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Electrochemical Behavior of Three CP Titanium Dental Implants in Artificial Saliva

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The electrochemical behavior of three titanium dental implants purchased on the Brazilian market was evaluated in artificial saliva using open-circuit potential measurements, electrochemical impedance spectroscopy and potentiodynamic polarization. The three implants are passive in this medium but their corrosion resistance and the stability of their passive oxide films are quite different. Although the three implants were made of commercially pure grade titanium, their corrosion current densities and passive current densities were shown to differ from one to two orders of magnitude.

Keywords: *dental implants, titanium, corrosion, electrochemical techniques*

1. Introduction

Titanium has been widely used for dental implants and restorations due to its good osseointegration, excellent corrosion resistance and biocompatibility in biological fluids and high resistance/weight ratio[1]. The influence of contaminants and surface treatments of titanium implants (alumina-blasting, acid etching, anodization, hydroxyapatite coating, for example) on osseous integration has been extensively studied. Many works have been also published on the corrosion behavior of commercially pure titanium in artificial saliva, Ringer, Hanks solutions and others[2-6]. All the authors agree that the titanium corrosion resistance in these media is due to the formation of an adherent and highly protective oxide film on its surface which is mainly formed of TiO_2[7]. Nevertheless, this oxide can lose its chemical stability under certain conditions. In fluoride medium for example, titanium can be severely attacked depending on the pH due to the formation of stable titanium fluoride and oxy-fluoride compounds[8]. In spite of the abundant bibliography on titanium corrosion properties, no study was found about the corrosion resistance of commercial titanium implants. Although titanium implants are considered as highly corrosion resistant materials for applications in body fluids, the determination of their corrosion rate is of great importance. Indeed, some studies indicated that titanium release in the organism, even at low levels, can lead from local discoloration of the tissues to serious inflammatory reactions[9-10].

The aim of the present work was to study the corrosion behavior of three titanium dental implants purchased on the Brazilian market in artificial saliva, using open-circuit potential measurements, electrochemical impedance spectroscopy and potentiodynamic polarization.

2. Experimental

The dental implants (namely A, B and C) investigated in the present work were obtained on the Brazilian market from three different suppliers and are made of grade 2, 3 and 4 CP-titanium, respectively. Their chemical composition according to ASTM F67-95 standard[11] is reported in Table 1.

Samples were cut from the implants for microstructure analysis, mounted in resin, grounded until 2400 grit, polished using an aqueous suspension of silica powder and finally etched in a modified Kroll solution (3 mL HF + 8 mL HNO_3 + 100 mL H_20). The three implants present a similar coarse-grained structure but differ in the mean Ti grain size (Figure 1). The Ti grain sizes of A, B and C implants are in the 50-100, 20-40 and 10-30 µm ranges, respectively.

The remaining materials were machined to nearly 3 mm-diameter cylinders. A copper wire was welded on one side of each cylinder in order to assure the electric contact. Then each cylinder was embedded in resin. The cross-section of the electrode (nearly 7 mm^2 exposed area) was mechanically ground with emery-paper up to 600 grit, rinsed with distilled water and dried.

The electrolytic solution used for the electrochemical study was the Fusayama artificial[12] saliva with the following composition: 0.4 g NaCl + 0.4 g KCl + 0.795 g $CaCl_2$–$2H_20$ + 0.690g NaH_2PO_4–H_2O + 0.005 g Na_2S-$9H_2O$ + 1.0 g urea in 1,000 mL deionized water. The Fusayama saliva has a natural pH of 5.5. The saliva was naturally aerated and the experiments were conducted without stirring. The temperature was maintained at 37 ± 1 °C using a thermostatic bath. The counter electrode was a square-shaped platinum sheet of 18 cm^2 area. All potentials were referred to the saturated calomel electrode (SCE) potential (= +0.242V/SHE).

Open-circuit potential, electrochemical impedance spectroscopy (EIS) and polarization measurements were performed using the Electrochemical Interface SOLARTRON® mod. 1287A and the Frequency Response Analyzer SOLARTRON® mod. 1260 A, controlled by the Ecorr/Zplot SOLARTRON® mod. 125587S software.

Prior to polarization experiments, the working electrodes were immersed in the Fusayama saliva for 3 hours, taking the moment of immersion as zero time. Then, impedance measurements at open-circuit potential were made using a sinusoidal signal of 10 mV amplitude and frequencies in the 0.1 Hz-100 kHz range. Cathodic and anodic polarization was then carried out potentiodynamically with 0.16 mV/s sweep rate. After each run, the samples were reground with emery papers to a 600-grit finish in order to remove any product formed on the metal surface which could affect the following tests, rinsed with distilled water and dried. Each experiment was repeated three times.

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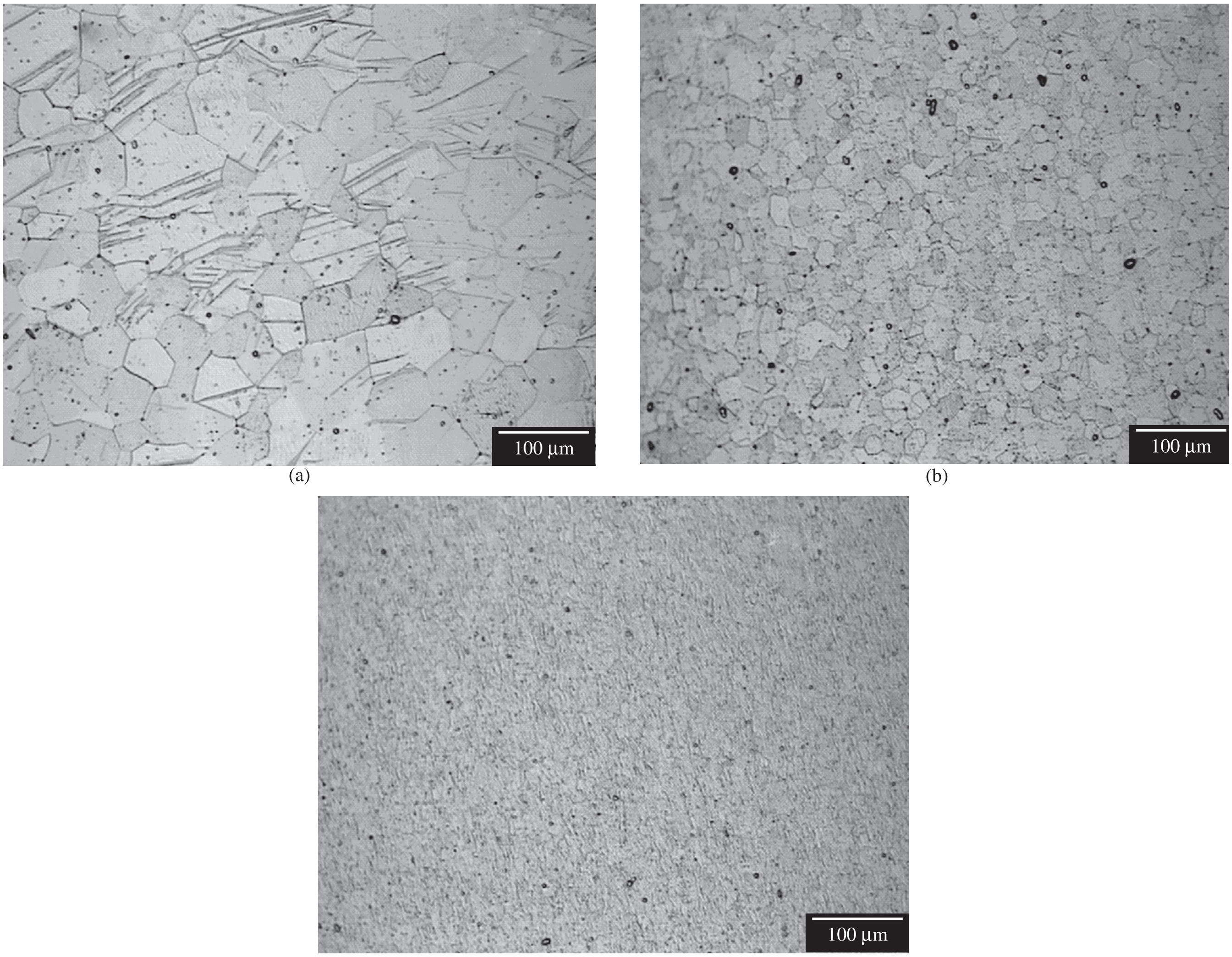
Table 1. Chemical composition of the A, B and C CP-Ti dental implants.

		Fe max	C max	N max	O max	H max	Ti min
A	Grade 2	0.10	0.03	0.015	0.15	0.005	99.7
B	Grade 3	0.15	0.03	0.020	0.25	0.005	99.6
C	Grade 4	0.20	0.05	0.040	0.30	0.010	99.4

wt. (%)



(a) (b)

(c)

Figure 1. Microstructures of (a) A, (b) B and (c) C implants.

3. Results and Discussion

Figure 2 presents the variation of the open-circuit potential (OCP) of the three Ti implants as a function of exposure time in artificial saliva. All OCPs shift in the noble direction with time which depicts the growth of a passive oxide film on the three implants in this medium. The potential of both A and B implants presents some oscillations, which can be related to some instability of their oxide films. These oscillations are not observed for C implant.

The open-circuit potentials tend to stabilize with time. Their values after 3h exposure, –0.235, –0.046 and +0.075 V/SCE for A, B and C implants, respectively (or 0.007, 0.196 and 0.317 V/SHE), show that C implant presents the noblest character, following by B implant and finally A implant. Nevertheless, all these potentials are found in the stability region of TiO_2 oxide in the Ti-H_2O Pourbaix diagram for solutions of pH 5.5[13]. A comparison of the implants corrosion potentials in artificial saliva with published data is a difficult task as the OCP of CP-Ti is highly dependent on heat- and mechanical treatments, surface preparation of the samples and exposure time. For example Schiff[14] and Al-Mayouf[15] reported OCPs of +0.025 V/SCE and –0.331 V/SCE for CP-Ti in Fusayama artificial saliva, respectively.

Figure 3 shows the polarization curves of the three Ti implants in artificial saliva. The anodic polarization curves have the same shape and are typical of passive behavior. Nevertheless, great differences in the values of anodic current density are evident and this suggests that the passive films formed on the three implants do not have the same stability and that these implants present difference in corrosion resistance.

The corrosion current density obtained by Tafel extrapolation method and the passive current density measured at 1 V/SCE are reported in Table 2. The results show that the increasing order of corrosion resistance of the Ti implants is: A < B < C.

There is difference of two orders of magnitude between corrosion current densities of A and C implants. Schiff[14] and Al-Mayouf[15] also reported very different corrosion current density for CP-Ti in Fusayama artificial saliva, 10^{-6} and 3.10^{-8} A cm^{-2}, respectively.

Considering the corrosion current densities reported in Table 2 and using the Faraday's law for a four-electron transfer, the calculated corrosion rates of A, B and C implants are 43.0, 5.0 and 0.5 µm/year, respectively. These values depict the excellent corrosion resistance of the three implants, since it is usually admitted that a metal or alloy presents an excellent corrosion resistance when its corrosion rate is in the 25-100 µm/year range[16]. Nevertheless, metallic implants generally do not fail due to corrosion damage but due to tissue irritation or infection caused by the corrosion products. Qualitative estimates suggest that implants must corrode at rates of 0.25 µm/year or less to avoid the possibility of tissue reaction[16]. Only C implant corrosion rate is close to this limiting value.

EIS experiments were carried out at OCP in artificial saliva. The Bode diagrams presented in Figures 4 a and b show that the metal/solution interface for the three Ti implants has a predominantly capacitive behavior, which is characteristic of passive materials. Nevertheless the capacitive behavior is limited to a narrower frequency range for A and B implants, 10^{1}-10^{2} and 10^{-1}-10^{2} Hz, respectively. The C Ti implant presents a capacitive behavior in a larger frequency range,10^{-1}-10^{3} Hz. This is related to the higher stability of the passive film formed on C implant, which has already been observed from its polarization curve (Figure 3) that shows the lowest values of the anodic current density. The impedance values measured at low frequencies (Figure 4a) indicate that the increasing order of corrosion resistance of the Ti implants in artificial saliva is: A < B < C.

The difference in chemical composition of the three Ti implants (grade 2, 3 and 4 for A, B and C, respectively) cannot explain the superior resistance of C implant and the lowest resistance of A im-

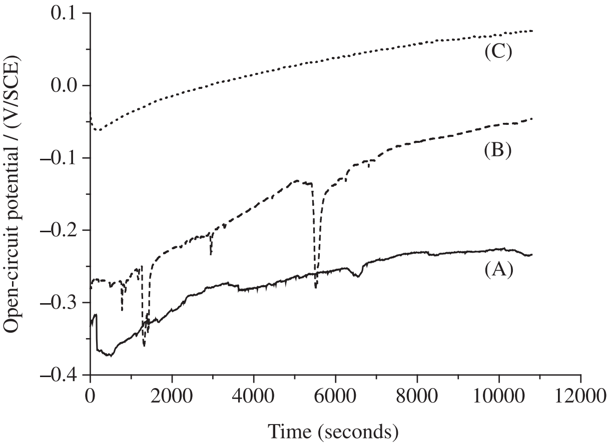


Figure 2. Variation of open-circuit potential for the three Ti implants in artificial saliva.

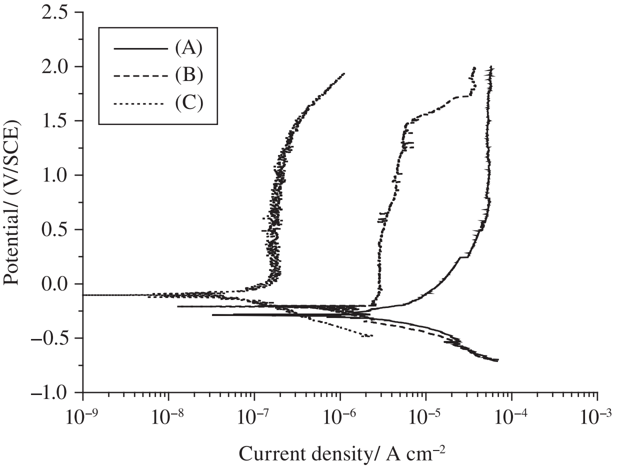


Figure 3. Polarization curves of the three Ti implants in artificial saliva.

Table 2. Corrosion potential, corrosion current density and passive current density (measured at 1 V/SCE) of the three different Ti implants in artificial saliva.

Ti implant	A	B	C
Corrosion potential/ V/ SCE	–0.235	–0.046	+0.075
Corrosion current density/ A cm^{-2}	5×10^{-6}	6×10^{-7}	6×10^{-8}
Passive current density/ A cm^{-2}	5.3×10^{-5}	4.7×10^{-6}	2×10^{-7}

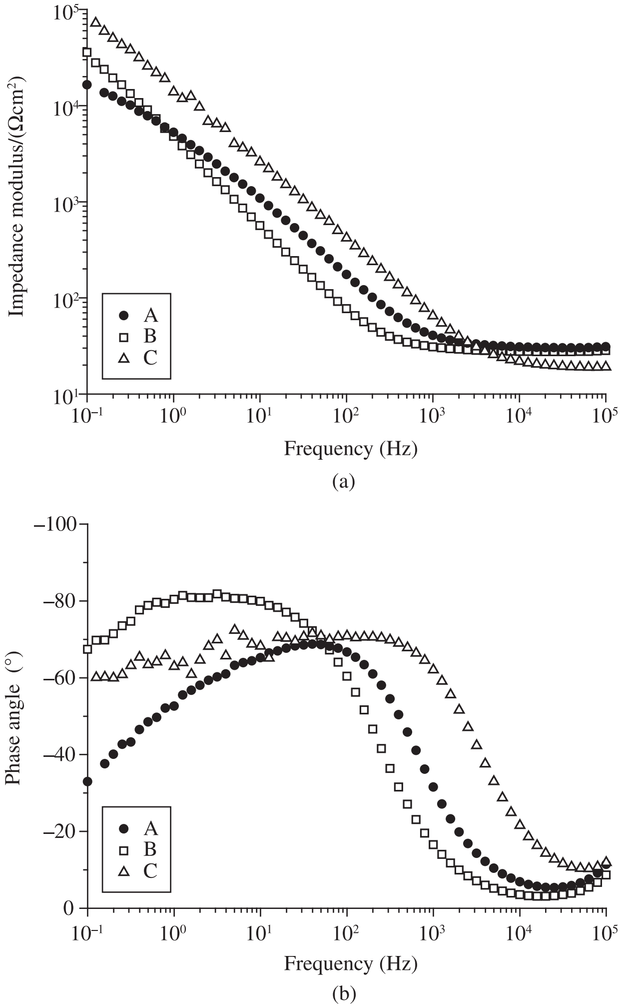


Figure 4. Bode diagrams of the three Ti implants obtained at OCP in artificial saliva: (a) impedance modulus vs frequency and (b) phase angle vs frequency.

plant. Indeed, the general corrosion resistance of commercially pure Ti grades is quite similar and our results showed differences of one to two orders of magnitude for corrosion current densities of the implants. ASTM grade 2 is only more resistant than ASTM grades 3 and 4 to stress corrosion cracking in chloride media. The difference in Ti grain size (Figure 1) cannot also explain the difference in corrosion resistance of the three Ti implants. Indeed, for most metals and alloys a decrease in corrosion resistance is usually observed when the grain size diminishes[17-18]. From the grain size standpoint, the increasing order of corrosion resistance should be C < B < A. An improvement in corrosion resistance of CP-Ti grade 2 in simulated body fluid was already observed but for ultra fine grained microstructure (sub-micron grain size)[19]. Then, other reasons such as heat- and mechanical treatments during manufacture of the implants may be raised to explain the significant difference in the corrosion resistance of the three implants.

4. Conclusions

The corrosion behavior of three commercially pure Ti dental implants purchased on the Brazilian market from three different suppliers was evaluated in artificial saliva using electrochemical techniques.

The three implants present a passive behavior in this medium and high corrosion resistance. Nevertheless their corrosion resistance and the stability of their passive oxide films are quite different.

The corrosion current densities of the three implants were shown to differ from one to two orders of magnitude.

Nor the chemical composition neither the Ti grain size of the implants could explain this difference in corrosion resistance.

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