

PRELIMINARY STUDIES FOR IN VIVO APPLICATION OF SURFACE TREATED Ti_6Al_7Nb PROSTHESES

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Abstract: *The aim of this paper is to compare the bioactive behavior generated by two different surface treatments on Ti-6Al-7Nb previous to the implant in the animal knee. One of the treatments consists in soak the sample with NaOH and followed by a subsequent heat treatment. The other treatment consists in immersion for 19 days in a SBF solution with additional PAW1 biovitroceramic (particles under 20 μm) content at 36 °C. After a long exposure (more than 100 days) of the samples to a simulated body fluid, the surfaces were investigated to clarify what bioactive structure forms on the alloy and how it changes in the body's environment. A knee plate was design for the samples of Ti-6Al-7Nb.*

Key words: *biomaterials, bone implants, prosthesis.*

1. Introduction

Titanium derives its corrosion resistance from the stable oxide film that forms on its surface, which can reform at body temperature and in physiological fluid if damaged. Increased use of titanium alloys as biomaterials is occurring due to their lower modulus, superior biocompatibility and high corrosion resistance. These attractive properties were a driving force for the early introduction of Ti and Ti-6Al-4V as implantable materials.

Titanium has a poor mechanical strength [9], [13] and when aluminium or vanadium are added to titanium in small quantities, the strength of the alloy is much increased over that of titanium [8]. Therefore, the Ti-6Al-4V alloy achieves considerably higher tensile properties than of pure titanium and

this alloy is used in high stress-bearing situations. But Ti-6Al-4V has a potential cytotoxicity and adverse tissue reactions caused by vanadium [4], [11] and for this reason has been required the development of new titanium alloys with non-toxic elements (Nb, Zr, Ta, Mo, Fe etc.).

The Ti-6Al-7Nb was developed around 1980 and proved to be highly biocompatible. In 1985 the Ti-6Al-7Nb was approved for clinical use, mainly in cementless femoral stem system and elastically deformable cup shells. Over the last twenty years it was demonstrated that Ti-6Al-7Nb is a real alternative to the well-known Ti-6Al4V which has been used for decades as an implant material [12].

Recently, it was revealed that titanium and its alloys spontaneously bond to living

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bone if they have been previously subjected to a treatment involving a soak in NaOH solution followed by a subsequent heat treatment [9]. These metals can therefore be called bioactive metals, and are already subjected to clinical trials for use in artificial total hip joints.

The aim of this paper is to compare the bioactive behavior generated by two different surface treatments on Ti-6Al-7Nb previous to the implant in the animal knee. One of the treatments consists in soak the sample with NaOH and followed by a subsequent heat treatment. The other treatment consists in immersion for 19

days in a SBF solution with additional PAW1 biovitroceramic (particles under 20 μm) content at 36 °C. After a long exposure (more than 100 days) of the samples to a simulated body fluid, the surfaces were investigated to clarify what bioactive structure forms on the alloy and how it changes in the body's environment.

2. Experimental Details

2.1. Materials

The composition of the investigated materials is given in Table 1.

Composition of the studied implant materials

Table 1

Type	Percent weight							Structure
	Al	Nb	V	C	O	N	Ti	
Ti-6Al-7Nb	6.12	7.06	-	0.08	0.15	0.03	Rest	$\alpha + \beta$

Three types of sample were used in this study: a) samples of Ti-6Al-7Nb without any surface treatment (named TAN); b) samples of Ti-6Al-7Nb with the first surface treatment (named TANEs) and c) samples of Ti-6Al-7Nb with the second surface treatment (named TANRo).

2.2. Knee plate design

The objective of the knee plate design are: a) obtain a surface where apply the treatment to be tested (a big surface is desirable); b) when the plate is implanted, the bone has to have a good blood supply after the cut in order to avoid the death of the bone. After the mechanical fabrication of the plate, the surface of the plate was embedded in a resin except 1 cm^2 which, starting from now, will be the active surface for study.

2.3. Electrolyte

The testing medium was an aerated Hank's solution whose composition is: NaCl

7.996 g/L, NaHCO_3 35 g/L, KCl 0.4 g/L, $\text{Na}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ 0.48 g/L, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.1 g/L, CaCl_2 0.18 g/L, KH_2PO_4 0.06 g/L, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.1 g/L, Glucosa 1 g/L.

2.4. Surface treatment

1. The samples were soaked in 10M NaOH aqueous solution at 60 °C for 24 h, washed with distilled water and dried at 40 °C for 24 h in air atmosphere. The substrates were subsequently heated up to 600 °C at a rate of 5 °C/min and kept for 1 h in an electrical furnace and then cool to room temperature.

2. The samples were immersed for 19 days in a SBF solution with additional PAW1 biovitroceramic (particles under 20 μm) content at 36 °C in order to form a HA layer formed by a multitude of HA nuclei originating on biovitroceramic precursor. The SBF was prepared by dissolving reagent grade chemicals of NaCl, NaHCO_3 , KCl, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 and Na_2SO_4 in distilled water, and buffered at *pH* 7.40 with tris-hydroxymethyl

aminomethane $((\text{CH}_2\text{OH})_3\text{CNH}_3)$ and hydrochloric acid at 36.5 °C [7].

2.5. Metallographical analysis

The metallographic technique used for titanium alloy implants consists of grinding up to 1000 grit with SiC, followed by polishing with alpha alumina of 0.1 μm to mirror finish. The specimens are ultrasonically cleaned using deionized water, and etched in Kroll's reagent containing 10 mL of HF, 5 mL of HNO_3 and 85 mL of water for microscopic observation, using an Olympus PME 3 - ADL microscope. For the samples with surface treatments, optical observations with the same microscope were made.

2.6. Electrochemical measurements

A conventional three-electrode electrochemical cell with a Pt grid as counter electrode and saturated calomel electrode (SCE) as reference electrode was used. AC impedance data were obtained at open circuit potential using a PAR 263 A potentiostat connected with a PAR 5210 lock-in amplifier. The amplitude of the AC impedance determinations the amplitude of the AC potential was 10 mV and single sine wave measurements at frequencies between 10^{-1} and 10^5 Hz were performed for each sample. The spectra were interpreted using the non-linear least square fitting procedure developed by Boukamp.

3. Results and Discussions

3.1. Optical metallography

The surfaces of untreated samples of the alloys were microstructurally analyzed. In the microstructures that would be presented, the alpha-phase appears light and the beta phase appears dark. The

microstructure of Ti-6Al-7Nb has been presented in Figure 1. The Ti-6Al-4Nb alloy possessed a two phase alpha-beta structure due to the presence of niobium which is a beta-phase stabilizer and aluminium which is an alpha-phase stabilizer.

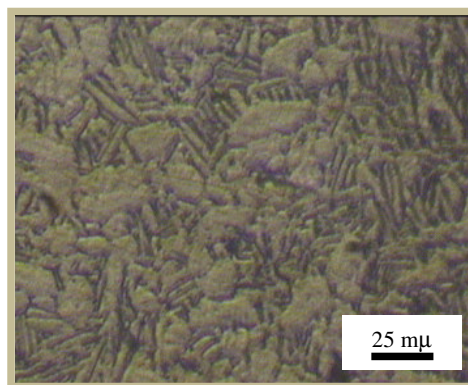


Fig. 1. *The microstructure of Ti-6Al-7Nb without any surface treatment*

3.2. Open circuit potential and electrochemical impedance spectroscopy

• Open circuit potential

The open circuit potential is a parameter which indicates the thermodynamically tendency of a material to electrochemical oxidation in a corrosive medium. After a period of immersion it stabilises around a stationary value. This potential may vary with time because changes in the nature of the surface of the electrode occur (oxidation, formation of the passive layer or immunity). The open circuit potential is used as a criterion for the corrosion behaviour. Figure 2 shows the E_{OC} curves for all the samples immersed in Hank solution at 25 °C in comparison with the actual implant alloy Ti-6Al-4V.

Open circuit potential variation is similar for all the samples. Initially, the potential of the samples presents approximately the

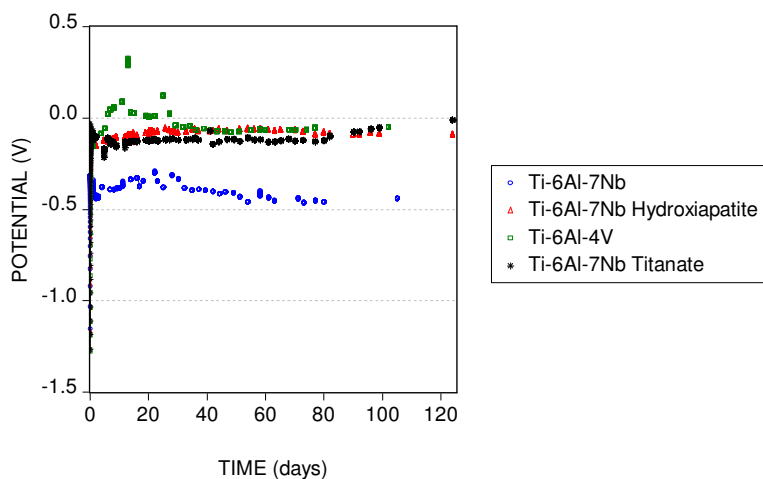


Fig. 2. Open circuit potential variation with time for Ti-6Al-7Nb with and without surface treatment in comparison with Ti-6Al-4V

same value: -1156 mV for TAN, -1266 mV for TANEs and -1168 mV for TANRo.

During the first moments of immersion, an abrupt E_{OC} displacement towards positive potentials was noticed in Figure 2 during a period of 30 minutes. This initial increase seems to be related to the formation and thickening of the oxide film on the metallic surface, improving its corrosion protection ability [1], [3], [5, 6]. Afterwards, the E_{OC} increases slowly suggesting the growth of the film onto the

metallic surface.

The studied samples did not exhibit potential drops associated with surface activation during more than 100 days exposure in the Hank solution. This kind of behaviour strongly suggests that the air-formed native oxide is thermodynamically resistant to chemical dissolution in Hank solution. Open circuit potential values are presented in Table 2 at the beginning of the test and after 100 days of immersion in Hank solution.

Table 2
Open circuit potential values of the tested samples: initially and after 24 hours of immersion in Hank's solution

Alloy	Open circuit potential, E_{OC} (mV vs. SCE)	
	Initial	After 100 days
TAN	-1156 ± 11	-44 ± 5
TANEs	-1266 ± 12	-11 ± 2
TANRo	-1168 ± 12	-88 ± 12

• Electrochemical Impedance Spectroscopy

The evolutions with time of the corresponding Bode spectra for each sample immersed in Hank solution are

presented in the next figures. The results for the alloy Ti-6Al-7Nb without surface treatment would be discussed first. The Bode-phase and Bode-magnitude plots have been provided in Figures 3a and 3b.

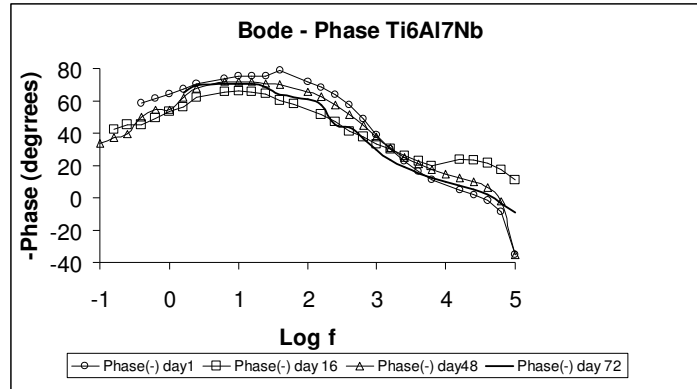


Fig. 3a. Bode-phase diagrams of Ti-6Al-7Nb without any surface treatment

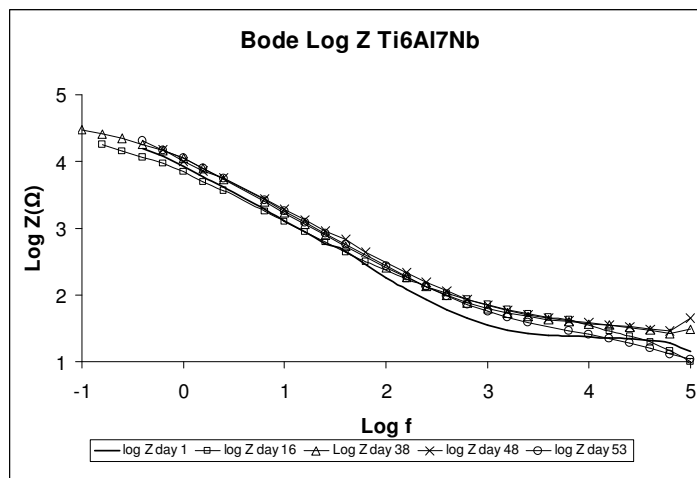


Fig. 3b. Bode- $|Z|$ diagrams of Ti-6Al-7Nb without any surface treatment

From the Bode-phase plots (Figure 3a) it can be noted that the phase angle drops towards zero degree at very high frequencies, indicating that the impedance is dominated by the solution resistance in this frequency range (no phase shift between current and potential results due presence of a resistor in AC circuit). Moreover, it can also be noted that the phase angle drops slightly towards lower values in the low frequency region with the immersion time indicating the contribution

of polarization resistance to the impedance. However, the phase remains at high values (close to -90°) in the middle frequency range indicating a near capacitive response. This behavior is indicative of a typical thin passive oxide film present on the surface. This high value of phase decreases with immersion time in Hank solution, suggesting a change in the nature of surface film with immersion time. This change could be due to the oxidation of TiO or Ti₂O₃ to TiO₂ [2], [10].

Bode-magnitude plots were characterized by two distinct regions (Figure 3b). In the higher frequency region (1-100 kHz), the plots exhibited constant $\log|Z|$ values vs. $\log(f)$ with a phase angle near 0° . This was due to response of the electrolyte resistance R_s (resistive region). In the broad and middle frequency range, the spectra displayed a linear slope of about -1 . This is the characteristic response of a capacitive behavior of surface film. The

flat portion of the curve (slope ≈ 0), present in high frequency region, marginally shifted its position during the time of immersion. This was due to minor changes in solution resistance (R_s) with immersion time in Hank solution. However, the solution resistance was quite low (generally below $2 \Omega \text{ cm}^2$).

In the Figures 4 and 5 are presented Bode spectra for the samples with surface treatment.

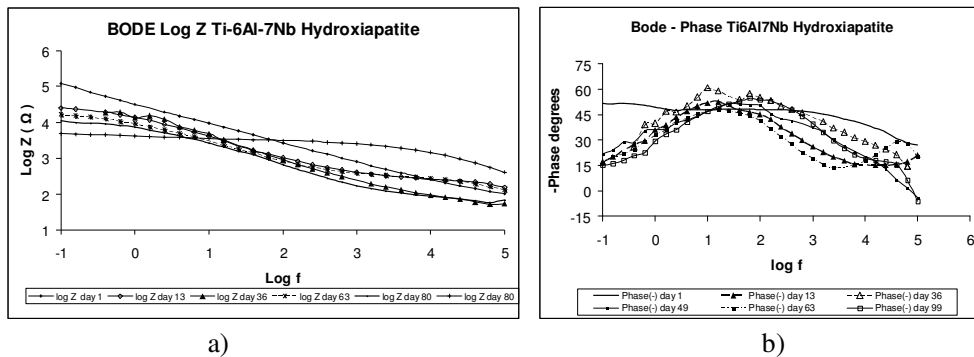


Fig. 4. Bode diagrams for TANRo

It can be observed a stable behavior during the period of immersion in physiological

fluid for the sample with biovitroceramic particles.

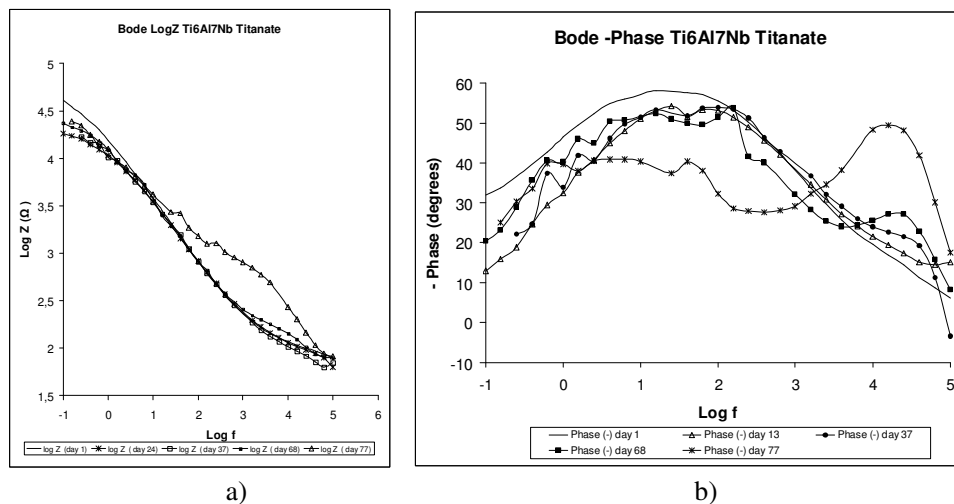


Fig. 5. Bode diagrams for TANEs

During the immersion of the sample with sodium titanate, this superficial layer is very active and the profiles of the Bode plots are continuously changing. The sodium layer is expected to form may Ti-OH groups on its surface in the physiological fluid via the ion exchange of its Na⁺ ions from the surface with H₃O⁺ ions in the surrounding fluid [9] and the obtained plots show a continuous activity at the layer surface.

4. Conclusions

The results emphasised that the surface treatment increases the passive layer adhesion to the metal surface and improves the biocompatibility of the biomedical devices inducing the bone growth on the implant surface. Both surface treatments increase the bioactivity of the passive layer formed during immersion in physiological fluid.

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