

Electrochemical corrosion behaviour of nitrogen ion implanted 316L stainless steel in Ringer Lactate solution

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ABSTRACT: Chemical stability, mechanical behaviour and biocompatibility in body fluids and tissues are the basic requirements for successful applications of implant materials in bone fractures and replacements. Corrosion is one of the major processes affecting the life and service of orthopaedic devices. The release of particles or elements from the metallic implants into the surrounding cells or tissues can cause inflammation, allergic reaction, toxicity and carcinogenicity. Therefore, surface modification is required for improving surface properties of materials. In this study, nitrogen was implanted by 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 316L stainless steel, Ti6Al4V, NiTi and ion implanted 316L stainless steel were investigated by an electrochemical test, at 37°C in Ringer Lactate 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 Ringer Lactate 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: Electrochemical corrosion, Elemental out-diffusion resistance, Ion implantation, Ringer Lactate solution.

I. INTRODUCTION

Continual research and development into new and improved materials is essential for successful utilisation of biomaterials. A leading stimulus in the development of new or surface modified alloys in medical field has always been the search for improved corrosion performance. In order to find the most adequate materials to be used as implants in living tissue, many alloys have been developed, beginning with austenitic stainless steel. It is noted that 316L stainless steel fall in higher grade in terms of anticorrosion [1]. However, the leaching out of the harmful ions to the body tissues and fluids inside the human body has been raising much safety concern [2, 3]. Its medical applications noted various medical complications such as allergic reactions, metallogenic and electrochemical reactions, metal toxicities and carcinogenicity [4-8]. Therefore, proper passivity to prevent surface layer degradation and ions release into the environment was considered crucial for its medical applications.

Ion implantation is the process which involves the introduction of a controlled amount of atoms of any element into the surface of any material with a beam of high velocity ions, without modifying the surface finish or the bulk properties of the underlying material and is independent of thermodynamic constraints. The bulk alloying techniques are limited by the equilibrium phase diagrams. Thus, if a potential alloying addition does not show extensive solid solubility in a base metal; there is little possibility of using it to improve the surface related properties such as corrosion and wear resistance properties. Surface alloying by conventional technique improve the corrosion resistance of metals with intrinsically inferior properties. Ion implantation is a versatile technique which at a controlled rate produces metastable-single phase-solid solution-surface alloys without any of the compositional limitations normally imposed by equilibrium phase diagrams.

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 [9-11].

Here, the studies were undertaken to evaluate the corrosion behaviour of surface modified 316L stainless steel by nitrogen ion implantation in Ringer Lactate solution conditioned by electrochemical method.

II. EXPERIMENTAL

Samples in the sheet form of NiTi-shape memory alloy, Ti6Al4V, 316L stainless steel were used in the present study. NiTi was procured from Johnson Metthey, USA. Chemical composition of NiTi, Ti6Al4V and

316L stainless steel is shown in Table 1, Table 2, and Table 3 respectively. The sheets were cut into 12 mm X 12 mm square samples and some 15 mm X 15 mm (used for corrosion study), each having thickness 0.5 mm. Samples were mechanically polished using polishing machine with silicon carbide paper in successive grades from 1000 to 2000 grit followed by a final mirror polish with a 0.5 µm grade diamond-lapping compound. Samples were ultrasonically cleaned with acetone before their surface modification.

The direct nitrogen ion implantation was done at LEIBF, IUAC, New Delhi, India. Nitrogen ion implantation on 316L stainless steel at energy of 60 keV was carried out at different fluences of 1×10^{16} , 5×10^{16} , 1×10^{17} and 5×10^{17} ions/cm². Corrosion resistance was investigated by Tafel extrapolation method. Tafel curves were obtained through Gamry-Potentiostat/Galvanostat (reference 3000). I_{corr} , E_{corr} , β_a , β_c and corrosion rate were obtained by Tafel fit and DC corrosion software. Before corrosion study, samples were ultrasonically cleaned with acetone. The electrochemical measurements were performed in a standard three-electrode cell with platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode with scan rate of 1 mV/s. The electrochemical tests were carried out at 37⁰ C in Ringer Lactate solution. The concentration of electrolytes in Ringer Lactate solution is shown in Table 4.

In dissolution test, six, each type nitrogen implanted and bare samples of surface area 1 cm² 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, 32nd and 64th weeks, the solutions were analysed by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICPAES) to determine amount of elemental concentration leached out from the surface of samples.

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. Average microhardness was calculated.

III. RESULTS AND DISCUSSION

Table 1
Chemical composition wt. % of NiTi

Ni	Ti	C	O	Total all others
55.74	44.24	≤ 0.05	≤ 0.05	≤ 0.20
All others are Al, Co, Cr, Cu, Fe, Mn, Mo, Nb, Si, and W				

Mechanical and Physical Properties of NiTi:

Temper: Flat Annealed; Surface: Pickled; Ingot A_p: 27⁰C; UTS(ksi): 178

Elongation (%): 11.4; Active A_f(⁰C): 22.7; A_f: 20-40⁰C

Table 2
Chemical composition wt. % of Ti6Al4V

C	Ni	Mn	Mo	V	Ti	N	Sn	Fe	Al
0.036	0.001	0.008	0.004	4.08	89.56	0.008	0.011	0.25	5.97

Table 3
Chemical composition wt. % of 316L stainless steel

C	S	P	Mn	Si	Cr	Ni	Mo
0.025	0.010	0.030	1.14	0.43	16.92	10.34	2.00

Table 4
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

Table 5
Corrosion rate of nitrogen implanted 316L SS in RL Solution

Sample code	Sample	Energy keV	Fluence ions/cm ²	β_a V/decade	β_c V/decade	E_{corr} mV	I_{corr}	Corrosion Rate in mpy
A	NiTi	--	--	7.608	3.173	-409.5	4.439 μ A	2.30
B	Ti6Al4V	--	--	3.793	5.673	-556.9	2.542 μ A	1.60
C	316L SS	--	--	1.942	6.413	-448.9	2.501 μ A	1.11
D	316L SS	60	1X10 ¹⁶	2.356	183.9 e ⁻³	-225.2	144.9 nA	64.96 e ⁻³
E	316L SS	60	5X10 ¹⁶	364.8 e ⁻³	112.9 e ⁻³	-200.7	7.372 nA	3.304 e ⁻³
F	316L SS	60	1X10 ¹⁷	472.3 e ⁻³	167.8 e ⁻³	-167.6	5.102 nA	2.287e ⁻³
G	316L SS	60	5X10 ¹⁷	188.7e ⁻³	144.3 e ⁻³	-168.5	17.28 nA	7.745 e ⁻³

The nitrogen ion implanted 316L SS samples showed variations in the corrosion rate with varying fluences and the sample implanted at fluence 1 X 10¹⁷ ions/cm² (sample F) showed an optimum corrosion resistance. The corrosion rate decreased with increasing fluences up to 1 X 10¹⁷ ions/cm² (sample F) beyond which the corrosion rate increased i.e. for sample G with fluence 5 X 10¹⁷ ions/cm². At this high fluence 5 X 10¹⁷ ions/cm², ion bombardment may induce local variations in sputtering yield resulting in major changes in surface topography and induce defects that build up within sample results in increase in corrosion rate. The corrosion resistance is greatly improved by nitrogen implantation due to nitride layer formation at surface. The E_{corr} potentials of the nitrogen implanted 316L SS samples showed the shift in noble direction in comparison with bare samples. The order of corrosion rate obtained in Ringer Lactate solution is,

$$F < E < G < D < 316L \text{ stainless steel} < Ti6Al4V < NiTi.$$

The corrosion rate of sample F was found to be 2.287e⁻³ mpy and E_{corr} was -167.6 mV

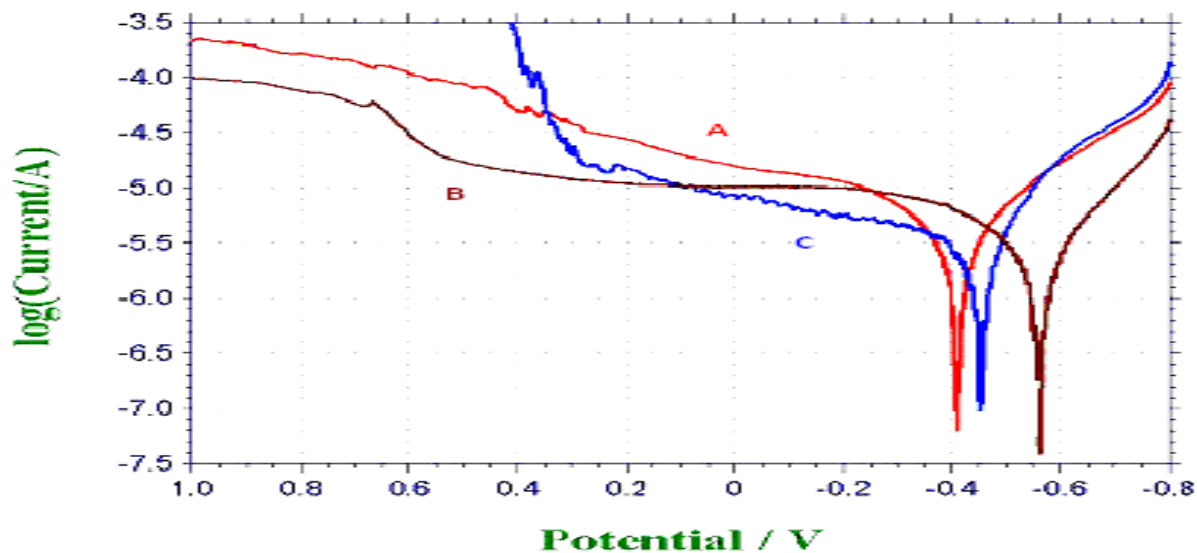


Fig. 1 Tafel plots of NiTi, Ti6Al4V and 316L SS in RL solution

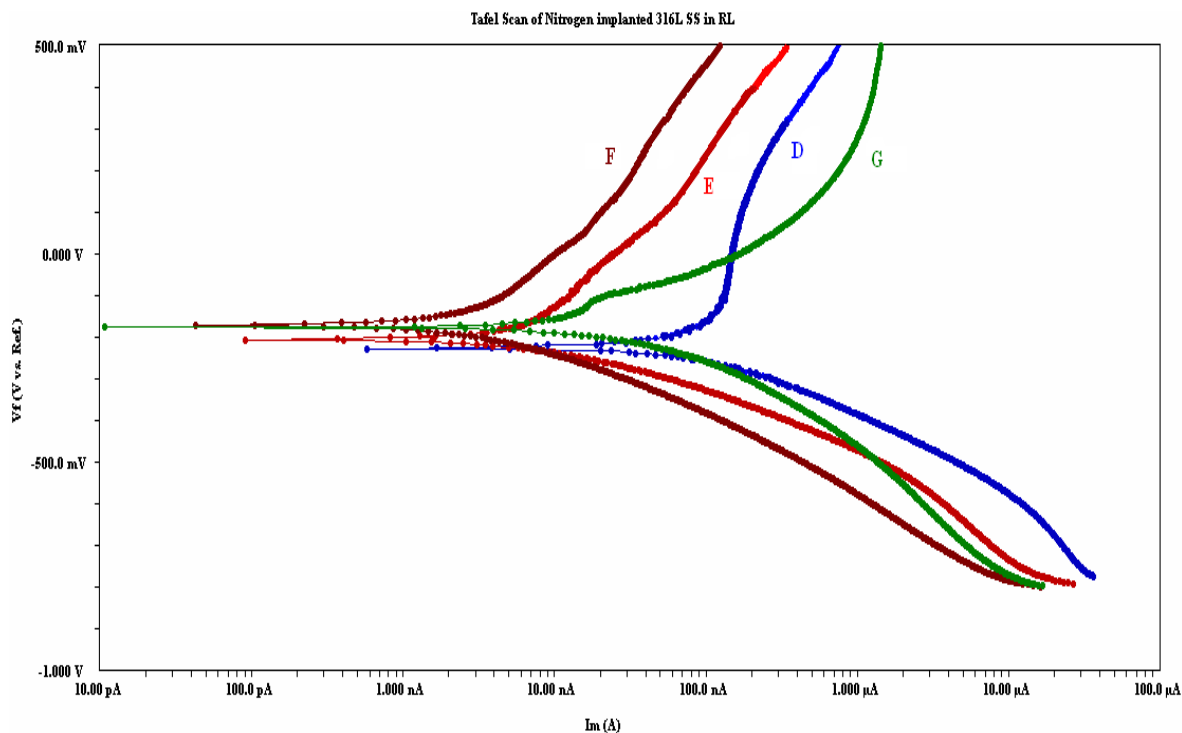


Fig. 2 Tafel plots of nitrogen implanted 316L SS in RL solution

The leaching out of Ni from nitrogen implanted 316L SS, bare 316L SS and NiTi are shown in Table 6. The comparative ICP-AES study of NiTi and 316L SS showed that after the end of 4th and 8th week, Ni concentration was nearly equal but after the end of 16th, 32nd and 64th week the Ni leached out of NiTi surface was increased more rapidly than 316L SS. In dissolution test only sample-D showed Ni concentration of 3.12 ppb in Ringer Lactate solution after the end of 64th week whereas all remaining nitrogen implanted samples showed Ni concentration to undetectable level (ND). All nitrogen implanted samples showed the improvement in elemental diffusion-out resistance.

Table 6
Dissolution test for nitrogen implanted 316L SS in RL solution

Sample code	Specimen	4 th week	8 th week	16 th week	32 nd week	64 th week
A	Ni	25.34 ppb	38.12 ppb	60 ppb	438 ppb	965 ppb
C	Ni	23.67 ppb	30.23 ppb	35.12 ppb	67.8 ppb	85.3 ppb
D	Ni	ND	ND	ND	ND	3.12 ppb
E	Ni	ND	ND	ND	ND	ND
F	Ni	ND	ND	ND	ND	ND
G	Ni	ND	ND	ND	ND	ND

Fig. 3 shows the microhardness study of nitrogen implanted 316L SS. Microhardness study of nitrogen implanted 316L SS showed that as fluences increased, microhardness increased. Sample-G showed the highest microhardness of 2975 Hv.

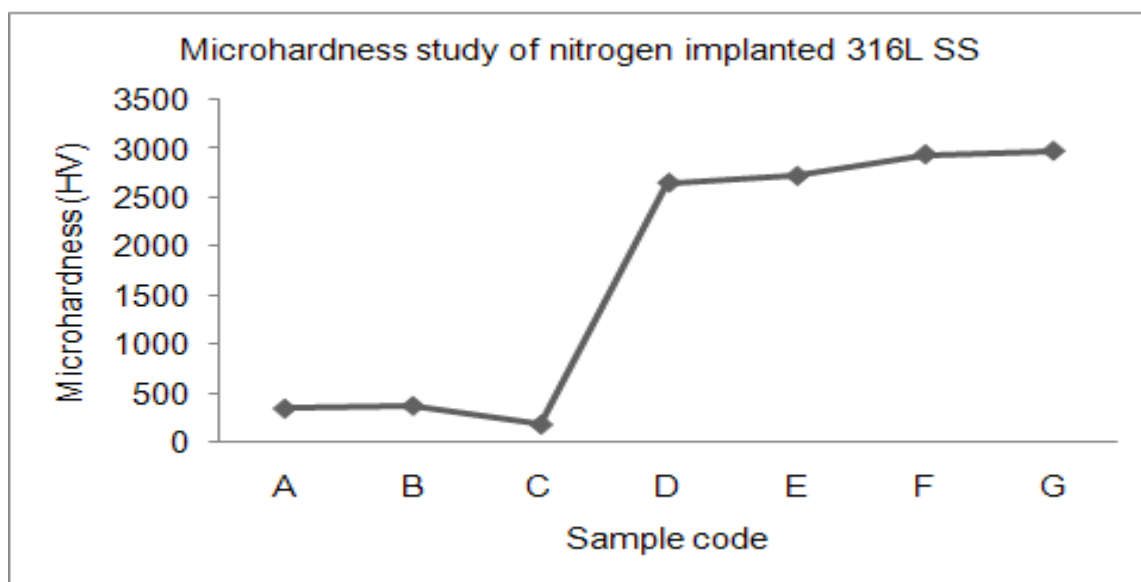


Fig. 3 Microhardness study

IV. CONCLUSION

Corrosion stability and elemental out-diffusion resistance was found to be increased by nitrogen ion implantation in Ringer Lactate solution. The ion 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. As fluences increased, microhardness of 316L SS increased.

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