

## INTRODUCTION AND LITERATURE REVIEW

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### 1.1 Surface Engineering

Engineering components interact with the environment and other engineering components primarily through their respective surfaces. Surface properties often dictate the lifetime, quality, and performance of the component and lead to the production of novel materials or materials with novel properties. For this reason, surface engineering is of considerable importance and has been the focus of extensive research investigation for the last few decades. The simplest definition of surface engineering is "The modification of a component surface to achieve a combination of properties in both the surface and the underlying bulk which may not be achieved otherwise (Seal and Dahotre, 2004)." The motivation for surface engineering or surface treatment may be the generation of components with improved durability or enhanced tribological properties or better anti-corrosion behavior.

Surface engineering may be imparted through various mechanisms. One such mechanism is to modify the microstructure of the surface layer and thereby bring about property changes (e.g. flame/induction hardening, carburizing, nitriding, etc.). Another mechanism might be to alter the shape or texture of the surface (e.g. surface texturing). Similarly, surface treatment could also be effected through the application of a layer of material over the component surface, the process generally referred to as coating.

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## 1.2 Classification of Surface Engineering Processes

Surface Engineering involves the tailoring of surface dependent engineering properties of a component. As an example, the surface properties of an engineering component may be modified for the betterment of its tribological performance. The surface engineering techniques may be divided into three basic categories (Shipway and Mellor, 2006).

1. Modification of surface microstructure without altering the chemical constitution.
2. Modification of surface microstructure and composition.
3. Application of new material to the surface - generally referred to as coating processes.

### 1.2.1 Modification of surface without altering the chemical constitution

A number of processes belong to this category of surface engineering. They can be subdivided as follows.

**1.2.1.1 By heating:** Transformation hardenable alloys, in particular, carbon steels, low alloy steels and cast irons, can be hardened (for improved wear properties) using flame, induction, laser or electron beam techniques. Here, instead of heating the whole component (as in through hardening), only the surface is heated, so that the bulk properties, specifically the toughness, remain unaffected, and component distortion is minimized. These processes produce parts which must be post ground to size and to provide a good surface finish.

**1.2.1.2. By mechanical working:** Several cold working processes, performed on the surface by peening, shot blasting or other specialized mechanical working processes, may produce deformed layers which increase the stored energy and compressive stress, thereby increasing the hardness, fatigue and stress corrosion resistance.

### 1.2.2 Modification of surface by altering the chemical constitution

**1.2.2.1 Thermochemical diffusion treatments** introduce interstitial elements, such as carbon, nitrogen and boron, or combinations of carbon and nitrogen, into a ferrous

metal surface at elevated temperatures. However, the processes are not confined to interstitial diffusion; metallic substitutional elements or metalloids are used in processes such as chromising, aluminising and siliconising.

**1.2.2.2 Electroplating and thermal diffusion treatments**, when used in combination, are included in this category. One process involves the electrolytic deposition of tin onto ferrous materials. This is followed by a diffusion treatment at 400 - 600 °C to form Fe/Sn compounds which resist scuffing and confer some corrosion resistance. Bronze coatings may be developed in a similar way to add a bearing surface to a steel substrate.

**1.2.2.3 Anodizing treatments** for aluminium alloys produce oxide layers which reduce adhesive wear and are significantly harder than the substrate. In this case, a layer of oxide up to 500 µm thick is produced.

**1.2.2.4 Parkerizing** (also called phosphating and phosphatizing) is a method of protecting a steel surface from corrosion and increasing its resistance to wear through the application of an electrochemical phosphate conversion coating. They are effective in reducing galling and scuffing. All phosphate coatings absorb oil and grease, thereby assisting 'running-in' by preventing adhesive wear and fretting.

### **1.2.3 Application of new material to the surface**

There are numerous processes which involve coating with a layer of material, not necessarily metallic, to meet specific service requirements. Depending upon the underlying mechanism of coating formation, processes of deposition of coatings are divided into four main groups.

**1.2.3.1 Coatings deposited in solid state:** Here the substrates are coated or clad with a material which remains in the solid state. These include the following.

- Explosive welding
- Cold-gas dynamic spraying
- Friction surfacing

**1.2.3.2 Coatings deposited in the liquid state:** In this process, coatings are applied in the liquid state (or a mixed liquid-solid state). Immediately after this the

solid coating is formed either by solidification from the melt or by evaporation of a solvent or carrier. Most wear resistant coatings in this category are applied in the molten or semi-molten state. The coating processes coming under this category are as following.

- Thermal spraying
- Weld hard-facing
- Laser cladding

**1.2.3.3 Coatings deposited from solution by reduction of ions:** Deposition of coatings is possible by the reduction of metallic (or complex) ions, normally in an aqueous solution, to form metal ions. On conducting this reaction at surface, the metal atoms build up to form a coating. There are two main methods for this reduction of ions.

- Electrodeposition
- Electroless deposition

**1.2.3.4 Coatings deposited from a vapour:** This technique is broadly divided in to two main methods as following.

- Physical vapour deposition
- Chemical vapour deposition

### **1.3 Lasers in Surface Engineering**

LASER is the acronym for light (L) amplification (A) by the stimulated (S) emission (E) of radiation (R). Laser is a coherent, collimated and monochromatic beam of light energy. A high power laser (typically in the range of kW) can be focused to attain a power density sufficient to melt metals and refractory materials. This property of the laser makes it an appropriate tool for surface engineering applications. This is further enhanced by the fact that the delivery of laser energy to a surface is extremely flexible and can be directed with high precision.

Originally, nearly all laser surface engineering applications were conducted with the help of CO<sub>2</sub> or continuous wave (CW) Nd-YAG lasers, but with the advent of the fiber (Lee *e. al.*, 2009) and diode lasers (Pashby *et al.*, 2003), a wider horizon in the

scope of laser surface engineering is envisaged. These lasers have the added advantage that their beams can be delivered by way of optical fibers.

Laser surface engineering offers a number of advantages over other surface engineering processes, like short processing time, localized treatment, precision in operation, low thermal distortion, precise control of treatment depth, ability to process complex shapes etc.

Some surface engineering applications involving lasers are listed as follows (Chattopadhyay, 2004):

- Laser transformation hardening
- Laser shot peening
- Glazing, homogenization, refining and polishing
- Laser Cladding
- Laser direct metal deposition (DMD) for component repair
- Modification of material surface by selective and controlled movement of melted material.
- Laser surface melting
- Laser surface ablation
- Laser assisted vapor deposition process
- Laser spraying
- Laser surface alloying

Typical industrial applications of laser surface engineering include:

1. Automotive:

- Hardening and cladding of engine cam shafts and valve seats
- Hardening of cutting and bending edges on press tools involved in manufacture of automotive parts
- Surface modification for various tribo-components

2. Aerospace:

- Repair and cladding of turbine blades
- Hardening of bearing surfaces on rotating shafts
- Promotion of adhesion between metallic and composite joints

### 3. Power Generation

- Hard-facing of steam turbine blades

### 4. Oil and Gas:

- Hardening and cladding of various parts of pumps, valves and tubular components

CO<sub>2</sub>, diode, Nd:YAG and fiber lasers are suitable for surface engineering applications because of their ability to achieve high power levels. Precise manipulation of the laser beam is possible with the help of immaculate optical modules, optic fibers, beam collimators or articulated arm robots. Laser can be integrated with multiple axis CNC worktables for better maneuverability of the work piece.

Selection of the appropriate laser for a particular application is of extreme importance in surface engineering. Factors like efficiency of laser, maximum power, spot size and shape, intensity distribution in laser beam, wavelength, absorption of laser beam by target material, maintenance requirements and cost influence the decision making process.

In the present work, the carbon-di-oxide laser and the diode laser have been made use of for laser surface alloying applications. Some of the important advantages and disadvantages of these lasers are listed below:

#### **1.3.1 Advantages and disadvantages of CO<sub>2</sub> and Diode laser**

##### **1.3.1.1 CO<sub>2</sub> lasers:**

Advantages:

- Ability to deliver high power levels at continuous wave mode
- High efficiency compared to those of gas lasers (Nd-YAG, Nd-glass etc)
- Low expenses needed to purchase, operate and maintain
- Excellent beam coupling characteristics to non-metallic materials
- Higher processing speed compared to those of other surface engineering processes
- High linear power density
- Capable of step-heating with special lenses

Disadvantages:

- Inability to achieve extremely small focal spot size due to high value of wavelength (10.6  $\mu\text{m}$ )
- Higher wavelength range results in poor absorption of laser energy by metallic materials
- Requirement of complex and expensive optical system to achieve uniform intensity distribution in laser beam cross-section

#### **1.3.1.2 Diode lasers:**

Advantages:

- High efficiency (~30 - 50%) compared to the conventional high power CO<sub>2</sub> and Nd-YAG lasers
- Uniform intensity distribution in laser beam cross-section
- Lower wavelength range 808 - 940 nm resulting in higher absorption of laser energy by metallic materials compared to considerably lower absorption in case of higher wavelength lasers like CO<sub>2</sub> lasers
- Compactness and portability, permitting easy relocation in work space and manipulation by robots
- Delivery of beam possible to remote work place by means of optic fiber
- Lower maintenance and cooling requirements (Maintenance-free period ~10000 h)

#### **1.3.2 Parameters affecting quality of laser surface engineering processes**

The thermal processes taking place at the surface of a part exposed to laser radiation depend on the laser power density (intensity), its distribution and the time of exposure of the surface to laser irradiation. The power density of a laser beam at a point on the material surface is controlled by focusing or defocusing of the incident beam on the material surface. Depth of heated or remelted layer for a given laser power density and distribution depends mainly on the exposure time. In case of a laser scanning a material surface, the laser spot size, its shape, the intensity distribution and the scanning speed of the laser define the exposure of the surface to laser radiation. Hence, for a given laser spot size, shape and intensity distribution, the laser power and

scanning speed are factors of significance that may affect the quality of surface treatment.

In laser surface treatment, the intensity distribution of the laser should ideally be uniform (referred to as ‘top hat’ intensity distribution in literature) and the shape of the spot should be rectangular, with the scanning direction perpendicular to the longer side of the rectangular spot. The intensity of a laser beam in the fundamental mode (TEM<sub>00</sub>) has a Gaussian distribution and hence is not appropriate for all surface engineering applications. Higher power lasers generally have a multimode structure and the intensity distribution can be of different types. However, uniform intensity distribution can be obtained in CO<sub>2</sub> and Nd-YAG lasers by the use of complex and expensive focusing systems (Kennedy *et al.*, 2004).

In comparison, high power diode lasers (HPDL), with a uniform intensity distribution (Kennedy *et al.*, 2004) and rectangular spot shape, are specifically suited for surface engineering applications. With the use of simple optics, the spot shape can be elongated to create wider scanning track of laser during surface treatment. This reduces the processing time of the surface provided that the power density remains sufficient for the particular operation.

### 1.3.3 Process description for some laser surface engineering techniques

Some of the laser surface engineering techniques are mentioned below:

**1.3.3.1 Laser heat treatment (LHT)** includes operations conducted using the laser beam as the source of energy needed for heating the surface layer of the processed material to change its structure for obtaining relevant mechanical, physical, or chemical properties and thus improving service life of the processed element. (Steen, 1998; Kusin'ski, 2000; Dobrzan'ski, *et al.*, 2003; Dutta Majumdar *et al.*, 2003; Dobrzan'ski *et al.*, 2005; Adamiak *et al.*, 2008).

**1.3.3.2 In case of Laser surface hardening** (Basu *et al.*, 2007), a high power laser performs fast scanning of the part surface. The fast heating by the moving laser gives rise to high cooling rates that result in a fine grained structure. This improves hardness and wear resistance. Surface hardening by laser gives a component the ability to resist wear, erosion, fatigue and corrosion. In case of iron base alloys, laser energy is employed to heat the surface above the austenite transformation



temperature. Rapid quenching associated with laser heating transforms the austenitic phase to martensite at the surface. In laser hardening, heating rates of  $10^3$  °C/s are common with high cooling rates of around  $10^4$  °C/s. The fast quenching rate is the result of the conduction of the heat to the cold surrounding bulk material due to extremely high thermal gradients resulting from laser heating.

Lasers offer the possibility of selective heat treatment of metal parts, where the working surfaces can be selectively and rapidly heated with laser and hardened without appreciably affecting the properties of the remainder of the part.

**1.3.3.3 In surface hardening by laser particle injection**, the surface of the substrate material is melted by a high-power scanning laser beam with simultaneous addition of hard, wear resistant particles (e.g. carbides) to the melt pool (Ocelik *et al.*, 2005; Rabitsch *et al.*, 1994). The short interaction time retains the carbides in solid state. The method is suitable for impregnation of materials which have poor wear resistance e.g. aluminium and titanium alloys.

**1.3.3.4 Pulsed laser deposition (PLD)** is a deposition process employing a pulsed laser in the nanometer wavelength range to ablate material from a target which is then deposited onto a substrate (Zergioti *et al.*, 1998; Cherukuri *et al.*, 2002). The whole process is carried out in vacuum. PLD can be used to deposit a wide range of materials from polymers to metals. PLD is not appropriate at present for large area deposition but is characterised by smooth, dense deposition of phases with correct stoichiometry. The process can achieve high rates of deposition and good adhesion of coating to substrate even at low substrate temperatures.

**1.3.3.5 Laser cladding** is the fusion of a material layer onto a substrate surface with minimum melting of the surface (Meng *et al.*, 2006; Xu and Liu, 2006). This is done with minimal heat input that also results in a small heat affected zone. The aim of cladding operations is generally to overlay one metal with another, producing a sound interfacial bond. Laser cladding enables a low dilution of the clad layer with the bulk material combined with a metallurgical bonding between the layer and the substrate.

There is a small zone of base material that does get melted with the clad and creates a metallurgical bond. This is in contrast to other cladding processes like thermal spraying where the material to be clad is literally sprayed onto the surface resulting in lack of proper bonding between the two layers.

A major benefit of laser cladding over conventional arc welding is that the thermal input can be precisely controlled, thus yielding minimal dilution and a small heat affected zone. This lower amount of heat input prevents distortion of base material and the properties of base material are not detrimentally affected.

**1.3.3.6 Laser can also be used to initiate SHS (Self-propagating High – temperature Synthesis) reaction** (Barzykin, 1992) like other heat sources, e.g., electric arc, electric filament etc. SHS is capable of producing fine grained reaction products of high purity. Inclusion of those pure and fine phases into the coating by subsequent laser surface alloying (LSA) may produce a coating with superior mechanical properties. By combining LSA and SHS, it may be possible to utilize the advantages of both processes.

#### **1.3.4 Laser surface alloying (LSA)**

Laser surface alloying is another surface engineering technique, and it is the subject of investigation in the present work. It is a laser assisted surface engineering technique that involves melting of a pre-/co-deposited layer of alloying element(s) along with a part of the underlying substrate leading to the formation of an alloyed zone confined to a very low depth from the top surface within a very short interaction time (Dutta Majumdar and Manna, 2003). The primary advantage of LSA over conventional coating deposition is that novel microstructures can be produced due to inherent rapid solidification and high concentration of key elements at or near the surface. Coatings having such microstructures cannot generally be developed by conventional means since metastable phases or extended solid solutions, which are characteristic of the rapid solidification rates, cannot be easily obtained. In addition, the coatings are metallurgically bonded to the substrate and their microstructures can be graded during processing to reduce thermal stress gradients occurring due to the thermal expansion mismatch between the coating and the substrate (Pei *et al.*, 2000). Since the microstructures as well as the compositions of the coatings strongly depend on the degree of mixing (dependant on convection and diffusion) and the cooling rates during liquid-to-solid and solid-to-solid phase transformation, the parameters controlling these mechanisms are of paramount importance to the laser surface alloying process (Komvopoulos and Nagarathnam, 1990).

Various publications have so far reported many favorable properties obtained by LSA. Pierantoni *et al.* (1989) reported improvement in hardness and excellence in surface smoothness through LSA. Pelletier *et al.* (1991) tried to correlate the microstructures with the solidification conditions in a LSA process. Molian (1983) described the characteristics of fusion zone defects, like porosity, cracks and irregular boundaries introduced by laser surface alloying applications. Tassin *et al.* (1996), Man *et al.* (2007), Zum Gahr *et al.* (1995) and many others have studied the improvement in wear resistance through the LSA route. Draper *et al.* (1981) found LSA effective in the passivation of titanium against corrosion. Watkins *et al.* (1997) have reported an account of the enhancement in anti-corrosion performance of Al and its alloys by the LSA technique.

#### **1.3.4.1 Laser surface alloying with preplaced powder**

Popular techniques like laser cladding, laser particle injection for the production of hard ceramic coating over metal substrates, encounter problems arising due to the difference between the melting temperatures of the hard ceramic phases and the metal substrates. Laser irradiation causes excessive melting of metal substrate as the ceramic materials require much higher temperature for melting. Apart from this, poor absorption of laser energy also causes low efficiency of energy usage. These difficulties might be solved, at least partially, by the powder preplacement method instead of powder injection in introducing the added material for alloying or cladding. The preplaced powder layer has considerably higher absorption of laser energy than a bulk material because of a less densely packed structure with a high proportion of inter-particle spaces. In addition, the powder layer has a low thermal conductivity, again due to its porous structure, so that most of the laser energy is deposited in the layer, ensuring that excessive melting of the substrate does not occur (Man *et al.*, 2007; Tam *et al.*, 2002). Apart from these, this technique provides the most economical way of producing coatings from tailor-made composition as the precursor powders can be mixed directly in the right proportions and applied onto the substrate to make the green coating.

This is the simplest method provided the powder can be made to remain in place until melted, while the area is shrouded by an inert gas. Some form of binder is usually used. The preplaced powder method involves scanning the laser beam over the surface covered with the layer of preplaced powder. The general theory for cladding

of pre-placed powder, according to Powell *et al.* (1988), is as follows. At ambient temperature, a layer of solid metal powder (of known depth, density and composition) rests on a substrate (of known composition). Laser irradiation heats up the surface powder particles and the majority of this heat is assumed not to conduct to the particles below because of low level of inter-particle contact (i.e. the bulk of the powder is assumed to act as an insulator). The insulated, irradiated particles melt and in the molten state conduct heat to neighboring particles experiencing wet contact (i.e. the powder layer  $> 2R_p$  distance from the molten front is an insulator, where  $R_p$  is the particle radius). The molten front progresses through the insulating powder layer. This process is faster in vertical direction than in the horizontal direction because the liquid flow is gravity assisted. Contact is ultimately established between the molten front and the substrate. Kim *et al.* (2000), Lusquinos *et al.* (2005) and many others have followed the idea.

There are some problems associated with the LSA technique. One is that of binder materials, introducing contamination and gas porosity in the alloyed layer. Secondly, this technique is limited to flat surfaces, unless some deposition techniques like PVD, electroplating or thermal spraying be employed to deposit the precursor powder on uneven surfaces. Preplacement of precursor powder mixture onto the substrate surface without binders does not generally produce good results as the powder mixture may get blown off the substrate surface due to shroud gas flow and gas evolution during laser scan. Laser alloying, followed by laser post-treatment (glazing) can make necessary correction in terms of porosity and unevenness of the coating.

### **1.3.5 Laser post treatment or laser glazing**

Laser post treatment is a very effective technique for improving surface quality and is also of relevance to the present investigation. It can be used to densify the topmost layer of the coating and thus increase its top hardness and seal it against penetration by corrosive agents. The process of laser surface melting was first described in 1976 (Hetzner, 1998). When a shallow skin of material is laser melted, the rapid self-quenching of materials due to very high cooling rates could lead to a range of microstructures encompassing amorphous metallic solids through very fine dendritic structures. Today the process is also referred to as laser glazing.

One major advantage of laser glazing is that the refined structure is created at or near surface where high load carrying capacity is required.

On the other hand, high-power laser beam may be used to melt the top layer of the surface, followed by rapid cooling leading to formation of refined microstructure with improved properties. The principle advantage of laser post-treatment is that it alters microstructures without changing the composition and provides a smooth, dense top layer. Dutta Majumdar and Manna (2010) reported the improvement of wear and corrosion resistance of steel and magnesium-based alloys by laser surface melting.

#### **1.4 Self-propagating High-temperature Synthesis (SHS)**

A short discussion on Self-propagating High-temperature Synthesis (SHS) is included here due to its relevance to the present investigation. SHS is a technique that leads to the *in-situ* formation of compounds from reactant substances through exothermic reaction (Subrahmanyam and Vijayakumar, 1992; Borovinskaya, 1992; Merzhanov, 1995; Morsi, 2001; Moore and Feng, 1995; Yang *et al.*, 2004). It generates sufficient thermal energy to sustain in the form of a reaction (combustion) wave through the extent of the reactants. The wave travels through the reactants, completely converting them to the final product. The temperature of the combustion wave and the speed of propagation of the reaction can be very high ( $\sim 5000$  K, 25 cm/s respectively). This process offers an opportunity to investigate reactions taking place at extremely high thermal gradients (as high as  $10^5$  K/cm). SHS provide an attractive, energy-efficient approach to the synthesis of simple and complex materials including solid solutions, composite materials, and metastable phases.

The specialty of this process is the conversion of chemical energy to thermal energy and once triggered, no further externally applied energy is necessary. Although such reactions are highly exothermic to be self-sustaining, they cannot self-initiate without the addition of external energy. For initiation of SHS reaction, it is required to heat one end of the sample either by thermal radiation or through the use of laser energy or by any other heat source. In order to ensure that the reaction would not get extinguished due to heat losses to the surroundings, the rate of heat dissipation (via conduction, convection or radiation) must be less than the rate of heat generation.

The products are generally of high purity due to volatilization of impurities (Tjong *et al.*, 2000; Daniel *et al.*, 1997).

SHS can be a very good process for the formation of nanocrystalline particles. Nersisyan *et al.* (2005) reported the synthesis of nano-tungsten powder in the range of 20-200 nm through molten salt-assisted SHS process. Laser assisted or laser triggered SHS has also been investigated by some researchers (James, 1990; Shilyeav *et al.*, 1994; Slocombe and Li, 2001).

In the present work it has been attempted to combine the two abovementioned phenomena of Laser triggered-SHS and Laser surface alloying. The reasons for selection of this specific combination are:

1. Possibility of formation of highly dispersed, nanoparticulate powder mixtures as SHS reaction products (and starting phases for laser alloying).
2. Formation of fine and pure powders of hard substances *in-situ* through SHS – which get incorporated as reinforcements into substrate surface by laser melting of substrate.
3. Chemical inertness of the products of SHS towards each other at subsequent high temperatures attained during laser alloying

### **1.5 Composite Materials and their Classification**

Composite materials represent a group of materials that consist of a discrete constituent (the reinforcement) distributed in a continuous phase (the matrix). Composite materials derive their distinguishing characteristics from the properties and behavior of their constituents, from the geometry and arrangement of the constituents, and from the properties of the boundaries (interfaces) between the constituents. The present investigation reports the development of a coating which is a composite with multi-component reinforcements. Hence, a short discussion on composites would be extremely relevant to the investigation reported.

Composites can be classified as follows.

1. Classification on the basis of the nature of the continuous (matrix) phase:
  - Polymer-matrix composites
  - Metal-matrix composites

- Ceramic-matrix composites
  - Intermetallic-matrix composites
2. Classification on the basis of the nature of the reinforcing phase:
- Particle reinforced composite,
  - Fiber reinforced composite,
  - Dispersion strengthened composite,
  - Laminated composite etc.

The properties of the composite can be tailored, and new combinations of properties can be achieved. It is usually sufficient, and often desirable, to attain a certain minimum level of reinforcement content in a composite to achieve or preserve many of the useful properties of the matrix. Other factors, such as the size, shape, distribution of the reinforcements, and properties of the interface, are also of significance.

The performance of ceramic-matrix composites (CMC) surpasses those of metal-matrix and polymer-matrix composites (MMC and PMC respectively) at elevated temperatures. There is considerable amount of interest in the development and testing of advanced ceramic composites based on oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ), nitrides (TiN,  $\text{Si}_3\text{N}_4$ , BN, AlN), borides ( $\text{TiB}_2$ ,  $\text{ZrB}_2$ ,  $\text{HfB}_2$ ), carbides (SiC, TiC), glass and glass-ceramics for a number of applications.

The strength of a composite is largely dependent on its structure; structural defects, brittle reaction layers, stress concentration, dislocation pileups, grain structure and texture. The strength also depends to a large extent on the size, distribution and spacing between the reinforcements; inhomogeneous distribution of the reinforcements lowers the strength.

Nanocomposites can be considered as solid structures with nanometer-scale dimensional repeat distances between the different phases that constitute the structure. These materials typically consist of two or more phases in some combinative form with the constraint that at least one of the phases or features is in the nanosize range. In general, nanocomposite materials can exhibit different mechanical, electrical, optical, electrochemical and structural properties than those of each individual component.

Interfaces play an important role in enhancing or limiting the overall properties of the composite. Due to the high surface area of nanostructures, nanocomposites present many interfaces between the constituent intermixed phases. Special properties of nanocomposite materials often develop from interaction of its phases at their interfaces. A noninteracting interface serves only to create weak regions in the composite, resulting in no enhancement of its mechanical properties. In contrast to nanocomposite materials, the interfaces in conventional composites constitute a much smaller volume fraction of the bulk material.

Processing plays an important role in the fabrication of nanocomposites with optimized properties (Ajayan *et al.*, 2003). Some examples of commonly used processes for creating nanocomposites are listed below.

- Nanocomposites by Mechanical Alloying
- Nanocomposites from Sol– Gel Synthesis
- Nanocomposites by Thermal Spray Synthesis
- Nanocomposites by SHS

### **1.5.1 Development of composites by *in-situ* and *ex-situ* routes**

The term “*in-situ* composite” is applied to those where the reinforcements of a composite are synthesized from their respective precursors or parent phases during composite fabrication by controlled melt growth, chemical reaction, transformation and deformation (Daniel *et al.*, 1997). This contrasts with *ex-situ* composites where the reinforcement(s) are synthesized separately and then inserted into the matrix through a secondary process such as infiltration or powder processing. *In-situ* composites have a number of advantages over conventional (*ex-situ*) composites as they avoid complicated additional steps in the process such as sorting, alignment, infiltration and sintering. These make the *in-situ* composites more cost-effective. The interfaces produced between reinforcement and matrix are relatively stable and most significantly, free of impurities. The mechanical strength of the *in-situ* composite is also found to be considerably higher than that of the *ex-situ* composite. Zuhailawati and Yong (2009) observed significant differences in the distribution and particle sizes of *ex-situ* and *in-situ* composites. *In-situ* composites have much finer particulates with better homogeneity in distribution. *Ex-situ* composites show the presence of gaps and



porosity suggesting poor adhesion between matrix and particulate interfaces. Tjong *et al.* (2003) showed the agglomeration of ceramic particulates during processing of *ex-situ* composites, leading to the formation of composites with poor mechanical strength and toughness.

There has been significant utilization of the *in-situ* route in the development of composite coatings for the associated mechanical and metallurgical advantages. However, substantial amount of investigation has also been carried out in developing CMC coatings with *ex-situ* reinforcements (Uenishi and Kobayashi, 1999; Xue *et al.*, 2009). The present work has investigated the relative merits and demerits of both these routes for the production of a nanocomposite coating.

## **1.6 Introduction to Wear**

Wear resistance is the ability to resist gradual loss of material from the surface of a material by the action of another surface in contact with it. Wear resistant coatings are frequently applied on material surfaces undergoing relative motion with other surfaces. In the present investigation, a coating has been developed with a view to impart high wear resistance to the substrate material. In order to understand and evaluate the wear resistive capability of the protective coating, it would be relevant to discuss in short the phenomenon of wear and wear resistance of materials.

### **1.6.1 Classification of wear: generalized approach**

There is no generalized rule that can be globally applied to all tribological phenomena for the prediction of the amount of wear from engineering surfaces over a given period of time. This is due to many factors those affect wear and the many mechanisms that cause wear. Wear can broadly be classified in three apparent ways. First one is by the observation and study of the visual aspects of the wear scar e.g., pitting, spallation, scratch, fretting, scuffing etc. The second one is by considering the physical mechanisms of material removal and damage like adhesion, abrasion, delamination etc. The third way is by studying the wear environment, e.g., lubricated or unlubricated wear, sliding wear, rolling wear etc. These classifications help the understanding of the behavior of any engineering component by means of extrapolating experience gained in one wear situation to a newer one.

A vital requirement for wear resistant engineering part may be a hard surface on a strong but tough base. This requires enhancement of certain properties of the surface of a component independently from those of its bulk. Resistance to wear being one of the most important of such properties, demands better understanding of the working environment, the type of service the part is going to deliver and most importantly, the possible ways in which it is going to get worn out or damaged. The four basic mechanisms causing wear are the following.

#### **1.6.1.1 Adhesive wear**

Asperities of one surface, while coming into contact with asperities of the counter surface, may adhere strongly to each other and form asperity junctions. Tangential motion of the surfaces causes separation of these junctions from the bulk of the weaker asperities and material is removed. In adhesive wear, the surface material properties, as well as possible protective surface films or contaminants and the atmospheric humidity play important roles. In failure modes like scuffing and seizure the role of adhesive wear is very important.

#### **1.6.1.2 Abrasive wear and asperity deformation**

Abrasive wear occurs in contacts where one of the surfaces is considerably harder than the other or where hard particles are introduced into the contact. The harder surface asperities are pressed into the softer surface which results in plastic flow of the softer material around the harder one. When the harder surface moves tangentially, ploughing and removal of softer material takes place resulting in grooves or scratches on the surface. Depending on the geometry of the harder surface and the degree of penetration, the removal of material can take different forms, such as ploughing, wedge formation or cutting. A distinction is often made between two-body and three-body abrasive wear, where the latter refers to situations in which hard particles are introduced between the moving surfaces.

A collision of two asperities results in plastic deformation or breakage of one or both of the asperities leading to material removal from the asperities. Asperity deformation is due to the roughness and waviness of the contacting surfaces. Sliding contacts deforming the surface plastically cause large plastic strains and strain hardening in the surface. The plastic deformation changes the near-surface microstructure so as to

make it resistant to shear. This leads to the transfer of pieces of material and elements from the surrounding to produce an ultra-fine-grained transfer film.

### **1.6.1.3 Fatigue and delamination wear**

Fatigue crack growth results from repeated loading and unloading of a surface, at a stress level lower than its ultimate strength. Fatigue can initiate large-scale cracking and may result in the liberation of surface material in the form of wear debris. At the points of concentrated contact, the Hertzian pressure at the surface creates a stress field beneath the contact zone where the maximum shear stress occurs at about one-third of the contact length beneath the surface in the case of pure rolling but is closer to the surface with increasing traction. In rolling, where the stress field moves repeatedly over the surface, fatigue of the near-surface material takes place. Material voids or dislocation pile-ups may form the nuclei for the first crack to occur. After that the crack will often propagate quite rapidly, unite with other cracks and liberate surface material. This often results in large craters in the surface. Delamination wear is a kind of fatigue wear that occurs on a more microscopic scale in sliding contacts when surface asperities repeatedly slide over each other. Small cracks are nucleated below the surface. Crack nucleation very near the surface cannot occur, due to the triaxial state of compressive loading which exists just below the contact region. Further loading and deformation causes cracks to extend, propagate and join with neighboring cracks. The cracks tend to propagate parallel to the surface, resulting in the delamination of long and thin wear sheets. In a reciprocating fretting wear contact, delamination by formation of parallel subsurface cracks and plate-like wear debris is one of the major wear mechanisms.

### **1.6.1.4 Chemical wear**

Chemical wear occurs due to detrimental chemical reactions in the contact, initiated by the influence of the environment in combination with mechanical contact mechanisms. Rubbing, in combination with the chemical reactions in the contact, results in removal of material and wear debris formation. The rubbing action results in increased temperatures at the surface and creates surface cracks which are favorable for further chemical reactions to occur. On the other hand, the chemical reactions at the surfaces may render them softer and weaker and thus decrease their resistance to new crack formation and liberation of surface material in the form of wear products.

Oxidation wear is the most common chemical wear process. A thin layer of oxides will be formed on metal surfaces. This is an important protective layer because without it both the friction and wear in metal contacts would be extremely high. If this layer is continuously removed by rubbing action and the contact is exposed to a humid environment, the formation of new oxide layers is speeded up and the result is typical oxidation wear. In certain cases wear can be due to chemical instability of the materials. Such phenomena are often found to occur in metal cutting processes where the chip moves rapidly along the tool surface. Temperatures at the interface can be well over 700 °C and the underside of the chip is freshly generated and may be partly molten. This process can result in two kinds of wear due to chemical instability. One is the solution wear due to dissolution of the tool material in the chip. The other is the diffusion of elements from the tool material into the chip, leading to weakening and ultimate failure of the cutting tool body

### 1.6.2 Classification of wear: Velocity accommodation approach

A different approach for the classification of wear mechanisms is the velocity accommodation approach. There are four basic mechanisms by which the velocity difference between two surfaces in relative motion is accommodated; namely: elastic deformation, fracture, shear and rolling. These basic mechanisms may occur in either of the two surfaces (first bodies) or in the layer between them (third body). The major advantage with this approach is that the fundamental tribological mechanisms are simplified to well-known mechanisms of material behavior that can be characterised by properties such as Young's modulus, fracture toughness and shear strength.

The different types of wear or wear failure modes describe a certain combination of wear mechanism with well-defined regular process of material removal that corresponds to a particular range of contact conditions (Holmberg *et al.*, 1994). The most common wear failure modes are:

1. **Fretting:** It occurs in case of short amplitude reciprocating, sliding motion between contacting surfaces, sustained for a large number of cycles. It results in two forms of damage: surface wear and deterioration of fatigue life.

2. **Pitting:** Pitting wear is due to surface failure of a material as a result of stresses that exceed the endurance (fatigue) limit of the material. Majority of pitting cracks initiate at or near the surface (Jiajun *et al.*, 1990).
3. **Scuffing and scoring:** The mechanism of material removal in scuffing and scoring is generally considered to be adhesive wear. It is opposite to pitting. It is the surface damage resulting from localized welding of rubbing surfaces of the mating elements with subsequent fracture in relative motion which does not result in immobilization of the parts (Budinski, 2007).
4. **Spalling:** Spalling is a phenomenon where friction and direct impact between mating components results in the creation of small flecks of metal. Mechanical spalling occurs at high stress contact points, for example, in a ball bearing. Spalling occurs where the maximal shear stress occurs not at the surface, but just below it, shearing the spall off.
5. **Galling:** Galling is a severe form of adhesive wear characterised by the formation of excrescences — macroscopic protuberances generated by adhesion between the rubbing surfaces. Excrescences result from localized solid-state welds between the rubbing surfaces. When galling occurs in sliding systems with very little running clearance, it can lead to seizure.
6. **Cavitation:** Cavitation is the erosion caused due to the collapse of entrained bubbles in a liquid. The collapse of bubbles forms energetic jets of the liquid impinging on the surface with extremely high local pressure.
7. **Solution wear:** It takes place due to dissolution of one material into another. This type of wear may take place in the tool material in a machining operation.
8. **Diffusive wear:** When there is intimate contact between the atoms of surfaces in contact with a high interface temperature, significant diffusion of chemical elements from one body to another can occur. In this situation, there is almost the perfect contact between the mating surfaces (e.g., tool and the metal chip) due to the extreme contact stresses and very high temperatures, reaching 700 °C or more. Diffusion wear is essentially a transient process. Diffusion wear is characterised by a smooth worn surface with no plastic deformation.

9. **Galvanic wear:** When two dissimilar metals are in contact with each other in a conductive solution (electrolyte), the more electropositive metal shall get corroded while the cathodic metal remains unaffected. For a metal pair in such a solution, the metal with anodic solution potential shall undergo accelerated galvanic wear.
10. **Melt wear:** Tribological properties of materials with low melting points are often governed by frictional heating effects. When the normal load or sliding speed between two mating surfaces increases to a high level, melt wear process appears.

Minimization of wear can lead to significant saving in the costs of replacement of worn machine components. Ceramic materials, owing to their high hardness and chemical inertness, have received considerable attention for their high resistance to wear, corrosion and high temperature oxidation. The high cost in production and their brittle nature, however, restricted the application of ceramics in industry for an extended period of time. Presently, various techniques of strengthening of ceramics in terms of toughness are established and well in practice. Ceramic coatings onto materials which are cheap and reliable in shock, such as steel, are widely employed. The ceramic coating serves as an anti-wear layer and the steel substrate acts as a shock-resistant support. One important and upcoming process for ceramic coating is laser surface alloying (LSA), since a coating of sufficient thickness and with low amount of porosity can be obtained. For proper evaluation of the application of a ceramic coating as a wear resistant coating, a comprehensive tribological investigation is required.

### 1.6.3 Time dependent behaviour of wear

A close look at the wear patterns of coatings with respect to time or sliding distance can give the idea of the development of a period of stable wear behavior after some initial wear has taken place. A period of stable wear behavior is one in which there is a stabilization of wear mechanisms. Typically, in such situations, the apparent contact area does not change with wear; this is also a period of lower and constant wear rate, after an initial period of higher and changing wear rate. In such situations, the initial period is usually referred to as break-in. Break-in behavior results from surface and

near-surface changes as a result of relative motion and wear and the emergence of different mechanisms. With nominally conforming contacts, there can be an apparent break-in period when a linear wear measure is used, such as scar depth or width. In this case, the depth wear rate decreases as true conformity is established by wear, even if there is no other change occurring. The morphology of the wear scar is generally different in the break-in and stable wear periods. Stable wear behavior is generally characterised by stable morphology. Volume wear rates are often constant in stable wear periods. However, short-term cyclic variations and slowly decreasing wear rates are also possible in these periods. This distinction between initial and long-term wear behavior is significant for several reasons. Suitable break-in may be required to obtain the stable period of low wear rate needed for long life. If this break-in does not occur, higher wear rates and unstable behavior might persist, resulting in reduced life. In some wear situations, initial wear rates might be lower than longer-term wear rates. This is generally the result of initial surface films or layers, which act as lubricants and are gradually worn away. Such an effect is more common with unlubricated tribosystems than with lubricated tribosystems. However, wear phenomenon in self lubricated coatings does not occur in such manner.

#### **1.6.4 Solid lubrication**

One potential way to reduce the coefficient of friction and wear in ceramics is to generate a thin film, *in-situ* rolls or highly shearable wear debris layer with viscous flow behavior between the counterfaces that can reduce the shear strength of the contacting surfaces and prevent opposing asperities from coming into direct contact. Easy shear at the interfaces is analogous to low friction, whereas fewer asperity-asperity interactions lead to lower magnitude of wear. With the lower value of friction, the magnitude of tensile stresses developing behind the moving asperities is also low. As a consequence, the location of maximum orthogonal shear stresses is displaced away from the plane of contact and the probability of microcrack initiation on contacting surfaces is reduced (Hamilton *et al.*, 1966). These microcracks act as stress concentration points in dynamic contact scenario. Because of the larger load-bearing area provided by the soft films, the magnitude of contact pressure acting in the normal direction is also reduced. This in turn reduces the probability of radial crack formation away from the contact zone. Lower values of coefficient of friction

effectively reduce the contact temperatures during dry sliding and thus have a high potential to reduce the thermal load for coating and substrate material. Considerable amount of efforts are being made to develop so-called low-friction protective layers to act as solid lubricants with the view to replace the commonly used expensive and hazardous coolant lubricants. For applications involving severe tribological conditions where conventional lubricants may be undesirable or impractical due to presence of excessive temperatures, load or speed, fluid contamination, vacuum environment, leakage or any other unacceptable circumstances, or there may be a requirement for a long shelf life, a viable alternative could be to employ a cage containing a solid lubricant. Cage material is sacrificed to produce the transfer film between the bodies in contact. This formation prevents counterbodies from direct metal contact. In the following, some of the popular solid lubricant coatings are summarized. Presently, mainly solid lubricants based on diamond-like carbon (DLC) and molybdenum disulfide ( $\text{MoS}_2$ ) are industrially applied.  $\text{MoS}_2$  and  $\text{WS}_2$  are known to have lubricating properties owing to the ease of shearing the bonds between the planes of atoms in the hexagonal structures of these materials (Mayrhofer *et al.*, 2006). DLC is the term commonly accepted for carbon-based coatings which have mechanical, optical, electrical, and chemical properties similar to natural diamond, but which do not have a dominant crystalline lattice structure. The H content determines film structure, which is amorphous and consists of a mixture of  $sp^3$  (diamond) and  $sp^2$  (graphite) carbon (Grill, 1999). Friction coefficients of DLC films, which typically range from 0.01 to more than 0.5, depend on the nature of the film and the conditions used for the friction test. The friction behavior of DLC is controlled by an interfacial transfer layer formed during sliding. This transfer layer of low shear strength ( $sp^2$ -type) is formed from the top layer of the DLC coating and is responsible for the low friction coefficients (Grill, 1999; Donnet, 1998).

Among lamellar solid lubricants,  $\text{MoS}_2$  and  $\text{WS}_2$  find the widest use and are known to have lubricating properties owing to the ease of shearing of the bonds between the planes of atoms in the hexagonal structures of these materials. The hexagonal structure of  $\text{MoS}_2$  (and, analogously,  $\text{WS}_2$ ) exhibits individual sheets of transition metal and sulphur atoms. There, atoms within a layer are bonded by strong covalent bonds, while the interaction between layers is a weak Van der Waals interaction. Due to these weak bonds between the layers, sliding occurs easily between sulphur layers.



Graphite was one of the first substances with lamellar structure to be used as a solid lubricant in several technological fields. Its ideal crystalline structure consists of parallel planes of carbon atoms arranged in a hexagonal lattice. Because of the low bonding energy between the atoms in adjoining planes and stronger binding of the atoms in the same plane, graphite has a distinctive anisotropy in mechanical properties. Under the action of a relatively small force, the planes with a high density of carbon atoms move and help to achieve low frictional properties. Graphite may have four relatively stable states of friction and wear behaviour, from which the average friction coefficient takes similar values: 0.1, 0.3, 0.45 and 0.6 (El Mansori *et al.*, 1998). Although there are many other solid lubricants present with excellent tribological properties, their application as coating, adherence to the substrate materials and inadequate workability at higher temperatures have posed obstacles to their adoption as solid lubricants. Advanced jet engines require lubricants that can function over a wide range of temperature, from room temperature to 800 °C. The highest working temperature for most of the common solid lubricants such as MoS<sub>2</sub> is limited to about 400 °C in air. WS<sub>2</sub> is stable to a higher temperature than MoS<sub>2</sub> (Singer, 1992; Donnet *et al.*, 1996; Hirvonen *et al.*, 1996; Rapoport *et al.*, 2005). Another common lubricant, graphite, generally works at room temperature and above 425 °C (Li and Xiong, 2008). A single solid lubricant cannot provide adequate lubrication over a wide range of temperatures and operating conditions and an approach towards the development of a coating with synergetic self-lubricating action (along with high wear resistance) can become very useful. Hexagonal boron nitride (hBN) has a lamellar crystalline structure which is similar to those of graphite and MoS<sub>2</sub>. This kind of structure of hBN can be easily sheared along the basal plane of the hBN and used as solid lubricant additives. It has been used in different anti-wear applications (Carrapichano *et al.*, 2002; Yi and Yan, 2006; Skopp *et al.*, 1995). Savan *et al.* (2000a, 2000b) and Chen *et al.* (2008) felt that it would be suitable to follow the methodology of improving tribological properties of hard coatings by addition of small amount of lubricant species like MoS<sub>2</sub> into hard and wear resistant matrix of TiN, CrN etc. Li and Xiong (2008) reported excellent self lubricating properties of Ni–Cr–W–Fe–C–MoS<sub>2</sub> composite, prepared by powder metallurgical process, over a wide range of temperature, as a result of synergistic lubricating effect of graphite and molybdenum disulfide. The corresponding friction coefficients were in the range of

0.14–0.27 and the wear rates were  $1.0\text{--}3.5\times 10^{-6}$  mm<sup>3</sup>/(N m) from room temperature to 600 °C. Walck *et al.* (1997) reported pulsed laser deposited ZnO-WS<sub>2</sub> solid film lubricant coating which exhibits adaptive lubrication behavior. An adaptive lubricant undergoes phase and/or chemical changes in response to thermal, environmental, and tribological conditions. The resulting phases or wear debris are also lubricious. This showed coefficient of friction of 0.04 or less, which is comparable to that of WS<sub>2</sub> films. The coating can withstand temperature in excess of 800 °C and retain its lubricious properties at such elevated temperatures.

## **1.6.5 Mechanical and tribological performance of some single phase composites**

### **1.6.5.1 Al<sub>2</sub>O<sub>3</sub>**

Al<sub>2</sub>O<sub>3</sub> (Alumina) coatings successfully improve the surface properties of materials. Such coatings have a high potential for many engineering applications such as surface coating for wear- and/or corrosion-resistant components. Due to the unique property combination of low weight, high strength, stiffness and temperature stability along with excellent resistance to wear and corrosion, Al<sub>2</sub>O<sub>3</sub> has become one of the most extensively used ceramics. The use of alumina coatings, produced by different processes for various tribological applications, is now well documented. Many research groups studied the wear performance of plasma sprayed alumina coatings (Bull *et al.*, 1996; Tao *et al.*, 2010; Mindivan *et al.*, 2009). Bull *et al.* (1996) found it to depend on the sliding counterface and the levels of residual stress within the coating. Tao *et al.* (2010) found that the better wear resistance of Al<sub>2</sub>O<sub>3</sub> coating than that of the Chromium Oxide (Cr<sub>2</sub>O<sub>3</sub>) coating is due to its better thermal conductivity which effectively facilitates the dissipation of tribological heat and alleviate the reduction of hardness due to the accumulated tribological heat.

Lee and Zum Gahr (1994) showed that lower friction coefficients and wear rates in unlubricated sliding pairs are attainable through improvement of surface properties by surface alloying of alumina ceramics. Frequently, the failure of brittle ceramics starts at stress raisers on surfaces, such as flaws, pores or scratches, and is promoted by tensile residual stresses. Laser remelting can reduce these surface defects, and may result in compressive residual stresses. Alloying can reduce grain growth during laser treatment owing to the Zener effect, and can provide toughening mechanisms as a

result of secondary phases. Zum Gahr *et al.* (1995) and Zum Gahr (1996) again showed that laser surface alloying of alumina ceramics can substantially improve tribological performance as well in unlubricated oscillating sliding contact as in abrasive sliding contact. A number of research groups have reported on the laser cladding of  $\text{Al}_2\text{O}_3$  on steel substrates (Feng *et al.*, 1996; Gao *et al.*, 2007; Wu *et al.*, 1995). Improvement in mechanical properties of  $\text{Al}_2\text{O}_3$  by LSA has also received considerable attention (Zum Gahr *et al.*, 1995). Gao *et al.* (2007) tested laser clad and remelted  $\text{Al}_2\text{O}_3$  coating for wear rate and found it to be less than that of plasma-sprayed  $\text{Al}_2\text{O}_3$  coating. The test revealed a linear relation between the mass loss of  $\text{Al}_2\text{O}_3$  coatings and the wear time. Hazra *et al.* (2009) obtained a laser cladding of  $\text{Al}+\text{Al}_2\text{O}_3$  on Mg alloy substrate by using  $\text{Al}+\text{Al}_2\text{O}_3$  powders and carried out wear test on the cladding with variable loads. They observed that the hard  $\text{Al}_2\text{O}_3$  particles effectively help in preventing grooving and ploughing during the wear process and the highly refined structure acts as a strong and ductile metal matrix to prevent the sudden failure of the alloy. Erdemir (1994) reported that  $\text{Al}_2\text{O}_3$  lacks the ability to rapidly dissipate the frictional heat from its sliding interface. As a result, plastic flow on these rubbing surfaces becomes feasible. Zawrah *et al.* (2002) studied the effect of surface treatment of slightly porous  $\text{Al}_2\text{O}_3$  by laser irradiation. Laser remelting without change of the chemical composition increased the hardness of various alumina ceramics slightly. According to the microscopic studies, laser remelting of the pure alumina resulted in reduction of porosity, an increase in grain size and formation of columnar grains.

The utilization and advantage of toughening mechanisms depend on the nature of mechanical stress on the ceramic. During unlubricated abrasive wear test, wear of ceramics was determined by intercrystalline microfracture, spalling of grains or particles of second phases, grain fragmentation, formation and quasi-plastic deformation of surface layers consisting of densified wear debris, detachment of these surface layers and delamination fracture due to sub-surface cracking. Sensitivity of the ceramics to surface pressure can be reduced in steps, which abate microcracking and spalling of grains or phases embedded in the matrix. A relatively soft phase exists between individual  $\text{Al}_2\text{O}_3$  grains. This effect together with the reduction in grain size contributes favorably to the markedly improved behavior of the composites during mechanical loading using the abrasive wear test.

### 1.6.5.2 TiB<sub>2</sub>

TiB<sub>2</sub> is a refractory compound exhibiting a unique combination of a number of useful properties. By virtue of its high hardness and modulus, good oxidation resistance and excellent strength at high temperature, TiB<sub>2</sub> is used in a number of widely used wear and thermal shock resistant coatings. These coatings have potential applications in boiler, tool materials and shoot-proof in the surface of arms (Darabara *et al.*, 2006; Wang *et al.*, 2006; Xu and Liu, 2006; Fang *et al.*, 2008). Hence, considerable research efforts have been carried out to prepare coatings with incorporation of TiB<sub>2</sub> particulates. These processing methods include high velocity oxy fuel spraying (HVOF), plasma spraying and magnetron sputter deposition. Metallic-based composite coatings with TiB<sub>2</sub> incorporation exhibited a combination of attractive properties (Fang *et al.*, 2008).

TiB<sub>2</sub> is characterised by high-melting point, low-specific weight, high hardness, high strength to density ratio, good wear resistance and excellent thermal and chemical stability up to 1700 °C (Vallauri *et al.*, 2008; Du *et al.*, 2008).

Kirk *et al.* (1981) reported the wear properties of electrodeposited TiB<sub>2</sub> coatings on Molybdenum, Inconel and Nickel in sliding applications at various speeds using hardened steel as the counterbody. The effects of sliding speed, lubrication and substrate material of the coating were investigated on the wear of TiB<sub>2</sub> coatings. Wear rate results indicate that TiB<sub>2</sub> coatings have a wear resistance comparable to that of Al<sub>2</sub>O<sub>3</sub> under the high speed (~30 m/s) unlubricated sliding wear (pin-on-disc) conditions. Under low speed (less than 5 cm/s) or high speed lubricated conditions, Al<sub>2</sub>O<sub>3</sub> is the more wear-resistant material.

Fang *et al.* (2008) reported the development of coatings containing TiB<sub>2</sub>, made by arc spraying. The coatings exhibit better wear performances than that of TiB<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> - coating.

### 1.6.5.3 TiN

Among various hard coating materials, Titanium Nitride (TiN) has been extensively studied and successfully commercialized as a protective coating material owing to its superior properties such as high hardness and wear resistance, high melting point, superior thermal stability, good chemical durability and high electrical conductivity (Kim *et al.*, 2003; Chou *et al.*, 2002). Such a combination of properties makes TiN a

potential candidate for wear-resistant components (Shen *et al.*, 2003). TiN is deposited as hard abrasion resistant coating on cutting tools and other material surfaces susceptible to wear and helps to extend the operating life and range of conditions for which they are used (Huang *et al.*, 1994; Wilson and Alpas, 1998). Its hardness increases with decreasing grain size, both for polycrystalline bulk materials and for thin films: hardness values of 17.2 and 45 GPa have been reported for a coarse-grained bulk material and for a nanostructured film, respectively. TiN coating is usually selected as a protective film for different varieties of metal surfaces. The major application of this protective layer is the coating of steels. Steels are the most widely used material in industry and daily life. The coating performance depends mostly on the film hardness and the adhesive strength.

Liu *et al.* (1995) reported that ion implantation into TiN coatings modified the mechanical properties of the near-surface region. Increase in hardness and reduction in friction coefficient has taken place by a considerable margin.

The tribological behaviour of TiN film is found to vary with substrate, deposition method, film thickness, stoichiometry, heat treatment and type of wear. Like most ceramic materials, TiN films are very brittle, and they have a high tendency to fracture and spall out from the substrate during wear, especially those on softer substrates. These tendencies increase as the film thicknesses and applied loads increase.

In the study on sputtered TiN films, Shimura *et al.* (1978) concluded that the friction coefficient appears to be controlled by gases absorbed on the surface rather than by the formation of an oxide film during frictional contact. Guu *et al.* (1996) tried to correlate the hardness and corrosion properties along with tribological behavior of PVD-TiN coating to the coating structure, thickness and test conditions. For titanium nitride (TiN) films, dependence of film thickness on the characteristics of the coating is reported and it is claimed that this is due to a decreasing defect density as the film grows thicker (Köstenbauer *et al.*, 2007; Machunze and Janssen, 2008).

#### **1.6.6 Ti-B-N based coatings**

Over the years Ti-B-N-based coatings have been studied extensively for their enhanced hardness, thermal stability, high wear and corrosion resistance and low friction characteristics (Peytavy *et al.*, 1979; Hammer *et al.*, 1994; Mayrhofer and

Stoiber, 2007). These properties make them potential candidates as protective coatings for various industrial applications (Lu *et al.*, 2005; Lu *et al.*, 2006; Neidhardt *et al.*, 2006; Mayrhofer and Stoiber, 2007). It is observed that the enhanced mechanical properties of this multiphase coating system (Broszeit *et al.*, 1993; He *et al.*, 1999) are determined by the presence of extremely fine crystalline and amorphous phases (Neidhardt *et al.*, 2006).

A considerable amount of research studies have already been reported regarding the process of formation of Ti-B-N coatings with PVD or CVD techniques. Gissler (1994), Veprek and Reiprich (1995), Veprek *et al.* (1996), Veprek (1999) and Lu *et al.* (2006) reported that the incorporation of boron into growing TiN film in a PVD process forms two- and/or three-phase Ti-B-N nanocomposites with microstructures comprising of nanocrystalline phases in an amorphous matrix. Zhu *et al.* (2002) reported the increase in the hardness of TiAlN coatings by boron implantation in the near-surface region in a cathodic arc evaporation process. Improved hardness and wear resistance and decrease in friction coefficient is attributable to the formation of TiB<sub>2</sub> and BN in the near-surface region by boron implantation.

In DC magnetron sputtering process, Ti-B-N based coatings can be produced by using TiB<sub>2</sub> target and controlling the nitrogen flux (Wiedemann *et al.*, 1999) or using Ti and BN targets (Garcia-Gonzalez *et al.*, 2007; Neidhardt *et al.*, 2006; Chaleix and Machet, 1997; Baker *et al.*, 1997; Aouadi *et al.*, 2002; Shtansky *et al.*, 2005; Son *et al.*, 2002; Djouadi *et al.*, 2004). Neidhardt *et al.* (2006) described that at low N<sub>2</sub> fractions, TiN lattice gets strained by the substitutional incorporation of boron. At higher fractions of N<sub>2</sub> this metastable phase is transformed to stable stoichiometric TiN, while the excess boron forms an amorphous BN phase surrounding those crystalline grains. Peytavy *et al.* (1979) and Pfohl *et al.* (1999) formed Ti-B-N based coatings in the Plasma-Assisted CVD (PACVD) process.

Regarding Ti-B-N systems, investigations are either directed to obtain superhardness ( $\geq 40$  GPa) or towards the study of the enhancement in the tribological properties. Neidhardt *et al.* (2006) reported maximum nanohardness of 34.5 GPa in nanocomposite Ti-B-N coatings synthesized by reactive arc evaporation. Lu *et al.* (2005) observed a hardness of  $\sim 44$  GPa in nanocomposite Ti-B-N thin film coating using unbalanced DC magnetron sputtering. Investigations have been carried out on the application of hBN, which is considered to be a potential solid lubricant (He *et al.*, 2001; Haltner, 1966). The lamellar nature of hBN, on getting integrated with TiB<sub>2</sub>,

makes it possible to completely remove the common severe compressive stress, decrease the friction and, as a result of property tailoring, improve the overall tribological performance (He *et al.*, 2001).

Ti-B-N system is generating considerable interest because of the possibility of the coexistence of hard TiB<sub>2</sub> and TiN with soft hBN. A surface might not exhibit good tribological characteristics by merely possessing a high hardness. It is well known that wear resistance gets influenced by many other factors like coefficient of friction, toughness, adherence, tribo-chemical reactions etc. It is difficult for a single phase coating material to meet with all these requirements. The presence of hard TiB<sub>2</sub> and TiN along with soft hBN provides a multiphase system with the appropriate property tailoring required in this case.

All the previous attempts to produce coatings of Ti-B-N system were made in the domain of thin films. For the first time, Chatterjee *et al.* (2010) have attempted to manufacture thick coatings by introducing free hBN in the final matrix of nanostructured Al<sub>2</sub>O<sub>3</sub>-TiB<sub>2</sub>-TiN composite coatings developed by combined SHS and LSA technique (Chatterjee *et al.*, 2008). The authors intend to investigate the potential of this free state hBN to act as a solid lubricant during relative motion of the developed coating with standard hard, wear resistant engineering materials. From another viewpoint, this would be attempted to achieve a particular composition of titanium, boron and nitrogen in the matrix so that a desirable combination of hardness and frictional coefficient is attained.

#### **1.6.7 Mechanical and tribological behaviour of multi-phase composite**

In Section 1.6.5.1, it has been discussed that Al<sub>2</sub>O<sub>3</sub> coatings successfully improve the surface property of the materials. Brittleness, lack of defect tolerance owing to low fracture toughness, and low resistance to thermal shocks can cause severe problems in case of components under mechanical and/or thermal loads. Microstructural parameters such as grain sizes, porosity and particularly, the size and density of flaws affect strength. Strength and toughness of alumina ceramics can be enhanced by various energy-dissipating mechanisms such as phase transformation, micro-cracking, grain bridging, and most importantly, by particle or fiber reinforcement. Particle reinforcement of alumina has been studied by adding, for example, TiB<sub>2</sub> as fine dispersed phase in the Al<sub>2</sub>O<sub>3</sub> matrix (Lee and Zum Gahr, 1994).

Addition of TiB<sub>2</sub> particles to Al<sub>2</sub>O<sub>3</sub> matrix improved fracture toughness, hardness, and strength over monolithic Al<sub>2</sub>O<sub>3</sub> and offered advantages with respect to wear and fracture behavior. Over the years, the Al<sub>2</sub>O<sub>3</sub>/TiB<sub>2</sub> composite have drawn the attention of research groups due to its high wear resistance. A considerable number of publications on the processing techniques and characterisations of this composite are available. Jianxin *et al.* (1996), Wang (2009), Fang *et al.* (2008), Meyers *et al.* (2001) and many others have reported processing techniques of Al<sub>2</sub>O<sub>3</sub>/TiB<sub>2</sub> composites using SHS (self-propagating High-temperature Synthesis) routes. Jianxin *et al.* (1996) studied the mechanical properties of TiB<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> composite powders with respect to the TiB<sub>2</sub> content and determined the optimum percentage of TiB<sub>2</sub> for the best mechanical performance. Zum Gahr *et al.* (1995) showed the high potential of laser-induced surface alloying for improving tribological performance of Al<sub>2</sub>O<sub>3</sub>, surface alloyed with TiB<sub>2</sub>.

Jianxin *et al.* (1996) studied the friction and wear behavior of Al<sub>2</sub>O<sub>3</sub>/TiB<sub>2</sub> composite sliding against cemented carbide both under the conditions variable atmospheres and temperature. It was found that the composition, temperature, and atmosphere had profound effects on the friction and wear behavior of Al<sub>2</sub>O<sub>3</sub>/TiB<sub>2</sub>. The presence of an oxide film in Al<sub>2</sub>O<sub>3</sub>/TiB<sub>2</sub> contributed to the improvement of the friction coefficient and wear resistance when sliding in air at 800 °C. The adhesion and diffusion of Cobalt (Co) to the ceramic surfaces resulted in a lower wear resistance when sliding in N<sub>2</sub> at 600 - 800 °C. This was attributed to the softening of the wear surface. Presence of higher TiB<sub>2</sub> content showed higher hardness and fracture toughness. The wear resistance was found to improve with increasing TiB<sub>2</sub> content. Du *et al.*, (2008) tested a laser surface modified AISI 1010 steel with precursor of TiB<sub>2</sub> + Al. The wear rate result of the coating shows that due to the presence of hard reinforcements, such as TiB<sub>2</sub> and iron–aluminide, the laser-coated samples demonstrate considerably better wear resistance than that of the steel substrate. The hard reinforcements (TiB<sub>2</sub>, Fe<sub>3</sub>Al, Al<sub>2</sub>O<sub>3</sub>) can play the role of hard barrier to interrupt the ploughing and scratching and therefore improve the wear resistance of the coating. Sivaprasad *et al.* (2008) tested wear properties of *in-situ* Al/TiB<sub>2</sub> composites. It was noticed that the abrasive wear rate increases with increasing load and decreases with increasing wt.% of TiB<sub>2</sub>. This is due to higher hardness of the composite. As the number of TiB<sub>2</sub> particles increases, the resistance to the penetration of abrasive particles into the composite increases and



hence the depth of penetration by the abrasives reduces leading to better abrasion wear resistance.  $\text{TiB}_2$  particles formed *in-situ* has an even dispersion in the matrix of alloy. This restricts removal or pulling out of grains in case of abrasion wear. In such a case, the wear mechanism appears to be a combination of micro-cutting, ploughing and grain pull-out. At the beginning of a test, a point contact prevails theoretically between the solid surfaces, which changes into an area contact with increasing time and wear. Increasing wear results in an increasing apparent area of contact and hence in a decreasing apparent surface pressure under a constant normal load.

In recent years, *in-situ* synthesized  $\text{TiB}_2/\text{TiN}$  has attracted considerable amount of attention (Li *et al.*, 2002). Combination of  $\text{TiB}_2$  and  $\text{TiN}$  may provide desirable combination of high-temperature hardness and stability with adequate ductility and fracture toughness (Olevsky *et al.*, 1996; Shim *et al.*, 2002). These properties are very critical to friction composites for enhancing wear resistance at high loads. However, *in-situ* synthesized  $\text{TiB}_2/\text{TiN}$  was mainly developed via mechanical milling (Chen *et al.*, 2008; Li *et al.*, 2002; Yang *et al.*, 1996) or combustion synthesis methods (Yeh and Teng, 2006). Chen *et al.* (2008) showed that the hardness and tribological properties of  $\text{TiB}_2/\text{TiN}$  composite are affected by the relative amounts of *in-situ* synthesized  $\text{TiB}_2$  and  $\text{TiN}$ .

Similar to  $\text{TiB}_2$ , addition of  $\text{TiN}$  phase in alumina matrix increases hardness, fracture toughness and thermal shock resistance up to 800 °C. In order to optimize the properties, the reinforcing particulate phase must be well dispersed in the matrix. Laarz *et al.* (2001) investigated on the possibility of the synthesis of composites with homogeneous microstructure by the densification of well dispersed powder mixtures in the  $\text{Al}_2\text{O}_3\text{-TiN}$  system. Shen *et al.* (2003) reported on the improvement of inherent low damage tolerance of  $\text{TiN}$  by addition of  $\text{Al}_2\text{O}_3$ .  $\text{TiN}$  matrix composite reinforced by dispersed  $\text{Al}_2\text{O}_3$  particles was hard and strong and its performance as cutting tool coating was comparable to those of cubic boron nitride (cBN) sintered tools. Noli *et al.* (2006) worked on the production of  $\text{Al}_2\text{O}_3/\text{TiN}$  protective coatings on stainless steel substrates and reported the substantially high corrosion resistance offered by such coatings. Pogrebnjak *et al.* (2006) studied the structure and element composition, as well as protection characteristics of the hybrid coatings based on  $\text{TiN}/\text{Al}_2\text{O}_3$  deposited on AISI 321 stainless steel substrate which were observed to have high corrosion resistance. Poser *et al.* (2005) studied the characteristics of ceramic

composites produced by embedding TiN particles into the surface of a commercial monolithic Al<sub>2</sub>O<sub>3</sub> ceramic using a laser-assisted process. Substantial improvement was observed in the stability of frictional behavior compared to that of monolithic alumina used for reference. Awad and Qian (2006) reported a duplex process of arc ion plating and microplasma oxidation, applied for deposition of duplex Al<sub>2</sub>O<sub>3</sub>/TiN coatings. The duplex coatings possessed very high hardness and wear resistance, and their mechanical and tribological behavior / characteristics were superior to those of single layer coatings alone and the untreated Al alloy substrate.

In recent years, *in-situ* synthesized TiB<sub>2</sub>/TiN has also attracted considerable research attention. Combination of TiB<sub>2</sub> and TiN may provide enhancement in high-temperature hardness and stability with adequate ductility and fracture toughness. However, the synthesis of *in-situ* TiB<sub>2</sub>/TiN was mainly carried out by mechanical milling (Shim *et al.*, 2002; Li *et al.*, 2002; Gutmanas and Gotman, 2000) or combustion synthesis methods (Yeh and Teng, 2006) through the reaction of Ti and hBN powders. Zhang *et al.* (1995) synthesized TiB<sub>2</sub>/TiN through the reaction of hBN and TiH<sub>2</sub> which decomposed into Ti and H<sub>2</sub> at a temperature range of 1000 - 1600 °C by reactive hot pressing. Becht *et al.* (1989) reported the development of laminar composites in TiN-TiB<sub>2</sub> system through chemical vapor deposition (CVD). TiB<sub>2</sub>/TiN might be synthesized *in-situ* through the reaction of Ti and hBN powders by powder metallurgy method in Cu matrix under proper hot pressing temperature and pressure. Molian and Hualun (1989) reported laser cladding of titanium alloy with boron nitride (BN) produce favorable structural features, excellent adhesion and formation of TiN, TiB<sub>2</sub>. This generated superior wear-resistant property when compared with age-hardened and laser surface-melted titanium.

The advantageous properties of Al<sub>2</sub>O<sub>3</sub>, TiN and TiB<sub>2</sub> in the field of surface engineering are utilized both in the form of individual ceramic phases as well as Al<sub>2</sub>O<sub>3</sub>-TiB<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-TiN and TiB<sub>2</sub>-TiN composites. The aforesaid composites were sometimes compounded with some third phase for better property tailoring. Pogrebniak *et al.* (2006) studied the structure and element composition, as well as protection characteristics of the hybrid coatings based on TiN/Cr/Al<sub>2</sub>O<sub>3</sub>. Chatterjee *et al.* (2008) reported production of composite coating consisting of all three phases (Al<sub>2</sub>O<sub>3</sub>-TiB<sub>2</sub>-TiN) for the first time following combined SHS and LSA route.

### 1.6.8 Effects of laser post treatment on composite coatings

Laser post treatment, as a secondary process, possesses the potential and promise to control and minimise problems like delamination, cracking, corrosion and erosion in plasma sprayed thermal barrier coatings (TBCs). All of these issues become more effective in the presence of corrosive species and high heat flux (Tsai *et al.*, 2007; Chwa and Ohmori, 2002; Zaplatynsky, 1982; Ahmaniemi *et al.*, 2005). Laser post treatment yielded improvement in the cyclic lifetime of the coating by exhibiting a higher thermal shock resistance and lower or no surface spallation even at temperatures as high as 900 °C (Zaplatynsky, 1982; Petitbon *et al.*, 1991; Miller and Berndt, 1984).

Zum Gahr *et al.* (2007) reported that laser induced remelting and alloying of ceramics ( $\text{Al}_2\text{O}_3\text{-ZrO}_2$ ,  $\text{ZrO}_2$ ) resulted in a reduction of friction coefficient.

Petitbon and Queriaud (1995) studied surface melting and over-cladding of the  $\text{Y}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3/\text{HfO}_2$  stabilized zirconia coatings by  $\text{CO}_2$  laser. The cladding was made using  $\text{Al}_2\text{O}_3$  powder. Laser treatment improved thermal cycling properties as well as friction and erosion resistance.

Khor and Jana (1997) performed laser glazing with Nd-YAG laser for  $5\text{CaO-ZrO}_2$  coatings. This resulted in the glazing region having distinctly different microhardness in comparison to that of the original as-sprayed coating.

Tsai *et al.* (2007) reported that the laser-glazed layer had a dense resolidified columnar microstructure with segmented cracks orthogonal to the surface. The microhardness, surface roughness and erosion results showed a marked improvement.

Laser post treatment imparts remelting and subsequent solidification of the surface which helps to seal pores and forms a network of controlled segmented cracks normal to the surface. Segmented cracks, orthogonal to the surface along the densified layer are characteristic features of laser melted ceramic materials and are generated by shrinkage and relief of thermal-induced stresses. These cracks, induced by laser treatment, improve thermal shock resistance by improving strain accommodation. Moreover, a considerable reduction in surface roughness is achieved, leading to considerable improvement in erosion resistance. On the other hand, densification and microstructural modification from lamellar to columnar structure can alter heat transfer by increasing thermal conductivity (Batista *et al.*, 2005; Batista *et al.*, 2006; Lawrence and Li, 2002). Besides, the columnar structure helps the coating in

achieving better wear properties as well as better thermomechanical resistance during thermal cycling (Antou *et al.*, 2003; Ouyang and Sasaki, 2002; Chwa and Ohmori, 2002).

Although laser-sealed layers exhibit a reduced degree of surface roughness and fine-scale resolidified structure, the major problem faced by laser post-treated coating is the formation of macroscopic cracks generated due to anisotropic thermal expansion mismatch combined with low toughness. As a matter of fact, cracks in the ceramic layer parallel to the surface are extremely detrimental as they lead to spallation (Ouyang *et al.*, 2001). Moreover, the existence of cracks may augment oxidative and corrosive degradation (Chang *et al.*, 1998; Batista *et al.*, 2005). Antou *et al.* (2003) tried to circumvent these problems by applying *in-situ* deposit remelting which densifies the coatings without generating high levels of cooling stresses incompatible with the mechanical and chemical resistance properties.

Laser post treatment has a great bearing on the microstructure of the coating. Laser post-treatment not only brings about columnar structure, but also results in homogenization of the composition in the remelted part (Tsai and Tsai, 1995). Wang *et al.* (2009) reported the formation of fine equiaxed grains in a laser remelting process of ceramic coating. This shape was different from the typical columnar crystals which grew along the direction of the heat flow. The formation of fine equiaxed grains is probably due to the nanoparticulate content in the coating proposed by Li *et al.* (2006). Laser imparts high speed heating and melting, followed by a rapid solidification process. During laser remelting, nanoparticles get easily diffused in the melting pool for its high diffusion coefficient. These nanoparticles act as nucleation sites during rapid solidification process resulting in non-direction growth of crystals. Fine equiaxed grains with homogenous distribution were obtained (Mingxi *et al.*, 2006; Li *et al.*, 2006). Meanwhile, the usual lamellar defect of the plasma-sprayed coating was erased, and the compactness of the coating was improved significantly after laser remelting.

Park *et al.* (2008) studied the effects of the laser treatment on TBCs. They found the crack size, crack width and remelting depth of the coating layer to be completely dependent on the laser power.

Wang *et al.* (2008) investigated the dependence of microstructure on the temperature gradient  $G$ , solidification front velocity  $R_s$  and ratio of  $G/R_s$  at the interface of solidification. In solidification process, high  $G/R_s$  ratio causes the formation of the

columnar structure. However, with decrease in  $G/R_s$  ratio, the microstructure will transform to the columnar dendrite, and finally, the equiaxed structure.

Chatterjee *et al.* (2008) reported the development and performance of nanostructured ceramic matrix composite coating consisting of  $\text{Al}_2\text{O}_3$ - $\text{TiB}_2$ - $\text{TiN}$  on steel substrates through combined SHS and LSA route. This thick hard protective coating with minor changes in the composition could also be made to perform as a self-lubricating coating Chatterjee *et al.* (2010). But all the aforesaid approaches reported are used without any posterior treatments.

In the present situation, looking at the concepts and the trends of results of all the laser post treatment or laser glazing experiments, improvement in the microstructure and tribological properties is anticipated.

The objective of the present work would be the development and performance study of laser post-treated nanostructured  $\text{Al}_2\text{O}_3$ - $\text{TiB}_2$ - $\text{TiN}$  coating produced by combined SHS and LSA technique.

### 1.7 Nanostructured Coating

Nanostructured coatings have recently attracted increasing interest because of the possibilities of synthesizing materials with unique combinations of mechanical, chemical and tribological properties due to size effect.

Types of nanostructured coatings are-

- Nanocomposite coating
- Nanoscale multilayer coating
- Superlattice coating
- Nanograded coating

Nanostructured materials are -

- A broad class of materials, with microstructures modulated in less than 100 nm.
- Materials with atoms arranged in nanosized clusters, which become the constituent grains or building blocks of the material
- Any material with at least one dimension in the 1-100 nm range

Hard materials usually refer to materials with hardness greater than 20 GPa. Materials with hardness above 40 GPa are classified as superhard, and those with hardness above 80 GPa are often called ultra-hard materials. It is possible to develop hard, superhard or even ultrahard nanocomposite coatings depending on coating design and application. Over the years, efforts have been made to synthesize and study these nanocomposite coatings, not only with high hardness but also with high toughness.

Nanostructured materials can be classified into two types,

- Nanocrystalline material
- Nanoparticles

Nanocrystalline materials are three dimensional solids, composed of nano-sized grains or crystallites. The grain size is considerably small (<100 nm) and a large number of atoms exist in the grain boundary, and the proportion of grain boundary is also considerably large. Nanocrystalline materials have remarkable properties owing to their unique structure.

Nanoparticle has ideally one or more dimensions of the order of 100 nm or less. Nanoparticles have extremely large surface-area/particle-size ratio and potentially different crystallographic structures which may lead to a radical alteration in chemical reactivity. If crystalline, each nanoparticle may be either a single crystal or polycrystalline giving rise to the presence of associated grain boundaries within the nanoparticle. In a small isolated nanoparticle, a large proportion of the total number of atoms will be present either at or near the free surface. For instance, in a 5 nm particle approximately 30–50% of the atoms are influenced by the surface, compared with approximately a few percent for a 100 nm particle. Similar arguments apply to nanocrystalline materials, where a large proportion of atoms will be either at or near grain boundaries. Such structural differences in reduced-dimensional systems would be expected to lead to very different properties from the bulk (Kelsall *et al.*, 2005).

Grain size has a profound effect on the mechanical behavior of materials, in particular, on the yield stress and hardness (Gleiter, 1989; Song *et al.* 1999). The Hall-Petch relationship is a well-known expression relating the variation in yield strength to the grain size of a material. It states that the yield strength increases monotonically with decreasing the average grain size  $d$  according to,

$$\sigma_y = \sigma_o + kd^{-1/2} \quad \dots (1.2)$$

Where,

$\sigma_y$  = Yield strength of polycrystalline sample

$\sigma_o$  = Overall resistance of lattice to dislocation movement or internal back stress

$k$  = Material dependant constant (Hall-Petch slope, considered to be a measure of the resistance of the grain boundary to slip transfer)

$d$  = Average grain size

The form of the equation indicates that a decrease in grain size will lead to an increase in the yield strength. According to the Hall-Petch equation, high yield strength may be attained by reducing the grain size of materials. For example, a drop in average grain size from 10  $\mu\text{m}$  to 10 nm should increase the yield stress more than thirty-fold. For pyramidal indenters, the microhardness ( $H_V$ ) of metals is empirically related to the yield strength ( $\sigma_y$ ) by the relation  $H_V/\sigma_y = 3$  (Qu *et al.*, 2008). Hence, for materials that exhibit Hall-Petch behavior, the hardness  $H_V$  should be related to grain size  $d$ , as

$$H_V = H_0 + k_H d^{-1/2} \quad \dots (1.3)$$

where,  $H_0$  and  $k_H$  are the correspondent terms in Eq. (1.2).

In this context it would not be irrelevant to mention that though, nanoparticles effectively strengthen the matrix but degrade its pseudo-elasticity. There exists an optimal volume fraction of nanoparticles above which the effect of nanoparticles becomes negative. Too many nanoparticles negatively influence the interfacial bond strength, leading to a decrease in the wear resistance (Chen and Li, 2007).

Hardness microscopically corresponds to the motion of dislocations. The hardness of a material, often measured by indenter techniques, is therefore determined by how resistant the bonds in the material are against distortions and how dislocations are able to move in the system. A hard material should ideally also be ductile to maximize potential use. However, dislocation movement, which determines the hardness and strength in bulk materials, has little effect when the grain size is less than approximately 10 nm. At this grain size, further reduction in grain size brings about a decrease in strength because of grain boundary sliding. Softening caused by grain boundary sliding is mainly attributed to large amount of defects in grain boundaries, which allow fast diffusion of atoms and vacancies under stress.

Further increase in hardness requires hindering of grain boundary sliding. This can be realized through proper microstructural design, i.e. by increasing the complexity and

strength of grain boundaries. A number of design methods have been put forth to produce a hard and tough nanocomposite

First, a combination of two or more nanocrystalline phases can provide complex boundaries to accommodate coherent strain, which result in the increase of coating hardness. In this case, the phases involved must show a wide miscibility in solid state, display thermodynamically driven segregation during deposition, and have certain chemical affinity to each other to strengthen the grain boundaries. This includes  $\text{TiB}_2$ -TiN and other metal nitride and boride/carbide systems (Mitterer *et al.*, 1999; Stuber and Schier, 1995). Second, by stopping the grain growth and strengthening the grain boundary, nanocrystalline phases can be segregated from grain boundaries of the other phase. Although this design is capable of causing significant increase in hardness and elastic modulus of the composite, it may not be able to improve toughness because dislocation movement gets prohibited and crack opening becomes the main mechanism of relieving strain. If the cohesive strength of the interface is not sufficient to withstand the local tensile stress at the crack tip, occurrence of unstable crack propagation and debonding may take place (Musil, 2000; Barna *et al.*, 2000). To counter this phenomenon, metal matrix composite coatings of one hard nanocrystalline phase into a metal matrix were formed (Mitterer *et al.*, 1999; Misina *et al.*, 1998). High hardness (~35-60 GPa) could be obtained for compounds having a wide miscibility gap in the solid state but a certain chemical affinity to each other to form high strength grain boundaries. In this case, both the dislocation mechanism and the grain boundary mechanism contribute to the hardness (Dieter, 1976; Gryaznov *et al.*, 1990), while the existence of a metal matrix improves toughness. But in some cases larger separations between nanocrystalline grains in the metal matrix fail to prohibit dislocation movements initiated from grain boundaries. This results in the lowering in the toughness of the composite. Thermal stability of nanocomposite coatings is yet another important property in mechanical applications. Some metal matrix nanocomposite coatings become unstable at high temperature. Both of these problems can be addressed in the following two ways. First, interface complexity can be introduced by using a ternary or quaternary system. This gives rise to, even at high temperatures, immiscibility and strong segregation into two binary compounds. Second, phases of high thermal stability can be included in the coating (Veprek and Reiprich, 1995). Veprek *et al.* (1996) and Zhang *et al.* (2003) embedded nanocrystalline phases in an amorphous phase matrix to produce superhard and



ultrahard composite coatings. Zhang *et al.* (2003b) commented that, to design a nanocomposite coating with both high hardness and high toughness, one must take all the above into consideration. Probably the best way is to use ternary, quaternary or even more complex systems, with high strength amorphous phase as matrix (such as a-SiN<sub>x</sub>, a-BN, a-C, etc.) and hard transition metal-nitride nanocrystals (such as TiN, W<sub>2</sub>N, BN, etc.) as nanocrystalline phase to increase grain boundary complexity and strength. These nanocrystalline phases should be refractory and immiscible in each other, and could result in compositional modulation, segregation and high thermal stability of the nanostructure. The aim is to maximize interfaces and form well-defined spinodal structure at interfaces.

### 1.8 Problem Definition

From the above discussion, it is observed that in-depth research has been carried out in the development of protective coatings for wear resistance applications. Composite materials with two or more hard ceramic phases as reinforcements have been under investigation as potential materials for wear resistant coatings, as some of these composites exhibit considerably better performance compared to those of single phase coatings and composites with only one type of reinforcements. Further, a number of coatings with the reinforcements developed *in-situ* are found to have better quality and performance in comparison to those with *ex-situ* reinforcements (Section 1.7).

For self-lubrication, coatings may incorporate phases of low shear strength (Section 1.6.4). Finally, composites with reinforcements in the nanometric size range provide unique property combinations that are otherwise not attainable (section 1.7).

Coatings may have a number of defects at and near the surface and laser post treatment has been successfully employed to reduce such defects, increase hardness and refine the microstructure (Section 1.6.8).

In view of this, the present study aims towards the development, characterisation and performance study of Al<sub>2</sub>O<sub>3</sub>-TiB<sub>2</sub>-TiN composite coating. The phase combination is selected with the aim of obtaining a multi-phase hard coating that has not been investigated till date. It is also aimed to obtain *in-situ* reinforcements by a laser triggered SHS process which would subsequently be incorporated in the coating matrix by laser alloying. It is further aimed to compare the performance of coatings with reinforcements developed *in-situ* and *ex-situ*. For self-lubrication, it is planned to

introduce free hBN in the coating so as to obtain a low coefficient of friction in sliding contact with other surfaces. A further improvement in the quality of coating performance is sought by a laser post treatment after laser surface alloying.

The advantageous properties of  $\text{Al}_2\text{O}_3$ , TiN and  $\text{TiB}_2$  in the field of surface engineering are utilized both in the form of individual ceramic phases as well as  $\text{Al}_2\text{O}_3$ - $\text{TiB}_2$ ,  $\text{Al}_2\text{O}_3$ -TiN and  $\text{TiB}_2$ -TiN composites. The aforesaid composites were sometimes compounded with some third phase for better property tailoring. In this respect, in the present investigation, it was aimed to develop a ternary composite ( $\text{Al}_2\text{O}_3$ - $\text{TiB}_2$ -TiN) that has not been developed or investigated by any research group till date. Apart from that, it is very important to mention that,  $\text{TiB}_2$  has little or no wetting or miscibility in  $\text{Al}_2\text{O}_3$  (Meyers *et al.*, 2001). This immiscibility may assist in the appearance of one phase ( $\text{TiB}_2$ ) as distinct particulate (frequently in nanometric size range) reinforcements in the other phase ( $\text{Al}_2\text{O}_3$ ) as matrix, thus augmenting the strength and hardness of the composite.

### 1.9 Objectives of the investigation

The detailed objectives of the present study include:

1. Development of  $\text{Al}_2\text{O}_3$ - $\text{TiB}_2$ -TiN composite coating on steel by combined SHS and LSA.
  - Feasibility study
  - Final experiments
2. Detailed characterisation of coating with an attempt towards structure-property co-relation.
3. Comparative analysis of composite coatings developed with *in-situ* and *ex-situ* reinforcements.
4. Study of the effect of free hBN in composite matrix on properties and tribological performance of coating.
5. Investigation of effects of laser post-treatment on structure and properties of coating, with and without free hBN.

### 1.10 Work Plan

The following work plan is formulated for carrying out the investigation in process sequence.

1. Process study, literature survey, problem formulation
  - SHS reactions and laser surface alloying
2. Feasibility study of problem by initial experiments
  - Experiments to obtain prior information about the effects of the experimental parameters
3. Experimental investigations

Experimentation with preplaced powder and scanning laser for

- Stoichiometric composition
  - Non- stoichiometric composition to incorporate solid lubrication
  - *In-situ* and *ex-situ* reinforcements
  - Laser post treatment
4. Physical and mechanical characterisation of coating

As indicated in the work plan, it was extremely critical to carry out a feasibility study of the proposed process of developing the  $\text{Al}_2\text{O}_3\text{-TiB}_2\text{-TiN}$  coating. The term stoichiometric composition refers to the proportions of the constituents ( $\text{Al}_2\text{O}_3$ ,  $\text{TiB}_2$  and  $\text{TiN}$ ) obtained by the SHS reaction adopted (to be discussed in detail in the next chapter).

The proposed work is fully experimental in nature, for the development of the coating. A number of tests are carried out to characterise the developed coating and determine its properties. In the next chapter, the complete details of the facilities utilized for the experiments and characterisation have been listed.