

In situ impedance spectroscopy study of the electrochemical corrosion of orthopedic Ti-6Al-7Nb in simulated body fluid

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ABSTRACT

The corrosion resistance of titanium alloy, Ti-6Al-7Nb, was investigated through electrochemical impedance spectroscopy (EIS), open circuit potential (OCP) measurements and scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis. The tests were done in Hank's solution at 37 °C for immersion periods expanded to 169 h. A high corrosion resistance was obtained for Ti-6Al-7Nb alloy in hank's solution due to the stable passive film formed on its surface. The EIS results indicated the presence of a single passive layer immediately after immersion. However, after 24 h of immersion in hank's solution, the EIS exhibited the presence of a bi-layered surface corresponding to an inner layer and an outer layer. Further, the film formed on the alloy after 169 h was confirmed by SEM and EDX analysis as calcium and phosphate may be due to apatite formation. Copyright © 2012 VBRI Press.

Keywords: Ti-6Al-7Nb; biomaterials; EIS; Hank's solution.

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Introduction

Titanium alloys are today one of the most important metallic materials used in orthopedics and dental surgery. Despite their high corrosion resistance in the physiological environment, the finding at revision surgery of damage at the metal surface and consequent periprosthetic metallosis indicates that failures of the implant occur in vivo. In vivo degradation of metallic biomaterials due to combined wear and corrosion processes results in the formation of particulate and ionic metallic debris, which are recognized as major factors limiting the lifespan of joint replacements [1]. In the case of titanium, it has been reported that levels of Ti are greater in patients with failed total knee and hip replacements [2,3] than in controls or in patients with stable prostheses.

The corrosion stability of titanium can be improved by alloying with resistant metals [4]. The implant biomaterials must exhibit excellent biocompatibility and corrosion resistance in biofluids, high mechanical resistance, low modulus, low density and good wear resistance [5].

The Ti-6Al-4V alloy originally developed for aerospace applications, and it is the first Ti alloy used as a biomaterial. Due to its excellent corrosion resistance and mechanical properties, this alloy is established as one of the major alloy used for manufacture of orthopaedic implants [6]. In various environments it spontaneously forms oxides, which play a decisive role in determining the biocompatibility and corrosion resistance of these implants [7].

Namely, the formation of a stable passive oxide film on metallic implants considerably reduces their corrosion [8]. The composition and thickness of the formed oxide determine the corrosion resistance of biometallic materials and release of metal ions from the implant that can affect health [9-11]. Various oxides are reported to form on Ti alloys surface [8,12]. The passive film on Ti implants is mainly composed of TiO₂, existing in a rutile-type tetragonal structure [8]. The presence of this thermodynamically stable and adherent oxide contributes to high corrosion resistance [12]. However, the structural changes in passive films of various Ti-based implants may alter their corrosion resistance. Metikos-Hukovic et al. [13] demonstrated that V can diffuse to the surface of Ti alloys and oxidize to form small amounts of V₂O₅, VO₂ and V₂O₃ at the outermost surface. Their formation deteriorates the passivity of Ti-6Al-4V alloy because they are not as protective as Ti oxides [13]. Thus, the V₂O₅ in the passive

film formed on Ti-6Al-4V alloy dissolves and results in the lower film corrosion resistance [14]. The release of aluminium and vanadium ions from the commonly used Ti-6Al-4V alloy was found to be toxic and their accumulation in the surrounding tissues was of great concern [15].

Vanadium can alter the kinetics of the enzyme activity associated with cells of the inflammatory response [16]. These metals may also influence the chemostatic mechanisms that are involved in the attraction of cells to the affected area; aluminium is found to be strongly positively chemostatic, possibly explaining the narrow but densely packed reaction zone. It has been reported that vanadium oxide formed on the surface of Ti-6Al-4V alloy dissolves, and this dissolution is further enhanced by the presence of Cl⁻ ions in Hank's solution [13].

Metal ions released from the Ti-6Al-4V implant to the bloodstream may cause local irritation of the tissues surrounding the implant [17]. Further, cell and tissue responses are affected not only by the chemical properties of the implant surface, but also by the surface topography or roughness of the implants [18]. Thus, there has been considerable interest in the use of the alloy Ti-6Al-4V for orthopedic implants because of its fatigue strength and biocompatibility, and this alloy has certain limitations.

In the light of these observations, further investigation of titanium alloys is increasingly important for gaining a better understanding of traditionally used alloys, and for helping in the search for new titanium alloys. Because of the possible risks associated with vanadium, Semlitsch developed the alternative alloy, Ti-6Al-7Nb, in which the vanadium was exchanged for niobium [19]. Today this alloy is the preferred choice for cementless total joint replacements [20]. Immunological studies have provided evidence that exposure of human monocytes to Ti-6Al-7Nb particles results in smaller release of cell mediators than does equivalent exposure to Ti-6Al-4V particles [21]. Corrosion stability is a prerequisite for in vivo applications, and the electrochemical properties and consequent corrosion resistance of Ti and Ti-based alloys under simulated physiological conditions have been the subject of numerous reports [22].

In order to avoid the possibility of V release and to explore further materials with suitable mechanical properties for biomedical applications, numerous alloys have been investigated: Ti-10Mo and Ti-10Mo-10Al [23], Ti-5Al-4.5V [23,24], Ti-6Al-7Nb [25,26], Ti-6Al-4Fe [24,26], Ti-13Nb-13Zr [27,28-31], Ti-45Nb [31], Ti-15Zr-4Nb [29] and Ti-Cu-Ag [32,33]. The passivation behavior of Ti-6Al-4Nb, Ti-6Al-4Fe and Ti-5Al-2.5Fe alloys in Hank's solution was comparable with that of Ti-6Al-4V [26]. Yu et al. demonstrated that addition of Zr or Nb (Ti-45Nb and Ti-50Zr alloys) results in strong covalent bond formation between neighbouring Ti, Nb and Zr atoms, through sharing of unpaired d level electrons [31].

The behavior of Ti-based alloys [13,23,25,27,34-44] has been studied under simulated physiological conditions. Ti-6Al-7Nb alloy exhibits a broader passive range than Ti-6Al-4V alloy in simulated physiological solution [13,38]. Based on EIS measurements, Metikos-Hukovic et al. proposed that the corrosion resistance increases due to incorporation of Nb cations into the TiO₂ matrix [13]. The high protectiveness of the passive layer formed on Ti-6Al-

7Nb alloy was ascribed to formation of a double oxide layer, a dense inner barrier layer and a porous outer layer [37,44].

One determining factor for the success of the alloys as biomaterials is their corrosion behavior. The corrosion behavior of a material strongly depends on the presence of a protective passive film, i.e. is mainly a surface phenomenon. Consequently, the determination of the passive film stability complements the in vitro corrosion evaluation. The stability of the surface oxide film is of high interest also because oxide layers of a biomaterial will be in direct contact with biological tissues. Despite numerous studies performed on Ti-6Al-7Nb alloy [13,27-29,37,38,40,42,43], there is little study about its behavior for long immersion time in simulated physiological solutions, and apatite formation on its surface. In previous study, we investigated the electrochemical behavior of the oxide film formed on the Ti-6Al-7Nb alloy in Hank's physiological solution, using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PD) measurements [25]. In this study, we investigate the corrosion resistance of Ti-alloy, Ti-6Al-7Nb in Hank's naturally aerated solution at 37 °C for one week (169 h) using electrochemical impedance spectroscopy, open circuit potential measurements, scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis.

Experimental

Materials

The material used in this study is a commercial Ti-6Al-7Nb alloy (purchased from Sulzer, Winterthur, Switzerland). For electrochemical measurements the test specimens were used in the form of discs with 1 cm² diameter. The samples surface was abraded to 2500 grid using Phoenix 4000 (Buehler, Germany) then polished with alumina paste. They were, then, washed with double distilled water followed by ultrasonic cleaning with ethanol for 10 minutes. To make electrodes, the specimens were embedded in a teflon holder, with a exposed surface area of 0.2 cm² to the solution.

All chemicals were purchased from Sigma Aldrich, Germany and were used without further purification. They are molecular biology grade with purity of ≥ 98%. Hank's physiological solution was prepared according to previous studies [28,42,45-48] (8 g/l NaCl, 0.4 g/l KCl, 0.35 g/l NaHCO₃, 0.25 g/l NaH₂PO₄ × H₂O, 0.06 g/l Na₂HPO₄ × 2H₂O, 0.19 g/l CaCl₂ × 2H₂O, 0.19 g/l MgCl₂, 0.06 g/l MgSO₄ × 7H₂O and 1.0 g/l glucose, pH 7.8) using doubly distilled water.

Methods

For electrochemical measurements an Autolab three-electrode corrosion cell was used. Saturated calomel electrode (SCE) and platinum plate were used as reference and counter electrodes, respectively. All potentials in this study were referenced to the saturated calomel electrode (SCE) scale. The temperature of the cell was adjusted to 37 °C by using thermostatically controlled water bath.

In the experiments, the electrode immersed in the electrolyte, and record the open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) after several times of immersion. The frequency ranged from 100 kHz to 10 mHz at 10 cycles per decade, with an AC amplitude of ± 10 mV. The absolute impedance and phase angle were measured at each frequency. The impedance data were interpreted on the basis of equivalent electrical circuits, using the Zsim program for fitting the experimental data. These measurements were done by using the electrochemical workstation Zahner IM6e (Zahner Elektrik, GmbH, Kronach, Germany).

Results and discussion

Open circuit potential measurements:

Fig. 1 shows the variation of open circuit potential (OCP) with immersion time of the TAN alloy in Hank's solution at 37 °C. As can be seen, the time profile of the OCP is typical for the formation of passive film on the alloy surface immersed in Hank's solution [49].

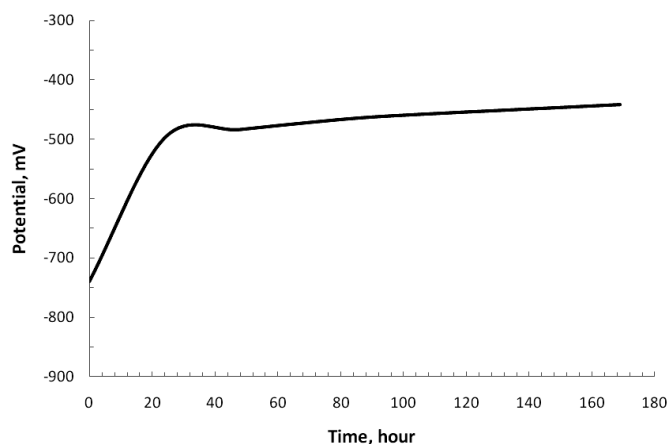


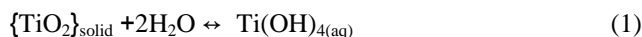
Fig. 1. The OCPs of TAN in aerated Hank's solution at 37°C measured for 169 hours.

Time (h)	0	3	24	48	72	96	169
OCP (mV)	-740	-586	-498	-484	-471	-461	-442

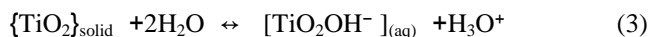
Immediately after immersion in the solution, the potential of the alloy is approximately -740 mV (SCE), then there is an initial shift of potential in the active direction within the initial few minutes followed by a continuous rise in potential towards noble direction, reaching the values around -500 mV (SCE) after 24 h of immersion. Then, it varies slowly towards more positive potentials until an approximately steady value reached, with variation rate less than 14 mV / day after 24 h, as indicated from **Table 1**. These results revealed a presence of competition between film dissolution and film formation.

It is known that, in clean, ambient, air a surface film of titanium oxide is expected to form onto the metal surface [50-52]. Since the time of exposure to air is very low, it is expected that the titanium substrate is partially covered with TiO₂ surface film which have a certain degree of

protection. On the other hand, dissolution of titanium oxide film in water is possible from the thermodynamic point of view according to the following reaction [53]:



Thus, the appearance of an initial shift of potential in the active direction within the initial few minutes could be attributed to the dissolution of the pre-immersion oxide film that formed on the surface in air upon immersion the electrode in the Hank's solution according to the following biochemical reactions [54]:



Generally, the formation of charged species (e.g. $[\text{Ti}(\text{OH})_3]^+_{(\text{aq})}$ and $[\text{TiO}_2\text{OH}^-]_{(\text{aq})}$) in Hank's solution is reflected in many publications [54,55].

The OCP shift in the noble direction indicates that an oxide film is passivating the metallic surface [56], suggests that a protective passive film forms rapidly and acts as a barrier for metal dissolution, reducing the corrosion rate. The thickness of the spontaneously formed protective oxide film on surfaces of alloy at open circuit conditions is 1–4 nm [57]. Although the OCP values of Ti alloy in physiological solutions were shown to be highly dependent on surface preparation [58], the stable value of OCP is found in the stable region of TiO₂ oxide in the Pourbaix diagram developed for the Ti–H₂O system at 37 °C [59], as seen in previous research [60].

Electrochemical impedance spectroscopy (EIS)

A set of impedance spectra recorded for the alloy at different time from immersion in Hank's solution presented as Bode plots, are shown in **Fig. 2**. The spectra at 0 h show that in the higher frequency region, log |Z| tends to become constant, with the phase angle values falling rapidly towards 0° with increasing frequency. This is a response typical of the resistive behavior and corresponds to the solution resistance, R_s. Inside the medium and low frequency regions, the system behaves differently. In the medium frequency range, a linear relationship between log |Z| and log f is observed, but with slope less than -1, and phase angle maxima (less than -90°), indicating that the passive film was not fully capacitive.

With the increase in the immersion time to 24 h, the alloy exhibited two distinct capacitive behaviors. After 169 h of immersion, the nature of Bode plots was similar to that of 24 h of immersion. The high impedance values and phase angle of -90° are indicative of a single thin passive oxide film present on the surface at 0 h of immersion. The increase in the impedance value observed for 24 and 169 h of immersion indicated an increase in corrosion resistance of the film. The two distinct capacitive behaviors can be attributed to the formation of a new layer in addition to the barrier layer. The unchanged Bode plots after 24 h of immersion indicated no further changes with increase in the

immersion time. This behavior may be due to the complete surface coverage of the new layer over the barrier layer. Substantial evidence from literature [4,54,61,62] shows that the film formed on surface, after prolonged immersion in SBF solution exhibits a two-layer structure composed of a dense inner layer and a porous outer layer.

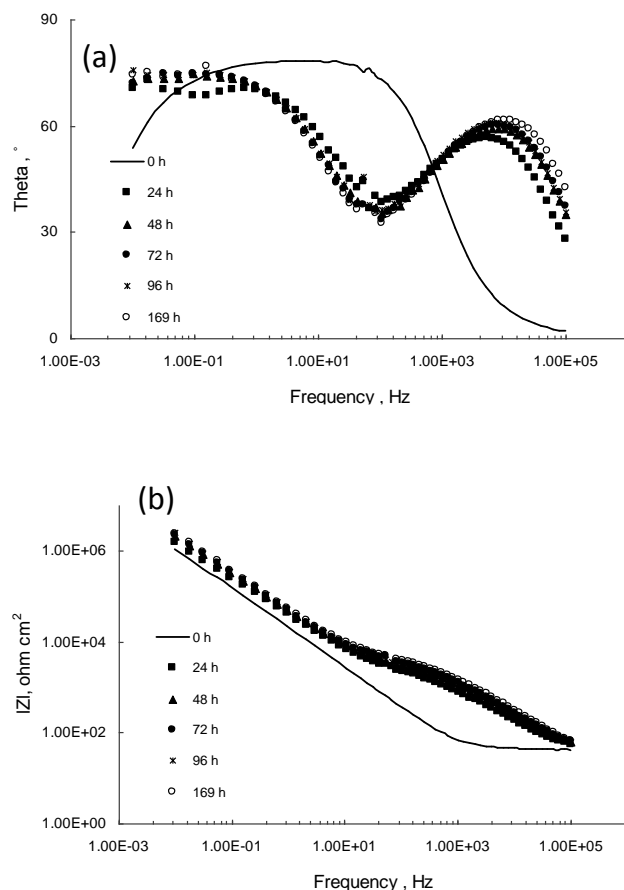


Fig. 2. (a, b) Variation of impedance plots with time for TAN in aerated Hank's solution at 37°C at different time.

Since any interface undergoing an electrochemical reaction is typically analogous to an electronic circuit consisting of a specific combination of resistors and capacitors, the electrochemical systems under the study can be described in terms of their electrical equivalent circuits (EECs). Thus, the first task was to identify the best-fit EEC, based on Zsim software, in order to establish the values of circuit elements. The usual guidelines for the selection of the best-fit EEC were followed: (i) a minimum number of circuit elements were to be employed; (ii) the error was suitably low (approximately 10^{-4}), and the errors associated with each element were up to 5%. The EECs that satisfied the above criteria were used to fit the experimental data and are presented in **Fig. 3a**. Since the measured capacitive response is not generally ideal due to the certain heterogeneity of the electrode surface [63,64], a constant phase element (CPE) was introduced for fitting the spectra, instead of an ideal capacitance element. Its impedance may be defined by: $Z(\text{CPE}) = [Q(j\omega)^n]^{-1}$, the constant Q accounts for a combination of properties related to both the surface and the electroactive species, $j\omega$ is the complex variable for sinusoidal perturbations with $\omega = 2\pi f$, and n

being the exponent of CPE, with values between -1 and 1 [65,66]. When $n = 1$, the CPE describes an ideal capacitor with Q equal to the capacitance (C). For $0.5 < n < 1$, the CPE describes a distribution of dielectric relaxation times in frequency space, and when $n = 0.5$ the CPE represents a Warburg impedance with diffusional character [67].

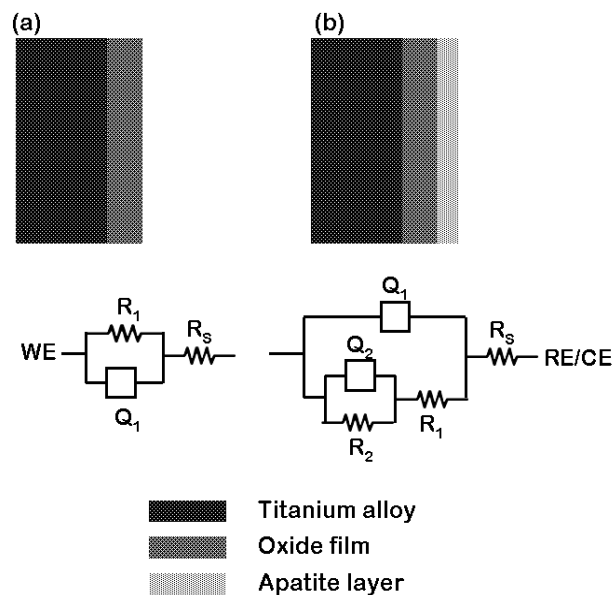


Fig. 3. Equivalent circuit fitted for TAN alloy in Hank's solution (a) 0 h and (b) 24 h.

Table 2. Values of fitting parameters obtained by fitting the EIS data for TAN at different time of immersion in Hank's solution at 37°C.

Time, h	R_s Ω cm^2	Q_1 $\mu\text{F cm}^2$	n_1	R_1 $\text{k}\Omega \text{ cm}^2$	Q_2 $\mu\text{F cm}^2$	n_2	R_2 $\text{M}\Omega \text{ cm}^2$
0	42.76	9.36	0.88	2.35×10^3	-	-	-
24	28.50	5.53	0.64	25.21	6.98	0.81	3.21
48	29.14	4.12	0.63	26.78	5.50	0.74	4.33
72	34.75	3.72	0.89	29.37	5.39	0.87	5.42
96	35.26	2.17	0.98	34.53	4.65	0.93	6.48
169	27.92	1.37	0.75	35.91	3.30	0.83	6.68

The physical meaning given to the circuit is association with the passive film/electrolyte interface and the passive film itself [67]. Some authors [23,54] proposed $R_s(Q_1R_1)$ as the equivalent circuit model to fit the EIS data in the case of a single passive film present on the alloy surface. Similarly, the equivalent circuit used for EIS for 0 h of immersion in Hank's solution, shown in Fig. 3a, consists of the following elements; a solution resistance (R_s) of the test electrolyte, (Q_1) the double layer capacitance and R_1 the charge transfer resistance of the barrier layer.

From **Table 2**, it can be seen that the values of n were very close to one ($n > 0.9$) for TAN alloy at 0 h of immersion in the solution. This indicated a near ideal capacitance of the passive films formed on the alloy [54]. As the immersion hours increased to 24 h, the equivalent

circuit fitted was $R_s(Q_1R_1(Q_2R_2))$, (**Fig. 3b**), where (R_s) represents solution resistance of the test electrolyte, Q_1 the double layer capacitance of the outer layer and Q_2 the double layer capacitance of the inner layer, R_1 and R_2 are the charge transfer resistance of the outer layer and inner layer of the metal/electrolyte interface, respectively.

The resulting parameters from best fitting of experimental EIS data were presented in **Table 2**. The constant phase element Q_2 represents the double layer capacitance, C_{dl} , as shown by the high value of the n_2 exponent. The values of R_2 are observed to increase with immersion time increased, confirming the formation of a barrier layer with high corrosion protection ability. Other authors obtained similar EIS results [54].

After 169 h of immersion in Hank's solution, the alloy showed higher values of charge transfer resistance, due to the newly formed layer that accounts for higher protection. The resistance of the outer layer increases with immersion time. Decrease in Q_1 and Q_2 , starting from the beginning of the immersion, can be attributed to thickening of the oxide layer. The thickening is more pronounced at 169 h. The observed to increase of R_1 with time indicate the establishment of stable passive conditions.

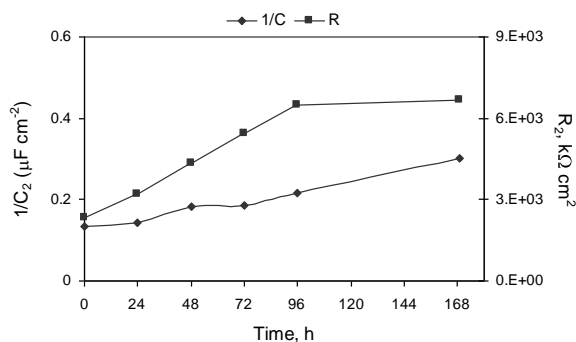


Fig. 4. Variation of the $1/C_{CPE}$ and R_{ox} of the oxide film with immersion time for TAN alloy in Hank's solution at 37 °C.

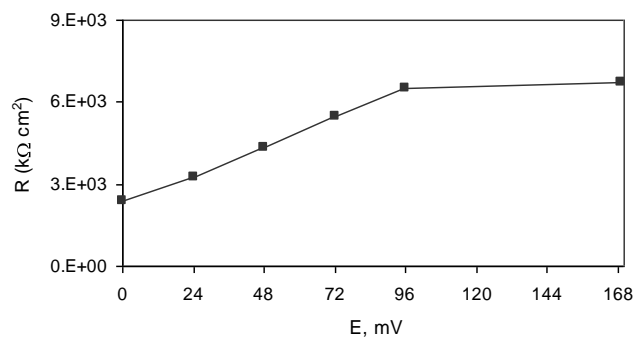


Fig. 5. Polarization resistance presented as the sum of partial resistances as a function of immersion time for TAN alloy in Hank's solution at 37 °C.

In **Fig. 4**, the variation of $(1/Q_2)$ and resistance (R_2) of the oxide films formed on titanium alloy surface as a function of the immersion time are drawn. Since the passive oxide film can be considered as a dielectric plate capacitor, the passive film thickness (d) in cm is related to the capacitance (C) by the equation [22,68]:

$$d = \epsilon_0 \epsilon_r A / C \quad (4)$$

where ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-12} \text{ Fcm}^{-1}$), ϵ_r is the relative dielectric constant of the film and A is the electrode area in cm^2 . Although the actual value of ϵ_r within the film is difficult to estimate, a change of C can be used as an indicator for change in the film thickness [69]. Hence, the reciprocal capacitance ($1/C$) of the surface film is directly proportional to its thickness [70–72]. The results in **Fig. 4** shows that R_{ox} and $1/C_{CPE}$ seem to be consistent with each other as they increase significantly with increasing immersion time.

The polarization resistance of the alloy equals the sum of the R_1 (Rct) and the passive film resistance, R_2 [22,67]. Its values estimated and presented in **Fig. 5** as a function of immersion time, which increase with immersion time increase indicating the increase in the corrosion resistance of this material in Hank's physiological solution.

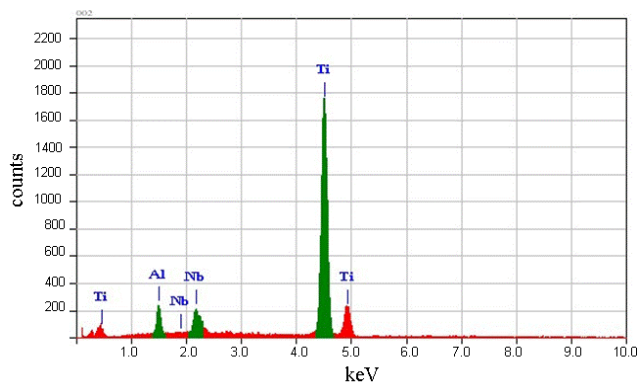


Fig. 6. EDX analysis of TAN before immersion in Hank's solution.

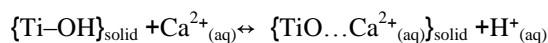
SEM and EDAX studies

Although TiO_2 is the predominant oxide of the passive film of Ti alloys, TAN contains Al- and Nb-oxides located mostly on top of the TiO_2 matrix, as shown by EDX results of TAN before immersion in Hank's solution (**Fig. 6**). Based on X-ray photoelectron spectroscopy (XPS) analysis, Milosev et al. [22], confirm that the layer is stabilized due to the incorporation of Al- and Nb-oxides, which increases the overall resistance of the layer.

The modification of the passive TiO_2 layer by Nb_2O_5 improves the structural integrity of the oxide film [73]. The formation of Nb_2O_5 oxide, which is chemically more stable and less soluble compared to V_2O_5 formed on the Ti–6Al–4V alloy, enhances resistance to dissolution of the surface film [14].

When TAN alloy immersed in Hank's solution, the oxide well start to dissolve. The dissolution of the titanium oxide film in water presented by equation (1), and in hank's solution by equation (2) and (3).

The calcium ions present in the Hank's solution tends to attach to the titanium oxide surface upon immersion. The concentrations of calcium and phosphate ions at the surface and therefore the thickness of the calcium phosphate were observed to increase with the immersion time [55]:



----- (5)

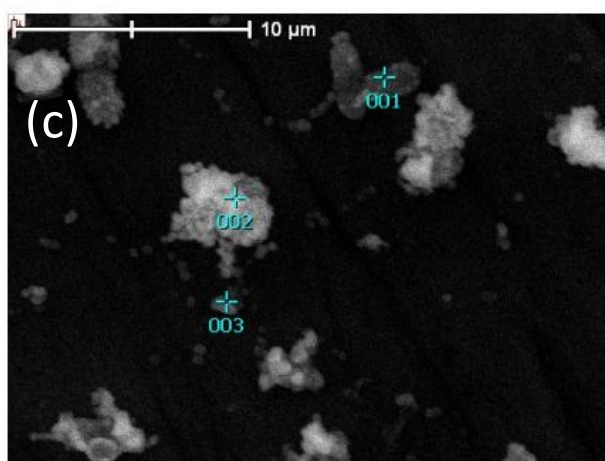
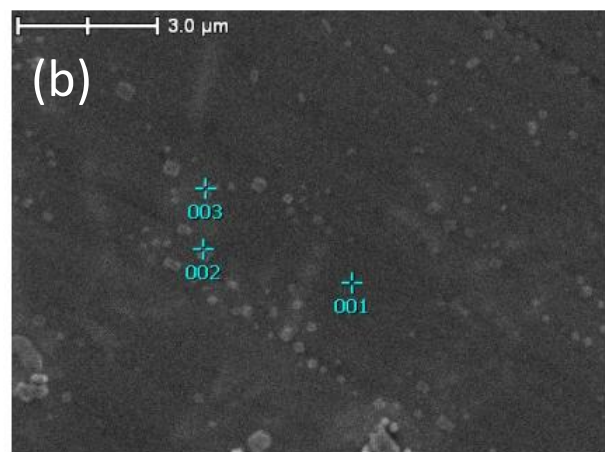
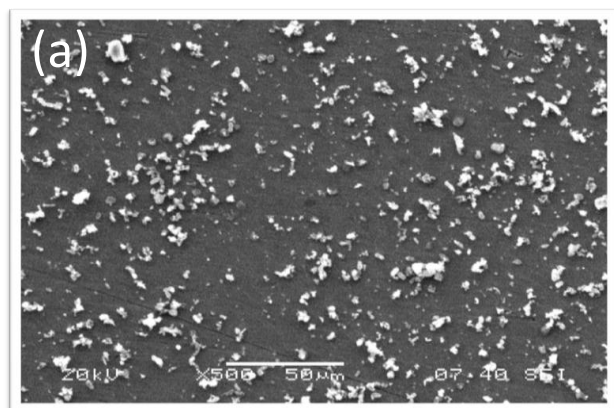
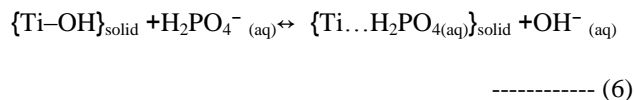
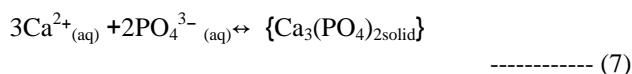


Fig. 7. (a-c) SEM of TAN after 169 hours of immersion in Hank's solution at 37°C.



Eq. (5) shows that the influence of cations (Ca^{2+} , Mg^{2+}) adsorption on the surface and Eq. (6) shows the exchange of basic hydroxide anions (OH^-) with phosphate anions:



Sitting [74] studied the immersion studies in the HBSS (Earle's balanced salt solution) using XPS on CpTi and Ti-6Al-7Nb samples. The alloys Ti-6Al-4V and Ti-6Al-7Nb behaved rather similarly to CpTi, although a slight tendency to slower kinetics for the calcium phosphate deposition out of HBSS (Hanks balanced salt solution) and EBSS (Earle's balanced salt solution), respectively, was noted [75].

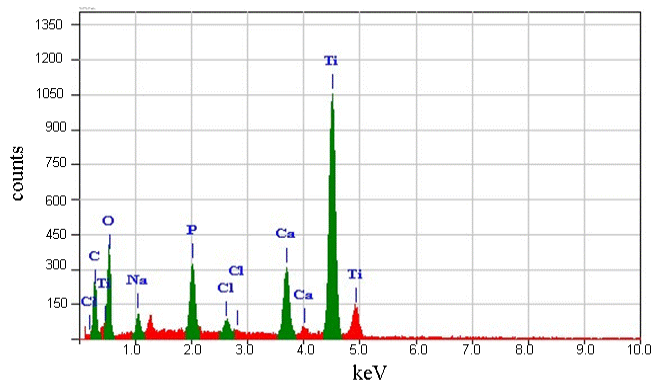


Fig. 8. EDX analysis of TAN after 169 hours of immersion in Hank's solution at 37°C.

Fig. 7 shows the SEM images of Ti-6Al-7Nb alloy after 169 h of immersion in Hank's solution. After immersion, apatite layer was formed on the surface of the alloy as shown. The composition of the particles was analyzed by EDX method and the results are shown in **Fig. 8**. The EDX results indicated that the Al and Nb peaks was suppressed for apatite formed on the alloys. This can be attributed to the prolonged interaction of Ca and P over the surface of the alloys, which in turn, increases the thickness of the layer. These results are in good agreement with the impedance spectroscopic studies.

As was suggested by Khan et al. [76], the Ti-6Al-7Nb alloy can be a better alternative to Ti-6Al-4V because of its corrosion resistance and resistance to loss of mechanical properties with changes in pH in simulated body fluid environment.

Conclusion

The electrochemical techniques used in this investigation led to the following conclusions. A high corrosion resistance was obtained for Ti-6Al-7Nb alloy in hank's solution due to the stable passive film formed on its surface. The EIS results indicated the presence of a single passive layer immediately after immersion. However, the alloy immersed for more than 24 h in hank's solution exhibited the presence of a bi-layered surface corresponding to an inner layer and an outer layer. Further, the films formed on the alloy were confirmed by SEM and EDAX analysis as calcium and phosphate may be due to apatite formation.

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