

## Electrochemical Studies on the Stability and Corrosion Resistance of Ti-5Al-2Nb-1Ta Alloy for Biomedical Applications

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Titanium and titanium-based alloys are employed widely in biomedical and dental applications. This is due to the stability and corrosion resistance exhibited by titanium, which is turn is due to the spontaneous formation of a passive titanium dioxide film, typically a few nm thick, which protects the metal from further oxidation. Electrochemical techniques viz., potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were carried out to investigate the corrosion behavior of titanium and Ti-5Al-2Nb-1Ta alloy in simulated body fluid (SBF) solution. All the measurements were made in the simulated body fluid solution at different duration. Electrochemical impedance spectroscopic results were compared with those obtained by potentiodynamic polarization techniques. Impedance spectra were represented in both complex impedance diagram (Nyquist plot) and Bode plots. The impedance spectra were fitted using a non-linear least square (NLLS) fitting procedure. Double layer capacitance decreases with increase of charge transfer resistance of the titanium alloys studied.

### Introduction

Metallic materials are being increasingly used in medical applications as implants to restore lost functions or release organs functioning below acceptable levels. Titanium alloys are among the most used metallic biomaterials; particularly for orthopaedic applications [1]. They possesses a set of suitable properties for these applications such as low specific weight, high corrosion resistance and biocompatibility [2].

The Ti-6Al-4V alloy with ( $\alpha + \beta$ ) structure was the first titanium alloy used as implant material. These alloy so far exhibited excellent corrosion properties, the metal ions released by corrosion or wear processes may induce aseptic loosening after long-term implantation [3]. For this reason studies on the corrosion and passivity of implants that simulate fluids from the human body: Ringer solution [4], phosphate saline buffered solution [5], artificial saliva [6] and Hanks solution [7].

Thus, a number of different titanium based alloys different Ti-Mo-Nb-Al, or Ti-Mo-Nb-Al-Cr-Zr alloy [8], Ti-Zr-Nb, Ti-Al-Nb [9], or Ti-Zr-Nb-Ta-Pd [10] that may become important for use as implant have

been investigated. In the present study, the electrochemical behaviour of newly developed Ti-5Al-2Nb-1Ta alloy in Hank's solution at different immersion hours.

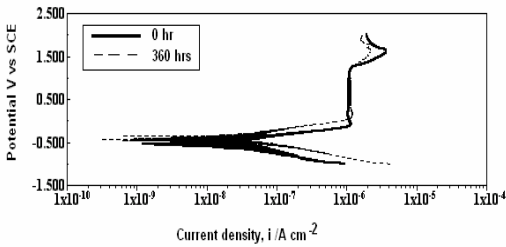
### Experimental Details

Ti-5Al-2Nb-1Ta (Kobe steel Ltd., Japan) used as substrate. The chemical composition (g/l) of the Hank's solution was 8.0 NaCl, 0.4 KCl, 0.185 CaCl<sub>2</sub>, 0.35 NaHCO<sub>3</sub>, 0.48 Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O, 0.1 MgCl<sub>2</sub>·6H<sub>2</sub>O, 0.06 KH<sub>2</sub>PO<sub>4</sub>, 0.1 MgSO<sub>4</sub>·7H<sub>2</sub>O and 1.0 Glucose. The pH was adjusted to 7.4 and temperature was maintained at 37°C. The substrate were ground with SiC abrasive paper upto 2500 grit, final polishing was done with 1µm diamond paste. The samples were degreased with acetone followed by ultrasonic cleaning with deionized water. Electrochemical potentiodynamic polarisation studies were carried out for titanium alloys in the Hanks solution. All the potential measurements were made with reference to a saturated calomel electrode (SCE). A platinum foil was used as the counter electrode and at a scan rate of 0.167 mV/s, in potentiostat (model PGSTAT 12 with FRA, Autolab, The Netherlands B.V) controlled

by a personnel computer with dedicated software (GPES version 6.0) was used for conducting the polarisation experiments. In order to obtain reliable results, the determination of potentiodynamic polarization measurements was repeated three times in Hanks solution. EIS studies were carried out using an electrochemical system Frequency Response Analyser (FRA), which included a potentiostat model PGSTAT 12. The titanium specimens with the exposed surface of 1 cm<sup>2</sup> were used as the working electrode. The impedance spectra were acquired in the frequency range 10 KHz to 10 mHz with a 10 mV amplitude sine wave generated by a frequency response analyzer. Nyquist and Bode plots were obtained after the specimens immersed in the Hank's solution for different hours 0 hr, 120 hrs, 240 hrs and 360 hrs.

**Results and Discussion**

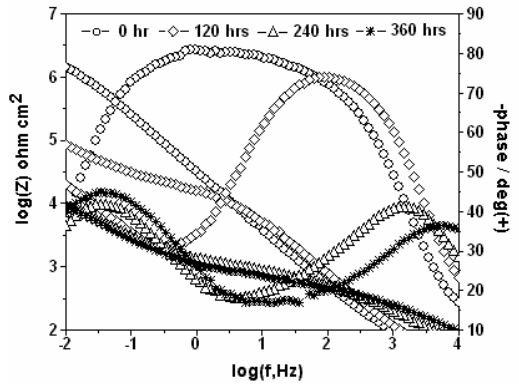
The corrosion potential ( $E_{corr}$ ), variation with time of immersion in Ti-5Al-2Nb-1Ta alloy in Hanks solution for a period of 0 hr and 360 hrs are shown in the Fig.1.



**Fig.1. Potentiodynamic polarization studies curves of Ti-5Al-2Nb-1Ta alloy at 0 hr and 360 hrs in Hanks solution**

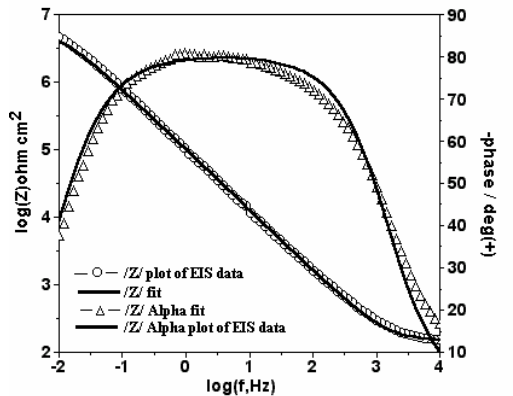
The initial  $E_{corr}$  for the alloy is -0.435 V (SCE) and then it gradually increases to noble potentials reaching a value of -0.247 V (SCE) after 360 hrs. The corrosion current densities ( $i_{corr}$ ) were obtained from the polarization curves by extrapolation of the cathodic branch of the polarization curves to the corrosion potential. The  $i_{corr}$  values were  $4.85 \times 10^{-7}$  A cm<sup>-2</sup> and  $2.39 \times 10^{-8}$  A cm<sup>-2</sup> for 0 hr and 360 hrs in Hanks solution respectively. The current density values show that stable passive film is formed on the surface and also due to the prolonged interaction in the Hanks solution. These results are in agreement with those of Zhnocai et al. [11]. The electrochemical

impedance data recorded for Ti-5Al-2Nb-1Ta alloy in Hanks solution followed by different immersion hours (0 hr, 120 hrs, 240 hrs and 360 hrs) are shown in the Fig.2.



**Fig.2. Bode plot of Ti-5Al-2Nb-1Ta alloy at different immersion hours in Hanks Solution**

From Fig.3a and 3b, it is observed that the phase angle approaches -90° and the phase angle remains constant between the higher and lower frequency ( $10^3$  to  $10^{-1}$  Hz), suggesting that a highly stable film are formed on the surface. At 120 hrs, phase angle decreases to near -70° due to the diffusion process (2). As the immersion hours from 240 to 360 hrs, the phase angle maximum is completely reduced to near -40° at high frequency; it may be due to the formation of the apatite layer on the titanium surface is shown in the figure 4a and 4b.



**Fig.3a. Impedance spectra for fitted Nyquist plot of Ti-5Al-2Nb-1Ta alloy at 0 hours in Hanks solution**

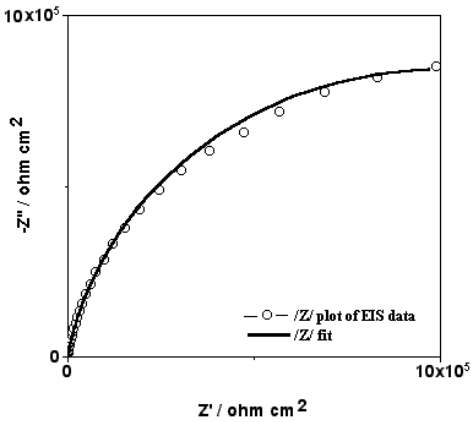


Fig. 3b. Impedance spectra for fitted Bode plot of Ti-5Al-2Nb-1Ta alloy at 0 hours in Hanks solution

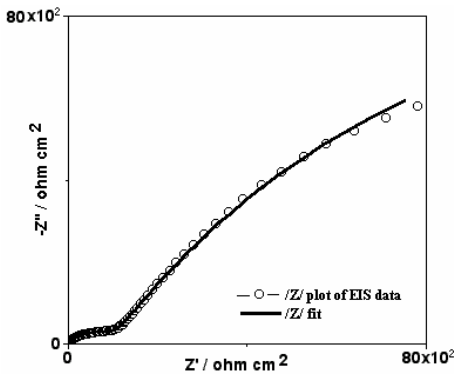


Fig.4a. Impedance spectra for fitted Nyquist plot of Ti-5Al-2Nb-1Ta alloy at 360 hours in Hanks solution

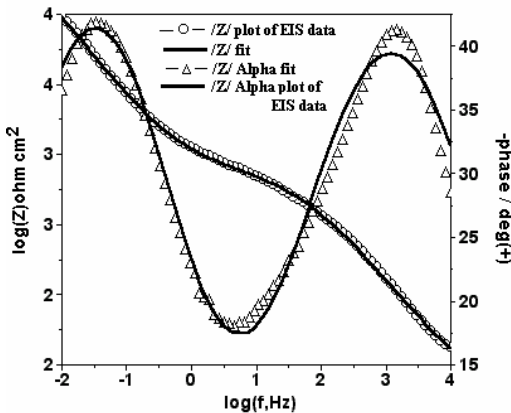


Fig.4b. Impedance spectra for fitted Bode plot of Ti-5Al-2Nb-1Ta alloy at 360 hours in Hanks solution

This was conformed by Lavos-Valereto et al. [12] with Ti-6Al-7Nb alloy, in Hanks solution, two relaxation time constants were clearly indicated by two peaks on phase angle plots.

The impedance spectra were fitted using a non-linear least square (NLLS) fitting procedure. The fitted impedance spectra (experimental and simulated data) generated using the equivalent circuit ( $R_s(R_1Q_1)$ ) and it consists of solution resistance ( $R_s$ ), charge transfer resistance ( $R_1$ ) and double layer capacitance ( $Q_1$  or CPE) (fig.5). This equivalent circuit is based on a model used by Pan et al. [5] to simulate data for titanium in a saline solution. The impedance of CPE is defined by

$$Z_{CPE} = 1 / (j\omega)^n Q$$

and the exponent  $n$  of the CPE is related to at non-equilibrium current distribution due to the surface roughness (porous) or non homogeneity (13). For interface behaviour is an ideal capacitor having  $n = 1$  and maximum phase angle equal to  $-90^\circ$ . The equivalent circuit for 120, 240, and 360 hrs are represented as  $R_s(R_1Q_1[R_2Q_2])$ . The two layers were formed on the metal surface in which  $R_1, R_2$  charge transfer resistance and  $Q_1, Q_2$  double layer capacitance. The outer layer consists of porous or apatite layer and inner layer consist of compact passive barrier layer (fig.5).

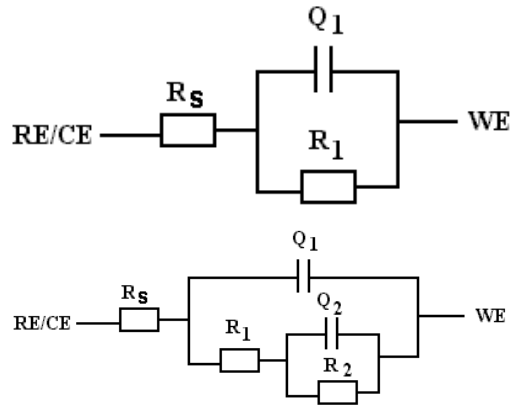


Fig.5. Equivalent circuit ( $R_s(R_1Q_1)$  and  $R_s(R_1Q_1[R_2Q_2])$ ) for Ti-5Al-2Nb-1Ta alloy in Hanks solution

### Conclusions

The electrochemical techniques used in this investigation led to the following conclusions.

Very low corrosion current densities were obtained for alloy at 360 hrs in Hanks solution showing that they are stable and passive film formed on the surface when compared to 0 hr.

The EIS results indicated that the layer film formed on the alloy is highly passive for 0 hrs and bilayered oxide consisting of an inner ( $\text{TiO}_2$ ) barrier layer and outer porous (apatite) layer, which apparently facilitates the osseointegration.

## References

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