ELSEVIER

Ceramics International 26 (2000) 709–713

CERAMICS
INTERNATIONAL

Microstructure and fretting behavior of hard TiN-based coatings on surgical titanium alloys

A. Shenhar[a], I. Gotman[a,*], S. Radin[b], P. Ducheyne[b]

[a]*Department of Materials Engineering, Technion, Haifa, 32000, Israel*
[b]*Department of Bioengineering, University of Pennsylvania, Philadelphia, PA 19104, USA*

Received 7 September 1999; received in revised form 5 October 1999; accepted 17 November 1999

Abstract

An original nitriding method [powder immersion reaction assisted coating (PIRAC)] for improving wear resistance of Ti-based surgical alloys was developed. CP Ti and Ti–6Al–4V alloy samples were annealed in sealed stainless steel containers that allow selective diffusion of nitrogen atoms from the atmosphere. The microhardness-microstructure and nitrogen concentration relationship were studied for TiN-based PIRAC coatings grown at 850–1100°C. Phase identification and microstructure characterization of nitrided samples were performed by XRD, SEM/EPMA and HRSEM. The effect of PIRAC coating on fretting behavior of Ti–6Al–4V was studied in vitro under conditions simulating in vivo conditions at the interface of modular orthopedic implants. A significant reduction in friction coefficient and fretted areas was measured for the coated samples. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Surgical titanium alloys

1. Introduction

Titanium and its alloys are widely used as implant materials and typically exhibit excellent biocompatibility. At the same time, Ti alloys suffer from inadequate wear resistance hampering their use as articulating devices. Adhesive and abrasive wear, as well as relative sliding at fretting–prone interfaces between mating modular components of orthopedic implants, generate particular wear debris jeopardizing the stability of the prosthesis.

An effective approach to reducing particulate-generating potential is providing an implant with a harder and more durable surface. Titanium nitride (TiN), whose favorable tribological properties (high hardness, low friction coefficient) are widely known, is one of the materials that are considered for use as wear-resistant coatings for orthopedic implants. Typically, TiN coatings are fabricated by CVD, PVD or plasma nitriding. The former two techniques suffer from poor bonding integrity of the substrate/coating interface, while the cost-effectiveness of the latter method is questionable.

In this paper, a new method (or, rather, a modification of the earlier developed powder immersion reaction assisted coating (PIRAC) method [1]) of growing thick TiN coatings on Ti-based surgical alloys is described. The method is based on annealing the sample in the atmosphere of highly reactive nitrogen which is supplied either by decomposition of unstable nitrides, or by selective diffusion of N from the atmosphere. Such PIRAC coatings are akin to oxide films on metals and alloys, and are characterized by strong adhesion to the substrate.

2. Experimental

In the present study, bulk commercially pure (CP) Ti and Ti–6Al–4V alloy were used. Samples 5×8×18 mm with a good surface finish were prepared by cutting and grinding. The samples were PIRAC-nitrided by annealing at 850–1100°C in sealed stainless steel containers that allow selective diffusion of nitrogen atoms from the atmosphere.

Microstructure characterization and coatings thickness measurements were performed using optical metallography, scanning electron microscopy (SEM) and high resolution SEM (HRSEM). Phase identification was done by means of X-ray diffraction. Diffusion profiles

---

* Corresponding author. Tel.: +972-4-829-2112; fax: +972-4-832-1978.
E-mail address: gotman@tx.technion.ac.il (I. Gotman).

PII: S0272-8842(00)00008-0

of N, V and Al in the surface layers of coated samples were measured by quantitative electron probe X-ray microanalysis (EPMA). All microhardness measurements were made under a load of 25 gf using a Knoop diamond indenter.

Fretting behavior of coated (950°C, 3 h) and uncoated Ti–6Al–4V was studied in vitro under conditions simulating in vivo conditions at the interface of modular orthopedic implants. Pin-flat pairs of either coated or uncoated samples were tested in a fretting apparatus at 90–100 μm displacement in tris buffered solution (pH 7.4 at 37°C) supplemented with electrolytes typical for plasma and 10% serum (TES) for up to 100,000 cycles. Prior to testing, uncoated samples were cleaned ultrasonically and passivated in 40% HNO_3 at 550°C for 20 min (according to ASTM F86). TiN coated Ti–6Al–4V alloy pin and flat were cleaned, but not passivated. The samples were stored in a dessicator before testing. The applied load varied from 1.5 to 6 N.

Fretting behavior was assessed by measuring friction coefficients and fretted surface areas as a function of applied load and number of cycles. Frictional force was calculated from the deflection of the loading rod and pin sample, using linear variable differential transformers (LVDTs). The frictional force was divided by the applied normal load to obtain the friction coefficient.

3. Results and discussion

PIRAC nitriding of CP titanium at $T \leqslant 900°C$ and of Ti–6Al–4V at $T \leqslant 950°C$ did not lead to significant grain growth or noticeable microstructural changes compared to the as-received materials. At higher temperatures, the coarsening of microstructure took place in both pure and alloyed Ti. In addition, annealing Ti–6Al–4V at $T \geqslant 1000°C$ (above β-transus) produced an (α-β) lamellar microstructure. Representative microstructures of Ti and Ti–6Al–4V after various nitriding anneals are shown in Fig. 1.

PIRAC nitriding of CP Ti and Ti–6Al–4V at $T \leqslant 1000°C$ yielded two layer coatings (Fig. 2). According to XRD analysis, the coatings consisted of the surface layer of δ phase, TiN_{1-x}, and the inner layer of ε phase, Ti_2N (Fig.3), with the fraction of ε phase decreasing with increasing treatment time and temperature. As seen in Fig. 2, the grains of the ε phase grew normal to the surface. Abnormal peak intensities suggest the preferred (002) orientation of ε-Ti_2N with its *c* axis parallel to the direction of growth. Such orientation of ε-Ti_2N has been previously reported for other nitriding methods [2,3].

Beneath the Ti_2N layer, a region of solid solution of nitrogen in Ti, α-Ti(N), was detected. Peaks of α-Ti(N) in the XRD pattern (Fig. 3) are shifted towards lower diffraction angles compared to those of pure α-Ti, indicating the presence of dissolved N in the lattice.

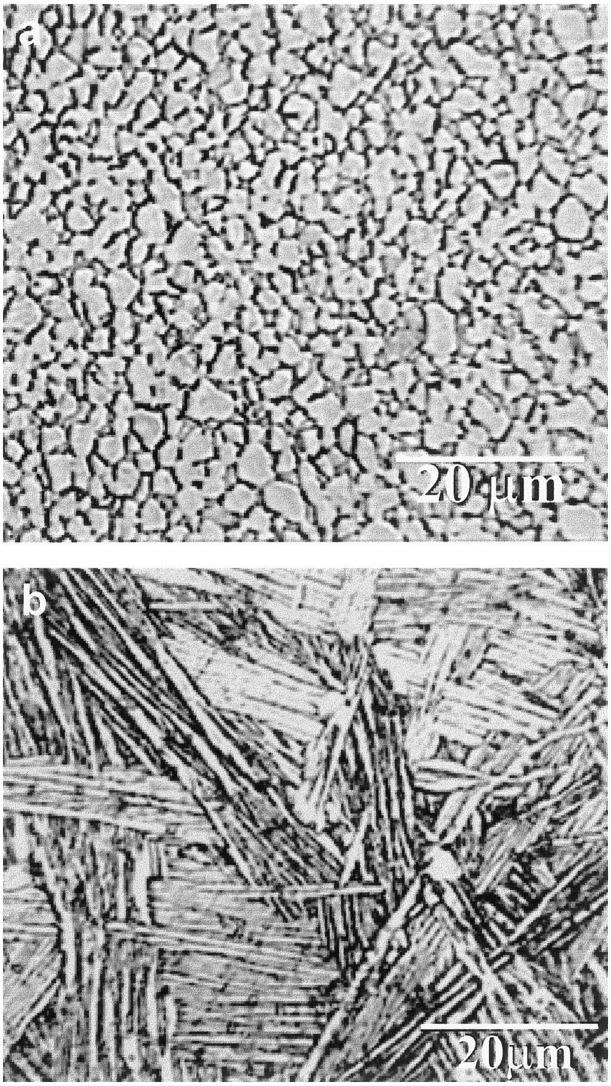

Fig. 1. Representative microstructures of Ti–6Al–4V alloy after PIRAC treatment at 900°C for 2 h (a) and at 1000°C for 1 h (b) (× 675, optical microscopy).

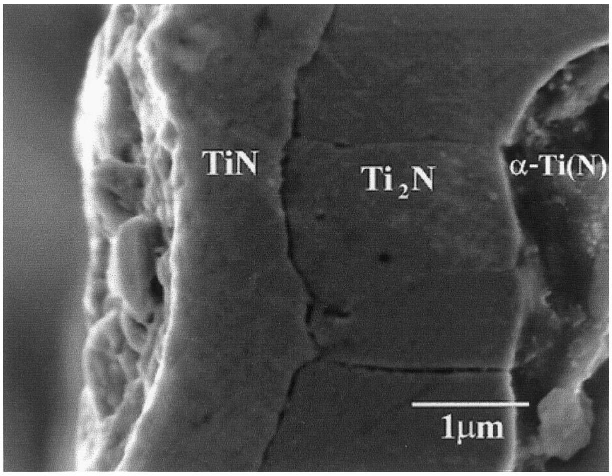

Fig. 2. HRSEM micrograph of PIRAC-nitrided Ti–6Al–4V sample (1000°C, 16 h), cross-section.

Longer anneals yielded thicker coatings, with the peaks of α-Ti(N) in the XRD pattern becoming weaker and the peaks of TiN becoming stronger.

After treatment at 1100°C, the compound layer consisted of the TiN phase only. This is in agreement with the Ti–N phase diagram indicating that Ti_2N decomposes above 1080°C. After short (2–4 h) anneals at all the temperatures, δ-TiN formed on the CP Ti surface had a (111) preferred orientation which disappeared after longer exposures.

In Figs. 4 and 5, EPMA scans for Ti, N, Al and V across the nitrided surface of Ti–6Al–4V and CP Ti (900°C, 4 h) are shown together with the corresponding SEM micrographs. For both materials, the surface layer with high N concentration is followed by a region characterized by gradually decreasing N content. The concentration profile of N in Ti–6Al–4V is much steeper and the diffusion depth of N is much shorter than in CP Ti. The surface layer of nitrided Ti–6Al–4V contains practically no Al or V. This must be due to the lower affinity of V and Al for N leading to the preferential reaction between Ti and N. The concentration profile of Al features a sharp peak immediately after the nitride layer, after which the profiles of both Al and V remain relatively smooth as long as some N is present. Most probably, this corresponds to the N-stabilized α-Ti. The profiles beyond the N diffusion depth feature large fluctuations corresponding to α- and β-Ti grains with their different solubility for Al and V. The absence of Al and V in the surface layer is significant, as both are known have certain toxic effects in the human body.

In Fig. 6, the thickness of the compound layer on CP Ti and Ti–6Al–4V formed at 850–1000°C is given as a function of the square root of time. The straight lines obtained suggest a volume diffusion controlled process. In contrast to coatings obtained by plasma nitriding [4], the compound layer on Ti–6Al–4V is always thicker than that on CP Ti after similar treatments. This could be due to the segregation of aluminum near the Ti_2N/α–Ti(N) interface, since Al was previously reported to inhibit the diffusion of nitrogen into Ti [5], leading to the increased local concentration of N and the formation of ε-Ti_2N.

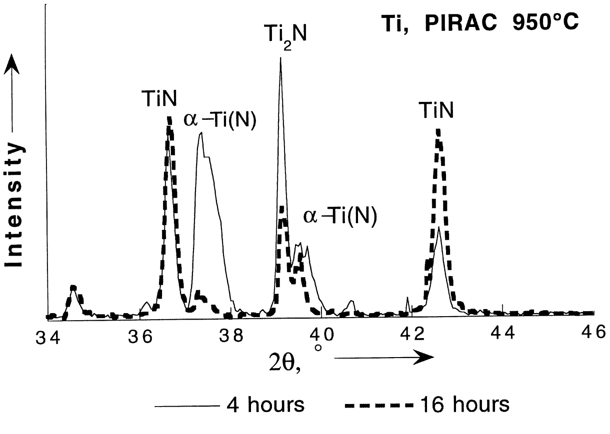

Fig. 3. XRD patterns of CP titanium nitrided via PIRAC at 950°C for 4 and 16 h.

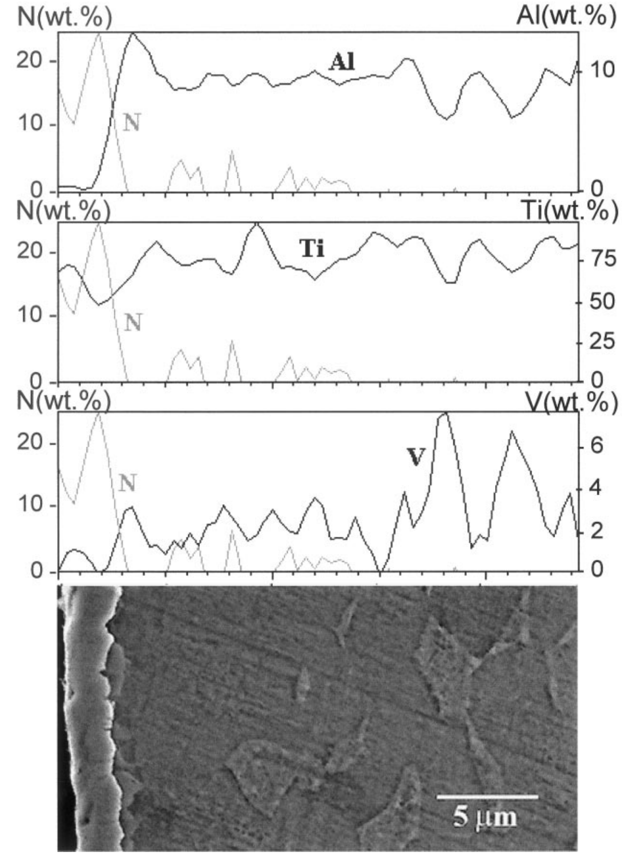

Fig. 4. EPMA line scans of N, Ti, Al and V across the surface layer of a Ti–6Al–4V sample nitrided via PIRAC at 900°C for 4 h, and the corresponding SEM micrograph.

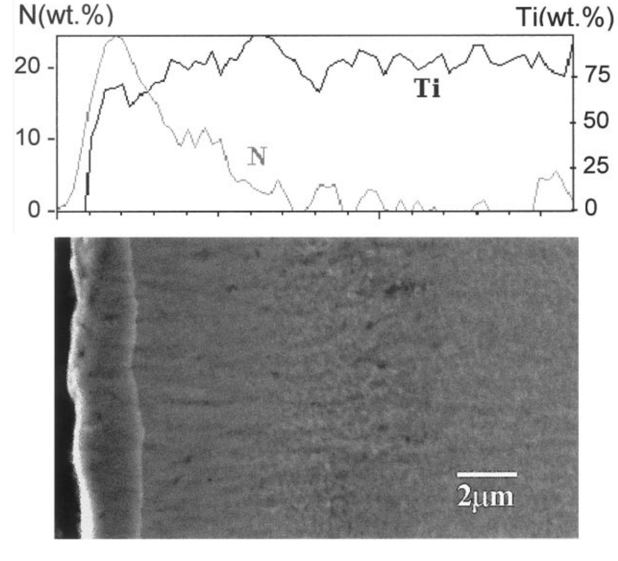

Fig. 5. EPMA line scans of N and Ti across the surface layer of a CP Ti sample nitrided via PIRAC at 900°C for 4 h, and the corresponding SEM micrograph.

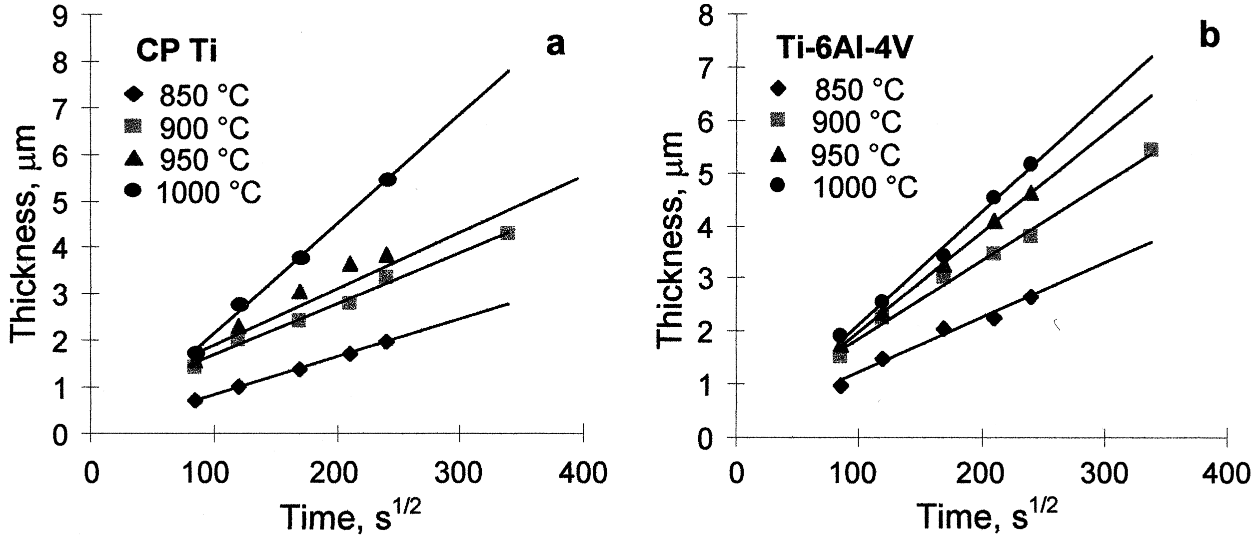

Fig. 6. Thickness of the compound layer versus square root of time for CP Ti (a) and Ti–6Al–4V (b).

The activation energies for the nitride layer growth obtained by the Arrhenius analysis of growth constants are ~166 and 117 kJ/mol for the CP Ti and Ti–6Al–4V, respectively. The value of 166 kJ/mol is comparable to the activation energies of N diffusion in both ε and δ phases [6] suggesting that diffusion through the compound layer is the rate controlling stage of the coating growth on CP Ti.

Continuous microhardness profiles were measured along the cross section of nitrided CP Ti samples (Fig. 7). The microhardness profiles match the N diffusion profiles obtained by EPMA scanning, suggesting that the decrease in microhardness is due to the reduction in N concentration. The gradual hardness decrease away from the surface is a very attractive feature of PIRAC-coated samples, since the hardened bulk material provides an optimal support for the hard surface layer. Much steeper microhardness profiles were measured in Ti–6Al–4V, again in agreement with the N concentration profiles.

In Fig. 8, the plots of fretted area, FA, as a function of applied load for coated and uncoated samples are presented showing a linear increase of FA with applied load in both cases. At the same time, a 6–7 fold decrease in FA was observed to result from the TiN coating at all loads applied.

Fig. 9 shows the effect of the coating on the change of the friction coefficient with fretting time for coated vs. uncoated similar pin-flat pairs. The data of Fig. 9 indicate that the friction coefficient of TiN-coated pairs was significantly lower than that of uncoated ones, at least at the initial stages of the fretting test. The reduction in the friction coefficient for TiN-coated pairs is due to the much harder surface of the coated alloy. At the same time, the tendency of the change of the friction coefficient with fretting time, i.e. increase at the initial stage followed

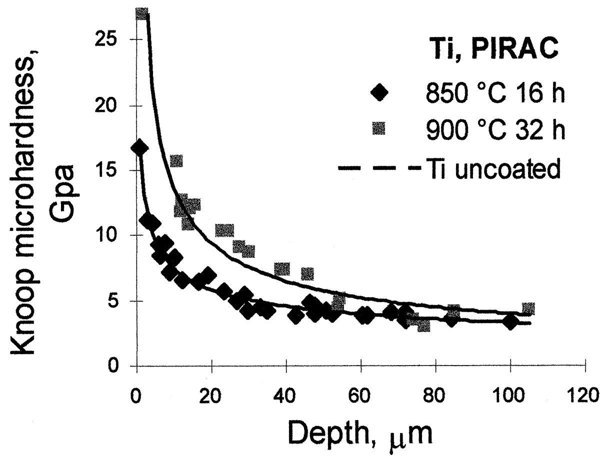

Fig. 7. Knoop microhardness as a function of distance from the surface of PIRAC-coated CP Ti.

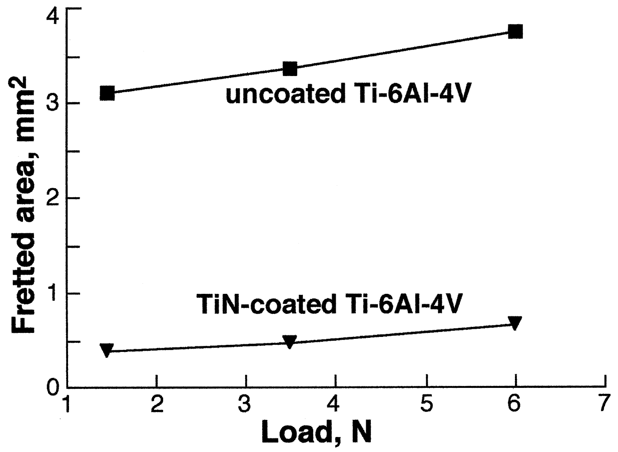

Fig. 8. Fretted area of uncoated and PIRAC- coated similar pairs (Ti–6Al–4V) as a function of applied load (100,000 cycles).

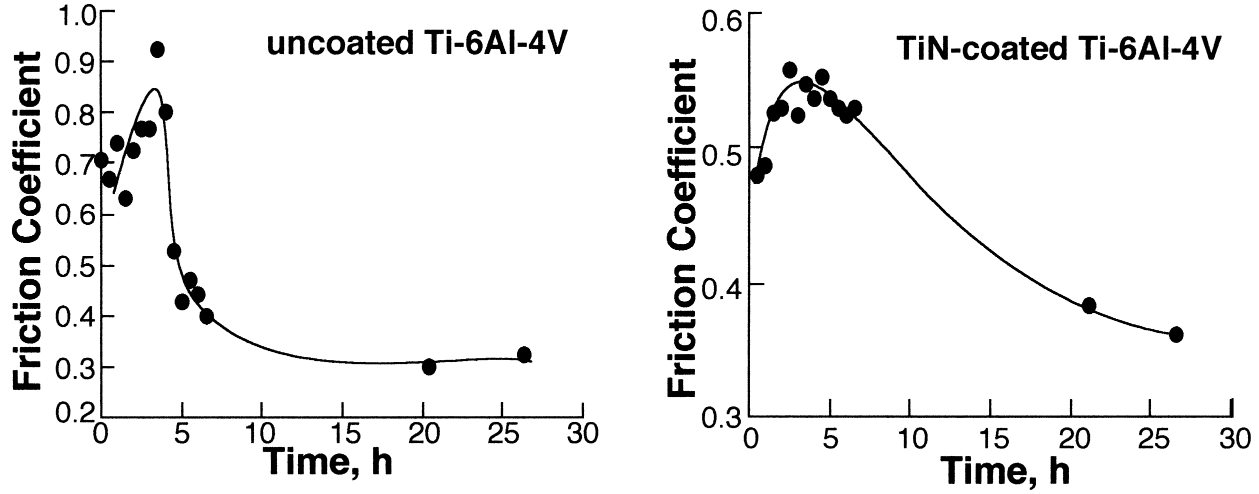

Fig. 9. Friction coefficient versus fretting time at 6 N for uncoated and PIRAC-coated Ti–6Al–4V pin-flat pairs (26.5 h correspond to 100,000 cycles).

by a subsequent decrease, was similar for both surface conditions, though the decrease occurred much more slowly for the coated samples. It was suggested earlier that boundary lubrication by absorbed serum molecules was responsible for the reduction in friction coefficient with fretting time in serum-containing solutions [7].

4. Conclusions

The surface of CP Ti and Ti–6Al–4V surgical alloy was modified by nitriding via an original PIRAC method. The method is based on annealing a Ti-based substrate under a low pressure of highly reactive nitrogen obtained by selective diffusion of atmospheric nitrogen through the reaction chamber walls. The modified Ti alloy surfaces were characterized in terms of phase composition, N diffusion and microhardness. Nitriding at 850–1000°C yielded two-layer coatings consisting of a TiN surface layer on top of a Ti_2N layer with a pronounced (002) preferred orientation. The coatings grown at 1100°C contained only one TiN layer. The growth of the nitride layers was controlled by diffusion, the activation energy of coating growth being 166 and 117 KJ/mol for CP Ti and Ti–6Al–4V, respectively (at 850–1000°C).

Beneath the compound layer, large amounts of dissolved nitrogen were detected, gradually decreasing away from the surface. The steeper N concentration profiles and shorter diffusion depths measured in Ti–6Al–4V (compared to CP Ti) may have an undesirable effect on the compliance of the coating to the substrate, a point to be further investigated. Microhardness profiles matching the N diffusion profiles were measured in both CP Ti and Ti–6Al–4V. The gradual hardness decrease in CP Ti is especially attractive, since the hardened bulk material provides an optimal support for the hard surface layer. No Al or V was detected in the nitrided surface of Ti–6Al–4V, which is quite important given the toxic effects of both elements in the human body.

The microstructure of CP Ti and Ti–6Al–4V remained practically unaffected by PIRAC treatment below 900 and 950°C, respectively. Encouraging fretting wear characteristics were obtained for PIRAC-coated pin-flat Ti–6Al–4V pairs with a lower friction coefficient and significantly smaller fretted areas compared to the uncoated alloy.

Acknowledgements

This work was supported by U.S.-Israel Binational Science Foundation (BSF) through grant No. 95-00486 and by the Israel Ministry of Health through grant No. 3789.

References

[1] E.Y. Gutmanas, I. Gotman, W. Kaysser, Coating of non-oxide ceramics by interaction with metal powders, Mater. Sci. Eng. A157 (1992) 233–241.
[2] C. Badini, C. Gianoglio, T. Bacci, B. Tesi, Characterization of surface layers in ion-nitrided titanium and titanium alloys, J. Less-Common Metals 143 (1988) 129–141.
[3] A. Raveh, P.L. Hansen, R. Avni, A. Grill, Microstructure and composition of plasma-nitrided Ti–6Al–4V layers, Surf. Coat. Techn. 38 (1989) 339–351.
[4] K.T. Rie, T.H. Lampe, Thermochemical surface treatment of titanium alloy Ti–6Al–4V by low energy nitrogen ion bombardment, Mater. Sci. Eng. 69 (1985) 473–481.
[5] A. Raveh, R. Avni, A. Grill, R.F. Plasma nitriding of Ti–6Al–4V alloy, Thin Solid Films 186 (1990) 241–256.
[6] E. Metin, O.T. Inal, Kinetics of layer growth and multiphase diffusion in ion-nitrided titanium, Metall. Trans. A20 (1989) 1819–1832.
[7] B. Smith, Parametric investigation of the fretting-enhanced corrosion of Ti–6Al–4V and Co–Cr–Mo in model physiological solutions, Ph.D. Thesis, University of Pennsylvania, Philadelphia, 1996.