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# An Overview of Metallic Biomaterials for Bone Support and Replacement

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# 1. Introduction

The National Institutes of Health Consensus Development Conference, USA defines a *Biomaterial* as – any substance (other than drugs) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments or replaces any tissue, organ, or function of the body (Dee et al., 2002). Biomaterials are distinct from other classes of materials because of special requirement of meeting biocompatibility criteria.

*Biocompatibility* is the ability of a material to perform with an appropriate host response in a specific application. The body tissues respond differently depending upon the type of foreign material. The type of foreign material and its corresponding tissue response is given in Table 1 below.

S. No	Type of Foreign Material	Tissue Response
1	Toxic	Surrounding tissue dies
2	Nontoxic/Biologically Inactive	Fibrous tissue of variable thickness develops
3	Nontoxic / Biologically Active	Interfacial bond forms
4	Nontoxic / Resorbable	Surrounding tissue replaces material

Table 1. Types of Tissue Response to Different Foreign Materials (Hench, L.L and Best, S., 2004).

In case of implant materials, closer it is in biochemical qualities to host's tissue, more difficult it will be for the host in discriminating this implant material as a foreign object in the body. As a result of this, the accepter tissue is likely to respond through the rejection phenomenon of immunoresponce which endangers the host's body. On the other hand, material farther away in biochemical characteristics from the accepter tissue is more likely to be a better biomaterial. The material closer to the host tissue in qualities would perform poorly as they are decomposed faster, digested and absorbed, whereas materials dissimilar in qualities are identified as foreign objects and are isolated from the host tissue by means of a new fibrous membrane (Chiroff et al., 1975). Any bone implant material when used either for joint replacement such as knee and wrist joint or total hip replacement (THR), it comes in contact with sinovial fluids. The sinovial fluid which is an aqueous colloid containing chlorides and phosphates of Na, K and Ca, albumins, globulins, amino-acids, sugars and bacterias, acts as a lubricant in natural joints and reduces friction. So, the implant material for bone must have no or very insignificant reactivity with body fluids (Holmes, 1979).

Modern biomaterials are getting benefited by the developments in the fields of traditional and non-traditional materials. However, there are still two major difficulties associated with biomaterials. The first is an incomplete understanding of the physical, chemical and mechanical functioning of many biomaterials and of the human response to these materials. The second difficulty is that many biomaterials do not perform as desirably as we would like. In view of this, special attention is now being focused on development of materials which are specially suited for specific biomaterial applications, such as for orthopaedic implant applications (Osborn and Newesely, 1980; Kitsugi et al., 1981; LeGeros, R. Z., 1988; Lavernia C. and Schoenung, J. M., 1999), i.e. the materials which show little or no inflammatory response and have sufficient mechanical strength when used as implant material. Therefore Orthopaedic implant material should exhibit: a) complete body stability, b) complete biocompatibility, c) high wear strength d) high mechanical strength, e) low friction (Krause Jr. et al., 1990).

# 1.1 Structure and properties of human bone

The bones of the body come in a variety of sizes and shapes. The four principal types of bones are long, short, flat and irregular. Bones that are longer than they are wide are called long bones. They consist of a long shaft with two bulky ends or extremities. They are primarily compact bone but may have a large amount of spongy bone at the ends or extremities. Long bones, as shown in Figure 1, include bones of the thigh, leg, arm, and forearm.

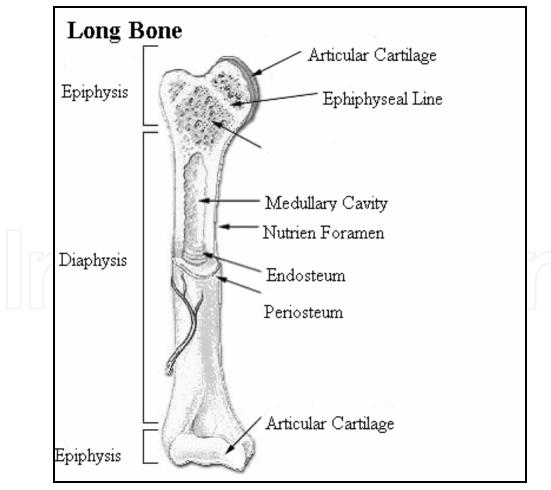


Fig. 1. Parts of a long bone (http://training.seer.cancer.gov)

There are two types of bone tissues: compact and spongy. The names imply that the two types differ in density, or how tightly the tissue is packed together. There are three types of cells that contribute to bone homeostasis. Osteoblasts are bone-forming cell, osteoclasts resorb or break down bone, and osteocytes are mature bone cells. An equilibrium between osteoblasts and osteoclasts maintains bone tissue.

#### 1.2.1 Compact bone

Compact bone, as shown in Figure 2, consists of closely packed osteons or haversian systems. The osteon consists of a central canal called the osteonic (haversian) canal, which is surrounded by concentric rings (lamellae) of matrix. Between the rings of matrix, the bone cells (osteocytes) are located in spaces called lacunae. Small channels (canaliculi) radiate from the lacunae to the osteonic (haversian) canal to provide passageways through the hard matrix. In compact bone, the haversian systems are packed tightly together to form what appears to be a solid mass. The osteonic canals contain blood vessels that are parallel to the long axis of the bone. These blood vessels interconnect, by way of perforating canals, with vessels on the surface of the bone. Human bone thus has a complex hierarchical microstructure that can be considered at many dimensional scales (Nalla et al., 2003). At the shortest length-scale, it is composed of type-I collagen fibres (up to 15 µm in length, 50-70nm in diameter) bound and impregnated with carbonated apatite nanocrystals (tens of nanometres in length and width, 2-3 nm in thickness). These mineralized collagen fibres are further organized at a microstructural length-scale into a lamellar structure, with roughly orthogonal orientations of adjacent lamellae (3–7  $\mu m$  thick) Permeating this lamellar structure are the secondary osteons (up to 200-300 µm diameter): large vascular channels (up to 50-90 µm diameter) oriented roughly in the growth direction of the bone and surrounded by circumferential lamellar rings.

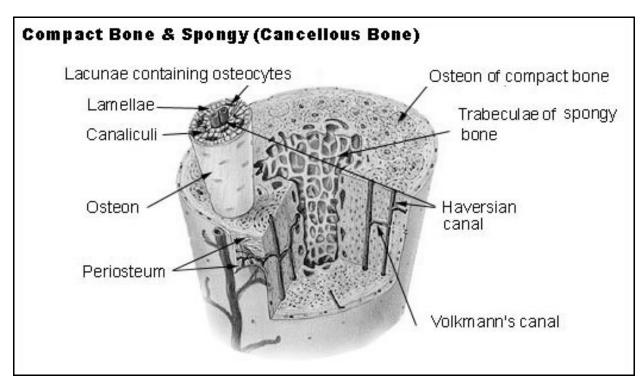


Fig. 2. Internal Structure of Bone (http://training.seer.cancer.gov)

#### 1.2.2 Spongy (cancellous) bone

Spongy (cancellous) bone is lighter and less dense than compact bone. Spongy bone consists of plates (trabeculae) and bars of bone adjacent to small, irregular cavities that contain red bone marrow. The canaliculi connect to the adjacent cavities, instead of a central haversian canal, to receive their blood supply. It may appear that the trabeculae are arranged in a haphazard manner, but they are organized to provide maximum strength similar to braces that are used to support a building. The trabeculae of spongy bone follow the lines of stress and can realign if the direction of stress changes.

# 1.2.3 Mechanical properties of bone

Bone consists of a collagenous framework upon which calcium salts are deposited mainly as hydroxyapatite. The mature bone is lamellar, its collagenous fibres building regular patterns. In the cancellous bone the collagen bundles lie parallel to the long axis of the trabecula and in the compact (cortical) bone the fibres are disposed in concentric rings around the vascular spaces. Bone can also be considered as consisting of cells and extracellular matrix, with 35% of the matrix being composed of organic and 65% of inorganic ones (Martin, 1998). The inorganic part comprises of calcium salts whereas that of the organic components is collagen and noncollagenous proteins. The noncollagenous proteins form 10% of the organic material. They modulate matrix organization, bind calcium and similar to bone growth factors, regulate bone formation and resorption (Sandberg, 1991).

The mature bone can be divided into cancellous (trabecular) or compact bone, depending of the degree of bone porosity. Compact bone has a porosity of 5-30% and cancellous bone is approximately 30-90% porous, which is the proportion of the volume occupied by non-mineralized tissue (Carter and Heyes, 1977). The diaphyses of long (tubular) bones are composed mainly of compact bone whereas the epiphyses and methaphyses consist of cancellous bone that is continuous with the inner surface of the cortical shell and exists as a three-dimensional, sponge-like lattice composed of plates and columns of bone. The trabeculae divide the interior volume of bone into interconnecting pores of different dimensions. The composition and true densities of compact and trabecular bone are thought to be similar (Galante et al., 1970) as are their microscopic material properties (McEiheney et al., 1970).

A key requirement in bone is compressive strength, and the most important factor in compressive strength is the degree of mineralization. Decreased mineralization results in increased risk of fracture (Wright and Hayes, 1977). A collagen and hydoxyapatite composite is advantageous from a mechanical standpoint. Mineralized tissue can be considered as a porous, two-phase composite consisting of hydroxyapatite crystals embedded in collagen matrix (Lees and Devidson, 1977). On the other hand, increasing collagen intermolecular cross-linking is associated with increased mineralization. The resulting composite structure is much stronger and stiffer due not only to the higher mineral content but also due to the stiffening of the collagen matrix caused by the greater cross-linked density (Memmone and Hudson, 1993; Carter and Springler, 1978). It has been suggested that the longitudinal strength and stiffness of mineralized bone tissue are approximately equal to the strain rate raised to the 0.06 power.

Structurally, bone can be considered as a composite having both solid and a liquid phase. The solid phase consists of mineralized bone tissue and the fluid phase comprises of blood vessels, blood and marrow, nerve tissue, miscellaneous cells and interstitial fluid (McEiheney et al., 1970).

The compressive strength of cortical bone in humans is around 200 MPa and for the femur it is around 17 GPa (Reilly et al., 1974; Reilly and Burstein, 1975). Cancellous bone is much weaker and the results obtained have varied, depending on the location of the bone (Goldstein, 1987). Compressive strengths of 0.15-27 MPa and elastic modulus from 50 to 350 MPa have been reported for cancellous bone (Carter and Heyes, 1977; Scoenfeld, 1974).

Composition	Enamel	Dentin	Bone	Hydroxyapatite (HAp)
Calcium [wt%]	36.5	35.1	34.8	39.6
Phosphorus [wt%]	17.7	16.9	15.2	18.5
Ca/P (molar ratio)	1.63	1.61	1.71	1.67
Sodium [wt%]	0.5	0.6	0.9	
Magnesium [wt%]	0.44	1.23	0.72	
Potassium [wt%]	0.08	0.05	0.03	-1
Total Inorganic [wt%]	97	70	65	100
Total Organic [wt%]	1.5	20	25	-1
Water [wt%]	1.5	10	10	
Elastic Modulus [GPa]	80	15	0.34-13.8	10
Compressive Strength	10	100	150	100

Table 2. Comparative composition and structural parameters of inorganic phases of adulthuman calcified tissues (Dorozhkin and Epple, 2002).

# 2. Metallic biomaterials

Metals are used as biomaterials due to their excellent electrical and thermal conductivity and mechanical properties. The metals and alloys are used as passive substitutes for hard tissue replacement such as total hip replacement and knee joints; for fracture healing aids as bone plates and screws, spinal fixation devices; and dental implants; because of their excellent mechanical properties and corrosion resistance. Some metallic alloys are used for more active roles in devices such as vascular stents, catheter guide wires, orthodontic archwires and cochea implants.

The orthopaedic surgeons, in dealing with the vast and complex problems of reconstructive surgery and some of the more complicated fracture problems, rely on the use of metallic biomaterials for fixation and replacement of portions of bone. Common use of metals for internal fixation is as old as early 1900s. Metal implants in the form of wire, bands, screws, bolts, staples, nails and plates are applied in the temporary fixation of fractures.

Metals are also used to fabricate implants which are designed to permanently replace the load-bearing function of a bone. Some of these metals and alloys are materials such as Al, In, Sn, Ti, Zr, Cr, Mo, Ta, Fe-Ni-Cr, Co-Ni-Cr, Co-Cr-Mo, Al-V-Ti and Ti-Mo-Pd, 316 L stainless steel and Cobalt based MP 35N alloy. Total hip replacement and joint replacement are some of the areas where these materials are required to remain in the body permanently.

The problems which are associated with these implant materials are not that severe with temporary fixation devices as they are with permanent implants. Some of the common problems associated with these implant materials are biocompatibility (involving local reaction in the tissues near the implant or a general reaction or an allergic reaction distant

from implant site) (Groot, 1980), wear and friction of load bearing implants in the presence of body fluids and effect of wear debris on the surrounding tissues, corrosion and fatigue in the presence of body fluids and lack of skeletal attachments (Rieu et al., 1990; Jarcho, 1981; Damien and Parsons 1990; Klein 1990; White and Shors 1986).

In its role of temporary fixation, the orthopaedic implant is used to bone fragments and keep them from being displaced during the healing process. Once healing is completed, the bone regains its original function and the implant is removed. Due to this reason, any of the aforementioned problems except for biocompatibilities are short-lived. However, any allergic reactions due to implant itself or wear debris or corrosion products cannot be neglected. Also, in future it is likely that orthopedic surgery including total joint replacement will be used in younger patients, who will not only be more active but will require their prostheses for a longer period (Barralet et al., 2002).

The main metals in clinical use are: Titanium and its alloys, Vitallium, Aluminium, Cobalt-Chromium alloys and various Stainless Steels, all of them being inert and biocompatible to acceptable levels (Mofid et al., 1997).

#### 2.1 Stainless steel

The first metal alloy developed specifically for human use was the "Vanadium steel" which was used to manufacture bone fracture plates and screws. Vanadium steel is no longer used in implant fabrication, as its corrosion resistance in vivo is inadequate. Later, another type of stainless steel (18.8 type 302) was used for the purpose due to its more strength and superior corrosion resistance than the vanadium steel. Subsequently, small amount of Mo was added to this type of steel to enhance its corrosion resistance and it became known as 316 stainless steel. After 1950, the percentage of Carbon in it was also reduced from 0.08 wt% to 0.03 wt% to further improve its corrosion resistance and thus it became 316 L stainless steel (Park, and Bronzino, 2000).

The 316 and 316L stainless steels are the most widely used for implant fabrication but ASTM recommends the use of 316 L stainless steel. The composition and important mechanical properties of general 316 L stainless steel are given in Tables 3 and 4 below:

S. No	Chemical Element	Composition (%)
1	Carbon	0.03 max
2	Manganese	2.00 max
3	Phosphorous	0.03 max
4	Sulfur	0.03 max
5	Silicon	0.75 max
6	Chromium	20.00 max
7	Nickel	14.00 max
8.	Molybdenum	4.00 max

Table 3. Composition of 316 L stainless steel (ASTM, F139-86, 1992)

Condition	Ultimate Tensile Strength (MPa)	Yield Strength (0.2% offset) (MPa)	% Elongation	Rockwell Hardness
Annealed	485	172	40	95 HRB
Cold-Worked	860	690	12	

Table 4. Mechanical properties of 316 L stainless steel implant material (ASTM, F139-86, 1992)

The high Young's modulus (approximately 10 times that of bone) of 316 L stainless steel (as can be seen in Table 8) leads to stress shielding of surrounding bone and hence causes bone resorption.

#### 2.2 Titanium and its alloys

The use of Titanium as implant material dates as late as 1930s. It is primarily due to its lightness (Table 5) and good mechano-chemical properties. There are four grades of unalloyed pure titanium, differentiated on the basis of amount of impurities such as Oxygen, Nitrogen and Iron present in them, which are used for surgical implant applications. The amount of Oxygen in particular affects the ductility and the strength of these grades.

Alloys	Density (g/cm³)
Ti and its alloys	4.5
316 L stainless steel	7.9
Co-Cr-Mo alloy	8.3

Table 5. Density of some alloys used as implant materials

Among the Titanium alloys, Ti6Al4V whose chemical composition is given in Table 6 is most widely used for implant applications. The main alloying elements in this material are Aluminium and Vanadium. The other alloys of Ti used are Ti13Nb13Zr whose main alloying elements are Niobium and Zirconium and Ti3V11Cr3Al, having Aluminium, Chromium and Vanadium as the alloying elements.

Element	Grade 1	Grade 2	Grade 3	Grade 4	Ti6Al4V
Nitrogen	0.03	0.03	0.05	0.05	0.05
Carbon	0.10	0.10	0.10	0.10	0.08
Hydrogen	0.015	0.015	0.015	0.015	0.0125
Iron	0.20	0.30	0.30	0.30	0.25
Oxygen	0.18	0.25	0.35	0.40	0.13
Aluminium					5.50-6.50
Vanadium					3.50-4.50
Titanium	Balance	Balance	Balance	Balance	Balance

Table 6. Chemical composition of different grades of Ti and its alloy (ASTM, F67-89, 1992; ASTM, F136-84, 1992).

It can be seen in Table 7, that Ti13Nb13Zr alloy is more ductile and has higher elastic modulus than the Ti6Al4V alloy, as well as pure grades of Ti.

Property	Grade 1	Grade 2	Grade 3	<b>Grade 4</b>	Ti6Al4V	Ti13Nb13Zr
Tensile Strength (MPa)	240	345	450	550	860	1030
Yield Strength (2% offset) (MPa)	170	275	380	485	793	900
% Elongation	24	20	18	15	10	15
% Reduction in area	30	30	30	25	25	45

Table 7. Mechanical properties of different grades of Ti and its alloys (ASTM, F67-89, 1992; ASTM, F136-84, 1992).

The success of Ti as implant material is related to its ability to osseointegrate into the surrounding bone which means it exhibits bioactive properties in the presence of tissue, allowing the growth of bone directly up to its surface. The reason for the success of Ti implants are (i) that it being highly reactive metal, forms a dense, coherent passive oxide film which not only prevents the ingress of corrosion products into the surrounding tissues in the initial stages of implantation (Sutherland et al., 1993) but also steadily grows in-vivo (Moor and Grobe, 1990) which is stoichiometrically similar to TiO<sub>2</sub> which is biocompatible (Kasemo, 1983; Lausmaa and Kasemo, 1990) and (ii) reformation of this surface coating to TiOOH matrix which traps the super oxide (O<sub>2</sub>-) produced during the inflammatory response thus preventing the release of hydroxyl radical (OH\*) (Tengvall and Lundstrom, 1989). Ti and its alloys are however more expensive than stainless steels.

These materials have poorer wear characteristics than other metals and alloys used as implant materials and therefore they are now not considered suitable for load bearing surfaces.

Titanium and its alloys have excellent resistance to corrosion. Their Elastic moduli are approximately half that of stainless steels (Table 8) and therefore create less risk of stress protection of bone.

Material	E (GPa)	Yield Strength (GPa)	Tensile Strength (MPa)	Fatigue Limit (MPa)
Stainless steel	190	221-1213	586-1351	241-820
Co-Cr alloy	210-253	448-1606	655-1896	207-950
Titanium	110	485	760	300
Ti6Al4V	116	896-1034	965-1103	620
Cortical Bone	15-30	30-70	70-150	

Table 8. Comparison of mechanical properties of metallic biomaterial with bone (Brunski, 1996).

# 2.3 Co-cr alloys

There are basically two types of Co-Cr alloys which are used as implant materials, (i) Co-Cr-Mo alloy which is castable and (ii) Co-Ni-Cr-Mo alloy which is forged. The Co-Cr-Mo alloy is in use in medicine particularly in dentistry since many decades and has found use in artificial joint applications also. The Co-Ni-Cr-Mo alloy is a recent development and has found application as an implant material for heavily loaded joints such as artificial hip and knee. As per American Society for Testing and Materials, the four types of Co-Cr alloys which are recommended for use as surgical implant materials are (i) cast Co-Cr-Mo alloy, (ii) wrought Co-Cr-W-Ni alloy, (iii) wrought Co-Ni-Cr-Mo alloy and (iv) wrought Co-Ni-Cr-Mo-W-Fe alloy. The chemical composition of these alloys is given in Table 9.

Amongst all the above discussed alloys, the Co-Ni-Cr-Mo is most corrosion resistant, whereas the abrasive wear properties are similar to Co-Cr-Mo alloy. However, it is not preferred for bearing surfaces of implants due to its poor frictional properties. The superior mechanical properties (particularly fatigue strength) make it useful for implants which require long service life.

# 3. Corrosion of metallic implants

The physiological environment is typically modelled as a 37 °C aqueous solution, at pH 7.2 (Healy, and Ducheyn, 1992), with dissolved gases (such as oxygen), electrolytes, cells and

Element	Co-Cr-Mo		Co-Cr-W-Ni		Co-Ni-Cr-Mo		Co-Ni-Cr-Mo-W-Fe	
Element	Min	Max	Min	Max	Min	Max	Min	Max
Cr	27.0	30.0	19.0	21.0	19.0	21.0	18.0	22.0
Mo	5.0	7.0			9.0	10.5	3.00	4.00
Ni		2.3	9.0	11.0	33.0	37.0	15.00	25.00
Fe		0.75		3.0		1.0	4.00	6.00
С		0.35	0.05	0.15		0.025		0.05
Si	74	1.00	\	1.00	( )	0.15	( <del></del>	0.50
Mn		1.00	=(	2.00	\ \ /	0.15		1.00
W			14.0	16.0			3.00	4.00
P						0.015		
S						0.010		0.010
Ti						1.0	0.50	3.50
Со	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance

Table 9. Chemical composition of different Co-Cr alloys (ASTM, F75-87, 1992; ASTM, F90-87, 1992; ASTM, F362-84, 1992).

proteins. Immersion of metals in this environment can lead to corrosion, which is deterioration and removal of metals by chemical reaction. During this electrochemical process of corrosion, metallic biomaterials release ions, which reduce the biocompatibility and jeopardize the life of an implant. Most metals such as iron (Fe), Chromium (Cr), Cobalt (Co), Nickel (Ni), Titanium (Ti), Tantalum (Ta), Niobium (Nb), Molybdenum (Mo) and Tungsten (W) that are used to make above discussed alloys to manufacture implants can only be tolerated by the body in minute amounts [51-53]. Sometimes, these metallic elements in naturally occurring forms, are essential in red blood functions (Fe) or synthesis of Vitamin B12 (Co), but cannot be tolerated in large amounts in the body. The biocompatibility of the metallic implants is therefore of considerable concern because these implants can corrode in an in vivo environment. The consequences of corrosion are the disintegration of implant material, which weakens the implant and the harmful effect of corrosion products on the surrounding tissues and organs.

Metallic implants used for load bearing purposes such as joint prostheses, screws and plates undergo different types of corrosion over time such as galvanic corrosion produced by two different types of metal, crevice corrosion and pitting (Gosain, and Persing, 1999;. Cohen, 1962; Traisnel et al. 1990). Further, fretting corrosion may also occur when the oxide film on the metal is damaged such as in case of a screw in a plate hole.

# 3.1 Corrosion of 316L stainless steel

316 L stainless steel, similar to Ti-6A1-4V and Co-Cr-Mo alloys, etc are known to be prone to corrosion and wear with sign of local macrophage reaction. Metallurgical and histological examination of implants made of biomaterials such as 316 L stainless steel, Co-Cr-Mo alloys and Ti-6AI-4V alloys, etc. show severe corrosion of the surface and even implant failure due to corrosion. In these cases, considerable amount of wear particles are released from metal-on-metal prostheses, which cause long term problems (Groot, 1980). Also, during examination of tissues adjacent to these failed implants, whole gamut of histopathological reactions from acute inflammation, through granulation of tissue to fibrosis, hyaline and a cellular collagens, and necrosis are observed (Jiang and Shi, 1998).

The characteristics tissue reaction to stainless steel implant is cylosiderosis. Stainless steel implants are also known to be associated with pain in its locality (when corroded).

In one of the detailed studies carried out on a retrieved bone plate and screw which was clinically used in-vivo to heal fracture in human patient, investigation was made to study the effect of actual body environment on the implants and to establish the reason for degradation or failure, if any (Srivastav et al., 1992).

For the study a retrieved commercially available standard 316L stainless steel bone plate and screw was selected which was implanted for a period of 2.5 months in a male human patient of about 30 years of age. These plate and screws were explanted as per routine after the healing of the fracture. The chemical composition of the implant material is given in Table 10.

<b>Elements Present</b>	Weight Present
Cr	17
Ni	12
Mo	03
Mn	02
Si	0.75
С	0.03
P	0.03
S	0.03
Fe	Balance

Table 10. Chemical composition of 316L stainless steel used in the study

# 3.2 Metallurgical investigation of corroded 316 L stainless steel implant

The 316L stainless steel plate and screw were examined by naked eye after cleaning in detergent solution. The areas warranting further examination i.e. those where corrosion was found by naked eye were prepared for observation under scanning electron microscope. Examination of retrieved implants (bone plate and screws) with naked eyes has shown

that the overall surface of the bone plate and the screws had neither any cracks nor fracture or any sign of corrosion, except clearly visible corrosion spots in and around the screw holes of the bone plate as shown in Figures 3 and 4 (Srivastav et al., 1992). It can thus be deduced that during the complete 3 months period of implantation, which can be termed as short in vivo period, 316 L stainless steel serves the purpose of bone support and helps in healing the fracture of the bone without any mechanical failure. Also, there is no significant effect of biological fluids on the material, except some localized effects around a few screw holes.

On closer investigation, it was however found that the screw hole at the top was most corroded and the bottom most hole was not at all corroded. This clearly means that the corrosion which is only localized in the screw hole, starts with the top most screw hole. In addition to this, the corrosion was found to be more pronounced inside and near the screw hole than away from the hole. The reason for this significant observation could be the fact that during this short period of implantation, the body fluids did not have as much effect on the corrosion of the plate as the physiological stresses. The load and the stresses were transmitted from the bone to the plate initially at the top. The stresses were more concentrated near the hole. This resulted in stress induced corrosion of the screw holes.

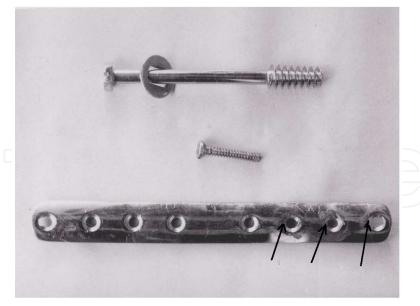


Fig. 3. Retrieved bone plate and screws showing corroded screw holes of the plate (arrow)

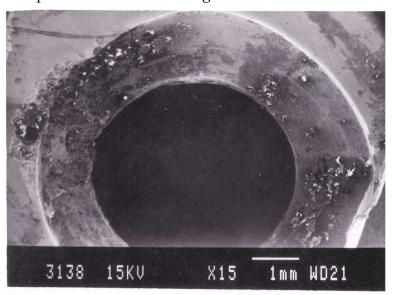


Fig. 4. Corrosion at the counter sunk of screw hole as seen at higher magnification

These corrosion spots are the potential source of metal ions and compounds which are known to have toxic effects on the tissues. The tissues adjacent to the failed or corroded implants have been reported to experience a whole gamut of histopathological reactions from acute inflammation, through granulation of the tissues to fibrosis, hyaline and a cellular collagens, and necrosis (Eggli, 1983).

Further, the improper positioning and mating of screw had resulted in crevice corrosion of the counter sunk of screw hole as has also been confirmed in other studies (Traisnel, 1990). A careful look at the corrosion area at higher magnification under SEM [Figure-5] revealed the presence of corrosion pitting and fretting, which is due to micro movements between the screw and the hole under load and which induces the crevice corrosion.

The reason for the corrosion in and around screw hole is clearly because the plate and screw surface acts as a bearing surface, where under the physiological loads, micromovements of the joint occurs, leading to formation of wear debris. The solubility of this small amount of

metal debris probably increases in presence of body fluids due to the large ratio of bearing surface area to the mass of the debris under higher stresses.



Fig. 5. Corrosion surface at higher magnification showing crevice and pitting corrosion at the countersunk (Srivastav et al., 1992)

Further, Figure-6 clearly indicates that the corrosion was spreading outwardly. This shows that eventually the whole area would have got corroded if implant was allowed to remain in the body for longer period, such as, in case of a permanent implant. This would have weakened the bone plate as found in other studies (Kwon, 2002) and if the use is continued for longer duration (six months to a year), then the bone plate would undoubtedly have fractured and failed under load as has been observed in other studies also. After the implant fails mechanically or functionally, it would require immediate removal as it has been found to induce severe pain and allergic reactions such as cytosiderosis, fibrosis in the adjacent tissues. Also, the release of Iron and its compounds, which are toxic and insoluble, may ultimately lead to cirrhosis of liver and damage to spleen (Jian and Shi, 1998).

It is most unlikely that 316 L stainless steel will behave like a safe metallic biomaterial and hence needs some kind of surface improvement or protection such as protective coatings to minimize the chances of corrosion. These materials also have their limitations and hence search for more biocompatible and reliable is needed.

# 3.3 An alternative to metallic biomaterials:

The integration of metallic implants to the host bone is promoted by coating them with biocompatible materials such as ceramics. These coatings are deposited by techniques such as PVD, ion plating, sputtering, etc. Using a variety of above mentioned techniques, a wide range of ceramic materials have successfully been deposited and it has been reported in many studies that these coatings significantly improve the wear characteristics of the materials on which they are deposited (Jamison, 1980; Hinterman, 1981; Asanabe, 1987). Similar bioceramic coatings can be effectively used for implants or prosthetic devices. These biocompatible coatings not only provide the implant the necessary tribological properties and the desired corrosion resistance, but also provide them with much desired superior biocompatibility.

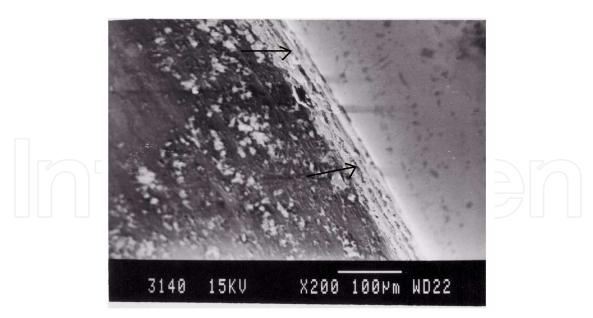


Fig. 6. Spreading of corrosion area from the screw hole to outer surface

Investigations carried out on Al<sub>2</sub>O<sub>3</sub> coatings have revealed that the coated implants obtain the necessary damping capability. The damping capability of Al<sub>2</sub>O<sub>3</sub> coating, which is an order of magnitude higher than that of the metallic materials used in joint prostheses, absorbs a significant energy before failure (Calderale and Vullo, 1977). The improvement of wear resistance by ion implantation on metallic joint prosthesis has also been studied in detail. Ion implantation is reported to bring improvement in other properties too such as fatigue, corrosion and fretting resistance of these metals and alloys (Rieu 1990). Similarly, the corrosion resistance of these alloys has been strongly enhanced by hard ceramic coatings when deposited by radio-frequency sputtering (Sella, 1990). In recent past, coating of plasma-sprayed apatite has been applied which leads to the formation of a strong bond between bone and metal implant (Geesink et al., 1998; Hamn et al., 199). This is particularly desired in cases such as hip arthroplasty, where implants have a tendency to detach with time. The presence of amorphous phase of HAp in these coatings is an inherent problem in manufacturing high quality implants (Zyman, 1993).

However, the life of a coated implant depends upon the life of these coatings. It is therefore desirable that the implant be coated with materials which are adherent to the implant surface as much as possible, so that it has a very slow and delayed delamination and flaking off. As a result of delamination and flaking off of these, ceramic coatings, hard ceramic particles come in between the rubbing surfaces and cause sudden and extensive damage to the interface. Once negligible or slow wear, thus becomes catastrophic. Hence, these ceramic coated surfaces are useful until the coating is intact (Komvopolouslos et al., 1987). The formation and accumulation of wear debris not only affects the life of the implant but also causes severe tissue reactions and pain, thus necessitating immediate removal. Even in case of implants which are used for non bearing surfaces, the degradation and or delamination of these coatings have been reported (Whitehead et al., 1993; Yie et al., 1995). To minimize this problem of delamination, solution such as use of composite coatings has been suggested (Srivastav and Prakash, 1992) which also has not been studied in detail and no permanent solution has been obtained except for using bulk bioceramics in place of metallic implants.

#### 4. References

- American Society for Testing and Materials (ASTM), (1992). F67-89, p.39.
- American Society for Testing and Materials (ASTM), (1992). F75-87, p.42.
- American Society for Testing and Materials (ASTM) (1992), F90-87, p.47.
- American Society for Testing and Materials (ASTM), (1992). F136-84, p.55.
- American Society for Testing and Materials (ASTM), (1992). F139-86, p. 61.
- American Society for Testing and Materials (ASTM), (1992), F562-84, p.150.
- Asanabe, S. (1987). Application of ceramics for tribological components, *Tribology International*, Vol.20, pp. 355-364.
- Barralet , J.E., Gaunt , T., Wright, A. J., Gibson I. R. and Knowles, J. C. (2002). Effect of porosity reduction by compaction on compressive strength and microstructure of calcium phosphate cement, *J Biomed Mater Res.*, Vol. 63 (1), pp. 1-9.
- Brunski, J. B. (1996). Metals In- *Biomaterials Science: An introduction to materials in medicine*, (eds.) Ratner, B.D., Hoffman, A.S., Shoen, F.J. and Lemons, J. E., pp. 37-50, Academic Press, San Diego.
- Calderale P. M. and Vullo, V. (1977). Damping capacity of alumina coatings for implants, Proc. 1st European Conf. on Biomaterials, Strasbourg, pp. 233-237.
- Carter D. R. and Heyes, W. C. (1977). The compressive behaviour of bone as a two phase porous structure, *J. Bone Joint Serg*, Vol. 59 A (7), pp. 954-962.
- Carter, D. R. and Springler, D. M. (1978). Mechanical properties and composition of cortical bone, *Clinical Orthopaedics*, Vol. 135, pp. 192-217.
- Chiroff, R. T, White, E. W., Weber, K. N. and Roy, (D. M., (1975). Tissue ingrowth of replamineform implant, *J Biomed Mater Res*, Vol. 9(4), pp. 29-45.
- Cohen, J. (1962). Corrosion testing of orthopaedic implants, J. Bone Jt. Surg., Vol. 44A, pp. 307-316.
- Damien C. J. and Parsons, J. R. (1990). Bone Graft and Bone Graft Substitutes: A Review of Current Technology and Applications, J. Appl. Biomaterials, Vol. 2, pp. 187-208.
- Dee, K. C., Puleo D. A. and Buzios, R. (2002). *An introduction to tissue-biomaterial interactions*, pp. 3, John Willey & Sons Inc., NJ.
- Dorozhkin, S. V. and Epple, M. (2002). Biological and Medical Significance of Calcium Phosphates, *Angew. Chem. Int.*, Vol. 41, pp. 3130 -3146
- Eggli, P. S., Muller W. and Schenk, R. K., (1983). Porous hydroxyapatite and tricalcium phosphate cylinders with two different pore size ranges implanted in the cancellous bone of rabbits, *Clin. Orthop.*, Vol. 232, pp. 127-138.
- Galante, J., Rostoker W. and Ray, R. D. (1970). Physical properties of trabecular bone, *Calcified Tisuue Research*, Vol. 5(3), pp. 236-246.
- Geesink, R. G., Groot, de K. and Klein, C. P. (1998). Bonding of bone to apetite-coated implants, J. Bone Joint Surg., Vol. 70B (1), pp. 17-22.
- Goldstein, S. A. (1987). The mechanical properties trabecular bone: dependence on anatomic location and function, *J. Biomech.*, Vol. 20(11-12), pp. 1055-1061.
- Gosain, A. K. and Persing, J. A. (1999). Biomaterials in the face: Benefits and risks, *J. Craniofac. Surg*, Vol.10(5), pp. 404-414.
- Groot, K. de (1980). Bioceramics Consisting of Calcium Phosphate Salts, "Biomaterials, Vol. 1, pp 47-50.
- Haman, J.D., Chittur, K.K., Crawmer D.E. and Lucas, L.C. (1999). Analytical and mechanical testing of high velocity oxy-fuel thermal sprayed and plasma sprayed calcium phosphate coatings, *J Biomed Mater Res.*, Vol. 48(6), pp. 856-60.

- Healy, K. E. and Ducheyn, P. (1992). The mechanisms of passive dissolution of titanium in a model physiological environment, *J. Biomat. Res.*, Vol. 26(3), pp. 319-338.
- Hench, L.L and Best, S.(2004). In-Ratner B.D., et.al., *Biomaterials Science-An Introduction to Materials in Medicine*, p-154, Elsevier Academic Press, U.K.
- Hinterman, H.E. (1981). Tribological and protective coatings by chemical vapour deposition, *Thin Solid Films*, Vol. 84, pp.215-243. http://training.seer.cancer.gov/anatomy/skeletal/tissue.html, (2004).
- Holmes, R. E. (1979). Bone regeneration within a coralline hydroxyapatite implant, *Plast Reconstr Surg*, Vol. 63(5), pp. 626-33.
- Jamison, W.E. (1980). Friction and wear reduction with tribological coatings, *Thin Solid Films*, Vol. 73, pp. 227-233.
- Jarcho, M. (1981). Calcium Phosphate Ceramics as Hard Tissue Prosthetics, *Clin. Orthop. Rel. Res.*, Vol.157, 259.
- Jiang, G. and Shi, D. (1998). Coating of hydroxyapatite on highly porous Al<sub>2</sub>O<sub>3</sub> substrate for bone substitutes, *J. Biomed. Mater. Res. (Appl. Biomater.)*, Vol. 43, pp. 77-81.
- Kasemo B. (1983). Biocompatibility of titanium implants: surface science aspects, *J. Proseth. Dent.*, Vol. 6, pp. 832-837, 1983.
- Klein, C., Groot, K de, Weiqun, C., Yubao L. and Xingdong, Z. (1994). Osseous substance formation induces in porous calcium phosphate ceramics in soft tissues, *Biomaterials*, Vol. 15(1), pp. 31-34.
- Kitsugi, T., Yamamuro, T., Kokubo T.and Ono, M. (1981). Mechanical properties of sintered hydroxyapetite for prosthetic applications", *J. Mater. Sci.*, Vol 16, pp. 809-812.
- Komvopolouslos, K., Saka, N. and Suh N.P., (1987). The role of hard layers in lubricated and dry sliding, *J. Tribol*, Vol.109, pp. 223-231.
- Krause, R. F. Jr., Fuller, E.R. Jr. and Rhodes, J. F. (1990). Fracture resistance behaviour of silicon carbide whisker-reinforced alumina composites with different porosities, *J. Am. Cer. Soc.*, Vol. 73 (3), pp. 559-566.
- Kwon, S. H., Jun, Y. K., Hong, S. H., Lee, I. S., Kim H. E. and Won, Y. Y. (2002). Calcium phosphate bioceramics with various porosities and dissolution rates, *J. Am. Cer. Soc.*, Vol. 85(12).
- Lausmaa, G.J. and Kasemo, B. (1990). Surface spectroscopic characterisation of titanium implant materials, *Appl. Surf. Sci*, Vol. 44, pp. 133-146.
- Lavernia C. and Schoenung, J. M. (1999). Calcium Phosphate Ceramics as Bone Substitutes, *Ceramic Bulletin*, Vol. 70 (1), pp. 95-100.
- Lees S. and Devidson, C. L. (1977). The role of collagen in elastic properties of calcified tissues, *J. Biomech.*, Vol. 10(8), pp. 473-486.
- LeGeros, R. Z. (1988). Calcium Phosphate Materials in Restorative Dentistry: A Review, *Adv. Dent. Res.*, Vol. 2 (1), pp. 164-180.
- Martin, T.J. (1998). Cell biology in bone. In- *Baillieres Clinical Endocrinology and Metabolism*, Ed.- Martin, T.J., Ng K. W. and Nicholson, G. C. PLC Press, NY, pp. 1-29.
- McEiheney, J. H., Fogle, J. L., Melvin, J. W., Haynes, R. R., Roberts V. L. and Alem, N. M. (1970). Mechanical properties of cranial bone, *J. Biomech.*, Vol. 3(5), pp. 495-511.
- Memmone, J. F. and Hudson, S. M. (1993). Micromechanics of bone strength and fracture, *J. Biomech*, Vol. 26(4-5), pp. 439-446
- Mofid, M. M., Thompson, R. C., Pardo, C. A., Manson, P. N. and Vander Kolk, C. A. (1997). Biocompatibility of the fixation material in the brain, *Plast Reconstr Surg*, Vol.100(1), pp. 14-20.
- Moor R. and Grobe, G. (1990), Auger analysis of biomaterials, PHI Interface, Vol. 13, pp. 6-9.

- Nalla R. K., Kinney J. H. and Ritchie, R. O. (2003). Mechanistic fracture criteria for the failure of human cortical bone, *Nature (Materials)*, Vol. 2, March, pp. 164-168.
- Osborn J. F. and Newesely, H. (1980). The material science of calcium phosphate ceramics, *Biomaterials*, Vol. 1 (2), April, pp. 108-111.
- Park, J. B. and Bronzino, J. D. (2000). *Biomaterials: Principles and applications*, p. 2, CRC Press LLC, USA.
- Reilly, D. T., Burstein, A. H. and Frankel, V. H. (1974). The elastic modulus of bone", J. Biomech., Vol. 7(3), pp. 271-275.
- Reilly D. T. and Burstein, A. H. (1975). The elastic and ultimate properties of bone tissue", J. Biomech., Vol.8(6), pp. 393-405.
- Rieu, J., Pichat, A., Rabbe, L.M., Chabrol C. and Robelet, M. (1990). Deterioration mechanism of joint prosthesis materials: several solutions by ion implantation surface treatments, *Biomaterials*, Vol. 11, pp.51-54.
- Sandberg, M.M. (1991). Matrix in cartilage and bone development: Current views on the function and regulation of major organic components. *Annual Medicine*, Vol. 23 (3), pp. 207-211.
- Scoenfeld, C. M., Lautenschlager E. P. and Mayer P. R. Jr. (1974). Mechanical properties of human cancellous bone in the femoral head, *Med. Bio. Eng.*, Vol. 12(3), pp. 313-317.
- Sella, C., Martin, S.C., Lecoeur, J., Bellier, S.P., Harmand, M.F., Naji, A.,. Davidas, J.P. and Chanu, Le A. (1990). Corrosion protection of metal implants by radio-frequency sputtering, *Clinical Materials*, Vol. 5, pp. 297-307.
- Srivastav A. and Prakash, R. (1992). Ceramic coated conventional implant materials as biomaterials, *TIB & AO*, Vol. 7(10), pp. 12-17.
- Srivastav, A., Prakash, R., Kapoor, A. and Kumar, S. (1992). Metallurgical observations on orthopedical surgical implants which were implanted in-vivo, *TIB* & AO, Vol. 7(1), pp. 18-20.
- Sutherland, D.S., Forshaw, P.D., Allen, G.C., Brown I.T. and Williams, K.R. (1993), Surface analysis of titanium implants, *Biomaterials*, Vol. 14(12), pp. 893-905.
- Tengvall, P. and Lundstrom, I., (1989). Physico-chemical considerations of titanium as biomaterial, *Clin. Mater.*, Vol. 9, pp. 115-134.
- Traisnel, M., Maguer, le D. and Hilderbrand, H. F. (1990), Corrosion of surgical implants, *Clinical Mater.*, Vol. 5, pp. 309-318.
- White, E. and Shors, E. C. (1986). Biomaterial aspects of Interpore-200 porous hydroxyapatite, *Dent. Clin. North Am.*, Vol. 30(1). pp. 49-67.
- Whitehead, R. Y., Lacefield W. R. and Lucas, L. C. (1993). Structure and integrity of a plasma sprayed hydroxyapetite coating on titanium, *J. Biomed. Mater. Res.*, Vol. 27, pp. 1501-1507.
- Wright T. M. and Hayes, W. C. (1977). Fracture mechanics parameters for compact bone effect of density and specimen thickness, *J. Biomech.*, Vol. 10(7), pp. 419-430.
- Yie, H., Hero, H., Solheim, T., Rorvik A. M. and Haanaes, H. R. (1995). Bonding capacity in bone of HIP-processed HA-coated titanium: Mechanical and histological investigations, *J. Biomed. Mater. Res.*, Vol. 29, pp. 1443-1449.
- Zyman, Z., Weng, J., Liu, X., Zhang X. and Ma, Z. (1993). Amorphous phase and morphological structure of hydroxyapetite plasma coatings, *Biomaterials*, Vol. 14(3), pp. 225-228.



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