Effect of Fluoride on the Corrosion Behavior of Ti and Ti6Al4V Dental Implants Coupled With Different Superstructures

Eman M. Anwar, PhD¹
Lamia S. Kheiralla, PhD¹*  
Riham H. Tammam, PhD²

The effect of fluoride ion concentration on the corrosion behavior of Ti and Ti6Al4V implant alloys, when coupled with either metal/ceramic or all-ceramic superstructure, was examined by different electrochemical methods in artificial saliva solutions. It was concluded that increased fluoride concentration leads to a decrease in the corrosion resistance of all tested couples. The type of the superstructure also showed a significant effect on the corrosion resistance of the couple.

Key Words: galvanic corrosion, titanium implants, titanium alloy implants, fluoride, all-ceramic superstructure

INTRODUCTION

Although it is unanimously agreed that titanium has proved its qualities as a material for endosseous implantation,¹ there is always a risk of coupling it with a superstructure made from a different material.² When a dissimilar couple is exposed to a corrosive environment, it will normally exhibit a galvanic corrosion.³ It has been stated that the galvanic corrosion of implant/superstructure systems is of alloy components and, second, that the current flow that results from galvanic coupling could lead to bone destruction.³⁴ Furthermore, Reclaru and Meyer⁵ stated that from an electrochemical point of view, an alloy that is potentially usable for superstructures in galvanic coupling with titanium must fulfill the following requisites: in coupling, the titanium must have weak anodic polarization and the current generated by the galvanic cell must also be weak.⁵ Thus, when choosing the implant-superstructure combination, the corrosion resistance of the couple and its biocompatibility must be taken into account.⁶

Since hygiene products such as toothpastes and prophylactic gels contain fluoride ions, the effect of different fluoride concentrations was evaluated, and it was stated that fluoride ions affect the corrosion behavior of Ti and its alloys and that the severity of the attack depends on both the concentration of fluoride ion and the pH value.⁷ It was added that the presence of NaF in concentrations

¹ Fixed Prosthodontic Department, Cairo University, Cairo, Egypt.  
² Chemistry Department, Cairo University, Cairo, Egypt.  
* Corresponding author, e-mail: lamisk@yahoo.com
DOI: 10.1563/AAID-JOI-D-09-00084

Journal of Oral Implantology 309
higher than 0.1% resulted in the destruction of the passive film on the Ti surface.\textsuperscript{8,9} Since in vitro electrochemical techniques have been proven to be sufficiently conveniently accurate, so they have been used to predict the corrosion of different alloys in a galvanic couple.\textsuperscript{10}

The aim of this study, therefore, was to investigate the effect of fluoride on the electrochemical behavior of titanium and titanium alloy implants coupled either with metal-ceramic or all-ceramic superstructures. Different electrochemical methods were employed: open-circuit potential (OCP) measurement, electrochemical impedance spectroscopy (EIS), anodic polarization, and potential difference.

**Materials and Methods**

In the present study, the corrosion behavior of Ti and Ti6Al4V screw-vent endosseous implants (Dentsply, York, Pa) coupled either with metal-ceramic or all-ceramic superstructures were tested. For this purpose, 4 electrodes were prepared, signifying 4 different groups: electrode I (Ti/MC), implant made of commercially pure titanium coupled to a metal-ceramic superstructure made of nickel chromium alloy (Wiron 99, BEGO, FRG) and fully veneered with feldspathic porcelain (Vita Zahnfabrile Bed, Sackingen, Germany); electrode II (Ti/all ceramic), implant made of commercially pure titanium coupled to an all-ceramic superstructure made of Inceram alumina and veneered with vitadur alpha porcelain (Vita Zahnfabrile Bed); electrode III (Ti6Al4V/MC), implant made of Ti6Al4V coupled to a metal-ceramic superstructure made of nickel chromium alloy and fully veneered with feldspathic porcelain; and electrode IV (Ti6Al4V/all ceramic), implant made of Ti6Al4V coupled to an all-ceramic superstructure made of Inceram alumina and fully veneered with vitadur alpha porcelain.

**Test solution**

Freshly prepared artificial saliva with pH 7.5 was used as an electrolyte. Its composition was 0.027 M KCl, 0.032 M NaCl, 0.007 M K\textsubscript{2}HPO\textsubscript{4}, 0.005 M KSCN, 0.002 M CaCl\textsubscript{2}, 0.0001 M tri basic citrate, 0.014 M NH\textsubscript{4}Cl, 0.013 M NaHCO\textsubscript{3}, and 0.0125 M urea.\textsuperscript{11} To test the effect of different concentrations of fluoride, NaF was added to the neutral saliva and 3 different concentrations were tested: 0.01 M NaF, 0.05 M NaF, and 0.1 M NaF.

Double-distilled water was used for the preparation and dilution of all of the solutions. The volume of the solution in the electrochemical cell was 50 mL. Measurements were conducted in unstirred solutions and at constant temperature (25 ± 2°C).

**Sample preparation**

Impressions of the implant abutments were made, and metal-ceramic and all-ceramic crowns were constructed with standardized dimensions to fit accurately on their corresponding abutments. Crowns were bonded to their corresponding implants using araldite to ensure that they would not be separated during the experiment. The exposed surface areas for different electrodes were made almost identical by using lacquer to cover the superstructures, except for a definite area designed to be left exposed cervically at the superstructure-implant junction. Then, samples were introduced into a Pyrex glass tube of an appropriate diameter and fixed in position using araldite at a fixed distance from the tube opening. To achieve high reproducibility, the electrodes were pretreated before each experiment using the same procedure: the electrode surface was mechanically polished with successive grades of emery papers 600–800 then 1200 grit, then washed with acetone and double-distilled water, and finally dried with fine tissue paper. The electrode was then immersed immediately in the test electrolyte. Measurements were performed in fresh
solutions, and in each run, the electrode pretreatment was carried out using the same procedure.

**Electrochemical tests**

The different electrochemical measurements were carried out using a computer-controlled potentiostat (IM6 Zahner Electric, Meßtechnik, Germany).

Open-circuit potential measurements were undertaken with a saturated calomel electrode as the reference electrode, and an auxiliary platinum sheet was used as the counter electrode. The working specimen was immersed in the electrolyte solution to form the electrolytic cell, which was then attached to the computer. The potential of the working electrode under open-circuit conditions was followed with time until a steady state was reached.

The impedance measurements were used to study the corrosion and oxidation behavior of the tested electrodes (I, II, III, IV) in artificial saliva without fluoride and another containing 0.1 M sodium fluoride. The method involves direct measurements of impedance of the electrochemical system in frequency domain from 0.1 to 100 KHz. The electrode impedance, Z, and the phase shift (θ) were presented in Bode and Nyquist formats. These experiments were carried out at steady state under open-circuit conditions and after anodization with +0.5 V for 30 minutes. Anodic polarization was performed to accelerate the corrosion and hence be able to predict the behavior of the couple after several years. The potential versus time for each couple after polarization was monitored and recorded until a steady state was reached.

Corrosion resistance (Rp) and potential difference (ΔE) were determined in kΩ and in Ev/SCE, respectively, and the results were fitted so that equivalent circuit models and appropriate plot formats can be obtained.

**Results**

Figures 1a, 1b, 2a, and 2b represent Bode plots, and Figure 3 represents the Nyquist plot for electrodes I, II, III, and IV. Inspection of Bode plots indicates that it is characterized by 2 distinct regions: in the higher frequency region (1–100 kHz), the impedance Z remained unchanged, exhibiting a constant horizontal line, with a phase angle (θ) near 0°, indicating high corrosion resistance of the couple. In the broad low and middle frequency range, the impedance started to increase with the decrease of frequency until reaching the end of the frequency limit, while the phase angle (θ) values were close to −90° over a wide frequency range, exhibiting a near capacitive response and indicating a compact passive oxide film. The maximum value of (θ) was in the frequency region from 0.01 to 10 Hz, depending on the type of the couple. This capacitive behavior was observed over nearly the whole measurements; in different conditions tested, in open circuit, and after anodization condition, in both Ti and Ti6Al4V implant/couples.

In our study, the equivalent electrical circuit can be shown in Figure 4.

The value of (1) Rcorr was calculated from the Bode plots at frequency 0.1 Hz by subtracting the value of Z (R0 + Rcorr) and from the Nyquist plot using the modulus Z = Rcorr and is listed in Table 1.

(2) The phase angle (θ) at f = 0.1 Hz was deduced from the Bode plots. These values were calculated for the electrodes I, II, III, and IV and are listed in Table 1. Inspection of these results reveals that (1) the Rcorr calculated either from Bode plots or Nyquist plots had almost similar values and (2) the values of Rcorr increase according to the following order: II > I > IV > III.

**Effect of Fluoride at OCP, Before Anodization**

In neutral saliva without fluoride. In OCP, it can be seen that the sequence of decrease in
Rp for the 4 studied electrodes is II > I > IV > III, which corresponds to the better corrosion resistance of electrode II compared with the other studied electrodes, as shown in Figure 1a.

The 4 electrodes exhibited a behavior typical of a thin passive oxide film (i.e., a near-capacitive response illustrated by a phase angle close to $-80^\circ$ over a wide frequency range). Furthermore, this did not change...
with exposure time, indicating that the oxide film is very stable under these conditions.

In 0.1 M NaF. After the addition of 0.1 M NaF, the 4 electrodes showed a marked decrease in their corrosion resistance values as shown in Table 1 and Figure 2a, when compared with those without fluoride.

**Effect of Fluoride After Anodization**

In neutral saliva without fluoride and in 0.1 M NaF. A marked increase was observed in the corrosion resistance (Rp) of the 4 couples with time after polarization (by +0.5 V from OCP), both in neutral saliva without fluoride (Table 1; Figure 1b) and in saliva with 0.1 M NaF (Table 1; Figures 2b and 3), indicating their high corrosion resistance, which increases with time. The Nyquist plot (Figure 3) was regarded as a plot of a semicircle with a length depending on the type of the couple and increases according to the order III > IV > II = I. It was deduced from these results that the corrosion resistance is different for the different electrodes, thus implicating the effect of the electrode composition on its corrosion behavior.

**Potential Difference of Different Electrodes After Polarization**

Figures 5 and 6 represent, respectively, the potential-time curves for the 4 electrodes, immersed in artificial saliva without fluoride and saliva containing 0.1 M NaF, after anodization.

The potential-time curve after anodization of different electrodes showed that initially it had positive values and then shifted sharply and then slowly to more negative values with time, until attaining a steady state, in a rate depending on the nature of the electrode.

To calculate the value of dissolution potential range, the Eimm, which is the starting potential of the electrodes, and the Es, which is the steady-state potential or the end potential, were deducted from the curves. The time required for the shift of potential from Eimm to Es, which is the time of dissolution (ts), was recorded. The rate of dissolution of oxides was calculated by dividing the value of dissolution potential range (Eimm-Es) by the time of dissolution ts. The obtained values are listed in Table 2.

The potential difference (ΔE) was in the order of electrode III > IV > I > II, indicating that electrode III showed the highest potential difference and consequently the lowest corrosion resistance (Rp), whereas electrode II showed the lowest potential difference (ΔE) and the highest corrosion resistance (Rp). That was true for electrodes immersed in neutral saliva without fluoride (Figure 5) and in saliva containing 0.1 M NaF (Figure 6).

The potential of different electrodes against time at 0.1 M NaF after anodization (Figure 6) showed that it shifted to more negative values to the end of immersion time. The potential difference (ΔE) differed

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**Table 1**

Corrosion resistance (Rp) (in MΩ) and phase angle (θ) for the 4 studied electrodes at open-circuit potential (OCP) and after anodization by +0.5 V in neutral saliva without fluoride and in 0.1 M NaF.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Rp Neutral Saliva Without Fluoride</th>
<th>Rp 0.1 M NaF</th>
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<tbody>
<tr>
<td>Ti/MC (electrode I)</td>
<td>Before anodization (OCP) 73.5 77°</td>
<td>168 81.7°</td>
</tr>
<tr>
<td>After anodization</td>
<td>79.9 75.2°</td>
<td>234.2 82.1°</td>
</tr>
<tr>
<td>Ti/all-ceramic</td>
<td>Before anodization (OCP) 228.2 80.1°</td>
<td>167.9 82.1°</td>
</tr>
<tr>
<td>(electrode II)</td>
<td>After anodization 405.5 81.7°</td>
<td>252 82.5°</td>
</tr>
<tr>
<td>Ti6Al4V/MC</td>
<td>Before anodization (OCP) 95.6 73°</td>
<td>81.62 80.2°</td>
</tr>
<tr>
<td>(electrode III)</td>
<td>After anodization 91.46 70.3°</td>
<td>88.2 79.3°</td>
</tr>
<tr>
<td>Ti6Al4V/all-ceramic</td>
<td>Before anodization (OCP) 189.7 81.1°</td>
<td>103.6 80.9°</td>
</tr>
<tr>
<td>(electrode IV)</td>
<td>After anodization 265.5 81.2°</td>
<td>104.7 71.6°</td>
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for different electrodes, yet it showed higher potential difference with 0.1 M NaF, when compared with those without fluoride (Figure 5). This might be attributed to a decrease in the oxide film thickness and consequently the corrosion resistance (Rp) according to the high-field theory, which relates the oxide thickness to the potential difference across the film.

**DISCUSSION**

A pilot study was performed on the 4 electrodes to determine the effect of different fluoride concentrations. The corrosion resistance of electrode I in the presence of 0.05 M NaF was almost equal to that in the presence of 0.01 M NaF and to those without fluoride. Yet the corrosion resistance decreased at 0.1 M NaF concentration after 1 hour immersion time, as shown in the Nyquist plot (Figure 7). All couples showed similar plots when compared under similar conditions at OCP and after polarization. So 0.1 M NaF was used throughout the study.

When a protective surface film is formed on metal, the electrode's impedance shown in the EIS plot predominantly corresponds to the capacitive effect of the surface passive

<table>
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<th>Table 2</th>
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<td>Electrode</td>
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<td>I</td>
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<td>III</td>
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**FIGURES 4-7.**

**Figure 4.** Equivalent electrical circuit for study of corrosion resistance of the 4 electrodes. C1 indicates double-layer capacitance; C2, capacitance of the oxide layer; R0, electrolyte resistance; R1, the charge transfer resistance; R2, resistance of oxide layer; Zw, Warburg impedance due to diffusion in the oxide layer. **Figure 5.** Potential-time curves for the 4 electrodes in neutral saliva without fluoride after anodization. **Figure 6.** Potential-time curves for the 4 electrodes in 0.1 M NaF after anodization. **Figure 7.** Nyquist plot showing electrode I in different fluoride concentrations after anodization. Electrode I; Electrode II; Electrode III; Electrode IV.
In this study, the large semicircles (or capacitive loops) observed in the Nyquist plots of both Ti and Ti alloy couples in artificial saliva at pH 7.5 without fluoride and with low fluoride concentrations, less than 0.1 M NaF (Figure 6), were mainly ascribed to the capacitive effect of the surface passive film, identified mainly as TiO₂ in the case of pure titanium implants or as TiO₂ with trace amounts of Al₂O₃ and V₂O₃ in the case of Ti₆Al₄V, indicating high corrosion resistance of the couples.

The results obtained at pH 7.5 in the presence of 0.01 and 0.05 M NaF indicate the ability of the electrodes to grow protective oxide layers on their surfaces, which caused the potential of the electrodes to be almost the same as the control, in absence of fluoride. This suggests that lower concentrations of fluoride ions did not hinder the formation of an oxide layer on the electrode surface, as reported by Wigg et al.

Nyquist plots obtained after the addition of 0.1 M NaF showed a decrease in the total impedance and a depression in the capacitive loop with a decrease in the diameter of the semicircles received, when compared with the ones without fluoride, as shown with electrode I, indicating a decrease in the corrosion resistance of all the couples after the addition of 0.1 M NaF (Figure 6), as all the electrodes showed similar results. This may be attributed to the fact that fluoride ions at high concentrations may have an influence on the properties of the oxide layer; fluoride ions interfere in titanium oxide formation, which changes the protective passive layer of the metal by exhibiting a 2-layer structure: one dense inner layer and a porous outer layer. This might indicate that the TiO₂-based passive film was significantly destroyed by the attack of fluoride ions via the formation of a soluble Ti-F complex compound, identified as Na₂TiF₆ as suggested by Huang and Lee, and as TiCl₆ and TiF₆, as suggested by Reclaru and Meyer, which leads to a decrease in the oxide layer resistance and increase in its capacitance. This shows that Ti and Ti alloys are susceptible to localized corrosion in solutions containing halide ions in a way dependent on their concentration.

It was also proved by Schutz and Thomas that a fluoride ion concentration of 20 ppm at 6 < pH < 7 suffices to produce localized corrosion on Ti. So titanium is not recommended to be used with fluoride-containing solutions, especially at pH less than 7.

Comparing the EIS plots of the 4 electrodes, almost similar results were obtained in the couples that had the same type of implant, as in case of Ti₆Al₄V couples that showed a remarkably decreased corrosion resistance when compared with those obtained for Ti couples. This result was in conjunction with Gonzalez and Mirza-Rosca, who studied the influence of alloying elements on the corrosion resistance of Ti and other Ti-based implant alloys and stated that Al, which is an alpha-phase stabilizer, was found to be detrimental to the passivity and corrosion resistance of Ti.

Comparing the order of the 4 couples according to their corrosion resistance, in neutral saliva without fluoride and after the addition of fluoride, our observations led us to the following conclusions. In saliva without fluoride, electrode I showed lower corrosion resistance than electrode II, and electrode III showed lower corrosion resistance than electrode IV. This can be attributed to the greater resistance to corrosion of all-ceramic crowns compared with the ceramic-capped Ni-Cr–based crowns, leading to a decrease in the corrosion resistance of its corresponding electrodes. These results are consistent with those of Amin et al., who showed that NiCr alloy degraded when placed in NaF solutions and that its corrosion resistance was affected by fluoride ion concentration in the solution. Moreover, it
was stated that fluoride molecules can react with CrO, forming chromium oxyfluoride in solid state, which cause a structure defect on the CrO layer, thereby indicating the effect of the material of the superstructure on its corrosion reaction with its corresponding implant couple.

**CONCLUSIONS**

Under the experimental conditions of this study, the following conclusions were drawn:

1. All samples showed good corrosion resistance to electrochemical corrosion under different tested conditions.

2. Commercially pure Ti couples showed significantly superior corrosion resistance properties than Ti 6Al 4V couples.

3. The use of fluoride therapy with concentrations higher than 0.1 M might cause a significant decrease in the corrosion resistance of different couples.

4. Ti 6Al 4V couples were more affected by fluoride than commercially pure Ti couples.

5. Ti and Ti 6Al 4V implants coupled with -ll ceramic crowns showed significantly higher corrosion resistance when compared with their corresponding couples that were coupled with metal-ceramic superstructures.

6. Ti implants coupled with all-ceramic crowns showed the highest corrosion resistance rates compared with the other tested couples.

7. The biological characteristics of each individual represent a variable that cannot be reproduced easily in vitro, in terms of composition, acidity of saliva, dental hygiene, eating habits, administration of medicine, and caries. For this reason, from our research we conclude that the best couple for corrosion resistance is electrode II, a Ti implant with all-ceramic crowns, as it was the most favorable implant-superstructure couple that is capable of resisting the most extreme conditions that could possibly be encountered in the mouth.

**REFERENCES**


