

Effect of Fluoride and Bleaching Agents on the Degradation of Titanium: Literature Review

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Abstract

The use of mouthwashes and dental gels containing fluorides has increased in recent years as well as the dental bleaching agents. However, such agents can be in contact with surfaces of dental restorative, prosthetic and implant systems at high concentration in the oral cavity. That can adversely affect the corrosion resistance of titanium and its alloys. The purpose of this review was to summarize the current data regarding the influence of fluoride and bleaching agents on the degradation of titanium and Ti6Al4V alloy surfaces. Books, chapters and full-text articles were identified on Medline and hand searches applying the following search items: "titanium and fluorides"; "titanium and hydrogen peroxide"; "titanium and ion release"; and "titanium and degradation". Thirty eight studies from an initial yield of 180 studies were selected. Results indicated that therapeutic substances used in dental practice such as fluoride, hydrogen and carbamide peroxides are related to corrosion and wear processes of titanium-based structures. Consequently, corrosive processes occurring on titanium lead to the release of ions and wear particles to surrounding peri-implant tissues and organs. However, the relation between ion release and inflammatory reactions into human tissues is not clear yet.

Keywords: Titanium; Hydrogen peroxide; Carbamide peroxide; Fluorides; Ion release

Introduction

Since the intensive work accomplished by Branemark [1], titanium and its alloys have been the first choice materials to fabricate dental implant systems and prosthetic infra-structures in oral rehabilitation supported by implants. Titanium and its alloys have a significant clinical performance due to their properties, such as low density around 4.5 g/cm³, low elastic modulus (110-140 GPa), high mechanical strength (tensile strength around 950 MPa), high corrosion resistance and excellent biocompatibility [2,3].

In fact, the corrosion resistance and biocompatibility of titanium and its alloys are resultant from the composition and structure of the titanium oxide film on the surface [3]. That oxide film primarily composed of TiO₂ acts like a protective and compact thin barrier ranging from 2 to 20 nm in thickness [1,3,4]. This layer is also named passive film due to its low reactivity with the surrounding environment [3,5]. This oxide layer can reduce ion release from bulk Ti to the biological environment [2]. Nevertheless, the titanium oxide film can be destroyed in the presence of corrosive substances or wear in the oral cavity [3,4,6].

The destruction of the titanium oxide film exposes fresh titanium to the corrosive environment leading to the degradation of titanium-based oral structures including dental implants and frameworks [3,7,8]. The simultaneous degradation by wear and corrosion can significantly increase the material loss and failures of those structures [4,9-12]. Recently, several previous studies have revealed corrosion of titanium and its alloys after exposure to therapeutic agents such as fluorides and hydrogen peroxide [3,13-16]. As a result from degradation process, the release of Ti ions and particles from CP-titanium or Ti, Al, V ions from titanium alloys to the surrounding tissues can stimulate an initial inflammatory response. The presence of released metallic ions and particles is considered a risk factor for the development of peri-implant inflammation [17,18]. Consequently, the diffusion of Ti, Al, V into the bloodstream can lead to cytotoxicity, mutagenic and or carcinogenic reactions considering previous studies in literature [18-20].

Implant-supported prostheses reveal microgaps at abutment-implant or abutment-prosthesis connections that can accumulate corrosive substances for long-term period [3,4,8]. In this sense, acidic substances with high corrosive potential such as fluorides or bleaching agents can get into the micro-gaps and promote corrosion. The degradation process of titanium and its alloys after exposure to therapeutic substances is a phenomenon that needs to be clarified in order to identify the consequences of this process and the eventual detrimental effects to patients.

Fluorides and corrosion of titanium

The use of mouthwashes and dental gels containing fluorides to prevent caries and to treat tooth hypersensitivity has been increased in recent years. However, high concentration of fluorides adversely affects the corrosion resistance of titanium and its alloys [4,14,21-23]. In fact, high concentrations of fluoride in an aqueous solution promote an association between H⁺ and F⁻ ions forming hydrofluoric acid (HF), which is corrosive to many materials including titanium. Although HF is considered a weak acid, the strong reactivity of HF molecules is extremely aggressive to metallic materials, glass-ceramics or living tissue. Thus, the corrosion resistance of Ti and its alloys depends on the fluoride concentration and pH of the surrounding solution. The possibility of corrosion is accurately predicted from the relationship between pH and F⁻ ions concentration as shown in the study of Nakagawa [22], whereas a linear threshold to localized corrosion at 30 ppm of HF [22,24]. The formation of HF concentration above 30 ppm

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revealed to have a destructive effect on the protective titanium oxide film [22].

In an acidic environment, it is suggested that localized corrosion occurs even at lower concentrations of fluorides [22]. Localized corrosion on titanium can take place in a solution containing 452.5 ppm F⁻ at pH 4.2 or in a solution containing 227 ppm F⁻ at pH 3.8. At higher pH, low F⁻ concentrations might not destroy the protective titanium oxide layer although can negatively affect the corrosion resistance of titanium [22,25]. F⁻ ions were detected at different concentrations up to 920 ppm F⁻ through the extracellular matrix in biofilms [26,27]. That can, slowly generate high F⁻ amounts close to dental surfaces. For instance, localized corrosion on titanium surface can occur at 227 ppm F⁻ and pH 3.8 [22,23]. On the other hand, gels, varnishes or solutions including high F⁻ content (9000-26000 ppm F⁻) often used for hypersensitivity treatment of natural teeth or after dental bleaching can also contact titanium-based surfaces of prosthetic structures or implant-abutment connections. For example, localized corrosion was detected on titanium surfaces in a solution containing 12300 ppm F⁻ at pH 6.5 due to the pitting corrosion process [23]. Some previous studies relating the effects of fluorides on titanium are shown in Table 1.

Thus, patients who wear titanium based implant and prostheses must be informed on the negative effect of high F⁻ concentration agents associated with acidic substances. So, it is of major importance that dentists check the clinical history of the patients in order to evaluate the presence and composition of dental implants and prostheses.

Previous studies also revealed that the chemical composition, structure and dielectric properties of titanium oxide film determine the corrosion resistance of titanium in corrosive substances [24]. A study has shown that adding 0.1-0.2% platinum (Pt) or palladium (Pd) in the composition of a titanium alloy cause dan effective improvement of the corrosion resistance of titanium in solutions containing up to 2% NaF.

Effect of bleaching agents on the corrosion of titanium

Hydrogen and carbamide peroxides are substances commonly used in dentistry as bleaching agents. Their concentrations vary between 1.5 and 35% depending on the use; that can be applied by patients under professional guidance or by dentists in the dental office. In the dental office, bleaching agents are used at high concentrations up to 35% hydrogen peroxide. A dissociation of carbamide and hydrogen peroxide takes place in the presence of high temperature or light, similarly to what occurs in the oral cavity. That promotes an effective reaction of the bleaching agent with the surface leading to the destruction of the titanium oxide layer and titanium corrosion [28]. Higher values of roughness were revealed on titanium immersed in 35% hydrogen peroxide solutions when compared with groups immersed in 16% carbamide peroxide solutions [29]. Concerning the last study, significant surface alterations were noticed on CP-Ti compared to those on Ti6Al4V [29]. However, other studies have shown no difference between the corrosion of commercially pure titanium (CP - Ti) and Ti6Al4V alloy. Previous studies relating the effects of bleaching agents on titanium are shown in Table 1.

Gingival barriers are used to avoid contact of the bleaching agent at high content with other areas that could promote damage to the surrounding soft tissues [30]. However, bleaching agents can reach the surfaces of restorative, prosthetic and implant systems. For example, titanium-based infrastructure and abutments as well as implant connections may come into contact with those substances. Materials with lower corrosion resistance are more susceptible to degradation in environment containing such corrosive substances [13].

Titanium degradation and its consequence

The degradation of titanium-based prostheses and implants

RESEARCH	ALLOY TYPES	FLUORIDE ORBLEACHING AGENT CONTENT (pH)	EFFECTS
Souza et al. [4,23]	CP titanium grade II, Ti6Al4V	20 ppm F (5.5)	OCP and EIS results on 0 upto 227 ppm indicated a passive film formation
		30 ppm F (5.5)	EIS and OCP results at 12300 ppm indicated an increase of the chemical reactivity on titanium
		227 ppm F (5.5) 12300 ppm F (6.5)	Significant increase of the weight loss up to 227 and 12300 ppm and consequently a localized corrosion of titanium
Mabilleau et al. [14]	CP titanium grade II	5000 ppm F	Corrosion of the surface was observed by SEM and AFM
		25000 ppm F 0.1% H ₂ O ₂ 10% H ₂ O ₂	Significant increase of Ra roughness occurred after immersion in the media
Mayouf et al. [21]	Ti-30Cu-10Ag CP titanium grade II Ti-6Al-4V	0.01M NaF (7.2)	The presence of 0.01 and 0.05M NaF at pH 7.2 had a higher negative effect on the corrosion resistance of TiCuAg than that recorded on Ti and TiAlV
		0.05M NaF (7.2)	TiAlV has a lower corrosion rate at 0,5M NaF in comparison with Ti and TiCuAg
		0.5M NaF (7.2)	The high concentration of NaF had a significant effect on TiCuAg
		0.01M NaF(3.0)	At pH 3,TiCuAa showed a lower corrosion rate than that of Ti and TiAlV
Nakagawa et al. [22]	CP titanium grade II	90.5 to 9048 ppm F (3-7)	Corrosion resistance of titanium was maintained in the 2% NaF at pH higher than 6,2 The titanium corroded in a solution at pH below 6,2
Nakagawa et al. [24]	CP titanium grade II Ti-6Al-4V Ti-6Al-7Nb Ti-0.2Pd	226 to 9048 ppm F (3-7)	CPTi, Ti-6Al-4V and Ti-6Al-7Nb alloys were easily corroded even at low fluoride concentration in acidic environment The corrosion resistance of Ti-0.2Pd alloy was higher
Nakagawa et al. [25]	CP titanium grade II Ti-6Al-4V Ti-6Al-7Nb Ti-0.2Pd Ti-0.5Pt	226 to 2262 ppm NaF (5-6,5)	CP Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys corroded in fluoride solutions containing 453 ppm F Ti-0.2Pd and Ti-0.5Pt revealed higher corrosion resistance than that recorded on the other alloys
Faverani et al. [30]	CP titanium grade II Ti-6Al-4V	16% carbamide peroxide 35% carbamide peroxide 35% hydrogen peroxide	Bleaching agents caused significant changes on the surfaces of both materials tested

Table 1: Summary of previous studies reporting the effect of fluorides or bleaching agents on titanium and its alloys.

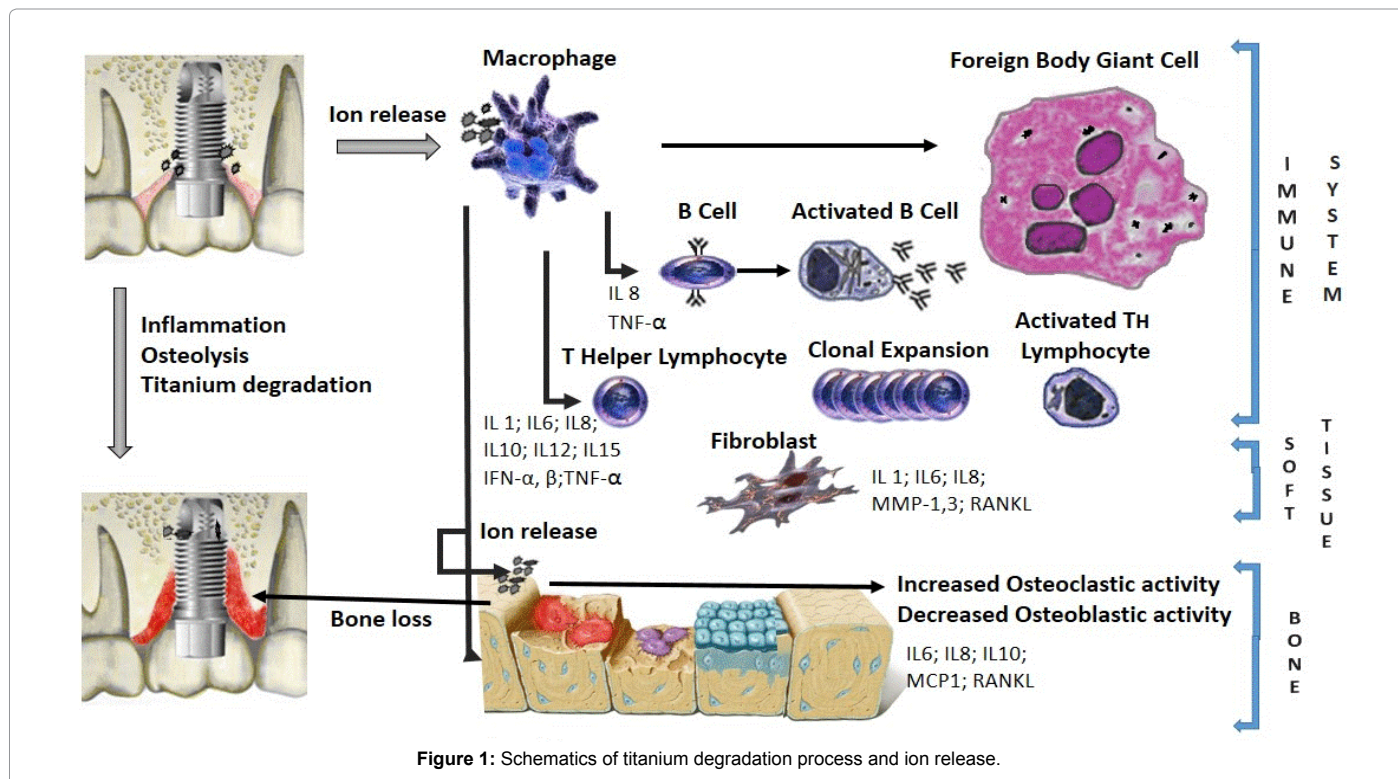


Figure 1: Schematics of titanium degradation process and ion release.

depends mainly on the conditions of the oral environment [3,31]. These conditions involve acidic pH, presence of reactive substances, oxygen concentration and temperature. Additionally, a corrosive physiological environment in combination with cyclic loads (fatigue) and wear can significantly increase the degradation of prosthetic infrastructures and dental implant connection systems [4,5,9-12]. Thus, the destruction of the titanium oxide film exposes the fresh titanium to mechanical and electrochemical interactions increasing the degradation of the Ti-based structure [4].

The degradation of titanium can cause four main phenomena: corrosion processes affecting mechanical integrity of structural materials; change in the electrochemical reactions; increase of roughness; and release of ions [11,12]. Mechanical aspects such as forces applied, the contact geometry and type (sliding, fretting, rolling or impact) determine the corrosion rate of titanium-based structures [5].

Although titanium and its alloys show higher corrosion resistance than several metallic materials applied in oral rehabilitation, simultaneous degradation by corrosion and wear takes place resulting in corrosion products such as ions and particles. Ions and metallic particles are deposited on surrounding tissues penetrating across tissues and the bloodstream that can promote local or systemic toxicity. In previous studies, Ti particles were detected at the peri-implant tissue as well as in organs like liver, kidneys and lymph nodes [19,32,33]. On peri-implant areas, high amounts of Ti particles were detected in the surrounding bone suggesting that metallic particles were released from wear, corrosion or fatigue phenomena [19,33]. Clinically, the release of metallic ions from titanium-based structures stimulate the attraction of macrophages and T lymphocytes from the immune system [18,32,34-36]. High amounts of inflammatory mediators involved in bone resorption and peri-implant disease have also been associated to metallic release as illustrated in Figure 1 [18,19].

Ions and particles composed of titanium are insoluble in physiological medium that results in high storage level and low content on the urine excretion [37]. However, aluminum and vanadium, are much more soluble leading to a high cytotoxic effect [38]. Ti6Al4V alloys used to fabricate abutments can release Al and V ions to surrounding tissues during wear, fatigue and corrosion processes [27]. Concerning the cytotoxic potential of those released metallic ions and particles, other titanium alloys have been developed to produce prosthetic structures and abutments for oral rehabilitation supported by implants.

Conclusion

Considering the literature data, dental therapeutic agents such as fluorides or hydrogen peroxide significantly influence to the degradation of titanium-based by corrosion and wear processes. The degradation rate of such structures is dependent of exposure time, pH and concentration of the corrosive substances. The deteriorative effect results in release of metallic ions and particles that stimulate the attraction of inflammatory cells from immune system. Such inflammatory process can be associated to peri-implant disease determining the long-term success of oral rehabilitation structures. In fact, the degradation of titanium and its alloys in the oral cavity is a phenomenon that needs to be clarified in order to prevent failures of dental implant and prostheses, to avoid eventual detrimental effects to the patients, and to improve the performance of titanium-based oral rehabilitation systems. Thus, it is of major importance that dentists check the clinical history of the patients in order to evaluate the presence and composition of dental implants and prostheses before use of fluorides or bleaching agents.

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