of interfaces should be considered as the main event, which is responsible for the mechanical properties of nano scaled materials. One of the most important crystal defects determining the mechanical properties are lattice dislocations. Interactions of dislocations with interfaces in nanocrystalline materials must be investigated in order to explain the strength properties. However, when the crystallite sizes are small lattice dislocations tend to leave the crystals and dislocation behavior is much more complicated. Recent years have seen attempts to model the dislocation interactions in nanocrystalline solids both theoretically and experimentally.[40,41,42,47] In the present dissertation attempt has been made to reinvestigate the existing model, developed by Williamson and Smallman, on dislocation interactions in polycrystalline materials for its possible application in nanocrystalline materials.[97]

Owing to the ultrafine scale of these materials' traditional experimental tools like X-ray and Electron diffraction and Electron microscopy are both necessary and useful to understand the structure of nanocrystalline materials. X-ray line profile technique of analysis is an effective means to understand the lattice defects in polycrystalline materials and have been used for last few decades.[168,196] With the advances made in the powder diffraction data analysis using Rietveld Refinement routine, lattice defect parameters are determined with precision.[199]

Phase stability and strength properties of nanomaterials are studied using the conventional analytical techniques like X-ray and electron diffractions, electron microscopy and X-ray photoelectron spectroscopy. Two types of materials have been selected ceramic nanopowders and metal/metal multilayers. Homogeneous nanocrystalline powders of TiO_2, Al_2O_3 and SiO_2 are selected for their size dependent phase stability and strength properties. These powders in nanoform now a day find wide range of applications. The oxides provide an opportunity to extend our knowledge of grain size dependent phenomena to newer dimension while multilayer systems give an opportunity to study the diffusion-controlled interface microstructure. The findings are important to explain the consolidation of fine powders and their thermal stability in terms of dislocation arrangements.

Nanotechnology more descriptively known as molecular manufacturing, involves the design, modeling, fabrication and manipulation of materials and devices at the atomic scale. Alumina has been used as a biomaterial implants due to its excellent biocompatibility and bioinert nature. Micro alumina is used for orthopedic and dental implants, and has the ability to be polished to a high surface finish and high hardness. It has been utilized in wear bearing environments such as the total hip arthroplasties (THA) as the femoral head generating reductions in wear particles from ultrahigh molecular weight polyethylene.[200] Total hip replacement (THR) is one of the most successful applications of biomaterials in the short term. However in the long term (>15 years) the current biomaterials, particularly polyethylene, fail because of a concurrent mechanical and biological process wear debris induced osteolysis, which leads to implant failure and to revision surgery.[201,202] Most importantly, to date, failure of conventional orthopedic and dental implant materials is often due to insufficient bonding to bone.[203-205]

CONCLUSION

Stability of the nanocrystalline materials synthesized by various processes is important for their possible technological applications. In order to obtain consolidated physical properties, these materials are treated under different environmental conditions. Physical processes of importance are growth and phase transitions, which are controlled by diffusion of atomic species through the grain boundaries of these tiny crystallites. It may also be stated that the microstructure of grain boundary or the interfaces plays important role in controlling the growth. Primary aim of the present investigation has been to undertake systematic studies in these directions. Two different types of materials have been selected. Nanocrystalline ceramic powders are studied for their growth. Growth, phase transition and diffusion dependent interface microstructure of some nanocrystalline materials in powder and also in thin film forms have been studied (1, 2, 3). Conventional method of X-ray diffraction studies of the lattice defects are done to explain the growth and phase transition in ceramic nanopowders. Williamson and Smallman developed a model to estimate the dislocation densities present in polycrystalline materials from the measured values of two important lattice defect parameters like crystallite size and rms strain. Following the changes in these parameters with annealing, it has been possible to infer about the nature of dislocation interactions and their arrangements in polycrystalline materials. Moreover, relation connecting dislocation densities and rms strain has a constant of proportionality, which depends on the elastic constants of the materials. Since X-ray diffraction pattern recorded from powder specimens, give information about the coherently diffracting domain only, such studies in nanodimensional powders is of importance as the information obtained will be limited to the crystalline fraction only. It has thus been felt necessary to reinvestigate the model for its possible application to nanocrystalline powder to explain the stability and strength properties. Based on the dislocation model, growth and phase transitions in nano powders of TiO_2 and Al_2O_3 have been explained. In nano powder TiO_2 phase transition (anatase to rutile) has been explained. It has been shown that polygonisation of dislocations takes place in rutile crystallites. Lattice distortion and high values of dislocation density at the grain boundary with marginal increase in crystallite size appear to cause structural transformation of anatase to rutile phase. Prior to transformation the anatase phase is found to prefer a random orientation of its crystallographic planes on the grain surface, whereas rutile phase has been seen to grow along plane. In the studies with nanocrystalline powder of Al_2O_3 it has been experimentally demonstrated that the nanopowder particles are not agglomerated and are made of single crystalline particles surrounded by highly strained distorted semicrystalline region. Grain size increases with heating the powder in ambient conditions. Increase in crystallite size has been attributed due to dislocation interaction similar to polygonization. The ratio of the elastic constants for both the oxides has been estimated. These constants are found to be close to their bulk values. However, in order that the estimated values of these constants correspond to the bulk values, a change in the ratio (ln r/r_o), a parameter term in the original expression derived by Williamson and Smallman has been made. The validity of such assumption needs further modeling. It has been shown that the phase transition in nanocrystalline powder of SiO_2 could not be explained by the above model. This has been attributed due to the amorphous nature of the nanopowder. On annealing at higher temperatures amorphous phase gradually transforms to small crystallites of α-crystobalite. The tiny crystallites subsequently form small domains in the structural form of β-crystobalite.

The above studies on ceramic powders have experimentally demonstrated that the metastable state of the interface microstructure gives rise to the growth and phase transition of nanocrystalline powders. In order to minimize such effect attempts need to be made to develop techniques to stabilize the interface microstructure. One of the methods could be low temperature annealing. However, recent trend in this direction is incorporation of an intervening medium, which restricts grain boundary interactions to a minimum. Temperature dependent growth behavior has been reported in the present work, however, influence of pressure on growth and phase transition need to be studied to further substantiate the above observations. Work in this direction is in progress.

Nano phase materials are new formulations of materials that are composed of grains of the same atoms but with fewer (less than tens of thousands) and smaller (less than 100nm) in diameter atoms than in conventional forms (which contains several billion atoms and have grain sizes of micrometers to millimeters in diameter). Moreover, Nano phase ceramics can be synthesized so they possess similar grain size, geometry and micro architecture as that of healthy, physiological bone. In this way Nano ceramic alumina is more effective than micro alumina for orthopedic application.

REFERENCES

1. H. Gleiter, Progr. Mater. Sci., 1989; 33: 223.
2. R.W. Siegel, Materr. Sci. Eng., 1993; A166: 189.
3. C.Suryanarayana, Int. Mater. Rev., 1995; 40: 2.
4. H. Gleiter, Acta. Mater., 2000; 7: 48.
5. H. Gleiter, Nanostructure Mater., 1995; 6: 3.
6. A. Inoue, Nanostructure Mater., 1995; 6: 53.
7. I.D. Morokhov, L.I. Trusov and S.P. Chizhik, Highly Dispersed Metallic Media, Atomizdat, Moscow, (1977).
8. R. Birringer and H. Gleiter, Encyclopedia of Materials Science and Engineering (edited by R.W. Cahn, W.A. Owen and M.B. Bever), vol 1, Pergamon Press, Oxford (1988), p339.
9. R.W. Siegel; Mater. Sci. and Tech., vol15, p583, (ed R.W. Cahn), Weinheim, Germany, VCH, (1991).
10. R. Birringer, H. Gleiter, H.P. Klein, and P. Marquart, Phys. Lett., 1984; 102 A: 365.
11. C.C. Koch, Nanostructure Mater., 1993; 2: 109.

12. B.H. Kear and L.E. McCandlish., Nanostructure Mater, 1993; 3: 19.
13. H. Chang, C.J. Alstetter, and R.S. Averback., Jl. Mater. Res., 1992; 7: 2962.
14. R.L. Bickerdike, D. Clark, J.N. Easterbrook, G. Hughes, W.N. Mair, P.G. Patridge, and H.C. Ranson, Int. J. Rapid Solidif., 1984-1985; 1: 305.
15. W. Chang, G. Skandan, S.C. Danforth, and B.H. Kear, Nanostructure Mater., 1994; 4: 507.
16. G. Palumbo, S.J. Thorpe, and K.T. Aust, Scr. Metall. Mater., 1990; 24: 1347.
17. D.S. Lashmore and M.P. Dariel, Encyclopedia of Materials science and engineering, (ed.R.W. Cahn), Suppl. vol 1, Oxford, Pergamon, 1988; 136-140.
18. M.J. Mayo, Mater. Design, 1993; 14: 323.
19. C.H. Chou and J. Phillips, Jl. Mater. Res., 1992; 7: 2107.
20. P. Taylor, S.A. Pirzada, D.L. Marshall, and S.M. Donahue, Plasma synthesis and processing of materials, (ed. K. Upadhya), Warrendale, PA, TMS., 1993; 215-225.
21. M.L. Mandich, V.E. Bondybey, and W.D. Reents, Jr., Jl. Chem. Phys., 1987; 86: 4245.
22. G.W. Kriechbaum and P. Kleinschmitt, Adv. Mater., 1989; 1: 330.
23. V. Haas, H. Gleiter, and R. Birringer, Scr. Metall. Mater., 1993; 28: 721.
24. D.J. Li, B.Z. Ding, B. Yao, Z.Q. Hu, A.M. Wang, S.L. Li, and W.D. Wei, Nanostructured Mater., 1994; 4: 323.
25. U. Köster, U. Schünemann, M. Blak-Bewersdorff, S. Brauer., M. Sutton, and G.B. Stephenson, Mater. Sci. Eng., 1991; A133: 611.
26. U. Köster, H.Alves, and J. Meinhardt: in Proc. of Int. Conf. on Advanced materials (ICAP-93), (ed. S. Somiya et al), Amsterdam, Elsevier Scientufic Publ. (1994).
27. K. Lu, R. Lück, and B. Predel, Acta Metall. Mater., 1994; 42: 2303.
28. R.W. Siegel, MRS Bull., 1990; 15: 10.
29. J.R. Thompson and C. Politis, Euro. Phys. Lett., 1987; 3: 199.
30. P.H. Shingu, B. Huans, S.R. Nishitani and S. Nasu, Proc. JIMIS-5: Non-Equilibrium Solid Phases of Metals and Alloys, JIM Trans. (Suppl.), 1988; 29: 3.
31. C.C. Koch: ‘Processing of metals and alloys’, Materials science and technology, vol.15, (ed. R.W. Cahn.), 193, Weinheim, Germany, VCH, (1991).
32. J.S. Benjamin, Sci. Am., 1976; 234, 5: 40.
33. J.J. Stiglich, T.S. Sudarshan, and R.J. Dowding, ‘Synthesis and consolidation of nanoparticles’, Army Research Laboratory Report No. ARL-CR-119, July 1994.
34. Alan F. Jankowski, Nanostructured Mater., 1995; 6: 179.

35. A. Singhal, G. Skandan, A. Wang, N. Glumac, B.H. Kear and R.D. Hunt, Nanostructure Material, 1999; 11(4): 545.
36. G. Skandan, Y. Chen, N. Glumac, B.H. Kear, Nanostructured Mater., 1999; 11(2): 149.
37. T. Mutschele and R. Kirchheim, Scr. Metall., 1987; 21: 1101.
38. V.G. Gryaznov and L.I. Trusov, Prog. Mater. Sci., 1993; 37: 289.
39. E.A. Fitzgerald, Mater. Sci. Reports, 1991; 7: 87.
40. V.G. Gryaznov, I.A. Polonsky, A.E. Romanov and L.I. Trusov, Phy. Rev. 1991; B, 44(1): 42.
41. A.E. Romanov, Nanostructured Mater., 1995; 6: 125.
42. V.G. Gryaznov, A.M. Kaprelov and A.E. Romanov, Scripta Met., 1989; 23: 1443.
43. E.O. Hall, Proc. Phys. Soc. (Lond.), 1951; B64: 747.
44. N.J. Petch, J. Iron Steel Inst., 1953; 174: 25.
45. V.G. Gryaznov, V.A. Solovev and L.I. Trusov, Scripta Met., 1990; 24: 1529.
46. T.G. Nieh and J. Wadsworth, Scripta Met., 1991; 25: 955.
47. C.S. Pande, R.A. Masumura and R.W. Armstrong, Nanostructured Mater., 1993; 2: 323.
48. S. Li, L. Sun and Z. Wang, Nanostructured Mater., 1993; 2: 653.
49. R.O. Scattergood and C.C. Koch, Scr. Metall. Mater., 1992; 27: 1195.
50. V.G. Gryaznov, M. Yu Gutkin, A.E. Romanov and L.I. Trusov, Jl. Mater. Sci., 1993; 28: 4359.
51. J. Lian and B. Baudelet, Nanostructured Mater., 1993; 2: 415.
52. G. Palumbo, U. Erb, and K.T. Aust, Scr. Metall. Mater., 1990; 24: 2347.
53. G.E. Fougere, J.R. Weertman, R.W. Siegel, and S. Kim, Scr. Metall. Mater., 1992; 26: 1879.
54. G.E. Fougere, J.R. Weertman, R.W. Siegel, and S. Kim, Nanostructured Mater., 1993; 3: 379.
55. X.D. Liu, J.T. Wang and B.Z. Ding, Scr. Metall. Mater., 1993; 28: 59.
56. K. Lu and M.L. Sui, Scr. Metall. Mater., 1993; 28: 1465.
57. J. Horvath, Diffus. Defect Data: Defect Diffus. Forum, 1989; 66-69: 207.
58. J. Horvath, R. Birringer and H. Gleiter, Solid State Commun., 1987; 62: 319.
59. R. Birringer, H. Hahn, H.J. Höfler, J. Karch, and H. Gleitier, Diffus. Defect Data: Defect Diffus. Forum, 1988; 59: 17.
60. H. Hahn, H.J. Höfler and R.S. Averback, Diffus. Defect Data: Defect Diffus. Forum, 1989; 66-69: 549.
61. S. Schumacher, R. Birringer, R. Strauss and H. Gleiter Acta Metalll., 1989; 37: 2485.

62. S. Schumacher, R. Birringer, R. Strauss, J. Appl. Phys., 1993; 74: 3822.
63. H.J. Höfler, R.S. Averback, H. Hahn, and H. Gleiter, Philos. Mag. Lett., 1993; 68: 99. J. Appl. Phys., 1993; 74: 3822.
64. R.S. Averback, H. Hahn, H.J. Höfler, J.L. Logas, and T.C. Chen, ‘Interfaces between polymers, metals and ceramics’ (ed. B.M. DeKoven et al), Mater. Res. Soc. Symp. PROC., 1989; 153: 3.
65. P.H. Shingu, B. Huang, S.R. Nishitani, and S. Nasu, Suppl. Trans. Japan Inst. Met, 1988; 29: 3.
66. U. Herr, J. Jing, U. Gonser, and H. Gleiter, Solid State Commun., 1990; 76: 197.
67. C. Suryanarayana and F.H. Froes, J. Mater. Res., 1990; 5: 1880.
68. J.Y. Huang, A.Q. He, and Y.K. Wu, Nanostructured. Mater., 1993; 4: 1.
69. R.W. Siegel and H. Hahn, in ‘Current trends in the physics of materials’, (ed. M. Youssouff), p.403-419, Singapore, World Science Publ., (1987).
70. R.W. Siegel, S. Ramasamy, H. Hahn, Z. Li, T. Lu and R. Gronsky, J. Mater. Res., 1988; 3: 1367.
71. H. Hahn, J. Logas, and R.S. Averback, J. Mater. Res., 1990; 5: 609.
72. M.J. Mayo, R.W. Siegel, A. Narayanasamy, and W.D. Nix, J. Mater. Res., 1990; 5: 1073.
73. M.J. Mayo, D.C. Hague, D.J. Chen, Mater. Sci. Eng., 1993; A 166: 145.
74. J.A. Eastman, J. Appl. Phys., 1993; 75(2): 770.
75. H. Hahn, J. Logas, H.F. Ho fler, Th. Bier, R.S. Averback, Mat. Res. Symp. Proc., 1989; 132: 35.
76. H. Hahn, R.S. Averback, J. Am. Cer. Soc., 1991; 74(11): 2918.
77. J. Moser, M. Gratzel, R. Gallay, Helv, Chem Acta., 1987; 70: 1596.
78. D.S. Bae, K.S. Han, S.H. Choi, Solid State Ionics, 1998; 109: 239.
79. R. H. French, J. Am. Ceram. Soc., 1990; 73: 477.
80. B. Holm, R. Ahuja, Y. Yourdshahyan, B. Johansson, and B. I. Lundqvist, Phys. Rep., 1999; 59: 12777.
81. F. H. Streitz and J. W. Mintmire, Phys. Rev. B, 1999; 60: 773.
82. J. Dutta, I.M. Reaney, C. Bossel, R. Houriet and H. Hofmann, Nanostructured Mater., 1995; 6: 493.
83. Th Demuth, Y. Jeanvoine, J. Hafner and J.G. Ángyán, J. Phys.: Condens. Matter, 1999; 11: 3833.
84. K.I. Hadjiivanov, and D.G. Klissurski, Chem. Soc. Rev., 1996; 25: 61.
85. A.L. Linsebigler, G. Lu, and J.T. Yates, Chem. Rev., 1995; 95: 735.

86. B.O’ Regan and M.Gr ä tzel, Nature (London), 1991; 353: 737.
87. A. Hagfelt and Gr ä tzel, Chem. Rev., 1995; 95: 49.
88. R.W. Siegel, S. Ramaswamy, H. Hahn, Z. Li, T. Lu and R. Gronsky, J. Mater. Res., 1988; 3: 1367.
89. H. Hahn, J. Logas and R.S. Averback, J. Mater. Res., 1990; 5: 609.
90. H.J. Freund, Faraday Discuss., 1999; 114: 1.
91. G.S. Heranan, M.R. Sievers and Y. Gao, Phys. Rev. Lett., 2000; 84: 3354.
92. R. Hengerer, P. Bolliger, M. Erbudak and M. Gr ä tzel, Surf. Sci., 2000; 400: 162.
93. M. Lazzeri, A. Vittadini and A. Selloni, Phys. Rev., 2001; (B) 63: 155409.
94. Handbook of Chemistry and Physics, edited by R.C. Weast (CRC, Cleveland, 1986), B-172.
95. H. Zhang and J.F. Banfield, J. Mater. Chem., 1998; 8: 2073.
96. J.R. Weertman, Mater. Sci and Engg., 1993; A166: 161.
97. T. Christman, Scri. Metall. Mater., 1993; 28: 1495.
98. G.K. Williamson and R.E. Smallman, Phil. Mag., 1956; B, 1: 34.
99. R.W. Cahn, Nature (London), 1990; 348: 389.
100. J. Karch, R. Birringer, and H. Gleiter, Nature (London), 1987; 330: 556.
101. T.M.H. Costa, M.R. Gallas, E.V. Benvenutti, and J.A.H. du. Jornada, J. Phys. Chem., 1999; B103: 4278.
102. S.N. Koruderlieva and B.R. Peatchkova, J. Mater. Sci. Lett., 1997; 16: 1662.
103. G.H. Li, Z.X. Hu, and L.D. Zhang, J. Mater. Sci. Lett., 1998; 17: 1185.
104. R.J. Hellming and N. Ferkel, Phys. Status Solidi, 1999; A175: 579.
105. J. Zhao, G.R. Hearne, M. Maaza, F. Lahu-Lacour, M.J. Witcomb, T.L Bihan, and M. Mezouar, J. of Appl. Phys., 2001; 90(7): 3280.
106. M. Kruger, B. Chen, D. Penwell, L. R. Benedetti, R. Jeanloz, Phy. Rev., 2002; B. 66: 144101.
107. P.J. Heaney, Rev. Mineral, 1994; 29: 1.
108. H. Zhang and C. G. Pantano, Mater. Res. Soc. Symp. Proc., 1992; 271: 783.
109. F. Babonneau, L. Bois, C. Y. Yang, and L. Interrante, Chem. Mater., 1994; 6: 51.
110. L. Bois, J. Maquet, F. Babonneau, and D. Balhoul, Chem. Mater., 1995; 7: 975.
111. G. D. Soraru`, Q. Liu, L. V. Interrante, and T. Apple, Chem. Mater., 1998; 10: 4047.
112. G. M. Renlund, S. Prochazka, and R. H. Doremus, J. Mater. Res., 1991; 6: 2723.
113. M. Hammond, E. Breval, and C. G. Pantano, Ceram. Eng. Sci. Proc., 1993; 14: 947.

114. G. D. Soraru`, E. Dallapiccola, and G. D'Andrea, J. Am. Ceram. Soc., 1996; 79: 2074.
115. D. Wolf, J. Wang, S.R. Phillpot, H. Gleiter, Phys. Lett., 1995; A, 205: 274.
116. J. Rupp, R. Birringer, Phys. Rev., 1987; B36: 7888.
117. E. Hellstern, H.J. Fecht, Z. Fu, W.L. Johnson, J. Appl. Phys., 1989; 65: 305.
118. N.X. Sun, K. Lu, Phys. Rev., 1996; B, 54: 6058.
119. L. Wang, Z. Tan, S. Meng, A. Druzhinina, R.A. Varushchenko, G. Li, J. Non. Cryst. Solids., 2001; 296: 139.
120. David A Keen and Martin T. Dove, J. Phys.: Condens. Matter, 1999; 11: 9263.
121. Petra Feichtinger, Mark S. Goorsky, Final Report 1998-99 for MICRO Project 98-047, Industrial Sponsor: Wacker Siltronic Corp., Portland.
122. A.F. Jankowski, Nanostructured Materials, 1995; 6: 179.
123. S. Hashimoto, Y. Ochiai and K. Aso, J. Appl. Phys., 1989; 66: 4909.
124. E. Devlin, J. Magn. Mater, 1993; 120: 236.
125. H. He, C. Lee, F. Lamleas, W. Vavra, D. Barlett and R. Clarke, J. Appl. Phys., 1990; 67: 5412.
126. L. Wu, N. Nakayama, B. Engel, T. Shinjo and C. Falco. Jpn. J. Appl. Phys., 1993; 32: 4726.
127. H. Holleck, C. Kuhl and H. Schulz, J. Vac. Sci. Technol, 1985; A, 3: 2345.
128. J. Ferreira, H. Seiroo, F.B. Ferrandes, R. Martins, E. Fortunato, A.P. Marvo, J.L. Martins, App. Surf. Sci., 2000; 168: 292.
129. C. DebiemmeChouvy, F. Ammeloot, E.M.M. Sutter, App. Surf. Sci., 2001; 174: 55.
130. V.K. Kaushik, App. Surf. Sci., 1991; 51: 27.
131. J.S. Kwak, H.K. Baik, J.H. Kim and S.M. Lee, App. Phys. Lett., 1998; 72: 22.
132. K.M. Chow, W.Y. Ng and L.K. Yeung, Surf. and Coatings Tech., 1998; 105: 1-2, 56.
133. S. Baunack, W. Bruckner, and J. Thomas, App. Surf. Sci., 1999; 144: 1.
134. Y. Yu, X. Wang, X. Hu, Appl. Surf. Sci., 2001; 172: 3.
135. T. Laurila, K. Zeng, J.K. Kivilathi, Thin Solid Films, 2000; 373: 1-2.
136. K.N. Tu, Acta Metallurgica, 1973; 21, April, 347.
137. Y.C. Chan, Alex C.K. So, J.K.L. Lai, Mate. Sci. Engg., 1998; B55: 5.
138. K.N. Tu, R.D. Thompson, Acta Metall, 1982; 30: 947.
139. Z. Mei, A.J. Sunwoo, J.W. Morris Jr., Metall. Trans, March 1992; A 23A: 857.
140. Y.G. Lee, J.G. Duh, Mate. Char., 1999; 42: 143.
141. K.H. Prakash, T. Sritharan, Acta. Mater., 2001; 49: 2481.
142. P.L. Tu, Y.C. Chan, J.K.L. Lai, IEEE Trans. CPMT-B Feb.1997; 20(1): 87.

143. Y. Wu, J. Elect. Mater., 1993; 22(7): 769.
144. R.E. Pratt, E.I. Stromswold, D.J. Quesnel, J. Elect. Mater., 1994; 23(4): 375. H.K. Kim, K.N. Tu, Phys. Rev., 1996; B53: 23.
145. J.K. Shang, dapping Yao, Trans. ASME-J. Elect. Packag, Sept. 1996; 118: 170.
146. P.J. Kay, C.A. Mackay, Trans. Inst. Metal Finishing, 1976; 54: 68.
147. Alex C.K. So, Y.C. Chan, IEEE Trans. CPMT-B., 1996; 19(3): 661.
148. A.J. Sunwoo, J.W. Morris Jr., G.K. Lucey Jr., Metall. Trans, 1992; A 23A: 1323.
149. W.K. Warburton and D. Turnbull, in Diffusion in Solids: Recent Developments, edts. A.S. Nowick and J.J. Burton, (Academic), Ny, 1974, Chap. 4.
150. B.F. Dyson, T. Anthony and D. Turnbull, J. Appl. Phy., 1966; 37: 2370.
151. B.F. Dyson, T.R. Anthony and D. Turnbull, J. Appl. Phys., 1967; 38: 3408.
152. C.K. Hu, H.B. Huttington, G.R. Gruzalski, Physical Rev, 15 July, 1983; 28(2): 579.
153. K.L. Lee, C.K. Hu, K.N. Tu, J. Appl. Phys., 1995; 78(7): 4428.
154. G. Contini, V.Di Castro, N. Motta, A. Sgarlata, Surf.Sc. 1998; L509: 405.
155. Antoni Bukaluk, Vacuum, 1999; 54: 279.
156. A. Bukaluk, Phys. Stat. Sol., 1990; (a)118: 99.
157. P. Barua, V. Srinivas, S. Dhabal, and T.B. Ghosh, Jl. of Mater. Res., Aug 2002; 17: 8.
158. C.J. Jenks and P.A. Thiel, Langmuir, 1998; 14: 1392.
159. J.M. Dubois, Mater Sci. and Engg., 2000; 4: 294.
160. T.A. Lograsso and D.W. Delaney, Jl. of Mater. Res., 1996; 11: 2125.
161. C.J. Jenks and P.A. Thiel, MRS Bulletin, 55, Nov. (1997).
162. S.S. Kang and J.M. Dubois, Jl. of Mater. Res., 1995; 10: 1071.
163. B.I. Wehner and U. Koster, Oxidation of Metals, 2000; 54: 445.
164. G.K. Williamson and W.H. Hall, Acta metal., 1953; 22.
165. B.E. Warren, and B.L. Averbach, J. Appl. Phys., 1960; 21: 595.
166. B.E. Warren, Progr. Metal. Phys., 1959; 8: 147.
167. D. Louër, J.P. Auffredic, J.I. Langford, D. Ciosmark and C.J. Niepca, J. Appl. Cryst., 1983; 16: 183.
168. G. Caglioti, A. Paoletti, F.P. Ricci, Nucl. Instrum., 1958; 3: 223.
169. H.P. Klug and L. Alexander, in X–ray Diffraction procedures for Polycrystalline and Amorphous Materials, 2nd edn., Wiley, New York, (1974).
170. M.A. Krivoglaz, O.V. Martynenko and K.P. Ryaboshapka, Phys. Met.Metall., 1983; 55: 1.

171. M.A. Krivoglz, in “Theory of X ray and Neutron Diffraction in Nonideal Crystals, Springer–Verlag, Berlin Heidelberg New York, (1996).
172. M. Wilkens, Proc. 8th Int. Conf. Strength Met. Alloys (ICSMA), Tempere, Finland, eds. P.O. Kettunen, T.K. Lepistö, M.E. Lehtonen, Pergamon Press, 1998; 47.
173. M. Wilkens, Phys. Stat. Sol.(a) 1970; 2: 359.
174. P. Klimanek and Jr. R. Kuzel, J. Appl. Cryst., 1988; 21: 59.
175. T. Ungár and and A. Borbély, App. Phys. Lett., 1996; 69: 3173.
176. P. Scardi and M. Leoni, J. Appl. Cryst., 1999; 32: 671.
177. R.W. Cheary, E. Dooryhee, P. Lynch, N. Armstrong, S. Dligatch, J. Appl. Cryst., 2000; 33; 1271.
178. F. Székely, I. Groma and J. Lendvi, Mat. Sci. Eng. A, IN THE press.
179. I. Groma, Phys. Rev.B, 1998; 57: 7535.
180. A. LE bail, A. Jouanneaux, J. Appl. Cryst., 1997; 30: 265.
181. R.E. Dinnebier, R.V. Dreele, P.W. Stephens, S. Jelonek, J. Sieler, J. Appl. Cryst., 1999; 32: 761.
182. P.W. Stephens, J. Appl. Cryst., 1999; 32: 281.
183. M. Wilkens, in Fundamental Aspects of Dislocation Theory, ed. J.A. Simmons, R. deWit, R. Bullough, vol.II, Nat Bur. Stand.(US) Spec. Publ.No. 317, Washington, DC, USA, 1970; 1195.
184. Jr. R. Kuzel and P. Klimanek, J. Appl. Cryst., 1989; 22: 299.
185. T. Ungár, I. Dragomir, A. Révész and A. Borbély, J. Appl. Cryst., 1999; 32: 992.
186. T. Ungár and G. Tichy, Phys. Stat. Sol.(a), 1999; 171: 425.
187. T. Ungár, J. Gubicaza, G. Ribarik and A.Borbely, J. Appl. Cryst., 2001; 34: 298.
188. T. Ungár, S. Ott, P.G. Sanders, P.G. Borbely, J.R. Wreetman., Acta Mater., 1998; 10: 3693.
189. B.F. Bertaut, Acta Cryst., 1950; 3: 14.
190. S. Rao, C.R. Houska, Acta Cryst., 1986; A 42: 6.
191. P. Chatterjee and S.P. Sengupta, J. Appl. Cryst., 1999; 32: 1060.
192. J.I. Langford, D. Louër, P. Scardi, J. Appl. Cryst., 2000; 33: 964.
193. J. Gubicza, J. Szépvölgyi, I. Mohai, L. Zsolods and T. Ungár, Materials Science and Engg. A, 2000; 280: 263.
194. C.E. Krill and R. Birringer, Phil. Mag. A, 1998; 77: 621.
195. W.C. Hinds, Aerosol Technology: Properties, Behaviour and Measurement of Airbone Particles, Wiley, New York, (1982).

196. The Rietveld Method, edited by R.A. Young, International Union of Crystallography, Oxford Univ. Press, (1996).
197. T. Ungár, M. Leoni, P. Scardi, J. Appl. Cryst., 1999; 32: 290.
198. P. Chatterjee and S.P. Sengupta, Phil. Mag., 2001; 81(1): 49.
199. L. Lutterotti, P. Scardi, P. Maistrelli, J. Appl. Crystallogr., 1992; 25: 459.
200. A. Rakngarm, Y. Mutoh, (2009) Characterization and fatigue damage of plasma sprayed HAp top coat with Ti and HAp/Ti bond coat layers on commercially pure titanium substrate, J. Mech. Behav. Biomed. Mater., 2: 444–453.
201. F. Pittella, M. Zhang, Y. Lee, H.J. Kim, T. Tockary, K. Osada, T. Ishii, K. Miyata, N. Nishiyama, K. Kataoka. Enhanced endosomal escape of siRNA-incorporating hybrid nanoparticles from calcium phosphate and PEG-block charge-conversional polymer for efficient gene knockdown with negligible cytotoxicity, Biomaterials, 2011; 32: 3106–3114.
202. Ghosh T.B., Dhabal S. and Datta A.K. On crystallite size dependence of phase stability of nano-crystalline TiO_2. Journal Of Applied Physics, 2003; 94(7): 4577-4582.
203. Dhabal S. and Ghosh T.B. Temperature dependent phase stability of nanocrystalline SiO_2. Journal of Nanoscience and Nanotechnology, 2004; 4(8): 1067-1070.
204. Sampa Dhabal. Grain boundary - dislocation interactions in nanocrystalline Al_2O_3. Journal of Material Research, 2007; 22: 4.