Corrosion Resistance Evaluation of PorousTitanium with Biomimetic Coatings

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Abstract: In this work, porous titanium samples processed by powder metallurgy and coated with biomimetic coatings, obtained during different periods of immersion in a simulated body fluid (SBF), were tested for corrosion resistance in a phosphate buffer solution (PBS). Uncoated samples were also tested for comparison. The corrosion resistance of both types of titanium samples was evaluated by electrochemical impedance spectroscopy and potentiodynamic polarisation curves. The electrochemical results indicated the formation of a surface film on the porous Ti samples with immersion in the SBF solution and this biomimetic film increased their corrosion resistance. This film helps osteointegration besides increasing corrosion resistance.

Introduction

Titanium is considered a highly corrosion resistance metal because its surface is permanently covered by an oxide film that is stable chemically and mechanically strong. Moreover it possesses properties for biomedical applications where the most important are osteointegration and biocompatibility. These properties are greatly enhanced in porous structures that favour bone in-growth providing anchorage for implant fixation. The porous structures allow the in-growth of body tissue, including bone tissue. Porosity is essential because it increases cellular adhesion and implant fixation. Moreover, interconnected macroporosity enhances osteointegration once it increases the specific surface in contact with bone, compared with smooth implants.

After a device is implanted in the body, fibroblasts surround the implant and then proceed to wall it off with a collagen-rich film. This effect of fibroblast growth into the pores with subsequent collagen formation serves to interlocks the porous structure and in-growing tissues, anchoring the material in the place within the body [1,2]. The chemical bonds between the implant and bone are additionally stimulated by bioactive materials such as calcium phosphates (eg. hydroxyapatite). It has been documented in the literature that calcium phosphate-like compounds can be nucleated and deposited on Ti and Ti alloys after immersion in different kinds of electrolytes [3-6]. Titanium implants can be bioactivated by a biomimetic precipitation process which is an alternative for other coatings methods. It is believed that this porous surface is capable of accelerating the biomimetic

process. According to Wang *et al*. [3] bone-like apatite forms on the surface of titanium pre-treated with NaOH solution after it has been treated in simulated body fluid (SBF). These authors used X-ray diffraction (XRD) and scanning electron microscopy (SEM) for microstructural characterisation and electrochemical impedance spectroscopy (EIS) to investigate the nucleation and growth of calcium phosphate (CaP) compounds. According to Tadakama *et al*. [7] NaOH solution and heat treatments are effective for inducing formation of CaP on Ti-6Al-4V. These authors investigated the process of apatite formation using XPS as function of soaking time in SBF and concluded that pre-treatments are able to produce an Al and V-free amorphous sodium titanate surface layer.

This paper reports the effect of calcium phosphate coatings deposition by biomimetic method on titanium produced by powder metallurgy on its corrosion resistance. The biomimetic methodology was studied in a previous research [8].

Materials and Methods

Porous cylindrical samples (Fig. 1) were produced by using as raw materials pure Ti powders ASTM grade 2, with irregular morphology and manufactured by hydrogenation-dehydrogenation process (Micron Metals, U.S.A) and an organic additive used as space holder, urea (Vetec, Brazil). The particle size range of Ti powders were 149-177 μm and 250-297 μm for the organic additive. The powders were mixed in a proportion of 70 % Ti/30 % urea. Subsequently, silicone molds were filled with this mixture and cold isostatic pressed at 300 MPa. For the full removal of the organic additive the samples were placed on a stove at 200 °C for 2 hours. Afterwards, they were submitted to sintering treatment on vacuum better 10^{-6} Torr (Thermal Technology, Astro, USA) at 1200 °C for 2 hours. Dense samples with 99.7% relative density were used as controls, were compacted by uniaxial and isostatic pressing and sintered without the space holder. A pure Ti powder ASTM grade 2 was used, which was milled under vacuum to an 8 μm powder medium size [9]. The pore volume fractions of the porous samples were performed by quantitative metallographic analysis, using an Image Pro Plus version 4.0 software. Thereafter, some samples were submitted to a biomimetic method in order to deposit a calcium phosphate (CaP) biomimetic coating. First they were pre-treated with 1 M NaOH solution at 130 °C in an autoclave for 60 min and heat treated at 400 °C for 1 hour. The pre-treated samples were immersed in a modified simulated body fluid (mSBF) solution (pH 7.0) at 37 °C for 14 and 28 days. The solution was replaced every two days, and the pH was controlled by the addition of calcium sulphate. The mSBF composition is composed by: $[Na^+]$ = 142.0 mM; $[K^+]$ = 5.0 mM; $[Mg^{2+}]$ = 1.5 mM; $[Ca^{2+}]$ = 2.5 mM; $[Cl^-]$ = 147.8 mM; $[HCO_3^-]$ = 4.2 mM; $[HPO_4^{2-}]$ = 1.0 mM and $[SO_4^{2-}]$ = 0.5 mM. Table 1 indicates the designation of the samples according to their treatment condition.

Table 1. Designation of the samples according to their treatment condition

| Sample	Treatment condition
P-1	Control – without pre-treatments or mSBF
P-2	Chemical and heat treatments [400 °C] and mSBF for 14 days
P-3	Chemical and heat treatments [400 °C] and mSBF for 28 days

Experimental set-up

Electrochemical tests were carried out using a Gamry potenciostat model PCI4. A three-electrode cell arrangement was used with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes. EIS and potentiodynamic polarisation tests were performed after 72 hours immersion in phosphate-buffered saline (PBS) solution, its composition is given in the Table 2. EIS measurements were performed in potentiostatic mode at the open circuit potential (OCP) with amplitude of the perturbation signal of the 10 mV and the frequency range varied from 10 kHz to 10 mHz, with acquisition rate of 6 points per decade. Potentiodynamic polarisation curves were obtained with sweep rate of 1 mV/s. and initiated from 600 mV (SCE) below the OCP and terminated at 2000 (SCE) mV above OCP.

**Table 2.** Composition (g/L) and pH of the PBS solution

NaCl	Na_2HPO_4	KH_2PO_4	pH
8.77	142	136	6.8

Results and discussion

Fig. 1 shows one of the porous samples (P-1) investigated in this study. Fig. 1a shows a general view of P-1 (without CaP coating), Fig. 1b shows the optical micrograph of its longitudinal section and Fig. 1c presents a SEM topographic view of P-1, both exhibiting the porosity morphology. Pores are the dark regions in the micrographs. The pore volume fractions were estimated in the range of 62.4 % to 71.9 %. From the optical and SEM micrographs, it can be observed that the porous microstructure is homogeneous and consists of dispersed small micropores (< 30 μm) and large interconnected macropores (> 100 μm). Fig. 2a presents the SEM image of sample P-3 (immersed 28 days in mSBF) and the corresponding EDX spectrum is shown in Fig. 2b, with high Ca and P peaks. The typical globular morphology of the calcium phosphate film formed during 28 days of immersion in mSBF is noticed at 10000X magnification.


(a)   (b)   (c)
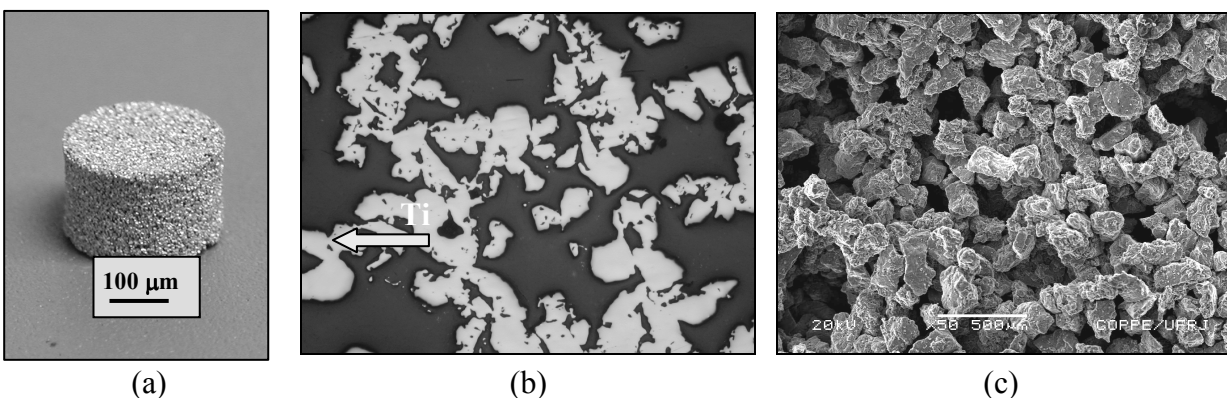
Fig. 1. Sample of porous Ti, without CaP coating: (a) general view; (b) optical micrograph; (c) SEM topographic view.

(a)   (b)
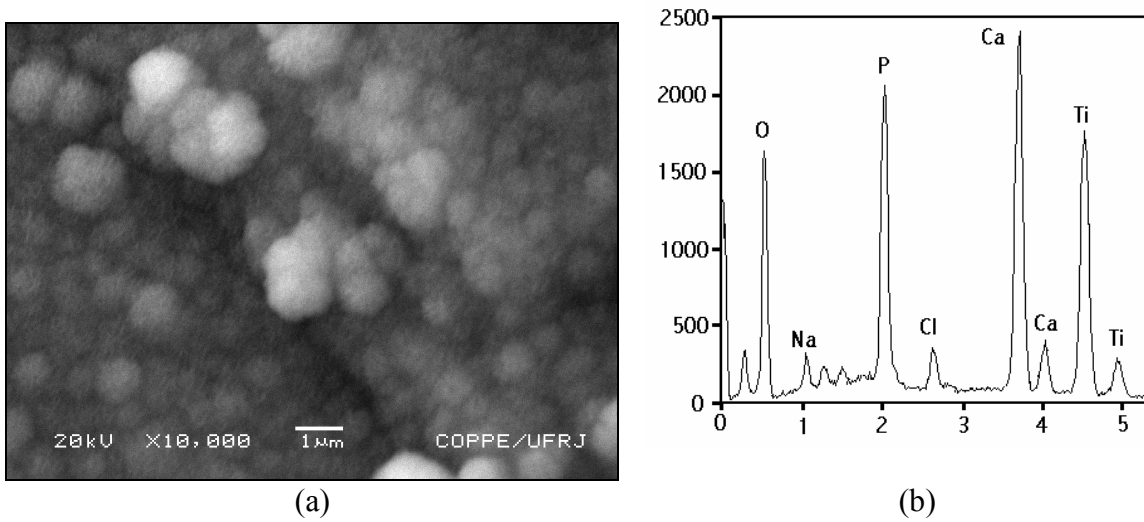
Fig. 2. (a) SEM image of P-3 samples with CaP film and corresponding (b) EDX spectrum.

Potentiodynamic polarisation curves for the three types of samples electrochemically tested (P-1, P-2 and P-3) are shown in Fig. 3. It shows very low corrosion rates, typical of passive materials.
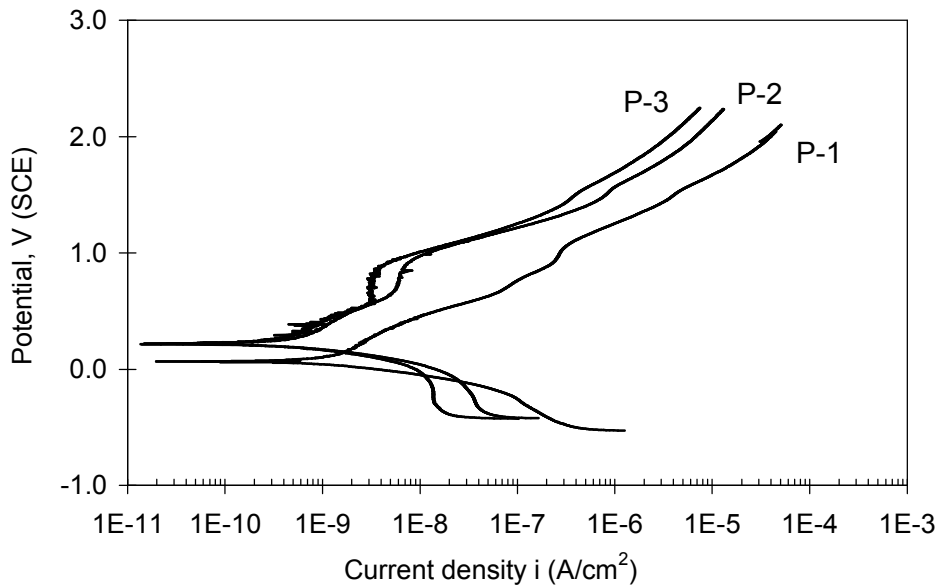
Fig. 3. Potentiodynamic polarisation curves for untreated porous titanium (P-1), porous titanium treated in mSBF for 14 days (P-2) and 28 days (P-3) sample for 72 hours immersion in PBS solution. Scan rate: 1mV/s.

The large surface area of the porous samples exposed to the electrolyte is the cause of the very low current densities estimated, once Ti is highly passive in the test medium. Corrosion potential estimated from these curves were: 64 mV (SCE), 214 mV (SCE) and 220 mV (SCE) for the untreated (P-1), treated in mSBF for 14 days (P-2) and treated in mSBF for 28 days (P-3) samples, respectively, indicating the ennoblement of the sample with growth of the surface film. The polarisation curves show similar results for the samples treated in SBF solution with only slightly lower corrosion rates associated to that treated for longer periods. The corrosion current density

(i_{corr}) values very were similar for both treated samples and of the order of nA/cm^2 showing that these are highly passive in the test solution. Although higher i_{corr} values were obtained for the untreated samples (0.3 μA/cm^2) they were also passive.

Fig. 4 shows the Bode phase diagrams of untreated (P-1) and treated samples (P-2 and P-3), after 72 hours in PBS solution.

The EIS results supported the polarisation ones. More capacitive results were associated to the treated samples (immersion in SBF) than to the untreated ones (Fig. 4). Higher impedances were obtained for the treated samples. The EIS data for the untreated samples suggested only one time constant with a peak at frequencies lower than 1 Hz. On the other hand, the treated samples (P-2 and P-3) clearly presented two time constants, the one at higher frequencies, likely related to the film deposited on the surface during immersion in the SBF solution. The Nyquist diagrams (results not shown here) confirmed that high impedances were associated to the SBF treated samples.

The electrochemical results show that the film formed in SBF solution, CaP, increases the corrosion resistance of porous Ti. It is known that this film helps osteointegration.
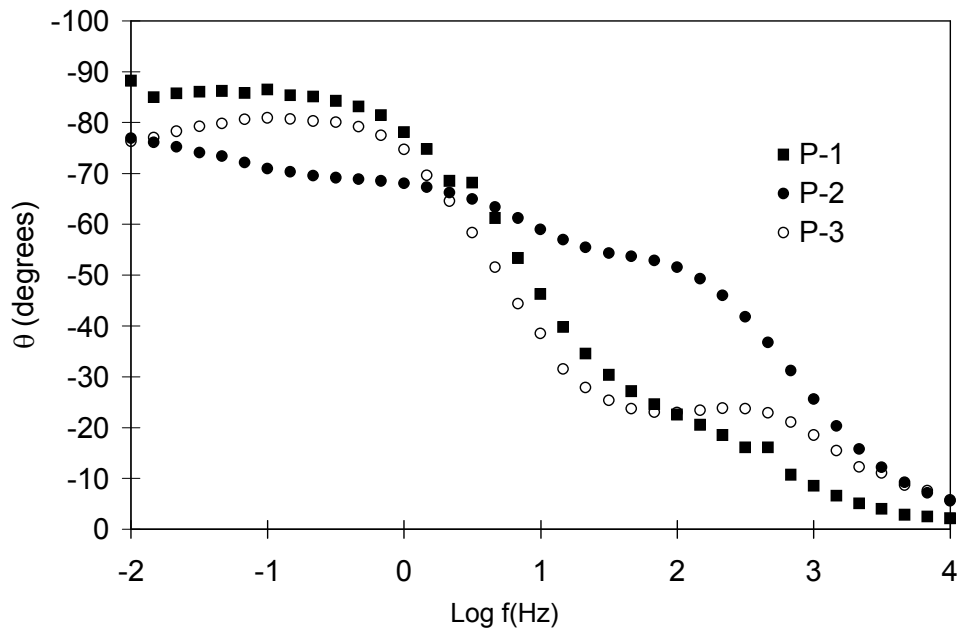

Fig. 4. Bode phase angle diagrams for P-1, P-2 and P-3 samples for 72 h in PBS.

Conclusions

The surface treatments and biomimetic process applied on porous Ti resulted in deposition of a CaP film on porous Ti samples. The electrochemical results indicated that the surface film formed improves the Ti corrosion resistance and consequently, immersion in SBF solution can be recommended as a pre-treatment for improving the corrosion properties of porous titanium.

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