



International Congress of Science and Technology of Metallurgy and Materials, SAM -  
CONAMET 2013

## Effect of Surface Modification on the Corrosion Resistance of Zr-2.5Nb as Material for Permanent Implants

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### Abstract

Zirconium is a potential material for permanent implants. In particular, surface modification induced by anodisation has proved to be effective to improve corrosion resistance while keeping good osseointegration. The combination of zirconium with niobium is supposed to develop a structure that presents a high corrosion resistance and continues having the mechanical resistance necessary for implants. The aim of the present work is to determine the viability of using anodised Zr-2.5Nb as implant material, and compare it with pure Zr. Electrochemical tests performed in the anodizing solution and in a simulated biological solution revealed that by anodising the materials a higher corrosion resistance is obtained. The improvement on the corrosion resistance is particularly noticeable in the case of the pure metal after a short period immersed in the simulated biological solution. But, after a long period of immersion, the alloy shows better performance.

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Selection and peer-review under responsibility of the scientific committee of SAM - CONAMET 2013

**Keywords:** zirconium alloys; anodisation; corrosion; permanent implants

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## 1. Introduction

In recent years, valve metals (Zr, Nb, among others) are receiving increasing attention both as alloying components of titanium and as base materials for biomedical applications. The promising results obtained of some in vitro and in vivo studies of zirconium have pointed out this metal as a potential material for permanent implants (Saldaña et al., 2007; Cabrini et al., 1993; Costa et al., 1994; Guglielmotti et al., 1997; Gomez Sanchez et al., 2012). The good performance of zirconium has been mainly attributed to its surface oxide film. The presence on the surface of zirconium of its native  $ZrO_2$  oxide (zirconia) determines the low corrosion rate of the material, and therefore the low metal ion release to the biological media (Hiromoto et al., 2002; Hanawa, 1999; Kohn, 1998; Patel et al., 1997). The combination of Zr with Nb made possible the development of a structure that supposedly presents a high corrosion resistance but continues having the mechanical resistance necessary for implants (Khan et al., 1999; Oliveira et al., 2005).

Increasing bioactivity while keeping low corrosion rates is one the main objectives of most of the research being performed on metallic materials for permanent implant applications. It has been extensively proved that the success or failure of the osseointegration process is determined by surface characteristics in different space length scales (Mendonça et al., 2008; Davies, 2007; Oliveira et al., 2003; Barrere et al., 2004; Gomez Sanchez et al., 2011a), and those materials where osseointegration occurs, have a lower implant replacement rate (Navarro et al., 2008).

Surface modification induced by anodisation in the conditions presented in this work corresponds to a surface design criteria based on the modification of chemical and topological features in the nanometric range with the aim of promote osseointegration of zirconium and Zr-2.5Nb as permanent implants. Since an additional requirement of metal implants is the corrosion resistance in body fluids for long periods, the electrochemical in vitro response of anodised samples was studied in order to determine the effect of the surface modification process on the corrosion resistance of these two candidate materials. A simulated body fluid (SBF) solution was selected from literature to investigate the resistance to corrosion. In this study we have assessed the corrosion resistance of the metals using anodic polarisation tests and electrochemical impedance measurements. The presence of Ca-P rich compounds, believed to increase the apatite formation capability in vivo, was also investigated in the as-received and anodised samples after immersion in the SBF solution.

## 2. Experimental

### 2.1. Materials and anodising treatment

Commercially pure zirconium and Zr-2.5Nb sheets were used, from which 20 x 15 x 0.127 mm specimens were cut. The electrodes were anodised for 60 minutes in 1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> at constant potential of 30 V.

### 2.2. Surface characterization

The crystalline phases corresponding to zirconium oxide on both metals were determined by Raman spectroscopy using an Invia Reflex confocal Raman microscope (Renishaw, UK). The Raman spectra were obtained using a 514 nm argon laser with a 50x objective lens. No thermal effects were observed for the samples during these measurements.

### 2.3. Simulated body fluid (SBF) solution

Electrochemical and immersion tests were performed in a solution with ion concentration similar to blood plasma, that has been extensively used to evaluate the in vitro behaviour of biomaterials (Kokubo et al., 1990a; Kokubo et al., 1990b). This SBF solution was prepared with reagents provided by Sigma-Aldrich (analytical grade, 85.0%) and deionised water (18.2 MΩ.cm, Millipore). The solution was buffered to pH 7.4 with concentrated HCl and tris(hydroxymethyl)aminomethane (tris).

#### 2.4. Electrochemical studies

Electrodes of both materials in the as-received condition and anodised at 30 V were electrochemically studied in the SBF solution and also in the anodising solution, using a conventional three electrode cell with a saturated calomel electrode (ECS) as reference and a platinum wire as counter electrode. Anodic polarisation tests and electrochemical impedance spectroscopy (EIS) measurements were performed in the anodising solution (1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>) to assess the effect of the oxide grown during the anodising process on the passivity state of the materials. Anodic polarisation tests were performed after 24 hours and 30 days of immersion in SBF at 37°C. In all cases new specimens were used for each test. Before each measurement, the potential was let to stabilise for 40 minutes at open circuit potential. A Reference 600TM Potentiostat-Galvanostat-ZRA (Gamry Instruments, USA) was used and potentiodynamic polarisation curves were measured from the open circuit potential to 1.5 V<sub>ECS</sub> or until the current density reached a value of 10<sup>-2</sup> A.cm<sup>-2</sup>, and backwards at a sweep rate of 0.002 V.s<sup>-1</sup>. EIS measurements were carried out using a PCI4 750/potentiostat/galvanostat/ZRATM (Gamry Instruments, USA). The amplitude of the perturbation signal was 10 mV rms and the impedance was measured between 10<sup>-2</sup> and 10<sup>6</sup> Hz. Tests were repeated three times with different specimens in each condition. Repetitive results were obtained in all electrochemical studies, and representative curves are shown in the Results and Discussion section.

#### 2.5. Immersion in SBF solution

Zirconium and Zr-2.5Nb samples in the as-received condition and anodised at 30 V were maintained in SBF solution following the recommendations of the ISO 23317:2007(E) standard (International Standard ISO, 2007). The specimens were kept in SBF solution for 30 days at a constant temperature of 37°C. The ratio of the sample area (in mm<sup>2</sup>) to the solution volume (in ml) was set equal to 10 (Kokubo et al., 2006). After 30 days the surfaces were observed by a Scanning Electron Microscope (SEM) and the presence of ions incorporated to the oxide from the SBF solution during this period was investigated by Energy-dispersive X-ray spectroscopy (EDS).

### 3. Results and discussion

In Figure 1 the Raman spectra corresponding to pure zirconium and Zr-2.5Nb samples in the as-received and anodised conditions are shown. Monoclinic zirconium oxide was identified as the main crystallographic phase in the anodised samples of both materials (intense peaks in Figure 1). No such peaks were observed for the as-received samples. In the case of as-received pure zirconium the spectrum can be reasonably assigned to tetragonal zirconium oxide. Zirconium pyrophosphates were also observed in the anodised samples at Raman shifts of 1060 cm<sup>-1</sup>. The incorporation of phosphate ions during the anodisation process has been reported previously (Khalil et al., 1994; Di Quarto et al., 1996). The presence of these compounds on monoclinic zirconium oxide may be beneficial for further apatite growing *in vivo*.

The anodic polarisation curves of zirconium and Zr-2.5Nb in aerated 1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> solution are shown in Figure 2 for both conditions studied: as-received and anodised at 30 V. The corrosion potential (E<sub>corr</sub>) increases when the materials are anodised. A large, weakly potential dependent current region, indicative of the passive state of the anodised surfaces, was observed. By contrast, untreated zirconium and Zr-2.5Nb showed a continuous increase of current with potential. This is not a consequence of an active corrosion process but evidence of the continuous growth of the oxide during anodic polarisation. The growth of anodic oxides of zirconium and its alloys is an irreversible process and applying potentials lower than the anodising potential after film growth does not lead to changes in its thickness.

Growth occurs by ion conduction through the film. The electric field controlling film growth is present only across the barrier layer, which provides the passivating characteristics to the film. Its thickness increases lineally with applied growth potential, consistent with the behaviour of other passivating oxide films (Shreir et al., 1995). Thus, the decrease of current density in the passive state when anodising the materials indicates an improvement of their corrosion behaviour. However, it should be mentioned that current densities are approximately one order of magnitude higher for the anodised alloy than for the anodised pure metal.

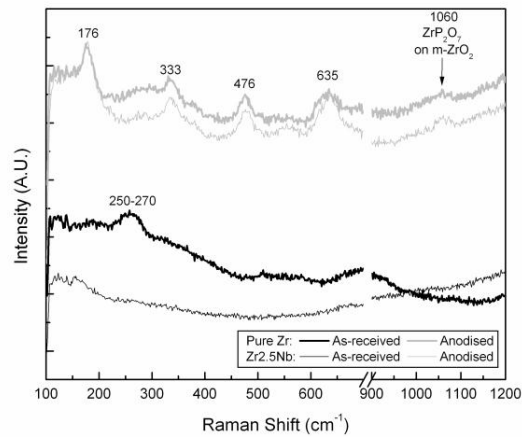


Fig. 1. Raman spectra of pure zirconium and Zr-2.5Nb alloy in the as-received condition and after anodizing at 30 V in 1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>.

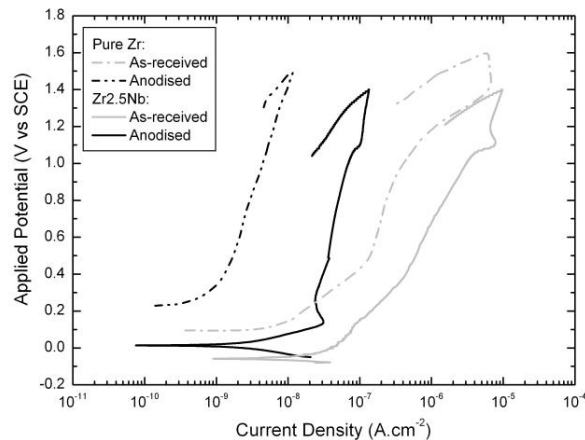


Fig. 2. Anodic polarisation curves in 1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> of pure zirconium and Zr-2.5Nb alloy in the as-received condition and after anodising at 30V.

EIS tests were carried out in 1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>. Bode plots of both materials in the as-received and anodised conditions are represented in Figure 3. In the as-received condition both materials present a capacitive behaviour, as expected due to the native oxide film on the surface. No significant differences were observed between the pure zirconium and the Zr-2.5Nb alloy. In the anodised samples, an increase of the total impedance modulus may be related to the thickening of the surface oxides. In accordance with the results obtained by anodic polarization, the anodised zirconium shows better performance than the anodised alloy. On both materials, two time constants are evidenced, and this can be related to a two layer structure of the oxide films, according to previous studies on titanium oxides and also in anodised zirconium (Gomez Sanchez, 2011b).

Anodic polarization curves in SBF solution of zirconium and Zr-2.5Nb as-received and anodised at 30 V are shown in Figure 4. The results correspond to polarization curves after 24 hs and 30 days of immersion in SBF solution at 37°C.

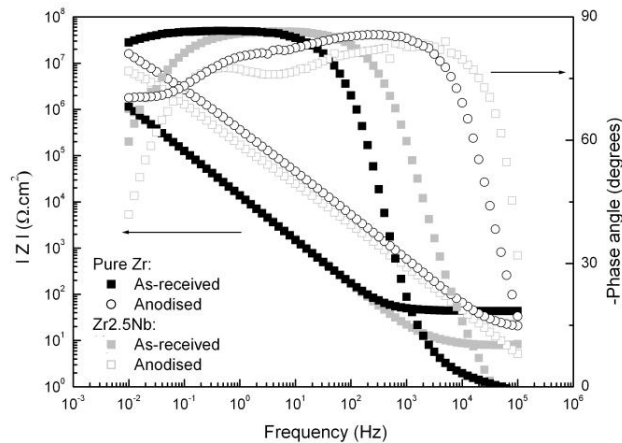


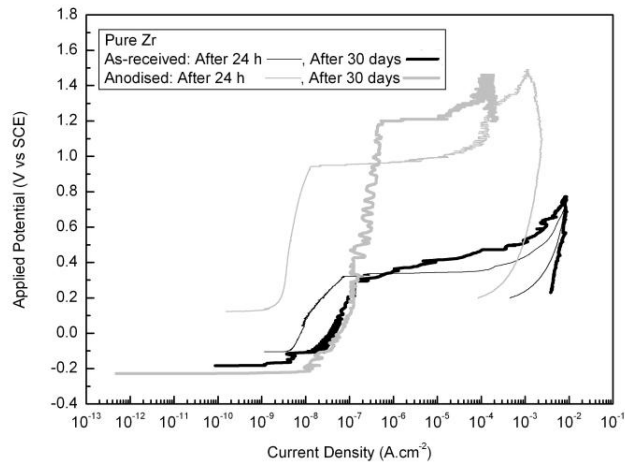
Fig. 3. Bode plots of pure zirconium and Zr-2.5Nb alloy in the as-received condition and after anodising at 30V.

For pure zirconium the  $E_{\text{corr}}$  after 24 hs of immersion in SBF solution increases (from  $-0.1$  to  $0.1 V_{\text{ECS}}$ ) when the material is anodised, showing evidence of a nobler surface of the anodic film as its thickness increases. However, after 30 days of immersion in the solution the  $E_{\text{corr}}$  decreases to  $-0.2 V_{\text{ECS}}$  in both conditions. This is indicative of certain degree of deterioration of the passive film during immersion. In the case of the alloy, the  $E_{\text{corr}}$  in the as-received condition is lower than in the case of the pure metal ( $-0.25 V_{\text{ECS}}$ ), but this value remains constant with time. When the alloy is anodised, the  $E_{\text{corr}}$  increases to  $-0.1 V_{\text{ECS}}$  and also remains constant with time. In conclusion, anodising the materials shifts the  $E_{\text{corr}}$  to nobler values due to the thickness increase of the oxide layer, particularly in the case of the pure metal after a short period immersed in SBF solution. But, after a long period of immersion, the alloy shows higher  $E_{\text{corr}}$  values and thus better performance.

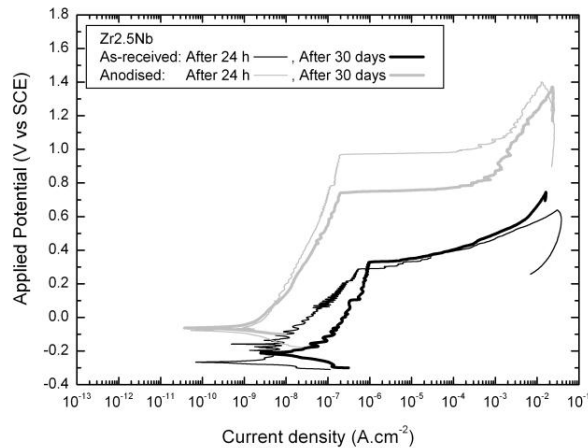
When the potential applied is higher than the  $E_{\text{corr}}$ , a zone where current densities increase weakly with the potential is observed in all cases. These current densities are relatively low, and are not associated to an active corrosion process but to a passive state. For pure zirconium the passive current ( $i_p$ ) decreases (from  $10^{-8}$  to  $10^{-9} \text{ A.cm}^{-2}$ ) when the material is anodised. However, after 30 days of immersion in the solution the  $i_p$  increases to  $10^{-7} \text{ A.cm}^{-2}$  in both conditions, indicating again some degree of deterioration. In the case of the alloy, the  $i_p$  in the as-received condition is higher than in the case of the pure metal (between  $10^{-8}$  and  $10^{-7} \text{ A.cm}^{-2}$ ), and increases even more after 30 days (between  $10^{-7}$  and  $10^{-6} \text{ A.cm}^{-2}$ ). But, when the alloy is anodised, the  $i_p$  remains constant with time at a value between  $10^{-8}$  and  $10^{-7} \text{ A.cm}^{-2}$ , showing a slightly better performance than in the case of the pure metal.

The rupture of the passive film during anodic polarization was observed for both materials in all cases. SEM observations of the samples after the polarization tests revealed the presence of pits. The localized rupture of the surface protective film and further anodic dissolution of the metal forming pits evidences the aggressiveness of this simulated biological media. The breakdown potential ( $E_b$ ) is higher for the anodised materials, an effect that can be attributed to an increase in thickness of the films obtained during the anodisation process. For pure zirconium and Zr-2.5Nb in the as-received condition, the  $E_b$  is similar ( $0.35$  and  $0.3 V_{\text{ECS}}$ , respectively), and does not vary with the immersion period in the SBF solution. On the other hand, for the anodised materials the  $E_b$  is higher after 24 hs of immersion in the SBF solution ( $1 V_{\text{ECS}}$  for both materials), and after 30 days of immersion, it increases in the case of the pure metal ( $1.2 V_{\text{ECS}}$ ) but decreases in the case of the alloy ( $0.75 V_{\text{ECS}}$ ). It is believed that these variations in  $E_b$  are inherit to the system studied, that in this aspect shows poor repetitiveness. In fact, some authors (Gomez Sanchez et al., 2012) have shown that in the case of anodised zirconium after 24 hs of immersion in SBF solution,  $E_b$  increases with the anodising potential (in the range  $0$ - $24 \text{ V}$ ) and no rupture of the passive film is observed when the anodising potential is  $30 \text{ V}$ . Regardless this point, what is important to stress is the fact that the anodising process improves considerably the resistance to corrosion of both materials. The resistance to uniform corrosion (measured

through the  $E_{\text{corr}}$  and  $i_p$ ) improves in both materials after anodising, but in the case of the alloy, the protective effect is maintained along time when immersed in SBF solution. As regarding the resistance to localized corrosion (measured through the  $E_b$ , or more precisely through the difference between the  $E_{\text{corr}}$  and the  $E_b$ ), the anodising process also offers a significant improvement in both materials, and this effect is maintained along time when the materials are immersed in SBF solution. In conclusion, both materials behave similarly, being the alloy slightly better after prolonged periods exposed to SBF solution. Similar results were found in the literature in other simulated biological media. Branzoi et al. (2008) found that alloying elements, such as niobium, increase the corrosion resistance of zirconium in Hank's solution. Similar results were obtained by Oliveira et al. (2005) in the Ringer physiological solution and the phosphate buffered saline (PBS) solution.



(a)



(b)

Fig. 4. Anodic polarisation curves in SBF solution of pure zirconium (a) and Zr-2.5Nb alloy (b) in the as-received condition and after anodising at 30V.

The different behaviour found among pure zirconium and the alloy, can be explained in terms of the different types of oxides formed in each case. Vittoz et al. (1999) investigated the surface properties of oxides on Zr-Nb

alloys. They found that the surface of Zr-Nb alloys presents an oxide layer composed of both zirconium and niobium oxides. It was observed that the surface is enriched in niobium oxide, presumably Nb<sub>2</sub>O<sub>5</sub> and it was proposed that Nb segregated during oxidation.

Specimens of both materials in the as-received and anodised condition were immersed in SBF solution at 37°C for 30 days and then observed by SEM and analysed by EDS. In the case of zirconium anodised at 30 V, the presence of acicular crystals was detected by SEM (Gomez Sanchez et al., 2011a). Analysis with EDS demonstrated the presence of Ca on the surface. Moreover, in a previous work (Gomez Sanchez et al., 2012) Ca-P compounds were detected on zirconium anodised at 30 V and ascribed to phosphates in apatite using Raman spectroscopy. On the contrary, on as-received zirconium specimens as well as on Zr-2.5Nb specimens no Ca compounds were detected on the surface after immersion. According to Kokubo et al. (2006) a material able to have apatite form on its surface in SBF has apatite produced on its surface in the living body, and bonds to living bone through this apatite layer. That is the reason why examination of apatite formation on the surface of a material in SBF is useful for predicting the *in vivo* bone bioactivity of the material. This method can be used for screening bone bioactive materials before animal testing and the number of animals used and the duration of animal experiments can be remarkably reduced. However, it is worth noting that *in vitro* tests regarding the apatite formation ability is not always in agreement with the *in vivo* results. There are a few materials that directly bond to living bone without the formation of detectable apatite on their surfaces. For instance, Gomez Sanchez et al. (2012) have found that both as-received zirconium and anodised zirconium showed similar bioactive behaviour *in vivo*, while zirconium shows no sign of being an apatite forming surface *in vitro* as anodised zirconium does. This discrepancy reinforces the importance of animal studies related to the bone formation ability.

The major use of zirconium has historically been by the nuclear community, and there has been a strong research focus on understanding zirconium oxidation mechanisms. Since the oxide layer that forms on zirconium and its alloys exhibits excellent wear behaviour as well as corrosion resistance, these materials may be compatible for use in biomedical applications. This study have shown the potentiality of using anodised zirconium and Zr-2.5Nb as implant materials. In further studies, the effect of anodic oxides on the surface of both materials on the bone formation rate will be studied *in vivo*.

#### 4. Conclusions

- Monoclinic zirconium oxide was identified as the main crystallographic phase in the anodised samples of both materials (zirconium and Zr-2.5Nb). Zirconium pyrophosphates, which may be beneficial for further apatite growing *in vivo*, were also observed.
- Electrochemical tests in the anodising solution (1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>) showed for both materials that the decrease of current density in the passive state and the increase of the total impedance modulus may be related to the thickening of the surface oxides when anodising the materials, resulting in an improvement of their corrosion behaviour.
- Polarization tests in SBF solution revealed that anodising the materials shifts the corrosion potential to nobler values, decreases the passive currents and increases the breakdown potential due to the thickness increase of the oxide layer. As a consequence a higher corrosion resistance in biological media is obtained.
- The improvement on the corrosion resistance is particularly noticeable in the case of the pure metal after a short period immersed in SBF solution. But, after a long period of immersion, the alloy shows better performance.
- Ca-P compounds were detected only on zirconium anodised at 30 V. Although the presence of these compounds may be beneficial for a good *in vivo* bone bioactivity of the material, their existence is not mandatory. Thus, *in vivo* tests are worth performing in the future to compare the bioactivity of the pure metal with the alloy.

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