

Characterization of Nitrogen Implanted pure Ti in Normal Saline (0.9% NaCl) Solution

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Abstract

Metallic biomaterial like stainless steel, Co- based alloy, Ti and its alloy are widely used as artificial hip joints, bone plates and dental implants. However; this alloy releases ions from the surface liable to do serious harm to human bodies. For overcoming surface originated problems, various surface modification technique have been used on the metallic implants. In this study, the nitrogen was implanted by a process of ion implantation at 60 keV with different fluences of 1×10^{16} , 5×10^{16} , 1×10^{17} and 5×10^{17} ions/cm². Corrosion resistance of Ti and ion implanted Ti were investigated by an electrochemical test, at 37^oC in normal saline solution. Tafel extrapolation method was used for calculating corrosion rate. ICP-AES studies were carried out to determine amount of ions leached out from samples when kept immersed in normal saline solution. Corrosion stability and elemental out-diffusion resistance was found to be increased by nitrogen ion implantation. The implanted samples showed variation in the corrosion resistance with varying doses and the sample implanted at 1×10^{17} ions/cm² showed an optimum corrosion resistance.

Keywords

Biomaterials; Ion implantation; electrochemical corrosion; microhardness.

1 Introduction

Metallic biomaterials like stainless steel, Co-based alloy, Ti and Ti alloys are widely used as artificial hip joints, bone plates and dental implants due to their excellent mechanical properties and endurance [1]. The performance of surgical implants is directly depending on their surface properties. Most implanted metallic biomaterials have a tendency to lose electrons in solution and, as a result, they show a high potential to corrode in the biological environments, which usually cause inflammatory and loosening of the implants [2]. In addition to that, their low surface hardness, high friction coefficient and poor wear resistance are also limiting their application of metallic biomaterials [3]. Commercially pure titanium

(C.P. Ti) is widely used as an implant in medical and dental material [4, 5] because of its suitable mechanical properties, excellent corrosion resistance and biocompatibility [6]. This high degree of biocompatibility and corrosion resistance of titanium in various test solution, saliva and other physiological media is attributed to the natural formation of very protective, stable oxide TiO₂ layer on the surface [7, 8, 9]. The clinical success is achieved not only because of implant material but also because of other properties as implant design, surgery technique, host bone quality, load bearing and the most important is surface quality. However, when titanium in contact with physiological solutions it tends to release metal ions which raises concerns about the possible cytotoxic effects associated with leaching of Ti.

Ion implantation serves as a versatile tool for surface modification of biomaterials, though it is similar to the coating process, it does not involve the addition of a layer on the surface of sample. It creates alteration in surface properties of solids or the bulk properties of the underlying material and is independent of thermodynamic constrains. Among the various ions to be implanted, nitrogen ion is the most suitable for biomedical applications. Using nitrogen ion implantation, properties such as hardness, corrosion resistance, wear etc. can be improved without adversely affecting the bulk properties of the materials.

2 Experimental procedures

2.1 Sample preparation

The commercially pure Ti was in the sheet form and sheet was cut into 15mm x15mm square samples with diameter 0.5mm. Prior, to study the Ti samples were polished using silica carbide emery paper of 320,800,1000,1500,2000 and 2500 grit followed by a final mirror polish with 0.5µm grade diamond lapping in order to produce scratch free mirror polished surface. The polished samples were subsequently cleaned in acetone, alcohol and de ionized water in turns. The samples are further subjected to ultrasonic cleaning in acetone for 20 minutes, rinse in de ionized water, dried and used for further studies. The elemental composition is shown in Table 1. The nitrogen ion implantation was done at LEIBF, IUAC, New Delhi, India. Nitrogen ion implantation on Ti at energy of 60 keV with different fluences of 1×10^{16} , 5×10^{16} , 1×10^{17} and 5×10^{17} ions/cm².

Table1 Chemical composition (wt. %) of Ti

C	Fe	N	O	H	Ti
0.08	0.03	0.03	0.18	0.015	99.67

Table 2 Sample code of Bare Ti and nitrogen ion implanted Ti

Sample code	Sample	Fluences ions/cm ²	Energy
Y	Ti6Al4V	Bare	
T	Ti	1×10^{16}	60 KeV
U	Ti	5×10^{16}	60 KeV
V	Ti	1×10^{17}	60 KeV
W	Ti	5×10^{17}	60 KeV

2.2 Electrochemical test

The electrochemical corrosion test was carried out using conventional three- electrode cell of 300 ml capacity by using Gamry-potentiostat/Galvanostat reference 3000, the Tafel extrapolation method was used to calculate the corrosion rate. The cell was fitted with working electrode, saturated calomel electrode (SCE) as the reference electrode and the platinum as a counter electrode. The studies were carried out in normal saline solution at 37 ± 10 C with scan rate 1 mV/s and electrode potential was raised from -800 mV to 1000 mV. The solution was de aerated with pure argon (Ar) gas throughout the experiment. The critical parameters like E_{corr} , I_{corr} , β_a , β_c and corrosion rate in mpy were calculated from the Tafel plots.

2.3 Dissolution test

In dissolution test, three samples each type, nitrogen implanted and bare samples of surface area 1cm^2 were immersed in 50 ml of normal saline solution in polypropylene bottles. The bottles were evacuated closed tightly and incubated in thermostatic chamber at 37 ± 10 C. All bottles were shaken and rotated at a speed of 72 rpm. After the end of 4th, 8th, 16th, 32 and 64th weeks the solution were analyzed by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to determine the elemental concentration of Ti leached out from the surface of samples.

2.4 Surface morphology

Microhardness measurement on six samples, each type were performed by mean of a microhardness tester of indenter type Vickers, duration time 5 seconds and test load of 20gm. and average microhardness was calculated. By means of XRD technique, the different phases present in the film were identified. The average grain size were estimated from full-width at half-maximum (FWHM) of peaks in XRD patterns by Sherrer formula,

$$t = k\lambda/\beta\cos\theta$$

Where, λ (1.540600 \AA in this case), θ and β are the X-ray wavelength, Bragg diffraction and FWHM in radians respectively.

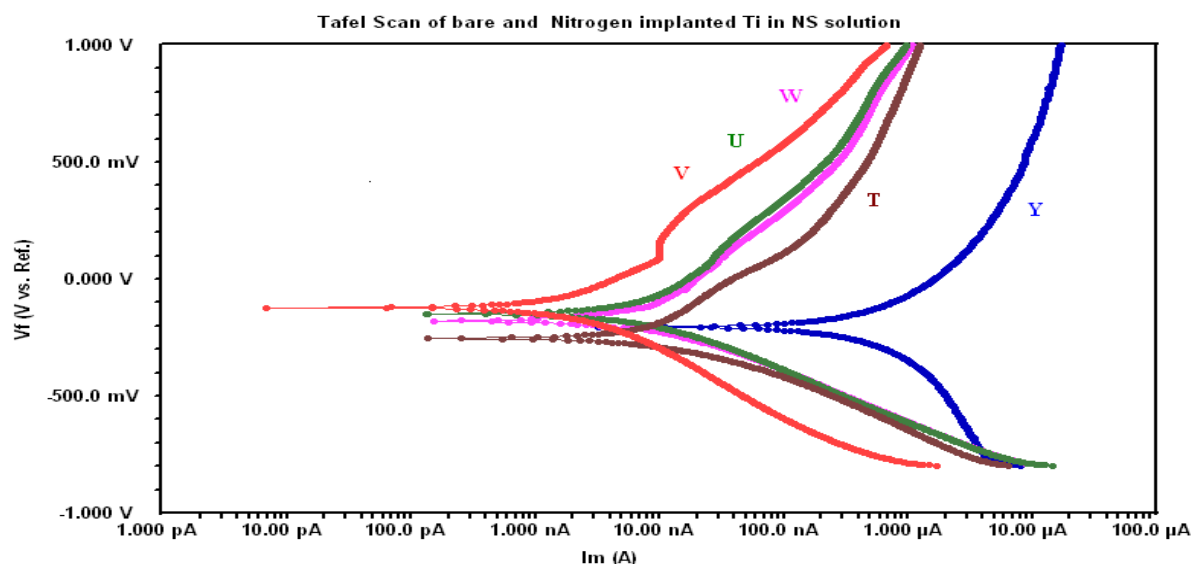
3 Results and Discussion

3.1 Corrosion behavior

Fig.1 shows the Tafel plots of bare and nitrogen implanted Ti in normal saline solution. The nitrogen implanted Ti showed variations in the corrosion resistance with varying fluences and the sample implanted with fluence of 1×10^{17} ions/ cm^2 (sample V) showed an optimum corrosion resistance beyond which corrosion resistance decreases. The E_{corr} potentials of the nitrogen implanted Ti showed the shift in noble direction. The order of corrosion rate obtained in normal saline solution is $V < U < W < T < Y$. The corrosion rate of sample V was found to be 2.217×10^{-3} mpy and E_{corr} was -121.9 mV in normal saline solution. Table 2 shows corrosion rate of nitrogen implanted Ti in normal saline solution.

Table 3 Corrosion rate of nitrogen implanted Ti in Normal Saline solution

Sample code	Sample	Energy	Fluence ions/cm ²	β_a V/decade	β_c V/decade	E_{corr} mV	I_{corr}	Corrosion Rate in mpy
Y	Ti	--	--	$807.6 e^{-3}$	$1.168 e^{-3}$	-203.5	1.460 μ A	$912.1 e^{-3}$
T	Ti	60 KeV	1×10^{16}	$393.2 e^{-3}$	$180.7 e^{-3}$	-246.2	10.55 nA	$8.762 e^{-3}$
U	Ti	60 KeV	5×10^{16}	$472.7 e^{-3}$	$227.7 e^{-3}$	-147.8	8.497 nA	$5.495 e^{-3}$
V	Ti	60 KeV	1×10^{17}	$531.4 e^{-3}$	$322.2 e^{-3}$	-121.9	3.234 nA	$2.217 e^{-3}$
W	Ti	60 KeV	5×10^{17}	$441.3 e^{-3}$	$200.7 e^{-3}$	-179.8	12.28 nA	$8.417 e^{-3}$

**Fig.1** Tafel plots of nitrogen ion implanted Ti in Normal Saline solution

3.2 Dissolution

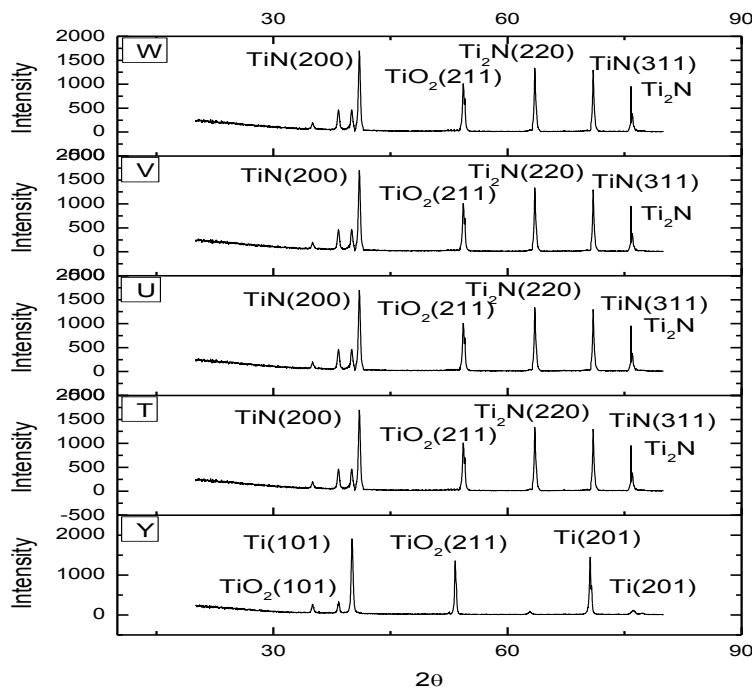
The dissolution test after continuous evaluation was carried out at the end of 4th, 8th, 16th, 32 and 64th weeks using ICPAES is shown in Table 4. At 64th weeks sample T shows leaching of Ti ions 13.12 ppb and rest of the samples shows no ions release from the surface of samples.

Table 4 Dissolution test of nitrogen implanted Ti6Al4V and Ti in Normal Saline solution

Sample code	Specimen	4 th week ppb	8 th week ppb	16 th week ppb	32 nd week ppb	64 th week ppb
A	V	ND	ND	ND	8.32	12.15
	Al	80.34	141.12	172.26	193.41	527.25
T	Ti	ND	ND	ND	ND	13.12 ppb
U	Ti	ND	ND	ND	ND	ND
V	Ti	ND	ND	ND	ND	ND
W	Ti	ND	ND	ND	ND	ND

3.3 Surface morphology analysis

Microhardness study of nitrogen implanted Ti showed that as fluence increased, microhardness increased [10-11]. The surface hardness of titanium also can be improved by irradiation [12 -14]. The XRD analyses of with and without implantation are show in Fig.2. The diffraction peak in the alloy reveals the noticeable phase changes in surface layer of implanted Ti. There are some new peaks are appearing at $2\theta = 38.56, 40.99, 54.335, 63.50, 70.98$ and 76.01° which shows the new phases are TiN, Ti₂N and rutile TiO₂. The TiO₂ peak is very small, suggesting a low volume fraction of this phase formed in this alloy. The formation of TiO₂ peak is due to low vacuum during nitrogen implantation. The average grain size were estimated from full-width at half-maximum (FWHM) of peaks in XRD patterns by Scherrer's formula and it was found it was to be 325 nm to 491 nm shown in figure 3. It was observed that as fluence increases from 1×10^{16} ions/cm² to 1×10^{17} ions/cm² the grain size decreases but for fluence 5×10^{17} ions/cm² it increases. The minimum grain size observed at fluence 1×10^{17} ions/cm².

**Fig.2** XRD overlay of nitrogen implanted Ti

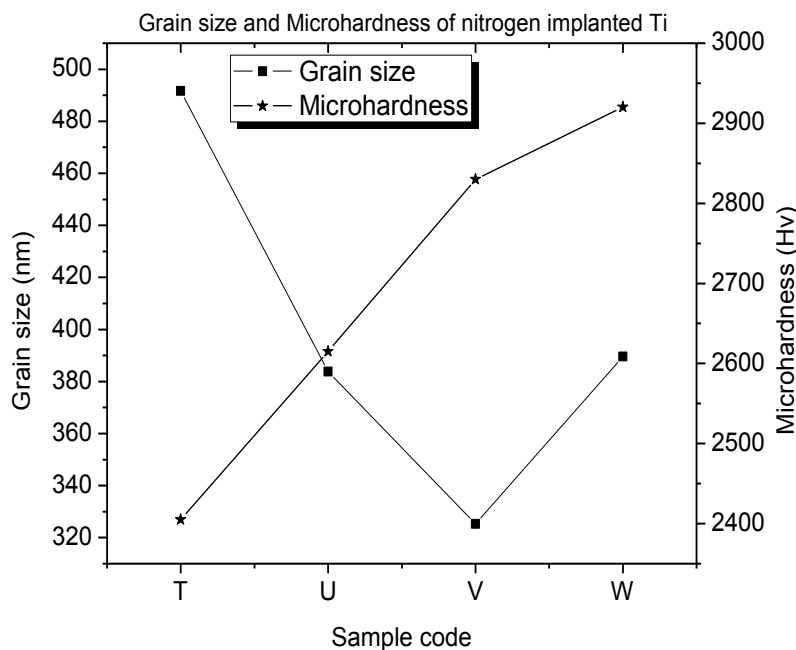


Fig. 3 Microhardness and grain size of nitrogen implanted Ti

4 Conclusions

The nitrogen implanted Ti showed improvement in corrosion resistance and elemental diffusion resistance in normal saline solution. As fluence increases from 1×10^{16} to 1×10^{17} ions/cm² the corrosion resistance increased beyond which corrosion resistance decreased. As fluence increases the microhardness increased and the grain size decreased. The increase in microhardness is due to formation of TiN on the surface of samples.

5 References

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