



Effect of galvanic coupling between titanium alloy and stainless steel on behavior of corrosion of dental implants

Larissa O. Berbel^{1*}; Bárbara V. G. de Viveiros¹; Ana Lígia Micelli¹; Jesualdo Rossi¹; Frederico Nigro¹; Luis C. Aranha¹; Isolda Costa¹

*Corresponding author: e-mail address: lari_berbel@yahoo.com.br

Abstract: Titanium and its alloys are widely used in dental implant manufacturing due its favorable properties, such as, biocompatibility, high mechanical strength and high corrosion resistance. This last one, is a result of the ability of titanium to form an oxide film (TiO₂) in contact with oxygen. However, a several factors can accelerate the corrosion process of implants in contact with the oral environment, such as, acidification of the medium, differential aeration, inflammatory conditions, presence of protein and the junction of diferent metals. The goals of this research is to investigate the corrosion effect of galvanic coupling between titanium alloy (grade V) and stainless steel 316L. The investigative technique adopted was the scanning vibrating electrode technique (SVET) in phosphate buffer solution simulating inflammatory conditions. The results showed detrimental effects of acidity of the environment, induced by inflammatory conditions, accelerate the oxidation of Ti-6Al-4V. SVET maps and SEM images for the junction of the different metals showed that the region with the highest electrochemical activity it is at the interface between the metals, mostly concentrated on the Ti-6Al-4V alloy, depending on the conditions of the medium.

Keywords: Biomaterials. Corrosion. Dental implants.

Introduction

Studies using metallic biomaterials have been conducted since the 19th century. In the beginning, the metals commonly used for organ replacement in the orthopedic area were iron, gold and silver. However, over the years, many researches have selected metallic materials capable of meeting the necessary requirements for use in the orthopedic and dental applications¹. It is necessary to attend the requirements for biomaterials to contact body fluids since the application of biomaterials requires biocompatibility, high corrosion resistance, high mechanical resistance, osseointegration, besides properties such as durability, fatigue strength and ductility are also required^{1,2}.

According to Manan *et al.*³, metals of high corrosion resistance may corrode when in contact with body fluids, depending on the environment conditions. The corrosion resistance of metallic biomaterials used in dentistry needs to be studied, since the buccal region presents favorable conditions to promote and accelerate the corrosive processes in dental implants. Metals inserted in oral region might be exposed to pH changes⁴. Also, the temperature and the presence of proteins⁵, bacteria⁶, might vary and the salts concentration might reach high values⁷. Also, fluoride ions in mouthwash affect the corrosion behavior of the material⁶.

According to the American Society for Testing and Materials (ASTM) G15-93⁸, corrosion occurs through chemical or electrochemical reactions between the metal and the environment to which it is exposed, resulting in the degradation of its properties. The environment conditions are of major importance the corrosion behavior of dental implants.

Several types of corrosion can be observed in dental implants, such as, pitting, crevice and galvanic corrosion. Galvanic corrosion in dental prostheses occurs when they are manufactured with dissimilar alloys. When different materials come into contact with corrosive fluids a potential difference is established between metals, creating in vivo galvanic cells^{9,10}.

The potential difference produces electric current flow that accelerates anodic dissolution of the less noble metal. Furthermore, electric current passing through the metal and tissue junction causes pain to the patient¹⁰.

In order to understand the behavior of metallic biomaterials when in contact with the buccal region it is necessary to evaluate the in vitro corrosion behavior of these metals by simulating inflammatory conditions around the dental implant.

The present study was carried out to evaluate the corrosion behavior of Ti-6Al-4V dental implant galvanically coupled with 316L stainless steel prosthetic abutment. The corrosion behavior was evaluated by open circuit potential measurements and scanning vibrating electrode technique (SVET), once the corrosion process is driven by electrochemical reactions between the metal and the medium to which it is exposed¹¹.

Materials and methods

The material used in this study consisted of a Ti-6Al-4V (Ti grade V) dental implant connected to a stainless steel 316 L prosthetic abutment. Samples of the connected materials were embedded in a cold curing resin and then sequentially ground with SiC paper #800, #1200, #2000 and #4000. Subsequently, the surface of the samples was polished with 1 µm diamond paste. Finally, the samples were degreased with acetone in a sonifier, rinsed with deionized water and dried under a hot air stream.

The tests were performed in phosphate buffered solution (PBS) with addition of 1% (mass) hydrogen peroxide (34 % Standard) and pH adjusted to 3. These characteristics are typical of inflammatory conditions. The area exposed to the electrolyte (test medium) was 0.05 cm². Hydrogen peroxide acts as a substitute for reactive oxygen species (ROS) often present in inflammatory processes¹². Under these conditions, pH are in the range of 3 to 4¹³.

¹Instituto de Pesquisas Energéticas e Nucleares (IPEN – CNEN/SP), São Paulo, SP, Brazil.



Figure 1– Dental implant of Ti grade V and a prosthetic abutment of stainless steel 316L.

Open circuit potential measurements

The open circuit potential was monitored as a function of immersion time in the electrolyte used in this study that comprised a phosphate buffer solution with 1% hydrogen peroxide and pH adjusted to 3 to simulate inflammatory conditions. Electrochemical tests were carried out using a three-electrode set up consisting of Ag/AgCl (3M KCl), as reference electrode, a platinum wire as counter electrode and the sample of Ti grade V and stainless steel 316 L, separately or coupled, as working electrode.

Scanning vibration electrode technique (SVET)

Scanning vibration electrode technique tests were carried out using an Applicable Electronics™, controlled by the Automated Scanning Electrode Technique ASET 4.0 software (Science Wares™). Insulated Pt–Ir probes (Microprobe Inc.) with a platinum black deposited were used as vibration electrode for the SVET system. The probe was placed (100 ± 3) μm above the surface, vibrating in the planes perpendicular (Z) and parallel (X) to the samples surface. The amplitude of vibration was 19 μm , vibration frequencies of the probe were 174 Hz (X) and 73 Hz (Z). A time lag between acquiring each current density data-point was 0.5 s. All experiments were performed in a Faraday cage at (20 ± 2) °C. The tests were carried for 24h.

Surface Characterization

After immersion tests, the exposed surface of the samples was characterized by optical microscopy, using a Leica DMLM, and scanning electron microscope (SEM), using a TM–3000, with 15 keV acceleration voltage, tabletop model, located at the Center of Lasers and Applications (CLA– IPEN–CNEN/SP).

Results e Discussions

Figure 2 shows the open circuit potential variation as a function of time of immersion of Ti–6Al–4V and 316 L stainless steel, either separately or coupled, in the electrolyte of this study.

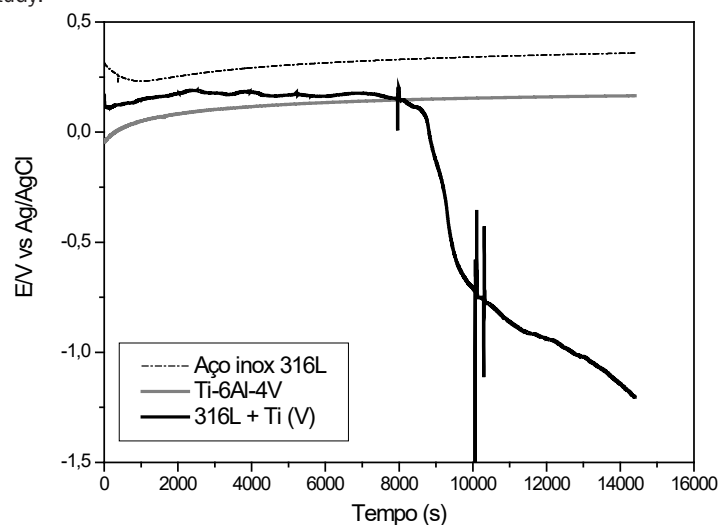


Figure 2 – Open circuit potential variation as a function of time of immersion of a dental implant (Ti grade V) and a prosthetic abutment of stainless steel, either separately or coupled.

According to OCP measurements, the stainless steel 316 presented more positive potentials compared to the titanium alloy, throughout the test. Therefore, when the Ti alloy is electrically connected to the SS 316L and exposed to the electrolyte of this study, the grade V titanium acts as anode while the stainless steel, behaves as cathode.

As expected, the open circuit potential of the sample with Ti alloy coupled to SS 316L showed an intermediate value between the two materials

tested separately, up to 8000 seconds (s) of the test. After this period of test, strong corrosion attack occurred in the sample with the galvanic couple that was evidenced by potential oscillations (indicated in Figure 2). Consequently, for longer periods than 8000 s, the potential largely decreased and values well below those of the two isolated alloys were measured. These results indicate a harmful effect of galvanically coupling the two tested alloys to the passive film promoting its attack when exposed to aggressive environments, and, consequently, corrosion of the material. The oscillations in potential of the galvanically coupled samples were supported by the intense localized attack observed at the exposed surface.

Figure 3 shows SVET maps of the galvanic couple during exposure to the electrolyte for 2h (A), 10h (B) and 14h (C). The immersion times corresponding to the maps of Figure 3(A), (B) and (C).

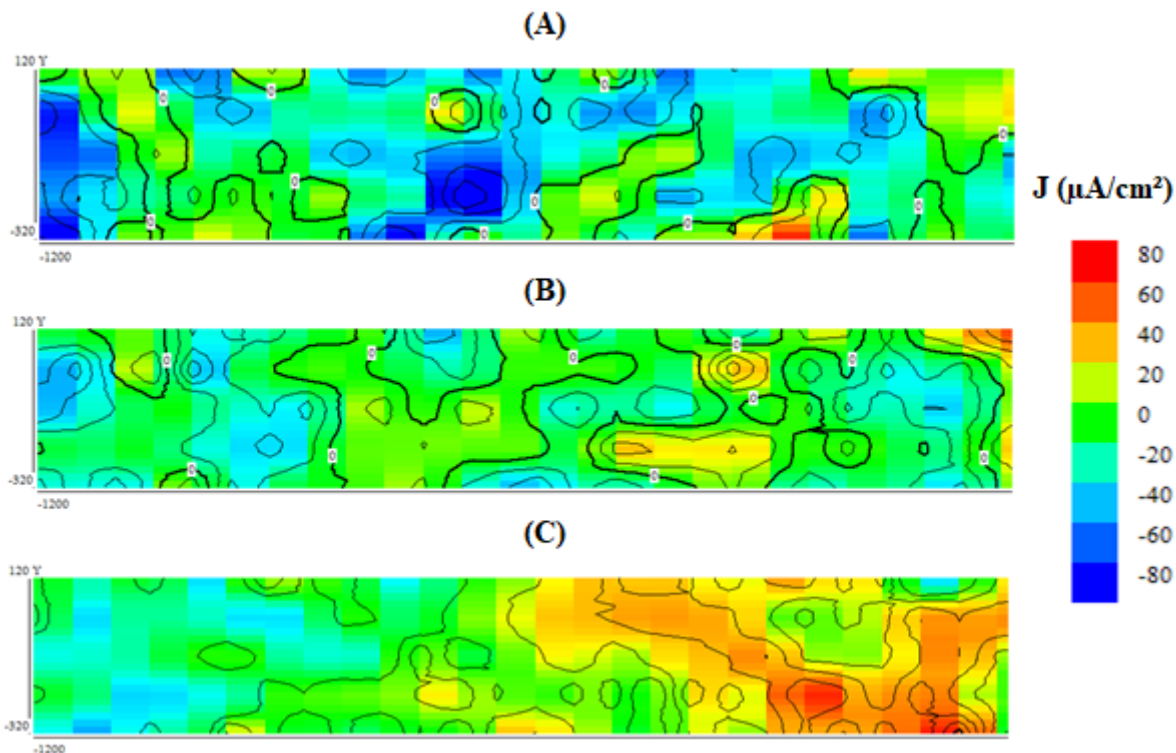


Figure 3 – SVET maps of the region of the galvanic coupling between the stainless steel 316 L abutment and the Ti grade V dental implant after (A) 2 hours, (B) 10 hours e (C) 14 hours of immersion in a PBS solution pH 3 and addition of 1% H_2O_2 .

After 2h of immersion, anodic areas were identified in the Ti alloy (see arrows). SVET maps (Fig. 3) showed that the anodic regions were related with the Ti-6Al-4V alloy. Anodic areas were clearly identified in the Ti alloy after 14h of test. Also, the anodic currents were related to the Ti-6Al-4V alloy. Consequently, the SS 316L was cathodically protected (blue regions). It is noteworthy that the conditions used in this study may occur in the buccal region in case of inflammatory processes.

Figure 4 shows the surface of the dental implants connected to the prosthetic abutment by (A) optical microscope and (B) scanning electron microscope (SEM) after the SVET assay.

The surface images of the galvanic coupling by scanning electron microscopy and optical microscopy (Fig. 4) after 24 hours of immersion test shows a large amount of corrosion products in the galvanic coupling region, mainly on Ti-6Al-4V alloy. Comparing the results of open circuit potential and SVET maps, it is observed that in acid medium (pH 3) and hydrogen peroxide addition, the titanium alloy grade V used with implant acts as anode in relation to stainless steel 316 L used as a prosthetic abutment, and latter being protected cathodically while Ti alloy corrosion is accelerated.

Mellado-Valero et al.¹⁴ analyzed the electrochemical behavior of five different alloy used to the manufactured of prosthetic abutments coupled to a titanium grade 2 used as dental implant from electrochemical assays in a solution of artificial saliva under different pH conditions (6.5 and 3.0) with the addition of fluoride ions. After the tests, was observed acceleration of corrosion of titanium alloy (grade 2) when coupled galvanically to the Co-Cr prosthetic abutment. The authors concluded that the effect of galvanic coupling is highly dependent on the conditions of the medium and the material in contact.

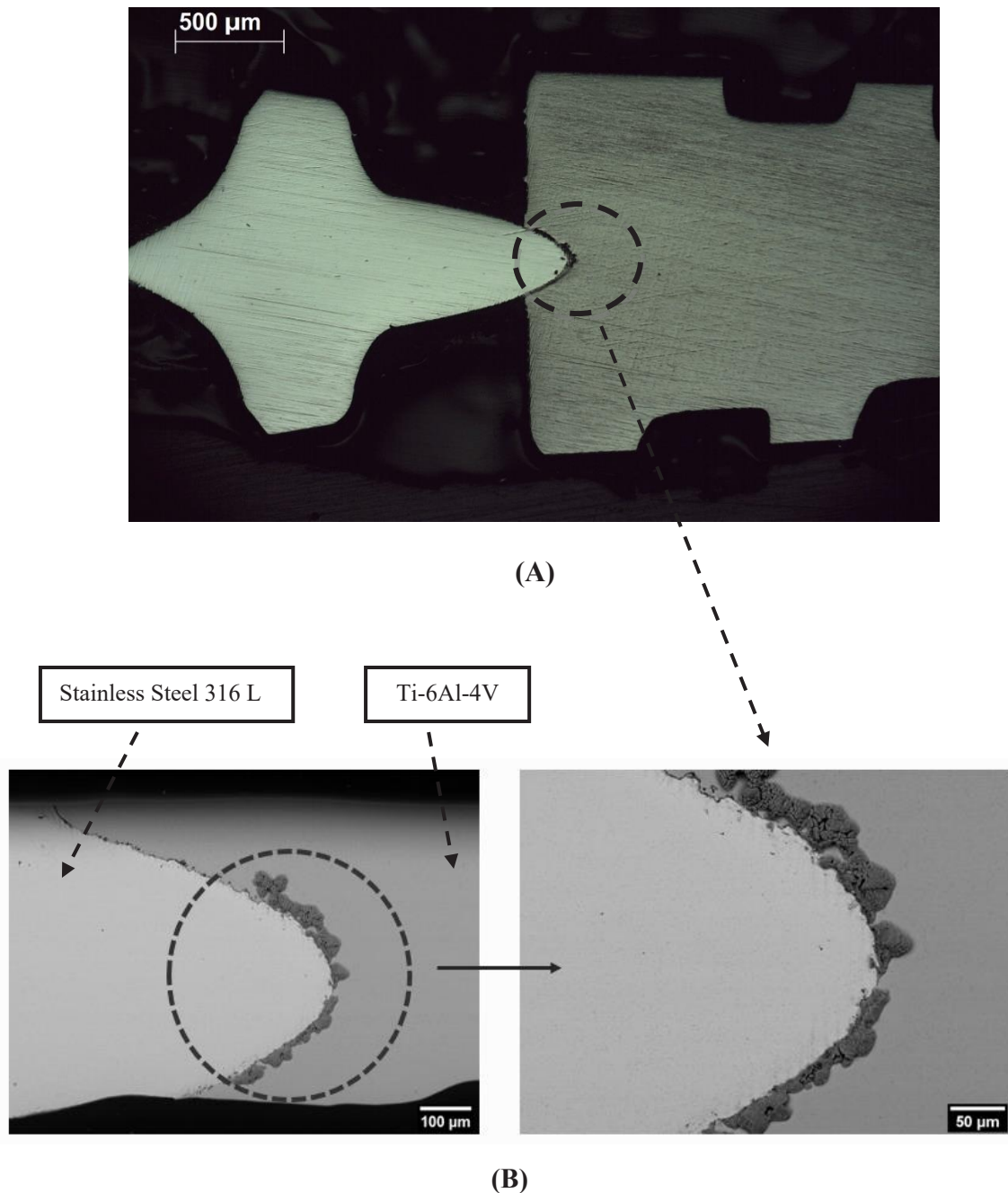


Figure 4 – Images of (A) optical microscopy and (B) scanning electron microscopy (SEM) after 24 hours of immersion in a phosphate buffer solution pH 3 and 1% H₂O₂.

Conclusions

The results of this study allow to concluding that Ti-6Al-4V alloy in galvanic contact with stainless steel 316 L acts as the anode in contact with a solution simulating inflammatory conditions in the oral environment. Galvanic coupling promotes an attack on the Ti alloy by attacking the passive film on the Ti alloy grade V when in contact with SS 316L, resulting in an intense attack on the coupling, as observed by a large amount of corrosion products under the area between these alloys.

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References

- [1]. Asri, R. I. M.; Harun, W. S. W.; Samykano, M.; Lah, N. A. C.; Ghani, S. A. C.; Tarlochan, F.; Raza, M. R. Corrosion and surface modification on biocompatible metals: a review. *Materials Science and Engineering C*, v. 77, 2017.

- [2]. Ravoiu, A.; Benea, L.; Chiriac, A. Metabolic albumin and its effect on electrochemical behavior on titanium implant alloy. *Materials Science and Engineering*, v. 374, 2018.
- [3]. Manan, N. S.; Harun, W. S. W.; Shri, D. N. A.; Ghani, S. A. C.; Kurniawan, T.; Ismail, M. H.; Ibrahim, M. H. I. Study of corrosion in biocompatible metals for implants: a review. *Journal of alloys and compounds*, v. 701, 2017.
- [4]. Moreno, J. M. C. Vasilescu, E.; Drob, P.; Osiceanu, P.; Vasilescu, C.; Drob, S. I.; Popa, M. Surface and electrochemical characterization of a new ternary titanium based alloy behaviour in electrolytes of varying pH. *Corrosion Science*, v. 77, 2013.
- [5]. Silva–Bermudez, P.; Rodil, S. E. Na overview of protein adsorption on metal oxide coatings for biomedical implants. *Surface & Coatings Technology*, v. 233, 2013.
- [6]. Apaza–Bedoya, K.; Tarce, M.; Benfatti, C. A. M.; Henriques, B.; Mathew, M. T.; Teughels, W. Souza, J. C. M. Synergistic interactions between corrosion and wear at titanium–based dental implant connections: A scoping review. *Journal of Periodontal Research*, v. 52(6), 2017.
- [7]. Revathi, A.; Magesh, S.; Balla, V. K.; Das, M.; Manivasagam, G. Current advances in enhancement of wear and corrosion resistance of titanium alloys: a review. *Materials Technology*, 2016.
- [8]. ASTM G15–93. Standard terminology relating to corrosion and corrosion testing.
- [9]. Bhola, R.; Bhola, S. M.; Mishra, B.; Olson, D. Corrosion in titanium dental implants/prostheses – a review. *Trends in Biomaterials and Artificial Organs*, v. 25(1), 2011.
- [10]. Chaturvedi, T. P. An overview of the corrosion aspect of dental implants (titanium and its alloys). *Indian Journal for Dental Research*, v. 20(1), 2009.
- [11]. Guo, H.; Callaway, J. B.; Ting, J. P–Y. Inflammasomes: mechanism of action, role in disease, and therapeutics. *Nature Medicine*, v. 21, n. 7, 2015.
- [12]. Izquierdo, J.; Bolat, G.; Mareci, D.; Munteanu, C.; González S.; Souto, R. M. Electrochemical behaviour of ZrTi alloys in artificial physiological solution simulating in vitro inflammatory conditions. *Applied Surface Science*, v. 313, 2014.
- [13]. Konstantinidis, I. A.; Kotsakis, G. A.; Gerdes, S.; Walter, M. H. Cross–sectional study on the prevalence and risk indicators of peri–implant diseases. *European Journal of Oral Implantology*, v. 8, n. 1, 2015.
- [14]. Mellado–Valero, A.; Muñoz, A. I.; Pina, V. G.; Sola–Ruiz, M. F. Electrochemical behaviour and galvanic effects of titanium implants coupled to metallic suprastructures in artificial saliva. *Materials*, v. 11, 2018.