ISSN: 2278-0181
Vol. 1 Issue 10, December- 2012

Electrochemical Study Of Nitrogen Ion Implanted Ti In Ringer Lactate Solution

Suresh Kadam [a], Kailash R. Jagdeo [b], M. R. Nair [c]

a. Dept. of Physics, KET's V. G. Vaze College, Mumbai(MS), India.
b. Dept. of Physics, DSPM's K. V. Pendharkar College, Dombivli(MS), India.
c. Principal, Model College, Dombivli(MS), India.

Abstract:

Titanium and its alloy are largely used biomaterials for implants despite of emerging new materials for application. There is still some ambiguity in corrosion behavior of metals in simulated body fluid. 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/cm^2. The corrosion resistance of Ti and implanted Ti was investigated by an electrochemical test, at 37^0C in Ringer Lactate solution. The unknown phases can be identified using X-ray diffraction (XRD). The Tafel extrapolation method was used for measuring corrosion rate. ICP-AES studies were carried out to determine amount of ions leached out from samples when kept immersed in Ringer Lactate solution. The result shows that new phases of TiN are formed after implantation in the surface region. Implanted samples showed variation in the corrosion resistance with varying fluence and the sample implanted at 1×10^{17} ions/cm^2 showed an optimum corrosion rate.

Keywords: Ion implantation, Ringer Lactate solution, Elemental - diffusion resistance, Biomaterials, Hardness.

1. Introduction

Commercially pure titanium (C.P. Ti) is widely used as an implant in medical and dental material [1, 2] because of its suitable mechanical properties, excellent corrosion resistance and biocompatibility [3]. 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 TiO_2 layer on the surface [4, 5, 6]. But 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 powerful tool of 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. Ion implantation creates alteration in surface properties of solids or the bulk properties of the underlying material and is independent of thermodynamic constrains. It has several advantages with other modification methods such as possibility of introducing any elements into any solids target, low temperature treatment [7], hence without dimensional change of treated compounds, no interface discontinuity as in film deposition, possibility of new structures in non equilibrium and new metallurgical phases. Nitrogen ion is the most suitable technique used to improve the corrosion resistance, hardness, wear and tribological properties [8, 9].

Here, the aim of study is to evaluate the corrosion behaviour of nitrogen implanted Ti in Ringer Lactate solution by electrochemical method.

2 Experimental procedures

2.1 Sample preparation

The commercially pure Ti was in the sheet form and sheet was cut into 12mm x12mm square samples and some 15mm x15mm with diameter 0.5mm. Prior, to the study the Ti were polished using silica carbide emery paper of 320,800,1000,1500,2000 and 2500 grit followed by a final mirror polish with 0.5 μm 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. They are further subjected to ultrasonic cleaning in acetone for 20 minutes rinsed 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 $1 X 10^{16}$, $5 X 10^{16}$, $1 X 10^{17}$ and $5 X 10^{17}$ ions/cm^2.

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 and Tafel extrapolation method. 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 Ringer Lactate solution at 37 ± 1^0 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 $E_{corr,}$ $I_{corr,}$ $\beta_{a,}$ β_c and corrosion rate in mpy were evaluated from the Tafel plots.

2.3 Dissolution test

In dissolution test, six, each type nitrogen implanted and bare samples of surface area 1 cm^2 were immersed in 50 ml of Ringer Lactate solution in polypropylene bottles. The bottles were evacuated and closed tightly and incubated in thermostatic chamber at 37±10C. All bottles were shaken and rotated at a speed of 72 rpm. After the end of 4th, 8th, 16th and 32nd week the solutions were analysed 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 Microhardness test

Microhardness measurement on six, each type samples were performed by mean of a microhardness tester of indenter type Vickers, duration time 5 seconds and test load of 10 g. and average microhardness was calculated.

3 Results and Discussion

Table 1
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

Concentration of electrolytes in Ringer Lactate solution (RL)

Ions	Concentration of ions mmoles/L
Sodium	131
Potassium	5
Calcium	2
Chloride	111
Bicarbonate (as lactate)	29

3.1 Corrosion behaviour

The nitrogen ion implanted Ti samples showed variations in the corrosion rate with varying fluences and the sample D implanted at fluence 1 X 10^{17} ions/cm^2 showed an optimum corrosion rate. The corrosion rate decreased with increasing fluences up to 1 X 10^{17} ions/cm^2 (sample D) beyond which the corrosion rate increased i.e. for sample E with fluence 5 X 10^{17} ions/cm^2. It was found that at high fluence 5 X 10^{17} ions/cm^2, ion bombardment may induce local variations in sputtering result in major changes in surface topography may induce defects build up within the sample results in increase in corrosion rate. The improvement in the corrosion resistance of nitrogen implantation Ti is due to nitride layer formation at surface. The corrosion rate of sample D was found to be 6.363 e-3 mpy and Ecorr was -147.8 mV. The order of corrosion rate obtained in Ringer Lactate solution is, D < C < E < B < A

Table 3

Corrosion rate of nitrogen implanted Ti6Al4Vand Ti in Ringer Lactate 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
A	Ti	--	--	1.286	1.339	-258.2	2.197 μA	1.372
B	Ti	60 keV	1X10^{16}	535.4 e^{-3}	201.9 e^{-3}	-277.2	17.28 nA	11.84 e^{-3}
C	Ti	60 keV	5X10^{16}	475.2 e^{-3}	124.3 e^{-3}	-179.8	9.620 nA	7.595 e^{-3}
D	Ti	60 keV	1X10^{17}	502.5 e^{-3}	231.4 e^{-3}	-147.8	9.282 nA	6.363e^{-3}
E	Ti	60 keV	5X10^{17}	754.2 e^{-3}	214.3 e^{-3}	-229.6	14.45 nA	9.905 e^{-3}

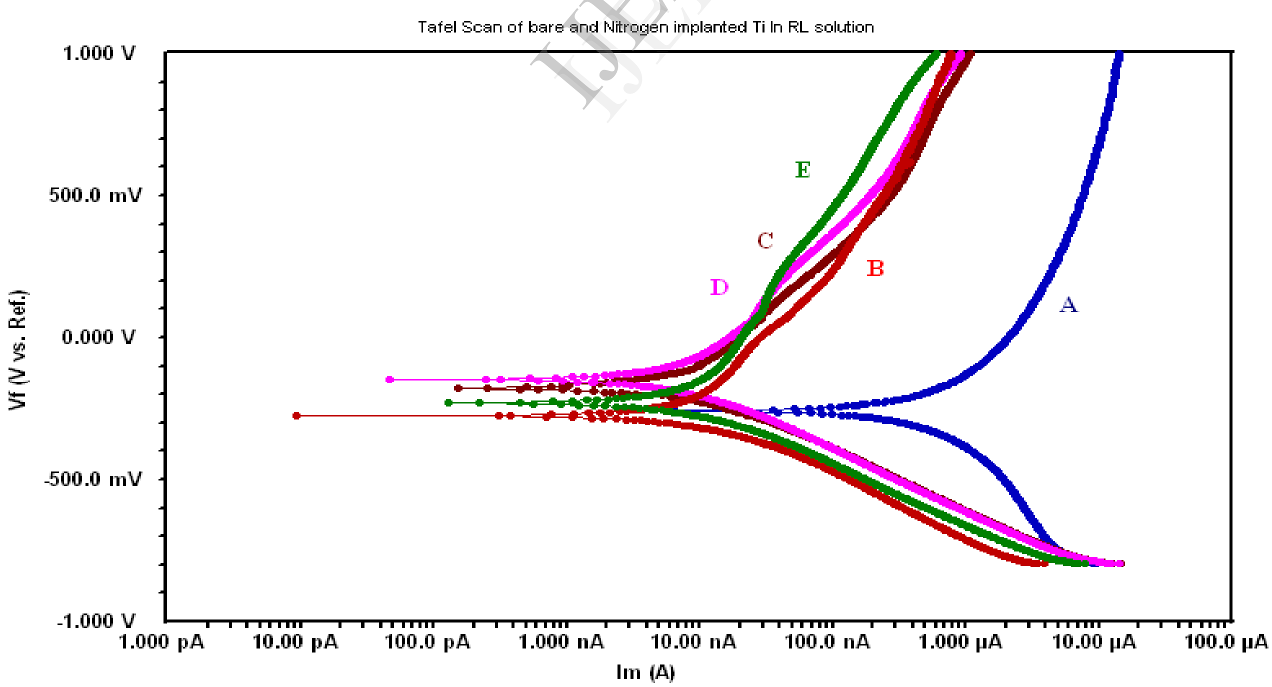

Figure 1 Tafel scan of nitrogen implanted Ti in RL solution

3.2 Surface morphology analysis

X-ray diffraction pattern of sample Ti with and with out implantations are show in Fig.2. It was observed for the sample without nitrogen implanted that all the peaks are attributed to alpha phases titanium, and there is no beta phase. The diffraction peak in the alloy reveals that noticeable phase changes in surface layer of implanted Ti. There are some new peaks are appearing at 2Θ = 38.56, 40.99, 54.335, 63.50, 70.98 and 76.01^0 which shows the new phases are TiN, Ti_2N and rutile TiO_2 as show in Fig.2. The TiO_2 peak is very small, suggesting a low volume friction of this phase formed in this alloy. The formation of TiO_2 peak is due to low vacuum during nitrogen implantation probably.

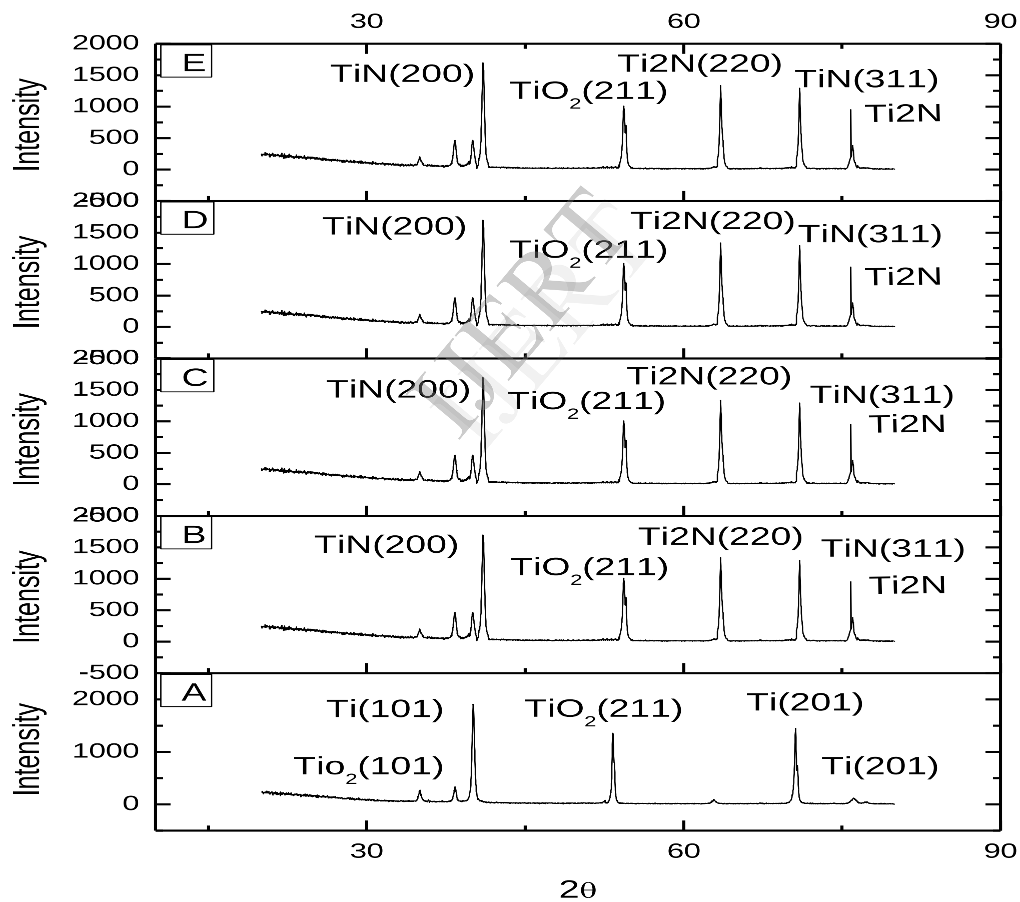

Figure 2 XRD pattern of Ti and nitrogen implanted Ti

3.3 Dissolution test

The ICP-AES study of bare Titanium and nitrogen implanted Ti is shown in Table 2. The Ti leached out from the bare showed that the elemental concentration of Ti increases every stage but the sample B shows

Ti concentration was 4.21 ppb in Ringer Lactate solution after the end of 32nd week whereas all remaining nitrogen implanted samples showed Ti concentration to undetectable level (ND). All nitrogen implanted samples showed the improvement in elemental diffusion-out resistance.

Table 2
Dissolution test for nitrogen implanted Ti in RL solution

Sample code	Specimen	4th week	8th week	16th week	32nd week
A	Ti	24.12 ppb	36.23 ppb	52.15 ppb	200.25 ppb
B	Ti	ND	ND	ND	4.21 ppb
C	Ti	ND	ND	ND	ND
D	Ti	ND	ND	ND	ND
E	Ti	ND	ND	ND	ND

3.4 Microhardness test

Fig. 3 shows the microhardness study of nitrogen implanted Ti. Microhardness study of nitrogen implanted Ti showed that as fluences increased, microhardness increased. Sample-E showed the highest microhardness of 2920 Hv.The XRD analysis shows that TiN and Ti2N are formed after N implantation and the TiN and Ti2N distributed as a small precipitates in the titanium matrix [10]. It is well known that the element distribution, new phase formation and microstructure change of the modification layer has a closer relationship with the surface properties of the implant alloy. The surface hardness of titanium also can be improved by irradiation [11, 12].

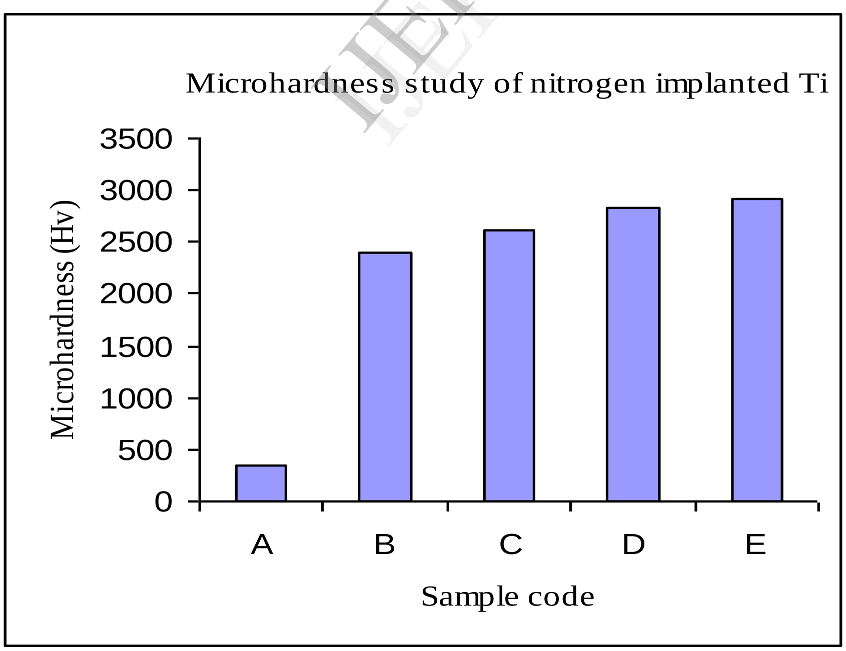

Figure 3 microhardness study of nitrogen implanted Ti

4 Conclusion

Nitrogen ion implanted Ti showed improvement in corrosion resistance and elemental diffusion resistance in Ringer Lactate solution. As fluence increases the corrosion resistance increases up to 1x 10^{17} ions /cm^2 beyond which corrosion resistance decreased and also as fluence increases microhardness increased. The enhancement in hardness related to the formation of TiN.

ACKNOWLEGEMENT

Many thanks to Dr. D. Kanjilal and Dr. Pravin Kumar, Inter University Accelerator Centre, New Delhi, India, for experimental support.

5 References

[1] B Rattner, A Hoffman, F Schoen, J Lemons. Biomaterials sci-70 SOBOYEJO ET AL.ence: An introduction to materials in medicine. New York: Academic Press; 1996.

[2] J L Ricci, J Charvet, SR Frenkel, R Chang, P Nadkarni, J Turner, H Alexander. Bone engineering. In: Davies JE, editor. Bone response to laser microtextured surfaces. Toronto: Em2 Inc.; (2000) 1–11.

[3] J L Ricci, J M Spivak, N C Blumenthal, H Alexander. Modulation of bone ingrowth by surface chemistry and roughness. In: Davies JE, editor. The bone–biomaterial interface. University of Toronto Press; (1991) 334–349.

[4] M. Long, and H. J. Rack, *Biomaterials*, 19(1998)1621-1639

[5] R. Narayanan, S. K. Seshadri, T. Y. Kwon, and K. H. Kim, *Scripta Mater*. 59(2007)229.

[6] A.M. Fekry, Rabab M. El-Sherif, *Electrochim. Acta* 54 (2009) 7280-7285.

[7] A.M. Al-Mayouf, A.A. Al-Swayih and N.A. Al-Mobarak, Effect of potential on the corrosion behavior of a new titanium alloy for dental implant applications in fluoride media, Materials and corrosion, Vol.55, 88 (2004) 524-530

[8] J. Jagielski, A. Piatkowska, P. Aubert, L. Thome, A. Turos, A. Abdul Kadar; Surface and Coating Technology, 200 (2006) 6355-6361

[9] X. T. Zu, Z. G. Wang, X.D. Feng, C.F. Zhang, S. Zhu, Q. Yu, ibid; 35(2003)114-118 [10] M.A. Arenas, T.J. Tate, A. Conde and J. de. Damborenea, Br. Corros. J. 35 (2000) 232-236.

[11] J. C. Oh, D.K. Choo, S. Lee, Surf. Coat. Technol. 127 (2000) 76–85.

[12] I. Nakamura, K. Matsui, M. Sasaki, I . Iakano and Y.Sawada, *Vaccum* **74** (2004) 659-663