
Wear-accelerated corrosion of Ti-6Al-4V and nitrogen-ion-implanted Ti-6Al-4V: Mechanisms and influence of fixed-stress magnitude

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Wear-accelerated corrosion rates at constant anodic potentials were evaluated for unimplanted and nitrogen-ion-implanted surgical Ti-6Al-4V while wearing against ultrahigh-molecular-weight polyethylene at stress levels up to 6.90 MPa (1000 psi). The ion implantation processing was found to reduce the wear corrosion rates in both saline and serum solutions at all applied stress levels. During wear testing, all of the ion-implanted surfaces remained visually

unchanged from the polished condition. However, many of the unimplanted surfaces developed damage zones characterized by wear tracks and black wear debris. A surface-damage mechanism is proposed and discussed which involves disruption of the Ti-6Al-4V protective oxide film, subsequent entrapment of oxide particles in the polyethylene, then self-perpetuating damage due to the abrasive action of the embedded particles.

INTRODUCTION

Ion implantation processing of the articulating surfaces of Ti-6Al-4V orthopedic joint prostheses offers the potential of significantly improving the wear resistances of both the alloy and the ultrahigh-molecular-weight polyethylene (UHMWPE) mating material.^{1,2} The ion implantation process offers several unique advantages over other surface modification techniques.^{3,4} With ion implantation, the properties of the near-surface volume can be enhanced through both chemical and structural modifications performed at room temperature with no distortions or changes in surface finish. Furthermore, no chemical or structural interface is created between the enhanced surface volume and the substrate material. On the contrary, a gradual transition in chemistry, structure, and properties is produced. Consequently, concerns about high-temperature processing and subsequent loss of sub-

strate properties, as well as concerns regarding interfacial cracking and spalling of applied coatings, are in effect negated.

With work beginning in 1981, the concept of utilizing ion implantation as a means to improve the corrosive wear behavior of surgical Ti-6Al-4V was introduced with supporting experimental data in 1983 by Buchanan, Bacon, Williams, and Beardsley.⁵ This and subsequent studies have compared the wear-accelerated corrosion behavior of unimplanted and nitrogen-ion-implanted surgical Ti-6Al-4V under *in vitro* conditions simulating the total artificial hip.^{1,6-10} In these investigations, a nominal stress of 2.30 MPa (333 psi) was applied with UHMWPE wear-pads rotating against samples of Ti-6Al-4V at an interfacial velocity of 5.0 cm/s. These parameters simulated an artificial hip under average walking conditions.¹¹⁻¹³

The purpose of the present study was to evaluate the wear corrosion behavior of Ti-6Al-4V at a number of applied stresses up to 6.90 MPa (1000 psi). The impetus for this work relates to the actual service conditions of articulating orthopedic implant devices such as total artificial hips and knees. The actual wear stress experienced by a device depends on a number of factors, including the type of device, and the body weight, level of activity, and type of activity associated with the patient. Furthermore, a given device in a given patient would be expected to experience a range of stress levels from zero to high values over any given time period, e.g., a day, year, or lifetime.

EXPERIMENTAL PROCEDURES

The wear-accelerated corrosion properties of surgical Ti-6Al-4V were evaluated with a test apparatus previously described in the literature, and schematically illustrated in Figure 1.¹⁴ Nominal contact stresses were applied with UHMWPE wear-pads at the same interfacial velocity as in previous studies, 5.0 cm/s. Either of two electrolytes was employed: isotonic saline (0.9% NaCl in distilled water) or 10% calf serum (GIBCO 200-6170) in isotonic saline, both at $37 \pm 1^\circ\text{C}$ and a pH of 7.00 ± 0.05 . Both electrolytes were continuously aerated with oxygen.

The ELI-grade Ti-6Al-4V material employed in this study conformed with ASTM F136-79 and had the following chemical composition: Ti, 6.07% Al, 4.07% V, 0.179% Fe, 0.02% C, 0.115% O, 0.009% N, and 0.0030% H. The tensile properties were: 943 MPa (136.7 ksi) ultimate tensile strength, 886 MPa (128.5 ksi) yield strength, 15% elongation, and 48% reduction in area. The UHMWPE had a molecular weight of 4.3×10^6 as measured by the intrinsic viscosity (IV) technique and tensile properties of 44.0 MPa (6.38 ksi) ultimate tensile strength, 23.7 MPa (3.44 ksi) yield strength, and 220% elongation. The surface preparation for the Ti-6Al-4V samples consisted of mechanical grinding and polishing to produce an average surface roughness of $0.3 \mu\text{m}$ RMS as measured by profilometry. All UHMWPE wear-pads had machined wearing surfaces with roughness values in the $6\text{--}8\text{-}\mu\text{m}$ RMS range.

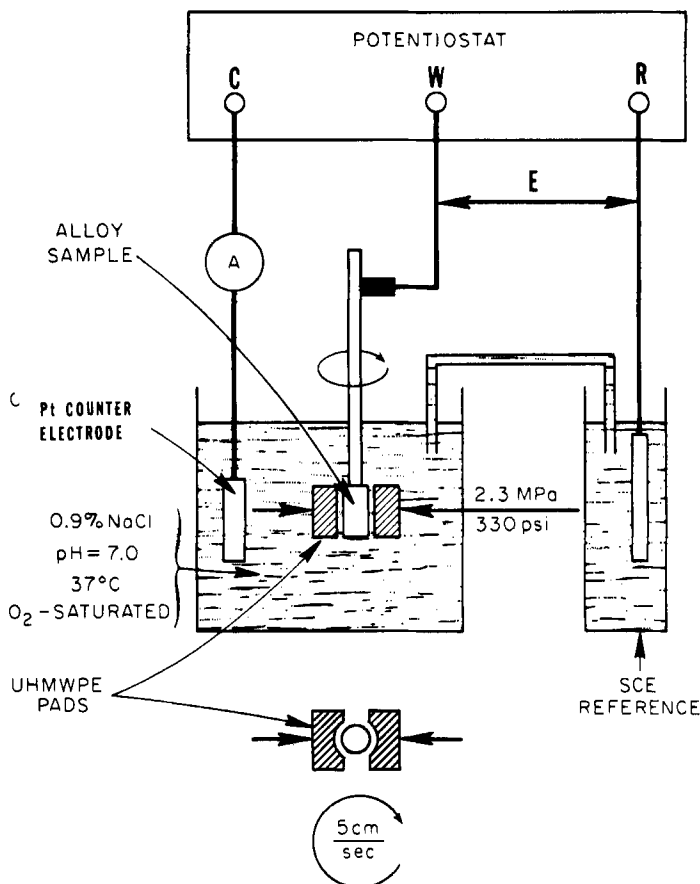


Figure 1. Corrosive wear test apparatus.

The ion implantation processing was performed with facilities in the Solid State Division, Oak Ridge National Laboratory. The nitrogen was implanted by utilizing a graded-energy technique. The ions were first implanted at 60 KeV with a fluence of 1.3×10^{17} ions/cm², then at 35.0 KeV with a fluence of 3.2×10^{16} ions/cm², and finally at 17.5 KeV with a fluence of 2.0×10^{16} ions/cm². This graded-energy technique provided a more uniform implanted-element concentration through the near-surface volume than would have been achieved by a single-energy implantation procedure, and produced an average 20 atomic % concentration through a surface-layer thickness of approximately 1000 Å.

In conducting each wear corrosion test, a sample was placed in the electrolyte and allowed to stabilize for 10 min while under rotation. The stress was then applied and the change in open-circuit corrosion potential noted. The sample potential was then potentiostatically set at a preselected anodic value. For the control samples, the anodic potential employed was -100 mV vs. saturated calomel electrode (SCE), and for the ion-implanted samples, +300 mV versus SCE. In each case, the value represented a change in

potential of approximately 550 mV in the anodic direction relative to the open-circuit corrosion potential under wear. While at the set potential, the anodic current density was measured at 2, 4, 6, 8, and 10 min, and averaged. The current density was a direct measure of the wear-accelerated corrosion rate under conditions enhanced by the applied anodic potentials.

RESULTS

The corrosion current densities produced by Ti-6Al-4V while wearing against UHMWPE at nominal stresses from zero to 6.90 MPa (1000 psi) are shown in Figure 2 for the saline electrolyte and in Figure 3 for the serum/saline electrolyte. Because considerable scatter was observed in the results, a large number of independent data points was generated.

With regard to the saline electrolyte, it is seen that applied stresses up to 6.90 MPa (1000 psi) had virtually no effect on the corrosion behavior of the nitrogen-ion-implanted Ti-6Al-4V. However, significant effects were observed for the unimplanted material. The wear stress was seen to accelerate corrosion by factors ranging up to approximately 1000. There did not appear to be a stress dependency *per se* in these results; but rather, at any of the stress levels evaluated the corrosion rate of the unimplanted material could be significantly greater than its zero-stress or static value. At the higher

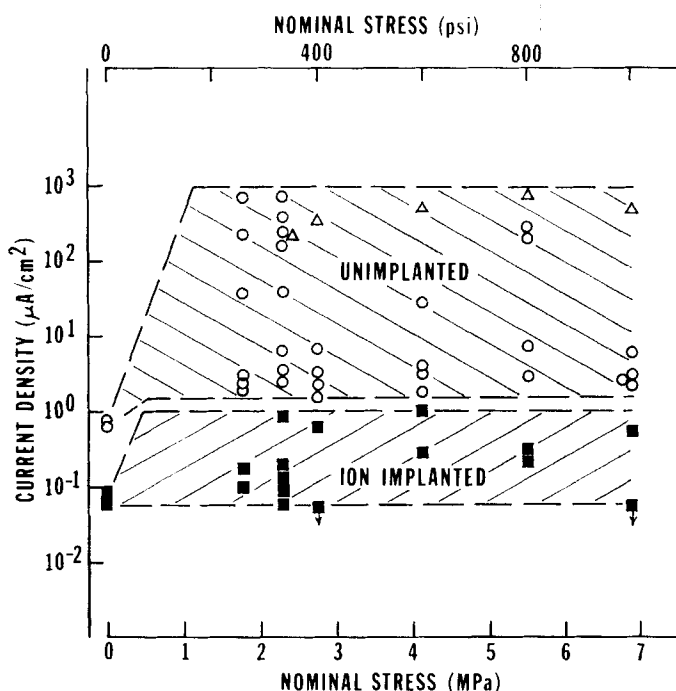


Figure 2. Average anodic current densities in saline solution as a function of nominal wear stress. \circ , \blacksquare Against PE, \triangle against SiC.

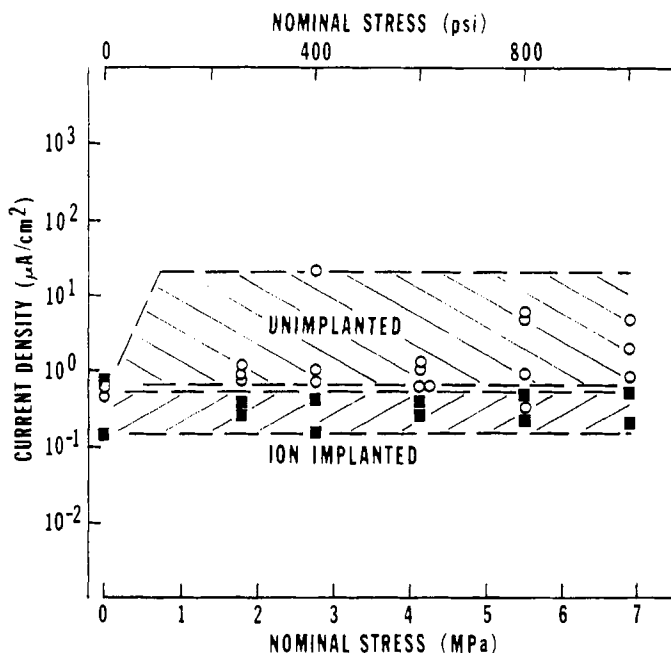


Figure 3. Average anodic current densities in serum solution as a function of nominal wear stress.

corrosion current densities, especially above approximately $10 \mu\text{amps}/\text{cm}^2$, the surface damage on the Ti-6Al-4V samples was visually obvious. Thin black bands of wear debris would initiate, then grow in width with time, as schematically indicated in Figure 4(a). A photograph of such a sample is presented in Figure 4(b). At a given stress level, the magnitude of the measured corrosion current was proportional to the extent of visual surface damage produced by this wear process. None of this surface damage was observed on any of the ion implanted samples.

In the serum electrolyte, Figure 3, again, the increasing stress levels had no effect on the wear corrosion behavior of the ion implanted material. The unimplanted control material demonstrated higher wear corrosion rates, but not as high as in the saline electrolyte. There was not an obvious stress dependency in the control results; but rather, as in the saline results, it appeared that a range of wear-accelerated corrosion rates was possible at all stress levels evaluated. Although the surface-damage features illustrated in Figure 4 were observed with the higher corrosion-current-density control samples in the serum electrolyte, they generally were less pronounced than in the saline electrolyte.

In order to gain more insight into the surface-damage mechanism associated with the unimplanted control material, additional wear corrosion tests were conducted with the Ti-6Al-4V wearing against an extremely abrasive material—600-grit SiC. Strips of 600-grit SiC grinding paper were cemented to the UHMWPE wear-pads. The tests were conducted in saline electrolyte

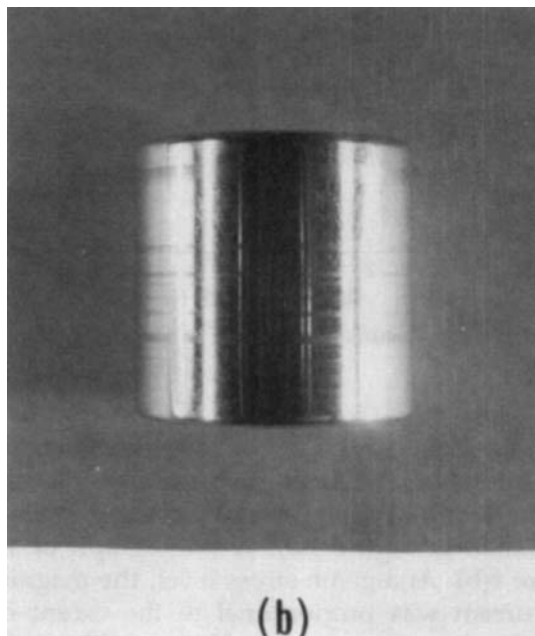
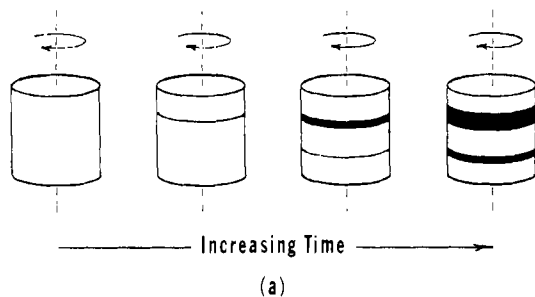


Figure 4. (a) Illustration of wear band development, (b) wear band development on Ti-6Al-4V.

under the same conditions as previously described. These results are also shown in Figure 2. It is noted that the wear corrosion rates produced by 600-grit SiC are at the top of the range of rates produced by UHMWPE, and that there appeared to be no obvious stress dependency. During this testing, black wear debris was generated over the entire Ti-6Al-4V wearing surface.

In previous studies, a limited number of anodic polarization curves had been generated for Ti-6Al-4V while wearing against UHMWPE at a nominal stress of 2.30 MPa (333 psi). Again, in order to gain insight into the surface-damage mechanism, a partial anodic polarization curve was generated for Ti-6Al-4V while wearing against 600-grit SiC at 2.30 MPa. These results are shown in Figure 5 along with static (nonwear) anodic polarization curves for Ti-6Al-4V in the nonpassivated and prepassivated (ASTM F86) conditions. It is seen that the wear against UHMWPE produced corrosion behavior which

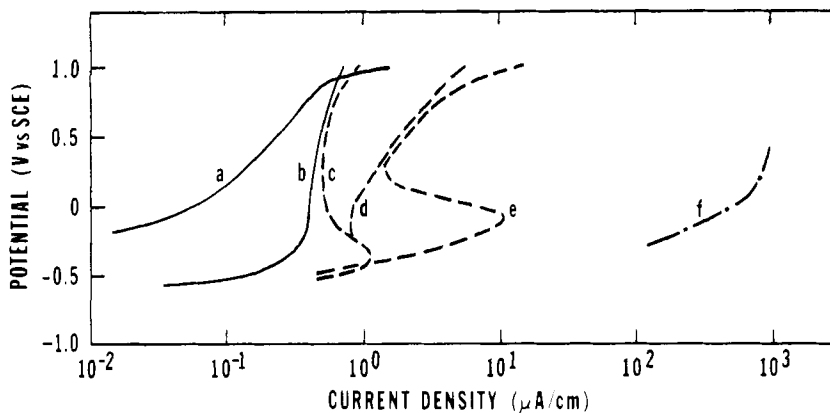


Figure 5. Anodic polarization curves for Ti-6Al-4V in saline solution: (a) static, prepassivated, deaerated solution; (b) static, nonpassivated, deaerated solution; (c, d, e) wear against UHMWPE with different degrees of surface damage, aerated solution; (f) wear against 600-grit SiC, aerated solution.

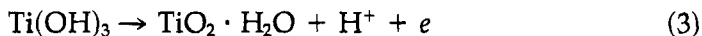
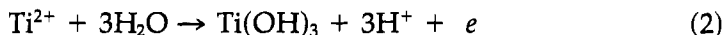
varied between the static values and the very high values associated with wear against SiC. The variability in the UHMWPE results were directly correlatable with the observed amounts of black wear debris on the Ti-6Al-4V surface, i.e., the greater the amount of black wear debris, the higher the measured corrosion current density.¹¹ In order to demonstrate the magnitude of the effects herein described, application of Faraday's law shows that a current density of 1000 $\mu\text{amps}/\text{cm}^2$ is equivalent to a corrosion penetration rate of 0.9 cm/year for Ti-6Al-4V.

DISCUSSION

To rationalize the results presented, one must first consider the observed behavior of the unimplanted Ti-6Al-4V. Furthermore, one must realize that the measurements in this study were of electrochemical corrosion rate, i.e., the rate at which material in the solid, principally titanium, was being lost through oxidation to ions, hydroxides, oxides, or other species. The study did not measure the amount of material lost through the strictly mechanical effects of wear. To emphasize this point—if a particle of material were removed, the corrosion rate would increase in proportion to the area of unprotected surface thus created (i.e., in proportion to the area of passive film removed), not in proportion to the total volume of material removed. Indeed, there has been evidence in prior studies that considerably more material is removed from the unimplanted Ti-6Al-4V than is predicted by the wear-accelerated corrosion rates.¹

In the case of titanium in an aqueous solution at a pH of 7 and over a range of electrochemical potentials normally observed under nonwear conditions, the thermodynamically stable situation consists of a TiO_2 or $\text{TiO}_2 \cdot \text{H}_2\text{O}$ pro-

protective surface film, or passive film. With the aid of the titanium Pourbaix diagram,¹⁵ one can predict the following sequence of reactions when the passive film is removed:



Other oxidation reactions are possible in the biological environment, e.g., complexing with proteins, enzymes, or other chemical species such as chlorine, phosphate, etc.

For the unimplanted Ti-6Al-4V alloy of the present study, while wearing against the very abrasive 600-grit SiC, it is assumed that the protective oxide film was totally and continuously removed, giving rise to the extremely large current densities shown in Figures 2 and 5. Obviously, the titanium-alloy substrate is extremely reactive; and if the oxide film is removed, very large corrosion rates will be produced. There was no stress dependency for the wear-accelerated corrosion rates against SiC, Figure 2, because the oxide film was completely removed under the SiC wear-pads at all stress levels evaluated.

For the wear corrosion of unimplanted Ti-6Al-4V against UHMWPE, it is proposed that partial removal of the oxide film is involved, and furthermore that the mechanism, once started, is self-perpetuating. With reference to the schematic drawings in Figure 6, it is hypothesized that a local or microevent occurs which results in removal of the oxide film, and that in this small area the oxide particles become embedded in the softer UHMWPE. As relative movement continues, the small band of Ti-6Al-4V substrate remains unprotected because of the abrasive action illustrated, and grows in width due to abrasion at the band edges. The corrosion current density measured would be directly proportional to the amount of unprotected surface area.

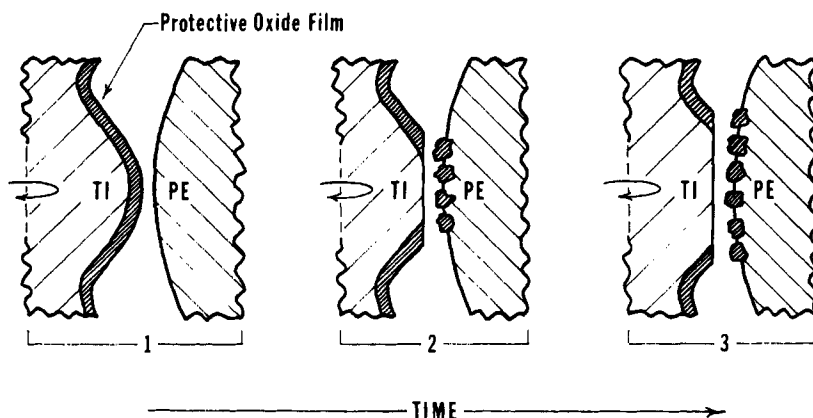


Figure 6. Proposed surface-damage mechanism: Ti-6Al-4V wearing against UHMWPE.

The microevents responsible for initiating the wear bands would be independent of each other. Their probability of occurrence would be statistical in nature and would depend on local surface geometries, local true contact stresses, local impact effects, local oxide film characteristics, and the degree and kinetics of polyethylene film transfer to the Ti-6Al-4V (if present). Over the conditions of the present study, the localized effects responsible for initiation of the wear bands were apparently more dominant than the controlled variations in nominal contact stress, such that no obvious nominal stress dependency was found (Figs. 2, 3). However, at a given stress level, the local effects controlled the initiation and subsequently the amount of wear corrosion damage from sample to sample. In comparing the generally less-severe serum electrolyte results (Fig. 3) with the saline electrolyte results (Fig. 2) for the unimplanted material, it is hypothesized that the large serum protein molecules acted to cushion or lubricate the interface between the UHMWPE and the oxide film on the Ti-6Al-4V, such that the microevent associated with wear band initiation was less likely to occur over the time interval employed in this study. However, as seen in Figure 3, the presence of serum protein molecules did not eliminate the wear corrosion effect. Furthermore, it could be argued that longer time intervals would lead to an enhanced probability that the self-perpetuating surface-damage mechanism would develop.

For the nitrogen implanted Ti-6Al-4V under the conditions of this study, in both saline and serum electrolytes, and in accordance with the proposed model under discussion, the protective film was never significantly disturbed or removed over the range of nominal stresses evaluated. Furthermore, since the film was not significantly disturbed, it follows that the underlying Ti-6Al-4V substrate was not subjected to mechanical wear. Consequently, it is hypothesized that one major effect of the nitrogen-ion-implantation process is to lead to major modifications in the character of the protective oxide film on Ti-6Al-4V. The modified film, possibly a titanium oxynitride rather than titanium oxide, is significantly more resistant to localized mechanical damage while still conferring a high level of corrosion protection. This modified passive film which is postulated to develop on nitrogen-ion-implanted Ti-6Al-4V has also been suggested by Hutchings and Oliver based on the results of their comparative mechanical wear studies.¹⁶

CONCLUSIONS

The wear-accelerated corrosion characteristics of unimplanted and nitrogen ion implanted surgical Ti-6Al-4V were evaluated as functions of applied nominal stress up to 6.90 MPa (1000 psi) against UHMWPE. Both saline and serum solutions were employed in this *in vitro* study. The wear corrosion rate for the ion-implanted material remained low and constant at all stress levels in both solutions. This result supplements the growing body of knowledge regarding the beneficial effects which can be achieved through ion

implantation of the articulating surfaces of Ti-6Al-4V orthopedic implants. The wear corrosion rate for the unimplanted material was higher, but showed no nominal stress dependence *per se*. Rather, the wear corrosion rate was found to vary significantly at each stress level from test-to-test. A surface-damage mechanism consistent with these results was proposed, and resulted in a tentative conclusion that one of the effects of the nitrogen ion implantation process is to lead to major modifications in the character of the protective oxide film on Ti-6Al-4V.

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