Preparation and Electrochemical Behavior of Ca-P Containing Porous Titania Coating on TiNbZrFe Alloy by Micro-arc Oxidation

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Ca-P containing porous titania coating was prepared on biomedical β-type TiNbZrFe alloy by micro-arc oxidation (MAO) in order to further improve the surface bioactivity and corrosion resistance of the alloy in simulated biological conditions. The phase structure, composition and morphology of the coating were investigated and the electrochemical behaviors in NaCl solution were investigated. The results indicate that the diameter of the pores of the coating is between 1μm and 8μm. The average size of pores and Ca/P ratio of the coating increase with the voltage from 250V to 400V. The Ca/P ratio is 1.61 similar to that of human bone (1.67), when the voltage is 400V. The porous coatings are mainly made up of anatase, rutile and amorphpous Ca-P compounds, a-Ca3(PO4)2 appears in the coating when the voltage is higher than 350V. The corrosion resistance of the alloy coated with anodic oxidation (AO) before MAO is higher than that of the alloy only coated with MAO. AO used in the present study results in thin and dense layer between the metal substrate and the MAO coating, which can improve the corrosion resistance.

Keywords: biomedical titanium alloy, porous coating, microarc oxidation, electrochemical impedance spectroscopy

1. Introduction

Many new β-type titanium alloys with non-toxic and allergen-free elements have been developed for biomedical implants, e.g., artificial hip joints, bone screws and dental implants, in order to obtain lower Young’s modulus and better biocompatibility. However, the surface of β-type Ti alloy is still encapsulated by fibrous tissue without producing any osseous junctions with the surrounding tissues after the implantation, although the surface is natural oxidized and covered with a thin titania layer. Therefore, many kinds of surface modification methods have been reported to improve the osteointegration of the titanium implants, such as physical, chemical, electrochemical and so on.

Microarc oxidation (MAO) is a recently developed technique which could produce a porous, relatively rough, and firmly adherent titanium oxide film containing Ca and P ions which could enhance the bonding between the implants and the tissue. However, the corrosion resistance of the MAO coated Ti alloy is not satisfactory because the out layer of the MAO coating is porous and loose. Therefore, Anodic oxidation (AO) is considered to be performed on the alloys before the MAO treatment, which is expected to add a dense film between the porous outer layer and the metal substrate so as to improve the corrosion resistance of the alloy.

In the present study, Ca-P containing porous titania coatings were prepared on new β-type TiNbZrFe alloy by MAO or AO+MAO treatment. The phase structure, composition and morphology of the coatings were investigated and the electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were measured to analyze the corrosion resistance of the alloy.

2. Materials and Experimental Procedure

An ingot of Ti-30Nb-8Zr-0.8Fe alloy (mass%), abbreviated as TNZF, was remelted in cold crucibles by vacuum electromagnetic suspension for 3 times. Then, the ingots were hot forged to square billet at 1100°C. The specimens with dimension of 30 mm × 30 mm × 2 mm were cut from the square billet, ground using SiC waterproof abrasive paper and finally ultrasonically cleaned with acetone, ethanol and distilled water.

The AO test was conducted in 0.5mol H2SO4 solution at 40V voltage for 1 hour. MAO tests were performed for the AO treated and untreated specimens in electrolytic solution containing 0.2mol/l CH3COO)2Ca · H2O, 0.12mol/l NaH2PO4 · 2H2O and 0.15mol/l NaOH. The stainless steel tank was used as cathodes. The frequency was 600 Hz and duty cycle was 20%. The MAO treatment was carried out at 250V, 300V, 350V and 400V, respectively, using a pulse power supply for 10 min. Thereafter, the specimens with MAO treatment at different voltages are abbreviated as M+Voltage, e.g., M300. The specimens with AO+MAO treatment at different voltages are abbreviated as AM+Voltage, e.g., AM300.

The morphologies of the coatings were observed by scanning electron microscope (SEM) with energy dispersive analytical X-ray spectrometer (EDS). The phase structures of the coatings were examined by X-ray diffraction (XRD) using Cu-Kα radiation.

Electrochemical tests were carried out by electrochemical workstation using three-electrode cell which consisted of the saturated calomel electrode as the reference electrode, the specimen as the working electrode and the platinum plate as the counter electrode. The specimens were immersed in 0.9% NaCl solution for 0.5 hour before the tests, and then embedded in an or-
ganic glass mould with exposing 1 cm² surface area to the solution, EIS tests were performed by applying a sinusoidal potential perturbation of 5 mV at the open circuit potentials. The impedance spectra were measured with frequency sweeping from 100 kHz to 10 mHz in logarithmic increment. The impedance data were analyzed using the ZSimpWin software, and were fit to appropriate equivalent electrical circuit. Different parameters obtained from the best-fit equivalent circuit were tabulated. Potentiodynamic polarization curves were measured from -0.8 V to 3 V at the scanning rate of 1mV/s.

3. Results and Discussion

3.1 Surface Morphology and Composition of MAO Coating

The surface morphologies of MAO treated TNZF alloys at different voltages are shown in Figure 1. It is clearly seen that the MAO coatings are porous. The diameter of the pores and the surface roughness gradually increase with increasing voltage from 250 V to 400 V. When the MAO voltage is 400 V, the average diameter of the pore is about 5 μm and the largest one is approximately 8 μm. The distribution of the pores is more inhomogeneous.

The Ca and P contents on the MAO coating surface at different voltages were analyzed by EDX. The Ca/P ratios were calculated as shown in Table 1. It indicates that this Ca/P ratio increases from 1.30 to 1.61 with increasing voltage from 250 to 400 V. The values are slightly lower than that of stoichiometric HA (1.67), indicating that the apatite formed is Ca-deficient HA.

![Figure 1. Surface morphologies of MAO coatings (a) AM250, (b) AM300, (c) AM350, and (d) AM400](image)

<table>
<thead>
<tr>
<th>Specimens</th>
<th>AM250</th>
<th>AM300</th>
<th>AM350</th>
<th>AM400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/P ratio</td>
<td>1.30</td>
<td>1.34</td>
<td>1.47</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Table 1. The Ca/P ratios of the of MAO coating formed on TNZF alloy

3.2 Phase Structure of MAO Coating

The XRD patterns of various MAO coatings at different voltages are shown in Figure 2. The MAO coatings mainly consist of metastable anatase, stable rutile and amorphous Ca-P compounds, α-Ca₃(PO₄)₂ appears in the coating when the voltage is higher than 350 V. With increasing reaction voltage, the content of α-Ca₃(PO₄)₂ and rutile increased, whereas the content of anatase phase decrease. It has been reported that the rutile rich titania coating exhibit the better biocompatibility and osteogenesis performance. From Figure 2, the largest intensity peaks of the rutile and anatase phase were compared and the intensity ratios of rutile (110) to anatase (101) in different samples were calculated. This ratio increases from 1.26 to 2.44 with increasing voltage. The rutile became the predominant phase in the coatings when the voltage increases to 400 V, although the weak XRD peaks of the anatase phase still can be observed.

![Figure 2. XRD patterns of MAO coatings of the sample AM300, AM350, and AM400](image)

3.3 Electrochemical Behavior

Impedance spectra of the specimens after MAO or AO+MAO treatment are shown as Bode and Nyquist plots in Figure 3. Impedance parameters obtained using equivalent circuit models shown in Figure 4 are given in Table 2. Bode plots (-θ vs. logf) behave two time constants, indicating a double layer structure of the coating. Based on the two layers model, the first time constant corresponded to inner barrier layer which dominated the impedance at low frequency and the relatively low phase angle and indicated the process of diffusion. The second time constant corresponded to the outer porous layer which dominated the impedance at high frequency and related to the ions exchange in the pores. It indicates that the phase angles of AM300 and M300 at high frequency are similar due to the same outer layer porous structure of the coatings, Figure 3 (b) is the characteristic response of a capacitive behavior of surface film, and the spectra displayed a linear slope of about -1. The impedance of AM300 specimen at low frequency is obviously higher than that of M300 specimen, indicating that the corrosion resistance of the
alloy coated AO before MAO is better than that of the alloy only coated with MAO. When the voltage is 400V, the same results can be obtained, as shown in Figure 3(d) and (e). Nyquist plots in Figure 3(c) and 3(f) also illustrate that the curvature radius, i.e., coating resistance of impedance spectra of AO+MAO coating is larger than that of only MAO coating. So the corrosion resistance can be improved by pre-AO treatment.

![Figure 3](image)

Figure 3. Bode and Nyquist plots of samples at different voltages: (a) (d) $\theta$ vs. Log $f$, (b) (e) Log $|z|$ vs. Log $f$, (c) (f) Nyquist plot

The equivalent circuit exhibit Warburg impedance characteristic as shown in Figure 4. The fitted EIS parameters $R_a$ are the electric resistance from the metal substrate and the inner dense layer. It can be seen from Table 2 that $R_a$ in AM300 and AM400 are higher than that in M300 and M400, respectively. This means the added AO layer between the metal substrate and MAO coatings increase the electric resistance of the inner layer.

Potential dynamic polarization curves of the coatings treated by MAO or AO+MAO are shown in Figure 5. No matter at 300V or 400V voltage, the corrosion potential of the alloy with AO+MAO treatment is higher than that of the specimens only by MAO. At the same time, the corrosion current becomes lower if the alloy were pre AO treated before MAO. The potential dynamic polarization curves also indicate that the corrosion resistance can be enhanced by pre AO treatment because the thin and dense layer produced by AO between the matrix and the MAO coating effectively hinders the penetration of corrosive medium.

4. Conclusions

(1) Titania coating surface of the TNZF alloy by MAO treatment are porous. The average diameter of
the micropores with the increase of MAO voltage, and approximately up to 5 μm when the voltage is 400V.

(2) The MAO coating comprised of anatase, rutile and amorphous Ca-P compounds, while α-Ca₉(PO₄)₂ appears in the coating when the voltage is higher than 350V. The rutile content and Ca/P ratio in the MAO coatings increase with increasing voltage. Ca/P ratio is about 1.61, close to that of stoichiometric HA (1.67) when the voltage is 400V.

(3) The impedance of the specimen by AO+MAO treatment at low frequency is obviously higher than those only coated with MAO. The thin and dense layer between matrix and MAO coating produced by AO effectively hinders the penetration of corrosive medium.

(4) The corrosion potential of the specimen with AO+MAO treatment is higher than that of the specimens only by MAO treatment. At the same time, the corrosion current becomes lower if the alloy were pre AO treated before MAO.

Acknowledgements

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