Corrosion in Titanium dental implants – a review

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ABSTRACT

Titanium (Ti) is the most widely used biomaterial for dental implants as it exhibits excellent mechanical properties and biocompatibility. The biocompatibility of titanium is related to thin, protective surface titanium dioxide (TiO_2) layer, which forms a boundary at the implant-biological medium interface, reducing its reactivity with the surrounding biological environment and prevents corrosion. However, the metallic materials used as implants are susceptible to corrosion due to variations in the internal electrolyte environment. The surface oxide layer can be destroyed during insertion of implant or micro-motion between implant and bone under loading conditions. The localized destruction causes corrosion of the implant and induces leak of metallic particles or ions into surrounding tissues. The presence of metallic particles in peri-implant soft and hard tissues may be due to frictional wear or corrosion, or simultaneous occurrence wear and corrosion, which is known as tribocorrosion. The released metal ions may remain in the intercellular spaces near the site where they were released, or maybe taken up by macrophages, or they can migrate systemically. This review article highlights various aspects of corrosion, biological response to corrosion products and prevention of corrosion of titanium dental implants.

1. Introduction

Most of the commercially available implant systems are made of pure titanium or titanium alloys Ti-6Al-4V [1-3]. Commercially pure titanium is available in four grades, based on the content of interstitial elements. Grade 1 is the most pure, and grade 4 contains the greatest amount of interstitial elements/impurities and has the highest mechanical resistance. The addition of Aluminum and Vanadium increases strength and fatigue resistance and might affect the corrosion resistance properties resulting in the release of metal ions [2]. Titanium (Ti) and titanium alloys exhibit superior biocompatibility, high strength to weight ratio, low modulus of elasticity (MoE)

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and enhanced mechanical properties such as high fatigue strength and fracture toughness [1, 2, 4-7]. The corrosion resistance of Ti & Ti alloys results from the high affinity of Ti towards oxygen, which results in the formation of a thin and stable passive oxide layer that protects the bulk material from reactive species [1-4, 8, 9]. The oxide layer formed on Ti alloys typically consists of titanium dioxide (TiO_2) but may coexist with other titanium oxides such as TiO and Ti_2O_3 [1, 2, 4, 7]. The passive surface oxide layer consists of anatase crystalline form or mixture of anatase and rutile. The thickness of the surface oxide film is approximately 4 nm, which offers protection against chemical attacks, acidic solutions and oxidising environments thereby making Ti-based implants highly corrosion resistant in the oral environment [2-4, 10]. Corrosion is the gradual deterioration of a metal due to interaction with the surrounding environment, resulting in the release of ions into the surrounding tissues [2, 11]. The metallic nature of the dental implants, corrosive environments in the oral cavity and cyclic, continuous loading of implants may initiate and accelerate corrosion process leading to release of metal particles into the peri-implant region [1, 12].

2. General concepts related to corrosion

The characteristics that determine corrosion of metallic materials are [2, 3, 13];

a. Thermodynamic forces correspond to the energy required or released during a reaction, which causes corrosion either by oxidation or reduction reactions.
b. Kinetic barriers to corrosion correspond to factors that prevent corrosion. The formation of metal oxide film on metal surface or passivation is an example of a kinetic barrier to corrosion.

3. Types of corrosion

The most common types of corrosion found in metallic dental implants are galvanic, fretting, pitting/crevice corrosion, and environmental induced cracking (EIC) [1, 3, 14, 15].

Galvanic corrosion occurs due to direct contact of two dissimilar metals in an electrolytic solution. The difference in electrochemical potential of the two metals promotes oxidation of the more reactive metal, which becomes the anode that generates flow of electrons and ions to the cathode. The surrounding tissue acts as a medium for electrical flow between metallic dental implants, and other types of alloys used intraorally for restorations, metal inlays, onlays, crowns and orthodontic devices. Though galvanic corrosion is not common in titanium dental implants because of the presence of protective, passive surface oxide layer, it could amplify the rates of corrosion initiated by other mechanisms.

Fretting corrosion is caused by repeated micromotion or friction of metal surfaces that cause mechanical wear and rupture of the passive surface oxide layer. Fretting can occur between dental implants and bone during implant placement and exposure to cyclic loads during chewing and parafunctional habits [15]. The release of metal debris and ions has been linked to inhibition of cell differentiation, cytotoxicity, phagocytosis of Ti particles by macrophages and other cells, inflammation, and neoplasia. Recent studies have shown that fretting and oxide disruption at the surface of load-bearing implants can cause an increase in corrosion. Abnormal electrical signals may affect the response and stability of the adjacent tissue, and fretting corrosion may amplify other types of corrosion by causing rupture of the passivating film and exposing bare titanium.

Pitting corrosion occurs as a result of the breakdown of the passive oxide film on a flat and evenly exposed area. Crevice corrosion is localized corrosion due to geometric confinement in the design of the device or from a previously corroded region on the surface. In pitting or crevice corrosion, the region undergoing active corrosion has restricted solution flow due to geometric confinement. It initially depletes local oxygen concentration, generating high levels of metal ions and electrons that are consequently consumed by the surface exposed to high levels of oxygen [15].

EIC is the brittle mechanical failure of metallic devices under stress levels significantly lower than their ultimate tensile strength. This occurs in susceptible materials in corrosive environments and under continuous loading. The magnitudes of the forces that can cause EIC to vary over a wide range. EIC include forces which would be considered negligible under non-corrosive conditions. EIC is the most common cause of corrosion in implants for bone applications, because of its localized nature, may go unnoticed until catastrophic failure.

4. Mechanism of degradation of Titanium dental implants

According to the theory of passivity, the surface oxide film inhibits dissolution of metal ions and is not always stable in the human body [16, 17]. Microscopically, the composition of oxide film changes due to the continuous process of partial dissolution and re-precipitation[18]. The surface oxide films must have certain characteristics to limit further oxidation [12, 13]; a) non - porous, b) atomic structure that will limit the migration of ions and electrons across the metal oxide-solution interface, and c) high abrasion resistance. After mechanical or electrochemical disruption of the surface titanium oxide layer, it can be reformed and easily leading to spontaneous re-passivation [12]. Any damage/wear of the surface oxide layer can occur due to low pH in peri-implantitis conditions. ISmplant micro movement resulting from extreme mechanical forces on implant and proximity of implant with other metals such as amalgam, gold, or chromium-cobalt alloys, leading to corrosion of Ti implants. [10, 13, 18].

The presence of protective oxide layer keeps the current flow and the release of corrosion products at a very low level. However, no metallic material is completely resistant to corrosion or ionization within living tissues [8]. The possible degradation mechanisms of surface oxide layer are wearing, corrosion or combination of both, i.e., which causes deterioration of the metal surface and release of metal ions/ debris into the peri-implant region [8, 19]. The implants are exposed to the electrolytic environment of blood and other body fluids which contain water, various anions such as chloride, phosphate, bicarbonate ions and cations like Na^+, K^+, Ca^{2+}, Mg^{2+} etc. proteins and dissolved oxygen [2]. The biological molecules disturb the equilibrium of the corrosion reactions of the implant by consuming the products of anodic or cathodic reaction [12]. Proteins can bind to metal ions and transport them away from the implant surface and disturb the equilibrium across the double surface layer formed by electrons on the surface and excess cations in the solution. Also, proteins absorbed on the surface found to reduce diffusion of oxygen at certain regions and can cause corrosion at those regions. Hydrogen formed by cathodic reaction acts as a corrosion inhibitor and the presence of bacteria in the vicinity of the implant enhances corrosion by absorbing the hydrogen. The literature described the presence of fluoride ions as a cause for the reduction in the protective quality of the oxide film [12, 20]. The composition of the surface oxide film changes according to reactions between the surfaces of the metallic implant and living tissues. According to literature, low concentration of dissolved oxygen, inorganic ions, change in pH values, proteins, and chemical properties of food and liquids may accelerate the release of metal ions from the implants leading to corrosion process [12, 16].

Many types of electrochemical corrosion are possible in the oral environment as the saliva contains aggressive anions such as chlorides which causes dissolution of the oxide layer and leads to the release of metal ions into the surrounding tissues. The electrochemical behaviour of Ti-based implants is dependent on various factors such as composition, the concentration of anions, pH, buffering capacity and surface-related properties of the implant [21]. Wear refers to the deformation of the surface of materials as a result of mechanical interaction between two opposite surfaces. The wear resistance of artificial dental materials is essential for the long-term stability of the implant. Generally, wear resistance is dependent upon the hardness, roughness, fracture toughness and Young's modulus of the interacting materials. As wear measurements in vivo are highly complex and time-consuming, wear analysis is usually performed in simulators in the presence of artificial saliva. Fretting corrosion refers to the small oscillating movements between two interacting materials (bone-implant, plates-screws) in the presence of corrosive oral environment [12]. Fretting results in the rupture of a protective oxide layer, initiation of cracks and formation of reactive metal atoms on the surface that are susceptible to corrosion [13, 14]. Simultaneous action of electrochemical and mechanical interaction occurring on materials subjected to relative movement is referred to as tribocorrosion [12, 22, 23].

5. Local effects of wear and corrosion of titanium dental implants

Despite high corrosion resistance of Ti, increasing evidence is found regarding the release of titanium related ions into surrounding peri-implant tissues[20]. During the healing process, a significant decrease in pH values (pH=4) has been found as a result of local inflammatory processes [14, 16, 24, 25]. The reduction in pH stimulates corrosion of metals by increasing aggressiveness of tissues towards metallic materials. The corrosion process may compromise the resistance of metal to fatigue, which eventually cause fracture of the implant. It has been reported that saliva leaking between suprastructure (Ni-Cr) and implant (Ti) may trigger galvanic corrosion due to differences in electrical potential. This generates leakage of ions such as nickel or chrome from crown or bridge to the peri-implant tissues, with consequent bone resorption and may compromise the mobility of the implant and its subsequent fracture [26].

5.1 Tissue response at the implant-bone interface and peri-implant soft tissues

Peri-implant mucosa consists of well keratinized oral epithelium, sulcular epithelium, and junctional epithelium with underlying connective tissue. The corrosion products may cause discolouration of peri-implant soft tissues [12], or type IV hypersensitivity reactions, where titanium microparticles are found inside macrophages [27-30]. Gingival hyperplasia, mucositis, and peri-implantitis have been described as the soft tissue complications associated with dental implants [10]. The reactive lesions of peri-implant mucosa reported in the literature were inflammatory angiohyperplastic granuloma and peripheral giant cell granuloma, in which the presence of metallic particles has been confirmed from histologic sections [31].

Numerous case reports in the literature describe histological evidence of the presence of metallic particles in the tissues adjacent to dental implants, orthodontic mini-implants, internal fixation devices for maxillofacial surgeries, orthopedic prostheses of titanium or titanium-based alloys [21,24]. The literature describes histologic evidence of inflammatory response and presence of metallic particles in the peri-implant soft tissues, osseointegrated bone tissue and bone marrow of failed dental implants, indicating the occurrence of corrosion process [21]. The size of Ti particles identified in peri-implant tissues ranges from 100 nm (or 0.1 μm) to 54 μm. Significant concentrations of Ti particles were noted around compromised implants than healthy implants. Microchemical analysis using X-ray dispersion (EDX) confirmed the presence of titanium in peri-implant soft tissues [24,30]. The presence of corrosion and wear products in the peri-implant tissues may cause per implant bone loss and aseptic loosening of implant. The decrease in the percentage of osseointegration was also noted in the areas corresponding to pits or surface defects on implant surface [24]. The observation of metal particles located intracellularly or in association with blood vessels may represent a biologic response aimed at eliminating the foreign material [33]. It was observed that increased mechanical stability during healing might reduce micromotion at the bone-implant interface and reduces fretting corrosion.

The presence of titanium particles has been found in saliva and gingival crevicular fluid of patients with titanium dental implants. The localized areas of gingival hyperplasia surrounding the transmucosal portions of titanium implants may be due to poor hygiene, lack of attached gingiva, and titanium allergy [28, 34-36]. In a case report, it has been emphasized that periodontal surgical procedures and chemotherapeutic agents failed to control the hyperplasia of epithelial tissue surrounding endosseous titanium dental implants. The hyperplastic response was reduced after replacement of titanium abutments with custom-fabricated gold abutments [28].

5.2 Dissemination of titanium to other biological compartments

The local effect of corrosion resulting in the passage of metal particles to the peri-implant tissues may compromise other biological compartments [24]. Experimental studies conducted on animal models showed titanium deposits in liver, spleen and lung with macrophagic activity [37, 38]. The detection of titanium in the blood cells and/or plasma of patients with titanium dental or medical prostheses could be used as an indicator of the possibility of corrosion process of the metal structures. It is known that traces of metal can increase the physiological production of reactive oxygen species, without a compensatory increase in antioxidant species, further leads to tissue damage.

6. Clinical significance of corrosion

Since titanium is highly reactive metal and corrosion-resistant; the superstructure is the probable cause for the initiation of the corrosion process. When titanium is coupled with other metals, may accelerate galvanic corrosion of less noble metal due to difference in electrolytic potential which can be minimized by fabricating the superstructure from a metal alloy that has similar/close electrolytic potential to that of titanium [12]. A case report from the literature reported metal fatigue is the cause for implant fracture, which is confirmed from metallurgical analysis and corrosion has been observed on the surface of Ni-Cr crown [13, 39].

The metallic ions released from the implant due to the corrosion process affects the peri-implant tissues. The dissolution of metal ions may lead to surface erosion which in turn leads to brittleness and fracture of the implant. As the implant fractures, corrosion gets accelerated due to the increase in the amount of exposed surface area and loss of protective oxide layer [11, 40]. If the fractured implant is not surgically removed, further dissolution and fragmentation can occur, which may result in inflammation of the surrounding tissues. The metal debris activates a cascade of signaling molecules that result in the activation and differentiation of osteoclast cells and leads to bone resorption/osteolysis of the peri-implant region [8, 11]. As a result, the bonding between the bone and implant is lost and results in implant loosening. The occurrence of implant loosening in the absence of bacterial infection is referred to as aseptic loosening. Metal ions such as Ti^{4+}, Co^{2+}, and Al^{3+} have been shown to decrease DNA synthesis, mitochondrial dehydrogenase activity, mineralization, and mRNA expression of alkaline phosphatase [1]. Smaller sized wear debris combines with biomolecules and elicit Type IV immunogenic response and causes eczema, prolongs bone healing and is also accompanied by pain [41]. Also, it has been found that the titanium implanted region turns black. This colour change is due to the surface of titanium undergoes repassivation when the oxide layer is disrupted. In certain conditions, the repassivation process forms so much TiO_2 oxide layer that the region turns blacker. This process is referred to as metallosis and has been considered to be harmful [41, 42]. It is therefore important to study the dental implants in-vitro under the physiological condition to understand their behaviour in the oral environment and develop strategies to combat the issues that lead to implant failure.

7. Prevention of wear and corrosion of Titanium dental implants

Bone-implant interface is considered to be significant in the retention of any implant and loss of metal ions from titanium implant surface may lead to corrosion, wear and poor osseointegration. Modification of implant surface microstructure improves biological response, chemical and mechanical properties, thus reducing the friction and corrosion of metallic implants [2, 4, 43-45]. Implant surface biomodification is a process limiting the loss of metal ions. It can be achieved by various implant surface modifications such as surface machining, sandblasting, acid etching, anodic oxidation, plasma-spraying, nitriding and biocompatible/biodegradable coatings [1, 11, 12, 45,46]. Literature states that biocompatible inorganic coatings, such as hydroxyapatite (HAP) can lead to delay in corrosion, wear and also minimizes the aseptic loosening of implants. Recently, nanoceramic hydroxyapatite coatings are becoming popular to promote osseointegration. These coatings prevent surface degradation of titanium dental implants.

CP-Ti has low wear resistance and strength than Ti alloys, and the mechanical properties of CP-Ti can be improved by different processing techniques to obtain nano-crystalline materials, which exhibit high strength and superior biocompatibility. The corrosion resistance of CP-Ti is improved when coated with nano Al_2O_3-TiO_2, and fretting wear also has been decreased by seven times [47].

Recently, laser-etching of dental implants is used to produce a high degree of purity with adequate roughness for better osseointegration. The corrosion resistance of Ti-6Al-4V alloy has been increased by seven times when the implant surface modified using the excimer laser [48]. Despite ceramics disadvantages like brittleness and high elastic modulus, these are becoming popular for their high biocompatibility and corrosion resistance.

8. Conclusion

Titanium is a promising metal in the field of implant dentistry. The potential risk of corrosion and release of corrosion byproducts into the surrounding environment is of clinical importance. The local biological effects caused by the presence of ions/particles in the peri-implant tissues might affect the implant outcome. If the corrosion resistance of titanium can be controlled by limiting the exchange of metal ions, may improve ultimate osseointegration. Implant surface modifications by addition or subtraction of metals to enhance the biocompatibility of the metal with the surrounding tissues and also to provide corrosion resistance by preventing the loss of metal ions from the surface.

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