



Biomedical Implants Corrosion

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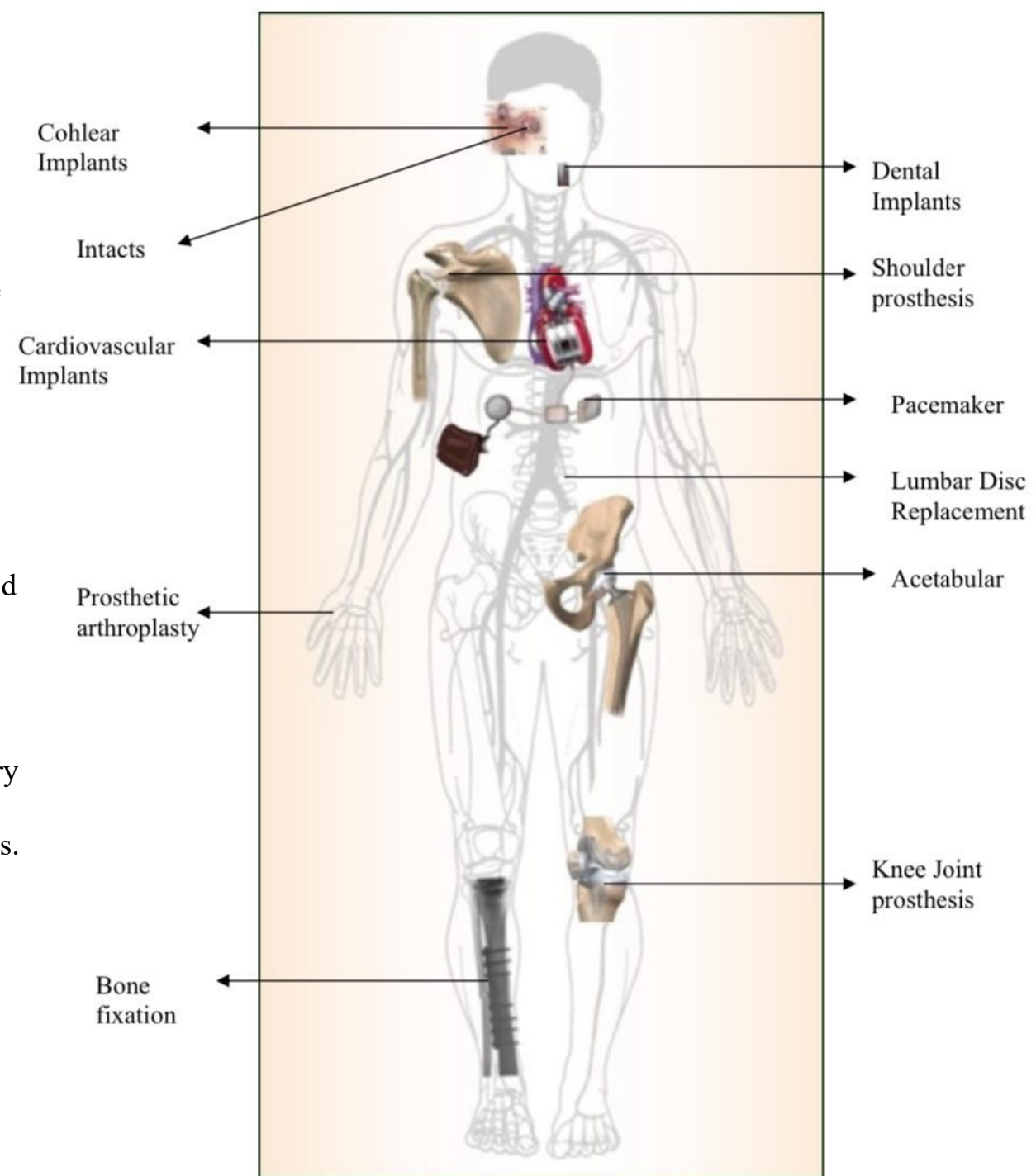
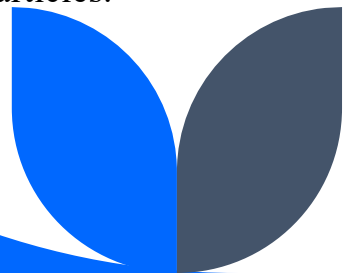


Introduction

Biomaterials play a crucial role in human life, particularly for the elderly population who require biomedical implants to increase their lifespan. The field of biomaterials has been used since ancient times, with materials like linen, gold, iron, and wood used for various purposes. Today, bioimplants are commonly used in various fields, including dentistry, orthopedics, plastic and reconstructive surgery, ophthalmology, cardiovascular surgery, neurosurgery, immunology, histopathology, experimental surgery, and veterinary medicine.

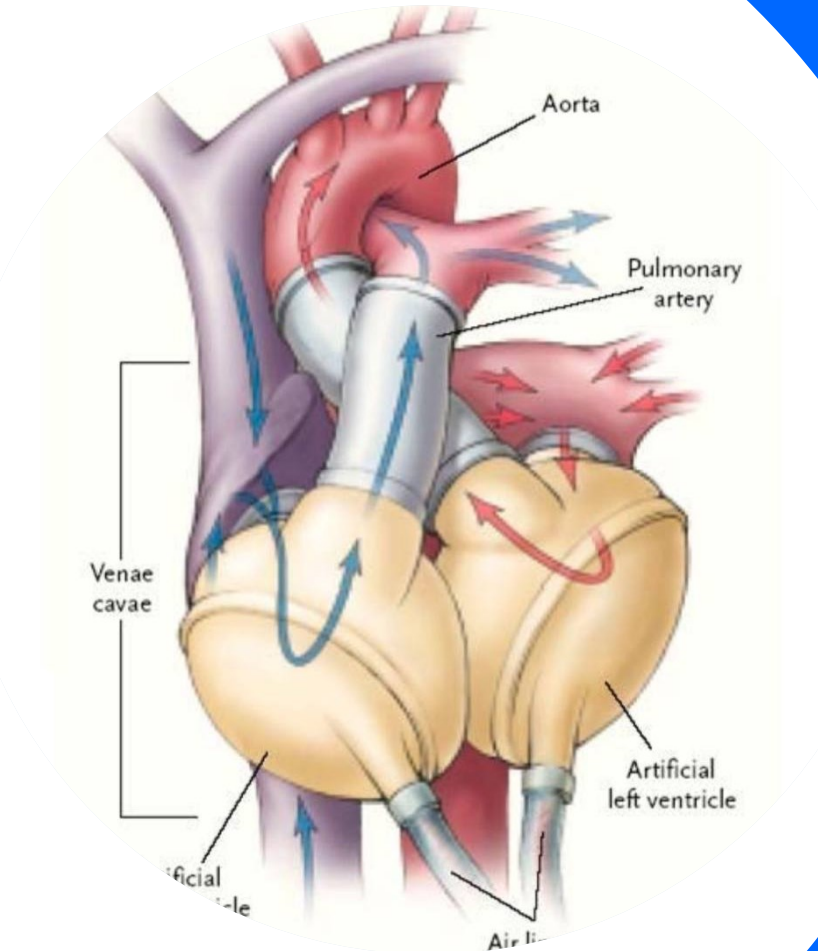
Biomaterials must be accepted by the human body, not causing adverse effects, possess sufficient mechanical strength, and have high corrosion and wear resistance in highly corrosive environments. The success of a biomaterial or implant depends on three major factors: the biomaterial's properties, the implant's biocompatibility, and the recipient's health condition and the surgeon's competence.

Currently used materials fail within 12-15 years, leading to revision surgery to regain functionality. The reasons for failure include mechanical, chemical, tribological, surgical, manufacturing, and biocompatibility issues. Corrosion is a challenging clinical problem, and research has been conducted on this topic in various forms, including books and comprehensive review articles.



WHY METALS CORRODE IN HUMAN BODY?

Corrosion is a significant concern in the human body, particularly when metallic implants are placed in the hostile electrolytic environment. The human body's aqueous medium contains various anions, cations, organic substances, and dissolved oxygen. Biological molecules can disrupt the equilibrium of corrosion reactions by consuming products due to anodic or cathodic reactions. Proteins can bind to metal ions and transport them away from the implant surface, causing preferential corrosion at certain regions. Hydrogen, formed by cathodic reactions, acts as a corrosion inhibitor, but bacteria can change this behavior and enhance corrosion by absorbing hydrogen near the implant. pH values also influence corrosion, with the tolerable rate for metallic implant systems being about 2.5×10^{-4} mm/yr or 0.01 mils/yr. Common forms of corrosion include uniform, intergranular, galvanic, stress corrosion, cracking, pitting, and fatigue corrosion. New materials are continuously being developed to replace implant materials, but clinical studies show they are also prone to corrosion to a certain extent. Materials should be tested for corrosion resistance under different conditions, such as reciprocatory wear, fretting, and stress corrosion.



SURFACE OXIDE FILM ON METALLIC MATERIALS IN BIOLOGICAL ENVIRONMENT

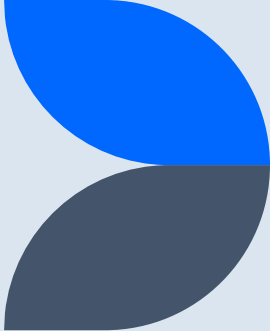
Surface oxide films on metallic materials play a crucial role in inhibiting the release of metallic ions and their behavior changes with the release of ions. The composition of these films changes according to reactions between metal surfaces and living tissues, and even low concentrations of dissolved oxygen, inorganic ions, proteins, and cells can accelerate metal ion release. The regeneration time of the surface oxide film after disruption also determines the amount of ions released. Tissue compatibility is determined by the initial stages of reactions after implantation, and the success of an implant depends on the reactions.

Biomedical implants should undergo both in vitro and in vivo studies for their applications. In vitro corrosion studies on orthopaedic biomaterials are conducted in Hank's solution or Ringer's solution, while corrosion resistance for dental materials is evaluated using synthetic saliva. The presence of organic compounds such as glycoprotein in saliva plays an important role in maintaining viscosity and affecting the diffusion of various ions.

The effect of the oxide film on corrosion of biomaterials remains to be understood, and understanding its behavior in in vivo conditions is essential for better insight into the corrosion phenomenon. The composition of the surface oxide layer and its interaction with the environment is highly dependent on the constituents of the material used. In general, a coating on implants is preferable as it reduces the corrosion rate.

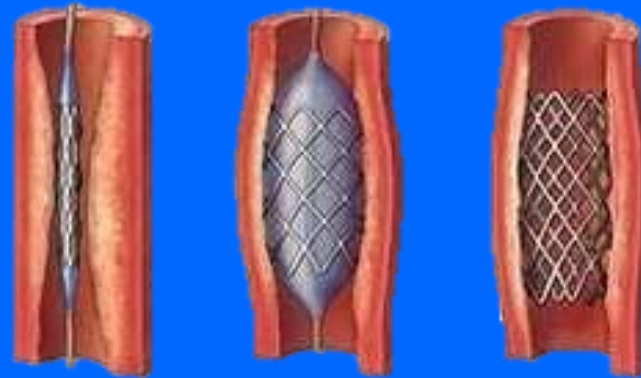
Table 2: Analysis of the Surface Oxide Film on Various Metallic Biomaterials

Metallic Biomaterial	Surface Oxides	Surface Analysis
Titanium(Ti)	Ti^{0+} , Ti^{2+} , Ti^{3+} , Ti^{4+}	<ul style="list-style-type: none"> • 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 Ni-Ti Ti-56Ni Ti-Zr	TiO ₂ TiO ₂ -based oxide TiO ₂ Titanium and Zirconium oxides	Surface consists of small amount of Al ₂ O ₃ , hydroxyl groups, and bound water and the alloying element Vanadium was not detected Minimal amounts of nickel in both oxide and metal states Very low concentrations of metallic nickel, NiO, hydroxyl groups and bound water on the surface were detected. 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 316L	Iron and chromium Oxides of Iron, chromium, nickel, molybdenum and manganese(thickness about 3.6 nm)	Only very less amount of molybdenum was observed on the surface and nickel was absent when tested in both the air and in chloride solutions. 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.


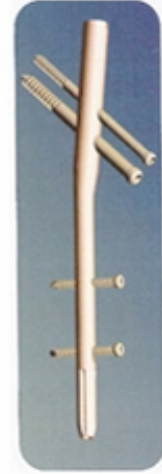



EFFECT OF CORROSION-FAILURE OF IMPLANTS

Corrosion in implants can cause brittleness, fracture, and inflammation of surrounding tissues. The release of corrosion products can lead to adverse biological reactions in the host, such as increased concentrations of corroded particles in the tissue near the implants and other parts of the body. Cobalt-chromium alloy, a commonly used biomaterial, can release toxins into the body, leading to cancerous tumors. There is a need to develop new and safer materials with extremely high corrosion resistance. Aksakal et al. investigated failed implants made of titanium alloy Ti-6Al-4V and 316L SS, revealing that failure occurred through corrosion fatigue, localized corrosion, and intergranular cracking. Stress corrosion cracking in biomedical implants can lead to the loss of structural integrity and function, leading to implant disintegration. Reducing the dissolution of metal ions can be achieved by using biocompatible inorganic coatings like hydroxy-apatite (HAP) coating with binders, reducing corrosion and wear and minimizing loosening of implants from bone.



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 <i>in vitro</i>	
Corrosion fatigue	316 SS, CoCrNiFe	Bone cement	

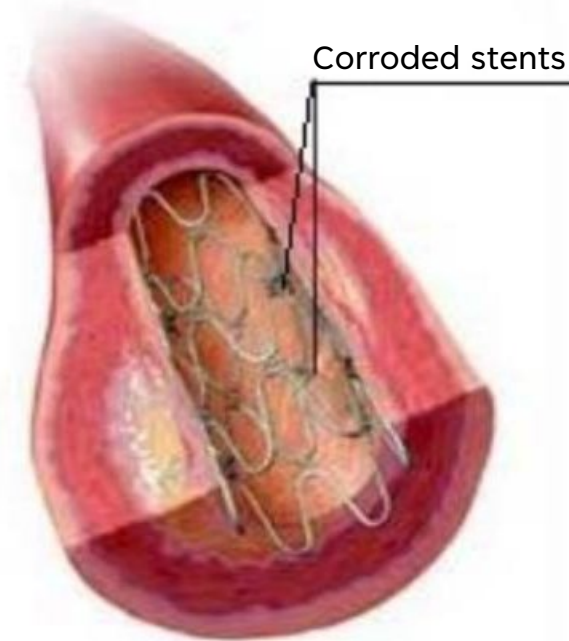
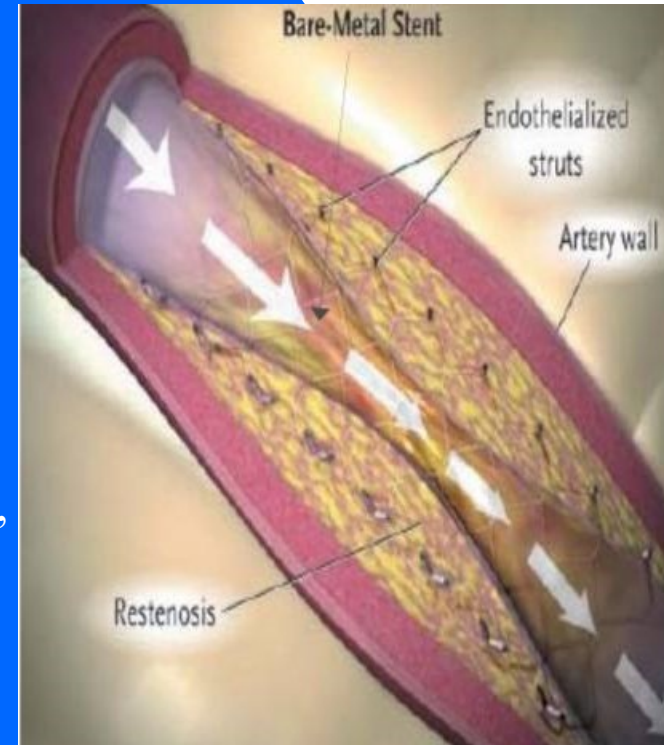
Types of Corrosion in the Conventional Materials Used for Biomaterial Implants

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

CORROSION OF VARIOUS IMPLANTS

• Cardiovascular Implants

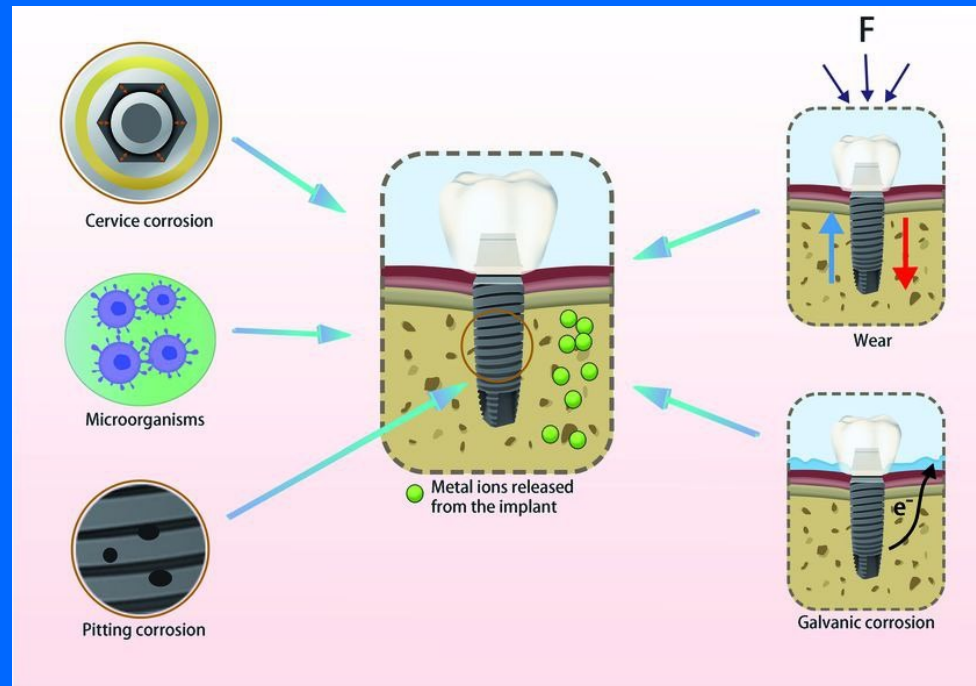
Heart diseases, particularly ischaemic heart disease, cause yearly deaths in the UK and USA, leading to premature death in middle-aged men and women. Artificial heart implants are considered a solution, consisting of polyurethane rigid outer housings that mimic the natural cardiac ventricle and auricle. However, bioprosthetic implants can cause calcification and stiffening, leading to clinical apprehension. Non-bioprosthetic implants are fabricated from materials like pyrolytic carbon-coated graphite, titanium, stainless steel, cobalt-chrome alloys, cobalt-nickel alloys, alumina coated with polypropylene, and Poly-4-fluoroethylene. These materials are prone to corrosion, with 316L SS being the most commonly used metal for stents. Co-Cr alloys, which conform to ASTM standards F562 and F90, are being used for stents due to their high elastic modulus. Biocorrosion of magnesium-based alloys is a new area of study for improving cardiovascular implants with local drug delivery functions.



CORROSION OF VARIOUS IMPLANTS

- **Corrosion of Dental Implants**

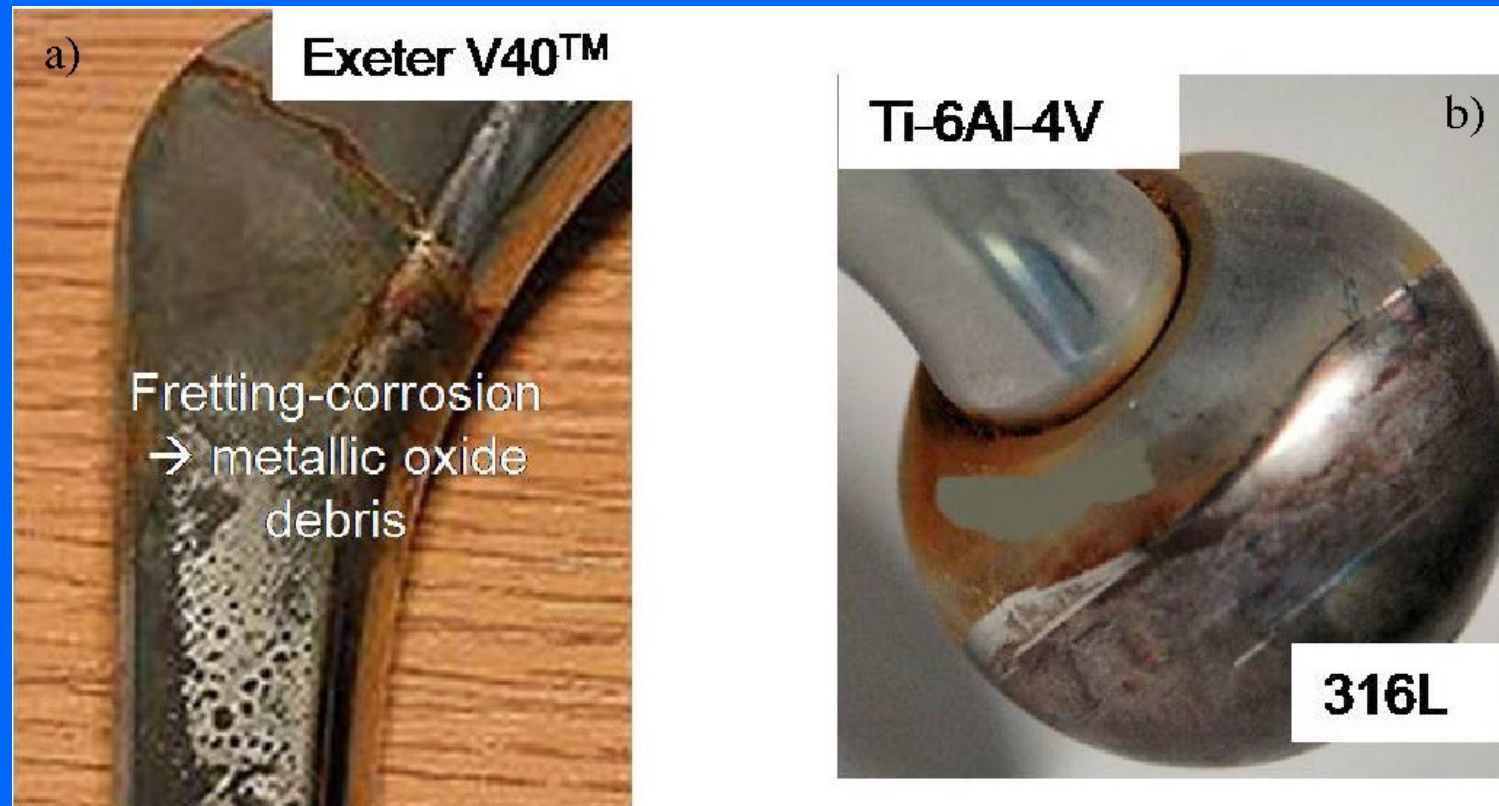
Dental implants are classified into endosseous and subperiosteal implants, with endosseous implants used for single crowns, fixed bridges, or retaining removable prostheses. They face an aggressive mouth environment, with saliva pH varying from 5.2 to 7.8. Factors causing corrosion include temperature, saliva quantity and quality, plaque, pH, protein, food and liquid properties, and oral health conditions. Galvanic corrosion occurs frequently between metallic implants, such as Co-Cr alloys, Ni-Cr, silver-palladium, gold, and Ternary Ti dental implants. Cobalt-based alloys release carcinogens, while titanium and its alloys are resistant to pitting corrosion. However, they undergo corrosion in high fluoride solutions during dental cleaning procedures. Osseointegration, the process of integrating metallic implants with surrounding bone, is crucial for preventing corrosion. Ti and its alloys are preferred due to their mechanical properties and resistance to extreme conditions.



CORROSION OF VARIOUS IMPLANTS

- **Corrosion of Orthopedic Implants**

Orthopedic implants, both temporary and permanent, can suffer from corrosion due to wear. High wear-resistant materials like ceramics and Co-Cr are often used for fabrication. In hip implants, Ti-based alloys are used for femoral components, with the ball made of Co-Cr or other hard ceramics. In vitro studies show that titanium with palladium exhibits high resistance to corrosion. However, the nature and distribution of corrosion products released into the body from these implants remain an important issue. Researchers are working on improving surface properties of titanium-based alloys.



SURFACE MODIFICATION IN BIOMATERIALS FOR CORROSION ALLEVIATION

Engineers and scientists have been working to improve the surface-related properties of biomaterials to reduce implant failure due to poor cell adhesion and corrosion. Various surface modification techniques have been adopted, such as chemical treatment, plasma ion implantation, laser melting, laser alloying, laser nitration, ion implantation, and physical vapor deposition. These methods lead to better interfacial bonding, non-equilibrium phases, faster processing speed, and reduced pollution.

In the case of Ni-Ti stents, the release of nickel ions from Ni-Ti has been reported, leading to endothelial cell damage. Various coating methods have been used, including passivation, plasma immersion ion implantation, electropolishing, and Diamond Like Carbon (DLC). Ti dental implants are surface modified to reduce corrosion, improve osseointegration, and increase biocompatibility. Laser-etching technique has been introduced to improve hardness, corrosion resistance, and other surface properties. Laser surface engineering (LSE) is a growing technique in biomaterials due to its high speed, low processing time, easy coating of complex geometry, higher adhesion between substrate and coated layer, and easy surface composition modification.

Nanoceramic materials have been studied for their superior properties compared to conventional coatings. Nanocrystalline diamond films coated Ti-6Al-4V provide significant protection against electrochemical corrosion in a biological environment, and nanoceramic HAP coatings are used to enhance osseointegration. Nanoceramic coatings are gradually receiving greater attention for their improved adhesion between metal and ceramic coatings



CURRENT AND FUTURE DEVELOPMENT

The field of corrosion in dental, orthopaedic, and cardiovascular implants faces numerous challenges. Recent research focuses on developing composite materials for implant applications that mimic nature, but more studies are needed to understand their behavior in in vivo conditions. Ceramics are used for total hip replacement, heart valves, dental implants, and tissue engineering, but are brittle and can fracture. Alumina and zirconia are considered alternatives for load-bearing applications but have mechanical failures. Bioactive glass, discovered in 1969, is widely used for bone repair and regeneration. However, a more sensitive method to study low corrosion rates of glasses is yet to be devised.

Uniform methodology should be adopted to compare the results of different research groups working in this direction. Surface modifications are often performed on biomedical implants to improve corrosion resistance, wear resistance, surface texture, and biocompatibility. A thorough understanding of the interactions between the implant surface, host, and biological environment, including micromotions of implants, is needed to obtain implants that can sustain for a longer period in the human system. The field of corrosion in biological systems is young and fertile, as humans know little about their physiology and interactions with foreign bodies.

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Thank you