In vitro corrosion behaviour of plasma nitrided Ti–6Al–7Nb orthopaedic alloy in Hanks solution

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Abstract
Titanium alloy (Ti–6Al–7Nb) used for orthopaedic applications was nitrided using a conventional dc plasma technique. Load-dependent microhardness measurements exhibit a hardness of 2087 H\textsubscript{v} at 25 g load for the alloy nitrided at 900 °C for 8 h. Cyclic polarization measurement in Hanks solution show maximum corrosion rate and minimum area of repassivation for the alloy nitrided for 8 h at 900 °C. Electrochemical impedance measurements show an increase in charge transfer resistance and decrease in double layer capacitance when compared to untreated alloy.

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1. Introduction
Titanium alloy Ti–6Al–4V has been extensively used for many years as an implantable material in the application of orthopaedic prostheses \cite{1,2}. It has been reported to have superior corrosion resistance when compared to stainless steel and cobalt chromium alloy \cite{3,4}. Recently, much concern has developed over the issue of biocompatibility of these alloys due to the dissolution of vanadium. So vanadium free alloys are recently developed to overcome the above issue. The alloy Ti–6Al–7Nb was developed using the non-toxic alloying element Nb to replace V since, both V and Nb are amorphous with bcc and thus both acts as suitable \textbeta phase stabilizers. Recent studies have also discussed the excellent short and long term biocompatibility of Nb \cite{5,6}. Though, the titanium alloy has excellent corrosion resistance and good mechanical properties, the toxicity of dissolved metal ions cause pain and restricted action in the tissues adjoining the implants. In order to avoid such a difficulty, surface nitriding has proved better biocompatibility for titanium alloys \cite{7}. Several methods are available for the production of TiN and plasma nitriding is a suitable surface modification tool due to its advantages of tailoring the properties of the layer \cite{8}. Very few reports are available on the corrosion behaviour of this alloy in simulated body fluid (SBF) \cite{9,10}. Based on this background, an attempt has been made to modify the surface of Ti–6Al–7Nb orthopaedic alloy by nitriding. The potentiodynamic cyclic polarization and impedance studies were carried out the nitrided alloy to provide information about the application of the alloy as a biomaterial.

2. Experiment
The sample used for the present investigation was the orthopaedic alloy Ti–6Al–7Nb obtained from GS titanium Inc., US. The samples were polished using SiC sheets and alumina paste up to 1 μm grain size. The plasma nitriding was performed in a low pressure DC plasma equipment with the sample working as a cathode. The plasma gas consisted of a N\textsubscript{2}–H\textsubscript{2} mixture (80:20%) controlled by mass flow controller. The treatment temperature was measured by a thermocouple inserted in the sample holder and controlled by varying the discharge current from the DC power supply.
Nitriding was carried out at 800 and 900 °C for 4 and 8 h. Vickers microhardness measurements were carried out using Leitz microhardness tester at loads of 25–500 g. Phases were identified by X-ray diffraction measurements using Cu Kα radiation. The corrosion behaviour was studied by cyclic polarization and electrochemical impedance spectroscopic measurements for both as received and nitrided samples. Hanks solution, which simulates the body fluid, was used as an electrolyte. The chemical composition of Hanks solution is (g/l) 0.185 CaCl₂, 0.4 KCl, 0.06 KH₂PO₄, 0.1 MgCl₂·6H₂O, 0.1 MgSO₄·7H₂O, 8.0 NaCl, 0.35 NaHCO₃, 0.48 Na₂HPO₄ and 1.00 D glucose. Saturated calomel electrode (SCE) and platinum foil were used as reference and auxiliary electrodes, respectively. Area of 1 cm² of the working electrode was exposed to the electrolyte. The corrosion behaviour was measured using AUTOLAB PGSTAT12 with frequency response analyser (FRA) designed for electrochemical examinations. Prior to the beginning of corrosion measurements, the specimens were maintained for 30 min in Hanks solution to attain equilibrium condition. The polarization curves were obtained by polarizing the samples from a potential of −500 to +1700 mV at a scan rate of 1 mV/s with respect to the open circuit potential (OCP). Impedance measurements were performed by applying a sinusoidal wave of 10 mV to the working electrode at a frequency range of 0.1 MHz–10 mHz.

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the X-ray diffractogram of the untreated alloy and alloys nitrided at 800 °C/4 h, 900 °C/8 h compared with untreated alloy. The nitried samples exhibit new diffraction lines identified as Ti₂N in addition to the base peaks. Similar results were obtained for samples treated at 800 °C/8 h and 900 °C/4 h. It is also found that the formation of phases depend on the experimental parameters [11].

3.2. Corrosion resistance experiments

Open circuit measurements were carried out for untreated alloys and alloys nitrided at different experimental conditions in Hanks solution. The potential was measured for 30 min prior to cyclic polarization experiments as shown in Fig. 2. OCP was found to move significantly towards noble direction for all the nitried alloys and maximum positive potential was obtained for the specimens treated at 900 °C for 8 h. The shift of OCP towards noble direction and its saturation at stable potential indicates the passive nature of the surface film during nitriding.

Fig. 3 show the cyclic polarization curves obtained for untreated titanium alloy and titanium alloy nitried at different experimental conditions in Hanks solution. It is clear from the figure that the passive current density is as low as 8.394 × 10⁻¹⁰ A/cm² for the alloys treated at 900 °C for 8 h compared to the untreated alloy with an Icorr of 2.58 × 10⁻⁶ A/cm². This is in accordance with the previous results obtained for the same alloy after nitrogen implantation in Ringers solution [12]. The increase in the corrosion resistance may be due to the formation of...
oxynitrides formed in the passive film, thereby preventing reaction of titanium with other ions. The electrochemical parameters were measured from Tafel analysis and the values are given in Table 1. The corrosion rate and area of repassivation are calculated and it is found that the area of repassivation is less for the alloys nitrided at higher temperature and longer durations compared to the untreated alloy indicating its immediate tendency to repassivate (Table 1).

3.3. Electrochemical impedance measurements

Impedance measurements are one of the most useful and informative methods of corrosion assessment [13,14]. The response for the corroding specimen to an applied small amplitude signal will depend on the frequency of the signal. The impedance behaviour of the specimen is expressed as in Nyquist plots. Fig. 4 shows the Nyquist plots obtained for untreated specimens and samples nitrided at different experimental conditions after immersion in Hanks solution for 96 h. The impedance values at lowest frequency of 10 mHz are presented in Table 2. It is seen that the impedance values of the nitrided alloy are higher than that of the untreated alloy. The polarization resistance and double layer capacitance values are calculated and the results are given in (Table 2). The polarization resistance was found to increase with increase in nitriding temperature and duration. The maximum resistance was exhibited by the specimen treated at 900°C/8 h. The double layer capacitance values were found to be minimum for the nitrided alloy indicating the stability of the nitrided layer [15]. The similar behaviour was obtained in the polarization measurements. The equivalent circuit for the impedance spectra obtained for untreated and nitrided alloys is given in Fig. 5.

Table 1
Electrochemical parameters and Area of repassivation of Ti–6Al–7Nb alloy nitrided at different experimental conditions

| Nitriding conditions | $E_{corr}$ V vs. SCE | $I_{corr}$ (A/cm²) | Corrosion rate (mm/yr) | Area of repassivation (mm²) |
|----------------------|------------------------|---------------------|------------------------|-----------------------------|
| Untreated            | -0.265                 | $2.58 \times 10^{-6}$ | $3.05 \times 10^{-2}$ | 320                         |
| 800°C/4 h            | -0.246                 | $9.96 \times 10^{-9}$ | $4.16 \times 10^{-4}$ | 260                         |
| 800°C/8 h            | -0.158                 | $1.96 \times 10^{-8}$ | $8.17 \times 10^{-4}$ | 240                         |
| 900°C/4 h            | -0.046                 | $1.04 \times 10^{-8}$ | $4.36 \times 10^{-4}$ | 255                         |
| 900°C/8 h            | 0.050                  | $8.39 \times 10^{-10}$ | $3.49 \times 10^{-3}$ | 136                         |

Table 2
Impedance and capacitance values for untreated and nitrided alloys

| Specifications | $Z$ at 10 mHz (ohms cm²) | $R_{ct}$ (ohms cm²) | $C_{dl}$ (μF cm²) |
|----------------|---------------------------|---------------------|-------------------|
| Untreated      | $1.64 \times 10^{4}$     | $1.64 \times 10^{4}$ | 1.490             |
| Nitrided at 800°C/4 h | $3.55 \times 10^{4}$     | $1.06 \times 10^{5}$ | $6.70 \times 10^{-3}$ |
| Nitrided at 900°C/8 h | $8.55 \times 10^{4}$     | $1.59 \times 10^{5}$ | $1.91 \times 10^{-3}$ |

Fig. 3. Cyclic polarization curves for Ti–6Al–7Nb alloy in Hanks solution: (a) untreated; (b) nitrided at 800°C/4 h and (c) nitrided at 900°C/8 h.

Fig. 4. Nyquist obtained for Ti–6Al–7Nb alloy after immersion in Hanks solution for 96 h: (a) Untreated and (b) nitrided at 800°C/4 h and (c) nitrided at 900°C/8 h.

3.4. Microhardness

The Vickers micro hardness was measured using Leitz micro hardness tester. Fig. 6 shows the micro hardness of

Fig. 5. Equivalent circuit for the impedance spectra obtained in Fig. 4.
samples nitrided in N₂:H₂ plasma measured normal to the surface as a function of load. The hardness was found to decrease with the increasing load. The maximum hardness obtained at 25 g load is 2087 Hv which is analog to the hardness of Ti₂N. It is seen from figure that the micro hardness is a function of treatment temperature and duration.

4. Conclusion

Plasma nitriding of Ti−6Al−7Nb orthopaedic alloy was conducted at different experimental conditions varying the temperature and duration. Polarization and impedance measurements were carried out to evaluate the corrosion behaviour of the nitrided alloys in Hanks solution. The maximum surface hardness was found to be 2087 Hv for the samples nitrided at 900 °C for 8 h. The formation of Ti₂N peaks were confirmed using XRD spectra indicating the diffusion of nitrogen ions into the surface. It is found that maximum corrosion rate and minimum area of repassivation are obtained for samples nitrided at 900 °C for 8 h. Electrochemical impedance measurements indicate decrease in the double layer capacitance value and increase in charge transfer resistance for the nitrided samples when compared to untreated specimens, indicating the formation of stable layer on the surface.

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References

[1] R. Boyer, G. Welsch, E.W. Collings, Materials Properties Handbook: Titanium Alloys, ASM International, 1994, pp. 165–167.
[2] J. Black, G. Hasting, Handbook of Biomaterial Properties, Chapman and Hall, London, 1998, pp. 179–200.
[3] P.J. Aragon, S.F. Hulbert, Corrosion of Ti−6Al−4V in simulated body fluids and bovine plasma, J. Biomed. Mater. Res. 6 (1972) 155–164.
[4] H.J. Muller, E.H. Greener, Polarization studies of surgical materials in ringers solution, J. Biomed. Mater. Res. 4 (1970) 29–41.
[5] M. Semlitsch, H. Weber, R.M. Streicher, R. Schon, Joint replacement components made of hot forged and surface treated Ti−6Al−7Nb alloy, Biomaterials 13 (1992) 781–788.
[6] H. Plenk, S. Schider, Tantalum and Niobium, Concise Encyclopedia of Medical and Dental Materials, Pergamon Press, Oxford, 1990, pp. 355–360.
[7] E. Mortiiner, Quantitative evaluation of bone opposition and in growth using porous metal implants with a titanium nitride surface, 17th International Biomaterials Symposium, Session 14, 1991, p. 151.
[8] E. Rolinski, Surface properties of plasma nitrided titanium alloys, Mater. Sci. Engng A 108 (1989) 37–44.
[9] M.A. Khan, R.L. Williams, D.F. Williams, In-vitro corrosion and wear of titanium alloy in biological environment, Biomaterials 17 (1996) 21117–21126.
[10] M.A. Khan, R.L. Williams, D.F. Williams, The corrosion behaviour of Ti−6Al−7Nb and Ti−13Nb−13Zr in protein solution, Biomaterials 20 (1999) 631–637.
[11] S.L.R. Da Silva, L.O. Kerber, L. Amaral, C.A. Dos, Santos, X-ray diffraction measurements of plasma-nitrided Ti−6Al−4V, Surf. Coat. Technol. 116–119 (1999) 342–346.
[12] L. Thair, U. Kamatchi mudali, N. Bhuvaneswaran, K.G.M. Nair, R. Asokamani, B. Raj, Nitrogen ion implantation and in vitro corrosion behaviour of as-cast Ti−6Al−7Nb alloy, Corros. Sci. 44 (2002) 2439–2457.
[13] F. Mansfield, M. Kendig, S. Tsai, Evaluation of corrosion behaviour of coated metals with AC impedance measurements, Corrosion 38 (1982) 478–485.
[14] F. Mansfield, M. Kendig, S. Tsai, Recording and analysis of AC impedance data for corrosion studies II. Experimental approach and results, Corrosion 38 (1982) 570–579.
[15] J. De Damborena, A. Conde, C. Palacio, R. Rodriguez, Modification of corrosion properties of titanium by N-implantation, Surf. Coat. Technol. 91 (1997) 1–6.