METAL CORROSION IN THE HUMAN BODY

LECTURE NOTE 9

DR.AMIR NAJAH SAUD AL-HUMAIRI
AL-MUSTAQBAL UNIVERSITY/ DEPARTMENT OF BIOMEDICAL ENGINEERING
CLASS: SECOND
SUBJECT : BIOMATERIALS SCIENCE
EMAIL: AMIR_NAJAH@MUSTAQBAL-COLLEGE.EDU.IQ

CORROSION

- Corrosion is the deterioration of a metal due to chemical reactions between it and the surrounding environment.

The types of corrosion in metallic implants are,

Pitting: Pitting corrosion occurs when localized areas of the metal surface are attacked, forming small pits or holes. This type of corrosion is often initiated by the breakdown of the protective oxide layer (e.g., on titanium or cobalt-chromium alloys) due to chloride ions in body fluids.

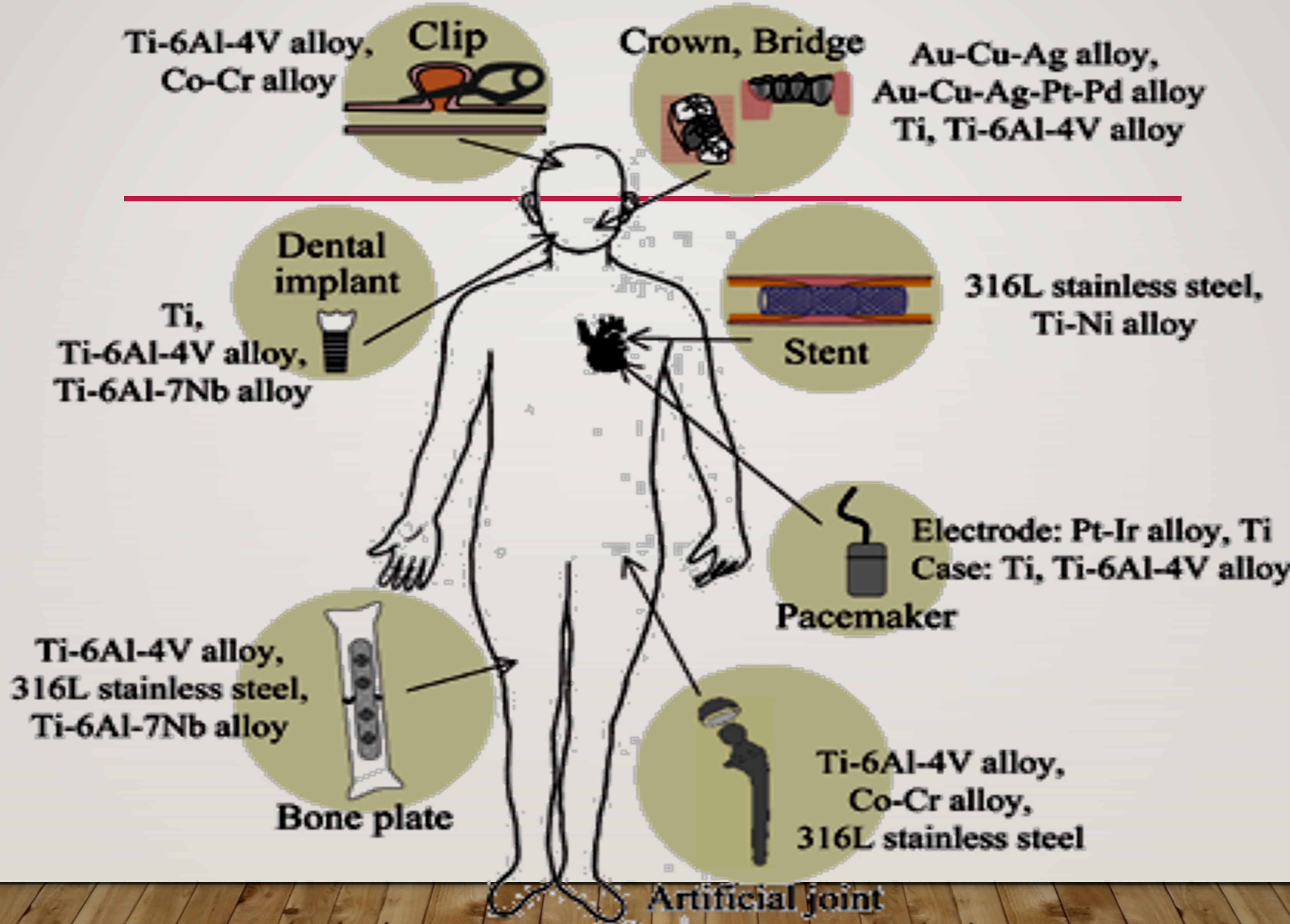
Crevice: Occurs in confined spaces or crevices, such as the gaps between screws, plates, or implant interfaces, where oxygen diffusion is restricted. This creates a difference in oxygen concentration, leading to localized corrosion.

Corrosion Fatigue: Corrosion fatigue results from combined cyclic mechanical loading and a corrosive environment. Repeated stress weakens the protective oxide layer, accelerating corrosion.

Stress-corrosion Cracking (SCC) : SCC occurs when tensile stresses (from mechanical loading or residual stresses) combine with a corrosive environment, forming and propagating cracks.

Fretting: Fretting corrosion occurs at the contact surfaces of two components (e.g., in modular implants or screws) due to micromotions that damage the protective oxide layer. This leads to wear and corrosion at the interface.

Galvanic Corrosion: Galvanic corrosion occurs when two dissimilar metals come into electrical contact in a corrosive environment (e.g., stainless steel and cobalt-chromium alloys in the same implant). The less noble metal becomes the anode and corrodes preferentially.


Ti-6Al-4V alloy,
Co-Cr alloy
Clip
Crown, Bridge
Au-Cu-Ag alloy,
Au-Cu-Ag-Pt-Pd alloy
Ti, Ti-6Al-4V alloy
Dental implant
Ti,
Ti-6Al-4V alloy,
Ti-6Al-7Nb alloy
316L stainless steel,
Ti-Ni alloy
Stent
Electrode: Pt-Ir alloy, Ti
Case: Ti, Ti-6Al-4V alloy
Pacemaker
Ti-6Al-4V alloy,
316L stainless steel,
Ti-6Al-7Nb alloy
Bone plate
Ti-6Al-4V alloy,
Co-Cr alloy,
316L stainless steel
Artificial joint

EFFECT OF CORROSION-FAILURE OF IMPLANTS

The reaction of the metallic ions that leaches away from the implant due to corrosion in the human body affects several biological parameters. As a material starts to corrode, the dissolution of metal will lead to erosion which in turn will eventually lead to brittleness and fracture of the implant.

Once the material fractures, corrosion gets accelerated due to increase in the amount of exposed surface area and loss of protective oxide layer. If the metal fragments are not surgically extracted, further dissolution and fragmentation can occur, which may result in inflammation of the surrounding tissues.

. The contents of the Table 1 amply illustrate the possible hazardous effects associated with the corroded implant material. The release of corrosion products will obviously lead to adverse biological reactions in the host, and several authors have reported increased concentrations of corroded particles in the tissue near the implants and other parts of the human body such as kidney, liver etc.

Effects of Corrosion in Human Body Due to Various Biomaterials

Biomaterial Metals	Effect of Corrosion
Nickel	Affects skin - such as dermatitis
Cobalt	Anemia B inhibiting iron from being absorbed into the blood stream
Chromium	Ulcers and Central nervous system disturbances
Aluminum	Epileptic effects and Alzheimer's disease
Vanadium	Toxic in the elementary state

SURFACE OXIDE FILM

The oxide film which inhibits the dissolution of metal ions is not always stable in the human body and hence a thorough understanding of the behavior of the oxide film in in vivo condition is essential to have a better insight of the corrosion phenomenon.

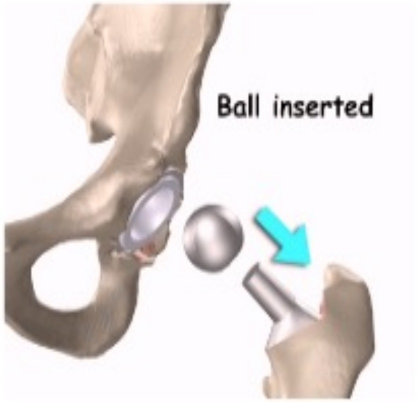
The analysis of the surface oxide film on various metallic biomaterials is given in Table

Table 5. Analysis of the Surface Oxide Film on Various Metallic Biomaterials

Metallic Biomaterial	Surface Oxides	Surface Analysis
Titanium(Ti)	Ti^{0+}, Ti^{2+}, Ti^{3+}, Ti^{4+}	• Ti^{2+} oxide thermodynamically less favorable than Ti^{3+} formation at the surface. • Ti^{2+} and Ti^{3+} oxidation process proceeds to the uppermost part of the surface film and Ti^{4+}observed on the surface outer most layer.
Titanium alloys		
Ti-6Al-4V	TiO_2	Surface consists of small amount of Al_2O_3, hydroxyl groups, and bound water and the alloying element Vanadium was not detected
Ni-Ti	TiO_2-based oxide	Minimal amounts of nickel in both oxide and metal states
Ti-56Ni	TiO_2	Very low concentrations of metallic nickel, NiO, hydroxyl groups and bound water on the surface were detected.
Ti-Zr	Titanium and Zirconium oxides	Titanium and zirconium are uniformly distributed along the depth direction. The thickness of the oxide film increases with increase in zirconium content.
Stainless steel		
Austenitic stainless steel	Iron and chromium	Only very less amount o f molybdenum was observed on the surface and nickel was absent when tested in both the air and in chloride solutions.
316L	Oxides of Iron, chromium, nickel, molybdenum and manganese(thickness about 3.6 nm)	The surface film contains a large amount of OH^-, that is, the oxide is hydrated or oxyhydroxide. Iron is enriched in the surface oxide film and nickel, molybdenum, and manganese are enriched in the alloy substrate just under the surface oxide film.
Co-Cr-Mo alloy		
Co-36.7Cr-4.6Mo	Oxides of cobalt and chromium without molybdenum(thickness 2.5 nm)	Surface contains large amount of OH^-, that is the oxide is hydrated or oxyhydroxidized. Chromium and molybdenum distributed more at the inner layer of the film.

Table 7. Types of Corrosion in the Conventional Materials Used for Biomaterial Implants

Type of Corrosion	Material	Implant Location	Shape of the Implant
Pitting	304 SS, Cobalt based alloy	Orthopedic/ Dental alloy	
Crevice	316 L stainless steel	Bone plates and screws	
Stress Corrosion cracking	C0CrMo, 316 LSS	Only in *in vitro*	
Corrosion fatigue	316 SS, CoCrNiFe	Bone cement	

Fretting	Ti6Al4V, CoCrSS	Ball Joints	
Galvanic	304SS/316SS, CoCr+Ti6Al4V, 316SS/Ti6Al4V Or CoCrMo	Oral Implants Skrews and nuts	
Selective Leaching	Mercury from gold	Oral implants	

CORROSION OF METAL ALLOYS

stainless steel is susceptible to localized corrosion by chloride ions and reduced sulfur compounds . The presence of micro organisms on a metal surface often leads to highly localized damages in the concentration of the electrolytic constituents, pH and oxygen levels .

Studies on corrosion and electrochemical behavior of 316L SS in the presence of aerobic iron-oxidizing bacteria (IOB) and anaerobic sulfate-reducing bacteria (SRB) reveal that the interactions between the stainless steel surface with the corroded products, bacterial cells and their metabolic products increases the corrosion damage and also accelerates

These localized corrosion attacks and leaching of metallic ions from implants necessitate improvement in the corrosion resistance of the currently used type 316L SS by bulk alloying or modifying the surfacepitting propagation

CORROSION OF METAL ALLOYS

Cobalt-based alloys have been widely employed in orthopaedic implants and biocorrosion of this alloy is one of the major problems to be dealt with as there is larger release of metal ions which causes adverse effects. Co-Cr-Mo alloy is used as a femoral head of joint prostheses in conjunction with an ultra high molecular weight polyethylene (UHMWPE) cup because of the high wear and corrosion resistance of this alloy. The problem with the metal-on-metal couple is that the release of metal ions is higher than that of the polymer-on-metal couple in in vivowhich will, over many years lead to toxicity problem.

Corrosion of metal alloys

it has been well established that titanium is completely inert and immune to corrosion by all body fluids and tissue and is thus completely biocompatible . High modulus of elasticity of the conventional alloys has resulted in the stress shielding effect and the failure of the implant. The modulus of elasticity of titanium based alloys is much lower and closer to that of the bone when compared to SS and Co-Cr alloys and hence they are more preferred for long term applications. As of now, they are used as implants for joint replacements, bone fixation, dental implants, heart pacemakers, artificial heart valves, stents and components in high-speed blood centrifuges because of their high specific strength and chemical stability . However, these implants such as artificial joints and bone plates are likely to be damaged mostly due to fatigue . The reason for this is due to the decrease in fatigue strength, which in turn should arise from the synergistic effect of the formation of corrosion pits on the surface, which arise from the dissolution of Ti2+ions in the living body, wearing at sliding parts and fretting

PROTECTION OF METAL IMPLANT

heat treatment is involved during the manufacturing process, the passivation oxide present on Nitinol is polycrystalline in nature, and has been found to exhibit severe pitting and crevice corrosion, whereas surface treatment to form amorphous oxide results in excellent corrosion resistance. Other surface treatments, such as electrochemical polishing, has also been found to be a good surface treatment prior to implantation, resulting in significantly increased corrosion resistance

PROTECTION OF METAL IMPLANT

Ti dental implants are generally surface modified to reduce corrosion, improve Osseo integration and increase the biocompatibility.

To achieve this, surface treatments, such as surface machining, sandblasting, acid etching, electro-polishing, anodic oxidation, plasma-spraying and biocompatible/biodegradable coatings are performed to improve the quality and quantity of the bone-implant interface of titanium-based implants .

Unlike the above treatments, laser-etching technique was introduced in material engineering originally which resulted in unique microstructures with greatly enhanced hardness, corrosion resistance, or other useful surface properties . Laser processing also is now being used in implant applications to produce a high degree of purity with enough roughness for good Osseo integration .

.

PROTECTION OF METAL IMPLANT

In addition to the above, nanoceramic HAP coatings are used to enhance the osseointegration.

Nanostructured graded metalloceramic coatings have also been tried to achieve better adhesion between the metal and ceramic coatings and thus nanoceramic coatings are gradually receiving greater attention