INTERPRETATION OF OPEN CIRCUIT POTENTIAL OF TWO TITANIUM ALLOYS FOR A LONG TIME IMMERSION IN PHYSIOLOGICAL FLUID

Y. SANTANA JIMÉNEZ[1] M. TEJERA GIL[1] M. TORRADO GUERRA[1] L.S. BALTES[2] J.C. MIRZA ROSCA[1]

Abstract: *Increased use of titanium alloys as biomaterials is occurring due to their superior biocompatibility and high corrosion resistance in the human body. Ti-6Al-7Nb was investigated compared with Ti-6Al-4V and two surface treatments were applied for increasing the bioactivity of the alloy. The results were interpreted from electrochemical and statistical point of view. It can be concluded that the alloy Ti-6Al-7Nb is a real alternative to the well-known Ti-6Al-4V alloy, which has been used for decades as an implant material and the obtained results are important for the safe long-term in vivo application of the Ti-6Al-7Nb alloy since niobium has the characteristics of an immunologically inert metal.*

Key words: *titanium alloys, OCP, biomaterials.*

1. Introduction

Measurements of an electrochemical potential is one of the more basic measurements in electrochemistry. The potential of a metal in an aqueous solution is a function of the inherent reactivity of the metal and the oxidizing power of the solution. The goal of potential measurements is to measure the potential of the specimen without affecting, in any way, electrochemistry reactions on the specimen surface. It is necessary to make the potential measurements with respect to a stable reference electrode so that any changes in the measured potential can be attributed to changes at the specimen/ solution interface [4]. The requirements of a reference electrode are that its potential be reproducible and stable. When a suitable reference electrode is used, the potential of the working electrode can be controlled reproducibly and any changes in the measured potential during the test can be related with confidence to changes in the working electrode potential. An unstable or contaminated reference electrode is unacceptable and will result in aborted tests or erroneous results.

In our work, a Saturated Calomel Electrode (SCE) with a potential V-SHE of +0.243 V (at 25 ºC) was used.

[1] Dept. of Mechanical Engineering, Las Palmas de Gran Canaria University, Spain.
[2] Dept. of Materials Engineering and Welding, *Transilvania* University of Braşov, Romania.

The aim of this paper is to compare the bioactive behavior of Ti-6Al-4V and Ti-6Al-7Nb previous to the implant in the animal knee. Two different surface treatments were tested on the surface of the Ti-6Al-4V. The Open Circuit Potential (OCP) of these materials was investigated during more than 2500 hours of immersion in Hank's physiological solution.

2. Experimental

2.1. Materials

The alloys present α + β bi-phase structure. 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-4V	6.15	-	4.10	0.08	0.20	0.05	Rest	α + β
Ti-6Al-7Nb	6.12	7.06	-	0.08	0.15	0.03	Rest	α + β

2.2. Electrolyte

The testing medium was an aerated Hank's physiological solution whose composition is: NaCl 7.996 g/L, $NaHCO_3$ 35 g/L, KCl 0.4 g/L, $Na_2HPO_4 \cdot 3H_2O$ 0.48 g/L, $Cl_2 \cdot 6H_2O$ 0.1 g/L, $CaCl_2$ 0.18 g/L, KH_2PO_4 0.06 g/L, $MgSO_4 \cdot 7H_2O$ 0.1 g/L, Glucosa 1 g/L.

2.3. Surface treatment

From every material we kept two samples without any surface treatment. For the others samples two surface treatments were performed:

1. The samples were soaked in 10M NaOH aqueous solution at 60 ºC for 24 h, washed with distilled water and dried at 40 ºC for 24 h in air atmosphere [3]. The substrates were subsequently heated up to 600 ºC at a rate of 5 ºC/min and kept for 1 h in an electrical furnace and then cooled to room temperature (the samples named Ti-6Al-7Nb titanate).
2. The samples were immersed for 19 days in a SBF solution with additional PAW1 biovitroceramic (particles under 20 µm) content at 36 ºC 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, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 in distilled water, and buffered at *pH* 7.40 [2] with tris-hydroxymethyl aminomethane ($(CH_2OH)_3CNH_3$) and hydrochloric acid at 36.5 ºC (the samples named Ti-6Al-7Nb hydroxyapatite).

2.4. Open circuit potential measurements

A conventional three-electrode electrochemical cell with a Pt grid as counter electrode and saturated calomel electrod (SCE) as reference electrode was used. The measurements of OCP were obtained with a PAR 263 A potentiostat. The statistic estimations and tests have been performed by SPSS v. 14 and E-Views v.6 statistics programs.

3. Results and Discussions

3.1. Open circuit potential from electrochemical point of view

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 1 shows the E_{OC} curves for all the samples immersed in Hank's solution at 25 ^{0}C.

From Figure 1, some conclusions can be obtained: Ti-6Al-7Nb behaves worse than Ti-6Al-4Nb Tit. and Ti-6Al-4Nb Hidr., so surface treatment improves corrosion process. On the other hand, Ti-6Al-4V has the highest corrosion potential but its tendency changes showing a decrease at the end of the sample period, reaching negative values, reaching the same levels as than Ti-6Al-4Nb Tit. and Ti-6Al-4Nb Hidr.

Open circuit potential variation is similar for all the samples. Initially, the potential of the two titanium alloys presents approximately the same value: −1277 mV for Ti-6Al-4V and −1156 mV for Ti-6Al-7Nb. For the samples with the two surface treatments, the potentials are also very closed: −1266 mV for the sample with titanate and −1168 mV for the sample with hidroxiapatite.

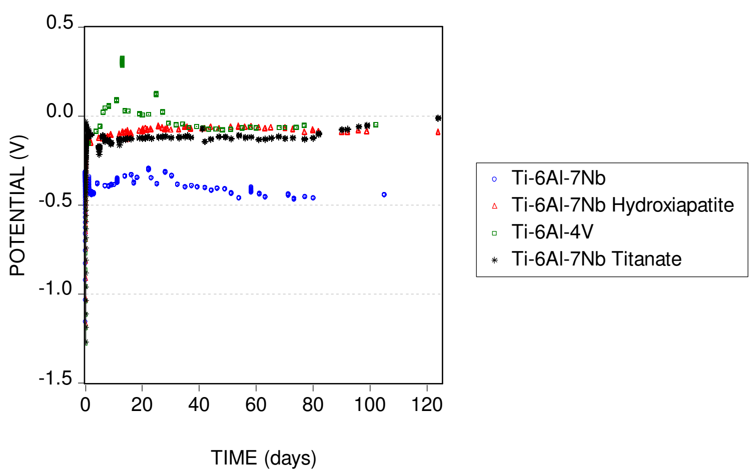

Fig. 1. *Open circuit potential variation with time for Ti-6Al-4V and Ti-6Al-7Nb with and without surface treatment*

During the first moments of immersion, an abrupt E_{OC} displacement towards positive potentials was noticed in Figure 1 during a period of around 2-3 hours. 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]. 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**
Ti6Al4V	−1277 ± 15	−49 ± 6
Ti6Al7Nb	−1156 ± 11	−44 ± 5
Ti6Al7Nb titanate	−1266 ± 12	−11± 2
Ti6Al7Nb hydroxyapatite	−1168 ± 12	−88 ± 4

3.2. Open circuit potential from statistical point of view

The following figure (Figure 1) shows the evolution of corrosion potential for every case throughout time. The time period goes from 0 days to 124 days and data were measured every 10 seconds with discontinuous periods. During the first day, the first 30 minutes were studied, and corrosion potential increases at a greatest speed in this period in every case study. It is important to point out that the series reach a level from which corrosion potential tends to stabilize. However, some outliers appear in some of the cases which alter the evolution of the corrosion potential as can be seen in Figure 2, which is restricted to the first 30 minutes. Concretely, Ti-6Al-4V alloy suffers a sudden increase around minute 25, and this behavior occurs in other occasions.

From Figure 1, some conclusions can be obtained: Ti-6Al-7Nb behaves worse than Ti-6Al-7Nb Tit. and Ti-6Al-7Nb Hydr., so surface treatment improves corrosion resistance. On the other hand, Ti-6Al-4V has the highest corrosion potential but its tendency changes showing a decrease at the end of the sample period, reaching negative values, reaching the same levels as than Ti-6Al-7Nb Tit. and Ti-6Al-7Nb Hydr.

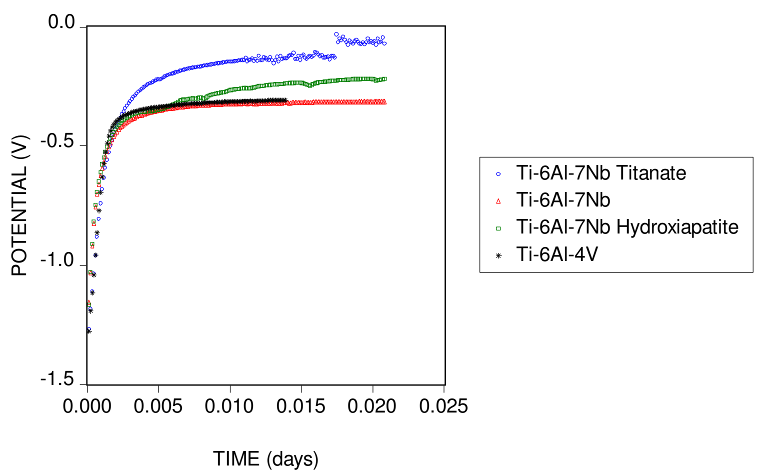

Fig. 2. *Evolution of corrosion potential for each case for the first 30 minutes*

Figure 3 shows Box Diagrams of the different alloys. Each box represents the difference between the third and first cuartiles. The fact that 50% central of the distributions are below zero for the first 3 cases (Ti-6Al-7Nb, Ti-6Al-4Nb Tit. and Ti-6Al-7Nb Hydr) is remarkable. The stars represent some atypical values and are most of them at the left hand side of the distribution. The Ti-6Al-4V alloy behaves differently, since there are also outliers in the right hand side of its distribution. The horizontal line inside the box denotes the median value, and the lowest value corresponds to Ti-6Al-7Nb alloy.

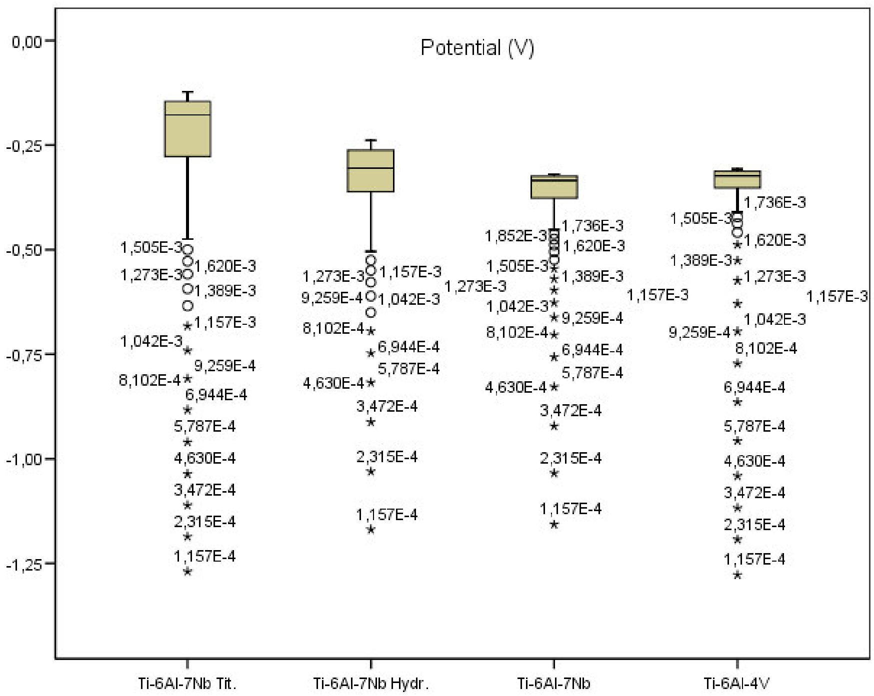

Fig. 3. *Boxes Graph of corrosion potential*

In order to test whether the samples come from different populations or not (concretely, whether the null hypothesis of corrosion process is equal for all cases) a non parametric test called Kruskal Wallis has been performed. Table 3(a) shows the relevant figures required to obtain the statistic. The Kruskal Wallis test joins the four samples and order the data from lowest to highest, assigning a rank to each observation. Next, the ranks corresponding to each sample are added and divided by the number of observations in each case. These data are shown in "Mean Rank" column from Table 3(a).

Its statistics follows a Chi-square distribution under null hypothesis, and since its associated probability is below 0.05 (concretely, 0.00), results show that null hypothesis is rejected, that is, corrosion processes are significantly different among the four samples. Additionally, some other tests where the equality of corrosion processes was tested in pairs of cases have been performed, and the conclusion was the same.

Kruskal Wallis test Table 3

Ranks (a)

Potential corrosion	N	Mean Rank
Ti-6Al-7Nb Tit.	2874	3597.27
Ti-6Al-7Nb Hydr.	2891	4919.72
Ti-6Al-7Nb	1218	683.87
Ti-6Al-4V	867	6252.29
Total	7850	

Statistic (b)

Potential corrosion	
Chi-square	4022.732
D.F.	3
Probability	0.000

3.3. Econometric models

A time series analysis of the first twenty minutes of potential evolution from the following four cases has been performed: Ti-6Al-7Nb, Ti-6Al-4V, Ti-6Al-7Nb with Hydroxiapatite, and Ti-6Al-7Nb with Titanate o. ARIMA time series analysis is usually applied to predict future data. However, the aim in this analysis is checking whether the corrosion potential follows a time series structure or not.

According to the results, in the four cases it was found that the corrosion potential is not random, but it depends on the previous values. Denoting by:

X_1 = Ti-6Al-7Nb with Titanate corrosion potential;
X_2 = Ti-6Al-7Nb corrosion potential;
X_3 = Ti-6Al-4V corrosion potential;
X_4 = Ti-6Al-7Nb with Hydroxiapatite corrosion potential.

The Box Jenkins time series methodology requires getting stationary series in order to model them. Thus, the series have been differentiated once or twice depending on each case. The following models have been estimated:

$$\Delta X_{1,t} = \phi_1 \Delta X_{1,t-1} + \alpha + \varepsilon_t - \theta_1 \varepsilon_{t-1}, \quad (1)$$

$$\Delta^2 X_{2,t} = \phi_1 \Delta^2 X_{2,t-1} + \alpha + \varepsilon_t - \theta_1 \varepsilon_{t-1} + \delta_1 D32_t + \delta_2 D31_t, \quad (2)$$

$$\Delta^2 X_{3,t} = \phi_3 \Delta^2 X_{3,t-3} + \alpha + \varepsilon_t - \theta_1 \varepsilon_{t-1}, \quad (3)$$

$$\Delta X_{4,t} = \phi_1 \Delta X_{4,t-1} + \varepsilon_t - \theta_2 \varepsilon_{t-2}. \quad (4)$$

Table 4 shows the results of the ARIMA estimations. The significance of the autoregressive coefficients indicate that corrosion potential depends positively on their past values, and their behaviour is not random in any case.

Finally, an OLS estimation of the different corrosion potentials has been performed, using time as regressor. It was found that an inverse relationship exists for the first day, while a linear relationship fits better from the second day on. Thus, in order to estimate the models dicotomic variables have been included in the model, where the data corresponding to the first day are denoted by 1 and the rest are denoted by 0. This way, different constant and tendency is allowed for the first day and the rest of the observations.

The general model estimated for each case is:

$$\textit{potential of corrosion}_t = \alpha_1 + \alpha_2 D1_t + \beta_1 \textit{time}_t + \beta_2 D1_t \frac{1}{\textit{time}_t} + u_t. \quad (5)$$

ARIMA models estimation Table 4

Coefficients	Ti-6Al-7Nb with Titanate	Ti-6Al-7Nb	Ti-6Al-4V	Ti-6Al-7Nb with Hydroxiapatite
α	0.0008 (0.014)			
ϕ_1	0.916 (0.00)	0.424 (0.00)		0.88 (0.00)
ϕ_3			0.449 (0.00)	
θ_1	–0.989 (0.00)	–0.897 (0.00)	–0.87 (0.00)	
θ_2				–0.43 (0.00)
δ_1		2.43 (0.01)		
δ_2		–0.0040 (0.00)		
R^2	0.275	0.54	0.49	0.55

P values are in brackets, showing that coefficients are significant if *P* value is lower than 0.05.

Table 5 shows the results of the OLS estimation for each case.

OLS estimations Table 5

Endogenous variable	Ti-6Al-7Nb with Titanate sódico corrosion potential	Ti-6Al-7Nb corrosion potential	Ti-6Al-4V corrosion potential	Ti-6Al-7Nb with Hydroxiapatite corrosion potential
α_1	–0.13 (0.00)	–0.38 (0.00)	0.026 (0.00)	–0.115 (0.00)
α_2	–0.17 (0.00)	0.062 (0.00)	–0.34 (0.00)	–0.153 (0.00)
β_1	0.000495 (0.00)	–0.0004 (0.00)	–0.001 (0.00)	0.00068 (0.00)
β_2	–0.000215 (0.00)	–0.000137 (0.00)	–0.00016 (0.00)	–0.00015 (0.00)
R^2	0.644	0.52	0.74	0.85
Mean abs. percent error	17.5	8.2	62	17

Results show a strong dependence of corrosion potential on time. In order to determine whether the corrosion process finally stabilises or not, we consider that it would be interesting to increase the sample period.

Analysis results seem to show that surface treatments of alloys behave better than alloys without treatment.

4. Conclusions

1. The alloy Ti-6Al-7Nb is a real alternative to the well-known Ti-6Al-4V alloy, which has been used for decades as an implant material.

2. Analysis results seem to show that surface treatments of the alloy behave better than for the alloy without any

treatment.

3. The obtained results are important for the safe long-term in vivo application of the Ti-6Al-7Nb alloy since niobium has the characteristics of an immunologically inert metal.

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