CHAPTER 1

INTRODUCTION

1.1 TITANIUM AND ITS PROPERTIES

Titanium was discovered by Gregor in 1791 and by Klaproth in 1795 (Boyer et al 1994), and named the metal after the Greek mythological god ‘Titan’ (Bomberger et al 1985, Ogdom and Gonser 1956, McQuillan and McQuillan 1956). Titanium is the structural metal which is available in abundance, making up about 0.62 % of the earth's crust. Though it exists in many mineral forms, its three main forms are leucoxene, rutile and ilmenite.

Titanium belongs to the fourth group and period in the Mendeleef’s periodic table. Its atomic number is 22 and its atomic weight 47.9. Being a transition element, it has an incompletely filled d shell in its electronic structure. This incomplete shell enables titanium to form solid solutions with the most substitutional elements having a size factor within ± 20 %. In its elemental form, titanium has a high melting point (1668°C). Titanium is exceptional among metallic elements, since, it exhibits various valencies, ranging from one to four because of the existence of numerous oxides. The high strength and low density of titanium are related to a specific electronic state, which allows the formation of relatively strong bonds between the titanium atoms (Koenoenen and Kivilahti 1988).
The increased use of titanium as structural material, began to accelerate in the late forties and early fifties of the last century, due to its unique set of properties (Refer Table 1.1).

**Table 1.1 Properties of Titanium**

<table>
<thead>
<tr>
<th>General Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Name, symbol, Atomic number</td>
<td>Titanium, Ti, 22</td>
</tr>
<tr>
<td>Element category</td>
<td>Transition metal</td>
</tr>
<tr>
<td>Group, period, block</td>
<td>4, 4, d</td>
</tr>
<tr>
<td>Appearance</td>
<td>Silvery grey-white metallic</td>
</tr>
<tr>
<td>Atomic weight (g/mol)</td>
<td>47.90</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>[Ar] 4s² 3d²</td>
</tr>
<tr>
<td>Electrons per shell</td>
<td>2, 8, 10, 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Solid</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>4.54</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>1668</td>
</tr>
<tr>
<td>Boiling temperature (estimated) (°C)</td>
<td>3260</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, α, at 20°C</td>
<td>8.4x10⁻⁶</td>
</tr>
<tr>
<td>Thermal conductivity (W/(mK))</td>
<td>19.2</td>
</tr>
<tr>
<td>Heat of fusion (KJ mol⁻¹)</td>
<td>14.15</td>
</tr>
<tr>
<td>Heat of vaporisation (KJ mol⁻¹)</td>
<td>425</td>
</tr>
<tr>
<td>Specific heat capacity ( J mol⁻¹ K⁻¹) (25°C)</td>
<td>25.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Miscellaneous</th>
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</thead>
<tbody>
<tr>
<td>Transformation temperature (°C)</td>
<td>882.5</td>
</tr>
<tr>
<td>Modulus of elasticity, α, (GPa)</td>
<td>105</td>
</tr>
<tr>
<td>Yield strength, α, (MPa)</td>
<td>692</td>
</tr>
<tr>
<td>Ultimate strength, α, (MPa)</td>
<td>785</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.32</td>
</tr>
<tr>
<td>Vicker’s hardness (MPa)</td>
<td>970</td>
</tr>
</tbody>
</table>
The properties of titanium are high strength to weight ratio, corrosion resistance, biocompatibility and low density which find application in the aerospace industry, chemical processing, oil refineries and manufacture of medical devices.

1.2 PHYSICAL METALLURGY OF TITANIUM

Titanium is an allotropic element which exists in more than one crystallographic form. At room temperature, titanium exhibits a hexagonal close packed (hcp) crystal structure, referred to as the "alpha" (α) phase. However, as the temperature is raised to 882.5°C (Collings 1994), pure titanium undergoes allotropic transformation from the α-phase (hcp) to a body-centered cubic (bcc) crystal structure, called the "beta" (β) phase. The temperature at which this transformation occurs is known as beta transus and is defined as the lowest equilibrium temperature at which the material is 100% β (bcc) phase.

1.3 CLASSIFICATION OF TITANIUM ALLOYS

Titanium alloys are classified based on their chemical composition, weight percentage of the alloying elements and its effect on the resultant microstructure at room temperature. The formation of two different crystal structures forms the basis for naming the three generally accepted classes of titanium alloys namely α, α+β and β (Donachie 1988).

1.3.1 Alpha Titanium Alloys

Commercially pure titanium (Cp-Ti) is alloyed with small amounts of oxygen to increase its hardness and tensile strength. It is possible to produce a range of commercially pure grades of titanium with strength levels between 290 and 740 MPa, by varying the amount of oxygen. Cp-Ti is
available in four different grades (American Society of Testing and Material grades I to IV), based on the incorporation of small amounts of oxygen, nitrogen, hydrogen, iron and carbon. The maximum impurity limits of grades I to IV pure titanium are listed in Table 1. The main disadvantage of α titanium is that it possessed low strength and poor wear resistance (Lautenschlager and Monaghan 1993). It must be alloyed with various elements to change its characteristics and to improve its mechanical properties.

Alloys of titanium with α stabilizing element maintain their hcp crystallographic structures at room temperature. The α stabilizers are aluminium, oxygen, nitrogen and carbon (Taira et al 1989). The strengthening effects in alpha alloys are achieved by solid-solution of the alloying elements. The α titanium alloy, generally used in aerospace industries, is easily weldable, more oxidation-resistant and superior in strength (Donachie 1982).

Table 1.2 Maximum impurity limits (wt.% of pure titanium)

<table>
<thead>
<tr>
<th>Type</th>
<th>N</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM grade I</td>
<td>0.03</td>
<td>0.20</td>
<td>0.18</td>
<td>0.10</td>
<td>0.015</td>
</tr>
<tr>
<td>ASTM grade II</td>
<td>0.03</td>
<td>0.30</td>
<td>0.25</td>
<td>0.10</td>
<td>0.015</td>
</tr>
<tr>
<td>ASTM grade III</td>
<td>0.05</td>
<td>0.30</td>
<td>0.35</td>
<td>0.10</td>
<td>0.015</td>
</tr>
<tr>
<td>ASTM grade IV</td>
<td>0.05</td>
<td>0.50</td>
<td>0.40</td>
<td>0.10</td>
<td>0.015</td>
</tr>
</tbody>
</table>

1.3.2 Alpha-Beta Titanium Alloys

Alpha-Beta alloys contain one or more α stabilizers or α soluble element and one or more β stabilizers. These alloys retain more of the β phase after solution treatment than α alloy. α-β alloys can be strengthened by solution treatment and aging. Solution treatment is usually done at high
temperature in two phases and is followed by quenching in water, oil or any other suitable quenchant. As a result of quenching, the β phase present at the solution treatment temperature may be retained or may be partly or fully transformed during cooling by either martensitic transformation or nucleation and growth. Solution treatment is followed by normal ageing between 480 to 650°C, to precipitate the α phase and produce a fine mixture of α and β phase in the retained or transformed β phase.

Alpha-Beta titanium alloys are commonly strong, owing to their duplex phase structure. The α-β alloys are more formable than alpha alloys but they are difficult to weld (Donachie 1982). The α-β titanium alloys contain various alloying elements such as aluminium, vanadium and niobium. The most popular alloy of α-β titanium alloys are Ti-6Al-4V and Ti-6Al-7Nb.

1.3.2.1 Aluminium

Aluminium, a typical α stabilizer, increases the α-β alloy transition temperature and maintains the improved mechanical properties over pure titanium. Other α stabilizers includes oxygen, which forms interstitial solid solutions to titanium.

1.3.2.2 Vanadium

Vanadium is a continuous solid-solution type β stabilizer (Donachie 1982). Ti-6Al-4V is the most commonly used titanium alloy especially in implant dentistry because of its lower elastic modulus. Although Ti-6Al-4V alloy is being widely used in dentistry, studies have shown that the release of aluminium and particularly vanadium ions from the alloy might cause long-term problems, such as peripheral neuropathy, osteomalacia and Alzheimer (McLachlan et al 1983 and Walker et al 1989).
1.3.2.3 Niobium

In early 1990’s niobium was introduced as an alloying element to lower the thermal expansion coefficient of pure titanium (Gibbesch et al 1989). Niobium is regarded as a useful alloying element for titanium because of its corrosion resistance and excellent biocompatibility (Plenk and Schider 1990, Semlitsch et al 1992). The heterogeneous Ti-6Al-7Nb alloy has α-β structure, with the enrichment of Al in the α-phase and Nb in the β-phase (Sittig et al 1999).

1.3.3 Beta Titanium Alloys

Beta titanium alloys are richer in β stabilizers and lesser in α stabilizers than α-β alloys. They are characterized by high hardenability, with the β phase completely retained by air cooling of thin sections or water quenching of thick sections. β alloys have excellent forgeability, cold-rolling capabilities and in sheet form, can be cold formed more readily than high strength α-β or α alloys. β alloys can be divided into two categories according to their constitutional behaviour with titanium: Beta – isomorphous elements and Beta – eutectoid elements.

Beta – isomorphous elements exhibit complete mutual solubility with beta titanium. Increasing addition of the solute element progressively depresses the transformation temperature. Molybdenum and vanadium are the most important beta isomorphous elements, while niobium and tantalum have also found application in some alloys (Collings 1994).

Beta – eutectoid elements have restricted solubility in beta titanium and form intermetallic compounds by eutectoid decomposition of the beta phase. The decomposition of beta phase in the titanium-iron, titanium-chromium and titanium-manganese systems is so slow that intermetallic
compound formation does not occur during normal commercial fabrication and heat treatment.

Beta alloys are strengthened by the solid solution effect of the β stabilizer additions. It is prone to ductile-brittle transformation. It has unique characteristics of low elastic modulus and superior corrosion resistance. It possesses good ductility and toughness, relatively low strength and excellent formability. Solution treated β- alloys begin to precipitate α phase at slightly elevated temperatures and are therefore unsuitable for elevated temperature service without prior stabilization or over ageing treatment.

1.4 SURFACE PROPERTIES OF TITANIUM AND ITS ALLOYS

There has been a considerable number of scientific and technical articles published on the structure, compositions, properties of titanium and its alloys and, many of the favorable properties that arise from the presence of surface oxide. It is well known that a native oxide film grows spontaneously on the surface upon exposure to air. The excellent chemical inertness, corrosion resistance, re-passivation ability and biocompatibility are due to the chemical stability and structure of the titanium oxide film that is typically a few nanometers thick. The composition and oxide thickness of mechanically polished Cp-Ti surface was characterized by X-ray photoelectron spectroscopy (XPS) (Textor et al 2001).

The characteristics of films grown at room temperature on Cp-Ti are as follows:

- The amorphous or nanocrystalline oxide film is typically 3-7 nm thick and mainly composed of a stable TiO₂ oxide layer.
The TiO$_2$ / Ti interface has an O to Ti concentration ratio that varies gradually from 2 to 1 from the TiO$_2$ film to a much lower ratio in bulk.

Hydroxide ions (OH$^-$) and chemisorbed water bonded with Ti cations leads to weakly bound physisorbed water on the surface. In addition, some organic species like hydrocarbons and metal-organic species, such as alkoxides or carboxylates of titanium also adsorb on the outermost surface layer whose concentration depends not only on the surface conditions, but also on the exposure time to air as well as the quality of the atmosphere during storage.

Hydroxide ions (OH$^-$) attached to metal cations possess acid/base properties depending on the type of the metal cations and the coordinate bonds with the cations. Hydroxides or hydro-complexes of multivalent cations are generally “amphoteric”, that is they exhibit both acid and base (or alkaline) properties. The underlying hydrolysis equations of titanium in an aqueous solution can be presented as follows

\[
\text{Ti} - \text{OH} + \text{H}_2\text{O} \Leftrightarrow [\text{Ti} - \text{O}]^- + \text{H}_3\text{O}^+ \quad (1.1)
\]

\[
\text{Ti} - \text{OH} + \text{H}_2\text{O} \Leftrightarrow [\text{Ti} - \text{OH}_2]^- + \text{OH}^- \quad (1.2)
\]

Reaction 1.1 leads to the formation of negative charges on the surface and reaction 1.2 yields positive charge (Boehm 1971, Schindler 1990, Parfitt 1976).

1.5  BIOMATERIALS

A biomaterial can be defined as any material used to make devices to replace a damaged part in a safe, reliable, economic, and physiologically
acceptable manner. The Clemson University Advisory Board for biomaterials has formally defined a biomaterial to be ‘a systemically and pharmacologically inert substance designed for implantation within or for incorporation with living systems’. Williams et al (1981) defined biomaterials as “non-viable materials used in medical devices, intended to interact with the biological systems”.

Biomaterials are widely used in repair, replacement, and augmentation of diseased or damaged parts of the musculoskeletal system. Common medical devices made of biomaterials include hip replacements, prosthetic heart valves, neurological prostheses and implanted drug delivery systems. These devices are placed inside the human body and termed as implants because they are intended to remain there for a fairly long period of time, and as prostheses they are permanently fixed in the body till the lifespan of the host (Von Recum 1999 and Hench 1985). The fundamental requirement of a biomaterial is that the material and the tissue environment of the body should coexist without any undesirable or inappropriate effect on each other.

The ultimate goal of using biomaterials is to improve human health by restoring the function of natural living tissues and organs in the body. It is essential to understand the relationships between the properties, functions and structures of biological materials, implant materials and interaction between the two in the body.

In the past few decades, there has been a significant increase among people in the use of self-operating machines, increased participation in sports, increased interest in motorcycles and bicycles and day-to-day increase in traffic, has ultimately resulted in the enormous increase in number of accidents. This in turn has led the people to inevitably opt for orthopaedic implants for early and speedy recovery to resume their routine activities.
The high strength, low weight, and outstanding corrosion resistance possessed by titanium and its alloys have led to a wide and diversified range of successful applications in the medical field, which demands high levels of reliable performance.

1.6 PROPERTIES OF TITANIUM AND ITS ALLOYS AS A BIOMATERIAL

The design and selection of biomaterials depend on the intended medical applications. In order to serve a longer period without any rejection, an implant should possess attributes such as excellent mechanical properties, biocompatibility, corrosion and wear resistance.

1.6.1 Mechanical Properties

Titanium and its alloys are used in orthopaedic surgery as wires, nails, plates and screws for the fixation and stabilization of fractures, or, in the form of artificial joints for the replacement of bones in the human body. Some implants are used for short time durations whereas, others remain in place providing continuous and trouble-free function for decades. To avoid a revision surgery caused by the implant materials, the materials must have certain chemical and mechanical requirements. Chemical requirements include high biocompatibility without altering the environment of the surrounding tissue even under deformation and sterilization. Mechanical property requirements are related to specific strength, modulus, fatigue, creep and fracture toughness which, in turn, are related to microstructures.

1.6.2 Biocompatibility

The European Society for Biomaterials, defines biocompatibility as “The ability of a material to perform with an appropriate host response in a
specific application” (Rocha 1996). It encompasses all aspects of the interfacial reaction between a material and the tissues of the body. The dependence of biocompatibility on several factors is presented in Figure 1.1.

![Diagram of various system parameters on biocompatibility]

**Figure 1.1 Schematic diagram of various system parameters on biocompatibility**

In accordance with Figure 1.1, biocompatibility involves physical, chemical, biological, medical and design aspects. The success of the biomaterial is mainly dependent on the reaction of a human body to the implant and this measures the biocompatibility of a material (Williams 2008). When compared to all the other properties of titanium, excellent biocompatibility is one of the most practical aspects considered in various replacements. This useful biological property of titanium is based on the existence of titanium oxide (TiO$_2$) layers, which are naturally formed in oxygen-containing environments. This oxide layer which is mainly TiO$_2$, forms so readily and is very adherent to the parent titanium.
Cp-Ti is considered to be the best biocompatible metallic material because its surface properties result in the spontaneous build-up of a stable and inert oxide layer. The main physical properties of titanium responsible for biocompatibility are: low electronic conductivity, high corrosion resistance, thermodynamic state at physiological pH, low ion-formation tendency in aqueous environments and an iso-electric point of the oxide. In addition, the passive film covered surface is only slightly negatively charged at physiological pH. Moreover, titanium has a dielectric constant comparable with that of water with the consequence that the coulomb interaction of charged species is similar to that in water.

1.6.3 Corrosion and Wear Resistance

Another important issue is the longevity of the biomaterial. In other words, the biomaterial needs good corrosion resistance, because corrosion can adversely affect biocompatibility and mechanical integrity. The biological environment is harsh and can lead to rapid or gradual breakdown of the passive film formed on the surface of the respective materials, by chemical corrosion. Titanium and its alloys are more corrosion resistant than other implant materials such as stainless steel, cobalt-chromium-molybdenum and cobalt-nickel- chromium alloys (Merrit and Brown 1981). All the commonly used titanium based biomaterials have extraordinarily good corrosion resistance for extended contact with the human bone, synovial fluids, soft tissue and plasma, when compared to other metallic biomaterials. However, there has been some concern regarding the toxicity of vanadium and the long term detrimental effects of aluminum, but until now these concerns have not been substantiated with data. The corrosion resistance of titanium is due to the formation of a protective oxide film which reduces the release of titanium or the alloying elements. The composition of this oxide film ranges from TiO$_2$-Ti$_2$O$_3$, TiO-TiO$_2$. Preliminary studies (Gangloff et al 1992) and tentative hypotheses (Mausli et al 1988) indicated that the oxide film results from bulk titanium and their alloying elements such as Mo, Nb, V and Cr, but, they are
not in the passive film to any significant extent. Titanium is a reactive metal, and disruption or damage to the oxide film is repaired immediately in the presence of air or oxidizing media. In applications where there is no oxygen or reducing media, as in the case of a crevice, titanium cannot form the passive film and therefore would not be corrosion resistant.

1.7 CLINICAL APPLICATIONS OF TITANIUM AND ITS ALLOYS

Titanium and its alloys are commonly used as biomaterials due to their excellent biocompatibility with little or no reaction to surrounding tissues. Titanium has an extreme reactivity to oxygen and promotes the formation of a stable oxide film on its surface, thus giving raise to corrosion resistance. These attractive properties, along with their low modulus of elasticity, were a driving force to the early introduction of some titanium alloys as biomaterials.

1.7.1 Hard Tissue Replacements

Hard tissues are often damaged due to accidents, ageing and other causes. It is a common practice to surgically substitute the damaged hard tissues with artificial replacements. The requirements of different endoprothetic materials are different, depending on the regions in which the implants are inserted. Hence, titanium and its alloys are widely used as hard tissue replacements in artificial bones, joints and dental implants.

One of the most common applications of titanium and its alloys are artificial hip joints that consist of an articulating bearing (femoral head and cup) and a stem as depicted in Figure 1.2.
Figure 1.2 Schematic diagram of artificial hip joints

The articulating bearing must be positioned in such a way that it can reproduce the natural movement inside the hip joints. Secure positioning of the femoral head in relation to the other components of the joint is achieved using the stem. The hip stem is anchored permanently to the intramedullary canal of the femur. The cup, which is the articulating partner of the femoral head, is used for fixing by reaming out the natural acetabulum to fit the design. Titanium and its alloys are also often used in knee joint replacements which consist of a femoral component, tibial component and patella.

For endosseous implant fixation in bones, such as in the case of artificial hip and knee joints two methods are currently employed. One is bone cement fixation and the other is cementless implantation. Consequently, prostheses can be classified into cemented and cementless in accordance with the fixation methods in bone tissues. The requirements that are related to the properties and design of the prostheses depend closely on the type of anchoring in the human body. For cemented prostheses, the components are fixed to another bony implant bed, employing bone cement based on polymethylmethacrylate (PMMA).
The cement is usually prepared at the time of surgery and applied with the aid of a syringe to the bony implant bed after blood and medullary fat have been removed. Penetrating into the cancellous bone structure, the cement hardens within a few minutes resulting from an exothermal reaction. This leads to a continuous cement mantle that is well anchored in the bone and lies closely against the implants (Morscher 1995).

In comparison with cementing, direct cementless anchoring of the prosthesis to the bone through osseointegration is a more recent technique. Cementless prostheses with the optimal surface structure and composition to enable osseointegration can produce lasting mechanical interlocking between the implant and the bone (Bobyn et al 1980). Rough surfaces, porous coatings and surfaces with osteoconductivity and osteoinductivity in body fluids have been shown to be good surfaces for osseointegration. Depending on the desired anchorage in the bone, partial osseointegration of the prosthetic components may be considered expedient. In such cases, the design is divided into functional zones that are optimized according to their functions. For a proximal anchored hip prosthesis stem, the solution may require the provision of a proximal surface that can be osseointegrated with the bone.

1.7.2 Dental Implants

Titanium and its alloys are commonly used as dental implants, which can be classified as sub-periosteal, transosteal and endosseous according to their position and shape. Sub-periosteal implants consist of a custom-cast framework resting on the bone surface beneath the mucoperiosteum. The prosthesis is secured on posts or abutments that penetrate the mucosa into the oral cavity. Transosteal implants can only be placed in the frontal lower jaw while endosseous implants can be placed in both the upper and lower jaws via a mucoperiosteal incision. They are the
most commonly used implant types and can be used as a single implant to replace one missing tooth as well as in cases of partial and total edentulism (Reclaru and Meyer 1998).

Most of the dental implants (Figure 1.3) are placed according to the “osseointegration” concept that allows dental implants to fuse with bones. Surface modification technologies, such as grist blast, chemical etching and plasma spraying are often utilized to improve the osseointegration ability of titanium.

![Schematic diagram of screw-shaped artificial tooth](image)

**Figure 1.3 Schematic diagram of screw-shaped artificial tooth**

1.7.3 **Cardiac and Cardiovascular Applications**

Titanium and its alloys are commonly used in cardiovascular implants viz., prosthetic heart valves, protective cases in pacemakers, artificial hearts and circulatory devices are shown in Figure 1.4a. Recently, the use of shape memory nickel-titanium alloy (NITINOL) in intravascular devices, such as stents (Figure 1.4b) and occlusion coils has received considerable attention. The advantages of using titanium in cardiovascular applications are strong, inert and non-magnetic. It also produces few artifacts
under magnetic resonance imaging (MRI), which is a very powerful diagnostic tool, but it is not sufficiently radio-opaque in finer structures. In artificial heart and circulatory assist devices, the materials are used both in the mechanical components of the pump and as a blood-contacting surface. Artificial hearts made entirely of titanium have not been very successful clinically due to problems with blood-clotting occurring on the device surface (Rintoul et al 1993).

![Figure 1.4 Artificial heart valve (a) and vascular stents (b)](image)

**Figure 1.4 Artificial heart valve (a) and vascular stents (b)**

### 1.7.4 Other Applications

Besides artificial bones, joints and dental implants, titanium and its alloys are often used in osteosynthesis (E.g. bone fracture-fixation). A bone fracture disables the function of an injured limb. Early and full restoration can be achieved by osteosynthesis, a method of treating the bone fracture by surgical method. Titanium and its alloys are attractive materials in osteosynthesis implants, in view of their special properties that fulfill the requirements of osteosynthesis applications (Rosenberg et al 2006). Typical implants for osteosynthesis include bone screws, bone plates and maxillofacial implants are shown in Figure 1.5.
Bone screws are used as single screws for direct bone fixation and then mostly applied as “lag screws” exerting compression on the fracture gap or they are used for the fixation of plates or other devices to the bones. Bone plates are applied to almost all skeletal areas mostly as bridging devices and as internal fixations. Titanium and its alloys with rough surfaces (blasted, plasma sprayed and etched) or bioactive surfaces can enhance the deposition of bone-like apatite to improve osteointegration, because they bond tightly to the bone thereby reducing relative motions that can otherwise lengthen the bone healing process.

1.8 COMMON FAILURES OF TITANIUM IMPLANTS

However, even today, the properties of titanium alloys do not meet the application requirements entirely. Many potential causes of failure of the implant is due to deficiencies in design (size and shape) of the device for a particular patient (Eg. an undersized noncemented stem), (Spector 1992) surgical problems (Eg. problematic orientation or problems in wound healing), host abnormalities or diseases (Eg. osteopenia), infection, material fracture, wear and corrosion (Wu 1996). Various causes for failure of implants that lead to surgery are presented in Figure 1.6.
Fracture happens often in bone and orthopaedic implants. Once fractured, biomaterials cannot be regenerated as natural bones. Therefore, structure and properties of the implanted material are particularly important to induce lubrication and to improve the biomaterial properties. The inducing of the lubricants could reduce wear, which is one of the main problems that leads to fracture of the materials. Some research work has been done in investigating the failure of the lubricant thin film (Luo et al 2000 and Jianbin et al 1999).

Wear of the articulating surfaces in artificial hip and knee joints give rise to production of wear particles with submicron. The negative biological effects of these wear particles are considered to be an important factor that limits the long term clinical performance of these type of devices. Therefore, an immediate need for the development of a novel and improved material combinations for the articulating surfaces in artificial joints is required. Such development is in turn dependent upon the improved understanding of the wear process involved and influences of the different material properties and conditions.

Total hip replacement is clinically successful with most designs that utilize an ultrahigh molecular weight polyethylene (UHMWPE) acetabular surface articulating with either a metallic or ceramic femoral head component (Wang et al 1997). However, aseptic loosening, often accompanied by osteolysis, continues to be the source of long-term clinical failure. It has been suggested that the macrophage response to phagocytosis of particulate wear debris, occurring in interaction between the cement and the bone, was an important causative factor in osteolysis, leading to eventual loosening (Willert and Semlitsch 1977). Particulate debris has emerged as a major factor in the long-term performance of joint replacement prostheses (Urban et al 1994).
Figure 1.6 Various failures of titanium implants
When present in sufficient amounts, particulates generated by wear, fretting or fragmentation, induce formation of an inflammatory, foreign-body granulation tissue that has the ability to invade the bone-implant interface (Amstutz et al 1992, Boss et al 1992, Willert et al 1990 and Mirra et al 1976). This may result in progressive periprosthetic loss of bone, a loss that threatens the fixation of prostheses inserted with or without cement (Nyquist and Kagel 1971, Willert 1990).

With regard to bone cement fixation, apart from the risk of necrotic damage of the living bone caused during bone cement fixation by the heat liberated during the polymerization of the cement, the lifetime of a cemented endoprostheses depends on the durability of the cement as well as its tensile bond strength on the implant surface. Failure begins with loosening at the interface accompanied by micro-movements between the metal and the cement, consequently initiating the formation of metal particles and release of metal ions.

Corrosive attack in the taper crevice of modular implants made of similar metals or mixed-metals combination can also occur (Buckley et al 1992, Collier et al 1991, Collier et al 1992, Mathiesen et al 1991, Gilbert and Jacobs 1997). The corrosive attack results in metal release and mechanical failure of the component (Urban et al 1993). Corrosive fatigue, on the other hand, is expected due to cyclic loading and the corrosive environment of the human body. The fractures occurring at the grain boundaries of the microstructure appear to be the result of three factors: porosity at the grain boundaries, intergranular corrosive attack initiated both at the head-neck taper and at free surface and cyclic fatigue-loading of stem (Gilbert et al 1994).

Implants are now expected to serve a much longer period of time or until lifetime without failure or revision surgery. Thus, the development of an
appropriate material to modify the surface of currently used materials with high longevity and excellent biocompatibility is highly essential.

1.9 NEED FOR SURFACE MODIFICATION

In order to avoid adverse tissue reactions arising from hard tissue replacements, a bio-inert material, which is stable in the human body and does not react with body fluids and tissues, is preferred. Bio-inert materials are generally encapsulated after implantation into the living body by fibrous tissues that isolate them from the surrounding bone. Some bioactive materials, such as hydroxyapatite and bioactive glasses are increasingly used as hard tissue replacements to improve the bonding between implants and bone tissues because the materials can bond to living bones without the formation of fibrous tissues by creating a bone-like apatite layer on their surface after implantation. Apatite formation is currently considered to be the main requirement for the bone-bonding ability of materials.

In this respect, titanium with its native surface oxide is known to be bio-inert, but it is difficult to achieve good chemical bonding with bones and form new bones on its surface at the early stages of implantation. Hence, titanium and its alloys do not meet all the requirements of an ‘ideal’ material. In addition, longer human life expectancy and younger patients requiring implants have driven biomedical research from original implant concerns, such as materials strength, infection and short-term rejection. For instance, wear, fatigue strength and long-term biocompatibility. Thus, the current trend is to use surface modification technologies to address a number of these ever-increasing clinical demands.

The material surface plays an extremely important role in the response of the biological environment to the artificial medical devices. In titanium implants, the normal manufacturing steps usually lead to an oxidized,
contaminated native surface layer that is often stressed, plastically deformed and non-uniform. Such native surfaces are not appropriate for biomedical applications and some surface treatment must be performed. Another important reason for surface modification to titanium medical devices is that specific surface properties that are different from those in the bulk are often required.

Proper surface modification techniques not only retain the excellent bulk attributes of titanium and its alloys, such as relatively low modulus, good fatigue strength, formability and machinability, but also improve specific surface properties required for different clinical applications. According to different clinical needs, the improvement of bioactivity, biocompatibility, blood compatibility, wear and corrosion resistance of implants using various surface modification technologies are discussed in the following section.

1.10 SURFACE TREATMENTS AND COATINGS

Mechanical methods for surface treatments involve removal of surface material by cutting (machining of the surface), abrasive action (grinding and polishing) and those where the treated material surface is deformed by particle blasting. Chemical methods are mainly based on chemical reactions occurring at the interface between titanium and a solution (solvent cleaning, wet chemical etching, passivation treatments and other chemical surface treatment). Electrochemical surface methods are based on different chemical reactions occurring at an electrically energised surface (electrode) placed in an electrolyte (electropolishing and anodic oxidation or anodising).

Improving the method for both wear and corrosion resistance of titanium implant surfaces, where the protection by natural surface oxide films is insufficient, can be done through the deposition of thin films. These
coatings should have a sufficient adherence to the substrate throughout the range of conditions to which the implant is exposed in service. They must tolerate the stress and strain variations that particular part of the implants normally impose on the coating. The coating process must not damage the substrate and must not induce failure in the substrate or introduce impurities on the surface, which may change interface properties. Coatings should be wear resistant, barrier layers preventive of substrate metal-ion release, to low-friction haemocompatible and non-thrombogenic surfaces. Such surface modification could be done by various processes such as sol-gel coatings, chemical vapour deposition (CVD) and physical vapour deposition (PVD).

The properties of PVD coatings exhibit certain thickness, roughness, hardness, strength and adhesion as well as structure, morphology, stoichiometry and internal stresses. PVD processes include evaporation, sputtering, ion plating and ion implantation. These techniques were carried out in vacuum, at back pressures of less than 1 Pa (Thull and Grant 2001). In CVD methods, they involve the reaction of volatile components at the substrate surface to form a solid product. Typical CVD coatings are depositions of TiN, TiC and TiC\(_x\)N\(_{1-x}\). The early coatings were deposited onto hard metal tools such as WC-Co. Good coating uniformity is an advantage of the CVD method and lower operating temperatures of the PVD method, it can be combined in the plasma-assisted CVD process. Biomaterials produced at low temperature CVD and PVD is Diamond-Like Carbon (DLC). DLC coatings can address the biomechanical problems in the implants currently used, for example, friction, corrosion and biocompatibility (Morshed et al 2003).

The bioactive coatings involve a principle of enabling an interfacial chemical bond between the implant and the bone tissues due to the specific biological response (Hench et al 1971). One of the most popular bioactive
coatings is hydroxyapatite (HA), which is similar to the mineral phase of natural hard tissue, that is, about 70% of the mineral fraction of a bone has a HA-like structure. HA can also be regarded as non-resorbable in a physiological environment, as long as it remains crystalline and is of high purity. It is the most stable calcium phosphate phase in aqueous solutions (de Groot et al 1990). It has weaker mechanical properties and low resistance to fatigue failure. The surface treatment techniques for HA are plasma spraying, Vacuum plasma spraying (VPS), electrophoretic deposition of HA and microarc oxidation.

1.11 LITERATURE REVIEW

The performance of titanium and its alloys in implant applications is mainly concerned with respect to the material’s biocompatibility and ability to withstand the corrosive fluids of the human body. A detailed review of available literature on the bioactivity and corrosion behaviour of titanium and its alloys is presented below.

1.11.1 Biological Behaviour of Titanium and its Alloys

The past years have seen the development of many synthetic bone replacements. To test their biocompatibility, ability for osseointegration, osseoinduction and osseoconduction requires that they be placed within bone preferably in an animal experiment. Various animal species are used for these biocompatibility tests, such as mouse (Endres et al 2004), rat (Ellier et al 1988, Thull et al 1992 and Benhuzzi 1996), guinea pig (Sousa et al 2004), rabbit (Jinno et al 1998 and Lopes et al 2001) and dog (Patka et al 1985, Choueka 1996 and Pal et al 1997). Furthermore, different implantation sites and methods have been used to examine biocompatibility issues.
When titanium was discovered as a biocompatible material with bone, extensive research was done to improve the osseointegration of the implant material. Early experimental work in which the unalloyed titanium samples was inserted into the femora of cats showed that titanium was well tolerated as stainless steel and vitallium. Further, it was also inserted into rabbits and rats, and the results showed that titanium was an inert metal and was ideal for fixation of fractures.

The clinical success of endosseous implant therapy is the formation of a direct contact between implant and the surrounding bone. The implant-bone response is thought to be influenced by implant surface topography. The composite effect of surface energy, composition, roughness and topography play a major role during the initial phases of the biological response to the implant, such as protein adsorption and cellular adherence (Schwartz and Boyan 1988). As a consequence, over the last 20 years, a large number of implant systems with different surface topographies have been introduced.

A variety of implant materials is used in bone with the expectation that osteogenesis will occur. Immediately upon implantation, the device becomes coated with a layer of organic and inorganic components from the plasma. These proteins, lipids, sugars and ions adsorb to the surface of the implant (Vroman and Adams 1969, Vroman et al 1980, Pearson et al 1988, Ziats et al 1988 and Pankowsky et al 1990).

Meyer et al (1988) demonstrated that the adsorption of lipids and proteins onto various biomaterials, including titanium, occurs within five minutes in vivo, while cell attachment does not occur until after several hours have elapsed. This suggests a requirement for prior conditioning of the surface before cell attachment can occur, a finding consistent with increased
attachment by osteoblasts to titanium after the metal is coated with extracellular matrix proteins (Schneider and Burridge 1994).

Although commercially pure titanium (Cp-Ti) is considered to have excellent biocompatibility studies have shown that cells can discern differences in surface characteristics (Beder and Eade 1956, Branemark 1985, Donley and Gillette 1991, Williams 1981). In a study utilizing human fibroblasts, Keller et al (1990) found that sterilization techniques significantly altered cell adherence characteristics. While the percentage of cells attached to acid-passivated Cp-Ti was approximately the same as that on tissue culture polystyrene after 15, 30 and 60 min in culture, those on surfaces sterilized by autoclaving, ethanol or ethylene oxide exhibited considerably less cell attachment.

Adherence to Cp-Ti is altered not only by sterilization techniques but also by surface roughness. Studies using osteoblast-like cells from rat calvarial explants have shown that cells are sensitive to differences in roughness (Bowers et al 1992). These cells were cultured on materials with roughness ranging from 0.14 µm to 1.15 µm. Of the various surfaces, a sandblasted surface with intermediate roughness had consistently higher levels of percent cell attachment than the other titanium surfaces. These data, in conjunction with the observation that cells grown on sandblasted surfaces were morphologically different from those on the other surfaces, support the premise that Cp-Ti surface roughness has an effect on initial cell attachment and subsequent spreading (Keller et al 1990 and Ben-Zeev 1991).

Hence, surface roughness and composition are considered to influence the properties of adherent cells. The bone formation in rabbit cortical bone around titanium implants with varied surface properties was investigated by Larsson et al (1996). They observed that a high degree of bone contact and bone formation was achieved with the titanium implants
which modified with respect to the oxide thickness and surface topography. However, the smooth surface exhibited a decrease in the rate of bone formation.

Recently, animal studies confirmed these early conclusions, and in fact, it appears that Ti and Ti-6Al-4V alloy may actually be better tolerated than stainless steel or the cobalt-chromium alloys. Deligianni et al (2001) studied the effect of surface roughness of the titanium alloy Ti-6Al-4V on human bone marrow cell response and on protein adsorption. They reported that cell attachment and proliferation were sensitive to surface roughness and increased as the roughness of Ti-6Al-4V alloy increased.

The first clinical trials on femoral stems with HA coatings were reported earlier (Furlong and Osborn 1985, Antonio et al 1989). Since then, hydroxyapatite coatings have been extensively used in both dental and orthopaedic prostheses, such as hip and knee implants as well as in screws and pins used in bone plates for fixing bone fractures. After about twenty years of clinical trials, there is general agreement that the originally pursued benefits of HA coatings, that is, earlier fixation and stability with more bone ingrowth or ongrowth, can be achieved. Most components become stabilized within 3 months with bone apposition. It has been suggested that migration of the femoral component within the first 2 yrs is related to the final outcome (Moilanen et al 1996 and Karrholm et al 1994). A large number of clinical trial experiments on HA coatings have also shown continued fixation for longer periods (2–10 yrs), but doubts still exist concerning the durability of the fixation.

The bone formation around titanium implants with varied surface properties was investigated after 1 yr in rabbits by Larsson et al (1997). They reported that a high degree of bone contact and bone formation is achieved
after 1 yr with titanium implants which are modified with respect to oxide thickness and surface topography.

Lee et al (2004) investigated the mechanical stability and in vivo behavior of implants of three surface designs: smooth surface (SS), rough titanium surface with a plasma-sprayed coating (PSC) and alkali and heat treated (AHT) titanium surface. Four weeks after the implantation into the dog bone, the pull-out forces of the SS, PSC, and AHT implants are 235±34.25, 710±142.25, and 823±152.22 N respectively. The AHT implant showed good bone-bonding strength after 4 weeks of healing because of the mechanical interlocking in the micrometer-sized rough surface and the large bonding area between the bone and implant as a result of the nanosized porous surface structure. During this healing period, new bone on the surface of AHT implant undergoes higher growth than that on the PSC implant.

Osteoblastic differentiation in bone marrow cells on the AHT titanium and apatite-formed titanium were examined by Nishio et al (2000) revealed that apatite formation played an important role. Alkali heat treated titanium bond to bones quickly, but titanium that is only alkali-treated failed to bond with the bone within a short period of time. Hence, alkali treatment with subsequent heat treatment is essential in order to acquire better bone bonding ability (Nishiguchi et al 1999). The detaching failure loads of untreated, alkali treated and alkali heat treated titanium after 8–16 weeks of implantation showed that after 8 weeks, the failure load of AHT titanium was 2.71±1.47 kgf. This was significantly higher than those of the alkali treated titanium and control titanium, the values being 0.51±0.52 and 0.02±0.03 kgf, respectively. After 16 weeks, the AHT titanium showed a failure load of 4.13 ± 1.25 kgf. This value was significantly higher than that of the same group at 8 weeks and those of alkali treated and control titanium groups at 16 weeks. The failure loads of alkali treated and control titanium groups did
increase over the 8 week loads, and their values were 0.49±0.38 and 0.33±0.36 kgf respectively.

In vivo bioactive performance of alkali and AHT titanium was examined mechanically and histologically after 4, 8, 16, and 24 weeks by Kim et al (1996). Sodium ion removal was found to enhance the bone-bonding strength of bioactive titanium at 4 and 8 weeks post operatively. However, its bone bonding strength was inferior to that of conventional alkali and heat treated titanium after 16 and 24 weeks. Histological examinations after detaching test revealed that the breakage of treated layer in the sodium free alkali and heat treated titanium. Sodium ion removal accelerated the in-vivo bioactivity of titanium and led to faster bone bonding, because of the anatase surface structure, but the loss of surface graded structure due to the complete removal of sodium ion decreased the adhesive strength of treated layer to the titanium substrate.

The bone formation on blood plasma modified titanium implants with varying surface topographies was investigated by Goransson et al (2002) using resonance frequency measurements. It was observed that the implant stability was lower in soft bone compared to dense and increased with time. Moreover, no significant differences were observed between the different surface modifications.

The literature on this topic is extensive and continuously increasing. However, the claims made in numerous publications about the effect of implant material on bone response are not straightforward as suggested.
1.11.2 Electrochemical Behavior of Titanium and its Alloys

Corrosion resistance is one of the main properties of a metallic material applied in the human body environment and the success of an implant depends on the careful examination of this phenomenon. The performance of an implant is directly related to its ability in functioning in the aggressive body fluids (Merritt et al. 1988 and William et al. 1988). In general, these fluids consist of a series of acids and certain amount of NaCl. In normal conditions, its pH is 7; however, it may be altered due to immune system response, like in the case of an infection or inflammation (Sugimoto and Omata 1995, Hench 1975). In the event of a corrosion process, the implant component may lose its integrity, leading to a failure. In addition, release of corrosion products may lead to undesirable biological reactions. Certainly, this will depend on the nature of chemical reactions on the implant surface in view of the fact that corrosion is essentially a chemical process.

It is commonly accepted that titanium exhibits high stability and corrosion resistance in-vitro (Mueller et al. 1970 and Gonzalez et al. 1999), although there have been reports showing the accumulation of titanium in tissues adjacent to the implant (Mu et al. 2000, Browne and Gregson 2000) that signifies metal release and some degree of corrosion in vivo. Aziz-Kerrzo et al. (2001) investigated the corrosion resistance of Ti, Ti–6Al–4V, and Ti–45Ni alloy in a buffered saline solution using electrochemical methods.

Ibris and Rosca (2002) reported the electrochemical behaviour of Ti, Ti-7Al-4.5V and Ti-5Al-2.5V alloys in Hank’s solution and Fusayama artificial solution. An equivalent circuit was also proposed for the impedance spectra and concluded that the alloying elements do not influence the charge transfer reaction but enhance the growth of the oxide film.

Zaveri et al (2008) reported that the laser treated Ti-6Al-4V alloy exhibited higher corrosion resistance than that of untreated alloy in SBF. The electrochemical impedance spectroscopic studies results indicated that the film formed on the Ti-6Al-4V alloy after the laser treatment was composed of a bi-layered oxide consisting of the outer porous layer and the inner barrier layer which was responsible for the corrosion protection.

Milosev et al (2008) studied the structure and composition of the passive film formed on Ti-6Al-7Nb alloy formed by electrochemical oxidation in Hank’s physiological solution using X-ray photoelectron spectroscopy and electrochemical impedance spectroscopic studies.

Oliveira and Guastaldi (2008) studied the electrochemical stability and corrosion resistance of Ti-Mo alloys used for biomedical applications. Alvarado and Sundaram (2006) evaluated the corrosion behaviour of Ti-48Al-2Cr-2Nb alloy in Ringer’s solution and evaluated its potential as a biocompatible material using potentiodynamic anodic polarization and electrochemical impedance spectroscopy.

1.11.3 Chemical Treatment of Titanium and its Alloys

Chemical treatment of titanium and its alloys are mainly based on chemical reactions occurring at the interface between titanium and a solution. The commonly employed chemical treatments are acid, alkali and H₂O₂ treatments.
1.11.3.1 Acid treatment

Acid etching removes the oxide and the contaminants which leads to clean and uniform surface finishes. A combination of acids are frequently used to pre-treat the titanium. A solution composed of 10-30 Vol. \% of HNO$_3$ and 1-3 Vol. \% of HF in distilled water has been recommended as a standard solution for acid pre-treatment. HF that readily attacks TiO$_2$ reacts with Ti to form soluble titanium fluorides and hydrogen. Incorporation of hydrogen in titanium can cause embrittlement of the surface layer, but a ratio of HNO$_3$ to HF of 10 to 1 can minimize the formation of free hydrogen (ASTM1997). Takeuchi et al (2003) investigated the decontamination efficiency of Na$_2$S$_2$O$_8$, H$_2$SO$_4$ and HCl, to the Ti surface. It was found that HCl is an excellent decontamination agent because it can easily dissolve titanium salts and not weaken Ti surfaces. Acid etching generally leads to a thin surface oxide layer (<10 nm), predominantly TiO$_2$, but residues from the etching solution are frequently observed, particularly chemicals containing fluorine. It is also known that some treatments can lead to hydrogen incorporation in the surface region below the oxide. These residues can remain even after post-thermal treatment to improve the properties of titanium and its alloys. Wen et al (1997) reported that the bioactivity of Ti alloy could be improved by two-step chemical treatments employing (HCl + H$_2$SO$_4$) and alkaline solution. Muller et al (2008) evaluated the influence of different acid etching conditions on the microstructure of Ti-13 Nb-13Zr alloy surface as well as on the rate of hydroxyl carbonated apatite formation during in vitro bioactivity tests in SBF solution.

1.11.3.2 Alkaline treatment

Kim et al (1996) first introduced alkali and heat treatment to improve the bioactivity. The method enables the formation of a biologically active bone-like apatite layer on the surface of the bioactive ceramics, such as
bioglass, hydroxyapatite and glass-ceramic. They studied the bioactivity of Ti, Ti-6Al-4V, Ti-5Al-2Nb-1Ta, Ti-15Mo-5Zr-3Al, SUS 316L and Co-Cr-Mo alloys by simple chemical surface treatments. They also reported that apatite was formed on the treated surface of Ti and its alloys only after 4 weeks in SBF solution.

Kim et al (1997) studied that the effect alkali (5 M) and alkali heat treatment on Ti metal. They reported that the sodium titanate gel layer was formed during alkali treatment and it was dehydrated and transformed into an amorphous sodium titanate at 400-500˚C, fairly densified at 600˚C and converted into crystalline sodium titanate and rutile above 700˚C. They finally confirmed that 600˚C as the optimum temperature for high apatite formation in a body environment.

As a preliminary test, Kim et al (1999) investigated the bonding strength of bonelike apatite layer to Ti substrate. They found that the apatite layer formed on the NaOH treated Ti metals in SBF showed higher bonding strengths to the substrates than those formed on Bioglass 45S5-type, sintered hydroxyapatite and glass-ceramic A-W. The graded surface structure of bioactive titanium prepared by chemical (5 M NaOH) and thermal treatment (600 or 800˚C) were studied. At 600˚C, a smooth graded interface structure with a tight bond was achieved. Whereas, at 800˚C the irregular graded structure, intervened by a thick titanium oxide and formed a less tight bond of the apatite layer to the substrate.

Lee et al (2002) investigated the bioactivity and surface changes of the alkali and alkali heat treated Ti-In-Nb-Ta alloy and Ti-6Al-4V ELI alloy that occurred during immersion in SBF solution. Porous networked layers of sodium titanate were formed on the surface of titanium alloys after surface modification by alkali and heat treatments. The pore size of the inner porous reticular structures in the Ti-In-Nb-Ta alloy was finer than that of Ti-6Al-4V ELI alloy. Whereas, the thickness of the sodium titanate layer on the Ti-In-Nb-Ta alloy was found to be half that of the Ti-6Al-4V ELI alloy.

Yang et al (1999) investigated that the alkali treated Ti in various aqueous solutions such as SBF solution, calcium aqueous solution, phosphate aqueous solution and accelerated calcification solution. Takadama et al (2001) proposed a mechanism for apatite formation on the bioactive Ti metal treated with NaOH and heat treatment in SBF solution using XPS results. The bone like apatite formation on bioactive Ti by TEM- EDAX analysis was studied by Takadama et al (2001a). They found that Ca/P ratio was 1.65 after 72 hr in SBF solution. Further, the surface characterisation of alkali treated titanium alloys and its electrochemical studies of surface modified titanium alloys were also studied by various authors (Tamil selvi et al 2007 and Raman et al 2007).

In summary, the available information indicates that titanium and its alloys may be the most biocompatible and corrosion resistance metallic implant materials in use present.

1.11.3.3 Hydrogen peroxide treatment

The insertion of an implant is inevitably associated with and inflammatory response due to the surgical trauma. Whether the reaction will subdue or persist is dependent on the materials selection as well as the site of implantation and the loads put on to it (Thomsen et al 1986, Salthouse and Matlaga 1980). In this respect, titanium has been shown by Branemark et al.
(1977) to give excellent long term clinical results when used for bone anchorage of dental bridges. Further, it has been observed that an oxide like layer grows on titanium implants in vivo during implantation (Sundgren et al 1986 and 1985). The experiments have indicated that hydrogen peroxide (H₂O₂) in buffered saline solutions in the millimolar concentration range produces and oxide like layer on titanium surfaces in vitro, and at higher concentrations several oxidation intermediates are distinguished in the Ti-H₂O₂ system (Tengvall et al 1987).

Tengvall et al (1988) first studied the interaction between H₂O₂ and titanium. They found that the hydroxyl radicals are formed from H₂O₂ during the inflammatory response and these are potent agent for cellular deterioration. Later a model was proposed by Tengvall et al (1989) for the titanium – tissue interface where the oxidized titanium surface is covered with a hydrated TiOOH matrix after the inflammatory reaction. This matrix is suggested to possess good ion exchange properties and extracellular components that may interact with the Ti(IV) – H₂O₂ compound before matrix formation. The TiOOH matrix is formed when H₂O₂ is coordinated to the Ti(IV) – H₂O₂. The complex is decomposed to water and oxygen. Superoxide (O₂⁻) may be bound therein and the oxide layer initially present may be partly reformed to a TiOOH matrix due to the interaction with H₂O₂.

Ohtsuki et al (1997) indicated that the treatment of Ti with a TaCl₅ containing H₂O₂ solution is an effective way of providing in-vitro bioactivity or the ability of the materials to be covered with apatite in SBF solution. Kaneko et al (2001) confirmed with in-vivo experiments that thus treated, Ti implants realized stronger bonding with bone tissue in a shorter implant period.

Pan et al (1996 and 1998) studied the enhanced oxide growth on titanium in phosphate buffered solution. The oxide growth at the titanium /
electrolyte interface was monitored in-situ by EIS measurements during periods of several weeks. The result suggested that the oxide layer can be described by a two layer model with a barrier inner layer and a porous outer layer. Moreover, H$_2$O$_2$ addition resulted in an increased dissolution/oxidation rate that leads to an enhanced oxide growth of the porous outer layer. As a result, the total oxide film can reach a thickness corresponding to an interference blue color.

Wang et al (2000) reported that the Ti substrates treated with the H$_2$O$_2$ / TaCl$_3$ solutions maintained at 400°C enhanced the bioactivity of the material, which may be due to an epitaxial effect of anatase precipitated on the surface oxide layer.

Wu et al (2002) pointed out that anatase and rutile phase were similar to the epitaxial effect on inducing apatite formation. Regardless of anatase, rutile or an amorphous phase, as Miyazaki et al (2001) proposed, heating reduces the number of M-OH groups (M: metals like Si or Ti) on the surface layers. The presence of the silanol (Si-OH) or titanol (Ti-OH) groups is accepted as one of the key factors for the apatite nucleation. The formation of apatite is favored due to the presence of Ti-OH groups created by chemical treatments, hence the Ti-OH functional groups play a crucial role in apatite formation.

Wang et al (2002) studied the microstructure and invitro bioactivity of titania gel layer formed by chemical treatment of the titanium substrate with higher concentration of H$_2$O$_2$ / HCl solution. They concluded that an amorphorous titania gel layer is formed and its thickness can be controlled by different time period. An anatase layer favorable for apatite deposition can be obtained by the heat treatment of H$_2$O$_2$ treated titanium above 300°C.
Anatase film with sub-micron porous structure were deposited homogeneously on Ti substrates treated with 15 wt.% of H$_2$O$_2$ solution maintained at 80°C for 1 hr followed by heating at 300°C for 1 hr in air by Wu et al (2002).

Reaction between titanium substrate and H$_2$O$_2$ can be explained by considering that the titania gel formation and Ti(IV) dissolution occur competitively. Shibata et al (2003) carried out the experiment with low concentration of H$_2$O$_2$ and subsequently thermally treated at 400°C for 1 hr. They reported that the titanium substrates were provided with in-vitro forming ability at an optimum concentration of H$_2$O$_2$ solution consisting of 6 mass% of H$_2$O$_2$ at 60°C for 3-6 hr. Moreover, the titania gel formation was controlled not only by the H$_2$O$_2$ concentration but also by pH of the solution. The formation of titania gel layer proceeded at a pH range of 4 to 4.6, while the corrosion of the titania gel layer was escated at a pH below 4.

Kawasaki et al (2004) reported that the high apatite forming ability derived from chemical treatments of titanium with H$_2$O$_2$ can be controlled by its morphology and concluded that apatite forming ability of titanium treated for 72 hrs with low roughness value was higher than that of titanium treated for 1 hr with high roughness values.

Julie Muyco et al (2006) characterised that the titanium peroxy gel during formation on titanium surfaces in H$_2$O$_2$ containing solution. They reported that the titanium peroxy gel formation was gradual (approximately 0.76 nm/min) and can be detected after 2 hrs. Moreover, corrosion rate was greater in the presence of H$_2$O$_2$ than in the absence of H$_2$O$_2$ solution.

Wu et al (2006) reported that H$_2$O$_2$ treatment is an effective method to provide Cp-Ti with bioactivity, which results in an anatase layer on the Ti surface through subsequently either a thermal treatment or a hot water
aging. Moreover, they suggested that a porous, thick anatase film and abundant Ti-OH functional groups are appeared to be more dominant factor in apatite deposition.

De Assis et al (2006) studied the effect of H$_2$O$_2$ on the electrochemical behaviour of Ti-13Nb-13Zr alloy in Hank’s solution. The results showed that the oxide layer formed on Ti-13Nb-13Zr alloy by immersion in Hanks solution without H$_2$O$_2$ is highly stable and protective. Chu (2006) and Gu et al (2006) studied the bioactivity of NiTi alloy oxidised in H$_2$O$_2$ solution followed by NaOH treatment, subsequently heat treated at 300-800°C.

Thus, the literature review shows that only few reports are available on the surface modification of titanium using H$_2$O$_2$. Hence, the present work is concerned with the optimization of H$_2$O$_2$ concentration for titanium and its alloys and to characterize the surface for biocompatibility and corrosion resistance.

1.12 SCOPE OF THE PRESENT INVESTIGATION

The scope of the present study is to develop new surfaces to obtain an improved osteointegration of titanium and its alloys as implants, which is one of the major goals in biomaterial research.

The reactions occurring at the bone-implant interface is of great importance when developing novel osteointegrative materials. Indeed, achieving good mechanical bonding without interposition of weak fibrous tissue at the bone-implant interface represents the goal of modern implantology. Upon implantation, the implant surface is conditioned by proteins, ions, sugars and lipids present in the blood and tissue fluids. Hence, there is a growing interest in shortening the process toward osseointegration,
and thereby reducing the healing time for patients with load bearing Ti implants. The implant osteointegration involves several complex factors including implant shape, surface topography and chemistry as well as surgical technique, mechanical loading and patient’s metabolic state. However, it has been recognized that the most important factor determining the degree of interaction of the implanted device is the physicochemical property of the surface. But until now, understanding about this field is very limited. A strong and durable bone to implant bonding can be achieved by the formation of a stable bone tissue at the bone-implant interface by proper implant surface treatments which provide the implant with a particularly suitable surface for bone cells to proliferate.

In general, bonding between the bone and the implant is achieved through mechanical interlocking enhanced by the porous surface that increases the interaction surface area. Various surface treatments such as plasma spray, chemical vapor deposition, physical vapor deposition etc., are capable of improving the osteointegration through better mechanical interface, but they do not provide a chemical bonding with the bone which is capable of speeding up the healing process.

Several chemical methods for surface modification of titanium implants have already been proposed to provide them with the ability of direct bonding to bone tissues. Chemical treatments of titanium surfaces proposed so far are primarily aimed at controlling the formation of titania or sodium titanates on the titanium substrates that induced apatite formation when those substrates were soaked in simulated body fluid solution. Hence, the present work is aimed towards an effective surface modification using H$_2$O$_2$, which will improve the corrosion and biocompatibility of implant materials in SBF solution.
1.13  OBJECTIVES OF THE WORK

The main objective of this research work is to modify the surface of titanium and its alloys using hydrogen peroxide, which are a simple, low temperature and a cost effective method. Further, to determine the biocompatibility and corrosion resistance of the material in SBF solution.

The specific objectives are to:

- Optimize the concentration of hydrogen peroxide solution and condition for heat treatment.
- Characterize the crystallographic structure, surface morphology and elemental composition of the modified specimens.
- Analyse the growth of apatite on the modified surface of the specimen in SBF solution.
- Study the morphological and elemental composition of the surface after immersion in SBF solution.
- Assess the biocompatibility and corrosion resistance of the modified specimens in SBF solution.

In order to achieve the above-mentioned objectives various techniques were employed.

1. Raman spectroscopy
   - To examine the phase composition of the surface.
2. Scanning Electron Microscopy (SEM) and Energy dispersive X-ray analysis (EDAX)
   - To examine the surface morphological change and to confirm the composition of element.

3. Fourier Transform -Infrared (FT-IR) spectroscopy
   - To confirm the chemical bond and functional groups of the surface.

4. Open circuit potential (OCP) measurements
   - To find out the stability of the passive film.

5. Potentiodynamic polarization studies
   - To study the corrosion behaviour of untreated and hydrogen peroxide treated titanium and its alloys in SBF solution.

6. Electrochemical impedance spectroscopy (EIS) measurements
   - To study the surface resistance and capacitance of titanium and its alloys in SBF solution and to understand the structure of the formed layer.