

## Corrosion of bio implants

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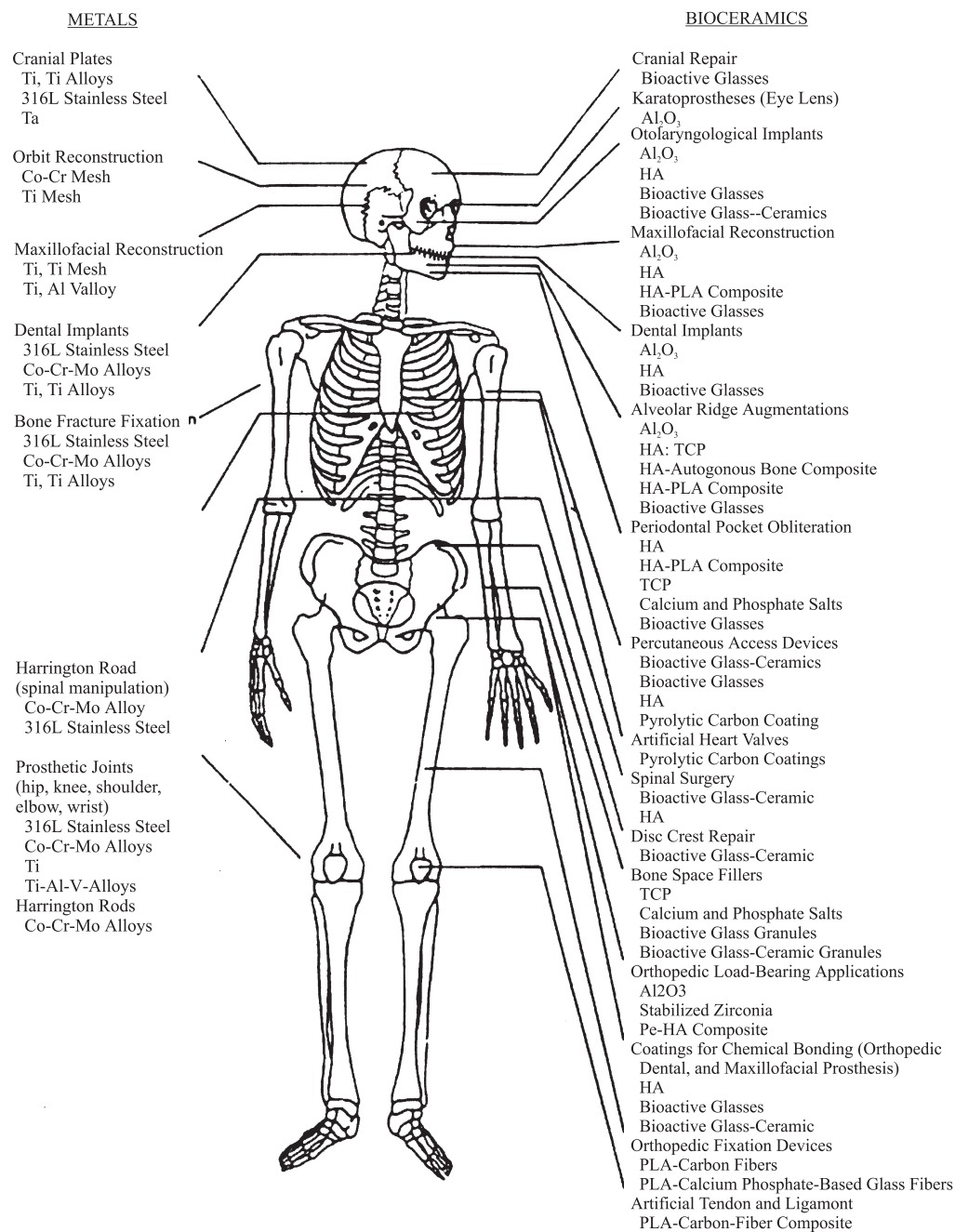
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**Abstract.** Chemical stability, mechanical behaviour and biocompatibility in body fluids and tissues are the basic requirements for successful application of implant materials in bone fractures and replacements. Corrosion is one of the major processes affecting the life and service of orthopaedic devices made of metals and alloys used as implants in the body. Among the metals and alloys known, stainless steels (SS), Co–Cr alloys and titanium and its alloys are the most widely used for the making of biodevices for extended life in human body. Incidences of failure of stainless steel implant devices reveal the occurrence of significant localised corroding viz., pitting and crevice corrosion. Titanium forms a stable TiO<sub>2</sub> film which can release titanium particles under wear into the body environment. To reduce corrosion and achieve better biocompatibility, bulk alloying of stainless steels with titanium and nitrogen, surface alloying by ion implantation of stainless steels and titanium and its alloys, and surface modification of stainless steel with bioceramic coatings are considered potential methods for improving the performance of orthopaedic devices. This review discusses these issues in depth and examines emerging directions.

**Keywords.** Orthopaedic implants; surface modification; hydroxyapatite; bio-ceramics.

### 1. Introduction

Biomaterials are materials used for making devices that can interact with biological systems to coexist for longer service with minimal failure. Williams (1981) defined biomaterials as “nonviable materials used in medical devices, intended to interact with the biological systems”. Biomaterials are widely used in repair, replacement, or augmentation of diseased or damaged parts of the musculoskeletal system such as bones, joints and teeth. A majority of the applications are summarized in figure 1 (Hench 1985). The fundamental requirement of a biomaterial is that the material and the tissue environment of the body should coexist without having any undesirable or inappropriate effect on each other. Biocompatibility, an essential requirement for any biomaterial, implies the ability of the material to perform effectively with an appropriate host response for the desired application. Common medical devices made of biomaterials include hip replacements, prosthetic heart valves and the less common neurological prostheses and implanted drug delivery systems. These devices when placed



**Figure 1.** Clinical uses of inorganic biomaterials (Hench 1985).

inside the body are termed implants when they are intended to remain there for a substantial period of time, and as prosthesis when they are permanently fixed in the body for long-term application till the end of lifetime (Von Recum 1999).

Orthopaedic implant devices are generally mounted on to the skeletal system of the human body for aiding healing, correcting deformities and restoring the lost functions of the original part. These are supporting bone plates, screws, total hip joints, knee joints, elbow joints, shoulder joints and reattachments for tendons or ligaments. The implants are exposed to the biochemical and dynamic environment of the human body and their design is dictated by anatomy and restricted by physiological conditions. In the past few decades, increase in the utilization of self-operating machines, participation of many persons in sports, defence activities, increased interest in motorcycles and bicycles, and day-to-day increasing traffic, has resulted in enormous increase in the number of accidents. This has necessarily led people to opt for orthopaedic implants for early and speedy recovery and resumption of their routine activities.

## **2. Materials for orthopaedic application**

Orthopaedic implants have improved the quality of life for millions of people over the last quarter of a century. The clinical objective is to relieve pain and increase ease of movement in the joint. The engineering objective is to provide minimal physiological stress to the remaining bone system so that the integrity and functionality of the bone and prosthetic materials are maintained over a long service life. Thus, materials suitable for implantation are those that are well-tolerated by the body and can withstand cyclic loading in the aggressive environment of the body. Materials that are selectively used in orthopaedics are ceramics, polymers and metals and alloys.

### *2.1 Ceramics*

Ceramics are inorganic compounds that can be classified into five categories of biomaterials by their macroscopic surface characteristics or by their chemical stability in the body environment. They are carbon, alumina, zirconia, bioactive glass (glass ceramics) and calcium phosphate. The limitations of ceramic materials are their low tensile strength and fracture toughness. Their use in bulk form is therefore limited to functions in which only compressive loads are applied. Results of ex-vivo push-out tests indicate that the ceramic/metal bond fails before the integration of the ceramic/tissue bond because of the weak link in the system (Hench 1982). Thus, there is reason for concern about the weak ceramic/metal bond and the integrity of this interface over a lengthy service-life under functional loading.

### *2.2 Polymers*

Polymers are considered for implant applications in various forms such as fibres, textiles, rods and viscous liquids. Recently, polymers have been introduced for hip socket replacement in orthopaedic implant applications due to its close resemblance to natural polymeric tissue components. However, polymers undergo degradation in the body environment due to biochemical and mechanical factors. This results in ionic attack and formation of hydroxyl ions and dissolved oxygen, leading to tissue irritation and decrease in mechanical properties.

### *2.3 Composites*

Composites are materials obtained by combining two or more materials or phases with a view to take advantage of the salient features of each constituent. It is essential that each component of the composite be biocompatible to avoid degradation between interfaces of the constituents.

Fibre-reinforced polymers (FRP) are the most widely investigated composites for biomedical applications. A few composites which are successfully used as implants are low stiffness femoral components for hip-joint arthroplasty, radiolucent and biodegradable fracture fixation devices, fracture-resistant bone cements and wear, creep and fracture-resistant articulation components. This uncertain lifetimes and degradation under complex states of stress, and their low mechanical strengths limit their applications. It is also difficult to shape them, and they are yet to attain technical maturity for these applications (Silver 1994).

#### 2.4 *Metals and alloys*

Metals and alloys have a wide range of applications including as devices for fracture fixation, partial and total joint replacement, external splints, braces and traction apparatus as well as dental amalgams. The high modulus and yield point coupled with the ductility of metals make them suitable for load-bearing without leading to large deformations and permanent dimensional changes. Although metals exhibit high strength and toughness, they are susceptible to chemical and electrochemical degradation. The implant materials may corrode and/or wear, leading to the generation of particulate debris, which may in turn aggravate the body environment and elicit both local and systemic biological responses. The application of metals and alloys is very important in orthopaedic, as they play a very predominant role in fulfilling almost every difficult factor that arises in implant applications.

#### 2.5 *Currently used metallic implant materials*

The fundamental criterion for choosing a metallic implant material is that it should possess biocompatibility. Metals and alloys have been widely used in various forms as implants, which provide the required mechanical strength and reasonable corrosion resistance. Metallic implants are usually made of one of the three types of materials: austenitic stainless steels, cobalt–chromium alloys and titanium and its alloys (Sivakumar *et al* 1992, 1994). The mechanical properties of these metals and alloys as recommended by ASTM are given in table 1. These materials are accepted by the body environment because of their passive and inert oxide layer formed on the surface. The main elemental constituents, as well as the minor alloying constituents of these materials are usually tolerated by the body in trace amounts, since most of these alloying elements have specific biological role. Cobalt–chromium alloys have the excellent corrosion resistance property. However, they are not recommended for joint prosthesis because of their poor frictional properties with itself or with other materials. They are susceptible to work hardening and special fabrication procedures need to be employed. Amongst all these materials, titanium and its alloys are the most corrosion resistant materials. Several ( $\alpha + \beta$ ) titanium alloys provide sufficient strength and corrosion resistance: Ti-6Al-4V, Ti-5Al-2.5Fe, Ti-6Al-7Nb, etc. However, the main disadvantages are their high cost, inferior wear properties, diffusion of oxygen into titanium during fabrication and heat treatment, and the dissolved oxygen embrittles titanium. Hence, special fabrication and welding procedures are required for joining. Titanium is regarded as highly passive and the passive film formed on titanium and its alloys are quite unreactive. In these alloys passive state is not entirely stable and under certain circumstances, localized breakdown on a highly microscopic scale has been found to occur. These deficiencies in applications have demanded the surface modification of the material, which would enhance corrosion and wear resistance without altering the mechanical properties. The presence of titanium in the surrounding tissues of these implants in the form of titanium compounds and subsequent failure of implants due to fatigue, stress corrosion cracking and poor wear resistance have been reported (Dobbs 1982).

**Table 1.** Mechanical properties of the implant alloys and human bone.

Material	Tensile strength (MN/m) <sup>2</sup>	Yield strength (MN/m) <sup>2</sup>	Elongation at fracture	Vickers hardness (H <sub>v</sub> )	Young's modulus (GN/m) <sup>2</sup>	Fatigue limit (GN/m) <sup>2</sup>
316L SS (annealed)	650	280	45	190	211	0.28
Wrought						
Co–Cr alloy	1540	1050	9	450	541	0.49
Cast Co–Cr alloy	690	490	8	300	241	0.30
Titanium	710	470	30	–	121	0.30
Ti-6Al-4V	1000	970	12	–	121	–
Human bone	137.3	–	1.49	26.3	30	–

Also, Ti6Al4V alloy contains aluminum which is well-known to cause certain bone diseases and neurological disorders. Vanadium is considered to be an essential element in the body, but may become toxic at excessive levels. The toxicity of vanadium is well-known, and can be aggravated when an implant is fractured and subsequently undergoes fretting. Release of titanium ions into the tissues adjacent to the implants results in discolouration of the tissues. This may also be detrimental to the bone attachment and further bone growth on the implant surface.

Austenitic stainless steels, especially AISI (American Iron and Steel Institute) Type 316L stainless steel is the most widely used material for implant fabrication in India for orthopaedic applications because of its lower cost, ease of fabrication and welding as compared to Co–Cr alloys and Ti and its alloys. Austenitic type 316L stainless steel possesses reasonable corrosion resistance, biocompatibility, tensile strength, fatigue resistance and suitable density for load-bearing purposes thus making this material a desirable surgical-implant material.

### 3. Detrimental factors affecting the performance of implant materials

#### 3.1 Mechanical forces imposed on the implant

The complicated service conditions and loads encountered on devices implanted in the human body are generally quite high. Implants are subjected to both static and dynamic loads depending on the activity of the patient. An implant introduced into a patient for the repair of a fractured bone must have sufficient strength to sustain and transmit the load actions resulting from joint and muscular forces. Simple calculation of static loading may be made to evaluate typical loading. For example, during body movement, the load on the head of the femur is approximately twice the body weight. The load varies with the position in the walking cycle and reaches a peak of about four times the body weight at the hip and three times the weight at the knee. The frequency of loading and load cycles encountered over a specific time period are also important. A fast rate of walking corresponds to one complete walking cycle (two steps) per second. Typically an average person may take one to two million steps per year. For an active person, the number of steps taken may be two or three times more than that taken by a normal person (Sivakumar *et al* 1995). The mechanical properties (Park & Lakes 1992) of implant alloys and human bone are given in table 1.

**Table 2.** Properties of bone.

Tissue	Direction of test	Modulus of elasticity (GPa)	Tensile strength (MPa)	Compressive strength (MPa)
<b>Leg bones</b>				
Femur	Longitudinal	17.2	121	167
Tibia	Longitudinal	18.1	140	159
Fibula	Longitudinal	18.6	146	123
<b>Arm bones</b>				
Humerus	Longitudinal	17.2	130	132
Radius	Longitudinal	18.6	149	114
Ulna	Longitudinal	18.0	148	117
<b>Vertebrae</b>				
Cervical	Longitudinal	0.23	3.1	10
Lumbar	Longitudinal	0.16	3.7	5
Spongy bone	Longitudinal	0.09	1.2	1.9
<b>Skull</b>				
	Tangential	–	25	–
	Radial	–	–	97

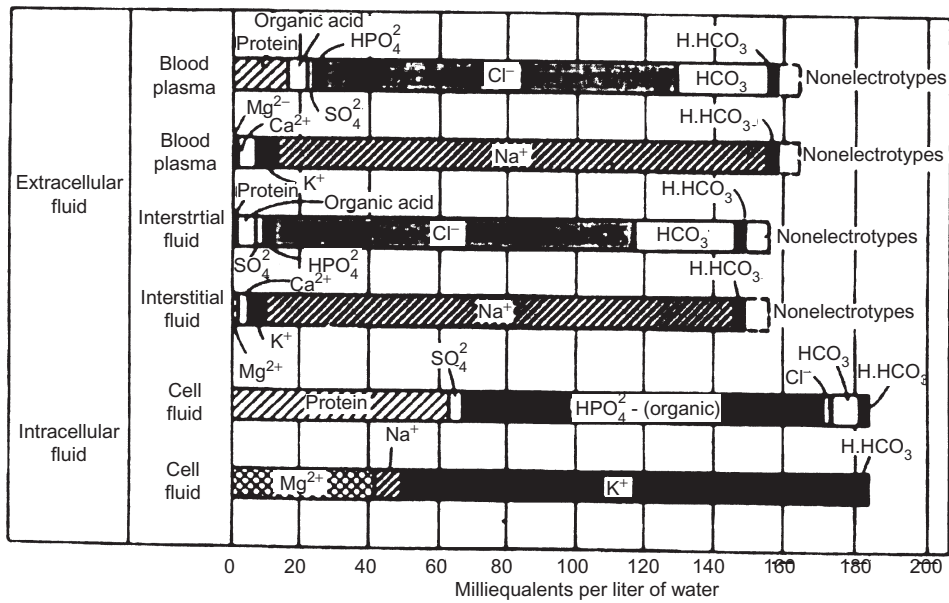
Source: Yamada (1970)

### 3.2 Biological environment

The human body is a harsh environment for metals and alloys having to be in an oxygenated saline solution with salt content of about 0.9% at pH  $\sim$  7.4, and temperature of  $37 \pm 1^\circ$  C ( $98.4^\circ$  F). When an orthopaedic implant is surgically installed into the human body, it is constantly bathed in extracellular tissue fluid (figure 2) (Pholer 1986). All the surgically implantable metallic materials, including the most corrosion-resistant materials, undergo chemical or electrochemical dissolution at some finite rate, due to the complex and corrosive environment of the human body. The body fluid constitutes water, complex compounds, dissolved oxygen and large amounts of sodium ( $\text{Na}^+$ ) and chloride ( $\text{Cl}^-$ ) ions and other electrolytes like bicarbonate and small amounts of potassium, calcium, magnesium, phosphate, sulphate and amino acids, proteins, plasma, lymph etc. The ionic species also perform numerous functions that include maintenance of the body pH and participation in the electron transfer reactions. On surgical implantation, the internal body environment is greatly disturbed i.e., the disturbance of blood supply to the bones and variation in the ionic equilibrium. Normal imbalance occurs in fluid compartment and transport of ions and non-uniform changes normally accompany disease states. From an electrochemical viewpoint, the initiation of corrosion can be due to the various conditions existing along the implant surface. These conditions may be responsible for the formation of electrochemical cells accompanied by active metal dissolution at favoured localized spots at the implant-body fluid interface. There are a series of other factors which can result in altering the local environmental conditions and lead to various forms of corrosion and/or failure of the implant. An orthopaedic implant is considered to have failed if it is prematurely removed from the body due to severe pain, inflammation and other reactions with the body like corrosion and wear.

### 3.3 Tissue-implant corrosion

In addition to the hostile environment and a significant load encountered by the implant, the interactions between the material and the tissues is of prime importance. Such interactions induce corrosion/ionization of the implanted device. Corrosion can have two effects. First

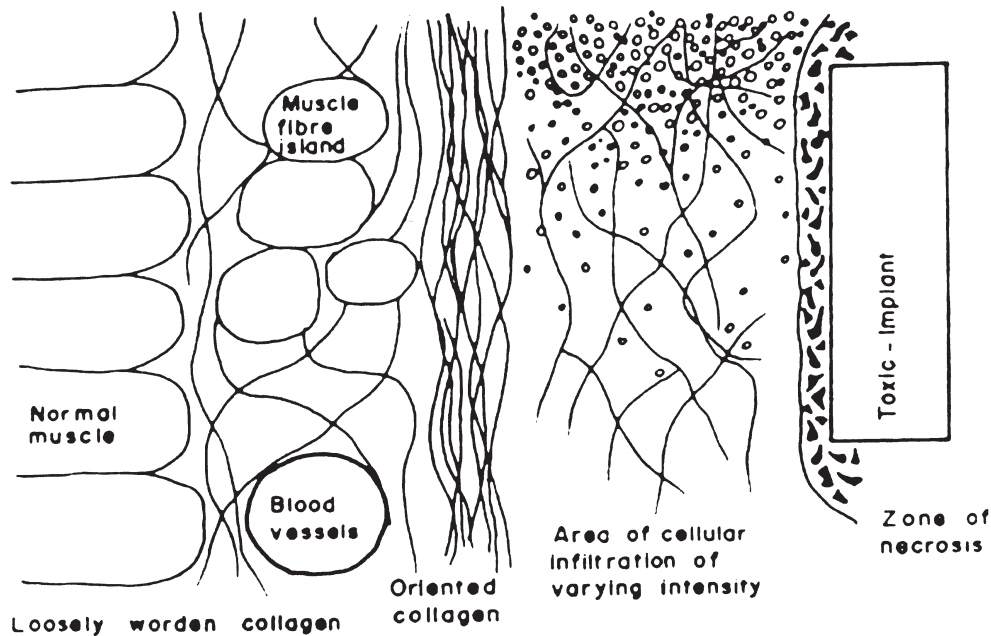


**Figure 2.** Ionic composition of blood plasma, interstitial fluid and intracellular fluid (Pholer 1986).

the implant may weaken and the premature failure will result. The second effect is the tissue reaction leading to the release of corrosion products from the implant. No metallic material is totally resistant to corrosion or ionization within living tissues. *In vivo* studies have shown that the implantation of the devices of most alloys significantly increase the concentrations of various ions adjacent to the tissues. Moreover, once a foreign material is implanted, there are several ways in which the body may react unfavorably. The presence of the implant may inhibit the defence mechanisms of the body leading to infection, necessitating the removal of the implant (Helmus & Tweden 1995). If infection does not occur or is controlled, the tissue response may range from mild edema to chronic inflammation and alteration in bone and tissue structures. This necessitates that the materials used in making implants must be inert or well tolerated by the body environment. The response of the body to an inert implant will be the development of a fibrous collagen sheath of low cellularity, which encapsulates the implant and separates it from the normal tissue. This obviously matures with time, varies in thickness in its organization and establishes a favourable relationship with the adjacent tissue (figure 3). The capsule may contain an area of necrosis adjacent to the implant surrounded by a region of chronic cellular infiltration. In some cases, the capsule has a well-defined boundary but in other cases, it extends irregularly and diffuses into the surrounding muscle. The thickness of the fibrous sheath depends on the corrosion resistance of the material. The materials producing the thinnest sheaths are regarded as the best tolerated by the body.

### 3.4 Other variables

Even though innovative metallurgical and technological advances have made striking progress in the design and the selection of implants, invariably failures occur due to underlying reasons. In every orthopaedic failure, the concerned patient is made to face the trauma of repeated surgeries besides the severe pain experienced during the process of implantation. Moreover,



**Figure 3.** Generalised fibrous capsule forming in response to intramuscularly implanted metal.

its replacement is expensive and causes hardship to the patient. Hence, it is highly desirable to keep the number of failures to a minimum. The prominent failures of stainless steel orthopaedic implant devices are discussed below.

**3.4a Direct overloading:** The intent of using a fixation device is to hold the ends of the broken bone in close proximity so that healing is promoted. The load is supposed to be shared between the bone and the fixation device. Even with a sharing of the load, it is necessary to limit the load placed on the affected bone until it heals. If excess load (due to the inept mobility of the patient) is transmitted to the implant fixed on the fractured bone slit, fracture of the implant is caused. Therefore, deformation and overload fracture results from a single overload or from a few cycles of overload on an orthopaedic fixation device such as a bone plate or a hip nail.

**3.4b Fatigue loading:** Fatigue failure is defined as failure due to dynamic as well as cyclic loading of stresses imposed on the implant. For fatigue crack to develop, it is not necessary for the implant to be loaded in the plastic deformation range. Local stresses that occur under the conditions of loading in the elastic deformation range of the implant are sufficient to initiate fatigue cracks on the surface of an implant. The majority of failures occurring in orthopaedic implants are fatigue failures (Williams 1981). Typical fatigue striations are frequently found on the fractured surfaces. Often fatigue crack nucleation sites are noticed to be present at design induced stress concentration or other structural defects. In many cases, cracks are initiated because of the corrosion phenomena and are propagated mainly by a fatigue mechanism (Sivakumar *et al* 1994). Fatigue failure may also occur due to improper installation and the presence of gap between the fractured bone fragments after implantation.



**3.4c Wear:** Wear is mechanical removal of materials during the process of relative motion between two or more contacting surfaces. The implant device may simply wear out in due course of its use. Wear can mainly affect the performance of joint prostheses. Four types of mechanisms may be implicated in the wear of metal components of joint prostheses. They are: (i) abrasive, (ii) adhesive, (iii) fatigue and (iv) corrosive modes. The adhesive wear is the most prominent on the metal-to-metal combinations. The metal to plastic system will exhibit a lower coefficient of friction but a higher volumetric wear rate. The volumetric wear of stainless steel–polyethylene combination is greater than cobalt–chromium–polyethylene systems. Higher wear rates are generally observed for a few metal-to-plastic combinations in an experimental system. The only combination used extensively in the metal-to-metal system is cobalt–chromium to cobalt–chromium. Neither stainless steel against itself or titanium against itself should provide a low wear rate and a low friction system because of their tendency to gall and seize. The severe wear followed by mechanical damage may lead to the premature removal of the prostheses.

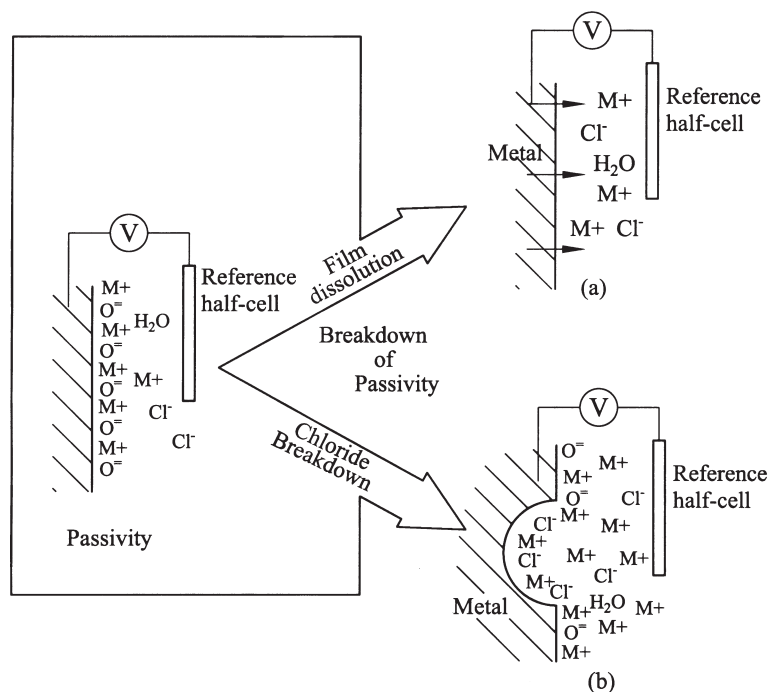
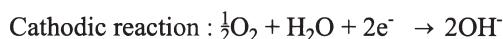
#### **4. Implant corrosion**

Corrosion is one of the major processes that cause problems when metals and alloys are used as implants in the body (Kruger 1979). To minimize these problems, better understanding of some of the basic principles involved in the degradative process of corrosion is required. Corrosion of implants in the aqueous medium of body fluids takes place via electrochemical reactions (Shreir 1994) and it is necessary to appreciate and understand the electrochemical principles that are most relevant to the corrosion processes. The electrochemical reactions that occur on the surface of the surgically implanted alloy are identical to those observed during exposure to seawater (namely, aerated sodium chloride). The metallic components of the alloy are oxidized to their ionic forms and the dissolved oxygen is reduced to hydroxyl ions. During corrosion process, the total rates of oxidation and reduction reactions that are termed as electron production and electron consumption respectively, must be equal. The overall reaction rate is controlled by the slowest step of these two processes.

The metals and alloys used as surgical implants achieve passivity by the presence of a protective surface passive film. This film inhibits corrosion and keeps current flow and the release of corrosion products at a very low level i.e. all the implantable materials undergo corrosion at some finite rate due to complex corrosive environment of the body, while in use. The types of corrosion that are pertinent to the currently used alloys are pitting, crevice, galvanic, intergranular, stress-corrosion cracking, corrosion fatigue and fretting corrosion.

##### *4.1 Pitting corrosion*

Pitting is a severe form of localised corrosion attack that results in extensive damage and release of significant amounts of metal ions. Pitting refers to the formation of small cavities/holes at the surface of a material, which is protected otherwise by the presence of an adherent, tenacious and self-healing thin passive film. The formation of such pits is attributed to the interaction of certain aggressive ions with the film at locations where it is defective or weak in nature. The pits may be visible to the naked eye in some cases but in general they are invisible, and dangerous to the extent they can allow the formation of stress corrosion cracking (SCC) or fatigue cracks, which can catastrophically fail the components in service. The importance of pitting significantly depends on the nature of the surface layer or the film that has formed on the surface due to the interaction of the material with the environment. Thus



**Figure 4.** Two principles of breakdown of passivity: (a) Metal undergoes general corrosion with film dissolution, (b) metal undergoes pitting corrosion.

a state of “passivity” is forced on the material, which safeguards the material from general corrosion by slowing down the dissolution process at the surface.

Pitting occurs when the anodic site becomes fixed on a small part of the surface due to a break in the passive layer, irregularities in the surface caused due to variations in the metal itself, incomplete coatings, scaling deposits that build up at selected areas, etc. The cathodic area can be anywhere outside the pit. This results in a high corrosion current density at the base of the pits. Movement of metal ions or  $\text{H}^+$  ions from the bottom of the pit is restricted by the film covering the top of the pit (Fontona & Green 1987). The depletion of oxygen creates a difference in electrochemical potential between the pit and the surrounding metal. The formation and breakdown of passivity and the mechanism of pitting attack are shown in figure 4. Once the pit is initiated, the metal ions form precipitates at the top of the pit and often form a film covering the pit. The film restricts entry of the solution and oxygen into the pit, and re-passivates, which could renew the protection. The importance of assessing pitting corrosion resistance by determining pit propagation rate (PPR) curves is discussed by Kamachi Mudali (1993), which also reviews the conventional tests for pitting. These tests involve anodically polarizing the specimen to a breakdown potential  $E_b$ , at which pitting ensues. After the pitting potential if the scan is reversed in the opposite direction, a protection potential  $E_p$ , is reached where the reversed curve meets the passive range, and below which pits re-passivate.

In implants, pitting occurs most often on the underside of screw heads. This form of attack occurs more frequently in media containing chloride ions (Sivakumar *et al* 1994). It is well established that the resistance to pitting in saline environment can be increased by molybdenum addition and keeping the inclusion contents to a minimum level.

#### 4.2 Crevice corrosion

Crevice corrosion is a form of corrosion, related to structural details. It occurs when a metal surface is partially shielded from the environment. It is usually encountered beneath the screw head that holds the plate or in similar locations such as the intersection of the components of two pieces, hip nail etc. The basic requirement for the occurrence of this process is the presence of a crevice, a narrow, deep crack: either an interface between parts of a device, such as between plate and screw head, or defects such as fatigue crack. Type 316L stainless steel is highly susceptible to crevice corrosion attack as compared to the other commonly used metallic implant material (Bates 1973). The occurrence of corrosion on the bone plate and screws made of stainless steels especially in the area of contact between screw heads and the counter sinks hole is a common feature. The presence of crevice corrosion in countersink portion of the bone plate can also induce crack propagation; though such type of crevice induced failures have been seldom identified. Crevice corrosion problem can often be eliminated by appropriate design of device and proper choice of the material.

#### 4.3 Galvanic corrosion

Galvanic or two metal corrosion takes place when two different metals are in physical contact in an ionic conducting fluid medium such as serum or interstitial fluid. The differential composition or process variables of a plate and the adjoining screws is responsible for the set-up of a galvanic couple, which results in galvanic corrosion. Galvanic corrosion depend on a large number of complicating factors including the relative areas of electronic and ionic contact, as well as the actual metal pair involved. However, it is safe to assume that some galvanic corrosion will occur in any dissimilar metal pair in acidic pH. In many practical applications, the contact of dissimilar materials is unavoidable. In surgical implants, galvanic corrosion can occur if a bone plate and bone screw are made of dissimilar metals or alloys. Corrosion is likely to occur between the plate and bottom side of the screw holes.

#### 4.4 Corrosion fatigue

Corrosion fatigue is a fracture failure of metal that occurs because of the combined interaction of electrochemical reactions and cyclic loading. Corrosion fatigue resistance is an important factor of consideration for load-bearing surgical implant metals or for metals used in cyclic-motion applications. Normally, a failure may not occur, but cracks can initiate from hidden imperfections, surface damage, minute flaws, chemical attack and other causes. The corrosive environment may result in local corrosive attack that accentuates the effect of the various imperfections. The corrosive attack will be influenced by solution type, solution pH, oxygen content and temperature. The body fluid environment may well decrease the fatigue strength of the implant. Fatigue striations are observed on the fractured surface of the device with coloured "beach marks" are indicative of corrosion fatigue. The presence of corrosion pit or pits could induce the fatigue to develop (Sivakumar *et al* 1994). Failures of mechanical origin in orthopaedic implants are most commonly due to fatigue or environmentally assisted fatigue. In some instances, however, the mechanism responsible for crack initiation and crack

propagation may be different (Hu *et al* 1993). For example, it has been suggested that cracks could be initiated by fretting and propagated by stress-corrosion cracking (SCC). It is also possible that cracks could initiate because of corrosion phenomena and propagated mainly by a fatigue mechanism.

#### 4.5 Fretting corrosion

Fretting corrosion occurs when two opposing surfaces such as bone plates and the screw heads of the prosthetic devices rub each other continuously in an oscillating fashion in the body environment. It is the result of small relative movements between the contacting surfaces in a corrosive medium. Even in the absence of corrosive medium, fretting can occur. Clinical significance of fretting attack lies in its intensity that may give rise to a large amount of corrosion products in adjacent tissues or it may be a major factor in crack initiation and fracture failure of an implant (Syrett & Wing 1978). Fretting corrosion at countersinks in plates and at hip nails may initiate corrosion fatigue, which occurs through screw hole. Quantification of weight loss of the implant due to fretting corrosion has been studied and was found to be directly proportional to the load transmitted across the surfaces, the number of cycle fretted and the amplitude of stresses. The weight loss has been reported to be inversely proportional to the hardness of the material and the frequency of stroke.

### 5. Problems associated with stainless steels

It is customary to use austenitic stainless steels, especially surgical grade type 316L stainless steels as temporary implants in several countries. Surgical grade type 316L stainless steel orthopaedic implants corrode in the body environment and release iron, chromium and nickel ions and these ions are found to be powerful allergens and carcinogens (Silver & Doillon 1989). Studies on retrieved implants show that more than 90% of the failure of implants of 316L SS are due to pitting and crevice corrosion attack (Sivakumar *et al* 1992). Hence, it is desirable that a better choice of material is made even for temporary use as orthopaedic devices. These localized corrosion attacks and leaching of metallic ions from implants necessitates improvement in the corrosion resistance of currently used type 316L SS by bulk alloying or modifying the surface.

In this background, a collaborative biomaterials research programme on the frontier areas of orthopaedic implants is in progress between Department of Analytical Chemistry, University of Madras, Department of Physics, Anna University, and Indira Gandhi Centre for Atomic Research, Kalpakkam. The programme included the survey and investigation of failed indigenous stainless steel implant devices, surface characterization, corrosion evaluation and various biocompatibility aspects of titanium and nitrogen modified stainless steels developed at IGCAR, kalpakkam, surface modification of stainless steels and titanium and its alloys by nitrogen ion implantation using the accelerator facility at IGCAR, Kalpakkam, evaluation of advanced titanium alloys, and hydroxyapatite coatings on type 316L SS for biocompatibility. Systematic *In vitro* and limited *in vivo* electrochemical studies in simulated body fluids and in albino rats respectively were conducted with the aim of ranking various metals and alloys according to their corrosion resistance and predicting biocompatibility.

### 6. Survey of failed stainless steel implant devices

Survey and examination of the 50 failed indigenous stainless steel implant devices retrieved from various patients of the local hospitals in Chennai (Madras), India was conducted over a

period of 4 years. The study has revealed the occurrence of 42% fracture failures, 24% failures due to corrosion attack, 14% due to onset of adverse tissue reaction, 6% due to bending of implants without fracture, 6% due to severe wear and 8% due to cracking without fracture. A classification of failures based on anatomical locations indicated that 74% failures were in the femoral area, 8% in the knee, 4% in the tibia, 2% in the humerus area and 6% in the radius and ulna. About 90% of the multicomponent devices had undergone visible crevice-corrosion attack (Sivakumar 1992). Severity of the corrosion attack increased with increased duration of implantation. Improvement in the design of the implants could reduce the number of metal-metal interfaces or modification of the crevice area could prevent crevice corrosion.

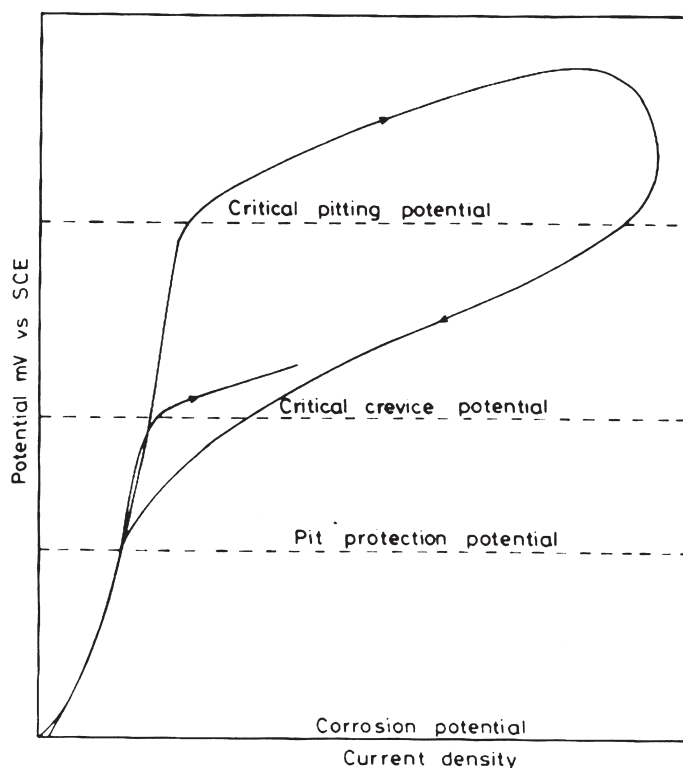
Pit-induced fatigue failure was observed in the compression bone plate and pit induced stress corrosion cracking was also noticed in the intramedullary nail in which the edges of the nail were severely pitted and most of the cracks were found to be associated with the pits (Sivakumar *et al* 1993, 1995). The pitting and crevice corrosion induced corrosion fatigue fracture was observed in the Sherman bone failure (Sivakumar *et al* 1994). Two hip prosthesis were also severely affected by pitting attack. The above facts indicate the necessity for the development of some innovative implant materials as device design exhibiting resistance to localized corrosion attack. Therefore, the manufacturer of the implant should ensure that the material supplied by them is within the ASTM specifications. The above approaches should be considered only as a temporary measures since they would only reduce the problem and will not completely eliminate it and the associated problems as mentioned in earlier part of this paper.

### 6.1 Electrochemical and surface characterization methods for orthopaedic materials

Electrochemical studies were carried out in simulated body fluids, namely Ringer's solution and Hank's solution. The pH of the solution was maintained at 7.4 and temperature at  $37 \pm 1^\circ\text{C}$ . Samples with dimensions  $10 \times 10 \times 2$  mm were mounted on an epoxy resin and polished to a mirror finish. A saturated calomel electrode (SCE) and a platinised platinum was used as the reference and auxiliary electrodes, respectively. The solution was deaerated with pure argon (Ar) gas throughout the experiment. The electrochemical measurements carried out on the coated samples are open circuit potential (OCP) – Time measurements, cyclic polarisation and electrochemical impedance spectroscopic (EIS) studies. The critical parameters like corrosion potential ( $E_{corr}$ ), the breakdown potential ( $E_b$ ) and repassivation potential ( $E_p$ ) were evaluated from the polarisation curves.

**6.1a Open circuit potential–time measurement:** The samples were immersed in the electrolyte and the potential was monitored as a function of time with respect to SCE, until the potential reached a stable value. The change in the potential in the anodic direction with time is termed the noble potential. This trend indicates the presence of a stable passive film, whereas, the shift in the potential in the cathodic direction, i.e. active direction indicates the onset of the corrosion process.

**6.1b Potentiodynamic polarization and impedance studies:** After the samples attained a constant potential, cyclic polarisation was started with an initial potential of 200 mV below the corrosion potential at a scan rate of 10 mV/min. The breakdown potential ( $E_b$ ) was reached when there was a monotonic increase in current beyond  $25 \mu\text{A}$  and above this value pitting nucleated on the metal surface. The sweep direction was then reversed after reaching an anodic current density of  $1 \text{ mA/cm}^2$  until the reverse scan reached the passive region. The potential at which the reverse scan reaches the passive region is called the pit protection potential



**Figure 5.** Idealized polarization curves indicating pitting and crevice potentials.

( $E_p$ ). The pitting potential is considered as the criterion for evaluating the pitting corrosion resistance of the materials. A typical cyclic polarization curve showing the pitting potential is given in figure 5. Pitting corrosion resistance and crevice corrosion resistance are interrelated as pitting corrosion resistance is generally accompanied by an improvement in the crevice corrosion resistance. The pitting potential of an alloy is directly influenced by the amounts of passivating elements present in the alloy. The area under the hysteresis loop in the cyclic polarization curve is a direct measure of the pit propagation kinetics. The hysteresis loop with significant observed area indicates extensive operation of the pit propagation mechanism. Higher pitting corrosion resistance of the implant can be obtained by increasing the pitting potential of the implant alloy in the noble direction. The impedance spectra of all the samples were recorded before and after polarization conditions, to evaluate the performance of the coating under equilibrium conditions and after the onset of the corrosion process respectively. The impedance parameters  $|Z|$ , polarisation resistance  $R_p$  and capacitance  $C$  were calculated from Nyquist and Bode plots.

**6.1c Passivation and surface characterization:** The samples were immersed in the electrolyte and allowed to attain the steady state equilibrium with the solution. Polarization was started at 200 mV below from the open circuit potential in order to remove the native oxide layer formed during specimen preparation and implantation. The potential was swept in the anodic direction with the scan rate of 1 mV/s up to 1.0 V, and kept at this potential for an hour in case of titanium and in the respective passive ranges for other alloys. (The reason for the

potential restricted to 1.0V is due to oxygen evolution at around 1.2V for the unimplanted specimen in this medium.) The passivated specimens were rinsed with deionised water and stored in a desiccator in an inert atmosphere before transfer to the ESCA surface analysis chamber. Depth profiling of the passivated samples was studied using secondary ion mass spectroscopy (SIMS) to understand the chemical composition of the surface layers.

The stability of the passive film of the specimen was evaluated by an accelerated leaching study. The specimens were held at a constant potential in the passive and active regions for an hour. The solution was analysed by ICP-AES, to determine the concentration of metal ions, namely Cr, Ni, Mo, Fe, leached out during the corrosion process. These results indicated the resistance of the alloys to the release of toxic metal ions.

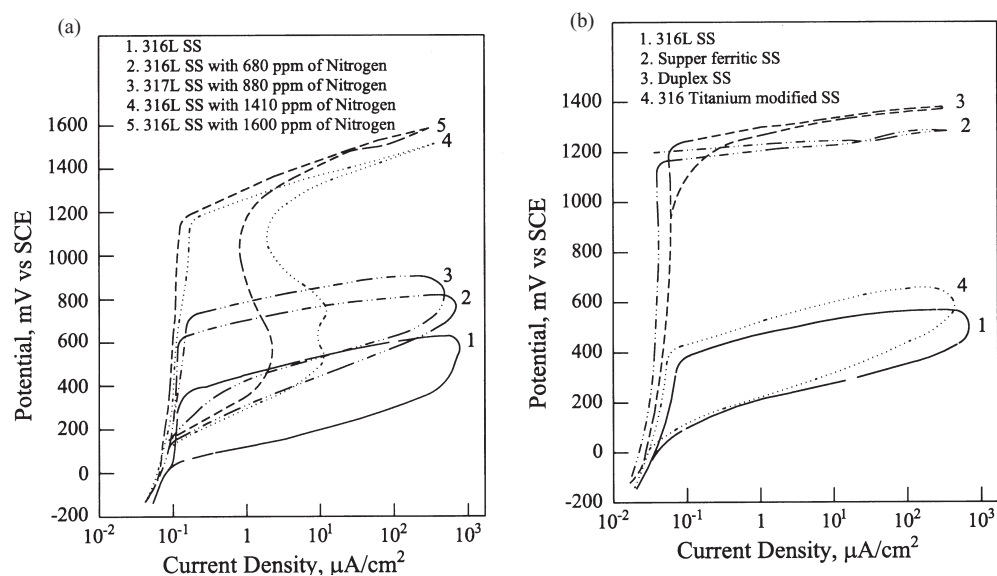
## 7. Frontier areas of research in orthopaedic implants: Alloy and surface modification

### 7.1 Modified stainless steels – a promising replacement for the currently used type 316L SS orthopaedic implants

The only way to reduce the corrosion of surgical implants is selecting an appropriate alloy with improved surface properties by addition of alloying elements, which improve the nature, composition and stability of the passive film; homogenization treatment to dissolve the second phase precipitates, production of cleaner varieties of steels using advanced steel-making processes in order to have control over inclusions; avoiding improper heat treatment and fabrication in order to eliminate the formation of second phases especially at grain boundaries. Also, the nature, composition, and chemical stability of passive films with superior corrosion resistance can be produced through surface treatment by ion beams. Stainless steels developed with the additions of alloying elements like nitrogen, titanium, molybdenum etc., for improving the corrosion resistance are termed modified stainless steels.

*7.1a In vitro and in vivo characterisation of modified stainless steel materials:* The *in vitro* corrosion studies were carried out on the modified stainless steels viz., type 316L SS with 680 ppm of nitrogen, 316L SS with 1600 ppm of nitrogen, 317L SS with 880 ppm of nitrogen, 317L SS with 1410 ppm of nitrogen, duplex (SAF 2205) and the newly modified super ferritic (Sea-cure) stainless steels in simulated conditions – Hanks solution (NaCl-8.0, CaCl<sub>2</sub>-0.14, KCl-0.40, NaHCO<sub>3</sub>-0.35, Glucose-1.00, NaH<sub>2</sub>PO<sub>4</sub>-0.10, MgCl<sub>2</sub>.6H<sub>2</sub>O-0.10, Na<sub>2</sub>HPO<sub>4</sub>.2H<sub>2</sub>O-0.06, MgSO<sub>4</sub>.7H<sub>2</sub>O-0.06 g/L respectively) at pH 7.4, and temperature 37 ± 1°C.

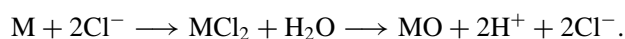
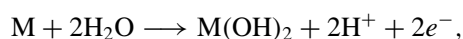
Cyclic polarization curves obtained for type 316L SS and modified stainless steels in simulated body fluid are given in figure 6a & b. The mean value of critical pitting potential ( $E_b$ ) for type 316L SS alloy was +365 mV. The presence of 680 ppm of nitrogen increased the value to +620 mV whereas the presence of 1600 ppm of nitrogen increased the  $E_b$  value to +1170 mV. A similar influence on the  $E_b$  was also found in the case of types 317L SS containing 880 and 1410 ppm of nitrogen (table 3). Thus, it is evident that austenitic stainless steels with higher nitrogen content exhibited increased  $E_b$  values indicating the improvement in the pitting corrosion resistance under simulated body fluid conditions. The super ferritic SS, duplex SS, 316L SS with 1600 ppm of nitrogen, 317L SS with 1410 ppm of nitrogen showed more than two fold increase in the pitting corrosion resistance as compared to the commonly used 316L SS (implant alloy) (Sivakumar *et al* 1993, 1994). The super ferritic stainless steel exhibited passivity up to +1120 mV and beyond this potential transpassive dissolution took place without showing any pitting attack on the specimen (Sivakumar *et al* 1993a). The titanium-modified stainless steels exhibited the pitting potential at +423 mV.



**Figure 6.** Potentiodynamic anodic polarization curves for (a) type 316L and nitrogen bearing stainless steels, and (b) type 316L superferritic, duplex and 316 Ti modified stainless steel.

The modified materials have shown improvement in high pitting corrosion resistance as compared to the currently used type 316L SS (implant alloy). For comparison, the pitting potential of the failed implants, 316L (ASTM standard specification for implant alloy) and the modified stainless steels are shown in figure 7.

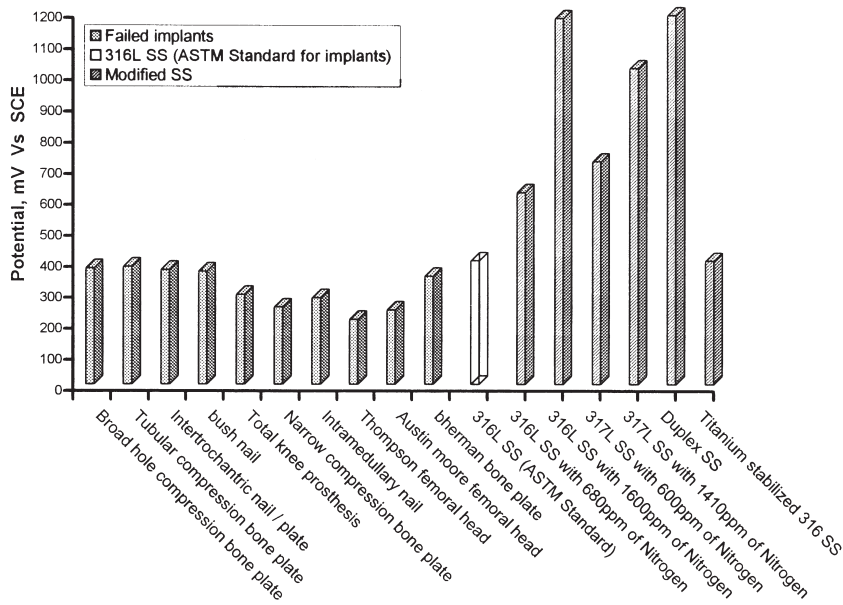
The higher pitting corrosion resistance of the above alloys could be attributed to the enrichment of chromium and bound water in the form of  $\text{OH}^-$  ions at the outermost layer of the passive film. Acidification of the pit could take place as a result of following reaction which accelerates the anodic reactions:



**Table 3.** Electrochemical parameters for modified stainless steel materials in Hank's solution.

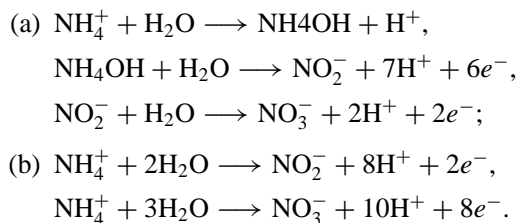
Materials	$E_{corr}$ (mV)	$E_b$ (mV)	$E_p$ (mV)	$E_{cc}$ (mV)
316L SS	-108	+365	+24	+272
316L SS (680 ppm of N)	-168	+620	+93	+459
316L SS (1600 ppm of N)	-159	+1170	+137	+730
317L SS (880 ppm of N)	-145	+720	+120	+580
317L SS (1400 ppm of N)	-155	+1152	+134	+756
316L SS (Ti)	-112	+723	+52	+332
Alloy 926	-120	+1189	+950	+972
Alloy 31	-200	Immune	-	Immune





**Figure 7.** Pitting behaviour of failed implants (10 cases studied), 316L stainless steel and modified stainless steels.

The presence of nitrogen in the above stainless steels improved the corrosion resistance due to the formation of ammonium ions at the pit site. The presence of ammonium ions,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , increased the  $\text{pH}$  which in turn slowed down the pit growth kinetics (Tanabe *et al* 1998). The XPS studies (Kamachi Mudali 1993; Sivakumar 1992; Clayton & Lu 1986) indicated the presence of  $\text{NH}_4^+$  in the metal/film interface, which may undergo any of the following reactions to form compounds that inhibit the initiation/propagation of the pit formation on the surface (Kamachi Mudali *et al* 1986, 1990, 1996).



During the initial stages of pit initiation, the presence of  $\text{NH}_4^+$  or  $\text{NH}_4\text{OH}$  in the passive film can help in immediate repassivation of the pit by increasing the  $\text{pH}$  of the solution inside the pits, and hence pit initiation and growth is avoided. The above results compliment our results (Kamachi Mudali *et al* 1986) and we have also shown (Kamachi Mudali 1993; Kamachi Mudali & Dayal 2000; Kamachi Mudali & Katada 2001; Kamachi Mudali *et al* 1986, 1990, 1996, 1997, 1999, 2000) that the dissolution of the nitrogen at the pit site and the subsequent formation of ammonium ions and nitrate compounds improves the pitting corrosion resistance. Clayton (1986) suggested a chemical, rather an electrochemical mechanism for the formation of ammonium ions and for the control of  $\text{pH}$  by the formation of nitrides from the anodically segregated nitrogen.

*In vitro* corrosion studies typically use artificial physiological isotonic saline solutions that match body fluids, except for the organic species. However, studies have indicated that organic species, such as proteins, play an important role in localised corrosion resistance, since proteins can interact with the metal surface and the corrosion products (Arumugam 1998). To simulate the organic components of body fluids for corrosion tests, bovine plasma or calf serum has been used, since amino acids analysed for human and bovine albumin indicate a remarkable similarity in molecular size and general composition. Further, their inclusions in test media would enable more realistic data to be obtained and provide an insight into the mechanism of *in vivo* corrosion. However, *in vivo* experimentation is inevitable to validate the applications as experimental results obtained by *in vitro* experiments. The *in vivo* experiments that provide the most complete information are those that consist of carrying out electrochemical measurements while the test material used as an electrode remains in the animal body. These tests are not generally used because they are more complex. It is also important therefore to establish how toxic these metals are and to assess the risk of localized tissue necrosis around the implant. To assess this risk of local toxicity through leaching of metals from metallic materials, it is important to carry out the histopathological tests.

Both, electrochemical *in vivo* (using albino rats) and *in vitro* studies (in Ringer's solution – NaCl, CaCl<sub>2</sub> and KCl, 8.6, 0.33 and 0.30 g/L respectively) on titanium modified stainless steels (316L with 0.21%, 0.34% and 0.42% titanium), nitrogen bearing austenitic stainless steels (316LN1, 316LN2 and 317L with 0.06%, 0.16% and 0.14% nitrogen respectively) and super austenitic stainless steels [alloy 926 (UNS N 08926), alloy 31(UNS N08031)] was carried to evaluate the corrosion resistance properties in comparison with the currently used type 316L stainless steel material. A cell assembly involving the electrodes in one piece was designed, fabricated and used for *in vivo* electrochemical measurements (Arumugam 1998).

Potentiodynamic cyclic anodic polarisation curve for the reference material type 316L SS, titanium-bearing stainless steels, nitrogen bearing stainless steels and super austenitic stainless steels in the Ringer's solution is summarized in table 4. The mean values of  $E_{corr}$ ,  $E_b$  and  $E_p$  for alloy type 316L SS were found to be at  $-373$  mV,  $+312$  mV and  $-221$  mV respectively. All the titanium bearing stainless steels exhibited passive condition right from the corrosion potential onwards similar to that of the reference material type 316L SS (Arumugam et al 1997). The critical pitting potential ( $E_b$ ) for all the three titanium bearing stainless steels were found to be shifted towards the noble direction compared to type 316L SS (Kamachi Mudali et al 1996). A proportionate anodic shift in  $E_b$  and  $E_p$  values were observed with

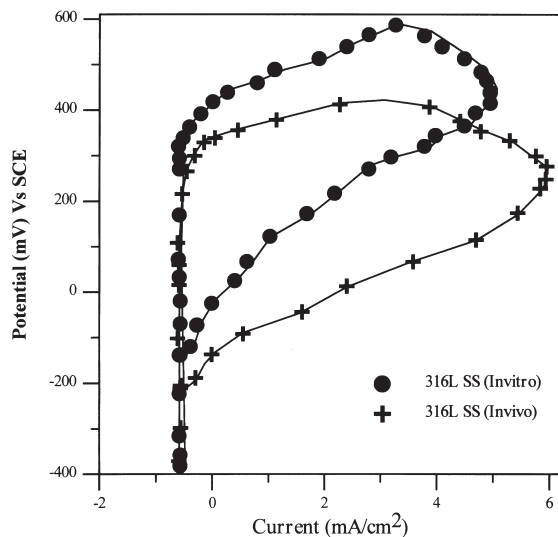
**Table 4.** Cyclic polarization data for modified stainless steel materials in Ringer's solution.

Materials	$E_{corr}$ (mV)	$E_b$ (mV)	$E_p$ (mV)
316L SS	-373	+312	-221
316L SS (0.21% Ti)	-341	+357	-204
316L SS (0.34% Ti)	-330	+391	-173
316L SS (0.42% Ti)	-317	+419	-161
316LN1 SS (0.06% N)	-304	+440	-112
317L SS (0.14% N)	-283	+518	+33
316LN2 SS (0.16% N)	-262	+546	+84
Alloy 926	-231	+834	+727
Alloy 31	-214	+891	+776

further additions of nitrogen (Pujar *et al* 1992; Kamachi Mudali *et al* 2000). Thus, the presence of 0.14% of nitrogen increased the  $E_b$  value to +518 mV, and the presence of 0.16% nitrogen increased the  $E_b$  value to +546 mV. Similar to the other modified stainless steel materials, the super austenitic stainless steels also showed passivity right from the corrosion potential ( $E_c$ ). The enhanced  $E_{corr}$ ,  $E_b$  and  $E_p$  values of the super austenitic alloys to the nobler region are indicative of improved corrosion resistance of these materials (Arumugam 1998).

The improved pitting resistance and repassivation characteristics seen in these alloys could be due to the excellent combination of alloying elements like chromium, molybdenum and nitrogen. The combined addition of chromium and molybdenum to stainless steels greatly improves their corrosion resistance in chloride solutions, with molybdenum interacting synergistically with chromium. The presence of molybdenum in stainless steel inhibits the corrosion process, which apparently increases the difficulty in breaking down the passive film. It forms a thin protective molybdenum oxide film under the hydrated chromium-rich oxide film and provides an impervious underlayer for the passive film. The presence of molybdenum along with chromium and nitrogen is able to increase the stability of the passive film, thus accounting for higher  $E_b$  and  $E_p$  values.

To compare the *in vivo* tests with those obtained under *in vitro* conditions, the polarisation curves of the reference material type 316L SS under both conditions are presented in figure 8. The cyclic polarisation curves obtained using the electrode cell assembly showed good reproducibility under *in vivo* and *in vitro* experimental conditions. The pitting potential of *in vivo* experiment was about +120 mV on the anodic region as compared to the *in vitro* experiments, and the repassivation potential also exhibited a shift of about +100 mV towards noble direction under *in vivo* condition. Many factors can be considered to explain the differences between *in vivo* and *in vitro* corrosion resistances. Amino compounds present under *in vivo* function as inhibitors (Arumugam 1998). Further, when a foreign material is inserted into a living system, almost instantaneously, specific blood proteins, consisting mainly of fibrinogen, adsorb onto the solid surface. This pattern of initial protein adsorption is encountered on all types of foreign materials inserted into a living system. Then, after continued adsorption of proteinaceous components, the surface of the solid becomes covered by a 'conditioning' film



**Figure 8.** Cyclic polarization curves of type 316L SS under *in vitro* and *in vivo* conditions.

of proteins (Sousa & Barbosa 1991). It is only after the build up of the protein film to generally about 200 Å in thickness, that other components participate in the adsorption process.

Among all the candidate materials, the super austenitic stainless steels exhibited the highest pitting resistance and repassivating tendency. Both *in vitro* and *in vivo* studies provide support to the idea that proteins inhibit corrosion and that they can be responsible for the lower corrosion rates found *in vivo* than in isotonic saline solution. The differences between the *in vitro* and *in vivo* experiments clearly demonstrate that the *in vivo* corrosion experiments in animals provide realistic data for the evaluation of corrosion resistance of the materials rather than the simulation of the complex conditions that exist within the human body via laboratory *in vitro* experiments.

### 7.2 Surface modification concept for enhancing corrosion resistance

The alternate ways to reduce corrosion and achieve the biocompatibility are via bulk alloying, surface alloying via ion implantation and surface modification by protective bioceramic coatings. Surface coating or modification by conventional techniques such as diffusion process, electrodeposition, physical vapour deposition, chemical vapour deposition and cladding, etc., often imparts satisfactory corrosion resistance to metals with intrinsically inadequate properties. They have only limited use for protecting implants since many are subjected to abrasion and wear, especially in orthopaedic implant applications. Ion implantation is a versatile surface alloying technique which produce novel metastable solid solution surface alloys without any compositional limitations normally imposed by equilibrium phase diagrams.

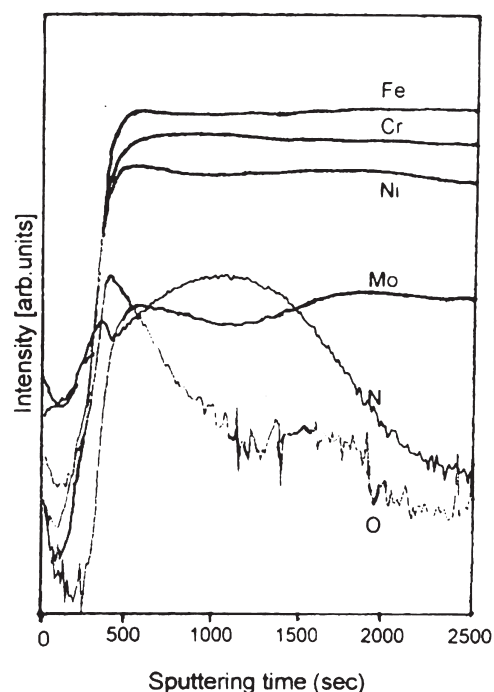
### 7.3 Ion implantation

Ion implantation is a process which involves the introduction of a small and economical amount of atoms of any element into the surface of the any material with a beam of high-velocity ions, without modifying the surface finish or the bulk properties of the underlying material and are independent of thermodynamic constraints. The bulk alloying techniques are limited by the equilibrium phase diagrams. Thus, if a potential alloying addition does not show extensive solid solubility in a base metal, there is little possibility of using it to improve the surface related properties such as corrosion and wear resistance properties. Surface alloying by conventional techniques improve the corrosion resistance of metals with intrinsically inferior properties. Ion implantation is a versatile technique which at a controlled rate produces metastable-single phase-solid solution-surface alloys without any of the compositional limitations normally imposed by equilibrium phase diagrams.

**7.3a Nitrogen ion implantation of stainless steels:** Among the various ions implanted, nitrogen ion implantation is the most suitable technology for biomedical applications. Properties such as hardness, corrosion resistance, wear etc. can be improved without adversely affecting the bulk properties of the materials (Veerabadran 1999).

Studies were undertaken to evaluate the corrosion resistance behaviour of type 316L SS and modified 316L SS on surface modification by nitrogen ion implantation in simulated body fluid conditions by electrochemical methods. Also, nitrogen ion was implanted at different doses at fixed energy, and implanted samples were subjected to electrochemical studies to get the optimum dose that can deliver a good corrosion resistance at simulated body fluid conditions.

Nitrogen ion implantations were carried out at different doses ranging from  $1 \times 10^{15}$  to  $2 \times 10^{17}$  ions/cm<sup>2</sup> at 60 KeV on type 316L SS and modified type 316L SS. Modified



**Figure 9.** SIMS depth profile of implanted-passivated advanced 316L SS at dose of  $1 \times 10^{17} \text{N}^+$  ions/cm<sup>2</sup>.

stainless contains higher percentage of Cr, Ni and Mo, lower carbon content and inclusions. Localized corrosion resistance behaviour was evaluated by *in vitro* electrochemical techniques namely open circuit potential (OCP) versus time measurements, pitting and crevice corrosion resistance studies and accelerated leaching studies were carried out for nitrogen ion implanted and unimplanted specimens in simulated human body fluid (Ringer's Solution) environment, in order to optimize the dose for producing maximum corrosion resistance to localized corrosion (Veerabadran 1999).

Nitrogen ion implantation on type 316L SS shifted the OCP to the noble potential (Subbaiyan *et al* 1996). A two-fold increase in pitting and crevice corrosion potentials was observed for the nitrogen ion implanted specimen compared to the unimplanted type 316L SS. Accelerated leaching studies showed a minimal dissolution of major alloying elements Fe, Cr, Ni and Mo from the surface of the specimen implanted at  $1 \times 10^{17}$  ions/cm<sup>2</sup>. This is attributed to the formation of protective passive film by the implanted nitrogen (Veerabadran 1996). SIMS depth profile (figure 9) studies showed the enrichment of nitrogen in the passive film. This inhibited the further dissolution of alloying elements and widened the passive range. The enhanced values, i.e., shift of OCP,  $E_b$ ,  $E_p$ ,  $E_{cc}$  to noble potentials arise from the incorporation of nitrogen in the passive film and widening of passive region consequent on nitrogen ion implantation.

Unimplanted modified 316L SS showed enhanced pitting and crevice corrosion resistance than the surgical grade 316L SS. The enhanced localised corrosion resistance is attributed to the high Mo content and low inclusion content of modified type 316L SS. Nitrogen ion implantation showed marked improvement in the corrosion resistance with pitting and crevice corrosion resistance increasing with the increase in the dose. A  $E_b$  of +219 mV and +500 mV was obtained for unimplanted and implanted sample at a dose of  $1 \times 10^{17} \text{N}^+$  ions/cm<sup>2</sup>. Accelerated leaching studies showed the minimisation of leaching of the alloying elements at

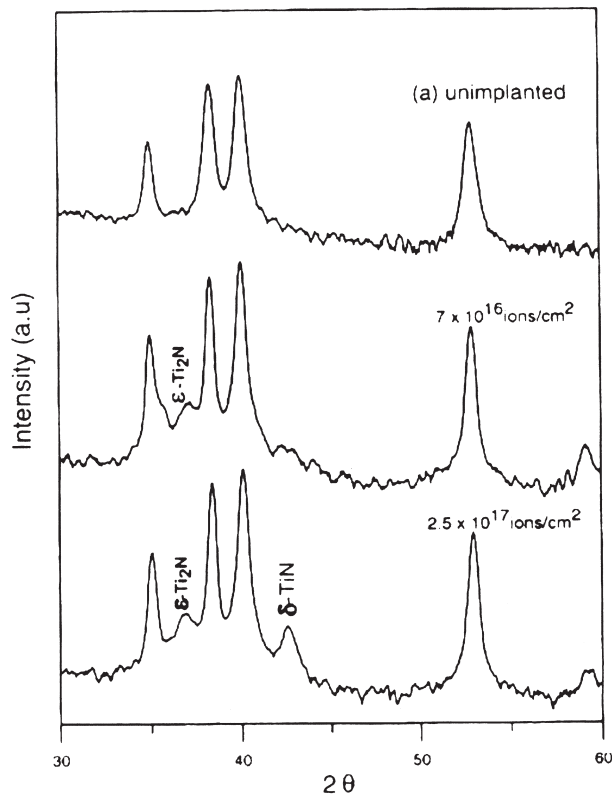
the dose  $1 \times 10^{17} \text{ N}^+$  ions/cm<sup>2</sup>. SIMS depth profile studies showed the enrichment of nitrogen at the surface. XPS studies have shown that Fe, Cr and Mo were present in their respective oxides in the passive film of both in unimplanted and implanted specimens whereas nickel was found to be in its metallic form (Veerabadrán *et al* 1999). Nitrogen is found to be present in solid solution for modified stainless steels in as-implanted specimen and partially converted into oxynitrides in the passive film. No nitride was found in both as-implanted and implanted-passivated specimens. Modified 316L SS is far more corrosion resistant than the currently used surgical grade 316L SS. All these critical parameters are indicative of the usefulness of modified stainless steel as an alternate material in place of the currently used surgical grade 316L SS, after the *in vivo* validation.

**7.3b Nitrogen ion implantation of titanium and its alloys:** The titanium and nitrogen modified type 316L SS, proposed for fast breeder reactor construction at IGCAR, Department of Atomic Energy, Kalpakkam, exhibited better corrosion resistance in neutral chloride medium (Kamachi Mudali *et al* 1996, 1999). Nitrogen ion implantation improved localised corrosion resistance of Ti-modified type 316L SS which showed better localized corrosion resistance compared to type 316L SS (Kamachi Mudali *et al* 1992, 1997). The implanted specimens showed variations in the corrosion resistance with varying doses and the specimen implanted at  $1 \times 10^{17}$  ions/cm<sup>2</sup> showed an optimum corrosion resistance. The specimens implanted at the dose of  $2.5 \times 10^{17}$  ions/cm<sup>2</sup> and above were found to be detrimental. This is attributed to the formation of Chromium nitrides during implantation and is present in the form of islands in the passive film that creates in homogeneties on the surfaces thus is more prone to corrosive attack (Sundararajan *et al* 1997).

Surface modification of CP (commercially pure) titanium was attempted through nitrogen ion implantation to increase its corrosion resistance in the simulated body fluid. The nitrogen ions of energy 70 keV were implanted between the dose varying from of  $1 \times 10^{15}$  and  $2.5 \times 10^{17}$  ions/cm<sup>2</sup> (Sundararajan *et al* 1996). Grating Incidence X-ray Diffraction (GIXRD) studies (figure 10) have been carried out on the modified materials to identify the phases formed after the implantation. Open circuit potential (OCP)-time measurement and cyclic polarization studies have been carried out to evaluate the corrosion resistance of the modified material. The specimen implanted to  $7 \times 10^{16}$  ions/cm<sup>2</sup> showed the optimum corrosion resistance. The results of the XPS investigations show that the implanted specimen exhibited enhanced corrosion resistance which is attributed to the enrichment of nitrogen on the surface to prevent further dissolution, and formation of oxynitride along with oxides in passive film.

Nitrogen ion implantation of Ti6Al4V alloy at the energy 70 keV was carried out at different doses ranging from  $5 \times 10^{15}$  to  $2.5 \times 10^{17}$  ions/cm<sup>2</sup> (Sundararajan *et al* 1996, 1998) The implanted samples were subjected to open circuit potential-time measurement and cyclic polarization studies to evolve the optimum dose. The results show that there was an increase in the corrosion resistance with increasing doses up to  $7 \times 10^{16}$  ions/cm<sup>2</sup> beyond which the resistance decreases. The stability of the passive film at higher potential was assessed by potentiostatic technique after impressing a constant potential of 1.5 V for three hours. The results of the present investigations indicate that nitrogen ion implantation can be used as a viable method to improve the corrosion resistance of the orthopaedic implant devices made of Ti6Al4V alloy.

Surface modification of Ti-6Al-7Nb alloy was carried out by nitrogen ion implantation at an energy of 70 and 100 keV using a 150 kV accelerator at different doses between  $1 \times 10^{16}$  and  $3 \times 10^{17}$  ions/cm<sup>2</sup> (Asokamani *et al* 2000, Thair *et al* 2001). The open circuit potentials of the implanted specimens were found to shift in the noble direction in comparison with



**Figure 10.** GIXRD studies of implanted and nitrogen ion implanted specimens.

unimplanted specimen. The passive current density and area of the repassivation loop were found to decrease as the dose values increased. The electrochemical impedance spectroscopic results indicate that the polarization resistance was higher for the of dose of  $2.5 \times 10^{17}$  ions/cm<sup>2</sup> implanted at an energy of 70 keV and at  $5 \times 10^{16}$  ions/cm<sup>2</sup> for an energy of 100 keV. Nitrogen ion implantation enhanced the passivability and reduced the corrosion kinetics of the alloy surface with increasing tendency for repassivation and thus enhanced corrosion resistance. This improvement arises from the formation of precipitates of TiN and Ti<sub>2</sub>N, which screen underlying titanium atoms, avoiding their migration and stabilizing the growth of the oxide film. GIXRD studies have shown that the implanted nitrogen present in the solid solution started to form nitride at the dose of  $1 \times 10^{17}$  ions/cm<sup>2</sup> whereas at the higher dose  $2.5 \times 10^{17}$  ions/cm<sup>2</sup> stoichiometric nitride had been formed. SIMS studies established the changes in the nature, composition of the implanted area as well as of the passive film formed after implantation that explain the enhanced corrosion resistance of the nitrogen ion implanted Ti-6Al-7Nb alloys in simulated body fluid. The study showed the depletion of Al, V and Nb in the passive film and the incorporation of nitrogen in the passive film which blocks the kink sites on the surface by the formation of oxynitrides along with oxides to prevent further dissolution (Thair *et al* 2001). Nitrogen implantation for both higher dose and energy ( $> 2.5 \times 10^{17}$  ions/cm<sup>2</sup>) was found to be detrimental from the electrochemical point of view, owing to the carbonitrides formed during nitrogen ion implantation.

#### 7.4 Hydroxyapatite coatings on type 316L SS

Bioactive ceramics are dense calcium phosphate based ceramics with a composition and structure similar to that of inorganic components of bone (Hench & Ethridge 1982). Of the various calcium phosphate ceramics, Hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (HAP) is the vital constituent present in bones and teeth. HAP is the most versatile material used for implantation purposes owing to their similarity with natural bone mineral and its ability to bond to bone. These materials are characterised by a certain solubility, which provokes the surrounding bone or tissue to form direct bonding to the implant. The solubility leads to gradual degradation and resorption by the surrounding tissue which stimulates the bone to grow on the material and through its pores, and in some cases it is believed to cause total transformation of the material into living bone (Von Recum 1999). This bonding is able to transfer shear and tensile stress along the interface, that could be an advantage in anchoring the implants and reducing the stress peaks in the bone. The main restriction of these materials lies in their low strengths so that they can be used as bulk materials only for low loaded devices (Lin *et al* 2001). The biological response to HAP has been characterised by clinical and laboratory studies (Park & Lakes 1992). HAP granules are used as fillers in large bone defects after resection of bone tumors.

HAP is also known to have a stimulating effect on bone formation, which is known as osseointegration. It enhances the osseointegration, and there are indications that chemical bonding may occur between HAP and bone. These attractive features of HAP are offset by the lack of strength necessary for load bearing applications (Chu *et al* 2001). Therefore to combine the bioactivity of HAP and the strength of the materials used in orthopaedic implants, it can be applied as coatings. Among the various modifications, the coating technologies have emerged as a viable process and have opened up a new possibility for implant and prosthetic devices (Pfaff *et al* 1993). Ceramic coated metal implants for prosthetic applications provide the necessary porosity for bone ingrowth, while the underlying metal substrate bear the load and the full weight bearing capacity is ensured soon after surgery. Thus, bioceramics play a twin (dual) role both in preventing the release of metal ions (rendering it more corrosion resistant) and also in making the metal surface bioactive.

The dominant requirements connected with the development of HAP coatings on metallic implants are – preparation of stoichiometric powder material with required chemical and phase composition established by their chemical identity (Ca/P ratio 1.66) and by close crystallographical affinity with bone tissue and their deposition as coatings without the presence of non-stoichiometric phases of the powder (Sridhar 2001). A number of novel methods (Sridhar *et al* 1997) for coating HAP have been proposed offering the potential for better control of film structure such as hot isostatic pressing, flame spraying, ion beam deposition, laser ablation and electrochemical deposition along with plasma spraying which has been widely studied over the decade. The major problems associated with plasma spraying process are that it is a line of sight process that produces non-uniform coating with heterogeneous structure and the high temperature involved alters the HAP and metal substrate phases. Hence, electrophoretic deposition of HAP on metal substrates has been used to overcome the above drawbacks and to achieve the uniform distribution of fine HAP deposits. The advantages of this technique include high purity of layers formed, ease of obtaining the desired thickness and high layer adhesion to the substrate. Hence, it is advantages to attempt to develop thin layers of HAP on the surface of type 316L SS by electrophoretic deposition and to studying their electrochemical properties for applications as orthopaedic devices.



**Table 5.** Electrochemical parameters of uncoated and HAP coated type 316L SS for various potentials at constant time duration of 3 minutes.

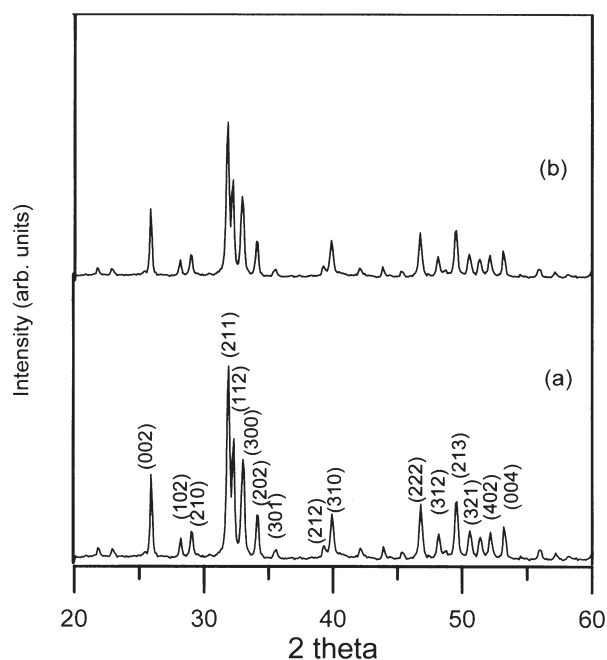
Coating potential (V)	Electrochemical parameters (V)		
	$E_{corr}$	$E_b$	$E_p$
Uncoated	-0.290	+0.323	-0.225
30	-0.015	+0.430	-0.031
50	+0.012	+0.465	+0.007
60	+0.035	+0.508	+0.025
70	-0.089	+0.455	-0.083
90	-0.110	+0.405	-0.120

**7.4a Development and characterisation of hydroxyapatite coatings by electrophoretic deposition:** HAP powder used for coating was chemically synthesised by wet method using  $H_3PO_4$  (0.3 M) and  $Ca(OH)_2$  (0.1 M) solutions at the optimum conditions. It was sintered at 1173 K and characterised by using IR, thermal and XRD studies to confirm its chemical nature (Ca/P ratio 1.66) and crystallographic structure (Sridhar 2001). HAP was electrophoretically deposited on type 316L stainless steel alloy surface ( $1\text{ cm}^2$ ) from a 2.5% suspension in isopropanol. The application of uniform HAP coatings on the surface of type 316L SS is affected by the suspension of HAP powder in isopropyl alcohol and coating variables, namely applied potential, time and thickness. The electrophoretic yield on type 316L SS substrate was determined at various applied voltages from 30 to 90 V at a constant time of 3 minutes, and also at a constant potential of 60 V at different time intervals. The sintering of the coatings after electrophoretic deposition was carried out at 1073 K for an hour in a vacuum furnace ( $10^{-5}$  torr) (Sridhar *et al*).

The coating parameters were optimized based on the corrosion behaviour of the coatings which was characterised by cyclic anodic polarisation studies (Sridhar *et al* 1999). The electrochemical parameters obtained from cyclic polarisation curves for the uncoated type 316L SS and HAP coated metal substrates, at coating voltages ranging from 30 to 90 V at a constant time of 3 minutes are presented in table 5. A nobler shift in the polarisation parameters namely  $E_{corr}$ ,  $E_b$  and  $E_p$  were observed for all the coated metal samples in comparison with the uncoated type 316L SS. The  $E_b$  (breakdown potential) for the sample coated at 60 V and 3 minutes was found to be around +0.508 V whereas for the uncoated type 316L SS it was around +0.323 V. The breakdown potentials ( $E_b$ ) for samples coated in the potential range from 30–90 V was found to be nobler than uncoated type 316L SS.

The surface of the coating becomes rougher with increase in coating time. During deposition, the electric field drives the particles towards the electrode and exerts pressure. The use of high voltage has the advantage of shorter deposition times and higher deposition thicknesses. However, higher voltages result in significant hydrogen evolution at the cathode, which in turn increases the porosity of the deposit (Sridhar 2001). The effective potential range for obtaining uniform HAP coatings was found to vary from 30 to 70 V. During the deposition process in the potential range of 30 to 70 V and coating time from 1–5 minutes, no significant  $H_2$  evolution was observed and the coatings obtained were uniformly adhered. This was found to be optimum at 60 V and 3 minutes.

Applied potential, current density and deposition times affect the development of HAP coatings (Sridhar *et al* 1998). Surface roughness, sintering temperature and atmosphere also

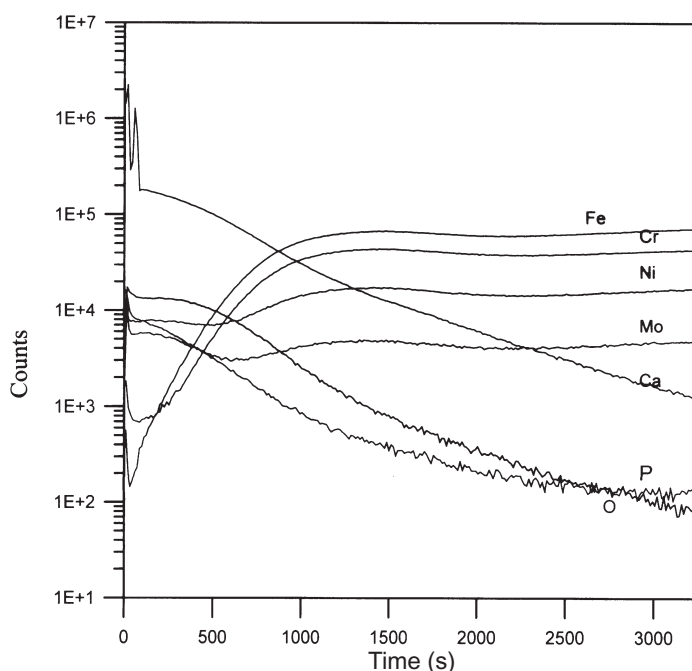


**Figure 11.** XRD patterns of HAP coated 316L stainless steel after sintering in vacuum at (a) 800°C in comparison with (b) stoichiometric HAP powder before coating.

affects the stability of HAP coatings on type 316L SS. No changes in stoichiometric structure of HAP (figure 11) were detected after deposition and subsequent heat treatments. The coating weight and thickness of the coatings increased with the increase in applied potential and time of the coatings. The coatings obtained above a potential of 70 V and 5 minutes resulted in thick porous deposits. Loss of thicker coatings from the metal surface was observed due to decohesion that occurs between the surface and the coating. Particle congestion at the cathode results in weakly bonded coatings. Higher electric field drives the particles towards the electrode and exerts pressure on the deposited layer.

SIMS studies show higher intensity levels of Calcium signal after sputtering for 3000 s, indicating the diffusion of the coating into the base alloy (figure 12). X-ray diffraction and Laser Raman studies further confirm the phase composition and characteristic vibrational modes of stoichiometric HAP. The optimum coating parameters for electrophoretic deposition of HAP on type 316L SS is deposition at 60 V for 3 minutes followed by vacuum ( $10^{-5}$  torr) sintering at 1173 K for 1 hour.

**7.4b *In vitro* corrosion studies:** A remarkable shift in the OCP-time, pitting potential and electrochemical impedance parameters towards the noble direction was observed in comparison to uncoated type 316L SS. OCP and pitting potentials shifted towards noble direction for HAP coated 316L SS in comparison with uncoated type 316L SS. A decrease in capacitance and a marginal decrease in polarisation resistance after cyclic polarisation indicate improved corrosion resistance. Electrochemical AC impedance spectroscopic data for the coated samples before and after polarisation indicate the increased corrosion resistance of the HAP coated samples (Sridhar *et al* 2000). Generally, higher values of total impedance, polarisation resistance and lower capacitance values were obtained for HAP coated samples in comparison with uncoated type 316L SS. The capacitance ( $C$ ) increased for uncoated type 316L SS samples and decreased for HAP coated samples after polarisation. Immersion studies carried



**Figure 12.** SIMS depth profile of HAP coated 316L SS.

out for a period of 30 days. This observation substantiates the stable nature of HAP coatings. The results indicate that HAP coatings obtained by electrophoretic deposition should be considered as a viable alternative for improving the corrosion resistance of type 316L SS for enhancing the biocompatibility of the implant devices.

## 8. Emerging areas of research to develop corrosion resistant biomaterials

Corrosion is one of the major problems resulting in the failure of these biodevices. The nature of the passive films formed and the mechanical properties, namely the modulus of elasticity, wear and bioactive natures of the surfaces form some of the essential criteria for selection of alternative and new materials. In this connection, the need for developing newer alloys with the addition of nobler metals to the currently used stainless steel and titanium and its alloys are proposed. The new class of super austenitic stainless steels have a higher percentage of chromium and molybdenum which strengthen the passive nature to enhance the corrosion resistance. Development of nickel-free stainless steels to eliminate the toxicity of nickel are also proposed and studied for implant applications.

The concern about the release of potentially harmful vanadium ions from Ti-6Al-4V has led to the development of V-free titanium alloy like Ti-6Al-7Nb alloy for providing improved corrosion and wear resistance as orthopedic implant device, since niobium is more biocompatible and cheaper than vanadium. Ti-6Al-4V contains aluminium, which is known to cause certain bone diseases and neurological disorders. The modulus of elasticity of metals and alloys should be equal or greater than that of the fractured bone as it varies for each part of the body (table 2). The currently used  $\alpha + \beta$  titanium alloy like Ti-6Al-4V possess high elastic modulus (120 GPa) as compared to that of bone (30 GPa). Toxicity of alloying elements

like V and Al, and high elastic modulus of conventional  $\alpha + \beta$  titanium alloys has necessitated development of new near-beta titanium alloys with non-toxic elements and low elastic modulus. Near- $\beta$  titanium alloys Ti-13Nb-13Zr, Ti-20Nb-20Zr, Ti-13Zr-20Nb containing non toxic alloying elements like Nb and Zr which promote lower modulus of elasticity have been prepared by using vacuum arc melting process. The modulus of elasticity of Ti-13Nb-13Zr is 79 GPa and theoretical investigations have shown that the elastic modulus of the other two alloys is around 30 to 40 GPa. Controlling microstructure by heat treatment is an effective way to improve the properties of these alloys and the corrosion properties (Geetha *et al* 2001). Defence metallurgical research laboratory, Hyderabad, India has taken the lead in the production of this class of alloys.

### 8.1 Laser nitriding

As the biomedical performance of titanium implants depends on their surface topography, production of hard surface by laser nitriding is proposed (Geeta *et al* 2001). Laser nitriding is a process by which surface hardness is increased by locally melting the surface of the alloy by laser excitation under a stream of nitrogen, and nitrogen + argon mixtures. This method of laser nitriding results in substantial increase in hardness of the treated material by the formation of titanium-nitrogen phases. Laser nitriding was carried out for Ti-13Nb-13Zr alloy in nitrogen atmosphere by utilizing a pulsed Nd:YAG laser with a pulse width of 4 ms at two different ambient pressures: 0.2 bar N<sub>2</sub>/Ar (S1), 1.0 bar N<sub>2</sub> (S2). The surface of the laser alloyed samples were generally uneven and consisted of ripples (Geetha *et al* 2001). There was no cracking observed in the laser alloyed region for both the samples treated at various partial pressure. The results of the OCP-time, passivation current density and area of repassivation of polarisation curves clearly exhibited high corrosion resistance for the laser alloyed samples as compared to the untreated hot-rolled alloy. Other modification methods, including laser glazing, plasma treating etc., can also used to enhance the surface hardness.

### 8.2 Hard coatings for orthopaedic implants

Total hip replacements sometimes fail due to aseptic loosening after relatively short periods of time. In order to reduce the wear of these surfaces, the feasibility of applying titanium nitride (TiN) coatings to Ti-6Al-4V alloy femoral heads is being investigated. Early results show that the wear is different for each wear couple. Titanium nitride (TiN) coated femoral heads offer an attractive alternative and research is in progress to assess the viability of TiN coatings for the protection of Ti-6Al-4V alloy and Co-Cr-Mo alloy femoral head components. It is hoped that other useful properties can be maintained while wear resistance can be improved by the use of a durable and biocompatible TiN coating. Similarly, stainless steel can be coated with layers of chromium nitride and evaluated.

Another viable alternative for enhancing the corrosion resistance, biocompatibility and mechanical properties of currently used implant materials is by surface modification. Surface modification techniques are related with ion implantation or deposition of ceramic layers (TiN, DLC, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>) by plasma spraying, chemical vapour deposition (CVD), physical vapour deposition (PVD), etc. Technical limitations of the ion implantation are related with its shallow penetration depth (0.1–0.3  $\mu$ m) that limit its utility when considering long-term applications. Ceramics coatings usually improve wear resistance of the implants but some disadvantages related to the processing (porosity, cracking) or mechanical behaviour of the coating/alloy system (delamination) have been reported. More recent

candidates for orthopaedic applications are: coated alloys by *in situ* thermal oxidation of zirconium base alloys or ferritic oxide dispersion strengthened (ODS) superalloys. Studies to evaluate feasibility of using deposited coatings are being focused on the following areas: adhesion to metallic substrate, integrity/dissolution rate, composition/structure and biocompatibility.

The production of many implant components includes surface modification treatments such as coating metal surfaces with metal/ceramic powders, wires or fibers using high temperature sintering to form porous-coated, textured components for tissue (usually bone) ingrowth (de Groot *et al* 1998). Plasma sprayed metal powders are used to form irregular surface geometry, again to allow tissue interlocking for implant fixation and different processes (plasma spraying, sputtering, precipitation from solution, sol-gel wet chemistry) are used for placement of coatings of so called bioactive ceramics (calcium hydroxyapatite and other calcium phosphate phases) over metallic substrates. Surface modification treatments involving physical or chemical vapour deposition process (PVD or CVD respectively) are also used for enhancing the corrosion and wear resistance of implants. These processes include ion implantation namely (with  $N^+$  [Sundararajan 1998; Veerabadran 1999],  $Ca^{2+}$ , Na and other elements) and plasma immersion ion plating (TiN coatings). The recent approaches also include the formation of  $TiO_2$  layers on the alloy surface followed by HAP coating and implantation of HAP on the surface of pure Ti by mechanical loading. The application of diamond-like carbon coatings (DLC) on Ti alloy substrates represent a more recent approach for developing superior wear resistant Ti alloy surfaces (Platon *et al* 2001).

### 8.3 Bioceramics

Bioceramics has evolved as an integral and vital segment of our modern health care delivery system (Hench 1991). The full potential is only beginning to be recognised. In the years to come, the composition, microstructure and molecular surface chemistry of various types of bioceramics will be tailored to match specific biological and metabolic requirements of tissues, cells and various parts of the body. Current interests also include the development of biphasic ceramics, like a composition containing two phases of calcium phosphates (like alpha, beta, tetra etc.) depending on the nature of application – short or long term.

### 8.4 Glass ceramics

Bioglasses are important class of biomaterials, which are prepared from a mixture of silica, alumina, magnesia, calcium oxide, sodium oxide and phosphorous oxide. The activity of bioglasses results from the formation of hydroxyapatite layer on the surface. In addition, calcium phosphate based glasses from CaO and  $P_2O_5$  also exhibit biocompatibility. The resorption property of calcium phosphates depends on the Ca/P ratio, degree of crystallinity and crystal structure. Partially resorbable sintered porous ceramic consisting of HAP and  $\beta$ -TCP (tricalcium phosphate) as well as HA-wollastonite (A-W) glass ceramic containing HAP and wollastonite phases have been suggested for bone augmentation (Kasuga *et al* 2001).

### 8.5 Coatings

The performance of bioceramic coatings on metals and alloys are influenced by biocompatibility, thickness, crystallinity, porosity, biodegradation, adhesion, strength, corrosion, wear and fatigue properties. Coating of metals and alloys is accomplished by a host of coating

techniques and processes for producing thin, bio-compatible films of calcium phosphate (Ca-P) materials on implant devices, has been the subject of investigation for the past several years. However, the high temperature involved during the coating process or the subsequent heat treatments after deposition causes alteration of the starting material by the creation of considerable amorphous material, the loss of OH from the HAP structure, and the formation of small amounts of other crystalline phases such as tricalcium phosphate. The bond strength is also somewhat less than that is desired in cases where high shear or torsional loading may occur. Bonding is almost exclusively by mechanical interlocking and thus is highly dependent on surface roughness of the substrate. New and advanced techniques should eliminate the pitfalls encountered. Recent development in the thermal spraying include high velocity oxy fuel spraying (HVOF) which gives significant improvement of coating quality. The higher kinetic energy of the spray particles generates very dense coatings with improved bond strengths compared to conventional plasma spraying (Lugscheider *et al* 2001).

The type of bioceramic coating depends on the intended nature of application such as resorbable, non-resorbable and surface active materials. Highly pure brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) coatings on porous Ti6Al4V substrate were prepared by electrodeposition from aqueous electrolytes. The influence of hydrothermal treatment temperature on brushite-to-hydroxyapatite conversion and the morphology and phase composition of hydroxyapatite (HAP) coatings studied. By means of sintering pure calcium-deficient hydroxyapatite coating on Ti6Al4V in air at 1073 K better bonding strength of coating with dense  $\text{TiO}_2$  film on the substrate surface was obtained.

### 8.6 Sol-gel coatings

The application of sol-gel processes in the preparation of single and mixed metal oxides, both in bulk powders and thin films, has increased dramatically over the last two decades and is currently attracting much global attention. Through the use of sol-gel methods, crystalline coatings of hydroxylapatite on substrates of vycor glass, polycrystalline alumina and single crystal magnesia have been successfully produced (Chai *et al* 2001). Results indicate that high quality hydroxylapatite coatings can be produced on ceramic substrates, with coatings deposited in this manner offering a number of benefits over other coating methods. In general the methodology involves the formulation of a homogeneous solution containing all of the component metals in the correct stoichiometry.

### 8.7 Ion implantation

Calcium-ion implantation technique was applied to improve the bio-compatibility of titanium. Calcium ions were implanted into titanium surfaces and the surface oxide of titanium grows after the calcium-ion-implantation (Ukai *et al* 2001). The amount of calcium phosphate forming on the surface increases with increase in the amount of implanted ion. The precipitation of calcium phosphate on titanium in the electrolyte solution is greatly accelerated by calcium-ion-implantation. This is a surprising property for the biomaterial. As a result of calcium-ion-implantation, the  $\text{TiO}_2$  film on titanium surface grows and the surface layer contains chemical states of  $\text{CaTiO}_3$  and CaO with increasing amount of implanted calcium ion. Implanted calcium ions exist as calcium oxide, and a complex oxide of calcium and titanium. Therefore, the structure of the surface-modified layer is  $\text{TiO}_2$  containing a calcium oxide and a complex oxide of calcium and titanium near the surface. This surface modification enhances significantly new bone formation under *in vivo* condition.

### 8.8 Quasicrystal thin films

Thin films of quasicrystals have attractive mechanical and electrical properties, which can be used as coatings for biomedical devices. They offer low friction and nonsticking surfaces. The coatings are applied to surgical blades and needles to improve their performance and even to extend their lifetime in certain applications. Although quasicrystals in general tend to be brittle, it is possible to take advantage of some of their properties by forming thin films deposited on a rigid substrate. Results on standard stainless steel blades coated with quasicrystalline AlCuFe with thickness up to 3000 Å show substantial improvements in the cutting and coagulation action of the blades over uncoated blades and Teflon covered blades (Syuko *et al* 2001).

### 8.9 Functionally graded coatings

Functionally graded materials (FGM) have the potential to meet the increasing demand for diverse functionalities within a single device. The potential value of FGM has attracted much attention in different fields in recent years. There has been much interest in recent years in HA because of its attractive bioactive properties. Functionally graded calcium phosphate coatings were produced on Ti-6Al-4V substrates by plasma spraying. It also involves the synergies of two types of calcium phosphates, namely,  $\alpha$ -tricalcium phosphate and HA, to form the FGM (Khor *et al* 2001).

### 8.10 Graded coatings

Graded coating of hydroxyapatite and titanium by plasma spraying was attempted as an alternative means to direct deposition of HAP in titanium. The application of multiple layers of HAP and titanium mixtures ensured a gradual change in the composition across the interface. As a result, the microstructure of the coating substrate interface showed a good adhesion between the coating and the substrate (Park *et al* 1999).

### 8.11 Composite coatings

In addition to the application of composites (Wang *et al* 2000) and composite coatings is also an emerging area of surface modification of metals and alloys. Titanium/porous titanium composites have advantageous mechanical properties, Ti/ceramic composites show special biological properties with improved osseointegration of the implants and the special physical properties of Ti/ceramic composites makes them suitable for heart pacemaker leads (Breme *et al* 2000).

### 8.12 Biomimetic coatings

Recently, calcium phosphate coatings have been grown from aqueous solution on to titanium metal substrate via surface induced mineralisation which involves modification of the surfaces to introduce surface functionalisation followed by immersion in a supersaturated calcium phosphate solution (Li *et al* 2001, 2002). This process is based on the idea of nature's template mediated mineralisation by chemically modifying substrates to produce surfaces that induce heterogeneous nucleation from aqueous solutions. In nature, organisms use various macromolecules to control the nucleation and growth of mineral phases.

New materials could extend the lifetime of implants, but surface modifications of traditional materials can also improve surface properties significantly. However, it is generally not possible to improve simultaneously all properties. Surface processing provides good biological

performance of implant materials, when special mechanical properties, such as low friction coefficient, high wear rate or high bonding with bone, are required. There are many possibilities, but the biocompatibility of these new systems must be carefully controlled during their evolution by means of quite simple *in vitro* tests or more difficult *in vivo* tests.

Standard test methods to determine the life term performance of biomaterials especially the new generation of alloys, surface modification by coatings, ion implantation, laser melting and other techniques, and bioceramics under realistic physiological loads are a few promising directions. Studies on *in vivo* corrosion measurements using single gadgets are met with uneven success and are seldom tried. Further work on this area towards the precise *in vivo* measurements will be fruitful. Due to corrosion the metal ions released into tissues surrounding implants may cause local cytotoxicity affecting the morphology and structure of the tissue, and may lead to systemic toxicity, carcinogenesis or allergenic reactions. Thus, *in vivo* screening of materials should also be carried out for evaluating adverse reactions. A sequence of systematic *in vitro* and *in vivo* studies are recommended and to be practised for the application of new biomaterials.

## 9. Summary

Survey of failed stainless implants indicate that about 70% of failures in type 316L SS implants are associated with corrosion related to pitting and crevice attack, pit induced fatigue crack and SCC. Alloy modifications of stainless steel with titanium and nitrogen effectively improves the corrosion resistance of the materials. Surface modification of stainless steels and titanium and its alloys by nitrogen ion implantation enhances the corrosion resistance properties of these orthopaedic implant materials. Surface modification of type 316L SS with hydroxyapatite bioceramics plays a twin (dual) role both in preventing the release of metal ions (rendering it more corrosion resistant) and also in making the metal surface bioactive. HAP coatings obtained by electrophoretic deposition prove as a viable alternative for improving the corrosion resistance of type 316L SS for enhancing the biocompatibility of the implant devices. The current areas of research mainly focus on surface modification of alloys by novel methods and processes which enhance the corrosion resistance and biocompatibility of the devices used. A new class of materials includes bioceramics, namely various types of calcium phosphates, glass ceramics, biphasic ceramics and functionally graded materials and their coatings.

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