

Galvanic Corrosion of Ti6Al4V Coupled With NiCr as a Dental Implant Alloy in Fluoride Solutions

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The aim of this study is to investigate the galvanic effect of NiCr on Ti6Al4V in fluoride solutions used on dental implants rehabilitations. The alloys were evaluated in solutions with different contents of fluoride and pH in similar conditions founded in oral environment. The electrochemical measurements were performed on two steps. On the first step, analysis of the open circuit potential of each alloy in combination with various fluoride concentrations and pH values were carried out. In the second step, galvanic measurements were performed between the coupled alloys using precision multimeters. Data were evaluated by one-way ANOVA tests ($\alpha=0.05$). Ti6Al4V presented a decreasing corrosion resistance with increasing fluoride concentration and decreasing pH, being in a thermodynamic corrosion domain for all evaluated solution combinations except 227 ppm F⁻ at pH 5.5. Despite this, an important result was obtained from the galvanic measurements. When coupled with NiCr, Ti6Al4V was able to achieve passivity and did not exhibit adverse galvanic effects with the different fluoride combinations tested. The possible galvanic effect in our study was an improvement in the Ti6Al4V

corrosion resistance in the presence of fluoride content when it was coupled with NiCr. This study provides a new important result for the safe use of Ti6Al4V with a possible fluoride presence in the oral environment since they are associated with NiCr-based prostheses and implant connections.

Keywords: galvanic corrosion, titanium, fluoride, implant, NiCr

1. INTRODUCTION

Titanium-based alloys are used for dental implants, prosthesis screws, and abutments because they have adequate properties, including a high mechanical resistance, a low density, and a modulus of elasticity that is closer to that of the bone than other alternative implant alloys, together with excellent corrosion resistance and biocompatibility [1-16]. Other alloys, based on Au, Ag, Pd, Cr, Co, and Ni, can be used in prosthetic restorations for both dental elements and implants. The low cost, ease of casting and finishing, and mechanical properties, such as yield strength, accuracy of fit, and good adhesion of ceramics, make NiCr and CoCr alloys attractive for castable abutments in implant rehabilitation [6,13,17-20]. The preference for castable abutments is related to subgingival prosthesis, single tooth, and limited prosthetic spaces for rehabilitations [21]. However, in some rehabilitations, the use of a premanufactured titanium alloy (Ti6Al4V) coping between the implant and the prosthesis framework may be necessary to improve the mechanical resistance [5]. This configuration is associated with a decreased cost and facilitated finishing of casting commonly used for dental alloys [5,6,22]. In this case, the prosthetic for rehabilitation is composed of two different alloys, a titanium alloy (Ti6Al4V) and a casting alloy (NiCr or CoCr) [6,21]. The success of implant rehabilitations and prosthetic structures is directly dependent on their resistance to mastication forces, preservation of precise fit, and resistance to electrochemical corrosion [5,7-9,21].

The corrosion resistance of these alloys is directly related to the formation of a passive film on the metal surface in contact with the environment [5,7-9,11,13,15,17-19]. The corrosion process depends on the chemical composition of the oral environment [1,5,6,8,9,11,17,18]. The corrosion resistance of an alloy used as a biomaterial depends on its electrochemical stability in the environment and the extent of adverse interaction with the surrounding tissues [18]. It is well known that an oral medium contains potentially corrosive substances such as acids, chlorides, and fluorides. Fluoride ions are found in daily mouthwashes (227 ppm F⁻), weekly mouthwashes (905 to 2270 ppm F⁻), professional dental gel/mousse (9050 ppm F⁻), professional acidified gel (12300 ppm F⁻), and professional fluoride varnish (22700 ppm F⁻) [1-3,9,10,11,13]. The use of acidulated gel can lead to a formation of calcium fluoride on the dental surface, which supports the reduction in dental demineralization [1-3,7,9,10,14,23-25]. The fluoride ions (F⁻) interact with the mineralized part of the tooth, hydroxyapatite, to form fluorapatite, which helps prevent caries [1-3,7-9,24,25]. The pH of the oral environment can change due to food, drink, acidic metabolites, the presence of inflammation, and the use of acidulated fluoride gels, which can achieve a pH value between 3 and 10 [9-11, 19, 23]. In summary, fluoride ions can be present in oral environments at different concentrations and pH in formulations ranging from 100 to 2000 ppm fluoride ions.

According to many studies, titanium alloys exhibit high chemical reactivity in the presence of fluoride ions and pH alterations [1,5,7,9,11,16,18]. An increase in the fluoride concentration may lead to a reduction in the corrosion resistance of titanium alloys. Decreases in pH or the oxygen reduction in the presence of fluorine can promote alterations in the surface roughness of the alloys due to the effect of fluoride ions in the titanium passive oxide layer [1,5,7,9,10,15,18,26]. The increase in roughness may also lead to microorganism adhesion or contribute to abutment screw loosening. Hydrofluoric acid (HF) dissolves the film protective layer on the surface of titanium alloys induced by the acid predominance in the medium [1,3,7,9-11,23,25]. The corrosion resistance of titanium alloys in fluoride environments depends on the combined impact of the fluoride concentration and pH [1,7-9,10].

The corrosion resistance of NiCr in simulated body fluids is generally lower than that exhibited by titanium alloys [7,18,19]. Oyar et al. [22] mentioned that in an acidic environment, NiCr can release Ni ions during the immersion period. Sampaio et al. [19] found that fluoride ions present in the oral environment could influence the formation of a NiCr oxide layer.

However, the use of titanium alloys in the oral medium, such as in implant bodies, screw prostheses, abutments, or prosthetic copings, or its contact with other alloys, such as NiCr in prosthetic restorations, prosthetic copings or abutments can cause galvanic effects, thereby significantly accelerating the corrosive process [7,12,13,20]. Zhodi et al. [13] mentioned that titanium alloys, when coupled with base alloys, acted as anodes, and additionally, an increase in fluoride content could lead to a decrease in the corrosion resistance of the alloys employed in oral rehabilitation. The corrosion mechanism is galvanic corrosion, which is triggered by any electrode potential difference between alloys. An electrochemical cell can be formed from the infiltration of saliva and fluoride ions between the implant and the prosthesis when the precise fit is lost. This gap can be associated with dimensional distortions and deformations occurring during the casting process. The galvanic cell may be formed between the two dissimilar alloys in the prosthesis structure or between the implant and the castable framework when they are screw-retained directly in the implant body [5,7,13]. Based on the different chemical compositions of the alloys investigated here, a difference between the electrochemical electrode potentials is expected. This potential difference is a basic requirement for the incidence of galvanic corrosion when NiCr is coupled with Ti6Al4V. A current generated by galvanic corrosion may result in discomfort to the patient and can be the onset of bone resorption [13]. A decrease in the corrosion resistance of alloys may influence their biocompatibility, generating an inflammatory response in the surrounding tissue and allowing environment infiltration into rehabilitation, leading to the loss of rehabilitation integrity and failure [1,6,8,9].

The present work aims to evaluate the galvanic effect on the corrosion resistance of Ti6Al4V when it is coupled with NiCr-based alloys in solutions at various fluoride concentrations and pH values.

2. MATERIALS AND METHODS

2.1 Preparation of the test specimen

The alloys used were Ti6Al4V ELI (extra low interstices) (ASTM F136/ISO 5832-3, ACNIS, Brazil) (Ti: balance; Al: 6.04%; V: 4.115%; Fe: 0.185%; O: 0.105%; C: 0.034%; N: 0.004%; H:

0.0028%) and NiCr commercial dental alloy (Neocast V, Dental Alloys, USA) (Ni: 70-77%; Cr: 11-14%; Mo: 8-10%; Al+Co+Ti: <5%). The NiCr casting conditions were the same as those used for the manufacture of a dental-supported implant. The casting process used was oxygen-gas flame melting and injection of the melted alloy into the mould by centrifugation in a dental prosthesis laboratory. The mould was made from a wax pattern embedded in a cast ring and covered by a coating. The wax pattern was removed at a temperature of 850°C. The alloy was heated within the melting range of 1150 to 1227°C by flame with oxygen and centrifuged for injection into the cast ring through feed channels. The casting test specimen was sandblasted with aluminium oxide to clean the surface, according to the manufacturer's recommendations. For the electrochemical measurements carried out to assess the corrosion process, 5 mm-diameter test specimens of machined Ti6Al4V and casting NiCr were used. The test specimens were assembled as working electrodes by using an electric contact through a welded copper wire on the backside of the test specimen. The test specimens were embedded in epoxy resin, including the backside electric contact. The surface of the working electrodes was prepared with 600 grit. The exposed electrode area was 0.196 cm².

2.2 Electrochemical measurements

The solutions used for corrosion resistance assessment were NaCl 0.9% (m/v) with three different NaF concentrations. The additions of NaF corresponded to 227 ppm F⁻, which is related to the concentration used in daily mouthwashes; 2270 ppm F⁻, used in weekly mouthwashes; and 12300 ppm F⁻, used in the form of acidulated gel in professional applications. These concentrations were used at pH 5.5, corresponding to the average pH found in the oral medium, and at pH 4.0, corresponding to inflammatory situations. Lactic acid was used for pH adjustments. All measurements were performed in triplicate.

The electrochemical measurements were performed in two steps. In the first step, open circuit potential (OCP) measurements of the isolated materials were performed as soon as the electrode was immersed in each solution. The OCP was recorded as a function of time until reaching a steady state. For this evaluation, a two-electrode cell was used. Silver/silver chloride (Ag/AgCl) was used as a reference electrode, and a resin-embedded material was used as a working electrode. The OCP measurements were carried out at 25°C using an Autolab PGA 302N multipotentiostat (Metrohm Autolab B.V., Switzerland), and the results were analysed using Autolab Nova 2.1 software. The measurements in this step were performed separately to obtain the OCP of each alloy in each solution tested.

In the second step, galvanic measurements of the coupled alloys were performed using a same exposed area for each alloy, which means an area ratio 1:1. Two high-precision digital multimeters (Fluke 8846A, USA) were used. The first multimeter operated as an ammeter, recording the galvanic current that flows between Ti6Al4V and NiCr. The second multimeter operated as a voltmeter connected between the coupled work electrodes and the reference electrode, recording the galvanic potential. The data acquisition frequency was 0.25 Hz. This measurement was long enough for the galvanic current to

achieve a value close to zero. The parameters extracted for this analysis were the initial (E_s) and final potential (E_f) and current values (I_s, I_f) of the pair.

2.3 Long-term immersion tests

The most and least aggressive combinations of fluoride concentration and pH were selected for long-term immersion tests with Ti6Al4V to evaluate the extent of ion liberation. The criteria used for solution selection were one that indicated active dissolution for Ti6Al4V and one that indicated a passive state of Ti6Al4V based on the literature.

Test specimens were obtained from an alloy rod with a diameter of 5 mm and a length of 12 mm. The immersion time was 15 days in 100 mL of solution.

2.4 Surface characterization

The Ti6Al4V specimens of the long-term immersion tests and of the galvanic tests were characterized by scanning electron microscopy (SEM) and confocal laser scanning microscopy. Surface inspections were made using SEM (JSM-6460LV) and a confocal microscope (LSM 800, ZEISS) in association with Conformap software (ZEISS). From the confocal analyses, Ra (arithmetic roughness) and Rq (quadratic roughness) roughness surface parameters were obtained by the mean of 3 profiles from 4 equidistant areas for each test specimen in each solution. All analyses were performed before the tests with a control specimen and then with the specimens obtained at the end of the tests.

2.5 ICP-MS

After the long-term immersion tests, the concentration of ions that leached in the solutions was determined by inductively coupled plasma mass spectrometry (ICP-MS). The analysis was performed using an iCAP Qc ICP-MS (Thermo Scientific, Bremen-Germany) equipped with a collision/reaction cell (QCell™) for kinetic energy discrimination, which was pressurized with 3.5 mL min^{-1} hydrogen and 0.1 mL min^{-1} helium and equipped with a skimmer and nickel cones, a quartz cyclonic spray chamber chilled by a Peltier system, a Meinhard™ micro-nebulizer and QTegra software for data acquisition. The operation conditions of the ICP-MS are listed in Table 1. The external calibration was performed with six standards made by simple dilution of stock solutions containing 1000 mg kg^{-1} standards (CertiPrep, SPEX, Metuchen, USA) with ultrapure water provided by a MilliQ™ System, Direct 8 model (Merck Millipore, Billerica, Massachusetts, USA). To attenuate transport and matrix interferences, ^{45}Sc was used as an internal standard. All solutions were stored at the end of the tests. A 100 mL solution was diluted with ultrapure water in the proportion required to become adequate for analytical calibration.

For this technique, the lower limit of detection (LOD) for each element was 1.75×10^{-3} ppm for Al, 0.23×10^{-3} ppm for Ti and 0.73×10^{-3} ppm for V.

Table 1. ICP-MS measurement parameters.

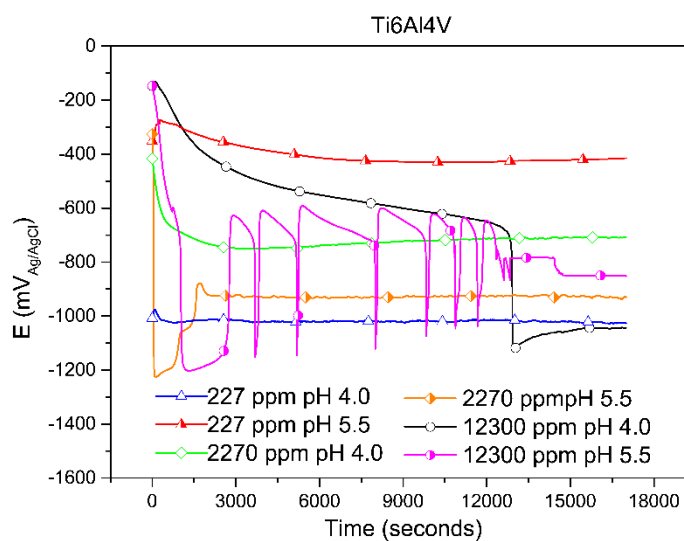
Parameters	ICP-MS
RF Power (W)	1550
Plasma Cool Gas (L min ⁻¹)	13
Auxiliary Gas (L min ⁻¹)	0.8
Nebulizer Gas (L min ⁻¹)	1.08
Sample Inlet Flow (mL min ⁻¹)	0.4
Dwell Time (s)	0.01
Measured Isotopes (<i>m/z</i>)	27, 44, 45, 46, 47, 48, 49, 51
Internal Standard (<i>m/z</i>)	45

2.6 Statistical Analysis

All evaluations were performed in triplicate and are reproducible. One result from each analysis is presented in the results and discussion section, with averages used for the results shown in tables. The obtained data from the electrochemical and surface characterization were statistically analysed by 1-way ANOVA.

3. RESULTS AND DISCUSSION

The first step was the analysis of the OCP for each alloy. The OCP values can vary as a function of time, as shown in Figure 1, where the OCP of Ti6Al4V and NiCr alloy is provided for all solutions. The results presented for each condition under investigation represent the behaviour of a triplicate set.



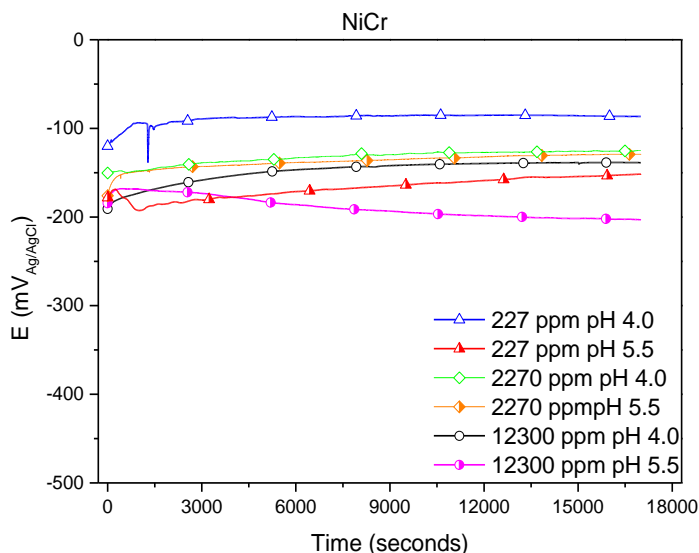


Figure 1. OCP of Ti6Al4V and NiCr in solutions with different fluoride concentrations and pH.

The OCP values of the NiCr alloy did not present significant variations ($p > 0.05$). However, the OCP obtained for Ti6Al4V exhibited unstable and complex behaviour with time ($p < 0.05$). Decreasing OCP values of Ti6Al4V were obtained with increasing fluoride concentration and decreasing pH. The OCP of Ti6Al4V in the solutions with fluoride at pH 4.0 was lower than that at pH 5.5. The stabilization of Ti6Al4V in a decreased potential range with an increase in the concentration of fluoride ions is attributed to active dissolution reactions. [1-3,8,24,26] This condition corresponds to rapid kinetics of metal dissolution without formation of a protective oxide layer. Souza et al. [8] cited that a decrease in OCP values indicates an increase in the chemical activity and increasing severity of alloy corrosion.

Another important aspect to be taken into account is based on thermodynamics. There is a potential limit for the stability of TiO_2 , which depends on the pH. It is possible to infer from the diagram that this potential limit for the corrosion-passivation transition is $-800 \text{ mV}_{\text{Ag}/\text{AgCl}}$ for pH 5.5 and $-600 \text{ mV}_{\text{Ag}/\text{AgCl}}$ for pH 4.0. Above these limits, Ti6Al4V is in the passivation domain, which implies a very high corrosion resistance. From the analysis of single Ti6Al4V OCP results plotted on an adapted E x pH diagram of the Ti- H_2O system [27], a single Ti6Al4V OCP remains in the corrosion range of the diagram, except for the 227 ppm F^- at pH 5.5, which remains in the passive range. The literature mentions that the corrosion resistance of titanium alloys can be affected by an increase in the fluoride concentration and can be aggravated when associated with a pH reduction. [2,4,7,8,13,15,16,24,26].

In addition to the thermodynamic analysis based on the E x pH diagram, the corrosion resistance of titanium alloys to the combination of fluoride concentration and pH could also be limited by equation (1) from immersion experiments developed by Nakagawa et al. [10]; combinations capable of promoting the destruction of the passive titanium film can be determined with the following equation:

$$pH = 1.49 \log F + 0.422 \quad (1)$$

Based on the Nakagawa equation, among the combinations used in this study, the most aggressive combination for Ti6Al4V was 12300 ppm F⁻ at pH 4.0, and the least aggressive combination was 227 ppm F⁻ at pH 5.5.

The OCP values registered for NiCr were higher than those obtained for Ti6Al4V for all conditions evaluated, indicating the possible occurrence of galvanic corrosion. The potential difference between the materials can generate galvanic effects among the alloys used in oral rehabilitations.

The preliminary requirement for galvanic interactions is an OCP difference between the alloys in the same environment. This difference is defined as E_d and was calculated from the E_{ocp} for the alloys and solutions shown above with equation (2). The obtained potential difference (E_d) is shown in Table 2.

$$E_d = E_{Ti}^{pHx} - E_{NiCr}^{pHx} \quad (2)$$

Table 2. Potential difference obtained from equation (2) using the OCP values of the alloys

Solution	Ti6Al4V E _{OCP} (mV _{Ag/AgCl})	NiCr E _{OCP} (mV _{Ag/AgCl})	E _d (mV _{Ag/AgCl})
227 ppm F ⁻ pH 4.0	-1019	-084	-935
227 ppm F ⁻ pH 5.5	-414	-151	-263
2270 ppm F ⁻ pH 4.0	-705	-125	-580
2270 ppm F ⁻ pH 5.5	-939	-128	-811
12300 ppm F ⁻ pH 4.0	-1027	-138	-889
12300 ppm F ⁻ pH 5.5	-852	-202	-650

The open circuit potentials resulted in different fluoride conditions, allowing us to observe the presence of the potential difference between the two alloys tested under the same conditions. This potential difference between the materials increases in proportion to the fluoride contents in solutions. This recognition is important because the alloy interfaces may be in contact or in closer contact in oral rehabilitations containing titanium implants or prosthesis structures and NiCr castings under *in vivo* conditions. The E_d values produced between the cast alloy of dental rehabilitation and the alloy of the implant can form a galvanic cell that can accelerate the corrosion process [5,12,15]. The occurrence of galvanic corrosion may affect the corrosion rate of the anodic alloy, leading to accelerated corrosion, while the cathode may present a decreased corrosion rate [12].

The second step evaluated the evolution of the galvanic interaction between the alloys when they were coupled. The results of the galvanic measurements of Ti6Al4V coupled with NiCr are shown in Figures 2, 3 and 4, separated by fluoride concentration and pH. The thermodynamic limit established by the E vs. pH diagram is also represented in the figures.

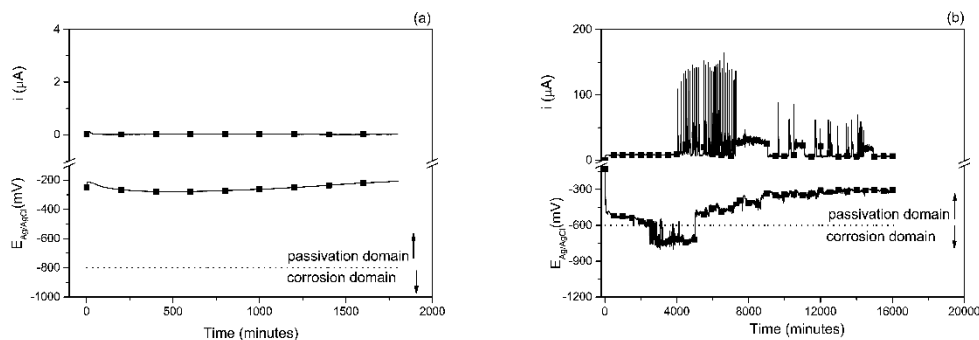


Figure 2. Galvanic measurements of current and potential of Ti6Al4V coupled with NiCr in solutions of 227 ppm F⁻ at pH 5.5 (a) and in 227 ppm F⁻ at pH 4.0 (b). The dotted line shows the thermodynamic limits of the corrosive and passive domains.

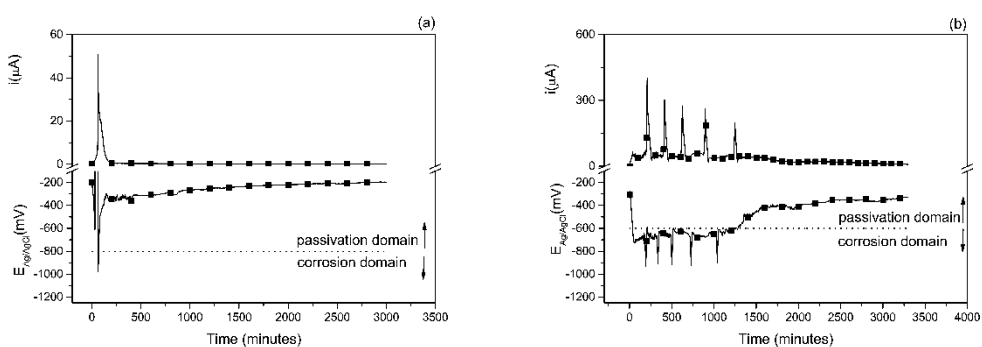


Figure 3. Galvanic measurements of current and potential of Ti6Al4V coupled with NiCr in solutions of 2270 ppm F⁻ at pH 5.5 (a) and in 2270 ppm F⁻ at pH 4.0 (b). The dotted line shows the thermodynamic limit of the corrosive and passive domain.

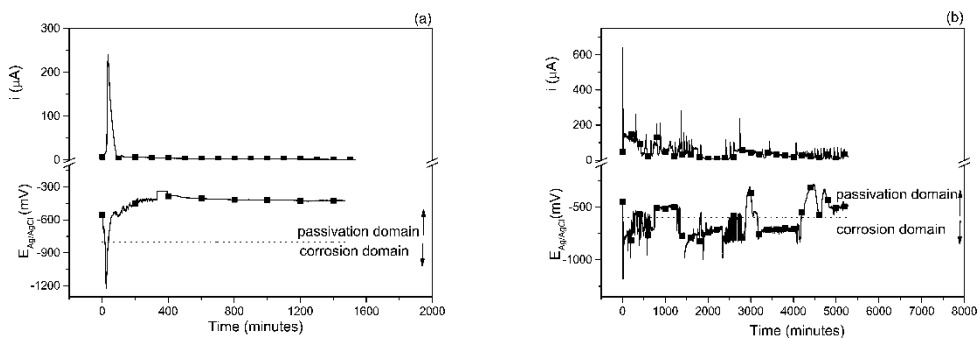


Figure 4. Galvanic measurements of current and potential of Ti6Al4V coupled with NiCr in solutions of 12300 ppm F⁻ at pH 5.5 (a) and 12300 ppm F⁻ at pH 4.0 (b). The dotted line shows the thermodynamic limit of the corrosive and passive domain.

The initial (E_s) and final potential (E_f) and current (I_s , I_f) values extracted from the galvanic measurements with the same combination of fluoride concentration and pH are shown in Table 3. The highest current and the lowest potential registered during the galvanic measurements are also in Table 3.

Table 3. Results obtained from the galvanic measurements of Ti6Al4V coupled with NiCr in solutions of various fluoride concentrations and pH values

Solution	E_s (mV _{Ag/AgCl})	E_f (mV _{Ag/AgCl})	I_s (μA)	I_f (μA)	Lowest potential (mV _{Ag/AgCl})	Highest current (μA)
227 ppm F ⁻ pH 4.0	-127	-312	6,2	5	-780	170
227 ppm F ⁻ pH 5.5	-130	-212	0.02	0.01	-212	0.133
2270 ppm F ⁻ pH 4.0	-495	-324	7.6	2.6	-918	403
2270 ppm F ⁻ pH 5.5	-210	-192	0.2	0.2	-968	50
12300 ppm F ⁻ pH 4.0	-449	-484	48.4	7	-1172	637.9
12300 ppm F ⁻ pH 5.5	-556	-423	7.4	6.6	-1214	240

The measured galvanic potential was the mixed potential generated by the alloys in contact, while the couple current was generated by the enhanced dissolution of one of the alloys, the anode. The galvanic current in this process is flowing from the anode to the cathode [7]. This current is detected by the ammeter, as represented in the graphs by current increases, current spikes and transients. The multimeter used in this step allowed us to detect all changes in data with increased sensitivity due to its acquisition frequency being higher than that of the potentiostat.

The galvanic tests presented significant variations in the initial and final couple potentials between the conditions tested ($p < 0.05$). The initial and final couple currents were at low magnitudes close to zero and did not present significant variations between the conditions ($p > 0.05$). The galvanic current had positive values under all conditions tested, which indicates that the Ti6Al4V acted as an anode when coupled with the NiCr alloy. In all solutions, an initial abrupt increase in the current and a corresponding decrease in the potential occurred. This behaviour indicated initial active dissolution of the Ti6Al4V electrode, which caused current flow to the casting electrode, except for the sample in 227 ppm F⁻ at pH 5.5.

The initial coupled Ti6Al4V potential migrated to values close to those measured for the single Ti6Al4V obtained in the experiments on the single materials. At 227 ppm F⁻ and pH 5.5, the initial peak did not represent the active dissolution of titanium; furthermore, its highest current of 0.133 μA was the lowest registered during the galvanic measurements, as shown in Table 3. With this solution combination, both alloys were in the passive domain when single or coupled. For other solution combinations of fluoride concentration and pH, the potential of single Ti6Al4V was lower, with a significant difference in comparison to single NiCr, thereby generating a transient current when coupled.

The results of OCP for single Ti6Al4V and of galvanic potential for Ti6Al4V coupled with NiCr were plotted on an adapted E vs. pH diagram of the Ti-H₂O system for all solution combinations evaluated, as shown in Figure 6 [27].

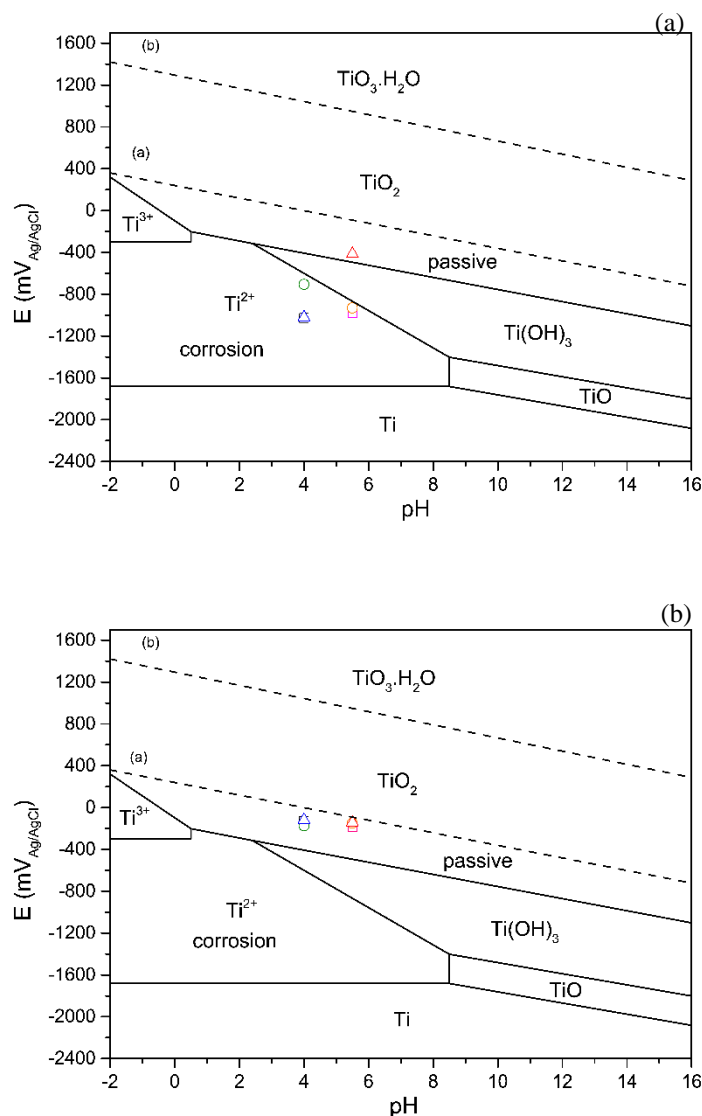


Figure 6. Electrode potential (OCP) of single Ti6Al4V (a) and galvanic potential of Ti6Al4V coupled with NiCr (b) as a function of solution composition (Δ 227 ppm F^- at pH 5.5; \triangle 227 ppm F^- at pH 4.0; \circ 2270 ppm F^- at pH 5.5; \circ 2270 ppm F^- at pH 4.0; \square 12300 ppm F^- at pH 5.5; \square 12300 ppm F^- at pH 4.0).

For the single Ti6Al4V for all solutions, except 227 ppm F^- at pH 5.5, the potential remained in the corrosion domain. In contrast to the single Ti6Al4V, the galvanic interaction of Ti6Al4V coupled with NiCr shifts the potential values into the range of TiO_2 stability, remaining in the passive domain for all solution combinations evaluated.

The NiCr alloy was not affected even when the potential decreased due to its connection with titanium during the galvanic action, remaining passive under cathodic conditions. For all conditions tested, the galvanic couple final potential stabilized at values closer to the OCP of single NiCr than to the OCP obtained for single Ti6Al4V in the same solutions. These results provide new important

information on the functional recommendation of the use of fluoride even if the patient has rehabilitations with titanium implants that are coupled with NiCr-based alloy components or prostheses. Although titanium alloys could be corroded by the presence of fluoride, as widely known and mentioned by studies in the literature [1-11,13,23-25], when coupled with Ni-Cr based alloys for oral rehabilitations, titanium alloys may still be passive due to galvanic interaction.

The galvanic current may flow not only through the metal but also through the surrounding tissue, resulting in discomfort and stimulating bone resorption. [5,7,13,18] Zhoid et al. [13] mentioned that a galvanic current greater than 20 mA was sufficient to cause sharp pain. The current-generated ions released from the corrosion process could also cause inflammatory and cytotoxic effects, mutagenicity and allergies. [6,20] The highest current of 0.638 mA found during the interactions tested in this study was inside the limit cited by Zhoid et al. [13] and thus would not cause deleterious effects. Although the occurrence of galvanic corrosion was detected, the interaction was not a risk effect since the coupled materials established a passive state in a short time, generating galvanic currents that were very low or close to zero.

Through the performed tests, it was possible to establish a relationship between the results obtained in the tests, as listed in Table 3, with the combination of fluoride concentration and pH. The final galvanic current values obtained in the test and the final couple potential were used to establish a relationship with the combination of fluoride concentration and pH, where the combination of high concentrations and low pH corresponds to the highest final current and the lowest final potential.

Another relationship was established between the maximum current peak and the respective potential with the concentration of fluoride and pH by comparing the results shown in Table 3. The highest fluoride concentration generated the highest current and was also influenced by the reduction in pH. This behaviour was attributed to the increased chemical reactivity of the titanium alloy and its protective film with the increase in the fluoride concentration and pH reduction in the oral environment [5,7,9,12,14,16,25]. Tuna et al.[14] mentioned that a high corrosion current indicates low corrosion resistance, whereas a low corrosion current indicates high corrosion resistance of a material. Therefore, a high concentration of fluoride ions leading to a high reactivity of titanium was indicated by the increase in value of the transient current generated by the increased release of Ti ions in active dissolution. The predominance of the acidic environment leads to the formation of HF, which reacts easily with the titanium surface; this process is exacerbated when in combination with a high concentration of fluoride [1,7,8,10,23,25].

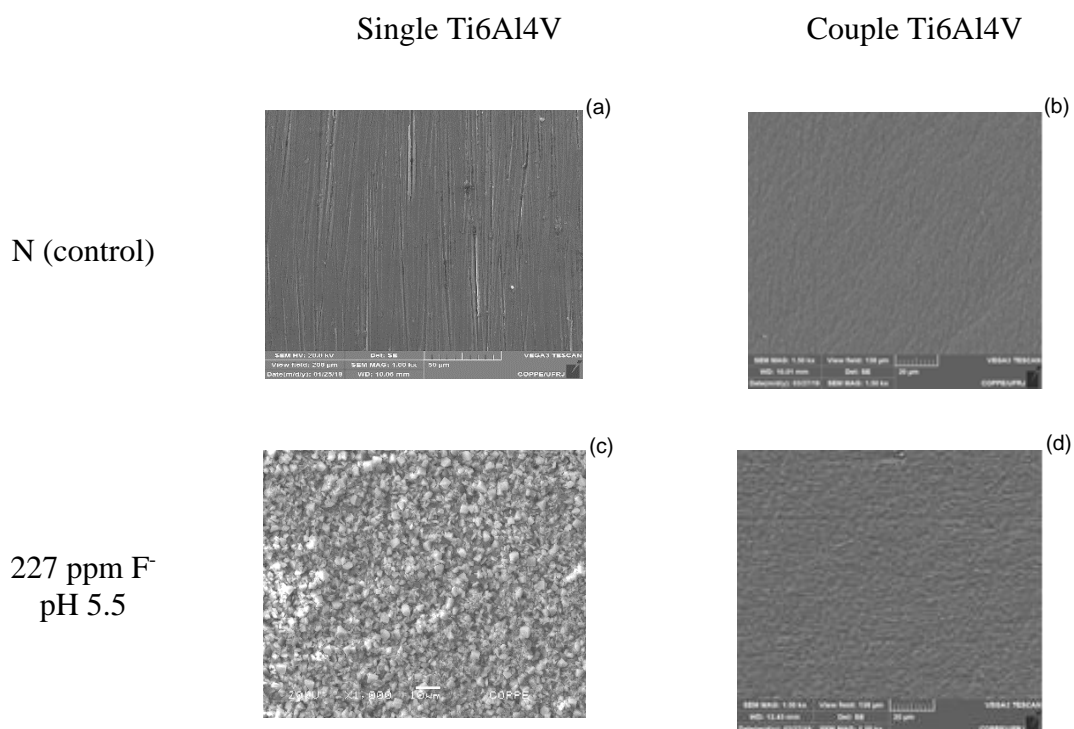
The galvanic test results at both pH 4.0 and 5.5 confirm the tendency of the galvanic couple to remain passive, which is represented by a rapid decrease in the current to values near zero, while the potential increases to values near those presented by an isolated NiCr alloy. The time necessary to stabilize the galvanic current was lower at pH 5.5 than at pH 4.0. In the evaluations of potential at pH 5.5, the couple presented an initial high spike of current, with a corresponding low spike of potential. After this, the subsequent increase in the galvanic potential indicated a tendency of the titanium alloy to reach a passive state under the influence of NiCr, in other words, the current returned to very low magnitudes, close to zero, and the potential stabilized. In contrast, in tests carried out for pH 4.0, after an initial high spike of current, with a corresponding low spike potential, the couple presented a subsequent period of intermittent variations in the current and potential, which corresponds to instability

of the electrochemical reactions, alternating between the active dissolution of titanium and the attempt to form an oxide protective film. The amplitudes of the variations in the current and potential decrease with the decrease in the fluoride concentration.

In summary, when coupled to NiCr, the Ti6Al4V alloy is less susceptible to corrosion than single Ti6Al4V components in the presence of fluoride solutions. Despite significant electrochemical potential differences, the galvanic interaction produced is mitigated by the limitation of the galvanic current. This galvanic interaction also shifts the potential to increased values for the Ti6Al4V/NiCr pair, which can promote titanium passivation, thereby avoiding active dissolution commonly observed for single titanium alloys in fluoride solutions.

Although the OCP and polarizations were important parameters for corrosion behaviour, they were not sufficient to define the corrosion resistance of dental alloys. In addition, the release of ions in long-term immersion tests could be a request for dental alloy employment because it considers the long-term interaction of alloys with the environment [18]. Due to the passive state on all evaluations of NiCr, this alloy was not evaluated in the long-term immersion tests.

The long-term immersion tests were carried out for Ti6Al4V in two solutions, 227 ppm F⁻ at pH 5.5 and 12300 ppm F⁻ at pH 4.0, for 15 days to characterize the corrosion products, the surface morphology and the number of ions released. The solutions represented the least and the most aggressive conditions of the combinations of fluoride and pH evaluated in our study.



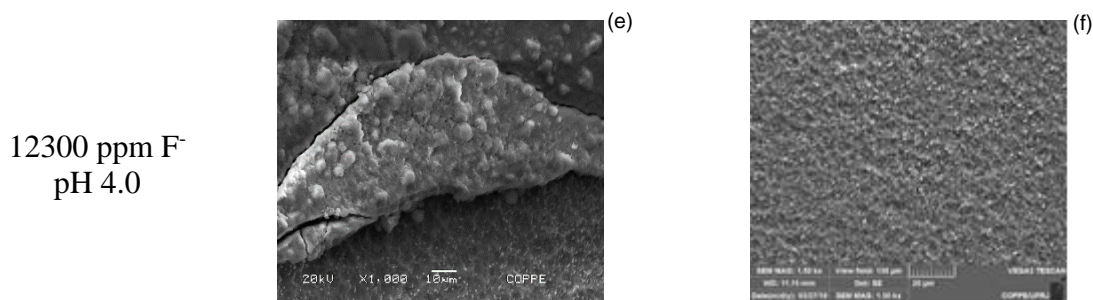


Figure 6. SEM images obtained before immersion tests of single Ti6Al4V (a) and Ti6Al4V coupled with NiCr (b) and after immersion tests of single Ti6Al4V in 227 ppm F⁻ at pH 5.5 (c), Ti6Al4V coupled with NiCr in 227 ppm F⁻ at pH 5.5 (d), single Ti6Al4V in 12300 ppm F⁻ at pH 4.0 (e) and Ti6Al4V coupled with NiCr in 12300 ppm F⁻ at pH 4 (f).

The main goal of this evaluation was to compare the surface morphology and roughness after galvanic interaction that maintained Ti6Al4V in a passive state, with the characterized surface found with long-term immersion tests in a less aggressive combination that represented the same passive state. The obtained SEM images are in Figure 6, and the 3D reconstruction by confocal analysis is in Figure 7. The obtained parameters of roughness are in Table 4.

For the immersed single Ti6Al4V alloy, a formation of a pseudofilm on the surface in test solutions containing 227 ppm of F⁻ at pH 5.5 and a damaged surface from tests in solutions containing 12300 ppm of F⁻ at pH 4.0 were observed. The SEM images of the films from a fluoride solution with 227 ppm F⁻ at pH 5.5, corresponded to a pseudopassive condition, which exhibited a preserved surface and suggested a formation of a protective film; this presented a different morphology than that seen on the control surface evaluated before the tests. After immersion tests in a F⁻ solution with 12300 ppm at pH 4.0, SEM images of single Ti6Al4V revealed a different morphology, showing cracks that were probably regions where the pseudofilm ruptured. Cracks observed at some points of this film suggested damage mechanisms and dissolved areas. The existing cracks from regions where loss of the pseudofilm integrity occurred on the surface from immersion tests in a solution of 12300 ppm F⁻ at pH 4.0 were also investigated. In evaluations of immersion tests after polarizations in solutions with 227 and 12300 ppm F⁻, Souza et al. [8] found similar differences in the SEM analyses. The authors found on surfaces of 227 ppm F⁻ only defects from polishing, while for 12300 ppm F⁻, they found cracked areas, which they explained to be associated with the excessive oxidation of the Ti film.

For Ti6Al4V coupled with NiCr in both the least and most aggressive combinations, the surface was preserved without damage or cracks on the surface, even in the most aggressive combination of 12300 ppm F⁻ at pH 4.0. The surface of Ti6Al4V coupled with NiCr from a solution of 12300 ppm F⁻ at pH 4.0 presented a morphology that suggested an increase in roughness when compared to that of the 227 ppm F⁻ at pH 5.5, which presented a similar morphology to that of the control surface. In the most aggressive combination, when coupled with NiCr, Ti6Al4V did not present a damaged surface when compared to the surface morphology found on single Ti6Al4V in the same aggressive combination of fluoride and pH. These results confirmed that the passive state allowed by the galvanic interaction

between the couple and were in agreement with the findings for single Ti6Al4V in 227 ppm F⁻ at pH 5.5.

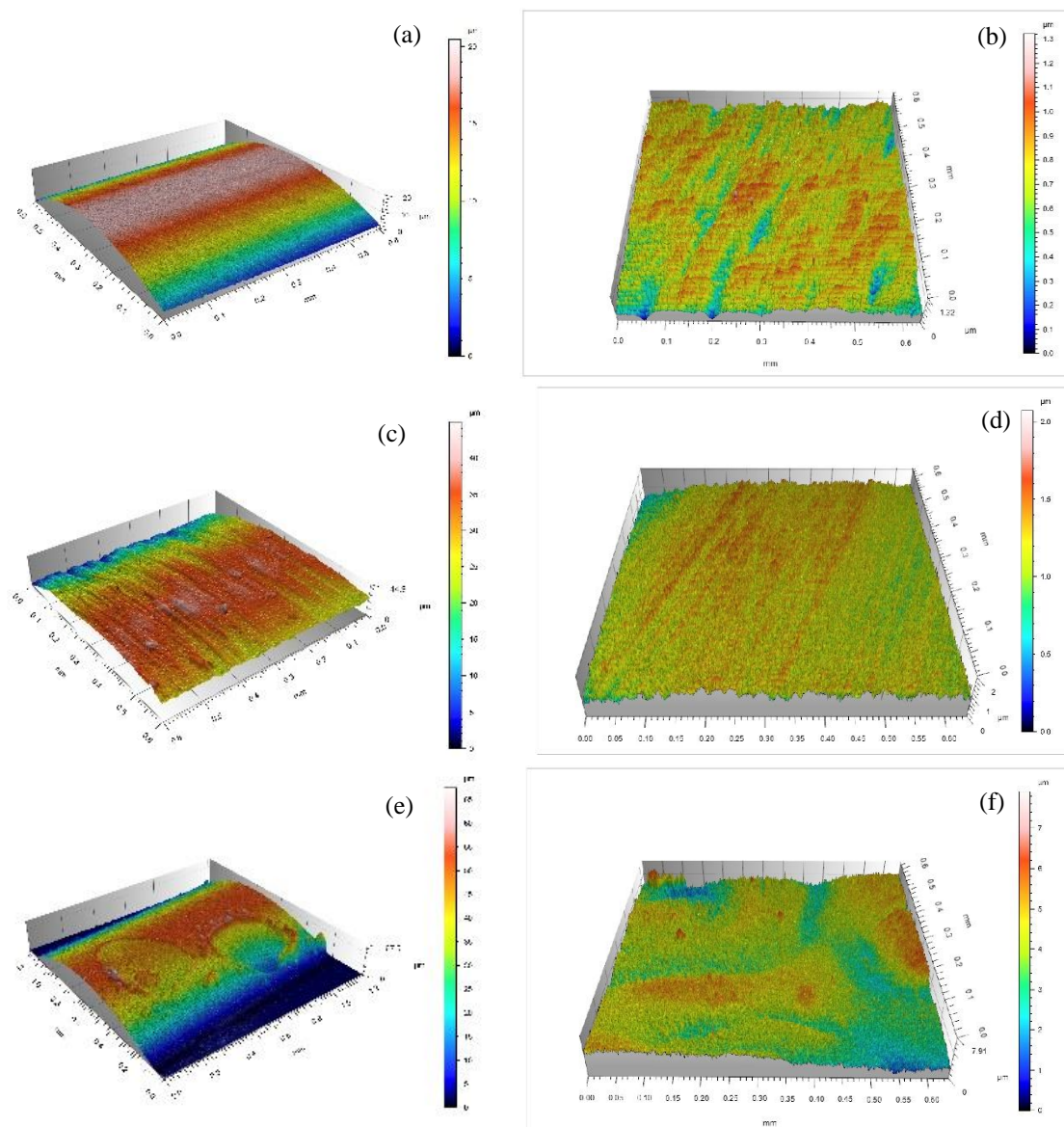


Figure 7. 3D reconstruction of single Ti6Al4V and couple Ti6Al4V: single Ti6Al4V before immersion (a), Ti6Al4V coupled with NiCr before immersion (b), single Ti6Al4V in 227 ppm F⁻ at pH 5.5 (c), Ti6Al4V coupled with NiCr in 227 ppm F⁻ at pH 5.5 (d) single Ti6Al4V in 12300 ppm F⁻ at pH 4.0 (e), and Ti6Al4V coupled with NiCr in 12300 ppm F⁻ at pH 4.0 (f).

Table 4. Mean roughness area (Ra, Rq) obtained with confocal analysis.

Solution	Single Ti6Al4V Ra (μm)	Single Ti6Al4V Rq (μm)	Couple Ti6Al4V Ra (μm)	Couple Ti6Al4V Rq (μm)
N (control)	0.098	0.118	0.087	0.106
227 ppm F ⁻ pH 5.5	0.104	0.137	0.108	0.132
12300 ppm F ⁻ pH 4.0	2.09	2.72	0.289	0.378

The confocal analysis, in addition to characterizing the surface, allowed us to obtain roughness parameters from these surfaces. Significant differences were found among the Ra (roughness arithmetical mean area) and Rq (roughness quadratic mean area) parameters for single Ti6Al4V between the surfaces after the long-term immersion tests in solutions ($p < 0.05$). Whereas for Ti6Al4V coupled with NiCr, no significant differences were found between the solutions ($p > 0.05$). For single Ti6Al4V, the roughness alterations identified in the Ra and Rq parameters presented a significant increase with increasing fluoride concentration. These differences may be associated with the presence of fluoride ions on the film surfaces and correlated with the corrosion behaviour presented in electrochemical tests, which is in agreement with literature data. The same correlation between the increase in roughness and fluoride content was previously found in the literature [4,5-8,10,23]. The changes in roughness could lead to biofilm accumulation on these surfaces, enhancing the surrounding tissue inflammation or accumulation of acidic metabolites from the biofilm in the oral environment. For Ti6Al4V coupled with NiCr, the galvanic interaction kept Ti6Al4V in a passive state for both solutions. Even in the most aggressive combination of fluoride concentration and pH, which represented an active dissolution for the single Ti6Al4V, for the galvanic couple, the values of roughness parameters were closer to the values found for the less aggressive combination. The above represents a passive state because this galvanic interaction kept the Ti6Al4V passive. This result was in contrast to the higher increase in the roughness parameter found for single Ti6Al4V with an increase in fluoride concentration and a pH reduction.

Since only the single Ti6Al4V alloy presented active dissolution, the evaluation of ions released by ICP-MS was performed only for a single alloy in long-term immersion tests. The ICP-MS analysis was performed on an aliquot of the solution at the end of tests to determine Ti, V and Al ions. The analytical technique was unable to quantify F ions. Al ions were not detected, and even if they were present, they were in a concentration lower than the lowest limit of quantification (LOQ) possible. Ti and V ions were found in the solutions tested. The concentration of the ions released showed a statistically significant difference between the solutions evaluated ($p < 0.05$). A larger difference was found for Ti ions, at 174.05 ppm in 12300 ppm F⁻ at pH 4.0 and 0.059 ppm in 227 ppm F⁻ at pH 5.5. The quantification for V resulted in 0.54 ppm in 12300 ppm F⁻ at pH 4.0 and 0.028 ppm in 227 ppm F⁻ at pH 5.5. The loss of titanium can be associated with the layer formed by corrosion products coming from active dissolution of the alloy in the presence of acidic fluoride. This environment can degrade the alloy surface, generating regions with active dissolution and an increase in corrosion products released into the surrounding tissue [1,8,24]. The literature reports that concentrations up to 11 ppm of Ti ions may present cytotoxic effects [8,28]. Wachi et al. [29] detected concentrations of up to 15 to 50 ppm of Ti ions in surrounding implant tissue after exposure to NaF for 30 min in animals. These detected ions were involved in the increased production of the expression receptor RANK-L (receptor activator nuclear kappa-L) and the ligand OPG (osteoprotegerin). These receptors and ligands are essential for osteoclast differentiation and increasing their activity consequently leads to bone resorption [28]. Although the previous results indicate a pseudopassivation of the alloy in fluoride solution with a concentration of 227 ppm of F⁻ at pH 5.5, it was possible to detect a release, but in a short concentration that did not represent a cytotoxic effect. Whereas in fluoride solution with a concentration of 12300 ppm of F⁻ at pH 4.0, the ions released could lead to cytotoxic effects.

The combined analysis of ICP-MS and the other techniques, SEM and confocal, supports the active interpretation that the Ti alloy has active dissolution process in fluoride solution at a concentration of 12300 ppm of F⁻ at pH 4.0 and supports the improvement of corrosion resistance when the Ti6Al4V alloy is coupled with NiCr, leading to a passive state even in the most aggressive combination of fluoride and pH.

4. CONCLUSIONS

Experiments on single materials demonstrated that variations in fluoride concentration and pH affected the corrosion behaviour of Ti6Al4V but not that of NiCr alloy. The occurrence of galvanic interaction between the Ti6Al4V and NiCr alloys in solutions with various fluoride concentrations and pH values is possible but without deleterious effects. The most important effects generated by this galvanic interaction are the protection of the NiCr alloy and the stabilization of the titanium alloy in a passive state. Ti6Al4V coupled with NiCr alloys shows improved corrosion resistance of the titanium alloy in fluoride environments and does not represent a risk to a patient. This study provides new important information on the application of fluoride to prevent caries or for sensible treatments when patients had rehabilitations with titanium alloys and such alloys coupled with NiCr-based alloy components.

The surface analysis of Ti6Al4V coupled with NiCr presented a morphology and roughness closer to that found in the long-term immersion tests for single Ti6Al4V when the alloy was in a passive state than in corrosive states, corroborating the results that galvanic interaction improved the corrosion resistance of Ti6Al4V in fluoride solutions when coupled with NiCr.

This work only evaluated the titanium alloy in configuration with the casting NiCr alloy, but for future areas of research, evaluations with other alloys, such as casting CoCr and zirconium alloys, should be performed with the same methodology.

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