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Corrosion behavior of pure titanium in artificial saliva solution

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ABSTRACT

The biocompatibility of commercially pure (cp) titanium stems from its chemical stability within an organism, due to a fine film of impermeable titanium oxide covering the metal surface, which guarantees its resistance to corrosion. Despite its biocompatible characteristic, this material does not promote the formation of a hydroxyapatite layer, therefore, many research groups have sought to alter the material's surface, introducing modifications that might influence corrosion resistance. The electrochemical behavior of cp Ti, with hydroxyapatite coating and without hydroxyapatite coating, commonly used in implant materials, was investigated using an artificial saliva solution at 25°C and pH=7.4. In the conditions of the study it was observed that the hydroxyapatite layer influences the properties of corrosion resistance. This study of the behavior of cp Ti with and without hydroxyapatite coating, in naturally aerated artificial saliva solution at 25°C, was based on open circuit potential measurements and potentiodynamic polarization curves. At approximately $1x10^{-6}$ A/cm^2 the potential for cp Ti with and without hydroxyapatite coating begins to increase at a faster rate, but at -74mV (SCE) for coated cp Ti and at 180mV (SCE) for uncoated cp Ti the increase in potential begins to slow. This behavior, characterized by a partial stabilization of current density, indicates that in those potential ranges a protective passive film is formed.

Keywords: corrosion, titanium, hydroxyapatite, biomaterials.

1 INTRODUCTION

Metallic materials used in orthopedics and implantology are classified as biotolerable. These materials come somewhere between bioinert materials and bioactive materials, however, they may be rendered bioactive through a surface activation treatment of their oxide, in the case of titanium, niobium, and tantalum, for example, or by the process of depositing bioactive coatings over the surface [1-3].

Commercially pure titanium (cp Ti) and its alloys were developed by William J. Kroll in 1946, and have demonstrated excellent biocompatibility, corrosion resistance and high mechanical strength, making them the most widely used of biomaterials. The biocompatibility of cp Ti stems from its chemical stability within the organism, which occurs through the spontaneous formation of a thin, adherent, and impermeable passive film of titanium oxide ($TiO_{2)}$ over the surface of the material, leading to high corrosion resistance [4-10].

Several applications of titanium can be found in biomedicine, for instance, in devices for artificial hearts, structural applications such as screws and dental implant pins, and prostheses.

However, despite its biocompatibility, there is no formation of a bioactive layer capable of bonding with bone tissue. Thus, several research projects have been developed, aimed at altering the surface of this material.

Efforts are underway to improve osseointegration. Moreover, different techniques are currently being used to obtain coatings of biotolerable materials with mechanical strength and with a bioactive layer [11, 12]. Coatings can be produced, for example, by ion sputtering, plasma spraying, sol-gel, electrolysis, and biomimetic methods [6].

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The main difficulty encountered is obtaining a good bond between the bioactive layers and the substrate. Abe and collaborators [13] propose a method called biomimetics to coat substrates of different substances with a layer of biological hydroxyapatite (calcium phosphate-based ceramic biomaterial).

However, the alterations introduced in this layer during the coating process can affect corrosion resistance, which is one of the main factors that renders titanium an excellent biomaterial [14-17]. Thus, physical properties of the coating, such as size, morphology, present phases, crystallinity, and thickness, must be evaluated.

In this work the corrosion resistance of commercially pure titanium with and without hydroxyapatite coating was investigated. A coating was produced by the biomimetic method using a technique that comprises a modification of conventional techniques, with sodium silicate solution as the nucleant agent. A synthetic solution to simulate artificial saliva was used for the corrosion test to verify whether the dental implant would be affected in real conditions [18-20].

2 EXPERIMENTAL PROCEDURE

Commercially pure titanium (cp Ti), ASTM F67 grade 1, was used for the experiments. The chemical composition of Ti used is given in Table 1.

Table 1: Chemical composition of cp Ti (% weight)

C	H	N	O	Fe	Ti
0.0090	0.0013	0.0060	0.1400	0.1100	Bal.

The biomimetic method was used to coat the cp Ti surface with hydroxyapatite. The biomimetic method used in this study involved two stages [13, 18]: the first step is nucleation, in which the substrate is immersed in a synthetic solution of simulated body fluid (SBF) along with bioactive glass particles as a nucleating agent; the second step consists of precipitation and growth of the apatite layer, with reimmersion of the substrate in 1.5SBF. In this study sodium silicate (SS) solution was used instead of bioactive glass in the nucleation stage.

The 1.5SBF and sodium silicate solutions were prepared as shown in Table 2. Their pH was adjusted to 7.25 at 37°C, with HCl 0.1M and tris(hydroxymethyl) aminomethane ($(CH_2OH)_3CNH_2$) 0.05M.

Table 2: Chemical composition of the solutions

Chemical reagent	SBF (g)	1.5SBF (g)	sodium silicate (g)
$(Na_2O)SiO_2$	---	---	0.276
NaCl	7.9946	11.9919	---
KCl	0.2236	0.3354	---
K_2HPO_4	0.1742	0.2613	---
$CaCl_2.2H_2O$	0.3676	0.5514	---
$MgCl_2.6H_2O$	0.3050	0.4575	---
$NaHCO_3$	0.3528	0.5292	---
Na_2SO_4	0.0701	0.1065	---
HCl 0.1M	10 ml	15 ml	pH=6.00
Tris 0.05M	pH=7.25	pH=7.25	pH=7.25

The microstructure of cp Ti was characterized by means of scanning electron microscopy (SEM) and semi-quantitative analyses by energy dispersive spectrometry (EDS).

The corrosion behavior was evaluated by electrochemical methods. Cylindrical samples (0.5 cm^2 of area) were used as working electrodes in the polarization technique. A slow-setting epoxy resin was used to insulate the samples in order to avoid the formation of air bubbles at the resin-metal interface.

Prior to testing, the samples without hydroxyapatite coating were mechanically polished with 1200 grit SiC sandpaper, rinsed in alcohol and dried before each measurement. The measurements were taken with a potentiostat, using a conventional electrode cell arrangement. A saturated calomel electrode (SCE) was used as reference electrode, and the counter-electrode was made of platinum (Pt).

The electrolyte used during the tests was a naturally aerated artificial saliva solution, the temperature was kept constant at 25ºC, and the pH was 7.4. The chemical composition of the artificial saliva solution is shown in Table 3.

The corrosion potential, Ecorr, was measured as a function of time over a 24 h period in artificial saliva solution at 25^{o}C, until its variation became negligible (open-circuit potential).

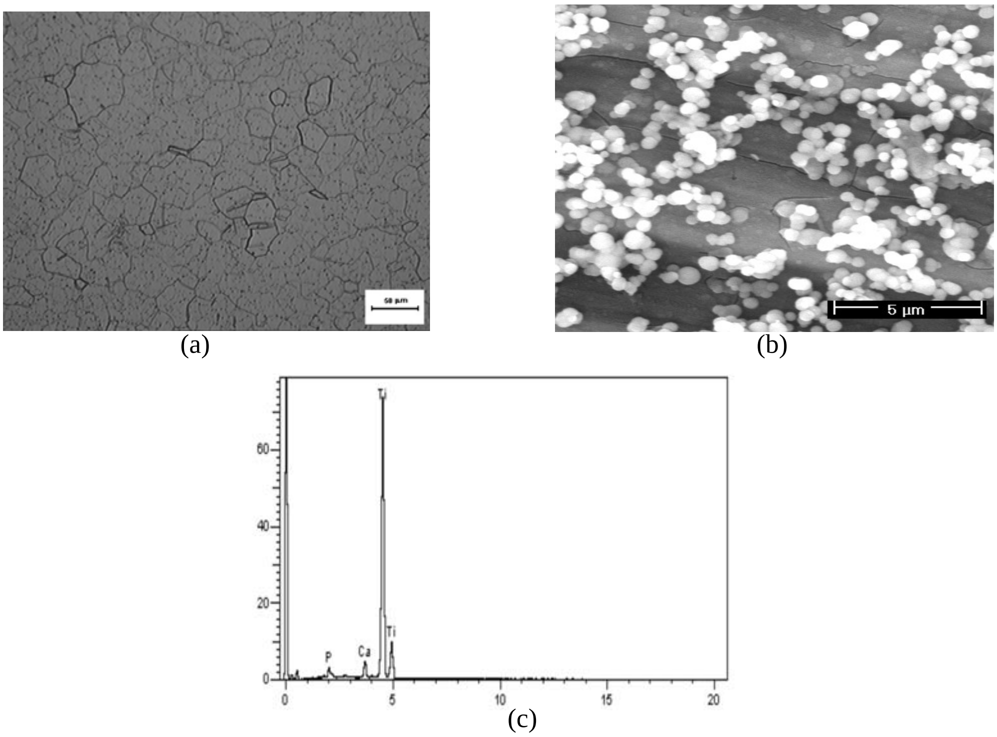
The potentiodynamic polarization curves were measured with a potential scan rate of 1 mV/s, from -1000mV (SCE) to 2000mV (SCE). The polarization tests were carried out in triplicate to evaluate the reproducibility of the results.

Table 3: Chemical composition of the artificial saliva solution [20]

Compound	**Concentration**
Na_2HPO_4	0.426 g
$NaHCO_3$	1.68 g
$CaCl_2$	0.147 g
H_2O	800 ml
HCl-1M	2.5 ml

3 RESULTS AND DISCUSSIONS

Figure 1a shows that the cp Ti had a typical cast microstructure, with non-homogeneous size distribution of α phase grains.



(a) (b)

(c)

Figure 1: Photomicrographs of the surface of cp Ti. (a) Without coating of the hydroxyapatite. (b) With coating of the hydroxyapatite. (c) EDS spectra of cp Ti with coating of the hydroxyapatite before immersion in the corrosion test.

Figures 1b and 1c show SEM and EDS of cp Ti with hydroxyapatite coating: it was possible to observe morphology composed of a dense layer and on top of this layer, a formation of globules.

The layers were analyzed using EDS, which was carried out over the entire area shown in the photomicrograph, confirming the presence of Ca and P.

The purpose of the hydroxyapatite layer is to improve the bioactivity and osteoconductivity during the initial period following implantation. The stability of these biomaterials derives from their electrochemical passivity, and their ability to avoid passivity breakdown in the highly aggressive physiological environment [18, 19].

The corrosion potential (E_{corr}) of cp Ti with and without hydroxyapatite coating is shown in Figure 2. The initial corrosion potential for cp Ti without coating was approximately -500mV, and it gradually increased to more noble potentials. After 24 h of immersion it remained stable, at around -225mV. For the coated cp Ti, the initial corrosion potential was +30mV, with rapid decrease. After 24 h of immersion, a value of approximately -70mV was reached.

Several authors have investigated the corrosion potential of Ti in artificial saliva, and different results have been reported. Kedici et al. [21] reported a corrosion potential of -425mV/SCE, while Schiff et al. [22] found a stable value of +50mV/SCE under similar conditions. In this work, the measured corrosion potential for non-coated Ti (-225mV/SCE) was higher than the value reported by Kedici et al. and lower than that reported by Schiff et al. However, differences in the composition of the artificial saliva solution must be considered.

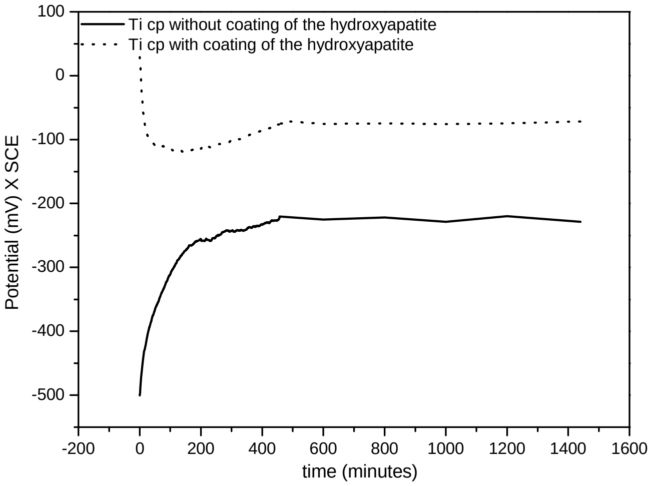


Figure 2: Potential corrosion against time curves of cp Ti with and without hydroxyapatite coating in naturally aerated artificial saliva solution at 25°C.

Figure 3 compares typical potentiodynamic polarization curves for cp Ti with and without hydroxyapatite coating after 24h of immersion in naturally aerated artificial saliva solution at 25°C. The polarizations test started at a cathodic potential in relation to the corrosion potential, therefore the surface passive film was at least partially removed due to the highly reducing initial potentials.

The corrosion current densities (I_{corr}) were obtained from the polarization curves by extrapolation of the cathodic branch of the curves to the corrosion potential (Tafel extrapolation). The average values and their deviations are shown in Table 4.

Table 4: Average values of E_{corr} and I_{corr} determined from the polarization curves in naturally aerated artificial saliva solution at 25°C

cp Ti	E_{corr} (mV (SCE))	I_{corr} (A/cm^2)
without hydroxyapatite coating	-585±20	$1x10^{-7}\pm0.3$
with hydroxyapatite coating	-460±15	$1x10^{-7}\pm0.4$

At approximately $1x10^{-6}$ A/cm^2 the potential for cp Ti with and without hydroxyapatite coating starts to increase faster, but at -74mV (SCE) for coated cp Ti and at 180mV (SCE) for uncoated cp Ti the potential increase becomes slower. This behavior, which is characterized by a partial stabilization of current density, suggests that it is in those potential ranges that a protective passive film is formed. This is in agreement with the low values I_{corr} shown in Table 4.

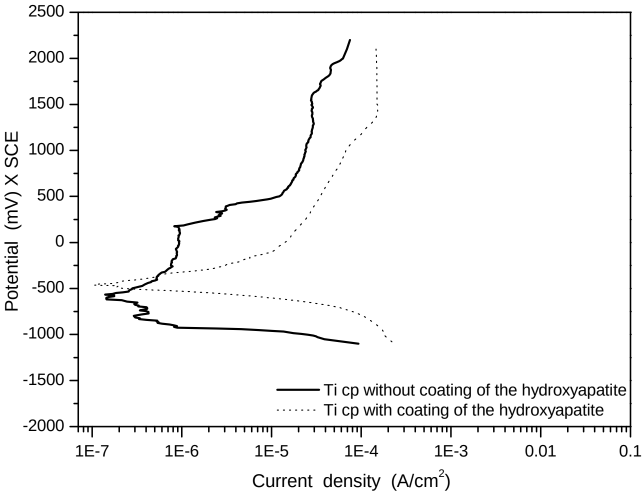
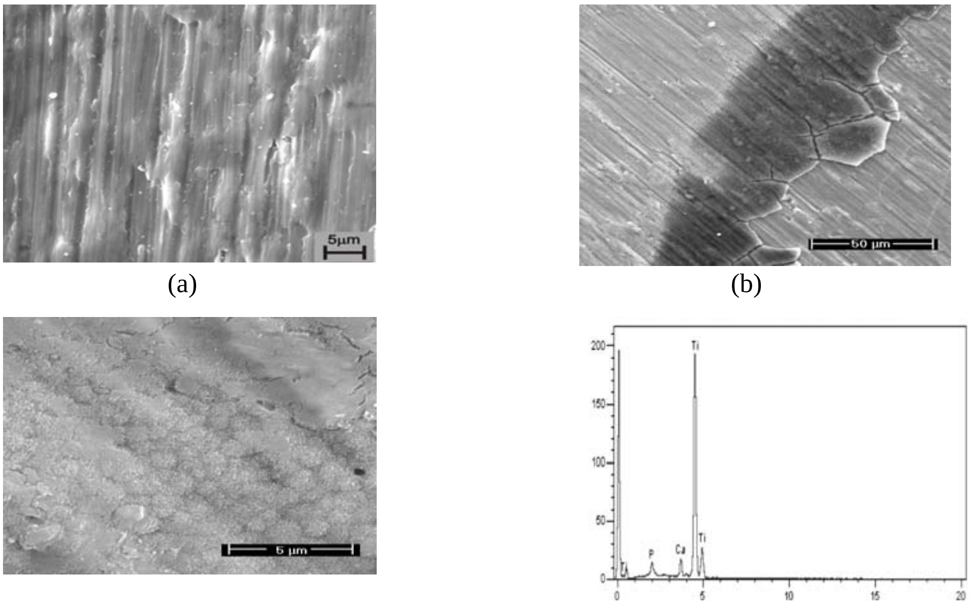


Figure 3: Potentiodynamic polarization curves for cp Ti with and without hydroxyapatite coating after 24h immersion in naturally aerated artificial saliva solution at 25°C.

However, at potentials above those values, a rapid increase in current density is observed, indicating that this film is gradually replaced by a less protective passive film, which becomes stable around 1300mV (SCE) for coated cp P Ti. For uncoated cp Ti, this point is 500mV. This film is characterized by passive current densities of the order of 0.1×10^{-4} to 1.5×10^{-4} A/cm^2. The smallest value of passive current density was shown by uncoated cp Ti (about 0.1×10^{-4} A/cm^2), and some current oscillations were also observed for potential above 1500mV (SCE), which could indicate passive film breakdown and repassivation.

Figure 4 shows photomicrographs of the surface of cp Ti after the corrosion test in artificial saliva solution.



(a) (b)

(c) (d)

Figure 4: SEM photomicrographs of the surface of cp Ti after the corrosion test in artificial saliva solution. (a) Without hydroxyapatite coating. (b) and (c) With hydroxyapatite coating. (d) EDS spectra coated with hydroxyapatite cp Ti.

Figure 4a shows that no signs of any type of localized attack (pitting) could be seen on the surface of the uncoated cp Ti specimens after the corrosion test in artificial saliva solution. For hydroxyapatite coated cp Ti, it was observed that the hydroxyapatite layer was partially dissolved during the test as shown in Figure 4b, but it is still possible to see the presence of the primary layer, as shown in Figure 4c.

These results are in agreement with the low corrosion current density measured in artificial saliva solution ($1x10^{-7}$ A/cm^2), for the conditions of each cp Ti specimen. An EDS analysis of the chemical composition of the precipitate layer of hydroxyapatite coated cp Ti after the corrosion test indicates that the precipitates consist mainly of calcium and phosphate, as shown in Figure 4d.

Thus, although the coating of the hydroxyapatite is not an effective anticorrosion layer, it hinders to some extent the electrochemical processes occurring at the metal substrate interface, hence contributing to a decrease in the metal ion release from the system.

4 CONCLUSIONS

It was concluded that sodium silicate solution (SS) proved to be effective for hydroxyapatite layer formation over cp Ti. Potentiodynamic polarization and open circuit potential are very useful techniques for studying the corrosion behavior of surgical implant alloys, even when they are coated with a ceramic material such as hydroxyapatite. This study of the behavior of cp Ti with and without hydroxyapatite coating in naturally aerated artificial saliva solution at 25^{o}C, shows that there is a passive region with low current density, indicating that under the conditions investigated, the formation of a surface protective film occurs. A low corrosion current density ($1x10^{-7}$ A/cm^2) was measured in this solution, for both coated and uncoated cp Ti. The lowest passive current density was measured for uncoated cp Ti (about $0.1x10^{-4}$ A/cm^2).

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