Original Article

Synergism between mechanical wear and corrosion on tribocorrosion of a titanium alloy in a Ringer solution

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\section*{Abstract}

The tribocorrosion behavior of a biocompatible ASTM-F67Gr1 titanium alloy was evaluated. An experimental pin-on-flat reciprocating sliding tribocorrosion setup was built which allowed the investigation of tribocorrosion phenomena in an electrolyte of a Ringer solution. Tests were performed at anodic and cathodic potential, and at two values of applied load and sliding speed. Potentiodynamic tests indicated a corrosion potential of $-0.368 \pm 0.082 \text{ V}_{\text{SCE}}$ and a passivation range between $0.344 \text{ V}_{\text{SCE}}$ and $2.932 \text{ V}_{\text{SCE}}$ was observed. After polarization tests, no pits were identified on the titanium alloy. The volume of worn material was higher at an anodic potential than in a cathodic potential, especially for the condition of the highest applied load and speed. Higher metal losses at a cathodic potential (pure mechanical wear) were observed in conditions of the highest speed. The mass loss due to the corrosion was similar for all conditions, and the synergistic factor was the highest for the condition of the highest applied load and sliding speed.

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1. Introduction

Biotribology is one of the most rapidly growing areas of tribology [1]. In recent years, many researches in tribology and tribocorrosion of materials used in implants were developed.
Loir et al. [2] studied the tribological behavior of diamond-like carbon coatings deposited on stainless steel by using pin-on-flat configuration in ambient air and Ringer solution, and by using a hip joint simulator during one million cycles corresponding to the human activities for one year. Diaz et al. [3] studied ion implantation of Ti alloys (Ti6Al4V) and the tribo-corrosion friction, wear and corrosion tests of these biomaterials. Xie et al. [4] reported that friction and wear occurring in cardiovascular devices may cause a failure of the implanted devices, and problems such as hemolysis and thrombus formation. Xie et al. [4] discussed typical tribological problems in various cardiovascular devices and mitigation methods [4]. Zhou and Jin [1] reported progress in joint tribology, skin tribology, and oral tribology.

Studies on tribocorrosion in the biomedical field have shown to be significant in two areas: orthopedics [2,5] and dentistry [6]. Titanium and its alloys are used as biomedical [7,8] and orthodontic materials [9] due to their excellent biocompatibility, low density, good mechanical properties and high localized corrosion resistance in many environments containing chlorides. The chemical environment of blood plasma is highly aggressive to many metals and alloys, mainly due to the presence of a high concentration of chloride ions and their ability to induce localized corrosion. In addition to the inorganic species, body fluids contain various types of biomolecules and cells that can adhere to the surface of biomaterials and affect surface corrosion reactions [10]. Despite their attractive corrosion and toxicological properties, titanium and titanium alloys generally exhibit poor fretting and wear resistance, which is attributed to the poor integrity of the TiO2 surface passive layer, or to the plastic deformation of surface and subsurface layers [11–13]. The release of wear debris may lead to cellular damage, inducing inflammation or encapsulation of the implant by fibrous tissue [11]. These environmental alterations may also alter the corrosion behavior of the material. Studies have shown the formation of a tribolayer in all types of metallic joints [11,14], and this dynamic layer is a mixture of metallic oxides, metallic nanocrystals and organic matter content. In this work, a vanadium- and aluminum-free alloy, which have been introduced for implant applications, was studied. Ti-6Al-4V has long been favored for biomedical applications. However, for permanent implant applications the alloy has a possible toxic effect resulting from a release of vanadium and aluminum [15]. Literature has reported different tribocorrosion setups based on specific objectives of their study [16–30]. Azzi and Szpunar [16] and Naghibi et al. [31] used a ball-on-plate device to study tribocorrosion of Ti for biomedical applications. Oliveira et al. [12] and Alves et al. [23] studied tribocorrosion of TiO2 anodic films for dental applications by using a pin-on-disk device. Serre et al. [32] used a ring-on-disk device to research tribocorrosion of graphite and titanium alloys for industrial applications. Chen and Yan [33] used a ring on block device for study the tribocorrosion behavior of titanium alloys for industrial applications. In this study, an experimental pin-on-flat reciprocating sliding tribo-electrochemical setup [13,15] was built to allow the investigation of tribocorrosion phenomena in the presence of corrosive solutions to simulate the movement observed in some applications of implants. The ASTM F67Gr1 titanium alloy was studied in a Ringer solution, a solution commonly used to simulate corrosion conditions in human body fluids.

2. Material and methods

The material studied in this work was the ASTM-F67Gr1 titanium alloy. The chemical composition, metallographic analysis and mechanical properties of the titanium alloy were provided by the manufacturer (Table 1). Samples were obtained from cold rolled and annealed titanium sheets with a thickness of 2.00 mm. The dimensions of the samples were 13 × 13 mm for the electrochemical tests and 20 × 5 mm for the tribocorrosion tests. Samples for electrochemical tests were covered with an artificial wax (Fluka), leaving an exposed area of 1 cm². For tribocorrosion tests the samples were cold embedded in resin. All the samples were polished using emery paper of 1200 mesh. The experimental device consists of a linear tribometer of reciprocating movement, provided with a silicon nitride indenter of 6 mm, and a sample holder which also acts as a reservoir for the corrosive solution (Fig. 1a). Fig. 1b illustrates the experimental device integrated to an electrochemical unit. The chemical composition of the Ringer solution is shown in Table 2. The electrochemical cell was composed of three electrodes, with a platinum counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and the titanium alloy as the working electrode (Fig. 2). The movement of the experimental device is generated from a 24 V direct current (DC) motor. The rotary motion motor drives a flywheel and, through a double rod system supported on an eccentric shaft, it is possible to generate the reciprocal linear movement of the shaft containing the penetrator. The length of the wear track can be adjusted from 2 to 50 mm by adjusting the eccentric shaft connecting the flywheel to the connecting rod. This rotary drive motor drives a flywheel and, by means of a double rod system supported on an eccentric axis (axis fixed on the opposite side of the axis driven by the motor); it is possible to generate the reciprocal linear movement of the shaft containing the indenter. The linear motion of the wear shaft is based on a system of linear guides by the double rod. The linear drive of the wear shaft is based on a system of linear guides driven by the double rod. The wear shaft is supported by linear ball bearings, which as well as the linear guides has an extremely low friction coefficient, allowing the minimum of loss in the applied loads. The wear axle is supported by a linear ball bearing, which as well as the linear guides has an extremely low friction coefficient allowing the minimum of loss in the applied loads. The tribological contact between the indenter and the sample must be completely submerged in the electrolyte. For security, the sample
should be fixed with the indenter moving, as it would be difficult to avoid splashing if the electrochemical cell is moving. The sample or working electrode was connected to an Autolab PGSTAT 302N potentiostat. In general, ceramic materials such as alumina and zirconia are usually used as indenters. The use of these materials prevents the formation of a galvanic couple between the sample and the indenter. The indenter body should also be made of insulating material in order to prevent electrical contact between the electrolyte and the wear device. If the indenter body is made of metallic material, it should be electrically isolated from the rest of the equipment at some point. The electrochemical behavior of the samples was evaluated using potentiodynamic polarization tests in five repetitions. The scan rate adopted for the tests was 1 mV/s. To evaluate the effect of the tribocorrosion in the titanium alloy, the wear-controlled test (potentiostatic) was selected [34]. In this test, the material is subjected to wear tests at cathodic and anodic potentials under the same conditions of speed, load and time. When subjected to an anodic potential, the removed material due to electrochemical events can be estimated by Faraday’s Law (Eq. (1)).

$$M = \frac{(i_A M_w) t}{(nF)}$$ (1)

where:

- $M$ (kg) = mass of metal;
- $t$ (s) = time, 1800 s;
- $i_A$ (A) = anodic current density;
- $M_w$ (kg/mol) = atomic mass of titanium, 0.0048;
- $F$ (C/mol) = 96,500;
- $n$ = number of electrons involved: 4.

The total area exposed to the electrolyte is $A_0$ (1 cm²), the wear track area is $A_w$, and the area without mechanical wear is $A_0 - A_w$. The anodic current was continuously monitored. When the current reached a stable value of $i_A$, the wear was started. The anodic current density during wear is $i_{w}$ (wear current density). A stabilization time of 5 minutes was adopted before the start of the wear. The removed material after the tribocorrosion test was:

$$M_{tot} = M_m + M_c + S$$ (2)
where: $M_m$ = material loss due to the mechanical wear; $M_c$ = material loss due to corrosion; $S$ = material loss due to the synergism between corrosion and wear. $M_{tot}$ represents the material removed from the wear track after the tribocorrosion test determined by using profilometry. The material loss due to corrosion, $M_c$, was calculated:

$$M_c = (i_a M_t) / (nf)$$  \hspace{1cm} (3)$$

In order to obtain values of $M_c$ which are characteristics of the degraded area, $A_w$, $M_c$ values were multiplied by $A_w/A_o$. $A_w$ represents the area of the wear track calculated from profilometry results. For obtaining the mechanical wear, $M_m$, the wear rate of the material in the absence of corrosion was measured. This measurement was performed by carrying out wear tests with the same tribological patterns (speed, load, and time). However, these tests were performed under the action of a cathodic potential ($−0.86 \text{V}_{\text{SCE}}$) and the $M_w$ value was obtained by using a profilometry analysis of the wear track. For this test, a cathodic potential of $−1 \text{V}_{\text{SCE}}$ was adopted as suggested in the ASTM G119 standard. However, to avoid hydrogen embrittlement, a value of $−0.5 \text{V}$ relative to the corrosion potential was used. After the determination of $M_{tot}$, $M_m$ and $M_c$, the synergism $S$ was obtained (Eq. (2)). The synergistic factor $S$ was decomposed into two parts: $M_{cm}$, which represents the increment in the corrosion degradation due to the mechanical wear, and $M_{nc}$, which represents the increment in the material wear due to corrosion. Eq. (4) represents the composition of tribocorrosive wear, expressing the synergistic term $S$ in function of $M_{cm}$ and $M_{nc}$. Eq. (5) shows the calculation of the term $M_{cm}$.

$$M_{tot} = M_m + M_c + M_{cm}M_{nc}$$ \hspace{1cm} (4)$$

$$M_{cm} = (i_w - i_a) M_t / (nf)$$  \hspace{1cm} (5)$$

After the determination of $M_{tot}$, $M_{cm}$, $M_m$ and $M_c$, $M_{nc}$ was calculated using Eq. (4). Tribocorrosion tests evaluated two levels of load and the wear rate was determined in four different conditions of load/speed (Table 3). Each condition was tested in regime of anodic potential ($2.3 \text{V}_{\text{SCE}}$) and cathodic potential ($−0.86 \text{V}_{\text{SCE}}$), with five replicates. Tukey test at an alpha level of 0.10 was used to compare the averages of the tribocorrosion results as well as the results of potentiodynamic polarization tests.

<p>| Table 3 – Tribocorrosion testing conditions. |</p>
<table>
<thead>
<tr>
<th>Condition</th>
<th>Applied load (N)</th>
<th>Speed (mm/s)</th>
<th>Potential (V_{SCE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.85</td>
<td>9.3</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>4.85</td>
<td>9.3</td>
<td>$−0.86$</td>
</tr>
<tr>
<td>2</td>
<td>4.85</td>
<td>23.3</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>4.85</td>
<td>23.3</td>
<td>$−0.86$</td>
</tr>
<tr>
<td>3</td>
<td>9.71</td>
<td>9.3</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>9.71</td>
<td>9.3</td>
<td>$−0.86$</td>
</tr>
<tr>
<td>4</td>
<td>9.71</td>
<td>23.3</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>9.71</td>
<td>23.3</td>
<td>$−0.86$</td>
</tr>
</tbody>
</table>

3. Results and discussion

The titanium potentiodynamic polarization curve (Fig. 3) confirms its excellent corrosion resistance in a physiological medium. The formation of pits on the alloy surface was not detected. The corrosion potential was $−0.368 ± 0.082 \text{V}_{\text{SCE}}$ and a passivation range between $0.344 \text{V}_{\text{SCE}}$ and $2.932 \text{V}_{\text{SCE}}$ was observed. From the $2.932 \text{V}_{\text{SCE}}$, there was an increase in current density values, but this increase was not sufficient to cause the appearance of pits, as reported in literature [35]. As seen in Fig. 3, the potential of $2.3 \text{V}$ corresponds to a passive region of Ti alloy. Most of the Ti alloys form a single compact layer which contains TiO$_2$ and traces of other oxides [12, 15]. According to Fig. 4, at the start of reciprocating sliding, the current increases due to depassivation of the metallic sample leading to anodic metal oxidation. At the end of sliding, the current decreases again due to anodic repassivation of the exposed bare metal. After rubbing, titanium alloy tends to recover the initial current density observed before sliding. This suggests that rubbing did not modify substantially their electrochemical properties or the surface composition. At applied potential, rubbing manifests itself by an enhanced anodic current due to depassivation by the counter body sliding on the alloy. Alves et al. [13] performed tribocorrosion measurements of titanium and anodic titanium oxides produced by plasma electrolytic oxidation (PEO) using a pin-on-disk reciprocating sliding configuration. They found the wear track of titanium samples without PEO treatment is characterized by sliding wear grooves aligned in the direction of the pin movement showing the occurrence of abrasion during rubbing. Results of wear testing with controlled potential in the four conditions are shown in Table 4. Fig. 5 shows results obtained by using a profilometry analysis of the wear track, used to calculate $A_w$ and worn volume shown in Table 4. Fig. 5 shows that the worn track presented a homogeneous roughness for samples submitted to tribocorrosion for all conditions. For the mechanical degradation, studied at a cathodic potential (Fig. 5B, D, F and H), a heterogeneous distribution of roughness of worn track was observed, except for the condition of the lowest load.
and speed. Fig. 4 shows the measured values of \( i_w \) and \( i_a \), evidencing the major difference between \( i_w \) and \( i_a \) for the most aggressive condition (Fig. 4D). From the analysis of the parameters listed in Table 4, a significant increase in wear compared to the volumes of worn material in regime of tribocorrosion in relation to those found when wear occurs at cathodic potential (purely mechanical wear) was observed, especially for the condition of the highest load and speed [36,37]. The corrosion current during wear increases with the increasing speed of the indenter and the applied load, with the highest values in condition 4 (high speed conditions) [36]. The highest value of current density during wear is due to a higher depassivation rate which depends on the contact pressure, sliding velocity, the counter body, and the mechanical properties of the passive film, e.g. the scratch resistance [15]. In condition 4, the contact pressure and sliding velocity are the highest. Table 5 shows the results of removed material after tribocorrosion tests. Higher metal losses at cathodic potential (pure

Table 4 – Volume of worn material, wear track area, and values of anodic and wear current density for the four studied conditions.

<table>
<thead>
<tr>
<th>Condition/potential</th>
<th>Volume (mm³)</th>
<th>( A_w ) (mm²)</th>
<th>( i_w ) (mA)</th>
<th>( i_a ) (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/anodic</td>
<td>0.32 ± 0.06</td>
<td>12.9 ± 0.9</td>
<td>1.11 ± 0.15</td>
<td>0.064 ± 0.020</td>
</tr>
<tr>
<td>1/cathodic</td>
<td>0.17 ± 0.03</td>
<td>11.4 ± 1.1</td>
<td>0.05 ± 0.04</td>
<td>–</td>
</tr>
<tr>
<td>2/anodic</td>
<td>0.59 ± 0.16</td>
<td>15.4 ± 1.4</td>
<td>1.93 ± 0.38</td>
<td>0.143 ± 0.137</td>
</tr>
<tr>
<td>2/cathodic</td>
<td>0.36 ± 0.02</td>
<td>15.1 ± 0.6</td>
<td>0.08 ± 0.03</td>
<td>–</td>
</tr>
<tr>
<td>3/anodic</td>
<td>0.50 ± 0.03</td>
<td>14.9 ± 0.8</td>
<td>1.44 ± 0.15</td>
<td>0.093 ± 0.056</td>
</tr>
<tr>
<td>3/cathodic</td>
<td>0.21 ± 0.02</td>
<td>11.4 ± 1.1</td>
<td>0.06 ± 0.02</td>
<td>–</td>
</tr>
<tr>
<td>4/anodic</td>
<td>3.58 ± 1.62</td>
<td>17.5 ± 1.1</td>
<td>2.65 ± 0.36</td>
<td>0.120 ± 0.075</td>
</tr>
<tr>
<td>4/cathodic</td>
<td>0.47 ± 0.08</td>
<td>15.3 ± 1.3</td>
<td>0.14 ± 0.03</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 5 – Total mass loss, values of wear rate of titanium in absence of corrosion (\( M_m \)) and the mass loss due to the corrosion process (\( M_c \)), and synergistic factor (S).

<table>
<thead>
<tr>
<th>Condition</th>
<th>( M_{int} ) (× 10⁻⁶ kg)</th>
<th>( M_m ) (× 10⁻⁶ kg)</th>
<th>( M_c ) (× 10⁻⁷ kg)</th>
<th>S (× 10⁻⁷ kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.46 ± 0.13</td>
<td>0.77 ± 0.01</td>
<td>1.13 ± 0.03</td>
<td>5.70 ± 1.31</td>
</tr>
<tr>
<td>2</td>
<td>2.68 ± 0.06</td>
<td>1.64 ± 0.03</td>
<td>1.93 ± 0.10</td>
<td>8.50 ± 0.42</td>
</tr>
<tr>
<td>3</td>
<td>2.28 ± 0.03</td>
<td>0.96 ± 0.01</td>
<td>1.16 ± 0.17</td>
<td>12.00 ± 0.17</td>
</tr>
<tr>
<td>4</td>
<td>1.63 ± 0.03</td>
<td>2.14 ± 0.06</td>
<td>1.53 ± 0.01</td>
<td>140.90 ± 29.00</td>
</tr>
</tbody>
</table>
mechanical wear) were observed in conditions 4 and 2, respectively (Table 5). In this case, speed plays the major role in the metal loss due to the heat generation in the contact area. The wear loss of condition 2 showed a higher value in relation to condition 3, which was submitted to a higher load but to a lower speed. In contrast, the synergy in tribocorrosion process suffered a greater influence of the applied load, as in conditions 1 and 2 (lower load) where synergistic factor was lower and did not vary much even under great variation in speed as shown in Table 5. In conditions 3 and 4, the synergistic factor showed considerably higher values, especially under extreme conditions (highest load and speed of condition 4), demonstrating the responsibility for 86% of total wear, highlighting the importance of this phenomenon in analyzing the wear of materials subject to simultaneous corrosion and mechanical wear. Depassivation/repassivation phenomena occurring on metallic surfaces in between mechanical contact events can result in an acceleration of the overall degradation process, observed mainly in condition of highest applied load and sliding speed. In general, in tribocorrosion systems, two mechanisms contribute to material degradation: wear accelerated corrosion and mechanical wear [15]. Wear accelerated corrosion of passive metals results from the periodic removal of the passive film by abrasion, followed by metal oxidation until repassivation occurs. Mechanical wear consists of the detachment and elimination of metal particles during sliding. Calculating $M_{cm}$ (increase in corrosion due to the mechanical wear) and synergism, values of $M_{mc}$ (increment in mechanical degradation due to corrosion) were obtained. The values of $M_{mc}$ and $M_{cm}$ are presented in Table 6. The profilometry analysis of the worn surfaces revealed that the greatest wear in conditions of purely mechanical wear (cathodic protection) occurred under conditions at the highest sliding speed (4 and 2) as shown in Fig. 5. In these conditions, the depth of wear process was higher for conditions 4 and 2 than conditions 1 and 3. Except for the condition of the highest applied load and sliding speed, the corrosion decreases the mechanical wear probably due to the corrosion product lubricant action. Alves et al. [13] reported that titanium oxide films can behave as lubricants. Some researchers determined that rutile-like oxide phases exhibited low shear strength and behaved as a solid lubricant [38]. However, the increment in corrosion degradation due to wear was positive for all conditions. At the most severe condition of wear, corrosion products cease to act as lubricants. However, wear increases the corrosion rate of the low alloy titanium due to the mechanical destruction of the passive film [12]. In fact, the nature of the tribological contact may change, as corrosion products become part of the contact region. This degradation process can result in the release of wear debris that may act as abrasive particles increasing the mechanical damage, and in the case of implants they can also be harmful for the human body [12].

**Table 6 – Values of the increment in corrosion degradation due to wear ($M_{cm}$) and the increment in mechanical degradation due to corrosion ($M_{mc}$).**

<table>
<thead>
<tr>
<th>Condition</th>
<th>$M_{mc}$ ($\times 10^{-6}$ kg)</th>
<th>$M_{cm}$ ($\times 10^{-6}$ kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-1.24 \pm 0.10$</td>
<td>$1.81 \pm 0.05$</td>
</tr>
<tr>
<td>2</td>
<td>$-1.76 \pm 0.10$</td>
<td>$2.61 \pm 0.14$</td>
</tr>
<tr>
<td>3</td>
<td>$-0.92 \pm 0.04$</td>
<td>$2.12 \pm 0.03$</td>
</tr>
<tr>
<td>4</td>
<td>$10.85 \pm 2.81$</td>
<td>$3.24 \pm 0.09$</td>
</tr>
</tbody>
</table>

$S = M_{mc} + M_{cm}$. 

Fig. 5 – Profilometry analysis for samples submitted to tribocorrosion in all studied conditions.
4. Conclusions

Tribocorrosion evaluated by using controlled potential tests at the anodic and cathodic region showed that the speed of the indenter and the applied load affect the titanium degradation. Higher metal losses at cathodic potential (pure mechanical wear) were observed in conditions of the highest sliding speed. The increment in corrosion degradation due to wear was positive for all conditions. Except for the condition of the highest applied load and sliding speed, the corrosion decreases the mechanical wear. The wear track presented a homogeneous roughness for samples submitted to tribocorrosion for all conditions. For the mechanical degradation, studied at a cathodic potential, a heterogeneous distribution of roughness of the wear track was observed, except for the condition of lowest load and speed. The synergistic factor was higher for the highest applied load condition.

Conflicts of Interest

The authors declare no conflicts of interest.

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