Chapter 1

Introduction

This chapter begins with an introduction to the field of science and engineering of biomaterials. The main focus is on orthopedic implant materials and their past and current scenario with a special attention to the Ti based biomaterials. This is followed by a brief description of the causes of failure of these materials and various preventive measures adopted to overcome the same. The need for the surface modification techniques such as laser nitriding and atmospheric plasma spraying that were undertaken in the current work is also discussed in this chapter along with the details of the spray drying process used to produce agglomeration of nanoparticles that is required for plasma spraying.

1.1 BIOMATERIALS

The field of biomaterials has evolved to save the life of human beings who suffer from various diseases or lost their mobility due to fracture of the joints and other parts due to ageing, accidents and diseases. The research and development of appropriate biomaterials in the past few decades have already saved millions of lives and improved the quality of life. This field involves researchers from various disciplines such as materials science, applied science, engineering, medicine and hence is of highly multidisciplinary in nature. From the commercial point of view, it has become a multibillion dollar business as the need for biomaterials has drastically increased in the recent past due to increase in the life span of human being. From the scientific point of view and especially with the emergence of nanomaterials which has actually pervaded all fields, the research and development on biomaterials have assumed new dimensions.

Biomaterials have been used in various clinical applications such as orthopedics, dentistry, plastic and reconstructive surgery, ophthalmology, cardiovascular surgery, neurosurgery, immunology, histopathology, experimental surgery and veterinary medicine and surgery. Thus knowledge from different fields and expertise are required to work in this area. The major implants used in the above mentioned fields include intraocular lens, contact lens, vascular graft, drug delivery
compounds, wound healing materials, hip and knee implants, catheter, heart valve, stent, breast implant, dental implant, surgical tools, pacemaker, renal dialyzer, left ventricular assisting devices etc.

As this is a very diverse field with various applications for the different parts of the human body, the requirements that are to be satisfied by the biomaterials vary for different applications. There are several subjective definitions given by various experts for biomaterial in this field and they are as follows:

(a) A biomaterial is a non-viable material used in a medical device intended to interact with biological systems. They may be distinguished from other materials in that they possess a combination of properties, including chemical, mechanical, physical and biological properties that render them suitable for safe, effective and reliable use within a physiological environment (Buchanan et al; 1987).

(b) A biomaterial is “a systemically and pharmacologically inert substance designed for implantation within or incorporation with living systems”.

(c) Biomaterials are materials used for making devices that can interact with biological systems to coexist for longer service with minimal failure (Williams et al; 1981).

(d) A Biomaterial is any systemically, pharmacologically inert substance or a combination of substances utilized for implantation within or incorporation with a living system to supplement or replace functions of living tissues of organs. In order to achieve that purpose, a biomaterial must be in contact with living tissues or body fluids resulting in an interface between living and nonliving substances (Sharma et al; 2005).

(e) Biomaterial is a bioactive material that elicits a specific biological response at the interface of the material which results in the formation between the tissues and the material (Hench et al; 1982)

A number of comprehensive review articles and several books extensively dealing with all the aspects related to biomaterials are available (Rack et al; 2006, Geetha et al; 2009, Kamachi Mudali et al; 2003, Buddy et al; 1997)
1.2 SELECTION CRITERIA FOR BIOMEDICAL IMPLANTS

Metallic materials that are used as biomaterial have to fulfill the following requirements

1. High specific strength.
2. Better mechanical properties, especially high fatigue strength in case of cyclic loading, high impact strength, low young’s modulus and high strength.
3. Good corrosion resistance in body environment.
4. Excellent biocompatibility.
5. Favorable tribological properties such as low friction and high wear resistance,
6. Better osseointegration (bone ingrowth)
7. Long term dimensional stability
8. Processability (casting, deformation, powder metallurgy, machinability, welding, brazing)

1.3 ORTHOPEDIC IMPLANTS

Over the years, the number of orthopedic implant surgery has increased several fold (Kurtz et al; 2007). The major cause for this increase is due to the fact that human joints are prone to degenerative and inflammatory disease that results in pain and joint stiffness, osteoarthritis, rheumatoid arthritis and chondromalacia apart from normal ageing of articular cartilage the most common degenerative process affecting the synovial joints (Dowson et al; 1987). In fact, 90% of the population over the age of 40 suffers from some degree of degenerative joint disease. Degeneration of weight bearing joints often requires surgery to relive pain and increase mobility. Various materials are being explored to replace the diseased joints and the most commonly used materials are metals, alloys, polymers, ceramics and composites. A schematic of a typical hip and knee implant system which uses various materials is given in figure 1.1. Amongst all the materials mentioned above, metals and alloys are
widely used as they are considered to be passive substitutes for hard tissue replacements due to their excellent mechanical properties and corrosion resistance. Alloys are also used for devices such as vascular stents, catheter guide wires, orthodontic arch wires and cochlear implants.

![Figure 1.1 Schematic diagrams of Hip and Knee joints](http://www.docstoc.com/docs/33562360/Total-Joint-Replacement)

1.4 CONVENTIONAL ORTHOPEDIC IMPLANT MATERIALS

1.4.1 STAINLESS STEEL AND COBALT CHROMIUM

During 1930’s, Stainless Steel containing 18% chromium and 8% nickel (18-8 steel) was first used for surgical implant purposes. Though this material possessed superior corrosion resistance than those available at that time, it showed some susceptibility to attack in the saline environment of the human body. Later, the 18-8 steel containing 2-4 wt% of molybdenum with the reduction in carbon content (0.08 wt%) was developed which showed drastic improvement in corrosion resistance in acidic and chloride environments (Man et al; 1981). This material formed the basis for the development of the most popular and extensively used alloy 316L SS (Brown et al 1988) as this alloy possesses required mechanical properties, reasonable corrosion resistance and biocompatibility for load bearing applications (Brown et al; 1988). Hence, 316L stainless steel is the most widely used material for implants in developing countries, because of its low cost, ease of fabrication and easy welding.
However, the 316L SS corrodes inside the body under certain circumstances especially in a highly stressed and oxygen-depleted region, such as the contacts under the screw of the bone fracture plate. In addition, Breme et al have observed poor osseointegration of 316L stainless steel implants when implanted on the legs of the pigs showing less bone formation and also the presence of granulated tissue between the metallic surface and the surrounding bone leading to the loosening of the implant (Breme et al; 1988).

This led to the development of two new cobalt-chromium alloys namely (i) the castable CoCrMo alloy and the CoNiCrMo alloy, which are highly corrosion resistant, because of their passive chromium oxide layer developed (Devine et al; 1975 and Lucas et al; 1982). The wrought alloy is used for making the stems of prostheses for heavily loaded joints such as the knee and hip. However, there was a significant release of nickel from the CoNiCrMo alloy also and it was about three times that of 316L SS. In addition, in vitro studies have indicated that the particulate Co that is released from the implant, is toxic to human osteoblast like cell lines and inhibits synthesis of type –I collagen, osteocalcin and alkaline phosphatase in culture medium.

Apart from the above said drawbacks, both stainless steel (210 GPa) and chromium cobalt alloys (240 GPa) possess high modulus compared to that of the bone (30 GPa) leading to bone resorption and loosening of implant after some years of implantation. Hence, presently, biomaterial research is focused on new materials with low modulus, high corrosion resistance and non-toxic alloying elements. Studies made in this direction showed that titanium and titanium alloys are superior compared to the alloys discussed so far.

1.4.2 TITANIUM AND ITS ALLOYS

Titanium and its alloys are found to be a better alternative to stainless steel and cobalt chromium alloys as they possess high specific strength and low modulus in the ranges of 55-110 GPa (Mitsuo Niinomi et al; 1998). Ti is a material of choice as an implant material because of its superior biocompatibility, resulting in no allergic reaction with the surrounding tissue and also no thrombotic reaction with the blood of the human body (Aragon et al; 1972). Titanium is a comparatively lighter metal with higher hardness and density between aluminum and steel (David hill, 1998). There are
various grades of Ti and amongst them grade 2 is the most commonly used for biomedical applications. However, as the strength of Ti was inferior to steel and cobalt based alloys, Ti-6Al-4V which was originally used for aerospace applications found its way into this field as it possessed high corrosion resistance and excellent biocompatibility. The range of applications of titanium and its alloys in medical area are truly astonishing as their applications cover a wide range of implants starting from dental implants and parts for orthodontic surgery, joint replacement parts for hip, knee, shoulder, spine, elbow and wrist, bone fixation materials like nails, screws, nuts and plates, housing device for the pacemakers and artificial heart valves, surgical instruments and components in high-speed blood centrifuges (Boehlert et al; 2005, Pilliar et al; 1991). Ti–6Al–4V ELI (Ti64, Extra Low interstitial) is the most commonly used grade for implant applications. Apart from the implant applications, titanium alloys are used in healthcare goods such as wheel chairs, artificial limbs, artificial legs etc owing to their excellent compatibility and non-allergic nature.

Though Ti-6Al-4V is far superior from stainless steel and cobalt based alloys, the release of large amounts of titanium, aluminum or vanadium from Ti-6Al-4V and their deposition in tissues, organs and body fluids, which obviously led to serious concern (Vinicius Andre Rodriques Henriques et al; 2010) vanadium contained in this alloy has been associated with potential cytotoxic effects and adverse tissue reactions (Silva et al; 2004). Further, aluminum present in the alloy was found to produce potential neurological disorders (Wapner et al; 1991) and if titanium itself is released into the tissue by passive dissolution or wear, it results in adverse tissue reaction. This is supposed to lead to either a mild response such as discoloration of the surrounding tissue or a severe one, leading to an inflammatory reaction causing pain and loosening of the implants due to osteolysis (Laing et al; 1967). The above said drawbacks of Ti-6Al-4V led to the development of second generation α+β alloys such as Ti-6Al-7Nb (Semlitich et al; 1992) and Ti-5Al-2.5Fe (Borowny et al; 1995, Zwicker et al; 1980).

The long-term clinical experience indicates that the high moduli α+β titanium implants transfer insufficient load to adjacent remodeling bone and this phenomenon termed as ‘stress shielding’ results in bone resorption and eventual loosening of the prosthetic devices (Long et al; 1999, Sumner et al; 1992). In order to achieve high degree of biocompatibility and lower modulus, near beta and beta titanium alloys
including Ti-13Nb-13Zr, Ti-35Nb-7Zr-5Ta (TNZT), Ti-15Mo-5Zr-3Al, Ti-15Mo-5Zr-4Nb-2Ta-0.2Pd (Steinemann et al; 1993) and Ti-12Mo-6Zr-2Fe (Oonishi et al; 1992) etc were introduced and the metallurgy of these alloys are discussed in detail by Geetha et al (Geetha et al; 2009) However, Mo is also found to cause severe tissue reactions in animal studies (Laing et al; 1967) and elements such as Pd, Sn do not seem to show complete biocompatibility. Ultimately, these led to focus on implants with elements such as Zr, Ta and Nb which are classified as non-toxic elements (Kovacs et al; 1993, Mishra et al; 1990) required by a biomaterial. In addition to biocompatibility requirements, several researchers are also working on further reduction of modulus by varying the beta stabilizing elements in Ti alloys in order to mimic the properties of the bone. The modulus of elasticity of various biomedical alloys is compared with bone and shown in Figure 1.2 and while their mechanical properties are compared in Table 1.1.

Figure 1.2 Modulus comparison chart

Geetha et.al; 2009
### Table 1.1 Mechanical properties of Ti and its alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tensile Strength (MPa)</th>
<th>Yield Strength ($\sigma_y$)</th>
<th>Elongation (%)</th>
<th>RA (%)</th>
<th>Modulus (GPa)</th>
<th>Type of alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-7Nb</td>
<td>900-1050</td>
<td>880-950</td>
<td>8.1-15</td>
<td>25-45</td>
<td>114</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>Ti-5Al-2.5Fe</td>
<td>1020</td>
<td>895</td>
<td>15</td>
<td>35</td>
<td>112</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>Ti-5Al-1.5B</td>
<td>900-1080</td>
<td>820-930</td>
<td>15-17.0</td>
<td>36-45</td>
<td>110</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>Ti-15Sn-4Nb-2Ta-0.2Pd (Annealed) (Aged)</td>
<td>715 919</td>
<td>693 806</td>
<td>28 18</td>
<td>67 72</td>
<td>94 99</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>Ti-13Nb-13Zr (Aged)</td>
<td>973-1037</td>
<td>836-908</td>
<td>10-16</td>
<td>27-53</td>
<td>79-84</td>
<td>Near $\beta$</td>
</tr>
<tr>
<td>TMZF(Ti-12Mo-6Zr-2Fe) (Annealed)</td>
<td>1060-1100</td>
<td>1000-1060</td>
<td>18-22</td>
<td>64-73</td>
<td>74-85</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Ti-15Mo (Annealed)</td>
<td>874</td>
<td>544</td>
<td>21</td>
<td>82</td>
<td>78</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Tiadyne 1610 (Aged)</td>
<td>851</td>
<td>736</td>
<td>10</td>
<td>-</td>
<td>81</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Ti-15Mo-5Zr-3Al (ST) (Aged)</td>
<td>852 1060-1100</td>
<td>838 1000-1060</td>
<td>25 18-22</td>
<td>48 64-73</td>
<td>80</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Ti-29Nb-13Ta-4.6Zr (Aged)</td>
<td>911</td>
<td>864</td>
<td>13.2</td>
<td>--</td>
<td>80</td>
<td>$\beta$</td>
</tr>
<tr>
<td>(Ti-15Mo-2.8Nb-0.2Si)</td>
<td>979-999</td>
<td>945-987</td>
<td>16-18</td>
<td>60</td>
<td>83</td>
<td>$\beta$</td>
</tr>
<tr>
<td>Ti-35.3Nb-5.1Ta-7.1Zr</td>
<td>596.7</td>
<td>547.1</td>
<td>19.0</td>
<td>68.0</td>
<td>55.0</td>
<td>$\beta$</td>
</tr>
</tbody>
</table>

Geetha et.al; 2009

### 1.5 Failure of Implants

The materials failed owing to various reasons such as infection, fracture, high corrosion and wear, high modulus, manufacturing defects, inaccurate surgical procedures and insufficient bone integration. Failure of an implant has often led to revision surgery in which the failed implant is removed and new implant is fixed. As the revision surgery is more expensive and its success rate is less compared to the first implantation, the surgeons look forward for the development of a long lasting implant to avoid the complications that arise due to the revision surgery. The number of
revison surgeries and the percentage of aged population in various countries are given in figures 1.3(a) and 1.3(b).

**Figure 1.3 (a) Number of Primary and Revision TJA Procedures Performed in US**

**Figure 1.3(b) Citizen of the age over 65**

Inspite of the fact that Ti and its alloys possess high biocompatibility and other advantageous properties, there are still few drawbacks which obviously reduce the service period to some extent. The major drawbacks of Ti and its alloys are
1. Low wear resistance and high friction coefficient
2. Wear accelerated corrosion
3. Poor osseointegration

The following section reviews the corrosion and wear behavior of various titanium alloys in use, in order to understand their failure mechanisms.

1.5.1 CORROSION CHARACTERISTICS OF TITANIUM AND ITS ALLOYS
1.5.1.1 TYPES OF CORROSION OCCURRING IN TITANIUM AND ITS ALLOYS

Titanium is a highly reactive metal and due to its strong chemical affinity to oxygen, it forms compact oxide layer within microseconds when exposed to the atmosphere (Kasemo et al; 1983). The oxides formed are primarily TiO$_2$ in addition to Ti$_2$O$_5$, Ti$_2$O$_3$ and amongst these, TiO$_2$ is more stable as it has the highest heat of formation (Dh=-915KJ/mol) (for 298.16-2000ºK) (Ashby et al; 1980, Weast et al;1966). Adhesion strength of Ti oxide layer which is few nanometer in thickness, is controlled by the oxidation temperature and the thickness of the oxide layer and the oxidation process is significantly influenced by the presence of nitrogen in air (Ashby et al;1980). All the three crystalline forms of TiO$_2$ (rutile, anatase and brookite) have been observed in the passive layer formed on Ti (Coddet et al; 1987). In the case of the titanium alloys such as Ti-6Al-7Nb and Ti-6Al-4V, the surface oxide films formed by chemical process are observed to be more complicated. The formation of Al$_2$O$_3$, Nb$_2$O$_5$ or V$_2$O$_5$, in addition to TiO$_2$ on these alloys are reported by several authors (Yoshiki Oshida, 2007). Though the thin oxide film formed on Ti surface is easily disrupted owing to mechanical or chemical damage, it will react quickly with the surroundings to reform the oxide film and thus Ti exhibits superior repassivation behavior within short time when compared to other metals and biomedical alloys. (Geetha et al; 2009)

Various types of corrosion are found to occur in implants depending upon the environment, loading nature and tribological conditions. Pitting corrosion of the implants is more predominant in the oral cavity due to the presence of oxygen and acidic food stuffs in the environment and this is the most common type of corrosion associated with 304 SS implants and Cobalt based alloys. Pitting corrosion of cobalt
based alloys leads to the release of carcinogens into the body (Clerc et al; 1997, Mueller et al; 1970). Though titanium and its alloys are highly resistant to pitting corrosion in different in vivo conditions encountered, they undergo corrosion in high fluoride solutions during dental cleaning procedures (Probster et al; 1992). Most of the medical implants are subjected to low frequency loads that may lead to corrosion fatigue as even simple walking results in a hip implant being subjected to a cyclic loading at about 1 Hz. Fatigue corrosion resistance of titanium is almost independent of the pH value while the fatigue corrosion strength of stainless steel declines to a value below pH 4. It has also been reported that the nitrogen implantation and heat treatment procedures enhance the corrosion fatigue of Ti6Al-4V alloy.

Fretting corrosion is very common in all load bearing metallic orthopedic implants. Fretting occurs at the interface of bone-stems, stem-cement and on the modular connection between implant components. The generation of ionic and particulate debris through fracture and abrasion of the metal oxide protective layers and their deposition in the local tissue are of clinical concern. (Geetha et al; 2009). Fretting corrosion, which takes place at modular junctions is due to relatively small scale motion (1 to100 µm) between implant components induced by cyclic loading. In total hip implants, the conical inserts on femoral stems are made either from Co–Cr–Mo alloys or titanium alloys and the heads which fit on these femoral stems are made of either cobalt based alloys, alumina or zirconia. Though there is a perfect interlocking mechanism between the head and stem, due to micro motions the body fluids often penetrate through this junction leading to fretting corrosion. The corrosion of the implant is largely reduced by the presence of protective oxide layer and the presence of the alloying elements. The structural changes in the film or the variation in the ionic or electrical conductivity of the film alters the passive film resistance against corrosion. The oxide film becomes thermodynamically unstable if the interface potential becomes negative or pH is low, resulting in the dissolution of the oxide layer. Willert et al have also reported the occurrence of crevice corrosion in the femoral components made out of Ti-6Al-4V or Ti-6Al-7Nb alloy that had been implanted with bone cement during total hip replacement (Willert et al; 1996).
1.5.1.2 EFFECT OF ALLOYING ELEMENTS, pH AND HEAT TREATMENT ON THE CORROSION BEHAVIOR OF Ti ALLOYS.

Apart from TiO$_2$, the oxides of the alloying elements present along with TiO$_2$, are found to influence the corrosion behavior of the alloy. In the case of Ti-6Al-4V alloy, vanadium oxide in the passive film dissolves and results in the generation and diffusion of vacancies in the oxide layer of Ti-6Al-4V (Metikos-Hukovic et al; 2003). On the other hand, addition of Nb as an alloying element instead of V, has a stabilizing effect on the surface film of Ti based alloys (Kobayashi et al; 1998). Thus the addition of Nb enhances passivation and also resistance to dissolution by the formation of Nb rich oxide which is highly stable in the body environment. Further, Nb addition improves the passivation property of the surface film by decreasing the concentration of anion vacancies. Apart from Nb, the addition of Ta is also found to increase the corrosion resistance of the Ti based alloys. Ta that has chemical properties similar to glass is also immune to all acid environments except HF (Ying Long Zhou et al; 2005). The comparative studies on the corrosion behavior of Ti–Ta and Ti-6Al-4V alloys showed that the addition of Ta remarkably reduces the concentration of metal release because more stable Ta$_2$O$_5$ passive film exhibits higher corrosion resistance than Ti–6Al–4V alloy (Jun et al; 2010). Thus the corrosion resistance of the passive film is greatly dependent on the alloying element and their oxides formed.

The corrosion behavior of various titanium alloys have been studied extensively in different environments and at various pH values, as the pH of the body may vary from 3.5 to 9 depending upon the condition of the area around the implant. Nakagawa et al studied the corrosion behavior of Ti-6Al-4V, Ti–6Al–7Nb and Ti–0.2Pd alloys and they observed that, amongst the three alloys, the titanium alloy with Pd exhibited higher resistance to corrosion over a wide range of pH due to enrichment of palladium on the surface (Nakagawa et al; 2001). The corrosion behavior of three titanium alloys viz. Ti-6Al-4V, Ti–6Al–7Nb and Ti–13Nb–13Zr alloys in phosphate buffered solution revealed that amongst the three titanium alloys, the alloy Ti–13Nb–13Zr was least affected by the change in the pH level and the hardness reduction due to corrosion in protein solution was less for this alloy when compared to other two alloys, thereby exhibiting its superiority compared to the other
two alloys. However, the work of Khan et al on corrosive wear studies of titanium alloys demonstrated that the Ti–6Al–7Nb and Ti-6Al-4V possessed best combination of corrosion and wear in *in vitro* accelerated corrosion test when compared with Ti-Zr-Nb and Ti-Mo alloys (Khan et al; 1999). The corrosion resistance of an alloy is not only affected by its bulk composition but also by the microstructures developed (Geetha et al; 2009). The redistribution of the alloying elements during heat treatment has been found to influence the corrosion resistance of the alloys. Though, the presence of the β phase with elements such as Nb, Ta, etc. in the two phase alloys improves their corrosion resistance, the heat treatments that lead to uneven distribution of alloying elements in either of the phase are found to be detrimental with respect to corrosion (Geetha et al; 2004).

The research on the interactions between material and biological system is relatively new and not yet matured; hence a systematic study based on physical chemistry and life science is required to understand the formation of the oxide film and repassivated layer obtained under different environments.

1.6 TRIBOLOGY OF TITANIUM AND ITS ALLOYS

Tribology is the science dealing with the interaction of surfaces in tangential motion. Hence tribology includes the nature of surfaces from both the physical and chemical point of view, including topography, the interactions of surfaces under load and the changes in the interaction when tangential motion is introduced. From macroscopic point of view, tribology includes (1) Friction (2) Lubrication and (3) Wear.

Loosening of total joint replacements made of metal head and polymer cup has been reported often and 10 – 20% of joints need to be replaced within 15 to 20 years (Malchau et al; 1998). Though there are reasons for the failure of orthopedic implants as mentioned earlier, the loosening of implants due to severe wear of polymer and some metallic components is of great clinical concern (Geetha et al; 2010). As the only solution available currently is revision surgery by which the loosened implants are replaced by newer implant, the major focus of orthopedic research is towards improving the fixation and study of the wear characteristics of total joint components.
The natural joints are well lubricated by the synovial fluid and both the mixed lubrication and boundary lubrication exists in human joints (Duncan Dowson, 2006). The average coefficient of friction of the load bearing synovial joints such as hip and knee is about 0.02 and the wear factor is about $10^6$ mm$^3$/N. On the other hand, the coefficient of friction for implant materials varies from 0.1 to 0.8 depending upon the materials that are in contact and the kind of lubricant used for testing. The most common type of hip joint comprises metallic femoral head articulating against an ultra-high-molecular weight polyethylene (UHMWPE) acetabular cup. From the implant retrieval studies of femoral head of cobalt–chrome–molybdenum (Co–Cr–Mo), 316L stainless steel (SS) and titanium –aluminium –vanadium (Ti–6Al–4V) alloy that were loosened by aseptic loosening, it was noted that titanium alloy femoral heads consistently had the maximum wear averaging 74.3% against ultra high molecular weight polyethylene acetabular component. Co–Cr alloy was found to wear the least and wear of stainless steel was in between Co–Cr and Ti alloy.

The high friction coefficient of titanium element is also one of the major reason for its poor wear resistance. From theoretical calculations, metals with low theoretical tensile and shear strength exhibit high coefficient of friction than higher strength materials (Collings, 1984). Within the class of hexagonal close packed (hcp) structure, titanium has relatively low values of these properties. Consequently, it is expected that titanium would exhibit high frictional values which has been demonstrated for titanium sliding against itself in air (Kustas et al; 2002). Low-tensile strength materials, including titanium also exhibits greater material transfer to nonmetallic counter faces than higher strength metals (Blau et al; 2001). The great affinity of titanium for oxygen results in the formation of an oxide surface layer, which is transferred and adheres to nonmetallic materials such as polymers, resulting in severe adhesive wear (Kustas et al; 2002). This is well demonstrated in the Ti-6Al-4V/UHMWPE combination used in Total Joint Replacement (TJR) prosthesis as the wear rate of UHMWPE against Ti-6Al-4V alloy is found to be 35% greater than for Co–Cr–Mo in hip simulator testing. This high wear rate of UHMWPE is attributed to the mechanical instability of metal oxide layer. Further, the wear of Ti-6Al-4V femoral head is observed due to the presence of foreign bodies in UHMWPE counterpart component. Surface oxides, thus play an important role in influencing the wear behavior and optimization of surface oxide properties through bulk or surface chemical modification is considered as one of the solution to alleviate this problem.
Titanium alloys such as Ti-29Nb-13Ta-4.5Zr with high Nb are found to be highly beneficial with respect to wear, as Nb$_2$O$_5$ possesses very good lubricating property (Aguey-Zinsou et al.; 2007).

Several types of wear include adhesive, abrasive and fretting wear and the types of wear occurring in hip implants are shown in figure 1.4. The wear mechanism of various implants is described in detail by Long et al (Marc Long et al; 2005). Fretting wear studies of Ti-6Al-4V, Ti–5Al–2.5Fe, Ti–13Nb–13Zr and Co–28Cr–6Mo alloys against steel ball in Hank’s solution showed that coefficient of friction was lowest for Ti–5Al–2.5Fe and maximum for Cp Ti (Animesh Choubey et al; 2004). Scanning electron microscopic investigation on the worn out surfaces suggested that wear was due to abrasion, plastic deformation and cracking. Sliding wear resistance of titanium alloys is found to vary with the stresses and alloy composition. Ti-6Al-4V exhibits superior wear resistance at high stress, whereas Ti–35Nb–8Zr–5Ta and Ti-15Mo–2.5Nb–0.3O also possess high wear resistance only at low stresses (Animesh Choubey et al; 2004).

Extensive studies were carried out on wear resistance of both the Cp Ti and Ti-13Nb-13Zr alloy at different nitriding temperatures at 500°C and 800°C (Johansson et al; 2004). There has been a substantial improvement in the hardness and wear resistance of T-13Nb-13Zr alloy, however it got benefited more from nitriding at both the higher and lower temperature than the Cp Ti.

In order to overcome this wear related problems and the revision surgery, continuous effort has been taken to change the cup material from polymer to metal or ceramic. The various combinations of materials used in hip implants and their wear rate are shown in Table 1.2.
Figure 1.4 Schematic diagram of Hip joint subjected to Fretting wear

Table 1.2 Wear rates of various combinations of materials in Hip joints

<table>
<thead>
<tr>
<th>Combination</th>
<th>Wear Rate (µm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal on Polymer</td>
<td>100-300</td>
</tr>
<tr>
<td>Ceramic on polymer</td>
<td>5-150</td>
</tr>
<tr>
<td>Metal on metal</td>
<td>2-20</td>
</tr>
<tr>
<td>Ceramic on ceramic</td>
<td>2-20</td>
</tr>
</tbody>
</table>

Amongst different combinations viz., metal vs polymer, metal vs metal, metal vs ceramic, ceramic vs ceramic, only metal vs metal and ceramic vs ceramic exhibited low wear rates. Metal vs metal prostheses are found to produce 20–100 times lower wear volumes compared to metal on polyethylene bearing (Mc Calden et al; 1995). Metallic wear particles are found to exhibit lower inflammation and the biological reactions to these metallic particles are markedly different from polymer debris in \textit{in vivo}\ (Tipper et al;1999). Both the \textit{in vivo} and \textit{in vitro} studies have shown that Co and Cr particles have toxic effects on different cells and tissues. In addition, it has also been observed that metal on metal prosthesis exhibits high frictional torques than the metal on polymer (Akahori et al; 2003). Ceramic on ceramic (Alumina) was introduced 20 years back as they exhibited much less wear than the metal (CoCr) on polymer and metal on metal. However, fracture of these implants and release of
ceramic wear particles are also observed frequently. The other ceramic material used for implant application is zirconia, which was considered to be a better alternative for alumina as alumina is highly brittle. Zirconia exhibits best mechanical properties and have high resistance to crack propagation and widely used. However, there are few cases in which these implants failed early due to ageing phenomena and issues related to manufacturing defects (Jerome chevalier et al; 2006).

1.7 MOTIVATION FOR THE CURRENT RESEARCH

Development of new materials or changing the currently existing materials have become very essential as implants with longer service period are required when compared to currently existing materials which last for 15-20 years. Several groups are focusing their attention on development of new ceramics or composites and porous materials to minimize the failure by increasing the wear resistance, biocompatibility and decreasing the modulus. Few other groups are working on surface modification of the existing materials to improve the corrosion, wear and osseointegration of the implant.

As Ti based biomaterials is the best choice for the orthopedic applications, the most important characteristics that has to be improved is their poor tribological property and inferior osseointegration. To realize the full benefit of titanium alloys in friction and wear applications, surface modification techniques are needed to effectively increase near-surface strength thereby reducing the coefficient of friction and lowering the tendency of material transfer and adhesive wear.

In the past few decades surface modification techniques such as CVD, PVD, plasma nitriding and ion implantation have been employed which resulted in improvement in hardness and other properties which are to be satisfied for biomedical applications. With the advent of the nanomaterials, there are several reports on nano phase materials for tissue engineering applications. Surfaces with nano features are preferred as they mimic the natural bone and also invoke higher cell reactivity. Nano hydroxyapatite (HA) coating on metallic implants is known to accelerate bone growth and enhance bone fixation and properties such as grain size, pore size, wettability etc could control protein interactions modulating subsequent bone adhesion. Though there are several reports on the development of nanoceramic bioactive coatings, very
few groups work on the wear resistant nanoceramic coatings. Nanoceramic coatings using alumina-titania and zirconia have proven to enhance the wear resistance of mild steel several times when compared to the substrates coated with micron sized powders. There are several applications of nano ceramic coatings in the field of automobile, naval, aerospace and biomedical sectors (Kabacoff et al; 2002). In the present work two different coating techniques namely laser nitriding on Cp Ti and Ti-13Nb-13Zr alloy as well as atmospheric plasma spraying of nanoceramic powders were carried out and their surface properties were evaluated. The detailed description of the two processes mentioned above is explained in the following sections.

1.8 LASER SURFACE ENGINEERING

The most commonly used methods employed for modifying the surface of the titanium alloys are Physical Vapor Deposition (PVD), Chemical vapour deposition (CVD), Ultra passivation of titanium and nitrogen ion implantation. The latter has become a standard procedure for titanium alloys, yet it cannot guarantee adequate wear resistance of critical TJR components and long-term service due to the rapid thinning of the < 10 μm thick hardened layer (Shenhar et al; 2000). Lately, there has been an increasing interest in using titanium nitride (TiN) coatings; the most commonly used being chemical vapor deposition (CVD) and reactive physical vapor deposition (PVD) (Morton et al; 1992). In both processes, TiN coating is grown from the vapor phase, with the reactions occurring on the substrate surface, as well as on the target and in the gaseous phase. The effective adhesion of coatings to titanium alloys is often poor because of the lack of load support provided by the relatively soft substrate beneath the coating. As a result, delamination of TiN coating has been observed on the articulating surfaces of Ti-6Al-4V orthopedic implants in in vitro wear simulations and clinical studies. For PVD coating deposited on titanium alloy, delamination could be partly due to compressive stress developed in TiN layer.

To prevent the failure of TiN coating adhesion, surface modification methods capable of producing a strong TiN coating/substrate interface, as well as providing a hard load-supporting subsurface layer, should be looked for. For many applications, laser surface treatment is an excellent alternative to PVD, CVD and ion implantation
processes. The following sections highlight the advantages, research scenario and technical challenges in the field of laser surface modification.

Some of the advantages of laser process over other techniques are described below.

1. Owing to high power density of a focused laser, treatment can be conducted at high speed and at low heat input resulting in the production of deeper case depth with narrow width of fusion and minimum thermal distortion and deformation.

2. A laser beam can easily be transmitted through air to an appreciable distance without serious attenuation or degradation and a vacuum is not required unlike other techniques. Further, the shape and size of the work piece is not restricted.

3. Shielding atmosphere and its pressure can be selected freely.

4. A laser beam can be readily shaped, regulated aligned, delivered, redirected, reflected, divided and focused by optics, therefore making it possible to perform alloying/other processes in localized and inaccessible areas.

5. Full automation and precise control can be achieved using computer and robot.

6. Time-sharing and high speed is possible and hence high efficiency production process can be achieved.

7. The depth of modification and hardness attained on the surface is very high compared to other techniques.

1.8.1 LASER NITRIDING

Laser nitriding is a process in which nitrogen gas is introduced along with the laser source which melts the surface during scanning. The presence of the nitrogen results in the nitride formation in the melted and resolidified surface. Laser surface engineering requires the protection of the molten surface by an inert gas, such as argon or helium, to prevent oxidation during processing. In the case of titanium
alloys, the replacement of the inert gas by nitrogen is a technique which has been developed over the past 30 years for modifying the near-surface region of alloys without altering the bulk characteristics of titanium alloys (Katayama et al; 1985, Mridha et al; 1991, Kloosterman et al; 1995, Xin et al; 1996, Nwobu et al; 1999, Abboud et al; 2008). Laser nitriding with 100% nitrogen atmospheres was used in most of the early works and this resulted in the formation of a thin 5-10 μm surface layer of titanium nitride. The highest hardness recorded closest to the surface was ~2000HV, and in addition, the TiN layers provided improved corrosion resistance, a lower coefficient of friction and higher wear resistance. However, in the surfaces with higher hardness, cracking was often observed. Several researchers found that when laser nitriding Cp Ti and Ti-6Al-4V alloy, it produced a surface with hardness > 600 HV, and cracking (Katayama et al; 1985). However, cracking could be avoided by preheating the substrate prior to nitriding, which reduced the cooling rate and controlled the level of the residual stresses developed on solidification (Katayama et al; 1985, Morton et al; 1991, Hu et al; 1997). An alternative method of alleviating this problem is the use of dilute nitrogen atmospheres, usually in the form of an argon-nitrogen mixture, together with lower nitrogen flow rates (Mordike et al; 1985, Grenier et al; 1997, Mohmad Soib Selamat et al; 2001). Dilute nitrogen atmospheres were found to reduce significantly or eliminate cracking, but at the expense of a decrease in surface hardness and a smaller melt depth. In the work of Selamat it has been clearly demonstrated that cracking was not produced when processed with a dilute nitrogen atmosphere (20%N- 80% Ar), while laser nitriding using a 50%N +50%Ar atmosphere led to a reduction in hardness (Xue et al; 1997). In addition to the environment, the scanning speed also affects the properties. The best results for laser processing Ti-6Al-4V alloy using a stationary beam were obtained with medium scanning velocities of 15-50 mms⁻¹ and with a minimum overlap of 50%, otherwise it was found that a part of each track will only be molten once (Morton et al; 1991). Apart from scanning speed and environment, the other factors which influence the properties are surface finish of the substrate and its temperature.
1.9 NANOCERAMIC COATINGS USING ATMOSPHERIC PLASMA SPRAYING

Nanoceramic coatings are found to tremendously improve the surface hardness and the wear resistance of the coated substrates (Richard et al; 2010). The advantages of the nanoceramic coatings are:

1) Higher longevity and reliability of the component.
2) Good replacement of hard chrome plating
3) Elimination of toxic hazardous materials
4) High adhesion strength
5) Higher fracture toughness

Nanoceramic coatings are usually achieved using thermal spray techniques and atmospheric plasma spraying is the most widely used technique to achieve the same. One of the main advantages of this process is the range of temperatures that can be used to make coatings on materials. This allows the range of materials from high to low melting temperatures to be used. Also, the plasma coatings obtained are generally denser and stronger when compared to the other thermal spray processes.

1.9.1 ATMOSPHERIC PLASMA SPRAYING

Plasma spray, a process used to fabricate ceramic coatings, is very simple in concept, but very complex in practice. The schematic diagram of atmospheric plasma spraying is shown in figure 1.5. An inert gas is passed through a region of electric discharge, where it is heated to very high temperature ranging from 10,000 to 22,000 K and which results in the production of plasma. A plasma is an electrically conductive gas which contains ions and electrons. The rapidly expanding plasma is forced out through a nozzle at velocities between 1,200 and 1,500 m/s and directed towards a substrate. Particles to be coated are injected into the plasma, where they are heated and then accelerated. Even though the particles and plasma temperatures are high, the temperature of the substrate is minimal. There are large number of parameters that must be properly selected as they can affect the structure and properties of the coating. The temperature and velocity of the plasma depend on the
power supplied to the gun, the type and the flow rate of the gas used. Usually, two gases are used, an inert gas such as helium or argon, and a secondary gas, such as hydrogen. Other factors include the morphology of the powder particles, distance from the gun to substrate, position and orientation of the powder injection ports, and surface preparation of the substrate. Taken all together, these parameters determine the thermal history of injected particles, velocity of impact, and flow and solidification characteristics after impact, thus giving the resultant coating and its microstructure. The details regarding the apparatus are discussed in the chapter 2.

![Figure 1.5 Schematic diagram for Atmospheric Plasma Spraying Technique](http://www.gordonengland.co.uk/ps.htm)

Various parameters such as carrier gas flow rate, stand off distance, argon gas flow rate, power input will control the quality of the coating. The mechanical properties of the plasma sprayed coating greatly depend upon what is termed as the Critical Plasma Spray Parameter (CPSP) which is a function of applied voltage, current and primary gas flow rate. The increase in the value of CPSP leads to the decrease in porosity in nanostructured coating whereas, the porosity of conventional coating is independent of CPSP. Similarly for nanostructured coating, the hardness, wear resistance and the spallation resistance increases with increase in CPSP (Jordan et al; 2001). On the other hand, the above properties are independent of CPSP for conventional coatings (Eun pil song et al; 2008) (figure 1.6). The superior properties of the nanoceramic coatings are associated with coatings that have a retained nanostructure, especially with unmelted nanoparticles.
Figure 1.6 Effect of CPSP on conventional and nano structured coatings

The quality of the coating is also affected by the stand off distance. Greater the stand off distance, the particles tend to grow during in-flight resulting in poor adhesion with high porosity. Similarly, lower stand off distance will also lead to poorly consolidated splats. Hence in order to ensure proper adhesion, the optimum stand off distance should be in-between 10 to 14 centimeters.

The size and shape of the powder have immense impact on the coating quality and properties. Fine powders tend to stick to the sidewall of the feed lines and spray nozzle tip causing reduction of powder passage area. Fine powders with strong surface interaction also tend to agglomerate leading to limited flowability. If the powder is too fine, it is difficult to maintain a constant powder flow rate during spraying. On the other hand, if the size of the powder is too large, insufficient melting can occur. However, the optimal powder size required depends on the melting point of the powder utilized, type of spray equipment and coating applications.
1.10 AGGLOMERATION OF NANOPOWDERS FOR ATMOSPHERIC PLASMA SPRAYING

Nanopowders as such cannot be fed into the plasma flame as small particles have very low mass and it has the tendency to fly away. Hence, it is necessary to agglomerate the powders into micron size to be utilized for plasma spraying. Recently, synthesis of nanopowders in insitu during the plasma spraying is also being tried, however, this research is in a very preliminary stage of investigation. There are various methods to obtain agglomeration of nanopowders and they are atomization technique, fusing and crushing technique, Sol gel technique and Spray drying technique. Amongst all, the best method for agglomerating the nanopowders is by spray drying technique, which is described below.

1.10.1 SPRAY DRYING

The production of particles from the process of spraying has gained much attention in recent years and it is the most widely used industrial process involving particle formation and drying. It is highly suited for the continuous production of dry solid powders, granulates or agglomerated particles from liquid feedstock as solutions, emulsions and suspensions. The schematic diagram of spray drying equipment is shown in figure 1.7.

Steps involved in agglomeration of nano particles

1) Preparation of stable suspension with appropriate solid loading, dispersant, binder and evaluation of the pH, viscosity and flow characteristics.

2) Atomization of a liquid feed into fine droplets.

3) Mixing of these spray droplets with a heated gas stream, allowing the liquid to evaporate and leave dried solid particles.

4) Separation of dried powder from the gas stream and collection.
1.10.1.1 SUSPENSION PREPARATION

The preparation and nature of suspension plays a major role in the formation of agglomerated powders and it highly influences the size and shape of the agglomerated powders. The solid loading (powders to be agglomerated) is added in an appropriate solvent and a suitable dispersant and binder is added to disperse the
particles. The concentration of the solid loading, dispersant and the binder are adjusted and the properties such as viscosity and flow characteristics are measured. Care must be taken with high solid loadings (above 30%) to maintain proper atomization to ensure proper droplet formation. The higher loading of solid contents will result in blocking at the nozzle openings. On the other hand, very low solid loading drastically affects the agglomeration of particles. Higher viscosity of the slurry results in clogging of nozzle openings which in turn hinders the correct drop formation. As the viscosity is lowered, less energy or pressure is required to form a particular spray pattern. Addition of a small amount of surfactant to the suspension (slurry) can significantly lower the surface tension and results in a wider spray pattern, smaller droplet size and higher drop velocity. Thus by trial and error, one has to develop a suspension with good flow characteristics.

1.10.1.2 ATOMIZATION

The main function of the atomizer is to break the bulk liquid into droplets, leading to the production of particles of the desired shape, size and density. Smaller the droplets, larger the surface area, easier is the evaporation with a better thermal efficiency. The ideal size from a drying point of view would be spraying of droplets of same size, which would mean that the drying time for all particles would be the same for obtaining equal moisture content. Further, the surface tension of the liquid causes the droplet suspended in air to form itself into a sphere.

1.10.1.3 MIXING AND DRYING

Once the liquid is atomized, it must be brought into intimate contact with the heated gas for evaporation to take place equally from the surface of all droplets within the drying chamber. The heated gas is introduced into the chamber by an air disperser, which ensures that the gas flows uniformly to all parts of the chamber.

1.10.1.4 AIR DISPERSER

Air disperser is used to disperse the hot air coming out of the heater. The air disperser uses perforated plates or vaned channels through which the gas is directed, creating a pressure drop and thereby equalizing the flow in all directions. It is critical that the gas entering the air disperser is well mixed and has no temperature gradient.
across the duct. Usually the heater used inherently produces a well-mixed gas stream, or a mixing section is placed between the heater and the air disperser to produce the same. The fine droplets are evaporated when they come in contact with the air. The contact time of the hot air with the spray droplets is only for a few seconds, during which drying is achieved and the air temperature drops instantaneously. The thermal energy of the hot air is used for evaporation and the cooled air pneumatically conveys the dried particles in the system.

1.10.1.5 DRYING CHAMBER

The largest part of a spray-drying system is the drying chamber and this vessel must be of adequate volume to provide enough contact time between the atomized cloud and the heated glass. Further, it is designed in such a way that all droplets must be sufficiently dried before they come into contact with the surface. Centrifugal atomizer requires larger diameter and less cylinder height. The size of this chamber is chosen based on the particle size that are to be produced in order to avoid wet deposition on the walls of the chamber.

1.10.1.6 POWDER SEPARATION

The dried powders consist of both coarse and fine powders. The coarse powders are collected at the bottom of the chamber which is provided with a conical outlet and fitted with a rotary valve, whereas the fine powders containing some amount of moisture will be separated using the cyclone separator. Spray dried powders that are obtained using above procedures should have the following properties to be utilized for plasma spraying.

[1] Nearly spherical shape
[2] Excellent flowability
[3] High compressibility
[4] Low bulk density
[6] Reduced moisture Content
[8] Increased thermal stability
In spite of the fact that spray drying is a conventional method which is extensively used for various applications, the agglomeration procedure to be adopted for nano ceramic Al₂O₃-13TiO₂ powders has not been reported so far. However, there are few manufacturers who produce these powders and the cost of the agglomerated nanoceramic powders is very high. It is also a very challenging task to achieve high yield using this technique.

Apart from this first introductory chapter, the thesis consists of five other chapters and the second one dealing with the experimental techniques. The third chapter dwells on laser nitriding on CpTi and Ti-13Nb-13Zr alloy and the characterizations performed on them. The fourth chapter deals with atmospheric plasma spraying technique which was adopted for coating and while the fifth one is devoted to the procedure followed for the agglomeration of nano particles in order to enable them to be coated on the implant substrate. The detailed discussions on the results obtained are dealt with in the last and final chapter.

Three phases of the work carried out in this thesis are summarized below.

![Figure 1.8 Flow Chart of Laser Nitriding](image_url)
Figure 1.9  Flow chart for Atmospheric plasma spraying

Figure 1.10  Flow chart for Spray drying