

Investigation of electrochemical behavior of plasma nitrided Ti-6Al-7Nb alloy in Hanks' Solution

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Abstract

Titanium alloy Ti-6Al-7Nb was plasma nitrided using inductively coupled RF Plasma with 100% Nitrogen at 750, 800 and 850°C for 4 h. Micro Raman studies show the formation of titanium nitrides. Potentiodynamic polarization studies in Hanks' solution show the corrosion resistance of the untreated samples to be better than the treated samples. Electrochemical Impedance Spectroscopy (EIS) studies show higher charge transfer resistance and lower double layer capacitance for the substrate compared to the nitrided samples. FESEM images of samples immersed in SBF show that growth of apatite is more and the size of deposits are larger on nitrided samples as compared to that on the untreated substrate. Nitrided samples immersed in Hanks' solution for 7 days show higher amount of calcium, phosphorous and oxygen than the substrate.

Keywords: Titanium alloy, Plasma Nitriding, corrosion, EIS, apatite

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1. Introduction

Titanium alloys are used in a large number of applications ranging from aerospace to marine to chemical industries because of their high specific strength and excellent corrosion resistance. Such a high and remarkable corrosion resistance is attributed to a very stable oxide film formed on the alloy surface.[1] Metallic materials are being increasingly used in medical applications as implants to restore lost functions or replace organs functioning below acceptable levels. Titanium alloys are among the most used metallic biomaterials, particularly for orthopedic applications.[2] They possess a set of suitable properties for these applications such as low specific weight, excellent mechanical properties and good resistance to corrosion in biological fluids and very low toxicity for the organism.[3]

In order to enhance the tribological properties of titanium alloys, surface modification is often performed. By means of physical and chemical vapour deposition, laser treatments, ion implantation and thermal nitriding it is possible to obtain surface layers consisting of titanium nitrides.[4] Titanium nitride (TiN) coatings, owing to high hardness allow improvement of the wear resistance of the substrate materials. Hence, they are widely used in many industrial coating technologies. TiN coatings can also improve the corrosion resistance properties of substrate materials in many aggressive environments.[5] TiN has been reported to enhance the corrosion resistance and biocompatibility of the Ti alloys.[6-8] Several methods are available for the formation of TiN and plasma nitriding is a suitable surface modification technology due to its advantages of tailoring the properties of the layer. [7, 8]

In the present work, titanium alloy Ti-6Al-7Nb was nitrided in low pressure RF plasma and characterized by electrochemical impedance spectroscopy, potentiodynamic polarization and immersion studies in Hanks' solution. The composition of the treated samples was analyzed by Micro Raman, FESEM and EDS.

2. Experimental Methods

2.1 Sample Preparation

Titanium alloy with nominal composition of Ti-6Al-7Nb samples of 10 mm diameter and ~3mm by thickness were cut from a rod and were ground with different grades of silicon carbide papers and finally polished using 0.1 μ m diamond paste. These samples were ultrasonically cleaned using acetone and dried prior to nitriding. Plasma nitriding was performed in a custom designed chamber which is made up of stainless steel. The chamber was pumped into 4 \times 10⁻⁶ mbar pressure by diffusion pump. Working gas flow was controlled by MKS make mass flow controllers. Nitriding was carried out 1.4 \times 10⁻⁴ mbar pressure. Plasma was generated using inductive coupling of 50W RF (13.56 MHz) power. The samples were kept in a heater box and heated to 750, 800 and 850°C. The temperature of the sample was measured using a thermocouple in contact with the sample. The nitriding time was counted when the sample temperature reached the desired temperature. After nitriding for 4h the samples were cooled in vacuum to room temperature.

2.2 Characterization Technique

The microhardness was measured using Buehler Micromet microhardness tester with Knoop indenter. MicroRaman analyses were carried out using Labram 010 Model of DILOR-JOBIN-YVON-SPEX Micro Raman spectrometer with 632 nm laser. The surface morphology of the samples were examined through Leica inverted vertical metallurgical optical microscopy and Carl Zeiss Supra 40 VP FESEM equipped with Inca Penta Fex3 (Oxford) EDS analyzer for elemental analysis. Immersion studies were carried out by immersing the

samples in freshly prepared Hanks' solution (SBF-Simulated Body Fluid) at pH of 7.4 to 7.6 for 7 days at room temperature.[7, 8]

2.3 Electrochemical measurements

Electrochemical studies on the substrate and nitrided samples were conducted using CHI604D Electrochemical Workstation supplied by CH instruments, USA. The conventional three electrode glass cell was used to carry out the electrochemical studies. The tests were conducted in 200 ml of Hanks' solution which simulates the body fluid (SBF) at room temperature. The sample was kept as the working electrode; Pt foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The reference electrode was kept very close to the surface of the working electrode. The sample was immersed in Hanks' solution for an hour in order to establish the open circuit potential (E_{OCP}) or the steady state potential. EIS measurement was carried out in the frequency range of 10 mHz to 100 kHz. The applied alternating sinusoidal potential was 10mV on the E_{OCP} . After each experiment, the impedance data were displayed as Bode plots. The Bode plot is a plot of $\log |Z|$ vs. $\log f$ and $\log f$ vs. - phase angle (θ), where $|Z|$ is the absolute impedance and f is the frequency. The acquired data were curve fitted and analyzed using ZSimpwin program (Princeton Applied Research, USA) to get suitable equivalent circuit parameters. The quality of the fit was checked by the χ^2 value. After EIS measurements, potentiodynamic polarization studies were carried out in a potential range of 200 mV below and above the OCP value with a scan rate of 1mV/s. The measured current–voltage data are plotted as Tafel plots in the form of potential vs. $\log (i)$ plot. The corrosion potential (E_{corr}) and corrosion current (I_{corr}) were deduced from the Tafel plot.

3. Results and Discussions

3.1 Surface Hardness

Fig. 1 shows the microhardness data of the samples at various applied loads of 25, 50, 100 and 200 gf. It can be observed that surface hardness of the sample increased 1200KHN at 50gf after nitriding. The hardness decreases with increasing load, indicating the formation of a hard layer near the surface. It can be also observed that the hardness increases with increasing temperature.

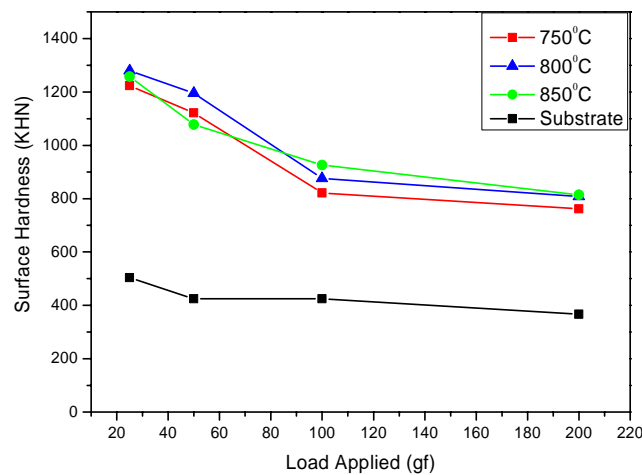


Fig.1. Surface hardness of Ti-6Al-7Nb substrate and nitrided samples

3.2 Raman Spectroscopy

Raman spectroscopic studies were carried out to confirm the formation of TiN due to nitriding. **Fig. 2** shows the Raman spectra of the sample nitrided in 100% nitrogen at 750°C, 800°C and 850°C for 4 h. In the figure, broad features corresponding to TiN are located in the 210-220, 300-350 and 500-600 cm^{-1} range, implying the formation of nitrides.[9] The intensities of the peaks show that effective nitriding takes place above 850°C.

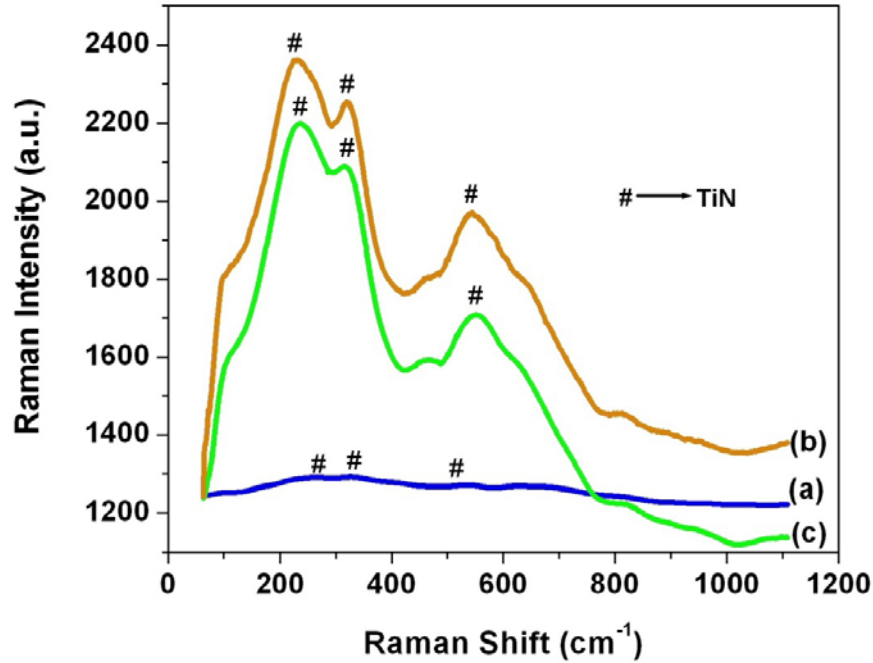


Fig.2. Raman spectra of samples nitrided at (a) 750°C, (b) 800°C and (c) 850°C

3.3 Immersion studies

Immersion studies were carried out on the substrate and nitrided samples by immersing them for 7 days at room temperature in a freshly prepared acellular SBF (simulated body fluid) Hank's solution with ion concentration that is nearly equal to that of human blood plasma ($\text{Na}^+ = 142.0$, $\text{K}^+ = 5.0$, $\text{Mg}^{2+} = 1.5$, $\text{Ca}^{2+} = 2.5$, $\text{HCO}_3^- = 4.2$, $\text{HPO}_4^{2-} = 1.0$, $\text{SO}_4^{2-} = 0.50$, and $\text{Cl}^- = 147.96$ mM). The chemical composition of the Hank's is as follows: 0.185g CaCl_2 , 0.4g KCl , 0.06g KH_2PO_4 , 0.1g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 8.0 g NaCl , 0.35 g NaHCO_3 , 0.48 g Na_2HPO_4 and 1.00 g D- glucose in 1 l of Milli-Q water. The pH of the solution was adjusted with 1 M HCl to 7.2-7.6.

Fig.3 (a) and (b) shows the FESEM images of the Ti-6Al-7Nb sample nitrided with 100% nitrogen and substrate after 7 days immersion in SBF, respectively. Insets in all the figures show images at a higher magnification. In these images, the apatite appears as white deposit. As can be seen in the images, the apatite deposit is more on the nitrided sample. These observations show that nitrided samples possess higher potential for growth of apatite on the surface. The wt.% of different elements obtained by EDS is given in **Table 1** for substrate and nitrided samples before and after immersion in SBF. The results show that wt.% of Ca and P is more on the nitrided sample after 7 days immersion in SBF.

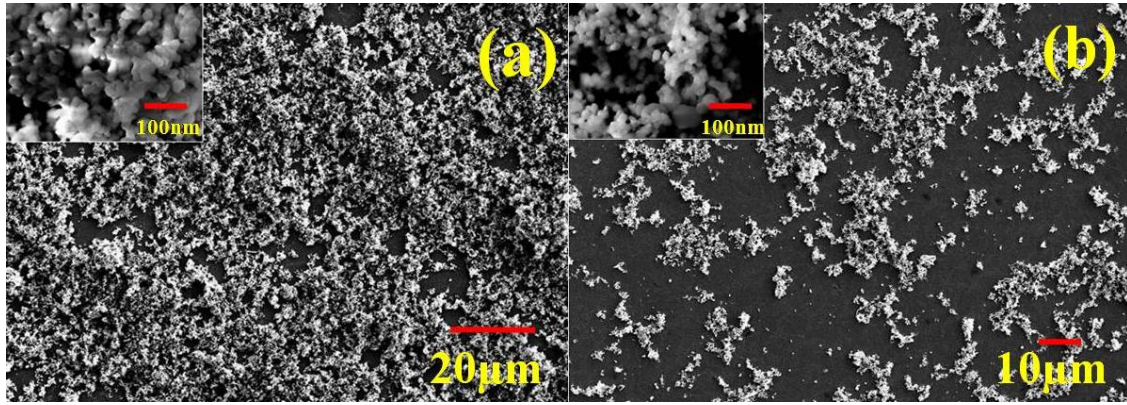


Fig.3. FESEM images of sample after 7 days immersion in SBF (a) sample nitrided at 800°C with 100% N₂ (b) substrate.

Table 1 EDS result of substrate and plasma nitrided sample for 4h at 800°C before and after immersion studies

Element	Substrate		Plasma nitrided at 800°C for 4hrs	
	Before Immersion	After Immersion	Before Immersion	After Immersion
	Wt%	Wt %	Wt%	Wt %
Ti	86.44	62.97	79.46	24.37
Al	6.17	4.43	3.94	2.03
Nb	7.05	5.23	6.20	2.65
O	0.17	21.40	4.94	46.17
N	-	-	5.46	-
Ca	-	3.56	-	15.01
P	-	2.41	-	9.77

3.4 Electrochemical Measurements

Potentiodynamic polarization curves of the substrate and sample nitrided at 800°C in freshly prepared simulated body fluid (SBF), Hanks' solution are shown in **Fig. 4**. The substrate and the treated sample were polarized up to 1V towards anodic potential to check their passive nature. The electrochemical parameters, that is, the corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) obtained for both the samples are listed in **Table 2**. For substrate, the corrosion current density, i_{corr} is about $0.0004\mu\text{A}/\text{cm}^2$ which is lower compared to those for nitrided sample. The lower i_{corr} value obtained for the substrate indicates that nitriding deteriorates the corrosion resistance. This shows that the native oxide layer provides better corrosion resistance and the nitrided layer formed by plasma nitriding is not as good as the native oxide layer [10]. The steadiness in anodic current density observed for the substrate and nitrided samples after 0.25V in **Fig. 4** indicates that the passive layer formed is very stable. In case of plasma nitrided sample there is an increase in anodic current

density compared to substrate. It can be seen in **Fig. 4** that the current for the formation of a passive film is an order of magnitude lower for plasma nitrided samples. This shows that the nitrided sample has better passivation compared to that of the substrate. The E_{corr} value shifted to much nobler value, -0.184V for nitrided sample, compared to the substrate value of -0.303 V.

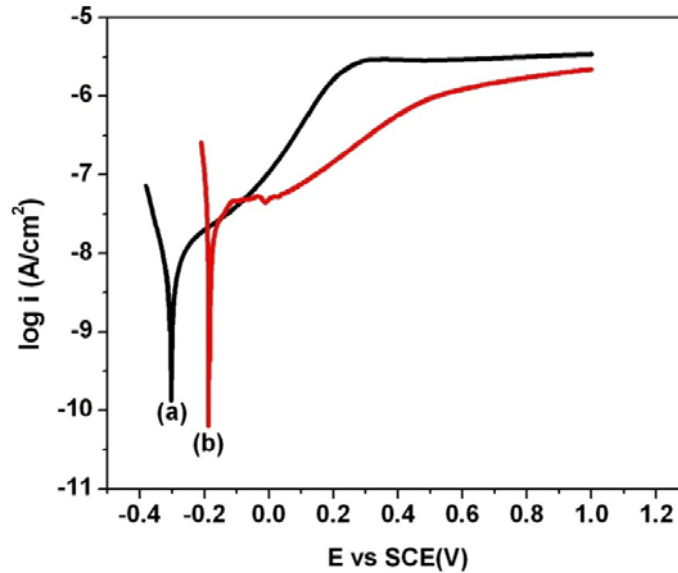


Fig.4. Tafel plots: (a) substrate, (b) sample nitrided at 800°C with 100%N2 for 4hrs

Table 2 Results of potentiodynamic polarization studies.

S.no	Sample	E_{corr} (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	R_p ($\Omega \text{ cm}^2$)
1.	Ti-6Al-7Nb substrate	-0.303	0.00047	3.2204×10^6
2.	Sample nitrided at 800°C with 100% N ₂	-0.184	0.00358	0.4592×10^6

Results of EIS studies carried out on the substrate and nitrided samples are shown in **Fig. 5(a)** and **(b)** in the form of Bode plots. In **Fig. 5(a)** and **(b)** the spectra show that in the higher frequency region $\log |Z|$ tends to become constant, with the phase angle values falling rapidly towards zero with increasing frequency. The limiting impedance at the high frequency end corresponds to solution resistance, R_e . In the low and medium frequency range (0.01-1 kHz), the phase angle is closer to -90° and remains nearly constant. In the same frequency range, nitrided sample have lower impedance value as compared to the substrate and a linear relationship between $\log |Z|$ and $\log f$ is observed for all samples with a slope approaching one. **Fig. 6** shows the equivalent circuit used for fitting the EIS data of the substrate and nitrided sample. The values of the parameters are given in **Table 3**. The Q symbol represents the possibility of a non-ideal capacitance, whose impedance is defined as $Z_{\text{CPE}} = [Q(j\omega^n)]^{-1}$ with 'n' less than one. For ideal capacitance 'n' is equal to one. In this figure R_e corresponds to the resistance of solution, R_1 to the resistance of the porous layer, R_2 to the resistance of the barrier layer, Q_1 to the capacitance of the porous layer and Q_2 to the capacitance of the barrier layer. The parameters, R_1 and Q_1 represent the properties of the porous film/solution interface i.e. the charge transfer resistance and double layer capacitance. A value of $10^6 \Omega \text{ cm}^2$ for R_2 in

the case of substrate suggests a high corrosion resistance and is higher than the value for treated sample. Such a high polarization resistance (R_p) was obtained for the substrate from polarization studies also. According to the model used for fitting EIS data of the substrate, R_2 is significantly higher than the value (R_1) associated with the outer porous layer. This indicates that the protection provided by the passive layer is predominately due to the barrier layer, which is in line with previous reports.[11, 14]

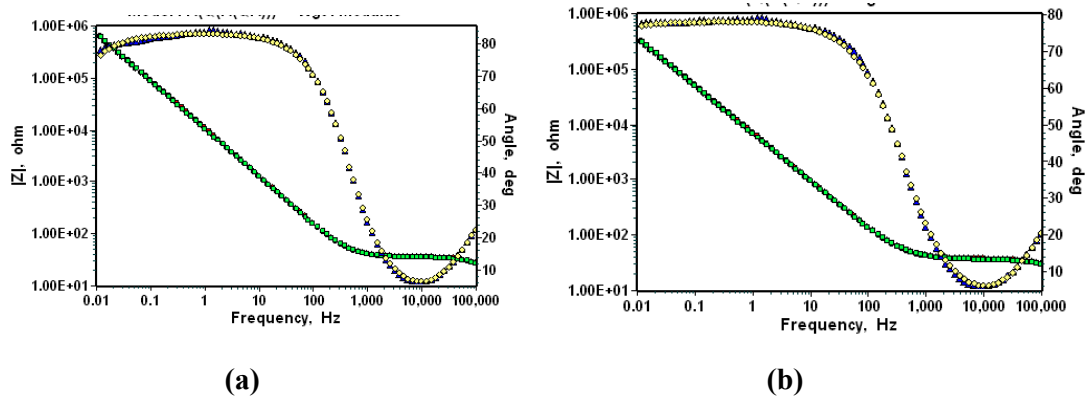


Fig. 5 Bode plots obtained for (a) substrate and (b) PN treated samples at 800°C in SBF solution

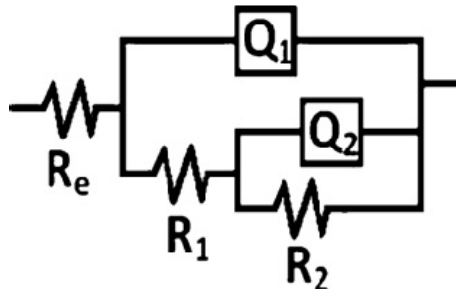


Fig. 6 Equivalent circuit (EC) diagrams used for fitting EIS data of Substrate and nitrided samples

Table 3 Electrochemical impedance parameters obtained by fitting equivalent circuit model for substrate and nitrided sample

Samples	R_e (Ω) cm^2	Q_1 S-sec ⁿ .cm ⁻²	n_1	R_1 (Ω) cm^2	Q_2 S-sec ⁿ .cm ⁻²	n_2	R_2 (Ω) cm^2	χ^2
Ti-6Al-7Nb Substrate	14.5	1.3×10^{-8}	0.98	22	1.72×10^{-5}	0.92	5.47×10^6	5.15×10^{-4}
800°C	15.6	6.5×10^{-8}	0.98	21	2.96×10^{-5}	0.86	1.08×10^6	5.57×10^{-4}

4. Conclusions

Ti-6Al-7Nb alloy was nitrided at different temperature and characterized for changes in hardness, composition and corrosion behavior in Hank's solution. From these studies the following conclusions may be drawn:

- a) The surface hardness improves after nitriding treatment.
- b) The Potentiodynamic polarization studies in Hanks solution show lower corrosion resistance for the nitrided samples as compared to substrate.
- c) FESEM shows formation of calcium phosphate phases on nitrided samples is higher compared to that of substrate after 7 days immersion in SBF.

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