Evaluating Corrosion behavior of Porous titanium in Artificial Saliva

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Abstract: Porous titanium has been used to improve osteointegration. However, porosity is inherent a defect responsible for decreasing mechanical properties and corrosion resistance, due to the large surface area exposed to the electrolyte, compared to solid titanium. In this work, porous titanium was obtained by uniaxial pressing followed by sintering. The corrosion behavior was evaluated using open circuit, electrochemical impedance spectroscopy, potentiodynamic polarization in artificial saliva at 37ºC. A typical passive behavior was not indicated in the results obtained, but low current densities were measured.

Introduction

During a person´s lifetime, teeth can fail to perform its regular functions properly, due to accidents, illness and even wear and tear of use. Therefore, dental implants can be used in order to mitigate or solve this situation [1]. The implant material must complain to the requirements of biocompatibility, biofunctionality, bioadhesion, low density associated with high mechanical strength, because the during of chewing efforts can reach 800N and high corrosion resistance, so pure titanium and its alloys meet these requirements [2,3].

Currently, the powder metallurgy technique has being increasingly used to produce porous implants and coatings. Interconnected pores can reduce the elastic modulus, allowing bone ingrowth and thus improving osteointegration [2].

Despite the claims in the literature that titanium has excellent corrosion resistance due to the formation of adherent and highly protective oxide film, titanium implants contacts fluorite ions of toothpaste and the oral rising. The ions can attack the oxide film depending on the pH due to the formation of aggressive compounds $[TiF6]^{2-}$,$[TiF6]^{3-}$,$[TiCl5(H2O)]^{-}$ $[TiCl6]^{2-}$ and $[TiCl5(H2O)]^{2-}$. [4].

Electrochemical techniques in ways that mimic the physiologic fluids is practice widely used to evaluate the corrosion behavior of metalic biomaterials, however, it´s difficult to determine the actual area of contact with electrolyte of the porous. On the other hand, according to Edwards and Higham that restriction for flowing of electrolyte can development corrosion rate is not corresponding to the actual area [5]. The aim of the present work was to evaluate corrosion behavior of porous samples compared molten titanium using open - circuit, electrochemical impedance spectroscopy, potentiodynamic anodic polarization.

Material and Methods

Powder of commercially pure titanium grade 1 (Cp-1) was obtained by hydrogenation-dehydrogentation (HDH) process with a 45μm mean particle size. The following composition of titanium powder was determined by infrared and thermal conductivity tests: 0.0 4 C, 0.02 N, 0.06 H, 0.08 Fe and 0. 03O (% wt).

The powder was then uniaxially pressed under 400 MPa, followed by a sintering process. It carried out in high vacuum condition (10^{-6} torr) at 1100 (batch 1) and 1150 ºC (batch 2) applying heating rates of 10°C/ min. All the sintered specimens were mechanically polished with 600, 800 and 1200 with a SiC paper, followed by polishing with 6, 3 and 1 μm diamond suspension.

All electrochemical techniques were performed at 37 ± 2 ºC in artificial saliva, characterized by the following composition : 0.4 mg/ L NaCl, 0.4 mg/ L KCl, 0.8 mg/ L $CaCl_2.H_2O$,1 mg/LCO (NH2) and 200μg/L NaF with pH= 7.

The measurements were conducted in a standard three-electrode cell 1 cm^2 working electrode, where platinum and saturated calomel (SCE) were used as counter and reference electrodes, respectively. Open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization anodic (PLA) were the chosen electrochemical techniques, performed on Parsat 2273 potentiostat. The open circuit potentials were monitored during 1 hour. The EIS were conducted in the frequency range of 10^5 -10^{-2} Hz with 10 mVs^{-1} amplitude and 10 points per decade. The potentiodynamic anodic polarization were carried out at with sweep rate of 1mVs^{-1}. The measurements started at -100mV_{SCE} and finished 2000mV_{SCE}.

Results and Discussion

Fig. 1 shows the open- circuit potential of three different Titanium samples as exposure in time in artificial saliva. The open - circuit potential tends to stabilization. Their values after one hour exposure are: -0,371 for molten titanium, -0,192 for porous samples of batch 1 (1100ºC) and -0,04 $V/_{ECS}$ for porous samples of batch 2 (1150ºC). All potentials are found within the thermodynamic stability region of TiO_2 oxide in Ti-H_2 pourbaix. However, the porous samples of (batch 2) are noblest than other samples, suggesting that the protective oxide film was already in place before the test.

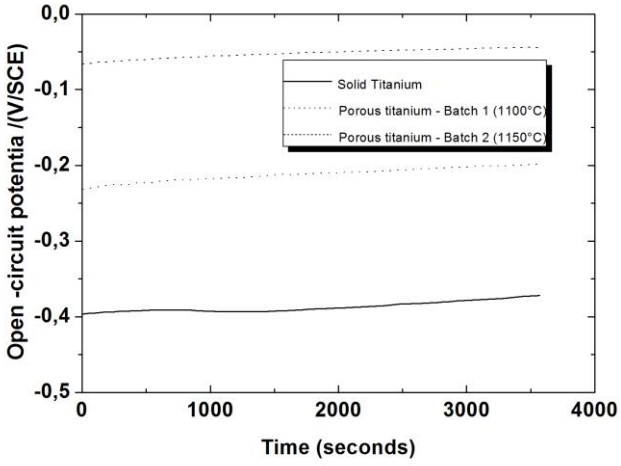

Fig. 1 Variation of open-circuit potential for three different titanium samples in artificial saliva.

The impedance spectra of solid and porous titanium in saliva artificial at 37°C are represented as Bode and Nyquist plots and shown Figs 2. The Bode diagrams show that metal/ solution interface

has capacitive behavior for solid titanium Fig 2 (a). Bode plots exhibit different behavior among porous titanium batches Fig. 2 (b) and Fig 2 (c). In the high frequency, the phase angle drops to 0°, indicating resistive behavior. In the low frequency, the phase angle decrease to lower, suggesting capacitive behavior. However, porous samples of batch 2 (sintered at 1150ºC) has the lowest capacitive behavior than other samples, because of angle phase, Z modulus (Fig 2 c) and Nyquist plots Fig 2 (f).

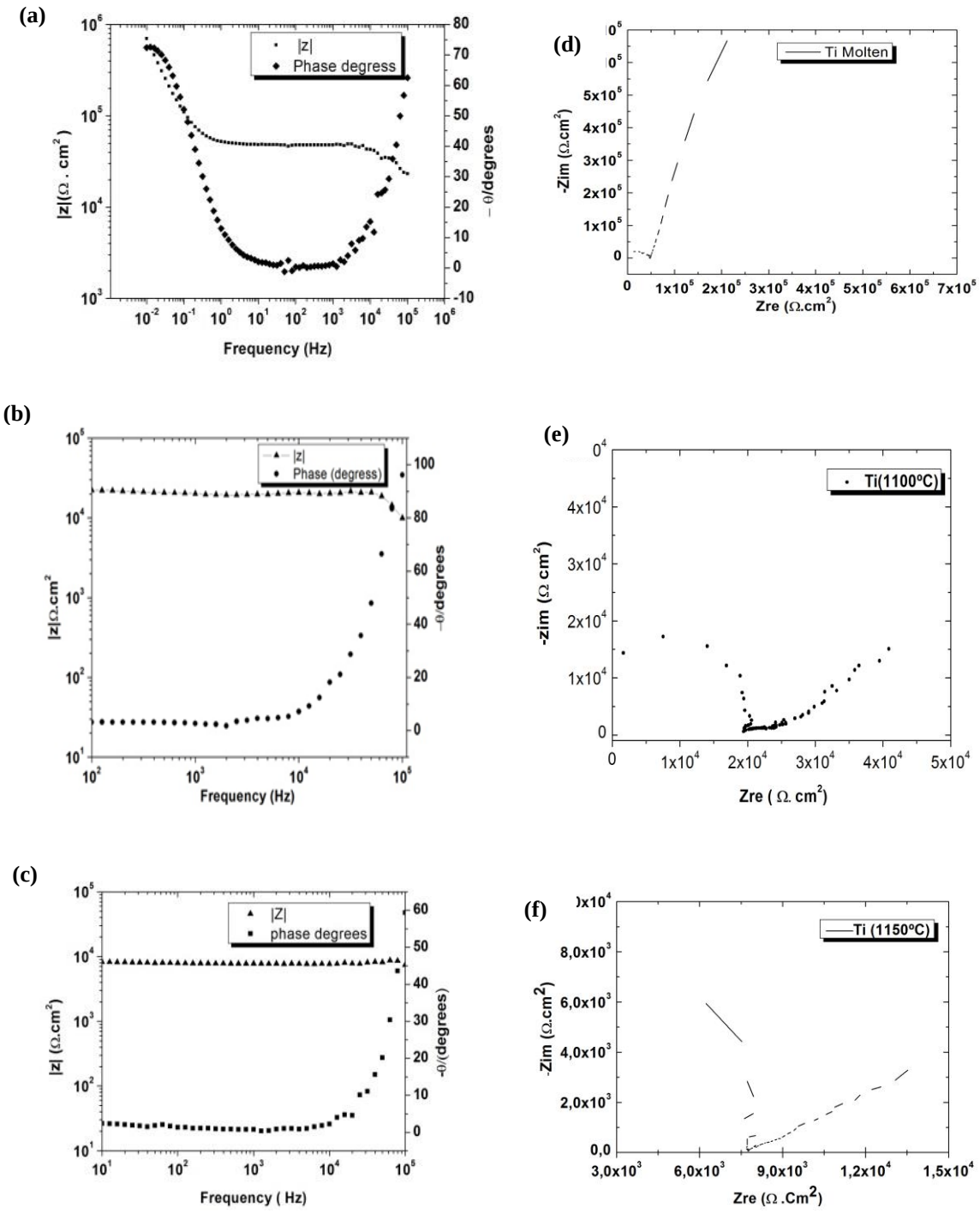

Fig. 2 EIS diagrams of different titanium specimens in artificial saliva at 37 ± 2 º: Bode plots – (a) molten titanium, (b) porous titanium 1100ºC and (c) porous titanium 1150ºC. Nyquist plots – (d) molten titanium, (e) porous titanium 1100ºC and (f) porous titanium 1150ºC.

The polarization curves of solid and porous titanium are shown in Fig. 3. As seen, the current density increase with potential from 0,2V for solid titanium, 0,42V for batch 1 and 0,50 for batch 2, suggesting that thickening the oxide film being insufficient to compensate the high filed effects of overpotential. In addition, it has been clearly shown abrupt increase of current density has not occurred which could suggest high corrosion resistance. However, in 1,2 -1,4V interval, the current density has slightly incresead, due to an oxygen evolution reaction [6]. Thermodynamic calculations showed that oxygen evolution could take place in lower potentials.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$E_{0/H_2O} = 1{,}222 - 0{,}059\ pH$$

$$E_{0/H_2O} = 0{,}809\ pH$$

$$E_{0/H_2O} = 0{,}569\ (ECS)$$

Porous titanium specimens exhibited lower resistance than solid titanium due to the larger surface area exposed to the electrolyte (Fig. 3). However, specimens of batch 1 were more resistant to corrosion than those of batch 2, which must be attributed to distinct pore morphologies. Batch 1is characterized by compact pores in an open and interconnected network, enabling the free flow of electrolyte. Batch 2 in turn has more small and isolated pores, resultant of the higher sintering temperature (1150º), trapping solution and exhausting oxygen supply, no helping to repair titanium oxide stability [6,7,8,9].

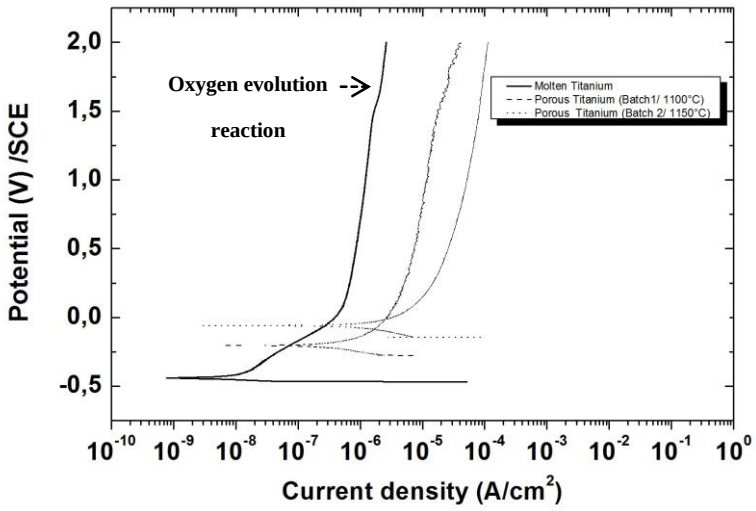

Fig. 3 Potentiodynamic polarization curve of molten and porous titanium in artificial saliva at 37± 2ºC.

Conclusions

Eletrochemical techniques have confirmed that corrosion behavior is influenced by porosity. In contrast to the expectations, the open-circuit curve has shown that the porous titanium of batch 2 (1150°C) was noblest than other samples, suggesting that the oxide film was formed during the sintering process. However, the electrochemical impedance spectroscopy and potentiodynamic anodic polarization tests confirmed that porous titanium of batch 2 has a lower corrosion resistance, as expected. It is suggested that denser and compact porosity, as found in batch 2, is more likely to trap the electrolyte, decreasing the oxygen supply needed for the preservation of titanium oxide film.

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