ORİJİNAL ARAŞTIRMA ORIGINAL RESEARCH

DOI: 10.5336/dentalsci.2020-77759

## Investigation of the Sodium Titanate Surface Behavior in Corrosive Oral Fluids by Comparing with Conventional Titanium Surfaces

## Sodyum Titanat Yüzeyin Koroziv Sıvılardaki Davranışının Konvansiyonel Titanyum Yüzeyler ile Karşılaştırılarak İncelenmesi

<sup>●</sup>Ahmet Kürşad ÇULHAOĞLU<sup>a</sup>,<sup>●</sup>Özkan ÖZGÜL<sup>b</sup>,<sup>●</sup>Umut TEKİN<sup>b</sup>,<sup>●</sup>Ercüment ÖNDER<sup>b</sup>

<sup>a</sup>Department of Prosthetic Dentistry, Kırıkkale University Faculty of Dentistry, Kırıkkale, TURKEY <sup>b</sup>Department of Oral and Maxillofacial Surgery, Kırıkkale University Faculty of Dentistry, Kırıkkale, TURKEY

This study is partially presented orally in AÇBİD 13th International Congress, 24-28 April 2019, Antalya, Turkey

ABSTRACT Objective: Titanium (Ti) and Ti alloys are suitable options as implant material because they are biocompatible and form a corrosion protective titanium oxide layer. However, the oxide layer is sensitive to corrosive ions such as fluoride (F) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which are normally found in human mouth. Commercially produced toothpastes, mount rinses and cariostatic gels contain between 0.1% and 1% content F concentration. Furthermore, H<sub>2</sub>O<sub>2</sub> can be secreted during inflammatory reactions by bacteria in oral environment. The corrosion of dental implants and components can cause failure of dental implant treatment. The aim of this study was to analyse the effects of different F and H2O2 concentrations on different treated Ti alloy (Ti6Al4V) in surfaces. Material and Methods: The effects of different F (0.5%, 2.5%) and  $H_2O_2$  (0.1%, 10%) concentrations on different treated Ti6Al4V surfaces [electro-polished, roughed, fine-roughed and sodium titanate-treated (NaTi)] were analysed. Scanning electron microscopy and inductively coupled plasma with optical emission spectrometer provided quantitative bulk elemental composition for Ti samples. Results: Median corrosion values of Ti (mg/L) and V (mg/L) corrosion levels in 10% H<sub>2</sub>O<sub>2</sub> and 2.5% F solutions were significantly higher than 0.1% H<sub>2</sub>O<sub>4</sub>, 0.5% F and control solutions. Median Ti corrosion values observed in electro-polished, roughed and fine-roughed groups were statistically higher than NaTi treated surfaces. Conclusion: This study shows that low ion release on NaTi surfaces causes the least amount of corrosion. Consequently, NaTi coating should be considered as the best alternative for protecting Ti surfaces from corrosion.

Keywords: Corrosion; titanium surface; NaTi titanium alloy; corrosive ions

ÖZET Amaç: Titanyum (Ti) ve Ti alaşımları biyouyumlu olmaları ve korozyon koruyucu titanyum oksit tabakası oluşturmaları sebebi ile implant malzemesi olarak uygun seçeneklerdir. Bununla birlikte, oksit tabakası diş hekimliğinde kullanılan koruyucu solüsyonların aşırı kullanımına ve florür (F) ve hidrojenperoksit (H<sub>2</sub>O<sub>2</sub>) gibi insan ağzında bulunabilen aşındırıcı iyonlara karşı duyarlıdır. Diş macunları ve ağız gargaraları %0,1-%1 içerik F konsantrasyonu içerir. Ayrıca H2O2 oral alanda bakteri tarafından inflamatuar reaksiyonlar sırasında salgılanabilir. Dental Ti implantların ve bilesenlerinin korozvonu dental implant tedavisinin başarısız olmasına neden olabilir. Bu araştırmanın amacı, farklı F ve H2O2 konsantrasyonlarının farklı muamele edilmis Ti yüzeyleri üzerindeki etkilerini analiz etmektir. Gereç ve Yöntemler: Farklı F (%0,5, %2,5) ve H<sub>2</sub>O<sub>2</sub> (%0,1, %10) konsantrasyonlarının, farklı şekillerde hazırlanmış Ti yüzeyleri [elektroliz ile parlatılmış, kumlanmış, ince kumlanmış, sodyum titanat (NaTi) ile kaplanmış] üzerindeki etkileri, taramalı elektron mikroskobu ve endüktif olarak eşitlenmiş plazma optik emisyon spektrometresi ile analiz edilmiştir. Bulgular: %10 H2O2 ve %2,5 F çözeltilerinde Ti (mg/L)] ve V (mg/L) elementlerinin ortalama korozyon değerleri, %0,1 H<sub>2</sub>0<sub>4</sub> ve %0,5 F ve kontrol çözeltilerinden anlamlı derecede yüksek bulunmuştur. Ayrıca elektroliz ile parlatılmış, kumlanmış ve ince kumlanmış gruplarda gözlemlenen ortalama Ti korozyon değerleri, NaTi ile işlenmiş yüzeylerden istatistiksel olarak anlamlı derecede daha yüksek bulunmuştur. Sonuç: Elde edilen verilere göre düşük iyon salınımı göstermesi sebebi ile NaTi yüzey kaplaması, Ti yüzeyleri korozyondan korumak için en iyi alternatif olabilir.

Anahtar Kelimeler: Korozyon; titanyum yüzey; NaTi titanyum alaşım; koroziv iyonlar

Available online: 22 Jan 2021

Correspondence: Ahmet Kürşad ÇULHAOĞLU Department of Prosthetic Dentistry, Kırıkkale University Faculty of Dentistry, Kırıkkale, TURKEY/TÜRKİYE E-mail: ahmetculhaoglu@hotmail.com



Peer review under responsibility of Turkiye Klinikleri Journal of Dental Sciences.

Received: 29 Jun 2020

Received in revised form: 28 Oct 2020 Accepted: 02 Nov 2020

2146-8966 / Copyright © 2021 by Türkiye Klinikleri. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). Titanium (Ti) and its alloys have been widely used in dental implantology, orthopedics and prosthodontics due to their high mechanical, physical properties and biocompatibility.<sup>1</sup>

The main feature of Ti metal biocompatibility is surface oxide film. Although a thin titanium oxide layer covering the Ti and Ti alloys would form an apatite layer on their surface for bonding to bone tissue, various surface treatment modifications have been proposed to enforce bone-bonding activity.<sup>2,3</sup> A thin layer of sodium oxide-titanium dioxide (Na<sub>2</sub>O-TiO<sub>2</sub>) is formed on Ti surfaces when sodium hydroxide (NaOH) is thermally applied to the surface. Emancipated sodium (Na) ions exchange with hydronium  $(H_3O^+)$  ions in simulated body fluids and form titania gel that stimulate apatite nucleation.<sup>2-4</sup> It had been previously reported that the apatite layer formed on Ti surfaces, which were subjected to NaOH and heat treatments, bonded tightly to surrounding bone tissues within 8 weeks, while non-treated Ti did not recover the same amount of the surrounding bone tissues despite the 12-week healing process.<sup>5</sup> Apatite layers found on sodium titanite (NaTi) immersed in simulated body fluid.<sup>6</sup>As an advantage of apatite nucleation and the short reported induction period for the apatite formation, alkali titanites can be used as bone substitutes under load-bearing conditions.<sup>7</sup>

Weakened wear resistance is the main mechanical consequence of the corrosion. Furthermore, dental plaque accumulation and increased element release are the long term biological devastating effects of abrasion. Regular use of dentifrices with different amounts of abrasives may cause abrading action on Ti surfaces due to the chemical alterations and degradation mechanisms. In addition to the devastating effect of toothpastes on the alloys, tooth brushing may result in superficial grooves on the titanium implant abutments.<sup>8,9</sup>

The presence of fluoride (F) and hydrogen peroxide ( $H_2O_2$ ) may cause corrosion of Ti alloys. F ions and  $H_2O_2$  are commonly found in oral environment. Flouride treatment is known to be the main method for preventing dental caries and plaque formation.<sup>10</sup> Commercially produced tooth pastes, mouth rinses and cariostatic gels contain between 0,1% and 1% of Turkiye Klinikleri J Dental Sci. 2021;27(1):89-97

F.<sup>11</sup> H2O2 can be produced by bacteria during inflamatory reactions in complex microbial system of the oral cavity.<sup>12</sup> Some oral hygiene products like toothpaste, mouth rinses, prophylactic gels, as well as some foods and water can contain high F concentrations (200 to 20.0000 ppm) and high F, H<sub>2</sub>O<sub>2</sub> concentrations may show detrimental effects on Ti.13-17 It is reported that even at these concentrations, corrosion on Ti was determined.<sup>10,18</sup> Moreover, F is not the only factor that causes titanium corrosion, also organic acids like lactic acid and formic acid can cause corrosion on Ti surfaces.<sup>19</sup> In addition, leukocytes and H<sub>2</sub>O<sub>2</sub> produced by bacteria during inflammation can cause corrosion on Ti surfaces.<sup>17</sup> High F and H<sub>2</sub>O<sub>2</sub> concentrations can change pH from neutral to acidic values. In this acidic environment, F ions form hydrofluoric acid (HF) which can be destructive on the passive film of Ti surface of dental restorations, implants and orthodontic wires over 30 ppm.<sup>20-22</sup>

Ti surfaces were treated with different surface characteristics such as surface topography and surface chemistry designed to enhance the biological response around different parts of implant. In addition, the corrosion resistance of titanium alloys mainly depend on the surface layer properties, and modifications of Ti surfaces may be required to improve.<sup>16</sup>

The corrosive effect of factors such as F and  $H_2O_2$  on refined Ti surfaces has been widely researched, yet the reactivity of these factors on different treated Ti surface has not been evaluated comparatively, especially on NaTi surface.

The aim of this study was to analyze the effects of different F and  $H_2O_2$  concentrations on different Ti surfaces. The analyses were conducted with scanning electron microscopy (SEM) and inductively coupled plasma (ICP), with optical emission spectrometer (OES) to provide quantitative bulk elemental composition for different Ti surfaces.

The null hypotheses of this research were that there will be no significant difference between the effects of different F and  $H_2O_2$  concentrations and different surface treatment methods such as electro-polished, roughed, fine-roughed, and NaTi coating does not have any effect on corrosion resistance on Ti surfaces.

## MATERIAL AND METHODS

### SURFACE PREPARATION OF SPECIMENS

Titanium alloy Ti6Al4V (ISO 5832-3, ASTM F67) specimens 1 mm of thickness and 10 mm diameter size were randomly divided into four experimental groups. The first group included electro-polished Ti. The second group included fine-roughed Ti treated with 100  $\mu$ m aluminic (Al<sub>2</sub>O<sub>3</sub>) sand-blasting procedure. In the third group, 300  $\mu$ m size aluminic (Al<sub>2</sub>O<sub>3</sub>) particles were used in order to acquire more roughed surfaces. The fourth group with sodium titanate (NaTi) was obtained by immersing specimens into 5N NaOH solution at 60°C for 48 hours which was then thermally treated at 600°C for 2 hours. The disks were ultrasonically cleaned in deionized water and sterilized in an autoclave at 121°C for 20 minutes.

### **TEST SOLUTIONS**

Every sample was tested in five different solutions to assess the corrosion rate. An artificial saliva was prepared based on the widely used Fusayama Meyer's solution, since it resembles the natural saliva.<sup>10</sup> The composition of the Fusayama's artificial saliva solution used is given in Table 1. The second and third mediums had the same content enriched with NaF at concentration of 0.5% (5 g/L) and 2.5% (25 g/L). The fourth and fifth mediums were prepared by enriching Fusayama's artificial saliva solution with H<sub>2</sub>O<sub>2</sub> at 0.1% and 10% H<sub>2</sub>O<sub>2</sub> concentrations.

Prepared specimens were dipped into the test solutions at a rate of 10 ml per sample area (10 cm<sup>2</sup>) for 9 days and sealed to prevent evaporation. Samples were incubated at 37°C under 100% humidity and rinsed daily. Test solutions were changed every 3 days.

TABLE 1: Composition of the Fusayama's artificial saliva.							
Compounds	(g/L)						
NaCl	0.4						
KCI	0.4						
CaCl <sub>2</sub> •2H <sub>2</sub> O	0.795						
Na <sub>2</sub> S•9H <sub>2</sub> O	0.005						
NaH <sub>2</sub> PO <sub>4</sub> •2H <sub>2</sub> O	0.69						
Urea	1						

# INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

The concentration of corrosion rate and elemental release of Ti, aluminum (Al), vanadium (V) ions at different corrosive solutions was analysed with static immersion test method according to International Standards Organization (ISO) 10271:2001by using ICP-OES. Detection limit was below 0.01 ppm.<sup>23</sup>

### SCANNING ELECTRON MICROSCOPY

Three samples in each group were examined with SEM analysis. Each sample air was dried for 1 minute and coated with 200 Å of gold-palladium for 5 minutes at a flow rate of 10 mA. Specimens were examined and photographed with SEM (Carl Zeiss AG-EVO 40) at 20-kV accelerating voltage under 500X magnifications.

### STATISTICAL ANALYSES

Release amounts of Ti, Al and V ions were compared between the experimental groups. Since the data were nonparametric, Kruskal-Wallis one-way analysis of variance tests were performed. Differences were considered significant at p<0.05. Relationships among the corrosion of Ti, Al and V values were analyzed by Spearman's correlation analysis with the significance set at 0.05. All analyses were performed using the SPSS Statistics 12 software pac.

## RESULTS

# INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROMETRY RESULTS

The release amounts of Ti, Al and V in each solution on different surfaces is shown in Figure 1. It was noticed that increased concentrations of Ti, Al and V are released from all surfaces with increasing concentrations of  $H_2O_2$  and F solutions. Furthermore, roughed and fine-roughed surfaces showed remarkable Ti dissolution at 10%  $H_2O_2$  and F solutions, whereas NaTi surface showed the least Ti dissolution.

Table 2 presents differences among four surface properties in terms of corrosion values. Although differences among the corrosion values of V (mg/L) and Al (mg/L) for both surface treatment groups were not statistically significant (p>0.05), statistically signifi-



FIGURE 1: Amount of released Ti, Al and V elements in each solution at different surfaces.

TABLE 2: Differences between four different surface   properties in terms of corrosion values.										
		Median	IQR	z	p value	Difference				
Ti (mg/L)	Electro polished	1.38	4.609	13.007	0.005*	1.3-4				
	Roughed	0.39	3.475							
	Fine roughed	0.55	5.030							
	NaTi	0.05	0.894							
V (mg/L)	Electro polished	0.07	0.074	2.926	0.403	-				
	Roughed	0.09	0.142							
	Fine roughed	0.12	0.156							
	NaTi	0.07	0.096							
AI (mg/L)	Electro polished	0.07	0.057	4.472	0.215	-				
	Roughed	0.08	0.075							
	Fine roughed	0.06	0.047							
	NaTi	0.08	0.052							

\*:p<0.01; IQR: Interquartile range

cant differences were observed for Ti (mg/L) values (p<0.05). Ti (mg/L) corrosion values on electro-polished and fine-roughed groups were statistically higher than Ti (mg/L) corrosion levels on NaTi surfaces.

Differences in corrosion values of five different solutions are presented in Table 3. Significant differences were observed for Ti (mg/L), V (mg/L) and Al (mg/L) corrosion levels at 10% H<sub>2</sub>O<sub>2</sub>, 0.1% H<sub>2</sub>O<sub>2</sub>, 2.5% F, 0.5% F and control solution groups. Median corrosion values of Ti (mg/L), V (mg/L) corrosion levels at 10% H<sub>2</sub>O<sub>2</sub>, and 2.5% F solutions were significantly higher than 0.1% H<sub>2</sub>O<sub>2</sub>, 0.5% F and control solutions. Also Al (mg/L) corrosion value at 0.1%  $H_2O_2$  was significantly higher than 2.5% F and 0.5% F solutions.

### SCANNING ELECTRON MICROSCOPY ANALYSES RESULTS

The surface micrographs of samples obtained from SEM are shown in Figure 2, Figure 3, Figure 4, Figure 5 and Figure 6. Overall changes were observed due to interaction between the solutions and specimen surfaces.

Characteristic surface textures of specimens are presented in Figure 2. Smooth, intact surface is

TABLE 3: Differences in corrosion values of five different solutions.								
		Median	IQR	Z	p value	Group differences		
Ti (mg/L)	10% H2O2	7.07	4.688	75.930	0.000*	1,3-2,4,5		
	0.1% H2O2	0.34	0.332					
	2.5% F	4.34	3.259					
	0.5% F	0.24	0.637					
	control	0.10	0.116					
V (mg/L)	10% H2O3	2.00	0.923	70.432	0.000*	1,3-2,4,5		
	0.1% H2O3	0.07	0.023					
	2.5% F	0.15	0.096					
	0.5% F	0.07	0.067					
	control	0.01	0.070					
AI (mg/L)	10% H2O4	0.86	0.361	78.779	0.000*	1-3,4,5		
	0.1% H2O4	0.10	0.033					
	2.5% F	0.06	0.011			2-3,4		
	0.5% F	0.06	0.019					
	control	0.07	0.025					

\*: p<0.001; IQR: Interquartile range



FIGURE 2: Scanning electron microscopy photomicrograph (×500) of specimens with different surface A) Electro polished, B) NaTi, C) Fine roughed and D) Roughed at control solutions.



FIGURE 3: Scanning electron microscopy photomicrograph (×500) of specimens with different surface A) degraded areas on electro polished surface, and unspecific surface changes observed at B) NaTi, C) Fine roughed and D) Roughed surfaces at 1% H<sub>2</sub>O<sub>2</sub> solution.

shown in Figure 2-A. Scattered swallow scratches and microcracks spread all over the observed surface on NaTi surfaces (Figure 2-B). Rough, wide and deep crater texture were detected on rough and fineroughed surfaces (Figure 2-C, Figure 2-D).

Although they were not substantial, degraded areas and nonspecific changes were observed on specimens immersed in  $0.1 \% H_2O_2$  solution (Figure 3-A, Figure 3-B, Figure 3-C and Figure 3-D).

Significant changes in the surface morphology and image of slits and cracks covering the entire surface were observed on all tested specimens at SEM images of 10%  $H_2O_2$  solutions (Figure 4-A). In addition, pits and fissures on the fin-roughed, roughed and NaTi surfaces were extremely abraded when compared with the samples in the control group (Figure 4-B, Figure 4-C, Figure 4-D).

Although less abrasion at pits and fissures of fine-roughed and roughed specimens immersed in 2.5% F solution was observed, a high amount of NaF sediments was detected in the sample (Figure 5-A, Figure 5-B, Figure 5-C, Figure 5-D). Despite that, within the minimal morphological changes, less amount of NaF sediments were observed on NaTi



**FIGURE 4:** Scanning electron microscopy photomicrograph (×500) of specimens with different surface A) slits and cracks covering the entire surface of electro polished surface, B) NaTi, extremely abraded C) Fine roughed and D) Roughed surfaces at 10%  $H_2O_2$  solution.



FIGURE 5: Scanning electron microscopy photomicrograph (×500) of specimens with different surface; less NaF sediments were observed at A) Electro polished and B) NaTi surfaces, minimal morphologic changes and more NaF sediments observed on C) Fine roughed and D) Roughed surfaces at 2.5% F.



FIGURE 6: Scanning electron microscopy photomicrograph (×500) of specimens with different surface; large sized and less amounts of NaF sediments observed on A) Electro polished, B) NaTi, C) Fine roughed and D) Roughed surfaces at 0.5% F.

surfaces (Figure 5-D), and electro-polished specimens (Figure 5-A).

When large size and smaller volume of NaF deposits were observed on surfaces of specimens at 0.5% F concentrations, smaller sized and more counted NaF deposits spread over the entire surface at 2.5% F concentrations (Figure 6-A, Figure 6-B, Figure 6-C, Figure 6-D) were observed. Importantly, NaF deposits which were easily noticeable on electropolished and NaTi surfaces were barely visible in deep craters of roughed and fine-roughed surfaces (Figure 6-C, Figure 6-D).

## DISCUSSION

Titanium and its alloys have been essential materials used in the dental industry due to their biocompatible nature and mechanical properties.<sup>1</sup> Given their outstanding properties, Ti and its alloys have just begun to be used for not only dental implants, but also for complex compounds like abutment, prosthetic bar and supporting substructure material for fixed partial dentures which were in direct contact with saliva, beverages, oral hygiene solutions, etc.

The present study examined decomposition and degradation risk of Ti materials in the clinical use evaluated in body simulating medias to specify the corrosion resistance of Ti alloy with different surface treatment methods. In this study, we used Fusayama Meyer artificial saliva in order to replicate the conditions of the human body, which is one of the most widely used artificial saliva. This is in line with the previous research in which the effects of conditions of the human body on the corrosion of the implant material has been investigated using solutions reproducing saliva and body fluids such as blood serum and tissue extracts.<sup>25</sup>

One of the important issues in the research regarding the corrosion of titanium and its alloys is the observation period. Previous studies lack consistency regarding this issue since there is no consensus over the optimal observation period. The effect of the surrounding environment on the corrosion behavior of dental alloys has been examined for various periods of time, ranging from 10 minutesup to 200 days.<sup>25,26</sup> Beline et al. reported that the corrosion resistance of CPTi against H<sub>2</sub>O<sub>2</sub> and NaF solutions was reduced at 7th and 14th days.<sup>27</sup> Also Mabilleau et al. noted a progressive degrading effect of F on titanium and its overlying oxide layer and 9 days of immersion at floriated solution was determined as a critical time at which roughness of Ti samples increased importantly.<sup>17,27,28</sup> Consequently, a 9-day of immersion was decided to be the most optimal period for this study.

In this study, ICP-OES and XRD were assumed to be the most suitable and mutually complementary methods to examine the biological degradation of metal alloys in body fluids.<sup>29</sup> Spectroscopic test methods like ICP-OES are beneficial for chemical analyzing of extracts of metallic biomaterials after immersing them in different solutions which simulate body fluids. Elemental release from biomaterials should be further investigated for allergic, inflammatory, toxic, carcinogenic effects and failure mechanism.<sup>30</sup>

Different percentages of  $H_2O_2$  concentrations were used to test the corrosion resistance of Ti and Ti alloys at peroxide containing environments.<sup>27</sup> High abrasion of 3%  $H_2O_2$  solution with pitting or crevice corrosion destruction on  $Ti_6Al_4V$  surface have been reported with the SEM analyses.<sup>31</sup> Furthermore, Yu et al. reported increased corrosion rates at different percentages of  $H_2O_2$  solutions.<sup>32</sup> The authors have reported that the presence of  $H_2O_2$  promotes corrosion of Ti<sub>6</sub>Al<sub>4</sub>V by increased anodic and cathode reactions. Besides, corrosion of Ti might have been occured due to the alteration of the passive film layer (2-6 nm) consisting of a thin oxide layer (2-6 nm), mainly TiO2. Corrosion of Ti occurs due to the alteration of the passivation oxide film.<sup>33</sup>

The study revealed signs of pitting corrosion with both H<sub>2</sub>O<sub>2</sub> concentrations. Importantly, the SEM and ICP-OES analyses revealed that the corrosion increased even in very low concentration of (0.1%)H<sub>2</sub>O<sub>2</sub> solutions. The more active corrosion attack of  $H_2O_2$  can be explained by temperature close to the oral cavity. Furthermore, it has been found that the effect of surface treatment was significant at corrosion resistance to  $H_2O_2$ . This finding is in concordance with Burnat et al. who showed higher corrosion in Ti<sub>6</sub>Al<sub>4</sub>V alloys at sandblasted specimens in comparison to machined samples.<sup>34</sup> Decreased corrosion resistance relates to sandblasting procedures on Ti surface which may increase surface activity and compromise the integrity and thickness of the oxide film; however, an increase in stability of the passive oxide layer and consequently a decrease in surface activation is observed for the titanium alloys.<sup>2,3,16</sup>

The corrosion resistance is reduced on rougher surfaces except for NaTi coated surfaces. Moreover, they showed better corrosion resistance than electro-polished surfaces. Although SEM images of the study revealed the devastating effect of high 10%  $H_2O_2$  concentrations on electro polished and sandblasted samples, less corrosive effects observed on NaTi surfaces were consistent with the ICP-OES findings.

Within the corrosive area of the oral cavity, F ions which are well known as effective at preventing plaque formation and dental caries, may potentially have a corrosive effect on Ti and Ti alloys.<sup>35,36</sup> Previous studies have shown that F ions can reduce corrosion resistance and cause localized and general corrosion on Ti and Ti alloys.<sup>27,37,38</sup>

Pits and cracks were observed on implant surfaces which were immersed in 0.1 or 0.2% NaF solutions, which is the concentration found in commercially available mouth rinses. Also, corrosion products were observed and they defined sodium aluminum fluoride (Na<sub>3</sub>AlF<sub>6</sub>).<sup>38,39</sup>

Mabilleu et al. reported a significant attack and increased roughness of the Ti surface in 0.5 F concentration.<sup>17</sup> Ca/P deposits were defined with presence of uniform attack at SEM observation. Crystalline deposits were observed on Ti surfaces at 2.5% high F concentration. Similar crystals at the cp-Ti surface have been found at 1% NaF solution.<sup>37</sup> Moreover, morphological damages characterized by pits and delamination on surface were obtained at atomic force microscopy images of 0.2%, 1.1% concentrated NaF.<sup>39</sup>. Our findings are supported with the previous results. It is important to note that the NaTi surface was also the least corroded and changed surface even at high F concentrations.

Unlike Ti element, vanadium is a toxic element with its high corrosive tendencies.<sup>40</sup> Furthermore, some adverse effects of Al have been reported.<sup>41</sup> We found that Al and V corrosion values were considerably lower than Ti. Our findings are in line with those of Rykowska et al. who reported similar, but slightly higher concentrations of Ti alloy than our study, 1.7 to 13.1  $\mu$ g g<sup>-1</sup> and 0.05 to 11.21 mg/l, respectively.<sup>41</sup> It is important to note that the corrosion concentrations reported by Rykowska et al. were determined at 1, 4 and 6-month periods from overlying mucosa.<sup>41</sup>

In-vitro conditions which include over simplifications in simulating oral area dramatically increased the results relative to the actual clinical conditions. Patients having Ti implants, orthodontic wire and wearing Ti based fixed or partial prostheses must be advised about the corrosion behavior of fluoride and H<sub>2</sub>O<sub>2</sub> containing solutions.<sup>42</sup> In addition, biological environment especially oxidants released by bacteria during inflammation can be aggressive for titanium implants and implant parts.<sup>17</sup> However, avoiding direct contact between Ti and saliva or corrosive solutions in oral cavity is virtually impossible; therefore, other alternatives must be developed to decrease the corrosion of titanium surfaces. The results of this study suggest that NaTi coated Ti surfaces are more resistant to corrosion than other surface treatment methods.

In addition to the titanium implants having conventional surface treatments, our study included the implants which received a hot NaOH solution treatment followed by thermal fixation. With this procedure, these implants, identified shortly as NaTi, became coated with a thin but firm layer of sodium titanite ceramic, consisting of Na<sub>2</sub>TiO<sub>3</sub>. The NaTi coating may cause a barrier effect on the Ti surface, which shows the ingress of anions in the electrolyte from attacking the metal surface.<sup>43</sup> The titanite layer protected the metallic implant from direct contact with the corrosive fluids, resulting in considerable reduction in corrosion.

## 

We have highlighted the behavior of different surfaces against corrosives. NaOH solution and heat treatments not only accelerate bone development, but also provide a bioactive macroporous titanium surface that is more resistant to corrosive oral fluids. It would be advisable to use NaTi surface treatment for dental implants and Ti prosthetic implant parts. However, more in-vivo experiments are required to determine the best surface treatment method for corrosion resistance.

### Source of Finance

During this study, no financial or spiritual support was received neither from any pharmaceutical company that has a direct connection with the research subject, nor from a company that provides or produces medical instruments and materials which may negatively affect the evaluation process of this study.

### **Conflict of Interest**

No conflicts of interest between the authors and / or family members of the scientific and medical committee members or members of the potential conflicts of interest, counseling, expertise, working conditions, share holding and similar situations in any firm.

#### Authorship Contributions

Idea/Concept: Ahmet Kürşad Çulhaoğlu, Ercüment Önder; Design: Ahmet Kürşad Çulhaoğlu, Ercüment Önder; Control/Supervision: Ercüment Önder, Ahmet Kürşad Çulhaoğlu; Analysis and/or Interpretation: Ahmet Kürşad Çulhaoğlu, Ercüment Önder; Literature Review: Ercüment Önder; Ahmet Kürşad Çulhaoğlu, Umut Tekin, Özkan Özgül; Writing the Article: Ahmet Kürşad Çulhaoğlu, Ercüment Önder; Critical Review: Ercüment Önder, Ahmet Kürşad Çulhaoğlu, Umut Tekin.

- Harzer W, Schröter A, Gedrange T, Muschter F. Sensitivity of titanium brackets to the corrosive influence of fluoride-containing toothpaste and tea. Angle Orthod. 2001;71(4):318-23.[PubMed]
- Pan J, Leygraf C, Thierry D, Ektessabi AM. Corrosion resistance for biomaterial applications of TiO2 films deposited on titanium and stainless steel by ion-beam-assisted sputtering. J Biomed Mater Res. 1997;35(3):309-18.[Crossref] [PubMed]
- Kokubo T, Yamaguchi S. Novel bioactive materials developed by simulated body fluid evaluation: Surface-modified Ti metal and its alloys. Acta Biomater. 2016;44:16-30.[Crossref] [PubMed]
- Zadpoor AA. Relationship between in vitro apatite-forming ability measured using simulated body fluid and in vivo bioactivity of biomaterials. Mater Sci Eng C Mater Biol Appl. 2014;35:134-43.[Crossref] [PubMed]
- Nishiguchi S, Kato H, Fujita H, Oka M, Kim HM, Kokubo T, et al. Titanium metals form direct bonding to bone after alkali and heat treat-

## REFERENCES

ments. Biomaterials. 2001;22(18):2525-33. [Crossref] [PubMed]

- Isaac J, Galtayries A, Kizuki T, Kokubo T, Berda A, Sautier JM, et al. Bioengineered titanium surfaces affect the gene-expression and phenotypic response of osteoprogenitor cells derived from mouse calvarial bones. Eur Cell Mater. 2010;20:178-96.[Crossref] [PubMed]
- Kim H-M, Miyaji F, Kokubo T, Nakamura T. Apatite-forming ability of alkali-treated Ti metal in body environment. J Ceram Soc Jpn. 1997;105 (2): 111-116.[Crossref]
- Acharya BL, Nadiger R, Shetty B, Gururaj G, Kumar KN, Darshan DD, et al. Brushing-induced surface roughness of two nickel based alloys and a titanium based alloy: a comparative study - in vitro study. J Int Oral Health. 2014;6(3):36-49.[PubMed] [PMC]
- Hossain A, Okawa S, Miyakawa O. Effect of toothbrushing on titanium surface: an approach to understanding surface properties of brushed titanium. Dent Mater. 2006;22(4):346-52.[Crossref] [PubMed]

- Schiff N, Grosgogeat B, Lissac M, Dalard F. Influence of fluoride content and pH on the corrosion resistance of titanium and its alloys. Biomaterials. 2002;23(9):1995-2002.[Crossref] [PubMed]
- Shim HM, Oh KT, Woo JY, Hwang CJ, Kim KN. Corrosion resistance of titaniumsilver alloys in an artificial saliva containing fluoride ions. J Biomed Mater Res B Appl Biomater. 2005;73(2):252-9.[Crossref] [PubMed]
- Houle M, Grenier D. Maladies parodontales: connaissances actuelles. Médecine et maladies infectieuses. 2003;33(7):331-340. [Crossref]
- Johansson BI, Bergman B. Corrosion of titanium and amalgam couples: effect of fluoride, area size, surface preparation and fabrication procedures. Dent Mater. 1995;11(1):41-6.[Crossref] [PubMed]
- Reclaru L, Meyer JM. Effects of fluorides on titanium and other dental alloys in dentistry. Biomaterials. 1998;19(1-3):85-92.[Crossref] [PubMed]

- Pan J, Liao H, Leygraf C, Thierry D, Li J. Variation of oxide films on titanium induced by osteoblast-like cell culture and the influence of an H2O2 pretreatment. J Biomed Mater Res. 1998;40(2):244-56.[Crossref] [PubMed]
- Rosalbino F, Delsante S, Borzone G, Scavino G. Influence of noble metals alloying additions on the corrosion behaviour of titanium in a fluoride-containing environment. J Mater Sci Mater Med. 2012;23(5):1129-37.[Crossref] [PubMed]
- Mabilleau G, Bourdon S, Joly-Guillou ML, Filmon R, Baslé MF, Chappard D, et al. Influence of fluoride, hydrogen peroxide and lactic acid on the corrosion resistance of commercially pure titanium. Acta Biomater. 2006;2(1):121-9.[Crossref] [PubMed]
- Boere G. Influence of fluoride on titanium in an acidic environment measured by polarization resistance technique. J Appl Biomater. 1995;6(4):283-8.[Crossref] [PubMed]
- Koike M, Fujii H. The corrosion resistance of pure titanium in organic acids. Biomaterials. 2001;22(21):2931-6.[Crossref] [PubMed]
- Nakagawa M, Matsuya S, Udoh K. Corrosion behavior of pure titanium and titanium alloys in fluoride-containing solutions. Dent Mater J. 2001;20(4):305-14. [Crossref] [PubMed]
- Pröbster L, Lin W, Hüttemann H. Effect of fluoride prophylactic agents on titanium surfaces. Int J Oral Maxillofac Implants. 1992;7(3):116-125.[Link]
- Yue TM, Yu JK, Mei Z, Man H.C. Excimer laser surface treatment of Ti6Al4V alloy for corrosion resistance enhancement. Mater. Lett.2002;52(3):206-212.[Crossref]
- ISO 10271 Standard. Dental Metallic Materials-Corrosion Test Methoda. 1st ed. Geneva, Switzerland: ISO; 2001.[Link]
- Cheng FT, Lo KH, Man HC. An electrochemical study of the crevice corrosion resistance of NiTi in Hank's solution. J Alloys Compd. 2007;437:322-328.[Crossref]
- Khan MA, Williams RL, Williams DF. Conjoint corrosion and wear in titanium alloys. Biomaterials. 1999;20:765-772. [Crossref]

- Gebert A, Roth S, Gopalan R, Kündig AA, Schultz L. Corrosion behavior of FePt-based bulk magnets in artificial saliva solution. J Alloys Compd. 2007;436(1-2):309-312.[Crossref]
- Beline T, Garcia CS, Ogawa ES, Marques ISV, Matos AO, Sukotjo C, et al. Surface treatment influences electrochemical stability of cpTi exposed to mouthwashes. Mater Sci Eng C Mater Biol Appl. 2016;59:1079-88.[Crossref] [PubMed]
- Schiff N, Grosgogeat B, Lissac M, Dalard F. Influence of fluoride content and pH on the corrosion resistance of titanium and its alloys. Biomaterials. 2002 May;23(9):1995-2002. [Crossref] [PubMed]
- Lesniewicz A, Gackiewcz L, Zyrnicki W. Biodegradation of metallic surgical implants investigated using an ultrasound-assisted process combined with ICP-OES and XRD. Int Biodeterior Biodegradation. 2010;64(1):81-5.[Crossref]
- Metikos-Huković M, Pilić Z, Babić R, Omanović D. Influence of alloying elements on the corrosion stability of CoCrMo implant alloy in Hank's solution. Acta Biomater. 2006;2(6):693-700.[Crossref] [PubMed]
- Faverani LP, Barão VA, Ramalho-Ferreira G, Ferreira MB, Garcia-Júnior IR, Assunção WG, et al. Effect of bleaching agents and soft drink on titanium surface topography. J Biomed Mater Res B Appl Biomater. 2014;102(1):22-30.[Crossref] [PubMed]
- Yu F, Addison O, Baker SJ, Davenport AJ. Lipopolysaccharide inhibits or accelerates biomedical titanium corrosion depending on environmental acidity. Int J Oral Sci. 2015;7(3):179-86.[Crossref] [PubMed] [PMC]
- Esposito M, Lausmaa J, Hirsch JM, Thomsen P. Surface analysis of failed oral titanium implants. J Biomed Mater Res. 1999;48(4):559-68.[Crossref] [PubMed]
- Burnat B, Walkowiak-Przybyło M, Błaszczyk T, Klimek L. Corrosion behaviour of polished and sandblasted titanium alloys in PBS solution. Acta Bioeng Biomech. 2013;15(1):87-95. [PubMed]
- 35. Cai Z, Shafer T, Watanabe I, Nunn ME, Okabe

T. Electrochemical characterization of cast titanium alloys. Biomaterials. 2003;24(2):213-8. [Crossref] [PubMed]

- Kassab EJ, Gomes JP. Assessment of nickel titanium and beta titanium corrosion resistance behavior in fluoride and chloride environments. Angle Orthod. 2013;83(5):864-9. [Crossref] [PubMed]
- Muguruma T, lijima M, Brantley WA, Yuasa T, Kyung HM, Mizoguchi I, et al. Effects of sodium fluoride mouth rinses on the torsional properties of miniscrew implants. Am J Orthod Dentofacial Orthop. 2011;139(5):588-93. [Crossref] [PubMed]
- Huang HH. Effects of fluoride concentration and elastic tensile strain on the corrosion resistance of commercially pure titanium. Biomaterials. 2002;23(1):59-63. [Crossref] [PubMed]
- Wheelis SE, Gindri IM, Valderrama P, Wilson TG Jr, Huang J, Rodrigues DC, et al. Effects of decontamination solutions on the surface of titanium: investigation of surface morphology, composition, and roughness. Clin Oral Implants Res. 2016;27(3):329-40.[Crossref] [PubMed]
- Okazaki Y, Ito Y, Kyo K, Tateishi T. Corrosion resistance and corrosion fatigue strength of new titanium alloys for medical implants without V and Al. Mater Sci Eng A. 1996;213(1-2):138-47.[Link]
- Rykowska I, Makuch K, Wasiak W. In vitro determination of titanium and other metals released from intraosseous dental implants into the mucosa. Anal Methods. 2015;7(21): 9226-36.[Crossref]
- Takemoto S, Hattori M, Yoshinari M, Kawada E, Oda Y. Corrosion behavior and surface characterization of titanium in solution containing fluoride and albumin. Biomaterials. 2005;26(8):829-37.[Crossref] [PubMed]
- Devi KB, Singh K, Rajendran N. Synthesis and characterization of nanoporous sodium-substituted hydrophilic titania ceramics coated on 316L SS for biomedical applications. Journal of coatings technology and research. 2011; 8(5):595. [Crossref]