CHAPTER 1
INTRODUCTION

1.1 TITANIUM AND TITANIUM ALLOYS

Titanium is a chemical element with the symbol Ti and atomic number 22. It is a lustrous transition metal with a silver color, low density and high strength. It is highly resistant to corrosion in sea water, aqua regia and chlorine. Titanium can be alloyed with iron, aluminium, vanadium, and molybdenum, among other elements, to produce strong, lightweight alloys for aerospace (jet engines, missiles, and spacecraft), military, industrial process (chemicals and petro-chemicals, desalination plants, pulp, and paper), automotive, agri-food, medical prostheses, orthopedic implants, dental and endodontic instruments and files, dental implants, sporting goods, jewelry, mobile phones, and other applications.[2]

A metallic element, titanium is recognized for its high strength-to-weight ratio. It is a strong metal with low density that is quite ductile (especially in an oxygen-free environment), lustrous, and metallic-white in color. The relatively high melting point (more than 1,650 °C or 3,000 °F) makes it useful as a refractory metal. It is paramagnetic and has fairly low electrical and thermal conductivity.

Titanium alloys are generally classified into three main categories: Alpha alloys, which contain neutral alloying elements (such as Sn) and/or alpha stabilizers (such as Al, O) only and are not heat treatable; Alpha + beta alloys, which generally contain a combination of alpha and beta stabilizers and are heat treatable to various degrees; and Beta alloys, which are metastable and stabilizers (such as Mo, V) to completely retain the beta phase upon quenching, and can be solution treated and aged to achieve significant increases in strength.[1]

Ti6Al4V alloy is known as the "workhorse" of the titanium industry because it is by far the most common Ti alloy, accounting for more than 50% of total titanium usage. It is an alpha+beta alloy that is heat treatable to achieve moderate increases in
strength. Ti6Al4V is recommended for use at service temperatures up to approximately 350°C (660°F). Ti6Al4V alloy offers a combination of high strength, light weight, formability and corrosion resistance which have made it a world standard in aerospace applications.[1]

Ti6Al4V alloy is the most popular Titanium α-β Alloy - its total production is about half of all titanium alloys. Aluminum (Al) is added to the alloy as α-phase stabilizer and hardener due to its solution strengthening effect. Vanadium (V) stabilizes ductile β-phase, providing hot workability of the alloy. Titanium α-β Alloys have high tensile strength and fatigue strength, good hot formability and creep resistance up to 570°F - 800°F (300°C - 425°C). Titanium α-β Alloys are used for manufacturing steam turbine blades, gas and chemical pumps, airframes and jet engine parts, pressure vessels, blades and discs of aircraft turbines, aircraft hydraulic tubing, rocket motor cases, cryogenic parts, marine components.[1]

Titanium (Ti) and Ti alloys are attractive for industrial applications because of their low density, high specific strength and stiffness, adequate creep and fatigue strength, good corrosion resistance and adequate fracture toughness [3]. However, the high price of Ti has been a major stumbling block for its wide use in some areas, such as the automotive industry. Powder metallurgy (PM) offers a viable tool to produce near-net-shape components with little machining, thus reducing the manufacturing costs and increasing the material yield, commonly referred to as the “buy-to-fly ratio” in the aerospace sector. The press and sinter processing is a traditional PM method and has been used to make titanium based alloy parts for a wide range of applications.[3]

1.2 COMPOSITE MATERIALS

Composed of two or more distinct phases-matrix phase-holds load and shares a load with it and dispersed phase-stronger than the matrix, called reinforcing phase.
1.2.1 Classification of Composite Materials

Based on matrix material:

(a) Metal Matrix Composites  – Aluminum, magnesium, cobalt and titanium
(b) Ceramic Matrix Composites – Ceramic matrix and other ceramic material
(c) Polymer Matrix Composites – Unsaturated polyester (UP), epoxy (EP)

Based on reinforcing material:

(a) Particulate Composites – Dispersed phase in the form of particles (random or preferred orientation).
(b) Fibrous Composites – Short (discontinuous fibers length < 100 diameter), long (continuous fibers of unidirectional orientation or bidirectional orientation).
(c) Laminate Composites – Several layers with different fiber orientations.

1.2.2 Fabrication Methods of Composites

a) Solid state fabrication of Metal Matrix Composites:

Solid state fabrication of Metal Matrix Composites is the process, in which Metal Matrix Composites are formed as a result of bonding matrix metal and dispersed phase due to mutual diffusion occurring between them in solid states at elevated temperature and under pressure. Low temperature of solid state fabrication depresses undesirable reactions on the boundary between the matrix and dispersed (reinforcing) phases.

Diffusion Bonding is a solid state fabrication method, in which a matrix in form of foils and a dispersed phase in form of long fibers are stacked in a particular order and then pressed at elevated temperature. The finished laminate composite material has a multilayer structure.

Hot Pressing Fabrication of Metal Matrix Composites, in which sintering under a unidirectional pressure applied by a hot press.
Hot Isostatic Pressing Fabrication of Metal Matrix Composites, in which sintering under a pressure applied from multiple directions through a liquid or gaseous medium surrounding the compacted part and at elevated temperature.

Hot Powder Extrusion Fabrication of Metal Matrix Composites, in which sintering under a pressure applied by an extruder at elevated temperature.

b) Liquid state fabrication of Metal Matrix Composites

Liquid state fabrication of Metal Matrix Composites involves incorporation of dispersed phase into a molten matrix metal, followed by its Solidification. In order to provide high level of mechanical properties of the composite, good interfacial bonding (wetting) between the dispersed phase and the liquid matrix should be obtained.

Infiltration is a liquid state method of composite materials fabrication, in which a preformed dispersed phase (ceramic particles, fibers, woven) is soaked in a molten matrix metal, which fills the space between the dispersed phase inclusions.

Gas Pressure Infiltration is a forced infiltration method of liquid phase fabrication of Metal Matrix Composites, using a pressurized gas for applying pressure on the molten metal and forcing it to penetrate into a preformed dispersed phase.

Squeeze Casting Infiltration is a forced infiltration method of liquid phase fabrication of Metal Matrix Composites, using a movable mold part (ram) for applying pressure on the molten metal and forcing it to penetrate into a performed dispersed phase, placed into the lower fixed mold part.

Pressure Die Infiltration is a forced infiltration method of liquid phase fabrication of Metal Matrix Composites, using a Die casting technology, when a preformed dispersed phase (particles, fibers) is placed into a die (mold) which is then filled with a molten metal entering the die through a sprue and penetrating into the preform under the pressure of a movable piston (plunger).

Stir Casting is a liquid state method of composite materials fabrication, in which a dispersed phase (ceramic particles, short fibers) is mixed with a molten
matrix metal by means of mechanical stirring. Stir Casting is the simplest and the most cost effective method of liquid state fabrication.

1.3 METAL MATRIX COMPOSITES (MMCs)

Metal matrix composites (MMCs) have been around for a long time, but have only been recognized as legitimate engineering composite materials in the second half of the twentieth century. From their humble research beginnings, MMCs have gone from "niche" materials to several high performance applications in aerospace, electronic packaging, automotive and recreational products. [4-6]

Metal matrix composites (MMCs) consist of at least two chemically and physically distinct phases, suitably distributed to provide properties not obtainable with either of the individual phases. Generally, there are two phases, e.g., a fibrous or particulate phase, distributed in a metallic matrix. Examples include continuous Al₂O₃ fiber reinforced Al matrix composites used in power transmission lines; Nb-Ti filaments in a copper matrix for superconducting magnets; tungsten carbide (WC)/cobalt (Co) particulate composites used as cutting tool and oil drilling inserts; and SiC particle reinforced Al matrix composites used in aerospace, automotive, and thermal management applications. [4]

With respect to metals, MMCs offer the following advantages:

* Major weight savings due to higher strength-to-weight ratio.
* Exceptional dimensional stability.
* Higher elevated temperature stability (creep resistance).
* Significantly improved cyclic fatigue characteristics.

With respect to Polymer Matrix Composites (PMCs), MMCs offer these distinct advantages:

* Higher strength and stiffness.
* Higher service temperatures.
* Higher electrical conductivity (grounding, space charging).
* Higher thermal conductivity.
* Better transverse properties.
* Improved joining characteristics.
* Radiation survivability (laser, UV, nuclear, etc.).
* Little or no contamination (no out-gassing or moisture absorption problems).

### 1.3.1 Types of MMCs

All metal matrix composites have a metal or a metallic alloy as the matrix. The reinforcement can be metallic or ceramic. In general, there are three kinds of metal matrix composites (MMCs):

(i) Particle reinforced MMCs.
(ii) Short fiber or whisker reinforced MMCs.
(iii) Continuous fiber or sheet reinforced MMCs.

Figure 1.1 shows, schematically, the three major types of metal matrix composites: Continuous fiber reinforced, short fiber or whisker reinforced, particle reinforced and laminated or layered composites. Table 1.1 provides examples of some important reinforcements used in metal matrix composites as well as their aspect ratios (length/diameter) and diameters. [4]

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![Particles](image1.png)

Particles

![Whiskers short Fibers](image2.png)

Whiskers short Fibers

![Continuous Fibers](image3.png)

Continuous Fibers

![Sheet Laminate](image4.png)

Sheet Laminate

Fig. 1.1 Different types of metal matrix composites
Table 1.1 Typical reinforcements used in metal matrix composites

<table>
<thead>
<tr>
<th>Type</th>
<th>Aspect Ratio</th>
<th>Diameter, μm</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle</td>
<td>1-4</td>
<td>1-25</td>
<td>SiC, Al₂O₃, BN, B₄C, WC</td>
</tr>
<tr>
<td>Short fiber or whisker</td>
<td>10-10000</td>
<td>1-5</td>
<td>C, SiC, Al₂O₃, Al₂O₃+SiO₂</td>
</tr>
<tr>
<td>Continuous fiber</td>
<td>&gt;1000</td>
<td>3-150</td>
<td>SiC, Al₂O₃, C, B, W, Nb-Ti, Nb₃Sn</td>
</tr>
</tbody>
</table>

Particle or discontinuously reinforced MMCs (the term discontinuously reinforced MMCs is commonly used to indicate metal matrix composites having reinforcements in the form of short fibers, whiskers, or particles) have assumed special importance for the following reasons:

- Particle reinforced composites are inexpensive than continuous fiber reinforced composites. Cost is an important and essential parameter, particularly in applications where large volumes are required (e.g., automotive applications).

- Conventional metallurgical processing techniques such as casting or powder metallurgy, followed by conventional secondary processing by rolling, forging, and extrusion can be used.

- High temperatures use than the unreinforced metal.

- Enhanced modulus and strength.

- Increased thermal stability.

- Better wear resistance.

- Relatively isotropic properties compared to fiber reinforced composites.

- Within the broad category of discontinuously reinforced composites, metal matrix composites made by liquid metal casting are somewhat cheaper to produce than powder metallurgy composites. There are two types of cast metal matrix composites:

  - Cast composites having impurities as reinforcement.

  - Cast composites in the form of a billet having uniform reinforcement with a wrought alloy matrix. Such composite billets are forged and/or extruded, followed by rolling or other forming operations. [4,6]
1.3.2 Characteristics of MMCs

One of the driving forces for metal matrix composites is, of course, enhanced stiffness and strength. There are other characteristics which may be equally valuable. As examples, we can cite the ability to control thermal expansion in applications involving electronic packaging. By adding ceramic reinforcements, one can generally reduce the coefficient of linear thermal expansion of the composite. Electrical and thermal conductivity characteristics may be important in some applications. Clearly, superconductors require superconducting characteristics. The metallic matrix provides a high thermal conductivity medium in case of an accidental quench, in addition to holding the tiny superconducting filaments together. Other important characteristics that may be of immense value include wear resistance (e.g., in WC/Co composites used in cutting tools or oil drilling inserts and SiC/Al rotor in brakes). Thus, although one commonly uses the term reinforcement by particle or fibers in the context of metal matrix composites, it worth pointing out that strength enhancement may not be the most important characteristic in many applications. [4, 6]

1.3.3 Matrix Materials

A wide range of metals and their alloys may be used as matrix materials. Examples: Aluminium and Aluminium Alloys, Titanium Alloys, Magnesium and its Alloys, Cobalt, Copper, Silver, Nickel, Niobium and Intermetallics.

1.3.4 Reinforcements

Reinforcement materials for metal matrix composites can be produced in the form of continuous fibers, short fibers, whiskers, or particles. The parameter that allows us to distinguish between these different forms of reinforcements is called the aspect ratio. Aspect ratio is nothing but the ratio of length to diameter (or thickness) of the fiber, particle, or whisker. Thus, continuous fibers have an aspect ratio approaching infinity while perfectly equiaxed particles have an aspect ratio of around one. Table 1.2 lists some important reinforcement materials available in different forms. [7]
Table 1.2 Some important reinforcements for metal matrix composites [7]

<table>
<thead>
<tr>
<th>Continuous Fibers</th>
<th>Al₂O₃, Al₂O₃+SiO₂, B, C, SiC, Si₃N₄, Nb-Ti, Nb₃Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discontinuous Fibers</td>
<td></td>
</tr>
<tr>
<td>(a) Whiskers</td>
<td>SiC, TiB₂, Al₂O₃</td>
</tr>
<tr>
<td>(b) Short Fibers</td>
<td>Al₂O₃, SiC, (Al₂O₃+SiO₂), vapor grown carbon fibers</td>
</tr>
<tr>
<td>Particles</td>
<td>SiC, Al₂O₃, TiC, B₄C, WC</td>
</tr>
</tbody>
</table>

1.3.5 Particulate Silicon Carbide

Silicon carbide in particulate form has been available for a long time. It is quite cheap and commonly used for abrasive, refractory and chemical purposes. Particulate SiC is processed by reacting silica in the form of sand and carbon in the form of coke at 2400°C in an electric furnace. The SiC produced in the form of large granules is subsequently comminuted to the desired size. Two types of SiC particulate reinforcement are shown in Figure 1.2, with angular and rounded morphology, respectively. [8]

![Fig. 1.2 SEM micrograph of SiC particulate reinforcement: (a) angular morphology and (b) rounded morphology (courtesy of Drake and S.M.K. Emanuelsen. Saint-Gobain)](image-url)

1.4 NANOTECHNOLOGY

Nanotechnology is the manipulation of matter on an atomic and molecular scale. The earliest, widespread description of nanotechnology[9, 10] referred to the particular technological goal of precisely manipulating atoms and molecules for fabrication of macro scale products, also now referred to as molecular nanotechnology. A more generalized description of nanotechnology was subsequently established by the National Nanotechnology Initiative, which defines nanotechnology as the manipulation of matter with at least one dimension sized from
1 to 100 nanometers. This definition reflects the fact that quantum mechanical effects are important at this quantum-realm scale, and so the definition shifted from a particular technological goal to a research category inclusive of all types of research and technologies that deal with the special properties of matter that occur below the given size threshold. It is therefore common to see the plural form "nanotechnologies" as well as "nanoscale technologies" to refer to the broad range of research and applications whose common characteristic is size.

Nanotechnology as defined by size is naturally very broad, including fields of science as diverse as surface, organic chemistry, molecular biology, semiconductor physics, micro fabrication, etc. [11] The associated research and applications are equally diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale.

Scientists currently debate the future implications of nanotechnology. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterials, [12] and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted.

1.4.1 Nanotechnology Applications

As of August 21, 2008, the project on emerging nanotechnologies estimates that over 800 manufacturer-identified nanotech products is publicly available, with new ones hitting the market at a pace of 3-4 per week. [13] The project lists all of the products in a publicly accessible online database. Most applications are limited to the use of "first generation" passive nanomaterials which includes titanium dioxide in sunscreen, cosmetics, surface coatings, [14] and some food products; Carbon allotropes used to produce silver tapes in food packaging, clothing, disinfectants and
household appliances; zinc oxide in sunscreens and cosmetics, surface coatings, paints and outdoor furniture varnishes; and cerium oxide as a fuel catalyst.

Further applications allow tennis balls to last longer, golf balls to fly straighter and even bowling balls to become more durable and have a harder surface. Trousers and socks have been infused with nanotechnology so that they will last longer and keep people cool in the summer. Bandages are being infused with silver nanoparticles to heal cuts faster. Cars are being manufactured with nanomaterials so they may need fewer metals and less fuel to operate in the future. Video game consoles and personal computers may become cheaper, faster, and contain more memory thanks to nanotechnology. Nanotechnology may have the ability to make existing medical applications cheaper and easier to use in places like the general practitioner's office and at home.

1.5 NANOMATERIALS

A nanomaterial is a field that takes a materials science-based approach on nanotechnology. It studies materials with morphological features on the nanoscale, and especially those that have special properties stemming from their nanoscale dimensions. Nanoscale is usually defined as smaller than a one tenth of a micrometer in at least one dimension [15] though sometimes includes up to a micrometer.

The nanomaterials field includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions.[16]

* Interface and colloid science has given rise to many materials which may be useful in nanotechnology, such as carbon nanotubes and other fullerenes, and various nanoparticles and nanorods. Nanomaterials with fast ion transport are related also to nanoionics and nano electronics.
* Progress has been made in using these materials for medical applications.
* Nanoscale materials are sometimes used in solar cells which combats the cost of traditional silicon solar cells.
* Development of applications incorporating semiconductor nanoparticles to be used in the next generation of products, such as display technology, lighting, solar cells and biological imaging; see quantum dots.
1.5.1 Bottom-up Approaches

These seek to arrange smaller components into more complex assemblies.

- DNA nanotechnology utilizes the specificity of Watson–Crick base pairing to construct well-defined structures out of DNA and other nucleic acids.
- Approaches from the field of "classical" chemical synthesis (inorganic and organic synthesis) also aim at designing molecules with well-defined shape (e.g. bis-peptides)[17].
- More generally, molecular self-assembly seeks to use concepts of supramolecular chemistry, and molecular recognition in particular, to cause single-molecule components to automatically arrange themselves into some useful conformation.
- Atomic force microscope tips can be used as a nanoscale "write head" to deposit a chemical upon a surface in a desired pattern in a process called dip pen nanolithography. This technique fits into the larger subfield of nanolithography.

1.5.2 Top-down Approaches

These seek to create smaller devices by using larger ones to direct their assembly.

- Many technologies that descended from conventional solid-state silicon methods for fabricating microprocessors are now capable of creating features smaller than 100 nm, falling under the definition of nanotechnology. Giant magnetoresistance-based hard drives already on the market fit this description, as do atomic layer deposition (ALD) techniques. Peter Grünberg and Albert Fert received the Nobel Prize in Physics in 2007 for their discovery of Giant magnetoresistance and contributions to the field of spintronics.
- Solid-state techniques can also be used to create devices known as nanoelectromechanical systems or NEMS, which are related to microelectromechanical systems or MEMS.
- Focused ion beams can directly remove material, or even deposit material when suitable pre-cursor gasses are applied at the same time. For example, this
technique is used routinely to create sub-100 nm sections of material for analysis in Transmission electron microscopy.

 Atomic force microscope tips can be used as a nanoscale "write head" to deposit a resist, which is then followed by an etching process to remove material in a top-down method.

1.5.3 Nanoparticles

Nanoparticles or nanocrystals made of metals, semiconductors, or oxides are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other properties. Nanoparticles have been used as quantum dots and as chemical catalysts such as nanomaterial-based catalysts.

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials.

Nanoparticles exhibit a number of special properties relative to bulk material. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper. The change in properties is not always desirable. Ferroelectric materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them useless for memory storage. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid. Nanoparticles often have unexpected visual properties because they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution.
The often very high surface area to volume ratio of nanoparticles provides a
tremendous driving force for diffusion especially at elevated temperatures.
Sintering is possible at lower temperatures and over shorter durations than for larger
particles. This theoretically does not affect the density of the final product, though
flow difficulties and the tendency of nanoparticles to agglomerate do complicate
matters. The surface effects of nanoparticles also reduce the incipient melting
temperature.

1.5.4 Nano Materials Applications

Since nanomaterials possess unique, beneficial chemical, physical, and
mechanical properties, they can be used for a wide variety of applications. These
applications include, but are not limited to, the following.[18]

- Phosphors for High-Definition TV
- Low-Cost Flat-Panel Displays
- Tougher and Harder Cutting Tools
- Elimination of Pollutants
- High Energy Density Batteries
- High-Power Magnets
- High-Sensitivity Sensors
- Automobiles with Greater Fuel Efficiency
- Aerospace Components with Enhanced Performance Characteristics
- Better and Future Weapons Platforms
- Longer-Lasting Satellites
- Longer-Lasting Medical Implants
- Ductile, Machinable Ceramics
- Large Electrochromic Display Devices

Phosphors for High-Definition TV

The resolution of a television, or a monitor, depends greatly on the size of the
pixel. These pixels are essentially made of materials called "phosphors," which glow
when struck by a stream of electrons inside the cathode ray tube (CRT). The
resolution improves with a reduction in the size of the pixel, or the phosphors.
Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride
synthesised by the sol-gel techniques are candidates for improving the resolution of monitors. The use of nanophosphors is envisioned to reduce the cost of these displays so as to render high-definition televisions (HDTVs) and personal computers affordable to be purchased by an average household in the U.S.[18]

**Tougher and Harder Cutting Tools**

Cutting tools made of nanocrystalline materials, such as tungsten carbide, tantalum carbide, and titanium carbide, are much harder, much more wear-resistant, erosion-resistant, and last longer than their conventional (large-grained) counterparts. They also enable the manufacturer to machine various materials much faster, thereby increasing productivity and significantly reducing manufacturing costs. Also, for the miniaturisation of microelectronic circuits, the industry needs microdrills (drill bits with diameter less than the thickness of an average human hair or 100 μm) with enhanced edge retention and far better wear resistance. Since nanocrystalline carbides are much stronger, harder, and wear-resistant, they are currently being used in these microdrills.[18]

**Elimination of Pollutants**

Nanocrystalline materials possess extremely large grain boundaries relative to their grain size. Hence, nanomaterials are very active in terms of their chemical, physical, and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.[18]

**High Energy Density Batteries**

Conventional and rechargeable batteries are used in almost all applications that require electric power. These applications include automobiles, laptop computers, electric vehicles, next-generation electric vehicles (NGEV) to reduce environmental pollution, personal stereos, cellular phones, cordless phones, toys, and watches. The energy density (storage capacity) of these batteries is quite low requiring frequent recharging. The life of conventional and rechargeable batteries is also low.
Nanocrystalline materials synthesised by sol-gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than their conventional counterparts. Furthermore, nickel-metal hydride (Ni-MH) batteries made of nanocrystalline nickel and metal hydrides are envisioned to require far less frequent recharging and to last much longer because of their large grain boundary (surface) area and enhanced physical, chemical, and mechanical properties.[18]

**High-Power Magnets**

The strength of a magnet is measured in terms of coercivity and saturation magnetisation values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume of the grains) of the grains. It has been shown that magnets made of nanocrystalline yttrium-samarium-cobalt grains possess very unusual magnetic properties due to their extremely large surface area. Typical applications for these high-power rare-earth magnets include quieter submarines, automobile alternators, land-based power generators, motors for ships, ultra-sensitive analytical instruments, and magnetic resonance imaging (MRI) in medical diagnostics.[18]

**High-Sensitivity Sensors**

Sensors employ their sensitivity to the changes in various parameters they are designed to measure. The measured parameters include electrical resistivity, chemical activity, magnetic permeability, thermal conductivity, and capacitance. All of these parameters depend greatly on the microstructure (grain size) of the materials employed in the sensors. A change in the sensor’s environment is manifested by the sensor material’s chemical, physical, or mechanical characteristics, which is exploited for detection. For instance, a carbon monoxide sensor made of zirconium oxide (zirconia) uses its chemical stability to detect the presence of carbon monoxide. In the event of carbon monoxide’s presence, the oxygen atoms in zirconium oxide react with the carbon in carbon monoxide to partially reduce zirconium oxide. This reaction triggers a change in the sensor’s characteristics, such as conductivity (or resistivity) and capacitance. The rate and the extent of this reaction are greatly increased by a decrease in the grain size. Hence, sensors made of nanocrystalline materials are
extremely sensitive to the change in their environment. Typical applications for sensors made out of nanocrystalline materials are smoke detectors, ice detectors on aircraft wings, automobile engine performance sensor, etc.[18]

**Automobiles with Greater Fuel Efficiency**

Currently, automobile engines waste considerable amounts of gasoline, thereby contributing to environmental pollution by not completelycombusting the fuel. A conventional spark plug is not designed to burn the gasoline completely and efficiently. This problem is compounded by defective, or worn-out, spark plug electrodes. Since nanomaterials are stronger, harder, and much more wear-resistant and erosion-resistant, they are presently being envisioned to be used as spark plugs. These electrodes render the spark plugs longer-lasting and combust fuel far more efficiently and completely. A radically new spark plug design called the "railplug" is also in the prototype stages. This railplug uses the technology derived from the "railgun," which is a spin-off of the popular Star Wars defense program. However, these railplugs generate much more powerful sparks (with an energy density of approximately 1 kJ/mm²). Hence, conventional materials erode and corrode too soon and quite frequently to be of any practical use in automobiles. Nevertheless, railplugs made of nanomaterials last much longer even the conventional spark plugs. Also, automobiles waste significant amounts of energy by losing the thermal energy generated by the engine. This is especially true in the case of diesel engines. Hence, the engine cylinders (liners) are currently being envisioned to be coated with nanocrystalline ceramics, such as zirconia and alumina, so that they retain heat much more efficiently and result in complete and efficient combustion of the fuel.[18]

**Aerospace Components with Enhanced Performance Characteristics**

Due to the risks involved in flying, aircraft manufacturers strive to make the aerospace components stronger, tougher, and last longer. One of the key properties required of the aircraft components is the fatigue strength, which decreases with the component’s age. By making the components out of stronger materials, the life of the aircraft is greatly increased. The fatigue strength increases with a reduction in the grain size of the material. Nanomaterials provide such a significant reduction in the grain size over conventional materials that the fatigue life is increased by an average
of 200-300%. Furthermore, components made of nanomaterials are stronger and can operate at higher temperatures, aircrafts can fly faster and more efficiently (for the same amount of aviation fuel). In spacecrafts, elevated-temperature strength of the material is crucial because the components (such as rocket engines, thrusters, and vectoring nozzles) operate at much higher temperatures than aircrafts and higher speeds. Nanomaterials are perfect candidates for spacecraft applications, as well.[18]

Better and Future Weapons Platforms

Conventional guns, such as cannons, 155 mm howitzers, and multiple-launch rocket system (MLRS), utilise the chemical energy derived by igniting a charge of chemicals (gun powder). The maximum velocity at which the penetrator can be propelled is approximately 1.5 to 2.0 km/sec. On the other hand, electromagnetic launchers (EML guns), or railguns, use the electrical energy, and the concomitant magnetic field (energy), to propel the penetrators/projectiles at velocities up to 10 km/sec. This increase in velocity results in greater kinetic energy for the same penetrator mass. The greater the energy, the greater is the damage inflicted on the target. For this and other reasons, the department of defense (U. S. Army) has conducted extensive research into the railguns. Since a railgun operates on electrical energy, the rails need to be very good conductors of electricity. Also, they need to be so strong and rigid that the railgun does not sag while firing and buckle under its own weight. The obvious choice for high electrical conductivity is copper. However, the railguns made out of copper wear out much too quickly due to the erosion of the rails by the hypervelocity projectiles and they lack high-temperature strength. The wear and erosion of copper rails necessitate inordinately frequent barrel replacements. In order to satisfy these requirements, a nanocrystalline composite material made of tungsten, copper, and titanium diboride is being evaluated as a potential candidate. This nanocomposite possesses the requisite electrical conductivity, adequate thermal conductivity, excellent high strength, high rigidity, hardness, and wear/erosion resistance. This results in longer-lasting, wear-resistant, and erosion-resistant railguns, which can be fired more frequently and often than their conventional counterparts.[18]
**Longer-Lasting Satellites**

Satellites are being used for both defense and civilian applications. These satellites utilize thruster rockets to remain in or change their orbits due to a variety of factors including the influence of gravitational forces exerted by the earth. Hence, these satellites are repositioned using these thrusters. The life of these satellites, to a large extent, is determined by the amount of fuel they can carry on board. In fact, more than 1/3 of the fuel carried aboard by the satellites is wasted by these repositioning thrusters due to incomplete and inefficient combustion of the fuel, such as hydrazine. The reason for the incomplete and inefficient combustion is that the onboard ignitors wear out quickly and cease to perform effectively. Nanomaterials, such as nanocrystalline tungsten-titanium diboride-copper composite, are potential candidates for enhancing these ignitors’ life and performance characteristics.[18]

**Longer-Lasting Medical Implants**

Currently, medical implants, such as orthopaedic implants and heart valves, are made of titanium and stainless steel alloys. These alloys are primarily used in humans because they are biocompatible, i.e., they do not adversely react with human tissue. In the case of orthopaedic implants (artificial bones for hip, etc.), these materials are relatively non-porous. For an implant to effectively mimic a natural human bone, the surrounding tissue must penetrate the implants, thereby affording the implant with the required strength. Since these materials are relatively impervious, human tissue does not penetrate the implants, thereby reducing their effectiveness. Furthermore, these metal alloys wear out quickly necessitating frequent, and often very expensive, surgeries. However, nanocrystalline zirconia (zirconium oxide) ceramic is hard, wear-resistant, corrosion-resistant (biological fluids are corrosive), and biocompatible. Nanoceramics can also be made porous into aerogels (aerogels can withstand up to 100 times their weight), if they are synthesized by sol-gel techniques. This results in far less frequent implant replacements, and hence, a significant reduction in surgical expenses. Nanocrystalline silicon carbide (SiC) is a candidate material for artificial heart valves primarily due to its low weight, high strength, extreme hardness, wear resistance, inertness (SiC does not react with biological fluids), and corrosion resistance.[18]
**Ductile and Machinable Ceramics**

Ceramics, are very hard, brittle, and hard to machine. These characteristics of ceramics have discouraged the potential users from exploiting their beneficial properties. However, with a reduction in grain size, these ceramics have increasingly been used. Zirconia, a hard, brittle ceramic, has even been rendered super plastic, i.e., it can be deformed to great lengths (up to 300% of its original length). However, these ceramics must possess nanocrystalline grains to be superplastic. In fact, nanocrystalline ceramics, such as silicon nitride (Si₃N₄) and silicon carbide (SiC), have been used in such automotive applications as high-strength springs, ball bearings, and valve lifters, because they possess good formability and machinabiltiy combined with excellent physical, chemical, and mechanical properties. They are also used as components in high-temperature furnaces. Nanocrystalline ceramics can be pressed and sintered into various shapes at significantly lower temperatures, whereas it would be very difficult, if not impossible, to press and sinter conventional ceramics even at high temperatures.[18]

**Large Electrochromic Display Devices**

An electrochromic device consists of materials in which an optical absorption band can be introduced, or an existing band can be altered by the passage of current through the materials, or by the application of an electric field. Nanocrystalline materials, such as tungstic oxide (WO₃·xH₂O) gel, are used in very large electrochromic display devices. The reaction governing electrochromism (a reversible coloration process under the influence of an electric field) is the double-injection of ions (or protons, H⁺) and electrons, which combine with the nanocrystalline tungstic acid to form a tungsten bronze. These devices are primarily used in public billboards and ticker boards to convey information. Electrochromic devices are similar to liquid-crystal displays (LCD) commonly used in calculators and watches. However, electrochromic devices display information by changing colour when a voltage is applied. When the polarity is reversed, the colour is bleached. The resolution, brightness, and contrast of these devices greatly depend on the tungstic acid gel’s grain size. Hence, nanomaterials are being explored for this purpose.[18]
1.6 NANOCOMPOSITES

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed,[19] <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement.

The field of nanocomposites is gaining a lot of momentum as researchers strive to enhance composite properties by using nanoscale reinforcements instead of particulate filled composites. This nanograin size plays a dominant role in influencing its mechanical properties. A reduction in grain size of 80 – 200 nm results in a hardness increase from 1600 – 1950 (Vickers) in WC 10% C cemented carbides. The strength of copper single crystals is 82 MPa which rises to 290 MPa at a grain size of 11 nm. Copper with a grain size of 27 nm had a tensile ductility of 30% even though the tensile strength was as high as 202 MPa. On rolling, copper with a grain size of 20 nm, an extensibility of 500 % was obtained.

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. Jose-Yacaman et al. [20] investigated the origin of the depth of colour and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a nanoparticle mechanism. From the mid-1950s nanoscale organo-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/claycomposites were the topic of textbooks, although the term "nanocomposites" was not in common use.[20]
In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Ajayan et al. [21] noted that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite. For example, adding carbon nanotubes improves the electrical and thermal conductivity. Other kinds of nanoparticulates may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage. In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called mass fraction) of the nanoparticulates introduced can remain very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers (e.g. nanometer-thin platelets, such as clays, or nanometer-diameter cylinders, such as carbon nanotubes)[21].

Despite considerable progress being made, the knowledge of mechanical properties of nanocomposite solids is in a state of infancy, one of the reasons being the inability to obtain large and defect free samples. Central to all is the understanding of the microscopic deformation and fracture mechanism in nanocomposite solids. There is a lot more needed to understand the dislocation activity in nanocrystalline solids. It is likely that for the longer end of the nanoscale grain size (50 – 100 nm) dislocation activity dominates for test temperatures less than 0.5 Tm. As the grain size
decreases, dislocation activity also decreases. There appears to be a lack of dislocation at grain sizes below 50 nm. This appears to be a new phenomenon, which controls the deformation behavior such as grain boundary sliding. There is a great need to explore the deformation mechanism in nanocrystalline solids and very little of it is understood.[21]

1.6.1 Classification of Nanocomposites

* Ceramic-matrix nanocomposites
* Metal-matrix nanocomposites
* Polymer-matrix nanocomposites

1.6.1.1 Ceramic-Matrix Nanocomposites

In this group of composites the main part of the volume is occupied by a ceramic, i.e. a chemical compound from the group of oxides, nitrides, borides, silicides etc. In most cases, ceramic-matrix nanocomposites encompass a metal as the second component. Ideally both components, the metallic one and the ceramic one, are finely dispersed in each other in order to elicit the particular nanoscopic properties. Nanocomposite from these combinations were demonstrated in improving their optical, electrical and magnetic properties [22] as well as tribological, corrosion-resistance and other protective properties.[23]

The binary phase diagram of the mixture should be considered in designing ceramic-metal nanocomposites and measures have to be taken to avoid a chemical reaction between both components. The last point mainly is of importance for the metallic component that may easily react with the ceramic and thereby lose its metallic character. This is not an easily obeyed constraint, because the preparation of the ceramic component generally requires high process temperatures. The safest measure thus is to carefully choose immiscible metal and ceramic phases. A good example for such a combination is represented by the ceramic-metal composite of TiO₂ and Cu, the mixtures of which were found immiscible over large areas in the Gibbs’ triangle of Cu-O-Ti.[24]

The concept of ceramic-matrix nanocomposites was also applied to thin films that are solid layers of a few nm to some tens of μm thickness deposited
upon an underlying substrate and that play an important role in the functionalization of technical surfaces. Gas flow sputtering by the hollow cathode technique turned out as a rather effective technique for the preparation of nanocomposite layers. The process operates as a vacuum based deposition technique and is associated with high deposition rates up to some μm/s and the growth of nanoparticles in the gas phase. Nanocomposite layers in the ceramics range of composition were prepared from TiO₂ and Cu by the hollow cathode technique [25] that showed a high mechanical hardness, small coefficients of friction and a high resistance to corrosion.

1.6.1.2 Metal Matrix Nanocomposites

Metal matrix nanocomposites can be classified as continuous and non-continuous reinforced materials. One of the more important nanocomposites is Carbon nanotube metal matrix composites, which is an emerging new material that is being developed to take advantage of the high tensile strength and electrical conductivity of carbon nanotube materials. Critical to the realization of CNT-MMC possessing optimal properties in these areas are the development of synthetic techniques that are (a) economically viable, (b) provide for a homogeneous dispersion of nanotubes in the metallic matrix, and (c) lead to strong interfacial adhesion between the metallic matrix and the carbon nanotubes. In addition to carbon nanotube metal matrix composites, boron nitride reinforced metal matrix composites and carbon nitride metal matrix composites are the new research areas on metal matrix nanocomposites.[26]

Another kind of nanocomposite is the energetic nanocomposite, generally as a hybrid sol–gel with a silica base, which, when combined with metal oxides and nano-scale aluminum powder, can form superthermite materials.[27]

1.6.1.3 Polymer-Matrix Nanocomposites

In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nanoscale filler (these materials are better described by the term nanofilled polymer composites). This strategy is particularly effective in yielding high performance composites, when good dispersion of the
filler is achieved and the properties of the nanoscale filler are substantially
different or better than those of the matrix. An example of this would be
reinforcing a polymer matrix by much stiffer nanoparticles [28-29] of ceramics,
clays, or carbon nanotubes. It should be noted that the improvement in mechanical
properties may not be limited to stiffness or strength. Time-dependent properties
could be improved by addition of the nanofillers.[30] Alternatively, the enhanced
crystallization behavior under flow conditions and other physical properties of
high performance nanocomposites may be mainly due to the high aspect ratio
and/or the high surface area of the fillers,[31-32] since nanoparticulates have
extremely high surface area to volume ratios when good dispersion is achieved.
Nanoparticle dispersibility in the polymer matrix is a key issue, which limits the
applicable particle volume fraction and therefore also the multi-functionality of
the composite material.[33] Recent research on thin films (thickness <50
micrometer) made of polymer nanocomposites has resulted in a new and scalable
synthesis technique, which allows the facile incorporation of greater nano-material
quantities [34] such advances will enable the future development of multi-
functional small scale devices (i.e. sensor, actuator, medical equipment), which
rely on polymer nanocomposites.

Nanoscale dispersion of filler or controlled nanostructures in the composite
can introduce new physical properties and novel behaviors that are absent in the
unfilled matrices. This effectively changes the nature of the original matrix (such
composite materials can be better described by the term genuine
nanocomposites or hybrids). Some examples of such new properties are fire
resistance or flame retardancy,[35] and accelerated biodegradability.

In a recent study, polymeric nanocomposites were fabricated using various
one-dimensional carbon nanostructures such as single- and multi- walled carbon
nanotubes, as well as two-dimensional carbon and inorganic nanomaterials such as
graphene platelets,[36] graphene nanoribbon,[37] single- and multi- walled
graphene oxide nanoribbons, graphene oxide nanoplatelets and molybdenum
disulfide nanoplatelets as reinforcing agents, to improve the mechanical properties
of poly(propylene fumarate) nanocomposites, for bone tissue engineering
applications. Significant mechanical reinforcement (i.e. increases in the Young's
modulus, compressive yield strength, flexural modulus and flexural yield strength) were observed at low loading concentrations (0.01-0.2 wt%) of nanomaterials. The results suggest that mechanical reinforcement is dependent on the nanostructure morphology, defects, dispersion of nanomaterials in the polymer matrix, and the cross-linking density of the polymer. In general, two-dimensional nanostructures can reinforce the polymer better than one-dimensional nanostructures, and inorganic nanomaterials are better reinforcing agents than carbon based nanomaterials. In addition to mechanical properties, multi-walled carbon nanotubes based polymer nanocomposites have also been used for the enhancement of the electrical conductivity.

1.7 THERMAL CONTROL SYSTEM

The purpose of a thermal-control system is to maintain all of a spacecraft's components within the allowable temperature limits for all operating modes of the vehicle; in all of the thermal environments it may be exposed. Establishing a thermal design for a spacecraft is usually a two-part process. The first step is to select a thermal design for the body, or basic enclosures, of the spacecraft that will serve as a thermal sink for all internal components. The second step is to select thermal designs for various components located both within and outside the spacecraft body. [38]

1.7.1 Thermal Design/Analysis Process Overview

The thermal-design process is a combination of design selection and supporting analysis. The spacecraft system requirements to minimize weight, cost, and test complexity while maximizing reliability are usually served best by keeping the thermal design as simple as possible and by avoiding the use of active components. The objective might be to develop a complete thermal-control system for a new spacecraft, to predict temperatures for an existing satellite in a new attitude, to modify the thermal design of a component in response to changes in component design, etc. [38]
1.7.2 Thermal Analysis

The study of the effect of heat on materials obviously has a long history, from man’s earliest attempts at producing pottery, extracting metals (about 8000 BC) and making glass (about 3400 BC) through the philosophical discussions of the alchemists on the elements of fire, air, earth and water, to early work on the assaying of minerals (about 1500 AD), followed by the development of thermometry and calorimetry. [39]

Excellent accounts of the basic, but difficult, concepts of “heat” and “temperature” and the development of temperature scales have been given by Wunderlich [40] and by Schuijff [41]. A detailed thermodynamic background to thermal analysis and calorimetry has been provided by Van Ekeren [42].

Whenever a sample of material is to be studied, one of the easiest tests to perform is to heat it. The observation of the behaviour of the sample and the quantitative measurement of the changes on heating can yield a great deal of useful information on the nature of the material. The analysis of thermal events may be approached in two ways, which overlap considerably. Either the experiment may be designed to measure thermal properties (heat capacity, enthalpy, entropy and free energy) with high precision and accuracy at particular temperatures and conditions, or we may study properties, including thermal properties, over a wider range of temperatures using a controlled heating procedure. [43]

To provide useful qualitative and quantitative information on the effect of heat on materials, experiments have to be carefully planned and use is often made of sophisticated equipment. The following formal definition of thermal analysis was originally provided by the International Confederation for Thermal Analysis and Calorimetry (ICTAC). [39] Thermal Analysis (TA) refers to a group of techniques in which a property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. A recent discussion of the above ICTAC definition by Hemminger and Sarge[44, 45] points out some of the difficulties and suggests some modification. Thermal Analysis (TA) means the analysis of a change in a property
of a sample, which is related to an imposed temperature alteration. Calorimetry means the measurement of heat.

Hemminger and Sarge [44, 45] explain that: (a) “analysis” means much more than “monitoring”; (b) in most experiments it is a change in a property, rather than the property itself which is monitored and (c) it is the temperature of the sample’s environment (e.g. a furnace), rather than the actual sample temperature which is programmed. A “temperature alteration” includes; (i) a stepwise change from one constant temperature to another, (ii) a linear rate of change of temperature; (iii) modulation of a constant or linearly changing temperature with constant frequency and amplitude; and (iv) uncontrolled heating or cooling. The direction of change may involve either heating or cooling and above modes of operation may be combined in any sequence. Isothermal experiments, other than at ambient temperature, are included in this definition under mode (i), where the first constant temperature is usually ambient temperature and the change is to the desired isothermal experimental conditions. The temperature may also be programmed to maintain a constant rate of reaction, such a mode is a sample-controlled programme.

1.7.3 Classification Principles for Thermal Analysis and Calorimetry

It is expedient to first develop a classification system that can be applied to the methods of thermal analysis and calorimetry. This will create an order structure in which both established and new measuring techniques can be incorporated. [46] There are many properties of the sample which can be measured; the number of techniques (and associated methods) is quite large. The main sample properties used and the associated primary techniques are listed in Table 1.3. [39] Absolute values of the sample property may be recorded, or the difference in the property of the sample compared to the same property of a reference material may be more convenient to measure, or the rate of change of the sample property with temperature (or time) may be of interest (derivative measurements). Further techniques (and methods) derived from those in Table 1.3 are listed in Table 1.4. [39, 43]
The range of samples is enormous, limited usually, but not necessarily, to initially solid substances. Studies on liquids provide less information of interest and studies on gases are not usually included under thermal analysis. The temperature programme to which the sample is subjected is most often a constant heating (or cooling) rate and the atmosphere is usually an inert gas, but studies in reactive gases also provide a wealth of information. [39, 43]

Like most techniques based on relatively simple principles, the interpretation of results is not always as straightforward and hence, it is important to combine information from several techniques whenever possible.

**Table 1.3 The Primary Thermal Analysis (TA) Techniques and Methods [39]**

<table>
<thead>
<tr>
<th>Property</th>
<th>Techniques</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Thermometry</td>
<td>Heating or cooling curve analysis</td>
</tr>
<tr>
<td>Temperature difference</td>
<td>Differential Thermometry</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td></td>
<td>(DT and DTA)</td>
<td></td>
</tr>
<tr>
<td>Heat flow difference</td>
<td>Differential Scanning</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calorimetry (DSC)</td>
<td></td>
</tr>
<tr>
<td>Mass</td>
<td>Thermogravimetry</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td></td>
<td>(TG and TGA)</td>
<td></td>
</tr>
<tr>
<td>Dimensions or mechanical</td>
<td>Thermomechananometry</td>
<td>Thermomechanical Analysis</td>
</tr>
<tr>
<td>properties</td>
<td>(TM and TMA)</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>Thermomanometry</td>
<td>Thermomanometric Analysis</td>
</tr>
<tr>
<td>Electrical properties</td>
<td>Thermoelctrometry</td>
<td>Thermoelctrical Analysis</td>
</tr>
<tr>
<td></td>
<td>(TE and TEA)</td>
<td></td>
</tr>
<tr>
<td>Magnetic properties</td>
<td>Thermomagnetometry</td>
<td>Thermomagnetic Analysis</td>
</tr>
<tr>
<td>Optical Properties</td>
<td>Thermoptometry</td>
<td>Thermoptometric Analysis</td>
</tr>
<tr>
<td></td>
<td>(TO and TOA)</td>
<td></td>
</tr>
<tr>
<td>Acoustic properties</td>
<td>Thermoacoustimetry</td>
<td>Thermoacoustimetric Analysis</td>
</tr>
<tr>
<td></td>
<td>(TAA)</td>
<td></td>
</tr>
<tr>
<td>Gas exchange</td>
<td>Thermally Stimulated</td>
<td>Thermally Stimulated</td>
</tr>
<tr>
<td></td>
<td>Exchanged Gas Measurement</td>
<td>Exchanged Gas Analysis</td>
</tr>
<tr>
<td></td>
<td>(EGM and EGA)</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.4 Special Techniques Derived From Primary TA Techniques [39]

<table>
<thead>
<tr>
<th>Primary Technique</th>
<th>Special Techniques (Methods)</th>
<th>Property or conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermomechanometry</td>
<td>Thermodilatometry (Thermodilatometric Analysis) (TD)</td>
<td>Dimension (negligible force)</td>
</tr>
<tr>
<td></td>
<td>Static Force Thermomechanometry (Static Force Thermomechanical Analysis) (sf-TM and sf-TMA)</td>
<td>Dimension (static force)</td>
</tr>
<tr>
<td></td>
<td>Dynamic Force Thermomechanometry (Dynamic Force Thermomechanical Analysis) (df-TM and df-TMA)</td>
<td>Dimension (dynamic force)</td>
</tr>
<tr>
<td></td>
<td>Modulated Force Thermomechanometry (Modulated Force Thermomechanical Analysis) (mf-TM and mf-TMA)</td>
<td>Dimension (modulated force)</td>
</tr>
</tbody>
</table>

Note: Static mode of operation means any quantity acting on the sample is constant with time.

Dynamic mode of operation means any alteration with time of any quantity acting on the sample. The alteration may be predetermined (programmed) or controlled by the sample.

Modulated mode of operation is a special variant of the dynamic mode of operation in which the alteration of quantity acting on the sample is characterized by frequency and amplitude. The modulated quantity has to be specified.

1.7.4 Thermal Analysis Instruments

All thermal analysis instruments have features in common illustrated in Figure 1.3. The sample, contained in a suitable sample pan or crucible, is placed in a furnace and subjected to some desired temperature programme. During this procedure, one or more properties of the sample are monitored by use of suitable transducers for converting the properties to electrical quantities such as voltages or currents. The variety of the techniques to be discussed stems from the variety of physical properties that can be measured and the variety of transducers that can be used.

Measurements are usually continuous and the heating rate is often, but not necessarily, linear with time. The results of such measurements are thermal analysis
curves and the features of these curves (peaks, discontinuities, changes of slope, etc.) are related to thermal events in the sample. (“Thermogram” is not a recommended term for a thermal analysis curves, because of its medical usage.) [39]

Fig. 1.3 Generalized thermal analysis instrument and resulting thermal analysis curve

1.7.5 Thermodynamic Background to Thermal Analysis and Calorimetry

Thermal Analysis is a series of techniques where physical properties of a material are measured as a function of time, while the material is subjected to a temperature programme. The physical properties are thus also measured as a function of temperature. In all calorimetric techniques the property that is measured is heat.[46]

1.7.6 Thermodynamic Systems

In thermodynamics, the part of the universe that is under investigation is called the system. This system is clearly distinguished from the rest of the universe, the surroundings. The system is separated from its surroundings by a wall (the wall may be real or imaginary). Depending on the properties of the wall three types of systems are defined:

* Open system: the wall between the system and the surroundings allows exchange of matter as well as heat;
* Closed system: matter cannot pass the wall between the system and the surroundings, exchange of heat between the system and the surroundings is
possible (normally, if the word 'system' is used without any indication, a closed system is meant);

* Isolated system: the wall completely isolates the system from its surroundings, i.e. no matter and no heat can be exchanged between the system and the surroundings.

In Thermal Analysis and Calorimetry it is usually interested in properties of materials. Therefore, the system is usually chosen as a certain amount of the material that is under investigation. Such a material may consist of a pure chemical component or of a mixture of two or more components. It is well known that a pure component can exist in different states of aggregation: solid, liquid and gas. These states of aggregation are sometimes also called phases, but, to be more precise, a phase must be defined as: a phase consists of all parts of the system that have identical intensive properties. If a system consists of a single phase, the system is called a homogeneous system. A system consisting of two or more phases is called a heterogeneous system. In heterogeneous systems, two different phases are separated from each other by an interface. Normally there is only one gaseous (or vapour) phase, but there may be several liquid and solid phases. More than one solid phase is also possible, even for pure component systems. [46]

1.7.7 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analyzer measures the energy changes that occur as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur. The energy changes enable the user to find and measure the transitions that occur in the sample quantitatively and to note the temperature where they occur and so to characterize a material for melting processes, measurement of glass transitions and a range of more complex events. One of the big advantages of DSC is that samples are very easily encapsulated, usually with little or no preparation, ready to be placed in the DSC, so that measurements can be quickly and easily made. [47]

A DSC is the most widely used of the thermal techniques available to the analyst and provides a fast and easy to use method of obtaining a wealth of information about a material, whatever the end use envisaged. It has found use in
many wide ranging applications including polymers and plastics, foods and pharmaceuticals, glasses and ceramics, proteins and life science materials; in fact virtually any material, allowing the analyst to quickly measure the basic properties of the material. [46, 47]

1.7.8 Heat Flow Measurements

The main property that is measured by DSC is heat flow, the flow of energy into or out of the sample as a function of temperature or time. Since an mW is a mJ/s this is literally the flow of energy in unit time. The actual value of heat flow measured depends upon the effect of the reference and is not absolute. Stable instrumental response or baseline is produced against which any changes can be measured. The starting point of the curve on the y-axis may be chosen as one of the starting parameters, and it should be set at or close to zero. [47]

Two different conventions exist for the display of the heat flow curve: one shows endotherms in the downward direction, the other upward. Traditionally, with heat flux systems endotherms are shown as going down, since endothermic transitions result in a negative temperature differential, whilst with power compensation systems, they are shown as going up since with this principle endothermic transitions result in an increase in power supplied to the sample [47]. The value of measuring energy flow is that it enables the analyst to identify the range of different transitions that may occur in the sample as it is heated or cooled.

1.7.9 Specific Heat (Cp)

The specific heat (heat capacity, Cp) of a material can be determined quantitatively using DSC and is designated Cp since values are obtained at constant pressure. The accuracy that can be obtained depends upon the instrument and method in use. [47]

In practice the traditional standard test method provides a fairly rapid method for determination of Cp and many manufacturers provide software specifically designed to comply with this. Three runs are required, each consisting of an isothermal period, temperature ramp and final isotherm. This method is applied identically to the succeeding runs:
1. First run: a baseline with uncrimped empty pans placed in the furnace.
2. Second run: as above but adding a reference (typically sapphire) to the sample pan.
3. Third run: replace the reference with your sample.

The three curves are brought up on the screen, isothermals matched, data subtracted and referenced against the standard. Most software packages will do this automatically, and if the differing weight and heat capacity of sample pans are taken into account then the baseline and reference runs may be used for subsequent samples, provided the DSC is stable. In fact, because the procedure is based on a subtraction technique between measurements made at different times, any drift will cause error. The DSC must be very stable and in practice it is best not to use an instrument at the extremes of its temperature range where stability may be compromised. The standard most often used is sapphire, and the mass used should be similar to the sample; in any event the sample should not be a great deal larger or errors will be increased. This method relies on the measurement of the heat flow of the sample compared to that of an empty pan. Whilst there may be a number of factors which dictate the scan rate of choice it should be noted that faster scan rates result in increased values of heat flow giving increased accuracy of measurement, and this also minimizes the time of the run and potential drift of the analyser. [47]

A similar principle is employed in stepwise heating methods where the temperature may be raised by only a fraction of a degree between a series of isotherms. This is reported to give a very accurate value for Cp because of the series of short temperature intervals. [47]

Specific heat data can be of value in its own right since this information is required by chemists and chemical engineers when scaling up reactions or production processes, it provides information for mathematical models, and is required for accurate kinetic and other advanced calculations. It can also help with curve interpretation since the slope of the curve is fixed and absolute, and small exothermic or endothermic events identified. Overall, it gives more information than the heat flow trace because values are absolute, but it does take more time, something often in short supply in industry.
1.7.9.1 Enthalpy

The enthalpy of a material is energy required to heat the material to a given temperature and is obtained by integrating the heat capacity curve. Again many software packages provide for the integration of the Cp curve to provide an enthalpy curve. Enthalpy curves are sometimes used for calculations, for example when calculating fictive temperature (see Glossary), and can help in understanding why transitions have the shape they do. [47]

1.7.9.2 Temperature Range

Make sure that the pan is specified for the desired temperature range and will not melt during a scan; remember that aluminium must not be used above 600 °C. Pan materials such as gold (melting point 1063 °C), platinum or alumina can be used at higher temperatures. [47]

1.7.9.3 Use without Pans

Occasionally, very stable samples may be run without pans, for example stable metals over a low temperature range. These benefit from increased thermal transfer to the sample. Thermally conductive pastes have also been used on occasion to try to improve thermal transfer, but such measures require great care and the use of helium or other highly conductive purge gas may be a better alternative. [47]

1.7.9.4 Sub-ambient Operation

A variety of cooling systems are available for most instruments and these are now mostly automatic in operation. Issues of filling liquid nitrogen systems and of availability mean that refrigerated coolers (intracoolers) are often preferred and some systems can operate at below − 100 °C. Intracoolers are preferred for use with auto samplers since there is no risk of the coolant running out. [47]

1.7.9.5 Power Compensation DSC

The various theories developed for Differential Thermal Analysis (DTA) and the closely related heat-flux DSC, are considered and extended finally to power compensation DSC. [46] Power compensation DSC has at its heart two small identical furnaces, one for the sample and one for the reference (normally an empty
pan), the reference being the right-hand furnace; Figure 1.4. These are both heated at a pre-programmed heating (or cooling) rate and power compensations are applied to either furnace as required to maintain this rate. In the resulting DSC trace the difference in energy flowing into the sample furnace is compared to the inert reference and plotted as a function of temperature or time. This design measures flow of energy directly in mW or J/s. The fundamental equation of DSC [47] is

\[
\text{DSC signal (W/g)} = \text{Heat Capacity (J/kg)} \times \text{Scanning Rate (K/s)}
\]

\[
dH/dt = dH/dT \times dT/dt
\]  

Therefore the raw heat flow signal can be viewed as a form of heat capacity. In practice, it reflects the changes occurring in heat capacity and the absolute value is obtained when the method used takes into account the contribution of the empty pans and reference together with the scan rate.

![Diagram of power compensation DSC](image)

Fig. 1.4 Diagram of power compensation DSC

In this system, both the sample and reference furnaces are heated at a programmed heating/cooling rate. In order to maintain this rate when transitions occur in the sample, power compensation circuit increases or reduces power to either furnace as required in order to maintain the heating rate. The power compensation circuit therefore reflects the energy changes occurring in the sample and is presented on the screen as a function of temperature or time. This technique measures energy changes directly.

The small furnaces of this system can be heated or cooled at very low rates to very high rates and are ideal for a range of different techniques, particularly fast scan DSC. Power compensated DSC also permits true isothermal operation, since under
constant temperature conditions both the sample and furnace are held isothermally. The temperature range of use is from liquid nitrogen temperatures to around 730 °C.

1.7.9.6 Heat Flux DSC

Heat flux DSC is of a single furnace design with a temperature sensor (or multiple sensors) for each of the sample and reference pans located within the same furnace; which is shown in Figure 1.5. Sample and reference pans are placed in their required positions and the furnace heated at the pre-programmed heating (or cooling) rate. When transitions in the sample are encountered a temperature difference is created between sample and reference. On continued heating beyond the transition this difference in temperature decreases as the system reaches equilibrium in accordance with the time constant τ of the system. It is the difference in temperature or Δt signal that is the basic parameter measured. Modern analyzers are carefully calibrated so that the Δt signal is converted to a heat flow equivalent and this is displayed as a function of temperature or time. The reason a difference in temperature is created is easily understood if melting is considered. When melting of a single crystal occurs the resulting mixture of solid and liquid remains at the melting point until melting is complete, so the temperature of the sample will fall behind that of the reference. Typical heat flux DSC analysers can be used from liquid nitrogen temperatures to a maximum of around 700 °C similar to power compensation DSC.

Fig. 1.5 Diagram of a heat flux DSC

In this system, both the sample and reference experience the same heat flux, but as energy demands differ, the heating or cooling effect will differ resulting in a difference in temperature between sample and reference. This difference in
temperature is converted to an energy equivalent by the analyzer giving the familiar DSC signal in mW. (This Figure 1.5 was produced by Anatech in Holland). [47, 48]

1.7.9.7 Heating and Cooling of Sample in DSC

The heating and cooling of sample in DSC instrument is as follows.

1.7.9.8 Heating

Graphite furnaces for high temperatures are maintained in an inert atmosphere and heated directly by passing a current through the electrically conducting graphite. At temperatures below about 1700 °C, an alumina lining tube may be inserted to allow controlled atmospheres which might attack the graphite [46].

1.7.9.9 Cooling

If the behavior of the sample is only studied under conditions of rising temperature, much useful information may be lost. The phase behavior of some organics, e.g. liquid crystals, may involve metastable states only found during cooling. Glass transition phenomena are very dependent on both heating and cooling rates. It is important that any DSC instrument should be capable of controlled cooling as well. Various cooling systems have been used to allow DSC measurements at temperatures below ambient. A typical cooling system is shown in Figure 1.6. A more elaborate method is to attach a container of liquid nitrogen to the assembly via a coolant controller. By means of a pressure gauge and a heater attached to a controller, a pressure of around 0.5 atm is maintained in the container. Cold gas is fed into a heat exchanger fitted over the DSC furnace and will allow cooling to -170 °C. [46]
1.7.10 Thermo Mechanical Analysis (TMA)

In this technique (TMA), dimensional changes in a sample are the primary measurement, while the sample is heated, cooled, or studied at a fixed temperature. A simple schematic figure of a typical TMA instrument is shown in Figure 1.7.

The sample sits on a support within the furnace. Resting upon it is a probe to sense changes in length, which are measured by a sensitive position transducer, normally a Linear Variable Displacement Transducer (LVDT). The probe and support are made from a material such as quartz glass (vitreous silica), which has a low, reproducible, and accurately known coefficient of thermal expansion, and also has low thermal conductivity, which helps to isolate the sensitive transducer from the changing temperatures in the furnace. A thermocouple near the sample indicates its
temperature. There is usually provision for establishing a flowing gas atmosphere through the instrument, to prevent oxidation for example, and also to assist in heat transfer to the sample. Helium is effective in this respect.

The load may be applied by static weights, as above, or by a force motor. This latter method gives the advantage that the applied load can be programmed to allow a greater range of experiments. The instrument is calibrated for position measurements by heating a sample whose expansion coefficient is accurately known. Aluminium is commonly used, in the form of small machined blocks or cylinders. Sample sizes are commonly around 5-10mm in height and width. It is important to prepare samples with clean, flat and parallel faces to avoid artifacts in the recorded curves.

There are a number of approaches to temperature calibration. One method uses small flat pieces of pure metals, e.g. indium, sandwiched between thin discs of quartz glass. Melting of the metal sandwich under the probe with a moderate load results in a sharp displacement of the probe. With care, a multi-layer sandwich can be built up using "fillings" of different metals, so that a multi-point calibration can be obtained in one experiment. The TMA curve for such an experiment is shown in Figure 1.8

![Graph: TMA Curve](image)

**Fig. 1.8 TMA Curve**

When the sample carries a zero, or negligible load, the experiment follows the free expansion or contraction of the material, and accurate coefficients of thermal expansion can be routinely determined. Under an appreciable load, softer materials
will be compressed, or slump at a glass transition, for instance, and the expansion measurements will be in error. Fortunately, modern instruments are able to apply loads that are sufficient to keep the probe in good contact with the sample, but small enough to avoid sample deformation. For troublesome samples, the ability to measure the underlying true expansion, is one of the advantages of the recent technique of Modulated Temperature TMA (MT-TMA). Sometimes the required information is about the deformation of the sample, and several types of probe are used for different types of study. A range of typical probes, available with most instruments, is shown in Figure 1.9.

![Diagram of typical probes](image)

**Fig. 1.9 A Range of Typical Probes**

The materials studied are usually rigid or nearly rigid solids, as implied by most of the experimental arrangements shown above. Liquids can be studied in the dilatometer-type accessory, which can also be used to measure the volume changes in an irregularly shaped samples, or powders, which are then submerged in an inert liquid such as silicone oil. Powders can also be studied as a layer with a loosely fitting lid on top, or when pressed into a pellet. Solid-state transitions can be followed in this way.
1.8 MODELLING AND SIMULATION

Modelling and Simulation in Engineering aims at providing a forum for the discussion of formalisms, methodologies and simulation tools that are intended to support the new, broader interpretation of Engineering. Competitive pressures of Global Economy have had a profound effect on the manufacturing in Europe, Japan and the USA with much of the production being outsourced. In this context the traditional interpretation of engineering profession linked to the actual manufacturing needs to be broadened to include the integration of outsourced components and the consideration of logistic, economical and human factors in the design of engineering products and services. [49]

Modeling and simulation (M&S) is getting information about how something will behave without actually testing it in real life. For instance, if we wanted to design a race car, but weren't sure what type of spoiler (A spoiler is an automotive aerodynamic device whose intended design function is to 'spoil' unfavorable air movement across a body of a vehicle in motion, usually described as turbulence or drag) would improve the traction most, we would be able to use a computer simulation of the car to estimate the effect of different spoiler shapes on the coefficient of friction in a turn. We're getting useful insights about different decisions we could make for the car without actually building the car.[49]

More generally, M&S is using models, including emulators, prototypes, simulators, and stimulators, either statically or over time, to develop data as a basis for making managerial or technical decisions. The terms "modeling" and "simulation" are often used interchangeably. [49]

1.8.1 Modelling

Modeling is the process of producing a model; a model is a representation of the construction and working of some system of interest. A model is similar to but simpler than the system it represents. One purpose of a model is to enable the analyst to predict the effect of changes to the system. On the one hand, a model should be a close approximation to the real system and incorporate most of its salient features. On the other hand, it should not be so complex that it is impossible to understand and experiment with it. A good model is a judicious tradeoff between realism and
simplicity. Simulation practitioners recommend increasing the complexity of a model iteratively. An important issue in modeling is model validity. Model validation techniques include simulating the model under known input conditions and comparing model output with system output. [50]

Generally, a model intended for a simulation study is a mathematical model developed with the help of simulation software. Mathematical model classifications include deterministic (input and output variables are fixed values) or stochastic (at least one of the input or output variables is probabilistic); static (time is not taken into account) or dynamic (time-varying interactions among variables are taken into account). Typically, simulation models are stochastic and dynamic.[50]

1.8.2 Simulation

A simulation of a system is the operation of a model of the system. The model can be reconfigured and experimented with; usually, this is impossible, too expensive or impractical to do in the system it represents. The operation of the model can be studied, and hence, properties concerning the behavior of the actual system or its subsystem can be inferred. In its broadest sense, simulation is a tool to evaluate the performance of a system, existing or proposed, under different configurations of interest and over long periods of real time.[50]

1.9 OBJECTIVES OF THE PRESENT STUDY

The present investigation is based on the following objectives.

a. Comminution of the silicon carbide powder in high energy ball mill.

b. Mechanical alloying for preparation of Ti6Al4V alloy.

c. Fabrication of Nano Silicon carbide reinforced titanium alloy metal matrix nanocomposites with different weight percentage (10, 15 & 20% of nano-SiCp) by powder metallurgy.

d. Thermal analysis of Ti6Al4V alloy and Ti6Al4V/SiCp nanocomposites to explore the stability and behavior of these materials for property development.

e. Study of specific heat property of Ti6Al4V alloy and Ti6Al4V/SiCp nanocomposites in differential scanning calorimeter (DSC).
f. Study of coefficient of thermal expansion of Ti6Al4V alloy and Ti6Al4V/SiCp nanocomposites in thermomechanical analyzer (TMA).

g. Effect of addition of nano-SiCp in different volume fraction sizes with Ti6Al4V alloy on thermal behavior.

h. Development of Micromechanical modeling by finite element method using ANSYS to study the thermal properties like specific heat capacity and coefficient of thermal expansion of Ti6Al4V alloy and Ti6Al4V /Nano-SiCp composites.

i. Validation of experimental data and with the finite element results of Ti6Al4V alloy and Ti6Al4V / Nano-SiCp composites.

Summary

The present study is focused on Fabrication of Nano Silicon carbide reinforced titanium alloy metal matrix nano composites with different weight percentage (10, 15 & 20% of nano-SiCp) by powder metallurgy and to study the thermal behavior of Ti6Al4V alloy and Ti6Al4V/nano-SiCp composites materials to explore the stability and behavior of materials for property development. The techniques include Differential scanning calorimetry (DSC) and Thermo mechanical analyzer (TMA).