



Insight Into Corrosion of Dental Implants: From Biochemical Mechanisms to Designing Corrosion-Resistant Materials

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Abstract

Purpose of Review Despite advanced technologies to avoid corrosion of dental implants, the mechanisms toward the release of metals and their role in the onset of peri-implant diseases are still under-investigated. Effective knowledge on the etiopathogenesis of corrosive products and preventive strategies mitigating the risks for surface degradation are thus in dire need. This review aimed to summarize evidence toward biocorrosion in the oral environment and discuss the current strategies targeting the improvement of dental implants and focusing on the methodological and electrochemical aspects of surface treatments and titanium-based alloys.

Recent Findings Recent studies suggest the existence of wear/corrosion products may correlate with peri-implantitis progress by triggering microbial dysbiosis, the release of pro-inflammatory cytokines, and animal bone resorption. Furthermore, current clinical evidence demonstrating the presence of metal-like particles in diseased tissues supports their possible role as a risk factor for peri-implantitis. For instance, to overcome the drawback of titanium corrosion, researchers are primarily focusing on developing corrosion-resistant alloys and coatings for dental implants by changing their physicochemical features.

Summary The current state-of-art discussed in this review found corrosion products effective in affecting biofilm virulence and inflammatory factors in vitro. Controversial and unstandardized data are limitations, making the premise of corrosion products being essential for peri-implantitis onset. On the other hand, when it comes to the strategies toward reducing implant corrosion rate, it is evident that the chemical and physical properties are crucial for the in vitro electrochemical behavior of the implant material. For instance, it is foreseeable that the formation of films/coatings and the incorporation of some functional compounds into the substrate may enhance the material's corrosion resistance and biological response. Nevertheless, the utmost challenge of research in this field is to achieve adequate stimulation of the biological tissues without weakening its protective behavior against corrosion. In addition, the translatability from in vitro findings to clinical studies is still in its infancy. Therefore, further accumulation of high-level evidence on the role of corrosion products on peri-implant tissues is expected to confirm the findings of the present review besides the development of better methods to improve the corrosion resistance of dental implants. Furthermore, such knowledge could further develop safe and long-term implant rehabilitation therapy.

Keywords Dental implants · Corrosion · Titanium · Dental alloys · Peri-implantitis

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Introduction

Since the introduction of titanium (Ti) dental implants in the 1960s by Branemark [1], the therapy with Ti-based dental implants has evolved from an accidental experimental

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discovery to a predictable standard of care for replacing missing teeth presenting a survival rate above 96% [2•]. This achievement is primarily due to the good mechanical properties as well as resistance to corrosion and excellent biological performance of Ti, which are mainly led by their inherent ability to form a spontaneous Ti oxide layer after exposure to oxygen atmosphere (mainly TiO₂) [3]. Nevertheless, the biomaterials currently used for dental implant design are still far from perfect. Although the passivation provided by the nano-scale amorphous TiO₂ layer is well known to act as a protective barrier against corrosion in physiological conditions (i.e., neutral pH), when dental implants are inserted into the complex in vivo oral environment, the constant exposure to acidic substances and microbial metabolites may proceed in reduced pH and consequent irreversible rupture of the passive film. Additionally, the TiO₂ barrier presents a poor tribological efficacy and can be easily removed/disrupted under loading [4]. As such, the implant becomes more susceptible to electrochemical reactions between the surface and oral fluids, resulting in partial or complete dissolution of the metal [5•, 6–8].

The endurance of these corrosive factors over time, along with wear induced by implantation procedures (e.g., friction, micro-motion), is the process that can cause the undesired release of metallic ions and particles from the implant to the surrounding tissues. In consequence, it may eventually lead to severe biological complications such as peri-implant diseases and even systemic toxicity, in a worst-case scenario [9•, 10–12]. Importantly, recent reports have hypothesized the contribution of the Ti particles to the onset and progression of peri-implant bone loss. In fact, it has been pointed out by the 2017 AAP/EFP World Workshop on the Classification of Periodontal and Peri-Implant Diseases and Conditions [13•] as a potential risk factor for peri-implantitis but with no conclusive evidence based on the currently available data. Thus, from this standpoint and considering the current prevalence of peri-implantitis (about 57% at patient-level) [14•], studying the influence of corrosion-induced release of ions and particles as a driving factor for peri-implant diseases and early/late failure of dental implants remains clinically relevant. Additionally, even though the problem of corrosion of dental implants has been successfully addressed through innovative surface modifications and alternative biomaterials using nobler metal alloys, the race for an ideal dental implant design capable of protecting the material from corrosion effects has disclosed numerous techniques and strategies that are stagnated in the bench, thus providing no consensus for a solid advance for clinical application.

Therewith, this review provides a close look at the available information regarding the corrosive factors/mechanisms of metal ions released from dental implants materials and their consequent biological side effects on peri-implant tissue and systemic health. Furthermore, a compilation of key

factors driving the anticorrosive effect of current surface modification techniques and metal alloys is presented, targeting a safer design of dental implants to ensure the long-term success of the implant rehabilitation therapy.

Search Strategy

A literature review focusing on the corrosion process of dental implants was undertaken aiming to answer the following focused question: “What is the current evidence toward the key factors influencing dental implants biocorrosion and driving the anticorrosive effect of implant surface modification techniques and titanium alloys?” For this, as a first step, two reviewers (B.E.N. and J.M.C.) searched for appropriate articles in the Pubmed (Medline) database using the combination of the terms “dental implants” OR “surface treatments” OR “alloys” AND “corrosion” OR “electrochemical” OR “degradation.” This was complemented by manual searches in peer-reviewed journals and snowballing approach to identify additional relevant studies in the reference lists of included articles. Finally, after screening the potential eligible titles and abstracts that addressed the focused question, relevant findings from the included articles were integrated into the following writing topics, as appropriate.

Dental Implants Meet the Challenges of the Reactive Oral Environment

From the moment dental implants are inserted in the oral cavity, the fate of maintaining their physicochemical properties, especially the integrity of the protective TiO₂ passive layer against corrosion, is highly dependent on the challenging conditions of the hostile electrolytic oral environment [8]. Usually, the oral fluids (i.e., saliva, blood plasma) are characterized by the presence of organic and inorganic substances in combination with a pH buffering mechanism that regulates the hypotonic and physiological condition of the medium (pH between 6 and 7) [15, 16]; however, some factors such as microbial metabolites and corrosive substances can reduce the pH, turning the environment acidic and highly reactive to chemically attack the metallic surfaces [7, 17, 18].

Corrosive substances, such as Cl⁻, F⁻, and H⁺, can be found in saliva, oral biofilms, prophylactic commercial formulations (e.g., toothpaste, mouth rinses, cariostatic gels), and foods [19–21]. Remarkably, the influence of F⁻ ion concentration in the medium adversely affecting the corrosion resistance of titanium-based materials has been widely studied [20–24]. Beline et al., for example, showed that 0.2% sodium fluoride mouthwash reduced Ti corrosion resistance

regardless of the surface treatment (machined, sandblasted, or acid etching) compared to fluoride-free mouthwashes [24]. Similar findings were reported by Chen et al. [25], in which results demonstrated that the Ti corrosion resistance decreased with the increasing concentration of fluoride (0–0.4 ppm F⁻) in Hanks' solution. That previous study also demonstrated the increase in surface roughness and acceleration of Ti ion release, which was even more pronounced in an acidic environment (pH 7.3 vs. 5.0) [25]. It is suggested that these corrosion results are mainly due to the formation of hydrofluoric acid (HF) from fluoride ions when the aqueous environment is acidified by eating habits or microbial metabolites (F⁻ + H⁺ → HF). HF is a well-known weak acid strongly reactive to metals because it has chemical characteristics prone to induce the breakdown of the TiO₂ protective layer (TiO₂ + 4HF → TiF₄ + 2H₂O) [26], thus promoting not only the degradation but also the discoloration of the metal surface due to the generated fluoride-titanium compounds (e.g., TiF₄(TiF₆)³⁻) [27].

Concurrently, besides the local acidification induced by foods and beverages, oral bacteria's promotion of acidic environment has been considered one of the major and intriguing causes to decrease the corrosion resistance of Ti [17]. The mechanism from which the microbial corrosion process occurs starts as soon as dental implants are inserted in the oral cavity. From this moment, not only the outer implant surface but also the micro gaps between the implant and abutments are immediately covered by protein-rich fluid pellicle—saliva and blood—that has remarkable specificity to bacterial components, thus promoting the adhesion of bacteria to these surfaces [28, 29]. As the biofilm develops, oxidation reactions due to bacterial acidic metabolites and oxygen level deficiency may occur between the biofilm-covered Ti surface (cathodic area) and the exposed Ti (anodic area), increasing the corrosion rate of the implant material [17]. Additionally, biofilm decontamination by mechanical debridement and chemical methods, such as citric acid rubbing, may also induce Ti release from the implant surface [30, 31].

In a nutshell, it is important to highlight that regardless of the etiologic factor driving the corrosion on Ti, bacterial cells and physicochemical factors act synergically for the implant surface degradation. For example, because biofilm development is influenced by the low pH microenvironment, the promotion of local acidification by modulating factors such as external acidic substances (e.g., foods, caffeine, cotinine, and nicotine) [4, 32, 33] and microbial components such as lipopolysaccharides [34] may accelerate the microbial corrosion process of Ti.

Furthermore, it is important to highlight that the literature has been increasingly reporting other chemical and biological substances to reduce implant corrosion, and it should not be neglected. Notably, Sousa et al. recently demonstrated

that hydrogen peroxide (H₂O₂) concentration in mouthwash was able to reduce the corrosion resistance of Ti6Al4V alloy under dynamic conditions simulating the hygiene protocol usually indicated in post-surgical implant placement [35]. Accordingly, other studies focusing on the role of H₂O₂ as a by-product of the peri-implant inflammatory process also demonstrated a reduction of implant corrosion stability [21, 36]. Yet, in a most unfavorable environmental condition, combining three oxidative agents (H₂O₂, lactic acid released from bacteria, and fluoride), the corrosion of the Ti surface considerably increased compared to the results of these substances alone [21]. In the same way, some studies have also assigned the role of albumin, the most abundant protein in blood plasma, to reduce the kinetic of Ti surface passivation and accelerate the dissolution of the material [36, 37].

Altogether, these physical, chemical, microbiological, and inflammatory corrosion processes promote the surface damage of dental implants and the release of corrosion by-products that may adversely alter the microenvironment conditions of peri-implant tissues, leading to cytotoxic and inflammatory reactions. Further, such event compromises the success of dental implant rehabilitation therapy.

Biointerface-Safety of Corrosive Products on Oral/Systemic Health—Should We Care?

With the growing aging world population and its expectation for a predictable long-term dental implant therapy, knowing the factors that contributes to the success/failure of the rehabilitation is of utmost importance. Since one of the main concerns towards implant therapy is the high prevalence of peri-implant disease [14•], unraveling the onset and pattern, as well as the risk factors for disease progression, remains clinically relevant. For instance, because it has been evidenced that metallic corrosive products are not fully bioinert; multiple studies have been raised concerns regarding the potential of wear and corrosion products to induce adverse biological reactions not only locally in the surrounding peri-implant tissues but also systemically throughout the human body [5•, 9•, 18, 33, 38•, 39].

Once corrosion products are released from the implant surface due to mechanical (wear particles/debris), electrochemical (corrosion-related free metal ions, organometallic complexes, and salts), and/or combination of both mechanical and electrochemical processes (i.e., tribocorrosion), a series of biochemical reactions might be triggered at the biointerface microenvironment [4, 38•, 40] (Fig. 1). In this context, several *in vitro* and pre-clinical experiments have demonstrated the role of Ti ions and particles to present toxic and/or pro-inflammatory effects [33, 41•]. In the case of mechanical wear, for example, Ti particles released by ultrasonic scaling of sandblasted

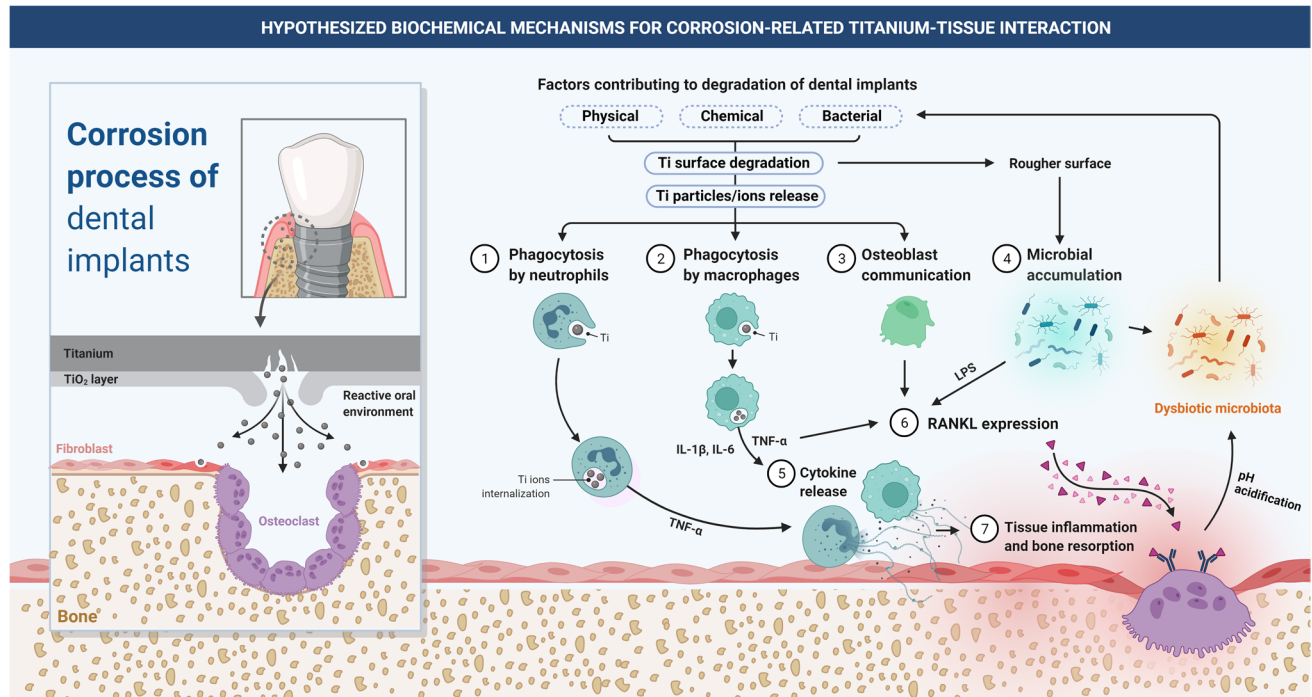


Fig. 1 Schematic depiction of hypothesized biochemical mechanisms for corrosion-related titanium-tissue interaction of dental implants. Corrosion process of dental implants leading to Ti particle/ion release arises from the electrochemical attack of the reactive oral environment to the implant surface by disrupting the protective oxide passive layer (TiO_2). As a consequence, there is an induction of inflammatory process in the soft tissue cells (e.g., fibroblasts) and bone cells, which is mainly led by signaling factors promoting the differentiation and recruitment of osteoclast cells responsible for peri-implant bone resorption (left panel). In a close look, there are several potential biochemical routes for the occurrence of these peri-implant inflammatory processes (right side). For instance, when dental implants are subjected to physical, chemical, and bacterial factors present in the reactive oral environment, it can be supposed that there is a multi-directional pathway loop for the Ti-tissue interaction. For example, once metallic particles/ions are released, the peri-implant inflamma-

tory process may occur by activating the function of phagocytic cells such as (1) neutrophils and (2) macrophages, (3) stimulating some communication pathways of osteoblastic cells, or even promoting (4) microbial accumulation in the degraded rougher surface region. In particular, the phagocytosis of Ti ions may lead to a (5) higher expression level of pro-inflammatory cytokines (e.g., $\text{IL1}\beta$, IL6 , and $\text{TNF}\alpha$), and all of these mentioned processes (3 to 5) may induce (6) RANKL expression within osteogenic cells, thus indirectly promoting RANKL-induced osteoclast differentiation and consequent (7) tissue inflammation and bone resorption. Once inflammation occurs, the pH level of the region is reduced with concurrent microbial dysbiosis, favoring the generation of bacterial acid products that, in the end, also negatively affect the corrosion resistance of Ti. Created and adapted from “Anti-neutrophil Cytoplasmic Antibody (ANCA)-associated Vasculitis” and “Proposed Therapeutic Treatments for COVID-19 Targeting Viral Entry Mechanism,” using BioRender.com (2021)

and acid-etched (SLA) surface induced a higher in vitro inflammatory response than the control LPS-treated human macrophages culture. In this case, a higher gene expression level of the pro-inflammatory cytokines $\text{IL1}\beta$, IL6 , and $\text{TNF}\alpha$ was noted, probably because macrophages may have phagocytosed Ti particles [30]. Interestingly, such inflammatory response due to Ti phagocytosis is an event that has been reported to occur not only with macrophages but also with neutrophil cells [33]. In addition, it seems that the macrophage-related expression of cytokine level may be directly dependent on the increasing concentration of particles and the type of implant surface treatment (machined, sandblasted, and SLA) [30]. Note that the in vitro cytokine level and in vivo bone resorption (mouse calvariae model) were more pronounced when particles were originated from sandblasted discs than from SLA and

machined surfaces, probably due to differences in chemical profile and particle sizes [30].

Choi et al. [42] reported that the larger the particle size, the more the expression of receptor activator of nuclear factor κB ligand (RANKL), a dominant signal for osteoclast recruitment, and the proteolytic activities of matrix metalloproteinases (MMP) 2 and 9, involved in the degradation of bone matrix and mineralization. The authors also demonstrated that although all particle sizes were able to induce the loss of implant integration with bone tissue in vivo (rat tibia model), large particle sizes ($\geq 10.0 \mu\text{m}$ and $< 15 \mu\text{m}$) were shown to maintain osteoblast in vitro viability whereas a reduction was observed for smaller particle sizes, indicating that different functional responses may be generated depending on the particle size present in the surrounding tissues, which is reported to vary from 100 nm to 54 μm [41•].

The cytotoxic effect of Ti products on the inflammatory response of human cells has been demonstrated for particles and Ti ions. Mine et al. showed that the concentration of Ti ions might have an impact on the bone remodeling of dental implants as 20 ppm Ti ions reduced cell viability of murine pre-osteoblastic MC3T3-E1, osteoclast-like RAW264.7, and epithelial cell-like GE-1 cells, and 9 ppm Ti ions increased the expression of RANKL and osteoprotegerin (OPG) in MC3T3-E1 cells [43]. In accordance, Wachi et al. [44] also demonstrated *in vitro* and *in vivo* (rat model) that, in the presence of bacterial LPS, 9 ppm Ti ions (limited concentration to induce a cytotoxic effect *in vitro*) can synergistically increase the ratio of RANKL to OPG and the level of CCL2, a chemokine related to activation of monocyte infiltration. Additionally, gingival epithelium loaded with Ti ions enhanced the localization of bacterial LPS endotoxin toll-like receptor 4, suggesting that Ti ions may play an important role in peri-implantitis onset by altering osteoclast differentiation due to changes in the sensitivity of the epithelium around microorganisms. In fact, in a previous study of our research group, Ti particles and ions demonstrated a striking influence on microbial growth in a dose-response manner, and Ti ions had the capacity to cause a dysbiotic change in the microbial community toward a profile similar to pathogenic biofilm-related to peri-implant infections [6].

Accordingly, evidence for Ti degradation in diseased peri-implant tissues has been demonstrated in human studies. As such, levels of released Ti were detected via ICP-MS (inductively coupled plasma mass spectrometry) in submucosal plaque [45], soft-tissue biopsies [46], and exfoliative cytologic samples [47, 48] in greater amount in diseased peri-implant mucosa than in healthy sites. Nevertheless, for both healthy and inflamed tissue biopsies, the Ti concentration found (7.3 to 38.9 μM) were reported to be within the levels needed to activate the IL-1 β secretion from human macrophage *in vitro*, which is a phenomenon closely related to stimulating an *in vivo* proinflammatory reaction [46]. Thus, these findings suggest poor specificity between the biological impact of Ti concentration and the pathological process of peri-implant diseases.

Indeed, there is some biological plausibility of the relationship between the origin of Ti ions/particles in the peri-implant tissue and the onset of biofilm-related peri-implant diseases. For instance, it can be supposed that there is a multidirectional pathway loop for the degradation of Ti surface in the oral environment: (i) wear, acidic substances, and metabolites released from bacteria (e.g., lactic acid) promote the degradation and acidification of the peri-implant microenvironment, thus allowing the passive oxide layer breakdown with consequent pitting and galvanic attacks; (ii) corroded Ti surface presenting increased roughness provides additional niches for bacterial recolonization; (iii) microbial accumulation promotes oxygen level deficiency

that jeopardizes the reformation of the passive oxide layer, thus promoting crevice corrosion on Ti surface; (iv) corrosion products induce microbial dysbiosis favoring the occurrence of inflammatory reaction and the consequent generation of acid products (hydrogen peroxide and H^+) that in the end also negatively affect the corrosion resistance of Ti. Nevertheless, it is of utmost importance to emphasize that among biofilm models used to assess microbial corrosion on Ti, only a few studies available in the literature considered the polymicrobial diversity of oral environment resembling the clinical situation [17], emphasizing the need for further *in vitro* and *in vivo* investigations on the cause-effect pattern between microbial accumulation and Ti surface degradation.

In addition, considering that all these corrosion processes occur in a complex biological environment, the transportation of corrosion by-products to remote organs is inherent. Ti ions have been related to ionically bind to blood proteins and be transported throughout the human body to distant organs such as kidneys, liver, and lung, thus extending toxicity concerns from local to a general health scope [39]. Therefore, as it is well known that corrosion and Ti release indeed occur and are correlated with inflammatory reaction induction and potential systemic cytotoxic effects, strategies to avoid the corrosion of dental implants are necessary and have been extensively studied.

Strategies to Avoid/Reduce the Corrosion of Dental Implants

Given what was mentioned in the above topics, some strategies have been drawn to avoid/reduce the corrosion of dental implants and the consequent undesired effects. Inhibiting corrosion of metals is an interdisciplinary approach in which engineering solutions are applied to the biomedical field to improve their applicability under a complex biological environment. Nevertheless, the race for novel approaches has led to numerous technologies that do not reach an endpoint consensus on the ideal strategy that could provide real progress for clinical application. In this way, knowing the key factors driving the corrosion resistance of current technologies is of great relevance for the guidance of future studies. Herein, we will review two main methods: the design of corrosion-resistant Ti alloys and the development of protective surface treatments.

The Search for Corrosion-Resistant Alloys for Dental Implants

When designing experimental alloys for dental implants to resist corrosion, the most straightforward strategy is altering their composition. Several alloying elements are known

to inhibit the degradation process by driving the growth of highly stable passive oxide films and microstructures [49]. From designing a new experimental alloy to improving already existing ones, the final goal is to create a material that can achieve passivity [50], regulate the hydrogen evolution reaction [51, 52], and reduce the anodic/cathodic activity directly [22, 53].

Stainless steel, cobalt-based alloys, magnesium (Mg), and its alloys have proven their applicability as bone implants [11]. However, Ti is the most popular material used for dental implant manufacturing, and its alloys have been widely applied clinically. Table 1 sums up the main alloying elements added to Ti and their role in improving the electrochemical properties of experimental metallic alloys proposed for dental implants. Herein, only studies investigating

binary alloys with high potential as implant materials were selected. In this way, it was possible to clearly state the effects of the alloying elements on Ti corrosion kinetics and microstructure.

Zirconium (Zr), tantalum (Ta), niobium (Nb), chromium (Cr), and molybdenum (Mo) are some of the elements normally added to Ti to form a stable and resistant oxide film when in contact with the environment. For example, Ta oxides (mainly Ta_2O_5) are known to be very stable, and their association with TiO_2 improved the structural integrity of the passive film leading to superior resistance to pitting corrosion [55]. Similarly, Mo showed concentration-dependent protection, in which higher concentrations arise the formation of a more compact inner oxide layer at the metal-oxide interface [67]. On the other hand, some elements such as Fe

Table 1 Effect of alloying elements on Ti alloy microstructure and electrochemical parameters

Alloying element	Effect on alloy microstructure and electrochemical parameters	Ref.
Zr	Zr acts reducing the anodic activity directly, stimulating a solid solution to strengthen and form a reinforced film containing ZrO_2 . Zr addition leads to higher polarization resistance (R_p) and lower values of corrosion current density (i_{corr}), corrosion rate, and capacitance parameters of Ti-Zr alloys.	[53, 54]
Ta	Ta incorporation forms a stable Ta_2O_5 passive film and a β phase in the Ti matrix, which reduces pitting initiations, the corrosion rate, and i_{corr} while enhancing the corrosion potential (E_{corr}) parameter of Ti-Ta alloys.	[55]
Nb	Nb promotes the formation of β and ω phases in the α -Ti matrix and contributes with NbO_2 to the passive film, enhancing the protective cathodic reaction. Nb addition lowers the corrosion rate, i_{corr} , and passivation corrosion density (i_{pass}) values, increasing the E_{corr} parameter of Ti-Nb alloys.	[56]
Cu	Cu provokes Ti_2Cu precipitation with a strong strengthening effect. Ti-Cu alloys exhibit a nobler E_{corr} and higher R_p , and the i_{corr} decreases with increasing Cu content.	[57, 58]
Ag	As the concentration of Ag enhances, it favors the precipitation of intermetallic components (Ti_2Ag and $TiAg$). With the increasing Ag content in Ti-Ag alloys, E_{corr} increases, and i_{corr} decreases. There is a tendency for the intermetallic to dissolve preferentially.	[58, 59]
In	In forms an α single-phase alloy with greater refinement of grains for higher concentrations. The corrosion rate and i_{corr} lower with In addition, enhancing R_p values of Ti-In alloy.	[60]
Pd	Pd favors the precipitation of β -phase, forming predominantly an α - β microstructure. Pd accelerates the protective cathodic reactions and inhibits the dissolution of Ti while decreasing i_{corr} and capacitance and enhancing the R_p of Ti-0.2Pd alloy.	[22, 58]
Cr	The addition of Cr in low concentrations forms an α - β structure, and then, for higher contents of Cr, a single β -phase alloy is observed. A Cr-rich oxide film improves the R_p and diminishes the i_{corr} of the Ti-20Cr alloy.	[58, 61, 62]
Mn	Mn stimulates the formation of an α - β structure, but at higher concentrations, a single β -phase can be obtained in association with the TiMn compound. Mn enhances the cathodic reaction but does not improve the corrosion resistance of Ti considerably.	[58, 63]
Mg	Ti-Mg alloys show Ti and Mg phases in their microstructure. The E_{corr} decreases with the content of Mg, while the i_{corr} increases.	[64]
Co	Co provokes the formation of an α - β structure, but as its concentration increases, only the β phase is observed associated with Ti_2Co . Ti-Co alloys show similar corrosion behavior to pure Ti.	[58]
Bi	Bi forms a single α -Ti phase, but Ti-20Bi alloy shows $BiTi_2$ and $BiTi_3$ intermetallic phases. Ti-Bi alloys slightly increases E_{corr} values but shows a significantly lower i_{corr} in an electrolyte containing fluoride and acid lactic.	[65]
Mo	The growth of primary β -phase dendrites with smaller sizes is observed with increasing Mo content in the alloy. Adding Mo to pure Ti improves the stability of the anodic oxides, increasing R_p and decreasing i_{corr} and i_{pass} as the content of Mo enhances in Ti-Mo alloys.	[66, 67]
Fe	Fe provokes the β phase formation as the concentration enhanced, improving the grain refinement of the Ti alloy. With the optimal concentration, Fe reduces the i_{corr} and increases the critical pitting potential (E_{pit}) and R_p parameters of Ti-Fe alloys.	[58, 68]

Note: A decrease in the electrochemical parameters, capacitance, i_{corr} , i_{pass} , and corrosion rate, reflects low electrochemical activity and high passivity. The higher the E_{corr} , E_{pit} , and R_p values, the greater the corrosion resistance properties and the stability of the oxide film

form oxides less stable than TiO_2 , impairing its protective behavior if added in high concentrations [68].

As seen in Table 1, not only the oxide film is changed when an alloying element is added to Ti. The alloy may go through a variety of phase transformation reactions, which can result in three microstructure phases (α , $\alpha+\beta$, and β) with intermetallic variants [69, 70]. There is no consensus in the literature regarding the best crystalline phase to prevent corrosion. While β crystalline phase is expected to be more resistant to dissolution and stabler than the α -phase [71, 72], the solid solution strengthening effect of the single α -phase in Ti alloys has revealed a better electrochemical behavior than $\alpha+\beta$ and β alloys [53, 73].

Regarding intermetallic phases, it tends to precipitate by incorporating high concentrations of alloying elements to Ti. Generally, intermetallic compounds will dissolve preferentially on the surface by developing a galvanic cell with the matrix [73–77], which impairs the alloy's electrochemical stability. In fact, the possible formation of a galvanic couple between Ti and Mg because of their dissimilar potential may accelerate the corrosion processes of Ti–Mg alloys [64]. Thus, single-phase alloys are likely to exhibit better electrochemical properties [78], but when more than one phase and/or diverse crystallographic orientations are present, it is indispensable to achieve grain refinement and an even distribution of the elements [49]. A fine microstructure provides an “enveloping effect” by modifying the cathode/anode area ratio between the intermetallic and the matrix to minimize the galvanic effects and provide corrosion protection of the less noble phase [57, 79]. Also, homogeneous microstructures and greater elemental distributions may result in better corrosion resistance due to the improved stability and durability of the passivation films formed on the matrices in these cases [50, 58, 74, 76, 77, 80]. For instance, the inhomogeneous distribution of the Ti_2Ag phase in Ti–Ag alloys resulted in more pores (e.g., imperfections) on the surfaces, favoring crevice corrosion attacks owing to localized disruption of the passive film [59].

The grain refinement of an alloy can be achieved from different approaches. Firstly, alloying elements such as Fe [68], In [60], and Sn [81] have shown a strong role in refining the grain size of the alloy, increasing its corrosion resistance. Another well-known approach to inhibit corrosion on alloy materials by microstructure refinement and homogeneous element distribution is applying alternative manufacturing techniques and thermomechanical/finishing processes [49]. Additive manufacturing or 3D printing (e.g., selective laser melting (SLM), electron beam melting (EBM), laser metal deposition (LMD), selective laser sintering (SLS), binder jetting (BJ), laser engineered net shaping (LENS), and wire arc additive manufacturing (WAAM)) [55, 82–86], as well as finishing (e.g., burnishing, laser surface treatments, and shot peening) [87–89], and thermomechanical processing

(e.g., aging and annealing) [90, 91] are a set of techniques that have been used to fabricate new alloys with protective properties against corrosion by (i) complete oxidation of alloying elements and growth of a uniform surface film, (ii) formation of defect-free microstructures with refined grain structures, and (iii) homogeneous distribution of alloying elements without solute segregation.

Although only binary Ti alloys are reviewed in Table 1, several other elements have been used to develop corrosion-resistant alloys. Some alloying elements (e.g., V, Al, and Sn) are more commonly associated in ternary, high entropy alloys (HEAs), or compositionally complex alloys (CCAs). The range of elements and combinations is wide. For this reason, researchers are first modeling a well-defined combination of elements and their concentrations by computational tools that consider first-principles calculations (e.g., *ab initio*, density functional theory) to predict material properties and electrochemical mechanisms before testing it by *in vitro* and *in vivo* studies [51, 92, 93]. Although this approach may increase the chance of success of metallic alloys, essentially, studies may have tested the progressive incorporation of an element to alloys empirically [53–55, 94–96].

Improving the Electrochemical Stability of Dental Implants by Surface Treatments

While the design of new alloys seeks to create a corrosion-resistant dental implant by improving the electrochemical properties of the bulk material, surface treatments are applied to the implant substrate after its manufacturing, aiming to minimize the corrosion damages by avoiding the penetration of corrodents on metal underneath and preventing the electrochemical reactions. Table 2 summarizes the treatment details and outcomes of the main technologies proposed to create a protective behavior against corrosion of dental implants surfaces.

Similar to the corrosive behavior of alloys, the electrochemical stability of coatings is also influenced by their elemental and crystalline composition. For instance, the growth of a TiO_2 rutile phase by surface treatments applied to Ti substrate has triggered superior electrochemical stability of the material [104, 111]. In addition, the reinforcement of the oxide layer with homogeneously distributed functional and stable compounds and crystal phases (e.g., TiN, TiH TiO_2 , Al_2O_3 , SiC) by coating/film deposition technologies has proved to enhance the corrosion performance of the implant material [54, 99, 110, 113]. In this context, Safavi et al. [113] and Ling et al. [119] listed a series of mechanism and ideal criteria that coatings and films deposited by magnetron sputtered and hydrothermal methods need to meet for corrosion inhibition, which may be considered regardless of

Table 2 Review of surface treatment technologies applied to dental implants surfaces to achieve protective behavior against corrosion

Method	Treatment details	Outcomes related to corrosion behavior	Ref.
Grit blasting	A high-pressure and high-speed sandblasting of micro- or nanoparticles creates a rough surface under micro- or nanoscale by physical deformation.	Some particles can leach from the surface, impairing the electrochemical stability of the material. An extremely irregular topography may disrupt oxide films, reducing corrosion resistance.	[38•, 97, 98]
Acid etching	Involves a chemical reaction of the acid with the implant surface provoking a rough surface under micro- or nanoscale by a subtraction process.	The electrochemical stability is positively affected by the formation of a TiH intermediate layer by the acid reaction with the Ti substrate, allowing the growth of a new stable oxide layer.	[38•, 54, 97]
Sandblasting/acid etching	Alters the surface morphology through deformations induced by physical contact (blasting) and irregularities induced by chemical action (acid etching).	Although the very irregular topography may decrease the corrosion resistance, the etching process acts cleaning any remaining impurities from blasting, also forming a TiH intermediate layer that can play a role in protecting the surface against corrosion.	[38•, 97, 99]
Sol-gel	This method uses an organic-inorganic solution applied to the substrate by coating techniques (e.g., dipping, spinning, and spraying), forming an adhesive layer after drying.	The formation of dense and crack-free coatings with adequate adhesion strength between coatings and substrate might cause a reduction in the corrosion rate due to a protective barrier effect. The addition of functional compounds to the layer can provide additional corrosion resistance.	[100–103]
Anodic spark deposition or plasma electrolytic oxidation	An electrochemical/anodic oxidation process uses a range of voltage to form nanotubes and micro- and nano-porous surfaces using electrolyte solutions with varied composition, temperature, and pH.	This process enables a thickening of the oxide layer that behaves as a barrier to ion diffusion. This method leads to the growth of a fully oxidized protective surface with different microstructures and compositions that might contribute to avoiding the electrochemical dissolution of the implant at the metal-electrolyte interface.	[73, 99, 104–106]
Electrophoretic deposition	It is based on the movement of charged particles or molecules in a suspension under an electric field, forming various surface features.	When compact and uniform, the coating causes a reduction of the penetration rate of the solution into the coating. Incorporating functional compounds as a reinforcement network might improve the local corrosion resistance of the coating matrix.	[107–109]
Physical vapor deposition (magnetron sputtering)	This deposition method generates thin, uniform, and defect-free films onto the substrate using a metal target and a mixture of gases. Topography can vary from smooth to complex and hierarchical nature.	The film formed onto the surface is more stable, compact, and homogenous than the natural oxide layer, reducing the penetration of ionic species through the film, thus, mitigating the electrochemical degradation process. Also, different crystalline phases and compositions may improve film density and chemical stability.	[110–113]
Chemical vapor deposition	Deposition of volatile organic or metalorganic precursors in the form of thin films with the specific nanostructure.	The formation of a dense and thin film acts as a physical diffusion barrier blocking the charge transfers between the substrate surface and the electrolyte effectively.	[114–116]

Table 2 (continued)

Method	Treatment details	Outcomes related to corrosion behavior	Ref.
Plasma spraying	The coating is deposited in a vacuum or low atmospheric pressure environment using a plasma system loaded with the desired material. The adherent micro- or nanoscale layer is formed by melting and sintering.	The coating formed by this method can consist of defects (e.g., pits, voids, microcracks, and pores) that are detrimental to electrochemical stability, but a close packing feature of the coating and reinforcement compounds may compensate for these disadvantages, enhancing the corrosion resistance.	[38•, 117, 118]
Hydrothermal- and alkali-based treatment	The implant surface is exposed to NaOH or KOH aqueous solutions, which can be submitted to a heating treatment or not, developing a layer with a range of morphologies features.	The dense and large coating thickness formed from this treatment physically isolates the substrate from the corrosive fluid, preventing its penetration into the coating underneath and providing effective initial protection.	[119–121]
Ion implantation	This surface modification process injects ions into a solid material by an ion implanter, causing a change in surface chemical composition.	The influence of this method on the electrochemical stability of implant materials is related to changes in the crystallinity of the microstructure or alterations in the oxide composition of the passive film, which can improve the corrosion resistance.	[122–124]
Polyelectrolyte multilayers	It is accomplished by the layer-by-layer technique that is performed by alternating the deposition of oppositely charged macromolecules to the desired number of layers, presenting different chemical nature, morphology, and thickness.	The presence of multilayers reduces the electrolyte permeability due to the strong ionic pairing between polyelectrolytes in adjacent layers. These coatings also can display an intrinsic self-healing behavior because of the introduction of nano-reservoirs or nano-reactors within the multilayer structure, exhibiting an improved corrosion behavior.	[125–127]

the surface treatment technology: (i) the formation of stabler oxide films containing TiO_2 , ZrO_2 , Nb_2O_5 , Ta_2O_5 , etc. and certain crystallinity potentially contribute to prevent the internal dissolution of the coating due to corrosive attacks; (ii) dense, compact, and defect-free layers can successfully fill the existing porosities of the substrate, preventing the corrosive fluid to reach the surface of the implant; (iii) thick layers may decrease and even mitigate the dissolution of the coatings in the immersion medium; (iv) an improved ability of substrates to form passive layers after coating/film deposition leads to better protective behavior; and (v) a strong bond strength between the coating and the substrate might avoid the coating cracking and peeling off in the body fluid, avoiding local corrosion.

Besides the intrinsic characteristics of the film/coating, it is important to consider the final alterations that the surface treatment will result in the physical-chemical properties of the dental implant that may hinder or improve the material's electrochemical stability. For example, some researchers have focused on creating a surface with hydrophobic nature to restrict or repeal the electrolyte solution at the surface, preventing liquid penetration through the coating and protecting the underlying substrate from corrosion [114, 117]. On the other hand, a detrimental behavior from the physicochemical alterations provoked by treatment techniques is also possible. For instance, increased surface roughness and surface area may impair the passive film formation and facilitate its damage, favoring pitting corrosion initiation [97–99]. Besides, increased electrochemical activity of treated surfaces may be incited by greater wettability, which results in lower contact resistance between the electrode and electrolyte that can have an even more negative outcome if a higher surface area is available for ion transportation [54, 128].

Conclusions and Remarks

Despite the need for further in vitro and in vivo in-depth elucidation regarding the effect and mechanisms of dental implant corrosion products on peri-implant tissue inflammation and systemic health, current evidence displays that there is room for the development of improved strategies toward the reduction of implant corrosion rate targeting real progress from the bench to the clinic. Regardless of the strategy, either designing experimental Ti alloys or developing new treatment surfaces, the aim converts to the same spotlight: to reduce the degradation level of the implants and prevent metal release in the tissue surrounding them to prolong their lifetime. It is evident that the chemical and physical properties are crucial for the electrochemical behavior of the implant material. Thus, developing an alloy or coating/layer for corrosion inhibition is mandatory to investigate these

features and consider biological applicability. For instance, incorporating some functional compounds into the substrate may improve the corrosion resistance of the implant material, but it can also be cytotoxic for tissues. On the other hand, although hierarchal structure topography with a greater surface area might improve the biological response of the implant, it may exhibit unwanted effects on the growth and stability of the oxide film, impairing its corrosion properties. The ultimate goal is to find reliable routes to conjugate in the same implant both characteristics, adequate stimulation of the biological tissues without weakening its protective behavior against corrosion. Therefore, based on the data discussed in this review, it can be suggested that an extensive understanding of the involved corrosion mechanism should be the basis for the design of dental implant devices. Full knowledge of the role of corrosion products and better methods to improve the corrosion resistance of dental implants can illuminate how to control peri-implant diseases and achieve safe and long-term implant rehabilitation therapy.

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Declarations

Conflict of Interest The authors declare no competing interests.

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