The electrochemical and mechanical behavior of passivated and TiN/AlN-coated CoCrMo and Ti6Al4V alloys

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Received 21 February 2003; accepted 14 July 2003

Abstract

The mechanical and electrochemical behavior of the surface oxides of CoCrMo and Ti6Al4V alloys during fracture and repassivation play an important role in the corrosion of the taper interfaces of modular hip implants. This behavior was investigated in one group of CoCrMo and Ti6Al4V alloy samples passivated with nitric acid and another group coated with a novel TiN/AlN coating.

The effects of mechanical load and sample potential on peak currents and time constants resulting from fracture of the surface oxide or coating, and the effects of mechanical load on scratch depth were investigated to determine the mechanical and electrochemical properties of the oxides or coating. The polarization behavior of the samples after fracture of the oxide or coating was also investigated.

CoCrMo had a stronger surface oxide and higher interfacial adhesion strength, making it more resistant to fracture than Ti6Al4V. If undisturbed, the oxide on the surface of Ti6Al4V significantly reduced dissolution currents at a wider range of potentials than CoCrMo, making Ti6Al4V more resistant to corrosion. The TiN/AlN coating had a higher hardness and modulus of elasticity than CoCrMo and Ti6Al4V. It was much less susceptible to fracture, had a higher interfacial adhesion strength, and was a better barrier to ionic diffusion than the surface oxides on CoCrMo and Ti6Al4V. The coating provided increased corrosion and fretting resistance to the substrate alloys.

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Keywords: Oxides; Mechanical properties; Corrosion; Surface modification; Scratch testing

1. Introduction

The oxides present on the surface of CoCrMo and Ti–Al–4V alloys are hard and compact, and provide wear and corrosion resistance to their parent alloys. However, these extremely thin films (≈ 1–4 nm) are susceptible to fracture due to scratches, dents, and fretting resulting from mechanical loading.

In an aqueous environment, oxide fracture produces oxide particles and exposes the reactive base alloy to water. Subsequent electrochemical events (oxidation) result in dissolution of the base alloy (producing metal ions) and reformation of the oxide film (repassivation), which produce current transients. During cyclic loading fretting of the contacting surfaces and corrosion continue and can lead to the release of large quantities of metal ions and oxide particles.

The structure and properties of the oxide film, substrate metal, and oxide–substrate interface may affect the oxide fracture process. The relevant properties include modulus of elasticity of oxide and substrate, hardness and thickness of the oxide film, and interfacial adhesion strength of the oxide–substrate interface. The important structural characteristics include the lattice mismatch between the alloy and oxide, morphology and chemistry of the oxide, and the defect structures within the oxide.

Fretting and corrosion have been observed in bone plates and screws, at the bone/stem and stem/cement interfaces of hip implants, and on the tapered interfaces of modular hip implants, and may also be occurring in titanium dental implants. Surface oxides and their
properties play a significant role in the fretting and corrosion processes that occur at the taper interfaces of modular hip implants. The mechanical properties and electrochemical behavior of the oxides affect the fracture/repassivation and corrosion processes and thus affect the degree of corrosion resistance they provide to the parent alloys.

Several investigators have developed methods for quickly fracturing oxide films and studying the subsequent repassivation events. Ratzer-Schiebe [1,2] and Buhl [3] used a microtome with an alumina knife to plane off a thickness of 5–50 μm from the surface of Ti6Al4V samples. Rubin [4] used a Vicker’s pyramidal hardness tester to create indentations in the surface of potentiostatically held titanium samples. These test methods involved disrupting the oxide on a potentiostatically held sample and measuring the resulting current transient to characterize the repassivation process. Fraker, et al. conducted repassivation studies of potentiostatically held samples of Ti6Al4V in Hanks’ solution at 37°C [5]. They used silicon carbide paper to remove the passive film and recorded the resulting anodic current transient immediately after film removal at applied potentials ranging from 600 to 7.0 V. In these studies, the applied load and area of oxide removed were not controlled. Ahila, Reynders, and Grabke used a sharpened quartz rod to scratch the surfaces of polished Cr–Mn and Cr–Ni steels in a deaerated Na2SO4/NaCl solution at a pH of 2.8, and record the resulting current transients due to repassivation [6]. Loads were not controlled.

Kolman and Scully [7] performed manual scratch tests and thin film fracture experiments on various titanium alloys in aqueous chloride solutions. The scratch test samples were imbedded in epoxy and the thin film fracture samples consisted of a 500 nm layer of titanium deposited onto a glass substrate. Current densities greater than 100 A/cm² were observed after fracture of titanium films in 0.6 M NaCl. In another study, they found the repassivation kinetics to be a function of depassivation speed, solution resistance, potentiostat response, and other factors [8]. The rate of oxide removal was shown to affect the shape of the current transient during repassivation. In scratch tests of Type 304 stainless steel in Na2SO4 solution, Bastek et al. [9] concluded that a large ohmic drop in the test solution could cause the filmed surface surrounding the scratch to decrease the peak current measured. Burstein and Gao [10] measured current transients produced by scratching rotating disk samples of AISI 304 stainless steel in deaerated 0.6 M NaCl and pure iron in deaerated 1.0 M K2CO3 solution. They found that the bare surface current density did not depend on the passive area surrounding the scratch.

Gilbert et al. [11] investigated the effects of scratch length, load, sample potential, solution pH, and aeration on the current transient response of potentiostatically held Ti6Al4V samples using a diamond stylus to fracture the surface oxide film. Goldberg and Gilbert [12] conducted similar investigations on CoCrMo samples. The methods they used to fracture the oxide and measure the resulting current transients were used in the present study.

Researchers have paid little attention to the mechanical and electrochemical behavior of oxide films and their importance to the in vivo corrosion process. Previous studies have investigated electrochemical behavior after oxide fracture [1–4,13,14]. Some of these studies have shown that sample potential, solution chemistry, and proteins [15] affect the repassivation process. However, only two attempted to characterize the mechanical properties of the oxide or its mechanical behavior during oxide fracture [11,12].

In order to understand fretting corrosion of medical and dental implants, it is important to determine the mechanical properties of the oxide and the electrochemical behavior of the surface during oxide fracture and repassivation. The objectives of the present study were to determine the mechanical and electrochemical properties of the oxide films present on the surface of nitric acid passivated and TiN/AlN-coated CoCrMo and Ti6Al4V alloys, and the electrochemical behavior of these alloy surfaces after mechanical fracture of the surface oxide or coating. The effects of mechanical load and sample potential on peak currents and time constants, and the effects of mechanical load on scratch depth were investigated to determine the mechanical strength of the oxides or coating. The polarization behavior of the samples after fracture of the oxide or coating was also investigated.

2. Materials and methods

Using a carbide abrasive cut-off wheel, samples were cut from 0.5 and 0.375 in diameter CoCrMo (ASTM F-1537) and Ti6Al4V (ASTM F-136) round stock, respectively. They were then mounted in acrylic and ground using 180–600 grit abrasive paper, and polished with diamond paste through 0.06 μm silica. The samples were washed with soap, ultrasonically cleaned, and rinsed in methanol after each application of diamond paste and silica. After polishing, a group of samples of each alloy were passivated in nitric acid per ASTM F-86 at room temperature. Another group of samples of each alloy was sent to the Basic Industry Research Laboratory (BIRL) at Northwestern University for plasma vapor deposition of a novel TiN/AlN coating. The samples were placed into a vacuum chamber and sputtered to remove the oxide film. Next, a 200 nm thick interlayer of titanium was deposited to enhance the coating/substrate interface. Alternating layers of
TiN and AlN were deposited until a coating thickness of approximately 5 \( \mu \text{m} \) was produced. Samples were mounted in the test cell of a Scanning Electrochemical Microscope and tested using the same apparatus used in a previous study and described elsewhere [12], with several procedural changes described here. In the present study, aerated phosphate-buffered saline (PBS) at pH = 7 was used for all test procedures. Variable load and variable potential tests were conducted. Topographic imaging of the scratched surfaces was performed to determine the effect of load on scratch depth. Table 1 lists the scratch test parameters. Variable load and variable potential tests for a particular alloy/surface treatment were conducted on the same single sample. Topographic imaging was conducted on a different unscratched sample.

To reduce background noise, acrylic nail polish (without metallic flakes) was used to seal test samples into the sample holder and cover most of the sample surface. An area of approximately 0.5 \( \times \) 0.5 cm\(^2\) of the alloy surface was left uncovered for scratching. Limiting the surface area for reactions to occur helped to reduce electrical noise in the current signal. The potentiostat was set at a smaller \( \mu \text{A/V} \) setting in order to reduce the magnitude of the noise in the current signal.

### 2.1. Variable load tests

In the variable load tests, a constant potential of 200 mV was applied to the sample and the load was varied from 0.0 to 8.0 N, depending upon the sample. Impedance spectroscopy of CoCrMo indicated that the resistance of the oxide reaches a peak at approximately 250 mV (versus Ag/AgCl) [16]. This suggests that at 250 mV the oxide may exhibit an optimum mix of mechanical strength and resistance to ionic diffusion. For the scratch tests, a potential of 200 mV was chosen to be close to this suspected optimum but not exceed it in case the oxide properties drastically deteriorated at potentials above it. Five 50 \( \mu \text{m} \) scratches were made at each load, each at a fresh unscratched location on the sample surface, 50 \( \mu \text{m} \) away from the previous scratch. The results of these tests were used to determine the constant load to apply to the samples during the variable potential tests.

When testing the TiN/AlN-coated CoCrMo test samples, loads from 0.0 to 0.6 N (the upper limit of the cantilever) were applied. A stiffer cantilever was then used to apply higher loads to the coated surfaces. The connection between the stylus containing the diamond tip and the LVDT apparatus broke at a load of 8.0 N. In order to avoid repeated damage, the stiffer cantilever was not used to apply scratches to the TiN/AlN-coated Ti6Al4V sample. Only loads of up to 0.6 N (upper limit of less stiff cantilever) were applied to the coated Ti6Al4V sample.

Custom written scratch test data analysis software was used to determine peak currents. Plots of mean peak current versus applied load were constructed. The background noise level for a particular series of scratch tests was determined by visual inspection of current signals resulting from scratch tests conducted with no contact between the diamond tip and the sample surface (load = 0 N). In these signals, the mean value represented the baseline current and the maximum deviation from this mean value represented the background noise. ANOVA was used to determine the first peak current that was significantly higher than the background noise. The lowest load that produced this peak current was considered to be the load at the onset of current transients. This load represented the minimum load required to fracture the oxide or coating.

### 2.2. Variable potential tests

Constant loads of 0.35 and 0.20 N were applied to the passivated CoCrMo and Ti6Al4V sample surfaces, respectively, and the potential of the samples were varied from \(-1.0\) to \(1.0\) V in 100 mV increments for the variable potential tests. These values were chosen because no multiple current peaks were observed when these loads were applied, the means of the peak currents were well above the background noise level but below the load where the diamond tip “sticks” in the sample surface, and the standard deviations of the peak current magnitudes at these loads were very small. A load of 0.6 N was applied to the surfaces of the TiN/AlN-coated CoCrMo and Ti6Al4V samples. Three 50 \( \mu \text{m} \) scratches were made at each potential, each at a fresh unscratched location on the surface of the sample, 50 \( \mu \text{m} \) apart from the previous scratch. At the start of the scratch test, samples were allowed to sit at \(-1.0\) V for 3–5 min prior to applying the first scratch. During the test, the potentiostat was adjusted to the next potential value, samples were allowed to sit for approximately 1 min prior to continuation of the scratch test.

The scratch test data analysis software was used to measure mean peak currents and time constants for

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Combinations of variables used in scratch tests</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Variable load test</strong></td>
<td></td>
</tr>
<tr>
<td>Load</td>
<td>0.0–0.6 N</td>
</tr>
<tr>
<td>Scratch length</td>
<td>50 ( \mu \text{m} )</td>
</tr>
<tr>
<td>Potential</td>
<td>200 mV</td>
</tr>
<tr>
<td><strong>Variable potential test</strong></td>
<td></td>
</tr>
<tr>
<td>Potential</td>
<td>(-1000) to (1000) mV (100 mV increments)</td>
</tr>
<tr>
<td>Load</td>
<td>0.20 N (Ti–6Al–4V)</td>
</tr>
<tr>
<td></td>
<td>0.35 N (Co–Cr–Mo)</td>
</tr>
<tr>
<td></td>
<td>0.6 N (TiN/AlN coated alloys)</td>
</tr>
<tr>
<td>Scratch length</td>
<td>50 ( \mu \text{m} )</td>
</tr>
</tbody>
</table>
repassivation. Background noise levels were determined at each applied potential by visual inspection of the current transient signals. Plots of mean peak current versus potential and time constants versus potential were constructed.

Current transients occur soon after the application of a scratch and quickly decay. Current magnitudes approach baseline levels within 20–30 ms after scratch initiation. Polarization behavior can be determined by measuring baseline currents at each potential. Measurement of baseline currents was done by collecting and averaging current data points occurring after approximately 30 ms. This average value was then plotted against the applied potential to produce a polarization curve for each sample.

2.3. Topographic imaging

Three scratches were made at each load, each at a fresh unscratched location on the surface of the test sample, 100 μm apart from the previous scratch. Topographic images of scratched surfaces were constructed as described elsewhere [12]. In the present study, custom written software was used to analyze each cross section of the scratch and determine the location where the greatest negative change in vertical displacement occurred between adjacent points in the cross section. The cross section containing the greatest change in vertical displacement between adjacent points was then plotted and the scratch depth was then measured directly from the plot. This software was validated by comparing scratch depths determined through use of the software to those obtained by the visual inspection method. Only those scratches deeper than the average surface roughness of the sample were detectable. Surface roughness, variations in surface flatness, and non-level sample surfaces were easily determined through visual inspection of the scratch depth plot. Scratch depth was determined by measuring the distance between a visually determined line representing the average surface roughness and the deepest point in the scratch. Plots of scratch depth versus load were then constructed. Curve fitting was used to characterize depth versus load behavior of the sample surfaces. The curves were extrapolated to the load axis to estimate the minimum load required to produce a scratch.

2.4. Microhardness tests

Hertzian contact stress equations were used to calculate experimentally derived hardness values for the base alloys, oxides, and coating from scratch test measurements. In order to determine the accuracy of these measurements, microhardness tests were conducted to provide a reference for comparison. Using a microhardness tester (Buehler Micromet II Microhardness Tester, Buehler, Lake Bluff, IL) with a Vicker’s pyramidal tip indenter, a 300 or 500 gm load was applied to previously untested samples of each of the four alloy/surface treatment combinations over a period of 5 s. A microscope was used to measure the lengths of the diagonals of the indented areas on the surfaces of the samples. Five indentations were made at different locations on the sample surfaces. The Vickers hardness (HV) in units of MPa was determined by

\[
HV = (9.8 \times 1.854 \times P)/(d_l^2),
\]

where \( P \) is the load (in kg) used to produce the indentation and \( d_l \) is the average diagonal length (in mm) of the indented area.

2.5. Microscopic evaluation of scratch test samples

After completion of the scratch tests, the passivated CoCrMo sample used for topographic imaging to investigate the effect of load on scratch depth and the coated CoCrMo sample used for the variable load test were inspected using optical and scanning electron microscopy. Electron micrographs were used to document the appearance of the coating and the shape and size of the scratches produced by the diamond tip during scratch testing.

3. Results

3.1. Variable load tests

The effect of load on mean peak currents for passivated CoCrMo is shown in Fig. 1. The first significant peak above the 0.5 μA noise level occurred at a load of 0.1 N. As the load increased, mean peak currents continued to increase somewhat linearly, reaching a maximum of 2.2 μA at a load of 0.45 N. At a load of 0.5 N, the peak current decreased due to sinking of the diamond tip into the sample surface.

The effect of load on mean peak currents for passivated Ti6Al4V is shown in Fig. 2. The first significant peak above the 0.7 μA noise level occurred at a load of 0.011 N. As the load increased, mean peak currents continued to increase somewhat linearly, reaching a maximum of 8.7 μA at a load of 0.20 N. At a load of 0.25 N, the peak currents decreased due to sinking of the diamond tip into the sample surface.

The effect of load on mean peak currents for TiN/AlN-coated CoCrMo is shown in Fig. 3. No significant peak currents were observed above the noise level of 0.5 μA for the entire range of loads. However, at a few of the load levels applied, random peaks of magnitude greater than 0.5 μA were observed. This may have been the result of the diamond tip scratching over a region of the TiN/AlN coating that was poorly adhered to the
CoCrMo substrate or an uncoated region of the substrate, allowing the diamond tip to fracture a portion of the substrate oxide.

The effect of load on mean peak currents for TiN/AlN-coated Ti6Al4V is shown in Fig. 4. No significant peak currents were observed above the noise level of 0.6 μA for the entire range of loads. No random peaks were observed suggesting that the adhesion strength of the TiN/AlN coating to the Ti6Al4V substrate may have been higher than that of the TiN/AlN-coated CoCrMo sample.

The results of the variable load tests for all four test samples are summarized in Table 2. At a potential of 200 mV, the minimum load required to produce a significant current transient due to fracture and repassivation of the oxide present on the surface of the passivated CoCrMo sample (0.1 N) was nine times as high as that of the passivated Ti6Al4V sample (0.011 N). At a potential of 200 mV and a load of 0.2 N, the magnitude of the mean peak current produced after fracturing the oxide present on the surface of the passivated Ti6Al4V sample (8.7 μA) was 11 times as high as that of the passivated CoCrMo sample (0.8 μA). No significant current transients were observed with either of the TiN/AlN coated samples at any of the loads used to apply scratches.

3.2. Variable potential tests

The effects of potential on mean peak currents, time constants, and baseline currents for passivated CoCrMo are shown in Figs. 5(a–c). Significant peak currents
Table 2
Summary of scratch test results for variable load tests, variable potential tests, and topographic imaging

<table>
<thead>
<tr>
<th>Variable load tests</th>
<th>Nitric acid passivated</th>
<th>TiN/AlN coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–Cr–Mo Ti–6Al–4V</td>
<td>Co–Cr–Mo Ti–6Al–4V</td>
<td></td>
</tr>
<tr>
<td>Load at onset of current transients (N)</td>
<td>0.1</td>
<td>0.011 N</td>
</tr>
<tr>
<td>Peak current at 0.2 N load (S.D.)</td>
<td>0.8 μA (0.09)</td>
<td>8.7 μA (0.73)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variable potential tests</th>
<th>Nitric acid passivated</th>
<th>TiN/AlN coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–Cr–Mo Ti–6Al–4V</td>
<td>Co–Cr–Mo Ti–6Al–4V</td>
<td></td>
</tr>
<tr>
<td>Potential at onset of current transients (mV)</td>
<td>500 to 400</td>
<td>800 to 700</td>
</tr>
<tr>
<td>Time constant (typical)</td>
<td>0–1 ms</td>
<td>1–2 ms</td>
</tr>
<tr>
<td>Peak current at 500 mV (S.D.)</td>
<td>5.8 μA (0.231)</td>
<td>12 μA (1.15)</td>
</tr>
<tr>
<td>Zero current potential (mV)</td>
<td>700 to 600</td>
<td>400 to 300</td>
</tr>
<tr>
<td>Potential at minimum current in passive region</td>
<td>300 mV</td>
<td>0 mV</td>
</tr>
<tr>
<td>Minimum current in passive region (density in μA/cm²)</td>
<td>0.4 μA (1.6)</td>
<td>0.08 μA (0.32)</td>
</tr>
<tr>
<td>Breakdown potential</td>
<td>550 mV</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Topographic imaging</th>
<th>Nitric acid passivated</th>
<th>TiN/AlN coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–Cr–Mo Ti–6Al–4V</td>
<td>Co–Cr–Mo Ti–6Al–4V</td>
<td></td>
</tr>
<tr>
<td>Scratch depth at 0.2 N load (S.D.)</td>
<td>0.163 μm (0.057)</td>
<td>0.255 μm (0.007)</td>
</tr>
<tr>
<td>Minimum load to produce scratch (nominal stress)</td>
<td>0.68 N (5.07 GPa)</td>
<td>0.35 N (3.09 GPa)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(&gt; 15 GPa)</td>
</tr>
</tbody>
</table>

Note: — = not applicable.

above the 0.5 μA noise level began to appear between −500 and −400 mV. As reported elsewhere [12], they continued to increase somewhat linearly until a maximum of 5.8 μA was reached at +500 mV. At potentials above +500 mV, mean peak currents decreased as the potential entered the transpassive region, but did not drop to zero. Time constants were fairly steady at 0.5–1.0 ms between −400 and +500 mV, began to increase at potentials above the breakdown potential of +550 mV, and then began to drop at +800 mV. The shape of the potential versus log baseline current curve seen in Fig. 5(c) resembles the polarization curve for the alloy, and correlates well with the transitions observed in the mean peak current versus potential plots. At −1000 mV, a cathodic current of 6.3 μA was measured. At a potential between −700 and +600 mV, the zero current potential (ZCP) was reached. Above the ZCP the alloy entered the active region where the currents became anodic. At a potential between −500 and −400 mV, the alloy entered the active/passive transition region. The alloy remained in the passive region, reaching a minimum current of 0.4 μA (1.6 μA/cm²), until the breakdown potential of +550 mV, where the sudden increase in dissolution current indicated entry into the transpassive region. At 1000 mV, the current was 631 μA.

The effect of potential on mean peak currents and baseline currents for passivated Ti6Al4V is shown in Figs. 6(a) and (b). Significant peak currents above the 1.0 μA noise level began to appear at potentials between −800 and −700 mV. These peak currents continued to increase linearly and did not exhibit transpassive behavior within the range of potentials. At +500 mV, the mean peak current was 12 μA. Time constants were very steady ranging between 1.0 and 1.7 ms at potentials of −900 mV and above and appeared to settle at the lower end of the time constant range at potentials above +100 mV. The transitions seen in the plot of potential versus log baseline current, shown in Fig. 6(b), are similar to those observed in Fig. 6(a). At the start of the test (−1000 mV), a cathodic current of 5.6 μA was measured. The ZCP was between −400 and −300 mV above which the sample quickly entered the passive region, without exhibiting well-defined active or active/passive transition regions. As the potential increased, current remained fairly steady reaching a minimum of 0.08 μA (0.32 μA/cm²). At 1000 mV, current began to slightly increase above levels observed within the passive region, reaching a maximum of 0.18 μA. However, this increase was very small and did not indicate transpassive behavior.

The effect of potential on mean peak currents and baseline currents for TiN/AlN-coated CoCrMo is shown in Figs. 7(a) and (b). No significant peaks above the 0.9 μA noise level were observed for the entire range of potentials. Time constants ranged between 0 and 1.5 ms but were representative of the time required for noise peaks to decay, not the decay of current transients resulting from repassivation of the fractured oxide or coating. The transitions observed in the plot of potential versus log baseline current (Fig. 7(b)) were different from those observed in Fig. 7(a), but similar to those observed in the passivated alloy (Fig. 5(c)). At −1000 mV, the sample was in the immune region and a cathodic current of 5 μA was measured. As the potential was increased, ZCP was reached between...
At potentials above this range, current became anodic, and the sample entered the active region and became passive at 100 mV with a current of 0.03 μA (0.12 μA/cm²). Current changed slightly with increasing potential until 600 mV where a sudden increase in current occurred. This apparently transpassive behavior continued until 900 mV where the current leveled off with increasing potentials to 0.63 μA, resembling a second passive region for the sample.

The effect of potential on mean peak currents and baseline currents for TiN/AlN-coated Ti6Al4V is shown in Fig. 6(a) and (b). No significant peaks were observed above the 1.5 μA noise level for the entire range of potentials. Time constants ranged from 0.5 to 1.5 ms, 

-400 and -300 mV. At potentials above this range, current became anodic, and the sample entered the active region and became passive at 100 mV with a current of 0.03 μA (0.12 μA/cm²). Current changed slightly with increasing potential until 600 mV where a sudden increase in current occurred. This apparently transpassive behavior continued until 900 mV where the current leveled off with increasing potentials to 0.63 μA, resembling a second passive region for the sample.

The effect of potential on mean peak currents and baseline currents for TiN/AlN-coated Ti6Al4V is shown in Figs. 8(a) and (b). No significant peaks were observed above the 1.5 μA noise level for the entire range of potentials. Time constants ranged from 0.5 to 1.5 ms,
but, as with coated CoCrMo, represented the decay of background noise, not peak currents resulting from repassivation of a fractured oxide or coating. There are some similarities between the transitions observed in the potential versus log baseline current plots of coated CoCrMo alloy (Fig. 7(b)) and coated Ti6Al4V alloy (Fig. 8(b)). At $-1000$ mV, the sample was in the immune region and a cathodic current of $7.9 \mu A$ was measured. The ZCP was reached between $-300$ and $-200$ mV. Between $-200$ and $+100$ mV, the sample entered a short active/passive transition region. A passive region began at $100$ mV with a minimum current of $0.025 \mu A (0.1 \mu A/\text{cm}^2)$. At a potential between $500$ and $600$ mV, current began to increase somewhat linearly, reaching a maximum of $1.0 \mu A$ at $1000$ mV. This sudden increase in current was probably not indicative of transpassive behavior as it represented a change of only one order of magnitude compared to the change of three orders of magnitude observed with the passivated CoCrMo sample (see Fig. 5(c)). Ti6Al4V does not exhibit this type of behavior. Thus, this sudden increase in current is probably reflective of the electrochemical behavior of the coating.

The results of the variable potential tests are summarized in Table 2. The mean peak current produced after fracture of the surface oxides at a potential of $+500$ mV for passivated CoCrMo was significantly lower ($5.8 \mu A$) than that of passivated Ti6Al4V ($12 \mu A$). It is important to note that these mean peak currents were produced by scratches applied with different loads, $0.35$ N (CoCrMo) and $0.20$ N (Ti6Al4V). Time constants typically ranged between $0$ and $1$ ms for passivated CoCrMo and $1$–$2$ ms for passivated Ti6Al4V. The minimum current measured in the passive region (passivation current) for passivated CoCrMo was higher than that of passivated Ti6Al4V and the TiN/AlN coated samples. The passivation currents of the coated samples were similar to each other but slightly less than that of passivated Ti6Al4V.

### 3.3. Topographic imaging of scratches

Fig. 9 is a plot showing the variation in depth along the surface of the scratched passivated Ti6Al4V sample. It represents a cross section perpendicular to the scratch direction located at the deepest point in the scratch. Measurements of scratch depth from similar plots constructed from topographic images of scratches made at various loads allowed construction of the graphs seen in Figs. 10 and 11. Both graphs indicate that as the load

![Image](image-url)
was increased, the depth of the resulting scratch also increased. For passivated CoCrMo, a load of 0.2 N produced a scratch that was 0.16 μm deep at its deepest point. This same load produced a scratch in the passivated Ti6Al4V sample that was 0.25 μm deep at its deepest point.

It can be shown that $d \propto L^{2/3}$, where $d$ is the scratch depth, and $L$ is the applied load [12,17]. Curves reflecting the depth versus load behavior of Figs. 10 and 11 were fit to the data and extrapolated to the load axes. Only those loads that produced scratches and did not cause the diamond tip to sink into the sample surface prior to producing the scratch were included in the curve fitting procedure. Due to the expected dependence of scratch depth on load($2/3$), the curve fitting software (SigmaPlot, Jandel Scientific) was initially instructed to attempt to fit a $2/3$ order power curve to the data. After completing several iterations, the software determined that power curves of order 0.0586 and 0.226 provided the best fit to the passivated CoCrMo and Ti6Al4V alloys, respectively. The intersections of these curves with the load axes were used as an estimate of the minimum loads required to produce measurable scratches in the surfaces of the test samples. This method indicated that these minimum loads were 0.068 N for passivated CoCrMo and 0.035 N for passivated Ti6Al4V.

Analysis of topographic images of scratched TiN/AlN coated samples of both alloys indicated that no measurable scratches were found at loads below 0.6 N. In order to apply loads of higher magnitude, use of the stiffer cantilever used in one of the variable load tests would have been required. However, during the variable load test, at loads above 1.0 N, the diamond tip produced dimples on the surface of the TiN/AlN coated CoCrMo sample. At the start of a scratch test, the diamond tip is lowered onto the surface until the desired load is applied, and the tip is then moved to produce a scratch. During the actual scratch test, the diamond tip sunk into the surface of the coating layer when the load was initially applied. When the test stage was moved by the scratch test software, the stylus bent with the diamond stylus trapped in the dimple, without a scratch being produced. Thus, at loads above 1.0 N, sinking of the diamond tip prevented scratches from being produced in the coating surface, making the use of the stiffer cantilever contraindicated for testing of TiN/AlN coated samples. For this reason, the less stiff cantilever was used to apply loads of up to 0.6 N for scratching and low loads for imaging of the TiN/AlN-coated Ti6Al4V surface.

During visual inspection of three-dimensional topographic images of scratched surfaces and plots of cross sections of scratches, it was noticed that the TiN/AlN coated alloy samples were smoother than their respective passivated alloy samples. While making several attempts to scratch the surface of the TiN/AlN-coated CoCrMo sample with a load of 0.6 N and immediately imaging the scratched surface area, a large current...
transient was observed after application of one of the scratches. Subsequent imaging of the scratched area indicated the presence of a deep hole instead of a scratch. This hole may have been a defect in the coating or the result of poor adhesion of the coating to the substrate. In general, the coating surfaces exhibited lower surface roughness and fewer polishing scratches than the surfaces of the passivated alloys.

3.4. Microhardness tests

The results of the microhardness testing of all four samples are listed in Table 3. Passivated CoCrMo had a higher hardness than that of passivated Ti6Al4V (4.09 versus 3.09 GPa)-coated CoCrMo had a higher hardness than that of coated T46Al4V (5.15 versus 3.89 GPa). TiN/AlN coated samples had significantly higher hardness values than the passivated samples.

A 300 gm load was used to obtain indentation measurements with the passivated alloy samples. For the coated samples, it was necessary to increase this load to 500 gm in order to produce a wide enough indentation that would allow for accurate measurement of the diagonals. Testing of a 700 HV blank control plate provided by the manufacturer of the microhardness testing equipment using the same test procedure and equations used to measure the hardness of the four test samples resulted in a measured hardness of 746HV. Thus, the hardness measurements reported here are most likely within 6.5% of their actual values.

3.5. Microscopic evaluation of scratch test samples

Fig. 12 is a scanning electron micrograph showing a typical scratch produced on the surface of the passivated CoCrMo sample used for topographic imaging to investigate the effect of load on scratch depth. The length of the scratch is 50 μm, and the width is approximately 10 μm. The scratch is not entirely straight and another small scratch can be seen almost perpendicular to the main scratch at the top of the main scratch. Wear debris can be seen piled along the edges of the scratch.

Inspection of the surface of the coated CoCrMo sample used in the variable load test was conducted with optical microscopy. In the area of the surface where loads up to 0.6 N were applied with the less stiff cantilever, narrow white lines, spaced approximately 50 mm apart were observed. In the area where loads from 1.0 to 8.0 N were applied, dimples were observed. These dimples were caused by the diamond tip sinking into the coating, as discussed previously. The white lines were thought to be scratches in the coating surface that were not deep enough to expose the substrate and produce a current transient due to passivation of the substrate surface. Inspection of this sample with scanning electron microscopy showed no evidence of any scratch or other plastic deformation of the coating surface at loads below 0.6 N. At loads ranging from 1.0 to 8.0 N, dimples of varying diameters were produced. The diameters of the dimples appeared to increase with increasing load. These dimples were evidence of plastic deformation of the coating. The lack of current transients resulting from these dimples indicated that the deformation was not deep enough to expose the substrate and result in passivation of the substrate surface.
4. Discussion

Current transients resulting from oxide fracture are due to the reformation of oxide and dissolution of reactive exposed substrate. They are an indication of the magnitude of the electrochemical events resulting from repassivation. Time constants are a measure of the kinetics of repassivation. Baseline currents are an indication of the electrochemical processes occurring at the surface of the repassivated alloy. Thus, current transients and time constants are indicators of how the electrochemical behavior of a sample surface is affected by mechanical loading, and baseline currents are indicators of the electrochemical behavior of the intact sample surface.

During the variable potential tests of the passivated alloys, the first peaks observed above the background noise levels indicated the potentials at which the oxides began to form and were able to reform after fracture. These potentials marked the beginning of the ranges of potentials where the surface oxides were stable. The linear increases in mean peak currents with increasing potentials were observed and discussed in a previous study [12].

As shown in Table 2, compared to passivated CoCrMo, surface oxides began to form at a lower potential for passivated Ti6Al4V, which did not exhibit the transpassive behavior observed with passivated CoCrMo. Thus, the oxide was stable within a much wider range of potentials for passivated Ti6Al4V than for passivated CoCrMo. The narrow ranges of time constants for repassivation indicated that the oxides present on the passivated alloys were fairly stable within their passive regions. However, the apparently higher time constants for passivated Ti6Al4V (1.5 ms) compared to CoCrMo (0.8 ms) suggest that its surface oxide takes longer to reform. The peak currents observed at 500 mV were higher for Ti6Al4V than for CoCrMo. The higher time constants and peak currents observed with Ti6Al4V indicate that more electrons were liberated during the repassivation of Ti6Al4V than with CoCrMo. This could also indicate that more metal ions were released during repassivation. However, due to the unknown composition of the oxide and multiple valences of the cationic oxide components, the quantities of metal ions released after oxide fracture and repassivation cannot be accurately calculated. It can be shown that for identical volumes of oxide removed during a scratch test, the total charge released from passivated Ti6Al4V would be approximately three times higher than the total charge released from passivated CoCrMo [11,12,18]. The baseline currents observed within the passive regions of each alloy were higher for CoCrMo, indicating that the oxide present on the surface of the CoCrMo sample is less of a barrier to ionic diffusion at potentials within the passive region than the oxide on the surface of the Ti6Al4V sample. This may be due to the lower defect density of the nearly stoichiometric oxide on the surface of Ti6Al4V.

The absence of peak currents above the background noise level for the TiN/AIN coated samples may be due to the mechanical and electrochemical behavior of the coating and the coating/substrate interface. First, the loads used during the scratch test may have been too low to fracture the hard coating or cause failure of the coating/substrate interface. Second, although the coating contains titanium and aluminum atoms with which to form oxides, fracture of the coating and any oxides on its surface may not have resulted in any significant release of electrons. The composition, concentration, and free energy of formation of oxides on the surface of the coating may be completely different than those of the oxides on the surfaces of the passivated alloys. Third, if the loads were high enough to fracture the coating layer and exposed substrate, the presence of the coating may have somehow inhibited the formation of the oxide on the exposed substrate surface, preventing the generation of current transients due to oxide formation. This is doubtful due to the large current transient observed after scratching an area of the coating that was poorly adhered to the substrate. The lack of current transients at loads of up to 8.0 N and the lack of any detectable scratches indicate that these loads were not of sufficient magnitude to plastically deform the coating surface and expose enough of the substrate to produce significant current transients.

Baseline currents for the coated samples were very similar to each other. Transitions within the potential versus baseline current curves occurred at similar potentials and passive current magnitudes were almost identical. Compared to the passivated samples, transitions occurred at different potentials and passive current magnitudes were lower for the coated samples. It appears as though the substrate had little or no effect on the shape of the potential versus baseline current curves and the current within the passive region. The TiN/AIN coating exhibited current limiting behavior. Within the current limiting region, when compared to the passivated alloy samples, the coating significantly reduced dissolution current magnitudes by as much as 93% and 69% for the CoCrMo and Ti6Al4V alloys, respectively. This indicated that the coating was an excellent barrier to ionic diffusion and can improve the corrosion resistance of each alloy.

During the variable load tests, the lowest loads resulting in the first significant mean peak current transients above the background noise level indicate the minimum load required to fracture the oxide or cause failure of the oxide/substrate interface. These loads are measures of the mechanical strength of the oxide or the oxide/substrate interface. The significantly higher load required to fracture the oxide on the surface
of the passivated CoCrMo sample indicates that this oxide is stronger than the oxide on the surface of the passivated Ti6Al4V sample. At a load of 0.2 N, the peak current transients resulting from repassivation of the fractured oxides were significantly lower for the passivated CoCrMo sample. This observation also indicates that the oxide on the CoCrMo sample was stronger and more resistant to oxide fracture. The stronger oxide and/or oxide/substrate interface resulted in a more shallow scratch at a load of 0.2 N, as seen in Figs. 10 and 11. This shallow scratch resulted in a smaller initial scratched area that reduced the peak current magnitude [12,18]. These results suggest that CoCrMo is more resistant to fretting than Ti6Al4V.

Microscopic evaluation of the coated CoCrMo sample used for the variable load test revealed the presence of dimples on the coating surface. These dimples were evidence of plastic deformation of the coating layer but may have been the result of a weaker substrate failing to support the stronger coating material. The minimum load required to deform the coating and expose enough of the substrate to produce a significant current transient was greater than 8.0 N. Thus, the TiN/AlN coating and its interfacial adhesion strength were significantly stronger than those of the oxides present on the surfaces of the passivated alloy samples. The hard, well-adhered TiN/AlN coating would be expected to improve the fretting resistance of CoCrMo and Ti6Al4V alloys.

The minimum load required to produce a detectable scratch is a measure of the strength of the oxide, coating, or their respective substrate interfaces. A higher load was required to plastically deform the surface of the passivated CoCrMo sample, and a load of 0.2 N produced a deeper scratch in the passivated Ti6Al4V sample. These results indicate that the oxide on the surface of passivated CoCrMo is stronger than that of passivated Ti6Al4V.

The lack of any measurable scratches produced in the surfaces of the coated samples with loads of up to 0.6 N indicates that these loads were not high enough to produce plastic deformations in the coating surface. The dimples created by loads above 1.0 N were unable to be analyzed using the topographic imaging methods used in this study. At loads between 0.6 and 1.0 N, the stresses developed in the CoCrMo substrate became high enough to plastically deform the coating. However, this may have been due to plastic deformation of the substrate that failed to support the coating and allowed it to deform.

The minimum load required to produce significant peak current transients and the minimum load required to produce a measurable scratch are both measures of oxide/substrate interface strength and in some cases, oxide strength. For passivated CoCrMo, the load required to produce current transients is slightly higher than but close to the load required to plastically deform the surface. This indicates that oxide fracture occurs when the supporting substrate is plastically deformed, and the oxide/substrate interface fails. For passivated Ti6Al4V, the load required to produce current transients is lower than the load required to plastically deform the surface. This indicates that the oxide is fractured prior to plastic deformation of the substrate. Thus, oxide fracture and repassivation is the result of failure of the oxide/substrate interface for passivated CoCrMo, and failure of the weaker oxide for passivated Ti6Al4V.

According to the Hertzian contact stress equations [17], at a load of 0.6 N, the contact width was 7 μm, which was greater than the coating thickness of 5 μm. This caused the coating to begin to behave as a “thin” coating where the coating had little effect on the contact stress field and only transmitted it to the substrate. In this situation, the stresses transmitted to the substrate caused the lower modulus substrate to deform. At loads above 0.6 N, this subsurface deformation resulted in a lack of support for the higher modulus coating and eventually allowed the coating to collapse into the deformed substrate, resulting in plastic deformation of the coating in the form of dimples.

Similar behavior has been reported in single layer TiN coatings comprised of fine columnar TiN that behaved like closely packed fibers [19]. In indentation tests, the TiN coating deformed elastically and transferred loads into the softer substrate resulting in substrate deformation. Coatings of this type do not conform to the deformation produced in the substrate. This caused sliding and splitting separation of adjacent TiN columns, resulting in cracking and sinking of the coating into the substrate.

The minimum loads required to produce a measurable scratch were used with the Hertzian contact stress equations to calculate the minimum stress required to produce plastic deformation of the test sample surfaces. These stress values are measures of the surface hardness of the samples and are shown in Table 3. The results of the microhardness measurements are included for comparison along with values cited in the literature. There is very good agreement between experimentally derived hardness values (scratch test apparatus and microhardness tester) and values published in the literature for CoCrMo and Ti6Al4V alloys. For CoCrMo, these values are 5.07, 4.09, and 4.50 GPa, respectively. For Ti6Al4V, these values are 2.89, 3.09, and 3.5 GPa, respectively. It is interesting to note that the stress required to produce the first significant current transient with a passivated Ti6Al4V sample was 1.97 GPa. Thus, the stress required to fracture the oxide (hardness) was less than the hardness of the substrate. This indicates that with Ti6Al4V, the oxide fractures prior to plastic deformation of the substrate.
The hardness value calculated for the TiN/AlN coating was based on results obtained with the coated CoCrMo sample. It was assumed that the minimum load required to plastically deform the coating was approximately 1.0 N, the load where dimples began to appear in the sample surface. This resulted in a calculated hardness of 18 GPa for the coating. The microhardness test yielded a hardness of 5.15 GPa and the literature cites values ranging from 40 to 45 GPa [19]. This lack of agreement between experimental and published values is probably due to the mechanical behavior of the coating/substrate interface, differences in how the scratch and hardness tests were conducted, and the relationship between coating thickness and testing depth.

The contact radius and depth of penetration predicted by the Hertzian contact stress equations were compared to scratch width and depth measured from topographic images for both passivated alloys. A load of 0.4 N was predicted to produce a 7.46 μm wide and 0.39 μm deep scratch in passivated CoCrMo, respectively. Scratch width and depth values of 6.9 and 0.26 μm respectively, were measured from topographic images. A load of 0.22 N was predicted to produce a 7.24 μm wide and 0.37 μm deep scratch in passivated Ti6Al4V. These values were found to be 6.2 and 0.31 μm, respectively. Thus, the calculated and experimental values were in good agreement with each other.

Comparisons of scratch depths were made between those determined from topographic images and those predicted by the contact stress equations. The dotted lines in Figs. 10 and 11 represent the predicted scratch depths and the solid lines represent the curves fit to the actual measured scratch depths. The curves are very similar in shape and the scratch depth values are consistently close to each other. It is interesting to note that the curve of predicted values includes the origin but the curve of measured scratch depths crosses the load axis at a positive load. The calculated values are based on the contact stress equations that determine the surface deformations resulting from an applied load. At very low loads, these equations would predict that a small, non-zero deformation will occur, and do not distinguish between elastic and plastic deformations. At loads that produce purely elastic deformations, the contact stress equations predict a deformation of the surface. However, when the load is removed, the deformation recovers to the non-deformed state, and the topographic image indicates that no deformation has occurred. At loads above the surface hardness of the sample, elastic and plastic deformation of the surface occurs, and the contact stress equations may predict scratch depths resulting from both types of deformations. When the load is removed, areas that were elastically deformed recover to their non-deformed state, but the plastically deformed areas are now permanently deformed. The topographic images reflect only the plastic deformation on the surface and do not yield any information regarding elastic deformation. Plastic deformation of the surface will occur at loads just above the load at which the curve for the measured scratch depths intersects the load axis, and the stress resulting from this load is equal to the surface hardness.

Inclusion of the elastic deformation component may explain why the predicted scratch depth values are consistently higher than the measured values. In Figs. 10 and 11, the intersection of the solid line with the load axis indicates the load where plastic deformation began for each passivated alloy. Thus, at loads just below the load where plastic deformation began, any deformations predicted by the contact stress equations were purely elastic, and completely recovered when the load was removed. From Figs. 10 and 11, these elastic deformations were determined to be 0.12 and 0.106 mm for passivated CoCrMo and Ti6Al4V, respectively. Subtracting these elastic deformations from the dotted lines representing the total deformation predicted by the contact stress equations should provide an estimate of the predicted plastic deformations. These predicted values are shown by the dashed lines in Figs. 10 and 11. Comparison of these predicted plastic deformations to the measured plastic deformations represented by the solid lines in Figs. 10 and 11 shows good agreement between predicted and measured scratch depths.

The results of the present study confirmed that oxide film thickness increases with potential. Pilling and Bedworth proposed that the ratio of the specific volumes of the oxide to its parent metal is a predictor of the ability of the oxide to protect the substrate from corrosion [20]. Oxides with Pilling–Bedworth ratios slightly greater than 1.0 were thought to develop protective residual compressive stresses. Those with very high ratios were thought to develop excessive compressive stresses that would cause buckling of the oxide [21]. This could decrease the load required to fracture the oxide or cause the oxide/substrate interface to fail. Thus, oxide strength may be dependent upon the potential at which it was formed and scratch tested.

5. Conclusion

In summary, CoCrMo has a stronger surface oxide and higher interfacial adhesion strength that make it more resistant to fracture than Ti6Al4V. With Ti6Al4V, repassivation takes slightly longer to occur and more electrons are released. However, if not mechanically disturbed, the oxide on the surface of Ti6Al4V significantly reduces dissolution currents at a wider range of potentials than CoCrMo, making Ti6Al4V more resistant to corrosion. The TiN/AlN coating has a higher hardness and modulus of elasticity than CoCrMo.
and Ti6Al4V. It is much less susceptible to fracture, has a higher interfacial adhesion strength, and is a better barrier to ionic diffusion than the surface oxides on CoCrMo and Ti6Al4V. The coating provides increased corrosion and fretting resistance to the substrate alloys. The scratch test and topographic imaging procedures provide a sensitive and useful method for assessing the mechanical and electrochemical stability of oxide films and surface coatings. Good agreement between calculated and measured scratch depths and contact radii was found for the test methods used. These methods can be used to determine the relative corrosion and wear resistance of surface oxides and surface modified alloys, and can be used to predict the effects of surface modifications on fretting corrosion.

Acknowledgements

The authors would like to thank Howard Freese of Teledyne Allvac for providing the alloys for testing, and the US Department of Education (NIDRR H133P0016-94) for their financial support of this work.

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