

# Corrosion behavior of PIRAC nitrided Ti-6Al-4V surgical alloy

D. STAROSVETSKY, A. SHENHAR, I. GOTMAN

Department of Materials Engineering, Technion, Haifa, 32000, Israel

Hard titanium nitride (TiN) coatings were obtained on the surface of Ti-6Al-4V alloy using an original PIRAC nitriding method, based on annealing the samples under a low pressure of monatomic nitrogen created by selective diffusion of N from the atmosphere. PIRAC nitrided samples exhibited excellent corrosion resistance in Ringer's solution in both potentiodynamic and potentiostatic tests. The anodic current and metal ion release rate of PIRAC nitrided Ti-6Al-4V at the typical corrosion potential values were significantly lower than those of the untreated alloy. This, together with the excellent adhesion and high wear resistance of the TiN coatings, makes PIRAC nitriding an attractive surface treatment for Ti-6Al-4V alloy surgical implants.

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## 1. Introduction

Titanium and Ti-6Al-4V titanium-based alloy are the most biocompatible and corrosion-resistant implant materials currently used in surgery. Implants made of Ti alloys rarely if ever show visible signs of corrosion; nevertheless, the release of potentially harmful metal ions, such as Al and V, and their accumulation in the body are of great concern. To reduce metal ion release and associated risks to the patient, several surface modification treatments have been suggested, such as prepassivation [1–5] and nitrogen ion implantation [5–10]. Although such treatments can substantially reduce corrosion rates under static conditions, they are hardly capable of providing long-term benefits under the conditions of wear that often prevail at the implant surfaces. Protective oxide layers are easily torn from the titanium alloy surface, whereas the thinning of ion-implanted layers quickly leads to their complete removal. As the inadequate wear behavior of Ti alloys is widely known, it would be advantageous if surface modification could simultaneously achieve the goal of wear and corrosion resistance improvement.

Lately, titanium nitride (TiN) has received considerable attention as a wear resistant coating for Ti alloy orthopaedic implants [11–14]. TiN coatings on surgical implants are grown by various physical vapor deposition (PVD) methods, and they often suffer from lack of adherence. As a result, delamination and failure of TiN coating adhesion have been observed in *in vitro* wear simulations and clinical studies [14, 15].

Recently, an original powder immersion reaction assisted coating (PIRAC) nitriding method has been proposed for the coating of complex shape Ti alloy parts [16]. In this method, a several micron thick TiN coating is formed by interaction of Ti-based substrate with highly reactive monatomic nitrogen. As the substrate is directly involved in the process of coating formation, TiN PIRAC

coatings are akin to oxide films on metals, and are characterized by an excellent conformity and strong adhesion to the substrate. TiN PIRAC coatings on Ti-6Al-4V have been reported to contain no toxic Al and V ions, and to significantly improve the fretting behavior of Ti-6Al-4V alloy [16, 17].

In this work, the resistance of PIRAC nitrided Ti-6Al-4V alloy to a localized corrosion attack occurring in chloride containing neutral media has been studied.

## 2. Experimental

Commercially pure (CP) Ti (99.7 wt% purity) and Ti-6Al-4V alloy (Al - 6.10, V - 3.95, Ti-balance, trace elements < 0.4 wt%) rectangular plates 30 × 10 × 2 mm were prepared by cutting and polishing with a 3 μm diamond paste.

Part of the samples were subjected to surface modification via an original PIRAC nitriding method. For this purpose, the samples were placed into containers made of a stainless steel with high Cr content, and annealed at 900 or 1000 °C for 2 h. Cr in the steel reacted with the atmospheric oxygen thus preventing its penetration into the container and protecting the Ti samples from oxidation. At the same time, nitrogen from the atmosphere could easily diffuse through the container walls due to the absence of strong nitride-forming elements in the steel. This resulted in a gradual build-up of a low pressure of monatomic nitrogen inside the container. Annealing Ti-based samples in the atmosphere of this highly reactive monatomic nitrogen resulted in the formation of Ti-N coatings on their surface. It is worth mentioning that since PIRAC coatings are formed by the reaction of the substrate with the surrounding nitrogen gas, the method is suitable for the surface modification of various complex shape or porous-coated surgical implants.

The corrosion and electrochemical behavior of coated and uncoated Ti-6Al-4V samples was studied in Ringer's solution: 9.00 g/l NaCl, 0.20 g/l NaHCO<sub>3</sub>, 0.25 g/l CaCl<sub>2</sub>·6H<sub>2</sub>O, 0.4 g/l KCl. The test solution was prepared from doubly distilled water and analytical grade reagents. The test cell was a 0.5l well-capped three electrodes electrochemical cell (working electrode, platinum wire as counter electrode, saturated calomel electrode, nitrogen inlet and nitrogen outlet). All the experiments were conducted at body temperature (37 ± 1 °C) under nitrogen atmosphere. Electrodes and gas bubblers were tightly inserted into the cell through glass grinds sealed with a silicone rubber sealant. Prior to testing, the medium was purged for 1 h with a pure nitrogen gas in the electrochemical cell. Subsequently, the working electrode that had been positioned in the cell head space during deaeration was immersed. The solution with the immersed sample was purged for 2 h, after which the experiment was started. Potentials were measured using Luggin capillary. The resulting potential values were referred to a saturated calomel electrode (SCE). The experiments were performed with a potentiostat M273 EG&G at the scan rate of 1 mV/s. The electrochemical behavior of PIRAC nitrided Ti-6Al-4V samples was compared with that of untreated Ti-6Al-4V and PIRAC nitrided CP Ti (1000 °C, 2 h).

To study the effect of PIRAC nitriding on metal ion release, the nitrided (1000 °C, 2 h) and untreated Ti-6Al-4V alloy samples were placed in 100 ml Ringer's solution and maintained at 37 ± 0.5 °C. The surface area of each sample group was approximately 10 cm<sup>2</sup>. Evaporation of the test solution was compensated by the addition of doubly distilled water. After 400 h, the Ti and Al concentrations in the saline solution were measured via atomic absorption spectrometry (AAS).

Phase identification and microstructure characterization of as-received and corroded PIRAC nitrided samples were performed employing X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS).

### 3. Results and Discussion

#### 3.1. Microstructure

PIRAC nitriding yielded characteristic golden-colored titanium nitride coatings on CP Ti and Ti-6Al-4V alloy surfaces. Representative SEM cross-sections of PIRAC nitrided Ti-6Al-4V samples surfaces are shown in Fig. 1.

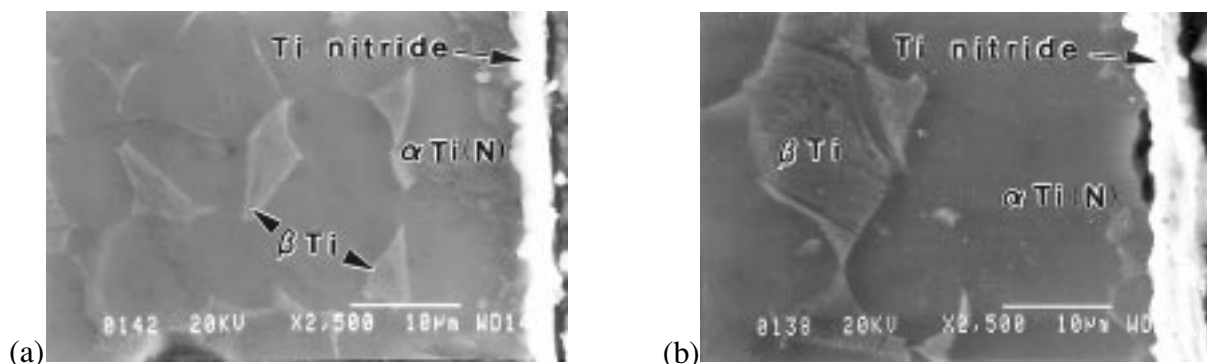


Figure 1 SEM of cross-sections of PIRAC nitrided Ti-6Al-4V samples: (a) 900 °C, 2h; (b) 1000 °C, 2h.

The coatings obtained on Ti-6Al-4V after 2 h nitriding at 900 and 1000 °C were ~ 2.5 and 3 µm thick, respectively. According to the XRD results (Fig. 2) and EDS analyzes, the coatings on both CP Ti and Ti-6Al-4V consisted of two layers: the surface layer of TiN, and the inner layer of Ti<sub>2</sub>N. This nitride coating was followed by a layer of nitrogen-stabilized α-Ti. The thickness of this α-Ti(N) layer in both CP Ti and Ti-6Al-4V samples increased noticeably with annealing time and temperature. In addition, a thin discontinuous layer of Ti<sub>3</sub>Al was present at the Ti<sub>2</sub>N interface in PIRAC nitrided Ti-6Al-4V alloy, which could only be resolved in a high resolution SEM after very long anneals. As the substrates were directly involved in the process of coating formation, the obtained PIRAC coatings were characterized by strong adhesion to the substrate.

#### 3.2. Corrosion studies

##### 3.2.1. Potentiodynamic test

Corrosion potential ( $E_{\text{corr}}$ ) transients for the untreated and PIRAC nitrided Ti-6Al-4V samples in deaerated Ringer's solution are given in Fig. 3. It can be seen that  $E_{\text{corr}}$  of uncoated Ti-6Al-4V decreases slightly after immersion reaching the value of approximately -0.45 V, Table I, after 2 h exposure. In contrast to this,  $E_{\text{corr}}$  values of PIRAC nitrided Ti-6Al-4V samples are much more positive already upon immersion, and even increase slightly during following exposure. As can be seen in Fig. 3 and Table I,  $E_{\text{corr}}$  of Ti-6Al-4V samples PIRAC nitrided at 900 and 1000 °C reached the values of -0.09 and -0.04 V, respectively, after two hours exposure, indicating stronger surface passivation compared to the untreated Ti-6Al-4V.

Potentiodynamic curves of untreated and PIRAC nitrided Ti-6Al-4V samples in deaerated Ringer's solution are presented in Fig. 4. The untreated Ti-6Al-4V sample was passive in the whole tested potential region up to +1.2 V, with the onset of anodic current seen at approximately -0.45 V. The current increased with potential up to 0.02 V and remained practically constant at the following positive potential sweep. With the potential scan reversed, a sharp current decrease typical of the strong passive behavior was observed.

Ti-6Al-4V samples PIRAC nitrided at 900 and 1000 °C were also passive in the whole tested potential region, as indicated by the sharp current decrease (similar to that of the untreated alloy) in the backscan part of their

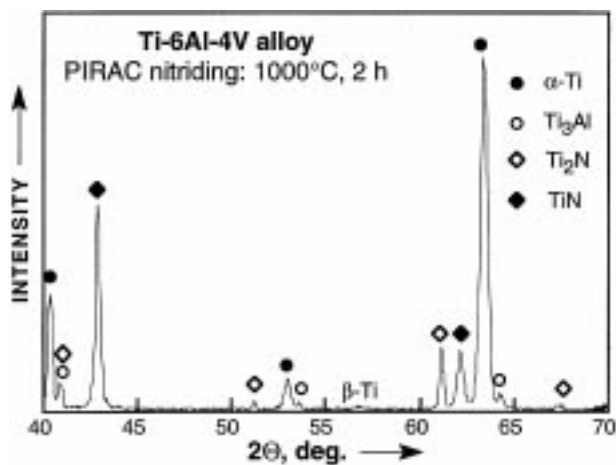


Figure 2 XRD pattern taken from the surface of PIRAC nitrided (1000 °C, 2 h) Ti-6Al-4V alloy.

potentiodynamic curves. At the same time, the anodic curves of these samples are noticeably different from those of the untreated Ti-6Al-4V. The onset of anodic current for the nitrided samples is seen at much more positive potentials. The measured values of current density at potentials below 0.43 V (SCE) are significantly lower than those of the untreated Ti-6Al-4V alloy indicating the stronger passivity of the nitrided material in this potential region. In contrast to the untreated material, the anodic current of PIRAC nitrided samples increases steadily with potential sweep until it equals, at  $E \approx 0.43$  V, the value of the anodic current of the untreated sample (the two curves intersect). At potentials above 0.43 V, the anodic current of nitrided samples can reach markedly higher values compared to the untreated alloy. A broad current peak appears on the curves of PIRAC nitrided samples at potentials above 0.7 V (SCE). As the nitriding temperature increases, the position of the peak is shifted towards higher currents and more positive potentials. The gradual increase of the anodic current of PIRAC nitrided Ti-6Al-4V alloy and the occurrence of the current peak at  $E \geq 0.7$  V could, possibly, be

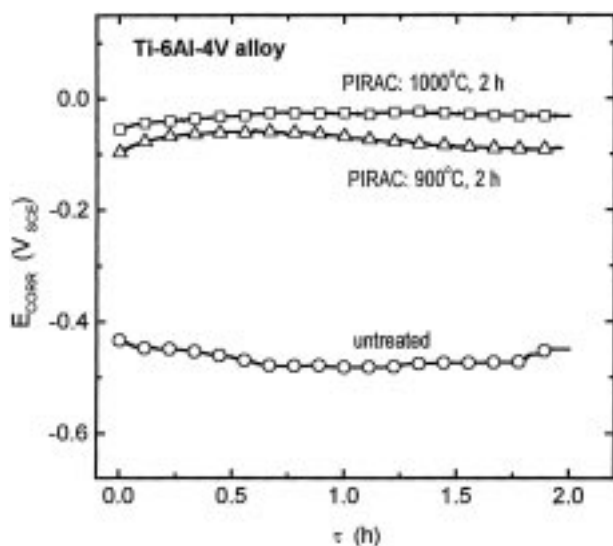


Figure 3 Corrosion potential ( $E_{\text{corr}}$ ) transients for untreated and PIRAC nitrided Ti-6Al-4V samples in deaerated Ringer's solution.

attributed to the oxidation of the nitrided surface accompanied by alteration of its structure and composition.

In order to better understand the effect of surface layer structure on corrosion behavior, similar potentiodynamic tests were carried out on CP titanium samples, both untreated and PIRAC nitrided at 1000 °C for 2 h. The obtained results are shown in Fig. 5. It can be seen that, similarly to Ti-6Al-4V alloy, PIRAC nitrided titanium is characterized by more positive values of corrosion potential (inset) and significantly lower values of anodic current (in the low potential region) compared to the untreated metal. Like in the case of PIRAC nitrided Ti-6Al-4V, the anodic current of PIRAC nitrided CP Ti increases steadily with potential sweep until the curves of the untreated and nitrided Ti intersect at  $E \approx 0.5$  V. At potentials above  $\sim 0.5$  V, the anodic current of nitrided CP Ti starts to exceed that of the untreated metal, however, contrary to Ti-6Al-4V alloy, no current peaks appear on the potential-current curve of the nitrided CP Ti at potentials above 0.7 V. It is assumed that the increase of anodic current with potential sweep in the passive region, which is the common feature of both materials, is caused by the oxidation of the surface nitride TiN/Ti<sub>2</sub>N layer. The appearance of current peak in the anodic curve of PIRAC nitrided Ti-6Al-4V alloy could possibly be related to the effect of small (undetected by EDS) amounts of Al and V in the surface nitride layer. The detailed investigation of the oxidation process of PIRAC nitrided Ti-6Al-4V alloy is currently underway.

### 3.2.2. Potentiostatic test

In addition to potentiodynamic test, the electrochemical behavior of untreated and PIRAC nitrided (1000 °C, 2 h) Ti-6Al-4V samples was examined by means of a stepwise potentiostatic test. The test was started at the applied potential of 0.2 V. The sample was held at this potential for 15 min, after which the applied potential was raised to 0.4 and, after an additional 20 min exposure, to 0.6 V.

Anodic current transients of the untreated and PIRAC nitrided Ti-6Al-4V samples obtained in the potentiostatic test are presented in Fig. 6. It can be seen that at all the applied potentials, the anodic current reached its maximum immediately after potential application and then decreased gradually with time. Very low anodic currents were measured during the potentiostatic tests at 0.2 and 0.4 V for both untreated and PIRAC nitrided Ti-6Al-4V, see Table I. Still, the current in the nitrided alloy was significantly lower than that in the untreated samples, indicating the enhanced passivity of PIRAC nitrided Ti-6Al-4V alloy in this potential region. At the higher potential of 0.6 V, however, the situation was quite the opposite, with the anodic current of the nitrided samples drastically increased and reaching values almost an order of magnitude higher than those typical of the untreated alloy at any exposure time. Such behavior indicates a reduction in protective properties of the passive film formed on the surface of the nitrided samples.

TABLE I Summary of corrosion characteristics of untreated and PIRAC nitrated Ti-6Al-4V alloy in deaerated and aerated Ringer's solution at 37 °C

Ti-6Al-4V	Deaerated solution			Aerated solution $E_{\text{corr}}$ , V
	$E_{\text{corr}}$ , V	$i_a$ at 0.2V, $\mu\text{A}/\text{cm}^2$		
		*p.d.	†p.s.	
Untreated	-0.450	5	0.01-0.02	0.04-0.07
PIRAC 900 °C, 2 h	-0.090	~ 0.6	0.0003-0.006	—
PIRAC 1000 °C, 2 h	-0.04	~ 0.7	0.003-0.006	0.14-0.17

\*Potentiodynamic test; †potentiostatic test.

### 3.2.3. Immersion test

Both potentiodynamic and potentiostatic tests indicated that PIRAC nitrated Ti-6Al-4V alloy was characterized by a significantly stronger passivity at potentials below 0.43 V compared to its untreated counterpart. It could, therefore, be expected that PIRAC nitrating treatment should reduce metal ion release from Ti-6Al-4V implants provided the corrosion potential doesn't exceed the value of 0.43 V during service life. To check this assumption, a long-term (400 h) immersion test was conducted at OCP for the PIRAC nitrated (1000 °C, 2 h) and untreated Ti-6Al-4V alloy. The long-term test was chosen since the passive dissolution rate of Ti-6Al-4V alloy in electrolyte solutions has been reported to be exceedingly low with no metal ions detectable at the early periods of immersion [18]. As the most pronounced shift of corrosion potential in the positive direction can be achieved in an aerated solution, and since blood and other extracellular body fluids to which Ti-6Al-4V implants are typically exposed are aerated solutions, the immersion test was conducted in an open electrochemical cell (without deaeration). Corrosion potentials of the samples were measured from time to time for the whole duration of the test.

Fig. 7 gives corrosion potential transients of PIRAC nitrated and untreated Ti-6Al-4V alloy during the immersion test. The corrosion potentials of both tested materials increase at the beginning of the experiment reaching constant values after approximately 50–80 h.

For PIRAC nitrated Ti-6Al-4V,  $E_{\text{corr}}$  does not rise above 0.16–0.18 V (SCE), i.e. the material remains within the strong passivity region ( $E_{\text{corr}}$  0.43V). As no changes of  $E_{\text{corr}}$  were measured for more than 300 h after the initial potential increase, it could be assumed that any PIRAC nitrated Ti-6Al-4V alloy implant will remain strongly passive during its whole service life. It should also be mentioned that previously discussed anodic current peaks observed in the potentiodynamic curves of PIRAC nitrated Ti-6Al-4V samples, Fig. 4, occur at potentials significantly higher than  $E_{\text{corr}}$  (0.7 vs 0.18 V) and thus should not impair the material's corrosion behavior in body fluids.  $E_{\text{corr}}$  values of untreated samples are ~ 0.1 V more negative at any exposure time, indicating their lower corrosion resistance.

Representative micrographs of PIRAC nitrated (1000 °C, 2 h) Ti-6Al-4V samples before and after 400 h immersion in Ringer's solution are shown in Fig. 8. A thin film repeating the surface topography of the nitride layer can be seen on the immersed sample. The film is too thin to be detected by XRD, however the large measured amount of oxygen (EDS) suggests a Ti oxide or oxynitride. The presence of the surface film indicates that the TiN PIRAC coating undergoes oxidation in the course of immersion. The initial increase of  $E_{\text{corr}}$  during the immersion experiment must be associated with the surface film formation. The presence of the oxidized layer on the surface of immersed PIRAC nitrated Ti-6Al-4V samples is noteworthy, since the surface oxide is

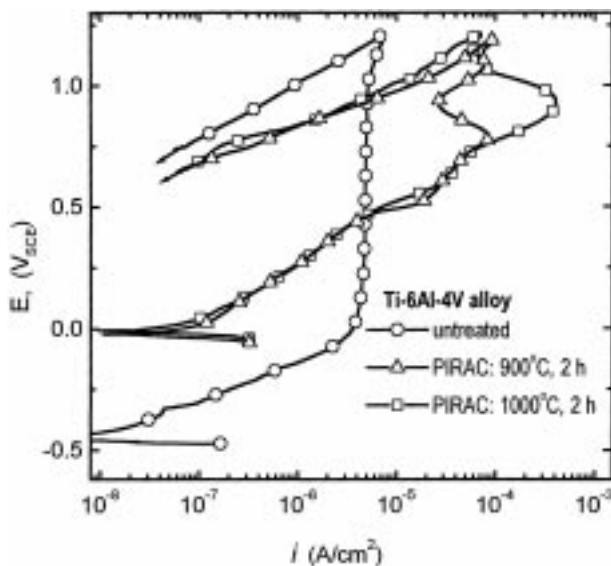


Figure 4 Potentiodynamic curves of untreated and PIRAC nitrated Ti-6Al-4V samples in deaerated Ringer's solution.

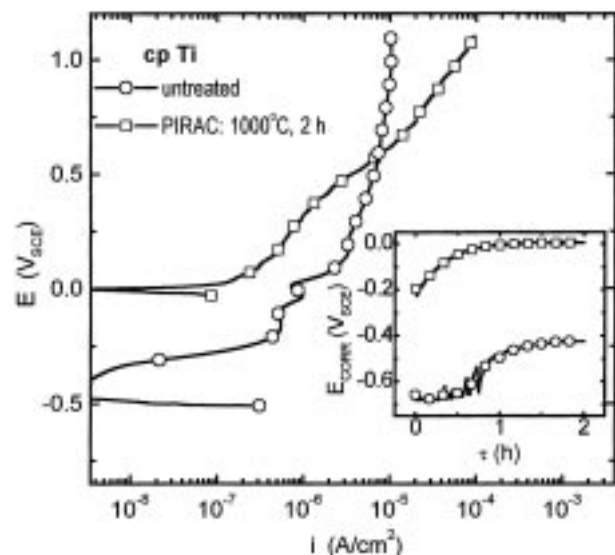


Figure 5 Potentiodynamic curves of untreated and PIRAC nitrated (1000 °C, 2 h) CP Ti samples in deaerated Ringer's solution.

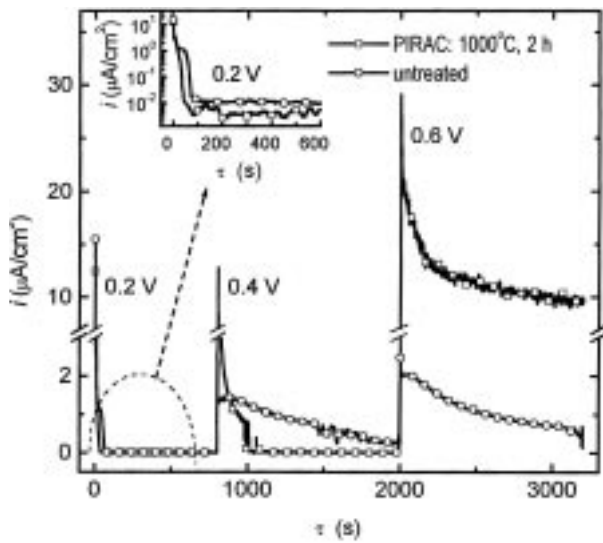


Figure 6 Potentiostatic curves of untreated and PIRAC nitrided (1000°C, 2 h) Ti-6Al-4V samples in deaerated Ringer's solution.

believed to be the key element of the favorable local tissue response to titanium-based implants.

The results of metal ion dissolution after 400 h immersion in Ringer's solution are given in Table II. It can be seen that small but measurable amounts of Ti and Al ions (2.5 and 0.8  $\mu\text{g}/\text{cm}^2$ , respectively) have been released from the untreated Ti-6Al-4V samples. For PIRAC nitrided samples (1000°C, 2 h) no Ti or Al was detected in the solution. The AAS detection limit under the conditions of experiment was  $\sim 20$  ng metal/ml, giving total metal ion release of 0.2  $\mu\text{g}/\text{cm}^2$  after 400 h immersion, which is at least an order of magnitude lower than for the untreated sample. These results confirm our earlier assumption that PIRAC nitriding significantly reduces metal ion release from Ti-6Al-4V alloy.

#### 4. Summary

The surface of Ti-6Al-4V alloy was modified by the original PIRAC nitriding treatment based on selective

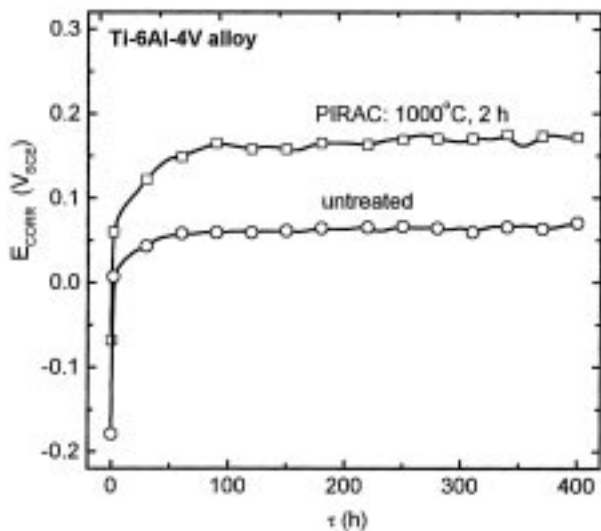


Figure 7 Long-term corrosion potential ( $E_{\text{corr}}$ ) transients for untreated and PIRAC nitrided (1000°C, 2 h) Ti-6Al-4V samples in aerated Ringer's solution.

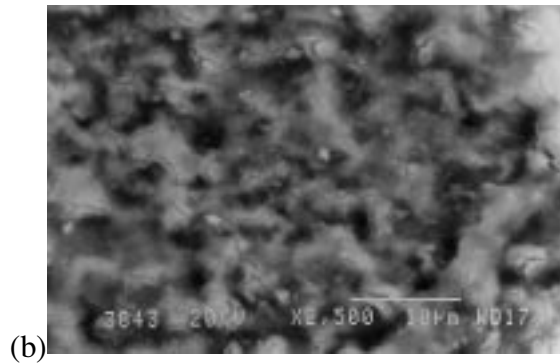
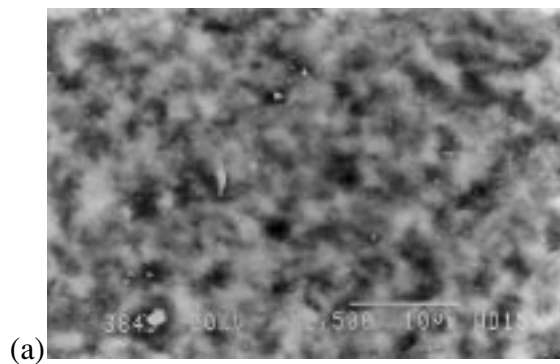


Figure 8 SEM micrographs of PIRAC nitrided (1000°C, 2 h) Ti-6Al-4V samples: (a) as-nitrided; (b) after 400 h immersion in Ringer's solution.

diffusion of nitrogen from the atmosphere. Thin and strongly adherent titanium nitride ( $\text{TiN} + \text{TiN}_2$ ) layers were formed on the alloy surface after PIRAC annealing at 900 or 1000°C for 2 h.

PIRAC nitriding allowed significant improvement of the corrosion behavior of Ti-6Al-4V in the saline (Ringer's) solution. The corrosion potential of PIRAC nitrided alloy was more positive than that of its untreated counterpart in both aerated and deaerated solutions indicating stronger surface passivation. A significantly lower anodic current was measured in PIRAC nitrided Ti-6Al-4V at the typical corrosion potential values compared to that of the untreated alloy. As a result of PIRAC nitriding treatment, an appreciable reduction in the dissolution of metal (Ti and Al) ions from Ti-6Al-4V alloy in Ringer's solution was achieved. The negligible release of potentially harmful metal ions, together with the excellent adhesion and high wear resistance of the TiN surface layers, makes PIRAC nitriding an attractive surface treatment for titanium-based surgical implants.

TABLE II Ti and Al ion release in aerated Ringer's solution after 400 h exposure at 37°C

Material	Released metal ions, $\mu\text{g}/\text{cm}^2$	
	Ti	Al
Untreated Ti-6Al-4V	2.4	0.8
PIRAC nitrided Ti-6Al-4V (1000°C, 2 h)	Not detectable	Not detectable

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