

Corrosion resistance evaluation of porous and dense titanium in Hanks' solution

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Abstract In this work, the corrosion resistance of porous titanium samples with porosity in the range from 40 % to 50 % was investigated in Hanks' solution. This type of material is used for clinical applications where porous structures allow the in-growth of bone tissue interlocking the porous body. The corrosion resistance was evaluated by open circuit potential measurements, electrochemical impedance spectroscopy and potentiodynamic polarisation tests. The corrosion resistance of dense Ti was also investigated for comparison. Porous Ti presents lower resistance than the dense Ti, but both types tested were passive in the electrolyte used. It was found that the corrosion resistance of porous Ti largely increases with time due to thickening of the passive film.

Introduction

The high corrosion resistance and biocompatibility of pure titanium are responsible for their widespread use in biomedical applications [1,2]. It is reported that porous materials are advantageous compared to their solid counterparts when considered for surgical purposes [3,4]. The presence of interconnected pores allows tissue in growths, anchoring the prosthesis to the surrounding bone [5]. The development of bioactive porous implants with suitable mechanical properties is a topic of major interest in the biomedical research [6-8]. The main concern with porous implants is related to their corrosion resistance. Generally, the corrosion resistance of porous metallic materials is inferior to that of dense ones due to the porosity in the first type. These can act as crevices sites hindering the access of oxygen from the environment and leading to aeration differential cells resulting in corrosion initiation with the breakdown of the protective oxide film. The literature has reported that porous titanium presents higher corrosion rates in simulated body fluids than non-porous titanium [9-11]. Most of these published works dealt with materials with porosity around 30 % or lower for

which the porosity might, in fact, act as crevices. However, there is no much understanding on the effect of bulky porosity on the corrosion resistance of passive materials such as Ti. In the present study, the corrosion resistance of porous Ti samples with porosity in the range from 40 % to 50 % was investigated. The results obtained with porous Ti samples were compared with that of dense Ti samples. The electrochemical techniques used were EIS and potentiodynamic polarisation tests. SEM was also used to analyse the surface morphology.

Materials and Methods

The materials used in this investigation were a porous Ti (p-Ti) and a dense Ti (d-Ti), both with ASTM B 265 Grade 2 designation. Porous Ti samples were prepared with titanium powders via hydrogenation-dehydrogenation (HDH) process. The powders were sieved into the 149-177 μm particle size range. An organic additive (urea) with 250-297 μm particle size range was used as pore maker. Titanium and urea powders were manually mixed in 70 % Ti and 30 % urea proportion and then, the powder mixture was filled into flexible moulds. Compacting was achieved with cold isostatic pressing, CIP, at 300 MPa. After removal from the mould, green compacts were heated at 200 °C for 1 h to eliminate the organic additive. The compacts were then sintered in a high vacuum furnace at 1200 °C for 1 h at 10^{-4} Pa. The porosity volume fraction range determined is 40-50 %.

Experimental set-up

A three-electrode cell arrangement was used for the electrochemical tests, with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The electrolyte was a Hanks' solution at 37 °C, whose composition is given elsewhere [12]. EIS measurements were accomplished in potentiostatic mode at OCP with a 1255 Solartron frequency response analyser coupled to an EG&G 273A. The amplitude of the perturbation signal was 10 mV, and the frequency range varied from 100 kHz to 10 mHz, with acquisition rate of 6 points per decade. EIS tests were carried out after periods of immersion corresponding to 3, 14 and 31 days. Moreover, potentiodynamic polarisation curves were obtained from -0.8 V to 3.0 V, after 31 days of immersion, with a sweep rate of the 0.1 mV/s. The polarisation tests were performed using an EG&G 273A potentiostat. The total surface area of the p-Ti samples exposed to the electrolyte was estimated by BET measurements and it was 550 cm^2 , and the area of the d-Ti was 0.29 cm^2 . Despite of the large differences in the surface areas of the Ti-p and Ti-d samples, the current densities referred to in all the graphs are based on the nominal exposed surface area (1 cm^2) to allow direct comparison of their corrosion resistance. Metallic surface of d-Ti was polished with SiC paper up to #2000. Porous Ti exposed for 31 days to Hanks' solution, after polarisation, was observed by SEM using a Philips XL30 microscope.

Results and discussion

SEM micrographs of the p-Ti surface immersed for 31 days in Hanks' solution and polarised are shown in Fig.1. This micrograph reveals the intrinsic porosity of the specimen, which was about 40-50 % (volume fraction range), with micro pores and interconnected macropores. The p-Ti shows micropores and interconnected macropores with different sizes, where the solution might have been retained, and therefore could act as crevices. This is a detrimental factor for materials with high susceptibility to corrosion and usually results in localised corrosion. Besides, the porosity also greatly affects the electrochemical behaviour of the material exposing a large area to the electrolyte solution. Porous materials are reported as having lower corrosion resistance than their solid counterparts [13-15]. However, a protective passive film is easily formed on Ti based materials and the large area of porous material exposed to the electrolyte could favour the oxide growth on greater areas of the porous electrodes comparatively to the dense ones. Porosity is also an important property for implant devices once it favours osteointegration when inserted in the human body, comparatively to compact ones.

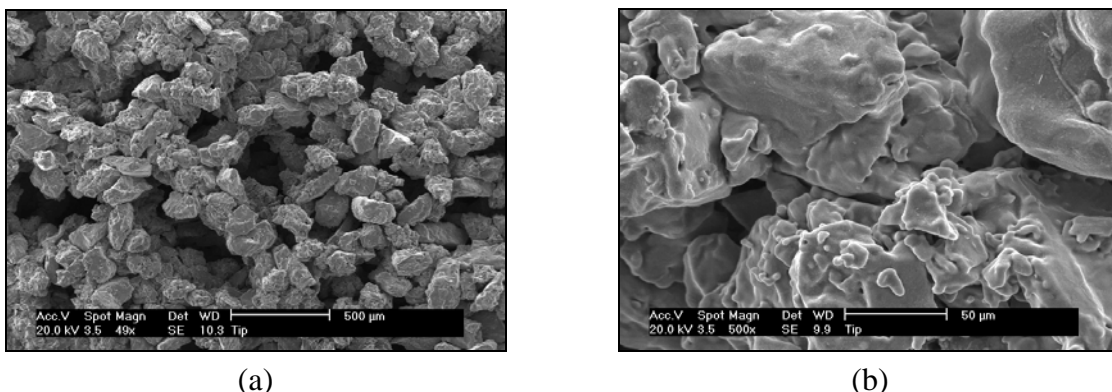


Figure 1. SEM micrographs of the p-Ti exposed for 31 days to Hanks' solution and polarised up to 3 V: (a) General aspect of the surface; (b) Same region as (a) with higher magnification

The Bode phase angle diagrams of the p-Ti specimens for 3, 14 and 31 days of immersion in Hanks' solution are shown in Fig. 2. For 3 days of immersion, the Bode phase angle diagrams clearly shows two time constants. The first one, at frequencies around 100 Hz, is characterised by a peak at approximately -60° , whereas the second one, at lower frequencies (10 mHz), shows a peak around -50° . For increasing immersion times the electrochemical behaviour presents significant changes. The two time constants observed in the Bode plot for 3 days of immersion are not easily separated for 14 days immersion period. For this last period, the Bode phase angle diagram indicates only one time constant, extending from frequencies around 10 kHz down to 1 Hz, with phase values approaching -80° (typical of passive materials). At lower frequencies, the phase angle sharply decreases. These results suggest the interaction of the two time constants, which were clearly separated for 3 days.

They also show the dislocation of the high frequency phase angle peak to higher frequencies. This could result from thickening of the oxide film with time. There was no indication in the Bode or Nyquist diagrams (results not shown here) of a diffusion controlled process at high frequencies, typical of porous materials. It has been reported in the literature [16,17] that the EIS response for porous electrodes at high frequencies depends on the ac signal penetrability. Angles near 45° at high frequencies were estimated by de Levie [16] for diffusion in porous electrodes of semi-infinite length. However, in the present study, angles approaching 0° were obtained at high frequencies, suggesting the high signal penetrability into the pores and that the electrode behaves as a flat one. This is explained by the large porosity present in the porous Ti (p-Ti) studied. The Bode (Z modulus) plots also showed that the impedance of the p-Ti largely increase between 3 and 14 days as a result of oxide growth. From this last period until 31 days, the results suggest further oxide film growth, but with lower kinetics. The corrosion resistance of titanium is attributed to the presence of a very stable TiO_2 layer on its surface [12,17,18]. The growth of this film is responsible for the EIS evolution with time of immersion and its kinetics is initially very fast. However, as the film thickens, the kinetics slows down due to the increasingly hindered access of oxidant agent to the substrate. This explains the large increase in impedance that occurs between 3 and 14 days, followed by a slower increase from 14 to 31 days. The high impedance values obtained for 31 days of test indicates the very high corrosion resistance of the oxide layer formed on the titanium surface. Potentiodynamic polarisation curves obtained for p-Ti and d-Ti, after 31 days of immersion in Hanks' solution are shown in Figure 3.

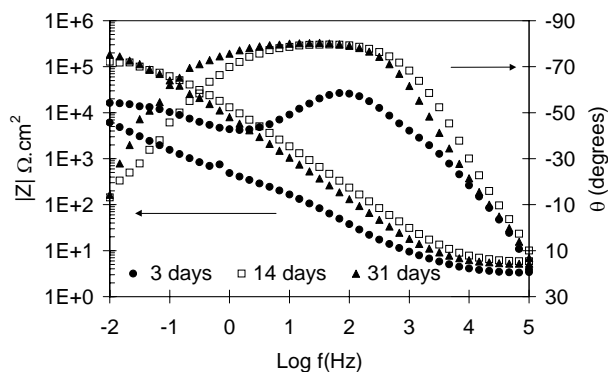


Figure 2. EIS diagrams obtained for p-Ti after 3, 14 and 31 days of immersion in Hanks' solution at 37°C .

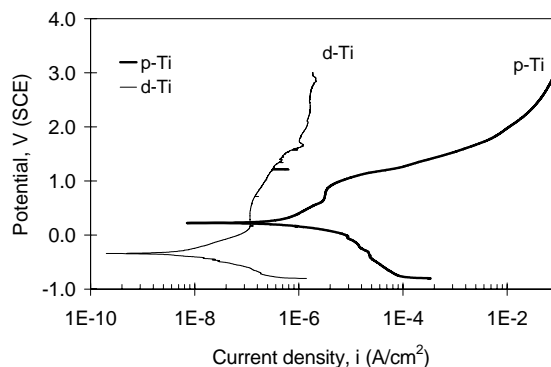


Figure 3. Polarisation curves for d-Ti and p-Ti after 31 days of immersion in Hanks' solution at 37°C . Scan rate: 0.1 mV/s .

The corrosion current densities obtained by the extrapolation of the cathodic part of the polarisation curves up to the corrosion potential are in the range of tenths of $\text{nA}\cdot\text{cm}^{-2}$ and $\mu\text{A}\cdot\text{cm}^{-2}$ for d-Ti and p-Ti, respectively, supporting the indication of a passive behaviour for

both types of materials in the electrolyte used. The polarisation curve for d-Ti shows a steady increase in current density with polarisation potential up to approximately 140 mV. The curve for this sample shows a potential range typical of highly passive materials with current densities in the order of 10^{-7} A/cm². At potentials around 500 mV the current density shows a slight increase with potential but it stabilises again from 1500 mV up to 3000 mV. In the whole range of polarisation the current densities associated to the d-Ti samples were always in the range of 10^{-6} A/cm² showing the high resistance to breakdown of the oxide film on this type of samples. For the p-Ti samples, on the other hand, the shape of the potentiodynamic polarisation curves after a small passive potential range, from 650 mV to 900 mV, exhibits a continuous current increase with potential, showing that the oxide film resistance to breakdown on this type of material is not sufficiently high. The current density values obtained up to approximately 1300 mV were in the range of tenths of μ A/cm², but they largely increased for larger potentials, suggesting that the oxygen evolution reaction could have contributed to the current increase. It can also be seen that the current density for d-Ti samples shows a further increase at potentials around 1300 mV. According to literature [19] this increase is due to the oxygen evolution reaction. The much larger current densities obtained for the p-Ti samples compared to d-Ti ones indicate that oxide film breakdown could occur on the first ones and this would also favour the oxygen evolution reaction on this type of material. The larger cathodic current densities seen on the polarisation curves of the p-Ti samples could also be explained by the larger exposed areas on this sample type.

Figure 4 compares the EIS diagrams of both types of Ti for 31 days in Hanks' solution at 37 °C. The Bode and Nyquist diagrams show higher capacitive behaviour at lower frequencies and higher impedance associated to the d-Ti, as expected.

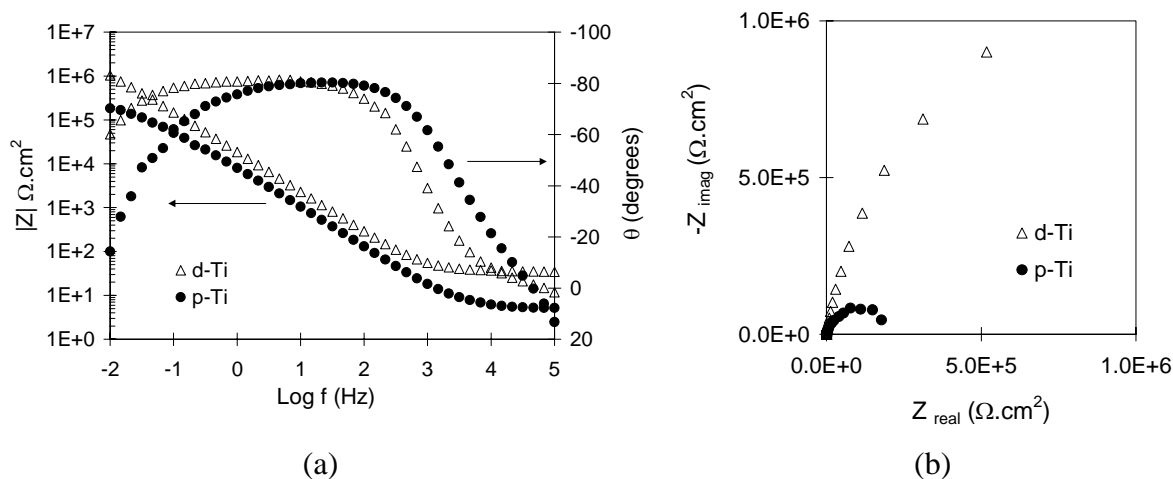


Figure 4. Comparison of the EIS diagrams obtained for p-Ti and d-Ti after 31 days of immersion in Hanks' solution at 37 °C: (a) Bode plots (b) Nyquist.

Conclusions

The results of the present study showed that the porosity in Ti samples has an important effect on their electrochemical behaviour. The large areas exposed to the electrolyte for the p-Ti samples favoured oxide film growth, leading to large impedance increase with time, but also produced an oxide film with lower breakdown resistance comparatively to d-Ti. Despite of the lower resistance to breakdown of the p-Ti samples comparatively to the dense ones, the very low corrosion current densities at open circuit potential to this type of samples, typical of highly passive materials, showed that they present high corrosion resistance in the test solution.

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