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Fretting Fatigue Studies of Titanium Nitride-Coated Biomedical Titanium Alloys

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Fretting fatigue is an adhesive wear mechanism caused by repetitive tangential micro-oscillation between two contacting materials pressed together under cyclic load. Bioimplants, such as hip joints and bone plates, are prone to undergo fretting fatigue failures during their service within the body. This article presents the fretting fatigue damage characterization of physical vapor deposition (PVD) TiN-coated biomedical titanium alloys (Ti-6Al-4V and Ti-6Al-7Nb) subjected to cyclic loads. The PVD TiN layer delayed the damage because of superior tribological properties compared with uncoated alloys. Delamination and abrasive wear damage of TiN at contact caused failure of the alloy. Friction coefficient curves of the PVD TiN-coated pair showed an irregular pattern caused by the influence of wear particulates and Ringer fluid at the contact.

Keywords biomaterials, fretting fatigue, physical vapor deposition (PVD) coatings, titanium alloys

1. Introduction

Components during service commonly encounter surface degradation due to corrosion, wear, and fretting. Wear and fretting normally begin when two contacting surfaces rub each other under normal load, causing shear force to act on the surface. Fretting is defined as a wear mechanism caused by very small oscillatory motion between two interacting surfaces under normal load (Ref 1). The result of fretting in engineering components under cyclic load is the reduction of life by premature initiation and propagation of cracks within the contact area.

It is generally understood from many years of medical investigation and experience that human joints, such as hip, knee, or shoulder joints, are highly prone to degeneration, leading to the acute pain and joint stiffness commonly termed as osteoarthritis. Osteoarthritis develops slowly over several years. The symptoms are mainly pain, swelling, and stiffening of the knee (Ref 2). This is generally caused by gradual degradation of membrane properties of the joints. Therefore, these load-bearing joints necessitates arthroplastic surgery involving complete replacement of diseased joint with biocompatible materials developed with metals, ceramics, and plastics. Biomedical-grade titanium alloys such as Ti-6Al-4V and Ti-6Al-7Nb are commonly used for artificial hip and knee joints because of their excellent biocompatibility and corrosion resistance. However, they are highly prone to fretting and wear damage during their service within the human body. Tapered contacts, frequently termed as modular junctions of hip prostheses (Fig. 1a), fret during walking movements and release debris, invoking hostile tissue response from the region surrounding the implants (Ref 3). Figure 1(b) shows the fretting area in bone plates. Elements such as Al and V are also known to cause neurological disorders and cytotoxicity (Ref 4-6). Fretting fatigue of titanium alloys also dramatically reduces fatigue life well below the yield stress (Ref 7). Kamachi et al. (Ref 8) have made an extensive analysis of failure of stainless steel orthopedic devices. According to their assessment, 74% of the hip implants failed at the femoral neck region due to fretting fatigue.

Load-bearing bioimplants are generally surface treated using, for example, physical vapor deposition (PVD) to improve wear resistance. Many other specialized techniques of surface modification are available, such as chemical vapor deposition (CVD), plasma nitriding, ion implantation, and thermal oxidation, for bioimplant applications. PVD coatings involve developing hard coatings on the surface of any material in a vacuum by deposition of evaporated coating material on the target substrate. PVD titanium nitride coatings are commonly used for industrial tools as well as bioimplants because of its high hardness, biocompatibility, and corrosion resistance within the biofluids. Nan et al. (Ref 9) have studied the fatigue behavior of titanium-based biomaterial coated with 1.4 μm titanium nitride by ion beam-enhanced deposition. Shenhar et al. (Ref 10) have characterized residual stresses and fretting wear behavior of 2 μm TiN coating developed on surgical titanium alloys using the powder immersion reaction-assisted coating (PIRAC) method. A major reduction in fretting damage was reported from the coated alloys. TiN coatings are characterized by high abrasion resistance, low coefficient of friction, and high hardness. TiN film with (111) preferred orientation has the highest hardness, which is also governed by its thickness and residual stresses (Ref 11). Therefore, an increase in film thickness increases the hardness because the increase in the thickness normally produces good packing of the film and increases the packing factor (Ref 12). The interfacial adhesion of coatings can be evaluated through simple tensile tests (Ref 12).

Fretting fatigue studies of titanium alloys is more meaningful in a physiological medium that represents the composition of the body fluids. Ringer solution, phosphate-buffered saline solution (PBS), Hank's balanced salt solution (HBSS) are some

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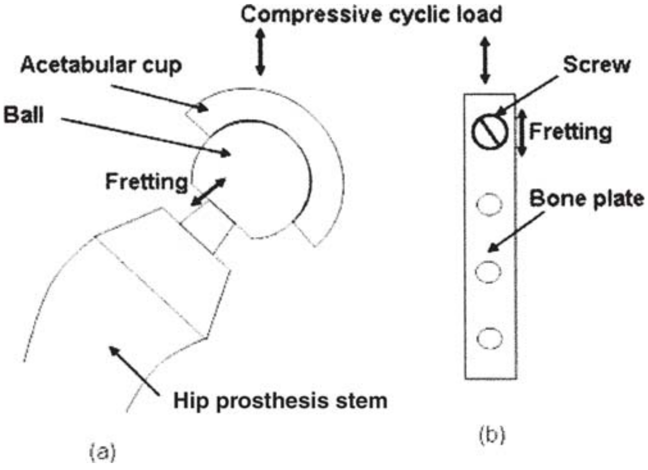


Fig. 1 Fretting fatigue areas in (a) hip joint and (b) bone plate

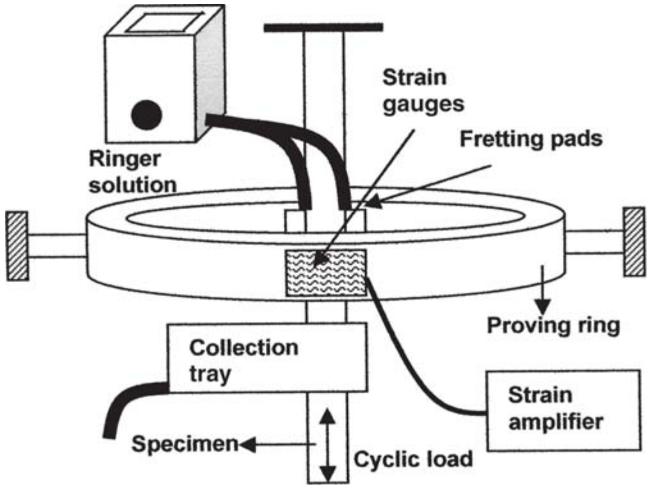
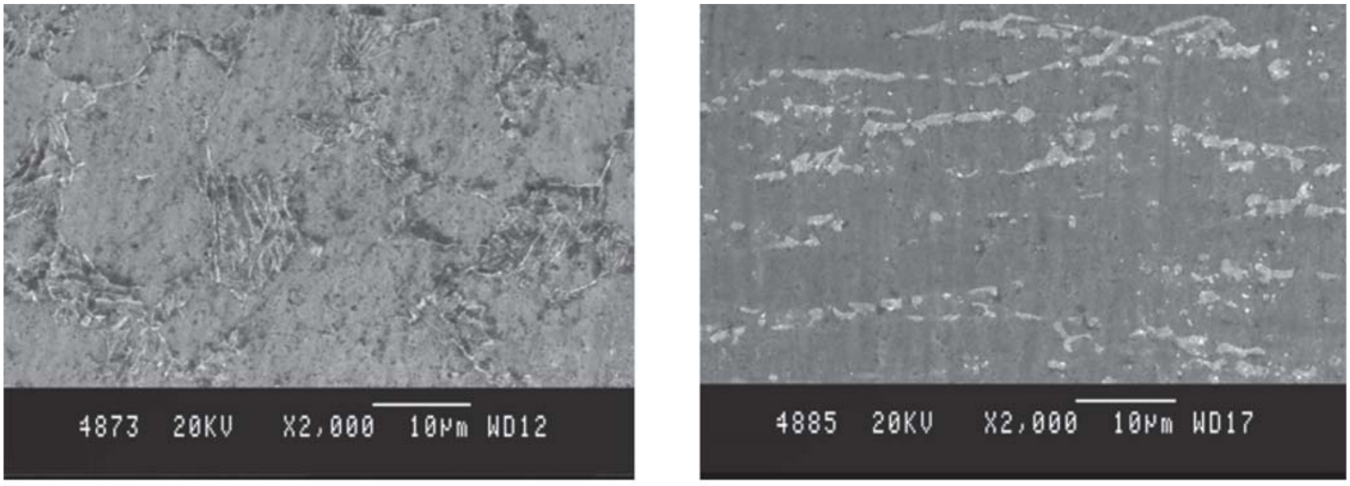


Fig. 2 Fretting fatigue experimental setup



(a) **(b)**

Fig. 3 SEM micrographs of (a) Ti-6Al-4V and (b) Ti-6Al-7Nb

of the widely accepted mediums for preliminary biomaterial fretting fatigue studies (Ref 12). Ringer solution is a saline medium with the following composition: NaCl (6.5 g/L), KCl (0.14 g/L), $CaCl_2$ (0.12 g/L), $NaHCO_3$ (0.2 g/L), and dextrose (0.4 g/L) (Ref 13). Starosvetsky and Gotman (Ref 14) have studied the corrosion behavior of 1 μm titanium nitride coating on Ni-Ti alloy in Ringer solution. Duisabeau et al. (Ref 15) have conducted fretting wear tests for Ti-6Al-4V and AISI 316L stainless steel in Ringer solution. The presence of a solution containing chloride ions activates a localized corrosion phenomenon, which leads to modification of the displacement regimen. In the current investigation, an attempt has been made to study the fretting fatigue behavior of PVD TiN-coated Ti-6Al-4V (fatigue specimens) and Ti6Al-7Nb (contact pads) in Ringer solution. The damage profile is studied with optical and scanning electron microscopy (SEM) micrographs and friction coefficient curves.

2. Experimental Details

Hot-rolled and annealed Ti-6Al-4V bars of dimensions 200 × 60 × 10 mm were procured from Vikram Sarabhai Space Center (VSSC, Tivandrum, Kerala State, India), and a Ti-6Al-7Nb rod of diameter 16 mm and length 127 mm was procured from Carpenter Technology Corp. (Wyomissing, PA). Fatigue specimens and fretting pads were profile cut with wire electrical discharge machining (EDM) as shown in Fig. 2 from Ti-6Al-4V and Ti-6Al-7Nb alloys, respectively. Both the specimens and pads were polished to mirror finish with alumina slurry (3 μm) and diamond paste (0.5 μm) and were later ultrasonically cleaned before the application of surface treatments.

For PVD TiN coating, the pads and the specimens were placed in a vacuum chamber maintained at a vacuum level of 10^{-4}. The samples were initially preheated to 280 °C and later bombarded with Ar and H (3:1 mixture) ions to clean the surface prior to deposition. The cathodic arc process evaporates the coating material from the commercially pure (CP) titanium disc target (100 mm diameter). When this material is evaporated, a high percentage of it is ionized. An electrical charge is then applied to the substrate (~250 V), which draws the ions to the surface. Nitrogen gas is steadily maintained at the pressure of 15 Pa within the chamber. The evaporated material reacts with nitrogen gas to form TiN. The process is continued until the required coating thickness (2 μm) has been obtained. The

Table 1 Mechanical properties of titanium alloys

Property	Ti-6Al-4V	Ti-6Al-7Nb
UTS, MPa	895	1027
YS, MPa	825	910
% El	10	17
% RA	20	48
Hardness, R_c	37	35

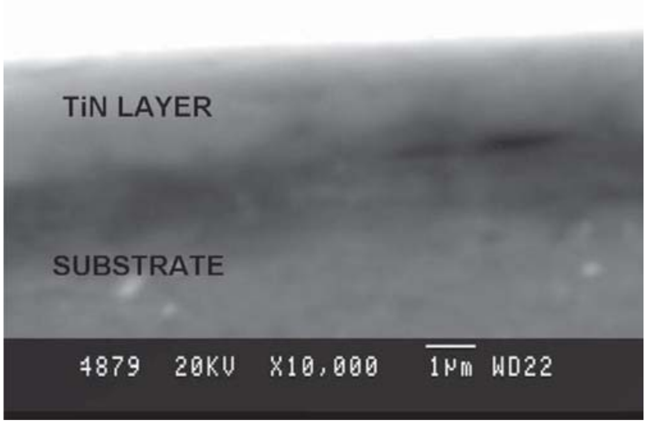


Fig. 4 SEM micrograph of TiN layer

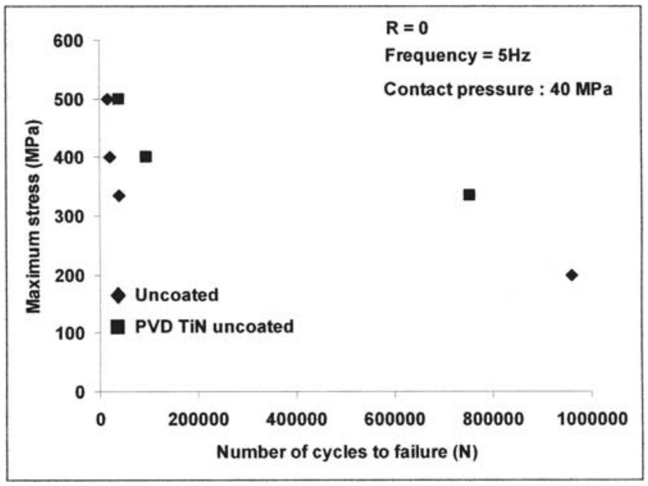


Fig. 5 *S-N* curve indicating the reduction in life caused by fretting

substrate was allowed to cool and later removed from the chamber. The TiN layer was characterized by SEM, profilometry, nanoindentation, and scratch testing.

Flat-on-flat contact fretting fatigue tests were conducted in a 100 kN DARTEC servohydraulic UTM. Fretting action was applied through the calibrated proving ring-contact pad arrangement (Fig. 2). The proving ring was calibrated according to ASTM E-74-02, which gives the standard practice for calibrating and verifying force measuring instruments. A network of strain gauges was affixed along the circumferential outer portion of the ring and underside of each of the pads. Calibration of the proving ring involved applying a series of tensile loads and recording the stain values corresponding to each load. The ring was calibrated in the servohydraulic UTM, and the pads were calibrated with a force transducer mounted on it. A multichannel strain amplifier was used to record the strains from the ring as well as pads. Friction coefficient curves were obtained from tangential and normal forces recorded from ring and pads. Cyclic loads of 3-7.5 kN at 5 Hz were applied during the test. A 40 MPa contact pressure was applied throughout the test. Ringer solution, maintained with a heater at 37 °C, is continuously streamed over the top of the pads and collected in a container below (Fig. 2). The flow is adjusted to obtain complete immersion of contact area similar to that of hip joints surrounded by a continuous flow of physiological medium.

3. Results and Discussion

Figure 3 shows SEM micrographs of Ti-6Al-4V and Ti-6Al-7Nb, respectively. The lamellar $\alpha + \beta$ colony of Ti-6Al-4V is more resolved compared with Ti-6Al-7Nb, with greater primary α size. Because the alloy is hot-rolled and annealed, it shows bimodal structure with primary α within the $\alpha + \beta$ matrix. Bimodal morphologies are generally known for high ductility and fatigue strength with well-balanced properties due to the combined influence of lamellar and equiaxed microstructures. Aluminum stabilizes the close-packed hexagonal (cph) α phase, and Nb and V stabilize the body-centered cubic (bcc) β phase in these alloys. Fatigue lives are also governed by the volume fraction of microstructural features. Initiation of fretting cracks is mostly localized along the weak points of the α-α or α-β interface (Ref 16). Table 1 gives the mechanical properties of titanium alloys. Ti-6Al-7Nb has higher strength and ductility compared with Ti-6Al-4V alloy.

Figure 4 shows an SEM micrograph of TiN layer on titanium alloy substrate. The average roughness of TiN surface was 0.3 µm. The adhesion strength of TiN layer was found to be 90 N. Nanoindentation studies show that the hardness and elastic modulus of the layer were 40 and 332 GPa, respectively.

A stress-to-number of cycles plot for fretting fatigue tests is shown in Fig. 5. PVD TiN-coated alloys improved the fretting fatigue life significantly compared with uncoated alloys. A large difference in fretting fatigue lives between uncoated and PVD TiN-coated pairs is observed with decreasing cyclic stress because the severity of fretting is more prominent at higher cyclic stresses. The TiN coating is hard and brittle by nature and is easily damaged at higher cyclic stresses due to its inherent inability to accommodate larger strains compared with the base material.

Figure 6(a) and (b) shows the fretting damage of uncoated alloys. Fretting direction is indicated by an arrow in Fig. 6(b) and (d). It can be clearly observed that uncoated alloys suffered severe damage from fretting. Oxidation and particle transfer commonly occurs during fretting of materials made of similar alloys. EDS spectra of this region also indicated a Nb peak, providing evidence of the transfer of wear particles from the pad material.

Figure 6(c) and (d) shows fretting damage of PVD TiN-coated alloy. The TiN coating has shown better fretting resistance compared with uncoated alloy. This is one of the localized areas along the surface. Damage cannot be similar at all the points because of the differences in contact behavior. At some areas, they were completely covered with heavy oxides. At higher magnification, delamination could also be observed along the failure edge, as shown in Fig. 6(d). TiN particulates can subsequently behave as abrasives in the contact zone when separated from the substrate. Oxidation, delamination, and particle transfer were common features of both TiN and uncoated

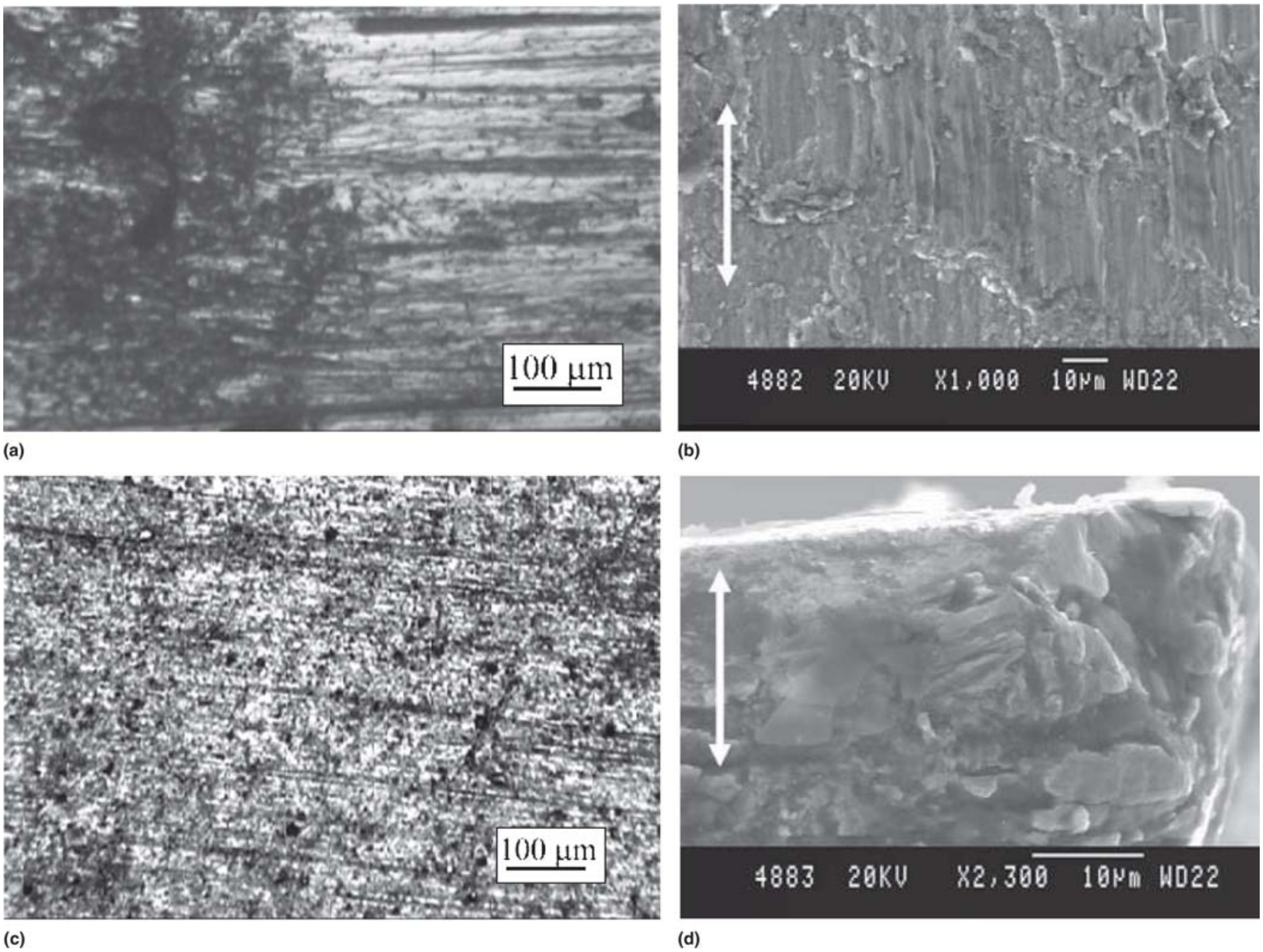


Fig. 6 Fretting scars of (a, b) uncoated and (c, d) TiN-coated Ti-6Al-4V at 500 MPa cyclic stresses

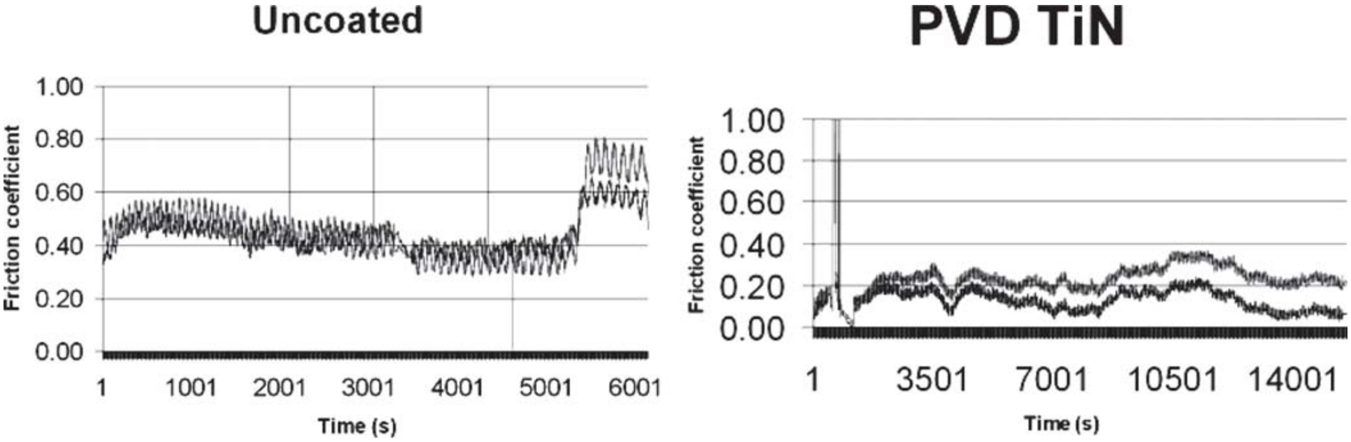


Fig. 7 Friction coefficients during fretting fatigue of (a) uncoated and (b) PVD TiN-coated alloy at 500 MPa axial loads

alloys. In the case of TiN, the damage severity is delayed compared with uncoated alloys due to superior tribological properties of the TiN layer, as explained earlier. The average roughness of fretted regions increased to 0.83 μm for uncoated alloys and 0.76 μm for TiN-coated alloys.

Figure 7(a) shows the friction coefficient curves for uncoated pairs. The friction coefficient for uncoated pairs varied from 0.3 to 0.8. The coefficient of friction between similar materials is always high due to high metallurgical compatibility. The initial increase in the friction coefficient is due to interaction of surface asperities of the contact pairs. High friction normally induces multiple cracks by plastic deformation of subsurface layer leading to generation of debris particles. The friction coefficient gradually decreased to 0.3 from 0.6 due to the combined influence of oxides and Ringer fluid. Oxidation and flow of Ringer fluid offer lubrication at the contact.

Figure 7(b) shows the friction coefficient curves for PVD TiN-coated pairs. The friction coefficient varied irregularly below 0.4 for PVD TiN-coated alloys. Initial variation in friction is generally due to interaction between surface asperities. Debris formed from these asperities contributes to further wear of TiN layer. High-friction events at the later stages can be attributed to delamination combined with third-body wear. Large variations in the friction coefficient between the TiN pairs are due to combined influence of TiN particulates, Ringer fluid, and oxides at the contact. It is difficult to understand the individual contribution of each of the above factors because the contact behavior is more complex compared with uncoated alloys.

4. Conclusions

- Fretting fatigue is a deleterious wear mechanism that leads to catastrophic failures of a loaded structure without warning. It is governed by several inter-related variables, which makes the process difficult to quantify. The main variables are the normal pressure and slip amplitude.
- Fretting damage of uncoated alloys is characterized by oxidation and particulate transfer due to the high metallurgical compatibility of the mating pairs. The friction coefficient is governed by the presence of oxides and Ringer fluid at the contact.
- PVD TiN coatings improved the fretting fatigue life of the titanium alloy. Improvement is achieved through delayed damage of the TiN coatings. The detached particles during fretting act as potential abrasives for further damage. TiN coatings exhibited reduced friction throughout the test compared with uncoated alloys.

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References

1. R.B. Waterhouse, Fretting Variables, *Fretting Corrosion*, Pergamon Press, 1972
2. J.D. Pomonis, J.M. Boulet, S.L. Gottshall, S. Phillips, R. Sellers, T. Bunton, and K. Walker, Development and Pharmacological Characterization of a Rat Model of Osteoarthritis Pain, *Pain,* 2005, **114**(3), p 339-346
3. M. Sumita, T. Hanawa, I. Ohnishi, and T. Yoneyama, Failure Processes in Biometallic Materials, *Compr. Struct. Integ.,* 2003, **9,** p 131-167
4. N.J. Hallab and J.J. Jacobs, Orthopedic Implant Fretting Corrosion, *Corros. Rev.,* 2003, **21,** p 183-214
5. S.H. Teoh, Fatigue of Biomaterials: A Review, *Int. J. Fatigue,* 2000, **22,** p 825-837
6. M. Long and H.J. Rack, Review: Titanium Alloys in Total Joint Replacement - A Material Science Perspective, *Biomaterials,* 1998, **19,** p 1621-1639
7. R.A. Antoniou and T.C. Radtke, Mechanism of Fretting Fatigue of Titanium Alloys, *Mater. Sci. Eng. A,* 1997, **237,** p 229-240
8. U. Kamachi Mudali, T.M. Sridhar, N. Eliaz, and B. Raj, Failures of Stainless Steel Orthopedic Devices: Causes and Remedies, *Corros. Rev.,* 2003, **21,** p 231-267
9. H. Nan, C. Yuanru, C. Guangjun, L. Chenggang, W. Zhongguang, Y. Guo, S. Huehe, L. Xianghuai, and Z. Zhihong, Research on the Fatigue Behavior of Titanium Based Biomaterial Coated with Titanium Nitride Film by Ion Beam Enhanced Deposition, *Surf. Coat. Technol.,* 1996, **88,** p 127-131
10. A. Shenhar, I. Gotman, S. Radin, P. Ducheyne, and E.Y. Gutmanas, Titanium Nitride Coatings on Surgical Titanium Alloys Produced by a Powder Immersion Reaction Assisted Coating Method: Residual Stresses and Fretting Behavior, *Surf. Coat. Technol.,* 2000, **126,** p 210-218
11. W.-J. Chou, G.-P. Yu, and J.-H. Huang, Mechanical Properties of TiN Thin Film Coatings on 304 Stainless Steel Substrates, *Surf. Coat. Technol.,* 2002, **149,** p 7-13
12. T. Ohmura and S. Matsuoka, Evaluation of Mechanical Properties of Ceramic Coatings on a Metal Substrate, *Surf. Coat. Technol.,* 2003, **169,** p 728-731
13. L. Thair, U.K. Mudali, S. Rajagopalan, R. Asokamani, and B. Raj, Surface Characterization of Passive Film Formed on Nitrogen Ion Implanted Ti-6Al-4V and Ti-6Al-7Nb Alloys Using SIMS, *Corros. Sci.,* 2003, **45,** p 1951-1967
14. D. Starosvetsky and I. Gotman, Corrosion Behavior of Titanium Nitride Coated Ni-Ti Shape Memory Surgical Alloy, *Biomaterials,* 2001, **22,** p 1853-1859
15. L. Duisabeau, P. Combrade, and B. Forest, Environmental Effect on Fretting of Metallic Materials for Orthopedic Implants, *Wear,* 2004, **256,** p 805-816
16. J. Takeda, M. Niinomi, T. Akahori, and Gunawarman, Effect of Microstructure on Fretting Fatigue and Sliding Wear of Highly Workable Titanium Alloy, Ti-4.5Al-3V-2Mo-2Fe, *Int. J. Fatigue,* 2004, **26,** p 1003-1015