

Influence of a Fluoridated Medium with Different pHs on Commercially Pure Titanium-Based Implants

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Abstract

Purpose: The objective of this study was to assess the influence of a fluoride medium with different pHs on the corrosion resistance of three commercially pure titanium-based dental implant commercial brands, under scanning electron microscopy (SEM) and EDS.

Materials and Methods: Forty-two dental implants, from three commercial brands, were used. Five years of regular use of mouth rinsing, with NaF 1500 ppm content and two different pHs, were simulated by immersing the specimens into that medium for 184 hours.

Results: SEM and EDS analyses demonstrated no evidence of corrosion on the specimens' surfaces after being submitted to fluoride ions or incorporation of fluoride ions to the set surface.

Conclusion: It was possible to conclude that both the fluoride concentration and the pH of the solutions did not exert any influence upon implant corrosion resistance.

The use of titanium and its alloys as biomaterials demonstrates a high success rate, due to a favorable combination of mechanical, physical, and chemical properties, such as low density, high mechanical resistance, low elasticity coefficient, high corrosion resistance, and excellent biocompatibility.^{1,2} The success of titanium and its alloys is directly related to these properties, as the biomaterial used will be constantly submitted to mechanical and thermal stresses, as well as to the harmfulness of the host medium.³

Besides mechanical stresses, it is presumed that implants will also be exposed to harmful elements, such as bacterial plaque and saliva, in the oral cavity. This environment is particularly favorable to metal biodegradation due to its thermal, ionic, microbiological, and enzymatic properties.⁴ Thus, the need for development and evaluation of materials resistant to both wear and corrosion is evident.

The high corrosion resistance of titanium is due to the formation of a dense and stable layer of titanium oxide on its surface. Titanium oxide is responsible for chemical stability in the human body.⁵⁻⁷ This layer is formed quickly because of the reactivity of the titanium with oxygen, which originates several oxides, with TiO_2 being the major oxide formed. The thickness of this layer ranges between 10 and 20 nm, and must not be disrupted under any condition.⁸ Considering this, commercially pure (cp) titanium, widely used in implant manufacturing, features a higher resistance to corrosion than other titanium alloys.⁹

This corrosion resistance level stands high when exposed to most of the mineral acids, even within rather harmful media, such as HCl (hydrochloric acid) or H_2SO_4 (sulfuric acid), resulting in extremely low corrosion under these conditions.^{3,8,10,11}

Fluoride ions are one of the few media that have the ability to provide a corrosive effect to a titanium surface. When titanium is exposed to fluoride, its oxide layer is damaged, and titanium is then easily degraded. This is due to the incorporation of fluoride ions in the oxide layer, considerably decreasing its protective properties.^{7,8,12-14}

Table 1 Dental implants used

Material	Manufacturer	
External hexagonal implant, smooth surface—Titamax Liso®	Neodent, Curitiba, Brazil	7
External hexagonal implant, treated surface—Titamax Poros®	Neodent, Curitiba, Brazil	7
External hexagonal implant, smooth surface—ICE®	3i Implant Innovations Inc., Palm Beach Gardens, FL	7
External hexagonal implant, treated surface—Osseotite®	3i Implant Innovations Inc., Palm Beach Gardens, FL	7
External hexagonal implant, smooth surface—MK III Ti®	Nobel Biocare AB, Göteborg, Sweden	7
External hexagonal implant, treated surface—MK III Ti Unite $^{\textcircled{B}}$	Nobel Biocare AB, Göteborg, Sweden	7

In the last 40 years, the use of fluorinated gels and solutions containing high levels of fluorides as prophylactic means in dentistry has increased every year due to the great impact on caries prevention.¹⁵ The presence of fluoride in materials used in dentistry on titanium surfaces has been studied. Fluoride has been reported to cause damage to implant surfaces.^{12,16} Solutions containing more than 20 ppm of fluoride ion can destroy the titanium oxide layer.¹⁷

Most of the studies found in the literature^{8,12,13,16} used cp Ti discs to evaluate the process of corrosion caused by the fluorides. High concentrations of fluoride associated with an extremely acidic pH initiated a corrosive process of titanium, which interfered in its mechanical properties, decreasing both the hardness and the resistance to fatigue.^{8,13}

Fluorides cause corrosion in titanium and make exposed surfaces in the oral cavity rougher. This surface facilitates the attachment of microorganisms, making mechanical debridement of plaque difficult (brushing movements, deglutition movements, and crevicular fluid flow). The presence of microorganisms can cause an inflammatory reaction, which may lead to the development of peri-implantitis. If not appropriately treated, this may lead to bone destruction around the implant.¹⁸⁻²⁰

The objective of this study was to evaluate if the fluoride concentration found in most dentifrices with varying pHs can cause deterioration of the surface of cp Ti-based dental implants.

Materials and methods

Forty-two dental implants, from three commercial brands, were used. They featured two types of surfaces, machined and treated, as described in Table 1.

Siirilä and Könönen¹⁶ established a model that simulated clinical conditions of ideal fluoride use. The sets were tested

Table 2 Groups tested (n)

	Group A Control	Group B NaF 1500 ppm (pH 5.3)	Group C NaF 1500 ppm (pH 7.4)
Titamax Liso—Neodent	7	7	7
Titamax Poros—Neodent	7	7	7
ICE—3i	7	7	7
Osseotite—3i	7	7	7
MK III—Nobel	7	7	7
MK III TiUnite—Nobel	7	7	7

in a simulation with a mean exposure to fluoride ions for a period of 5 years of use within the oral environment and were compared to groups referred to as control, that is, with no fluoride ion exposure. The sets were then divided into groups (Table 2), according to the pH of the fluorinated solution and to the type of implant surface, where group A (control) was immersed in distilled water, group B (test) was immersed in a fluorinated solution with 1500 ppm and pH 5.3, and group C (test) was immersed in a fluorinated solution with 1500 ppm and pH 7.4.

In the test groups, the sets were statically submerged (Fig 1) in a fluorinated medium for 184 hours (7.5 days), simulating contact with fluoride ions for a period of 5 years, i.e., 21 times per week, with an average of 2 minutes each time (estimate of brushing average three times per day with fluoride-content dentifrice). The solution was changed every 12 hours, and the sets submerged were then washed in tap water for an interval of 30 seconds before being submerged again into the replaced solution. In the control group, the same procedure was repeated with the sets submerged in distilled water.

Scanning electron microscopy (SEM)

All implants were evaluated under SEM (JEOL-JSM T-330^A) before and after exposure to the fluorinated solutions to verify the corrosive action of fluoride ions. All images were evaluated by one examiner blind to implant brand and immersion solution.

Energy dispersive X-ray spectrometric (EDS) assessment

The implants were evaluated under EDS before and after exposure to the fluorinated solutions to verify the incorporation of fluoride ions to the titanium surface.

Results

Macroscopically, loss of brightness and stains on the surface could be observed in all the implants of all commercial brands exposed to the fluorinated solution; the alterations were more evident in the groups exposed to the more acidic fluorinated solution (Fig 2).

SEM assessment confirmed that the surface of the control group titanium implants showed that irregularities originated from either surface treatment or machining process; however, there were no traces of corrosion (Figs 3–5).





Figure 1 Implant submerged in the solution.



Figure 2 Implant $3^{(B)}$. Left—implant before exposition. Right—implant after exposition.



Figure 4 SEM of Neodent implant, treated surface-control group.

Nevertheless, in the groups exposed to the action of fluorides, it was possible to observe that Nobel, 3i, and Neodent implants showed some dark spots on the titanium surface, regardless of fluorinated solution pH and superficial treatment (Figs 6–8).

Under EDS assessment, all implants, regardless of brand, group, or surface, predominantly demonstrated titanium (99%). None of the groups showed presence or incorporation of fluoride ions to the titanium surface (Fig 9).

Discussion

The titanium oxide layer, highly stable chemically and comprising several oxides, TiO_2 among them, provides high corrosion resistance to titanium and chemical stability in the human body.^{6,7} Even in contact with mineral acids, such as HCl, H₂SO₄, and HNO₃, this oxide layer of 10 to 20 nm in thickness maintains its stability, featuring an extremely low corrosion rate during those situations.^{3,8} However, this layer cannot maintain its stability in contact with fluoride. Fluorides are incorporated in the oxide layer, forming compounds of titanium oxide fluoride, titanium fluoride, or titanium sodium fluoride, disorganizing the oxide layer stability and reducing its protective properties.^{7,8,12-14,21} In other words, fluoride ions can form



Figure 3 SEM of 3i implant, smooth surface—control group.



Figure 5 SEM of Nobel implant, smooth surface—control group.



Figure 6 SEM of Neodent implant, treated surface, after fluorinated solution

a soluble complex with titanium ions derived from the oxide layer. Without the oxide layer, the corrosive process acts upon titanium.

Several studies^{16,22-24} have demonstrated the effective action of fluoride on the titanium corrosive process, although in this present study, using a fluorinated solution (NaF) at a concentration of 1500 ppm, no evidence of corrosion was found. This concentration is used in dentifrices, gels, and mouth-rinsing solutions currently in the market.

Several studies have found differences in the corrosion between the pH of fluorinated solution and gel, as demonstrated in studies by Toumelin-Chemla et al,⁸ Schiff et al,²² and Nakagawa et al;²³ nevertheless, in the present study, no degradation of the superficial structure was observed under SEM in the implant/component sets submitted to fluorinated solutions with different pHs. Only macroscopic discoloration of the sets submitted to fluorinated solutions could be observed. This was probably due to alterations in the oxide layer caused by the chemical reactions of oxygen, hydrogen, and fluoride, which did not favor the biomaterial degradation. The difference between the present study and those mentioned above can be attributed to the fluoride concentration used (concentrations



Figure 7 SEM of 3i implant, treated surface, after fluorinated solution.



Figure 8 SEM of Nobel implant, smooth surface, after fluorinated solution

higher than 1500 ppm) and to a more acidic pH (lower than 5.3).

In a study by Reclaru and Meyer.¹⁴ the corrosive process was observed under SEM only when the pH of the fluorinated solution was below 3.5, which is in accordance with this study, where the pHs used were 5.3 and 7.4, respectively. The statement that corrosion by fluoride ions is enhanced when the solution pH decreases was confirmed by Strietzel et al.¹²

In situations where the pH is extremely low, it is possible to observe stains and dark spots on the specimens under SEM, which can be interpreted as imperfections in the oxide layer, representing the initiation site of a corrosion pit, which is a form of corrosion observed mainly in passive metals such as titanium.¹⁰ This corrosion is characterized by the formation of grooves, in which there is no reestablishment of the oxide layer by oxygen inhibition; an anodic process is otherwise established.

Although neither corrosion evidence through SEM nor fluoride incorporation to the surface of the specimens through

Results Filter Fit Method Chi-sqd = 5.03 Livetime = 100.0 Sec. Standardless Analysis Error Net. Element Relative Error (1-Sigma) Counts (1-Sigma) k-ratio C -K 430 +/-29 726 +/-57 Ti-L 0.00055 +/- 0.00020 54 A1-K 148 +/-0.99945 +/- 0.00549 532 Ti-K 96798 Adjustment Factors Z-Balance: 0.00000 0.00000 0.0000 1.00000 Shell: 1.00000 1.0000 PROZA Correction Acc.Volt.= 15 kV Take-off Angle=31.9 Number of Iterations = 3 Ŀ. Flor LI+

LIGHEILC	V I GUIO	201	HCOM A	LIGHEUC	NO A LIT.
	(calc.)			Wt %	(1-Sigma)
A1-K	0.0006	1.559	0.15	0.09	+/- 0.03
Ti-K	0.9990	1.000	99.85	99.91	+/- 0.55
Total			100.00	100.00	

Figure 9 Result of EDS on the samples.

EDS has been observed, the macroscopic discoloration observed suggests that a partial corrosive process may be taking place. In Huang's study,⁷ all titanium specimens showed evidence of corrosion when the concentration of NaF was higher than 1000 ppm.

Nakagawa et al²³ suggest that instead of fluoride ions, hydrofluoric acid (HF) is the major factor responsible for the destruction of the titanium oxide layer. Initially, NaF is split into sodium ions and fluoride ions in the solution. The fluoride ion is partially converted into HF depending on the solution's pH, and after it is converted to HF, HF starts to affect titanium. The pH of the solution used in the present study was probably not acidic enough to convert sufficient amounts of fluoride ions into HF, thus having no effect on the titanium oxide layer.

Considering an in vivo situation in the oral cavity, there are other factors that may be acting not only to accelerate the process of corrosion but also to retard or abrogate the corrosive process, such as incorporation of hydrogen ions to the titanium surface²¹ as well as deposition of albumin.²⁴ However, given the variability of the oral environment, without further investigation, recommending the use of topical applications of fluorinated gels on cp Ti-based implants and structures should be done with caution.

Conclusion

Within the limitations of this study, it is possible to conclude that there were no significant alterations in the corrosion resistance of dental implants with the use of fluorinated solutions, regardless of the solution pH, the implant brand, or surface type.

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