Evaluation of the Tribocorrosion Behavior of Ti-6Al-4V Biomedical Alloy in Simulated Oral Environments

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Abstract: The sliding wear of Ti-6Al-4V alloys coexisting with dental amalgam in a simulated temperature-controlled cell was evaluated. Disc-shaped samples of Ti-6Al-4V (n = 30) and spherical silver amalgam (n = 30) were prepared. Discs were subjected to wear while immersed in artificial and fluoridated saliva as follows: Ti-6Al-4V–Ti-6Al-4V (G1); amalgam–amalgam (G2), and Ti-6Al-4V–amalgam (G3). Samples were analyzed for mass variation, volume loss, and surface roughness. Wear tracks were characterized by scanning electron microscopy. Wearing induced significant mass loss for all groups except G3 in fluoridated saliva: Ti-6Al-4V (p = 0.045) and amalgam (p = 0.732). These samples presented an increase in mean surface roughness (p = 0.032 and 0.010, respectively). Overall, Ti-6Al-4V showed 0.07 mm³ (95% CI: [0.06–0.07]) higher wear track volume. Ti-6Al-4V has a higher mass loss when subjected to fluoridated media but no significant roughness variation. Fluor-containing substances should be avoided over Ti-6Al-4V alloys placed in areas of mechanical wear, especially if dental amalgam is also present.

Keywords: dental alloys; wear; surface roughness; Ti-6Al-4V; tribocorrosion

1. Introduction

Metal alloys used in the oral cavity for restorative or prosthetic purposes are subjected to a wet environment, where saliva can act as an electrolytic solution that promotes electrochemical reactions between the different alloys. Therefore, metal restorations permanently held in saliva can undergo progressive degradation due to corrosion [1]. Up to now, however, there is little evidence that multiple metal restorations on the same medium increase wear. Nonetheless, empirical clinical observations frequently detect signs of wear in dental restorations; this phenomenon could be intensified by the coexistence of different metal alloys in the oral cavity, such as amalgam, cobalt–chromium, and titanium alloys.

The expansion of dental implants and implant-supported prostheses increased the development and optimization of metallic alloys [2], namely titanium alloys, such as Ti-6Al-4V. This alloy has higher strength than commercially pure grade IV titanium and can be used to manufacture implant components (namely abutments) and the frameworks of fixed and removable prostheses (tooth and implant-supported).

In the oral cavity, Ti-6Al-4V biomedical alloys are subjected to a process called tribocorrosion, which is the combination of corrosion and wear action, culminating in irreversible material degradation, in which wear probably contributes to the initiating mechanism [3–6]. Adequate wear resistance is a requirement of a dental alloy used in oral rehabilitation to
ensure the durability of the restorations. On the contrary, a high wear rate may be related to the elongation of antagonists, tilting, and movement of teeth and other dysfunctions [7].

Although titanium and its alloys are considered corrosion-resistant, they are susceptible to acidic environments and to the presence of fluoride ions [8,9]. According to the literature, fluoride ions present in toothpaste, mouthwashes, and fluoridated acidic prophylactic gels may be harmful to the corrosion resistance of titanium-based materials for dental use. The fluoride ion can disrupt the protective oxide layer present on the surface of Ti alloys, which has been considered responsible for the corrosion resistance of the mentioned alloys [3,10–12]. This is an issue to take into account, because fluoride is a fundamental agent in the prevention of tooth decay [13].

Several studies evaluate the effect of fluoride on the corrosion behavior of titanium isolated or coupled with amalgam but understatic conditions [1,14–16]. Other authors also evaluated tribocorrosion, particularly stress corrosion [11], fretting corrosion [17,18], fatigue [19–22], and elastic tensile strain [10] but on dental alloys isolated.

The literature is sparse regarding the evaluation of different alloys in the same medium under dynamic wear testing conditions, with and without fluoride. Thus, the purpose of the present study was to evaluate the sliding wear of two dental alloys coexisting in a simulated temperature-controlled cell containing artificial saliva, in the presence and absence of fluoride ions. The fluoridated saliva with a concentration of 225 ppm of fluoride was used since almost all fluoride mouthwashes on sale have this concentration [13]. We hypothesized that due to the galvanic phenomenon, the simultaneous presence of amalgam and Ti-6Al-4V samples in a wet medium leads to higher wear and surface roughness in amalgam and lower wear and surface roughness in Ti-6Al-4V, compared to the samples isolated. Additionally, we hypothesized that the fluoridation of the wet medium would contribute to an increase in the wear of Ti-6Al-4V samples due to the disruption of the superficial oxide layer, regardless of the presence of the amalgam.

2. Materials and Methods

2.1. Preparation of Test Materials

To carry out this study, 10 mm × 3 mm disc-shaped samples of two metallic alloys with application in Dentistry were prepared: a titanium alloy (Ti-6Al-4V) and a spherical silver amalgam alloy with the following composition in percent weight (wt.%): Ag—60 wt.%, Sn—28 wt.%, and Cu—12 wt.%. 

Ti-6Al-4V samples (n = 30) were obtained by machining metal rods (titanium/aluminum/vanadium Ti-6Al-4V Rod, Lot LS2782375JP, Goodfellow Cambridge Limited®, Huntingdon, UK). Samples were then mechanically polished for 1 min using abrasive sandpaper grit 1000 (Struers Inc., Cleveland, OH, USA) at 150 rpm and 10 N pressure.

Amalgam samples (n = 30) were prepared using self-activating capsules (Tytin, Kerr Manufacturing Co., Romulus, MI, USA; Lot 3-3069), as indicated by the manufacturer. The capsule was placed and secured in the amalgamator and triturated for 8 s. The mix was immediately condensed after trituration according to Specification No. 1 ANSI/ADA into a 10 mm × 3 mm cylindric mold. After setting, the samples were polished for 15 s using abrasive sandpaper grit 2500 (Struers Inc., Cleveland, OH, USA) at 300 rpm and 5 N pressure.

The polished samples were enclosed in an acrylic resin cylinder, subjected to a mass loss study, and then stored in water for 14 days at 37 °C. After storage, samples were cleaned using distilled water in an ultrasonic cleaner and stored for another 7 days at room temperature.

2.2. Initial Characterization of the Samples

Before being subjected to tribological experiments, the samples were analyzed with regard to initial mass, surface roughness, and Vickers hardness.
2.2.1. Initial Mass

All samples were weighed before the wear tests using an analytical electronic scale (Model AA-200Ds, Denver Instrument Co, Denver, CO, USA), with a 0.0001 g sensitivity.

2.2.2. Surface Roughness

The surface roughness of the samples was determined in a profilometry device (Perthometer Mahr, model Perthen S4P, Götttingen, Germany), using a filter LT (0.800x5) 5600 Mn. The amplitude parameters used were arithmetic average height (Ra) and ten-point height (Rz).

Ra is defined as the average absolute deviation of the roughness irregularities from the mean line over one sampling length [23].

Rz is more sensitive to occasional high peaks or deep valleys than Ra. The ISO system defines this parameter as the difference in height between the average of the five highest peaks and the five lowest valleys along the assessment length of the profile [23].

2.2.3. Vickers Hardness Measurement

Vickers hardness test is based on the resistance that the material offers to the penetration of a diamond pyramid with a square base and an angle between faces of 136°, under a given load. The samples were subjected to forces of 1, 2, 5, 10, and 20 N in a micro Vickers hardness tester (model HMV-2, Shimadzu, Japan) that allows the acquisition, recording, and processing of data for the evaluation of hardness. Five repetitions were performed for each force. This test followed ISO 6507 standards [24].

2.3. Tribocorrosion Experiments

The samples were tested in couples: Ti-6Al-4V + Ti-6Al-4V (G1); amalgam + amalgam (G2); and Ti-6Al-4V + amalgam (G3) and subjected to a wear test.

The wear was carried out in alternative sliding equipment with customizable stroke, speed, and load (Figure 1) (Pedro Nunes Institute, Coimbra, Portugal), which simulates the conditions of use usually given to these materials in the oral cavity. The wear equipment operates by applying a vertical load to the specimen using a counter body, sliding horizontally, and then repeating the cycle. The counter-body type was made of a chemically inert ceramic material (95% Alumina spheres (Al₂O₃) ¼ Helmut Kreutz, Haiger, Germany) [25], with a hardness similar to dental enamel; the contact is a punctual type using a counter-plane sphere. The parameters for this test were as follows: a load of 15 N and 2400 cycles at 0.7 Hz.

![Figure 1. Schematic representation of the equipment customized to perform wear testing of the samples.](image)

During the tests, the samples were immersed in an electrolyte solution kept in circulation at 310.15 K, simulating the conditions found in the oral cavity. After the tests, the samples were washed with distilled water, ultrasonically cleaned for 5 min, and dried, before final characterization.

Two electrolyte solutions were considered: artificial saliva and artificial fluoridated saliva; the latter was prepared by using sodium fluoride (NaF) at 225 ppm. Artificial saliva
was prepared according to the following composition [26,27]: potassium chloride (KCl, 20 mmol/L), sodium hydrogen carbonate (NaHCO₃, 17.9 mmol/L), sodium dihydrogen phosphate (NaH₂PO₄·H₂O, 3.6 mmol/L), potassium thiocyanate (KSCN, 5.1 mmol/L), and lactic acid (0.10 mmol/L). All solutions were prepared using Milli-Q ultrapure water of resistivity >18 MΩ·cm and analytical grade reagents. The laboratory temperature was 25 ± 1 °C in all experiments.

2.4. Final Characterization of the Samples

After the tribocorrosion experiments, all samples were subject to weighing in the same equipment described in Section 2.2.1, and the wear track profile was acquired by Perthenometer Perthen S4P, previously described in Section 2.2.2, in order to evaluate the final surface roughness and the volume of the wear tracks.

The wear track morphology was also observed by scanning electron microscopy (SEM JEOL JSM-5310, Tokyo, Japan) with a voltage of 20 kV.

2.5. Statistical Analysis

All statistical analyses were carried out on SPSS Statistics Version 27.0 (IBM, New York, NY, USA). Data on the variation in mass, wear track volume, and surface roughness variation (Ra and Rz) of the samples were analyzed using a three-way factorial design (three-way ANOVA), considering as independent variables, the material, the electrolyte, and the cylinder combination (pairs of cylinders simultaneously tested). Data were checked for normality and homoscedasticity and for three-way and simple two-way interactions.

Simple comparisons (pre–post and between levels of the independent variables—between alloys or between electrolyte solutions) were performed with non-parametric tests (Kruskal–Wallis and Mann–Whitney U for independent groups, Wilcoxon for paired data), followed by post hoc Bonferroni correction where applicable. The significance level was set at 0.05.

3. Results

3.1. Specimen Mass Variation

The mean and median values of the registered initial and final mass of the Ti-6Al-4V and amalgam samples tested in artificial saliva (AS) and fluoridated artificial saliva (FS) are detailed in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>T0</th>
<th>T1</th>
<th>ΔT0–T1</th>
<th>p-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Mean (SD), g</td>
<td>Mean (SD), g</td>
<td>Mean (SE), mg</td>
</tr>
<tr>
<td>AS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>10</td>
<td>2.4 (0.2)</td>
<td>2.4 (0.2)</td>
<td>820 (300)</td>
</tr>
<tr>
<td>G2</td>
<td>10</td>
<td>3.6 (0.4)</td>
<td>3.6 (0.4)</td>
<td>3070 (300)</td>
</tr>
<tr>
<td>G3</td>
<td>5</td>
<td>3.5 (0.5)</td>
<td>3.5 (0.5)</td>
<td>3040 (400)</td>
</tr>
<tr>
<td>FS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>10</td>
<td>2.4 (0.3)</td>
<td>2.4 (0.3)</td>
<td>3560 (200)</td>
</tr>
<tr>
<td>G2</td>
<td>10</td>
<td>3.7 (0.4)</td>
<td>3.7 (0.4)</td>
<td>5620 (300)</td>
</tr>
<tr>
<td>G3</td>
<td>5</td>
<td>2.4 (0.3)</td>
<td>2.4 (0.3)</td>
<td>7200 (2500)</td>
</tr>
</tbody>
</table>

* is the usual indication of what is statistically significant.

Wearing induces a statistically significant mass loss for all groups, except for the amalgam samples in G3 (simultaneous testing of Ti-6Al-4V and amalgam specimens) when submerged in fluoridated saliva (p = 0.732).
There were statistically significant differences in mass loss between G1 and G2 regardless of the electrolyte solution (AS or FS, \( p = 0.004 \) and \( p = 0.026 \), respectively).

However, there were no statistically significant differences between TiAlV samples (G1 and G3, \( p > 0.05 \)) or amalgam samples (G2 and G3, \( p = 0.205 \)) after immersion in artificial saliva.

Three-way ANOVA detected a statistically significant three-way interaction between cylinder material, cylinder combination in testing setup (Ti-6Al-4V–Ti-6Al-4V or amalgam–amalgam or Ti-6Al-4V–amalgam), and type of electrolyte solution: \( F(1, 52) = 5.40, p = 0.024 \). There was a statistically significant simple two-way interaction between material and type of electrolyte solution for cylinder combination Ti-6Al-4V–amalgam, \( F(1, 52) = 8.56, p = 0.01 \), but not for cylinders of the same material, \( F(1, 52) = 0.012, p > 0.05 \). Such findings are graphically replicated in Figure 2, in which it is possible to notice that the fluoridation of saliva promotes a similar increase in mass loss for the samples of Ti-6Al-4V and amalgam when tested separately (full thickness lines representing G1 and G2) but not when tested simultaneously (dashed lines representing Ti-6Al-4V and amalgam samples of G3). In this case, saliva fluoridation leads to higher mass loss of the Ti-6Al-4V samples (approximately twice that of G1) and lower mass loss of the amalgam samples (4 to 5 times lower than that for G2).

![Figure 2](image-url)  
**Figure 2.** Mean mass loss (micrograms) of G1, G2, and G3 samples tested in artificial saliva and fluoridated saliva. Notice the cylinder combination and electrolyte solution interaction.

### 3.2. Vickers Hardness

The Vickers test revealed that Ti-6Al-4V samples present hardness superior to 3 GPa regardless of the applied load (up to 20 N). Under the same conditions, amalgam samples show lower test values, i.e., approximately 2 GPa.

### 3.3. Surface Roughness

Prior to the wear test (T0), all groups are characterized by similar arithmetic average surface roughness (Ra). The exceptions are Ti-6Al-4V samples of G3, tested in fluoridated saliva, for which lower Ra values were obtained, as depicted in Table 2.

The wearing test induced an increase in Ra values for all amalgam samples, statistically significant for G2 in saliva (\( p = 0.001 \)) and G3 in FS (0.010). After the wear test (T1), the Ra values of titanium samples remained relatively similar to those of the pre-test (T0) despite the slight increase in Ti-6Al-4V samples of G3 in FS.

At T0, there were no statistically significant differences in the average maximum height of the profile (Rz) (\( p = 0.426 \)). After the wear test (T1), there was an increase in Rz of all amalgam samples, as detailed in Table 2 and graphically represented in Figure 3. The analysis of data shows that G3 amalgam samples, after immersion in FS, lead to statistically higher Rz than their counterpart Ti-6Al-4V samples (\( p = 0.036 \)).
Table 2. Mean values of the registered initial (T0) and final (T1) Ra and Rz to Ti-6Al-4V and amalgam samples tested in artificial saliva and fluoridated artificial saliva. Values in micrometers. † p-value for the T0–T1 comparison within each group (Wilcoxon test); †† p-value for the group comparison at T0 and T1 (Kruskal–Wallis test).

<table>
<thead>
<tr>
<th>Group Material</th>
<th>N</th>
<th>T0 Mean (SD), µm</th>
<th>T1 Mean (SD), µm</th>
<th>p-Value †</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial saliva</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 (Ti-6Al-4V)</td>
<td>10</td>
<td>0.43 (0.07)</td>
<td>0.5 (0.1)</td>
<td>0.431</td>
</tr>
<tr>
<td>G2 (Amalgam)</td>
<td>10</td>
<td>0.49 (0.05)</td>
<td>0.59 (0.09)</td>
<td>0.001 *</td>
</tr>
<tr>
<td>G3</td>
<td></td>
<td>Ti-6Al-4V</td>
<td>0.47 (0.05)</td>
<td>0.5 (0.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amalgam</td>
<td>0.49 (0.05)</td>
<td>0.53 (0.07)</td>
</tr>
<tr>
<td>Fluoridated saliva</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 (Ti-6Al-4V)</td>
<td>10</td>
<td>0.43 (0.08)</td>
<td>0.44 (0.09)</td>
<td>0.659</td>
</tr>
<tr>
<td>G2 (Amalgam)</td>
<td>10</td>
<td>0.47 (0.05)</td>
<td>0.5 (0.1)</td>
<td>0.146</td>
</tr>
<tr>
<td>G3</td>
<td></td>
<td>Ti-6Al-4V</td>
<td>0.38 (0.06)</td>
<td>0.43 (0.03)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amalgam</td>
<td>0.50 (0.05)</td>
<td>0.68 (0.07)</td>
</tr>
</tbody>
</table>

| p-value †† | 0.042 * | 0.024 * |

Table 3. Mean values of the registered initial (T0) and final (T1) Ra and Rz to Ti-6Al-4V and amalgam samples tested in artificial saliva and fluoridated artificial saliva. Values in micrometers. † p-value for the T0–T1 comparison within each group (Wilcoxon test); †† p-value for the group comparison at T0 and T1 (Kruskal–Wallis test).

<table>
<thead>
<tr>
<th>Group Material</th>
<th>N</th>
<th>T0 Mean (SD), µm</th>
<th>T1 Mean (SD), µm</th>
<th>p-Value †</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial saliva</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 (Ti-6Al-4V)</td>
<td>10</td>
<td>4.6 ± 0.7</td>
<td>5 ± 1</td>
<td>0.679</td>
</tr>
<tr>
<td>G2 (Amalgam)</td>
<td>10</td>
<td>5.1 ± 0.4</td>
<td>6 ± 1</td>
<td>0.009 *</td>
</tr>
<tr>
<td>G3</td>
<td></td>
<td>Ti-6Al-4V</td>
<td>5.0 ± 0.4</td>
<td>6 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amalgam</td>
<td>5 ± 1</td>
<td>5.6 ± 0.6</td>
</tr>
<tr>
<td>Fluoridated saliva</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 (Ti-6Al-4V)</td>
<td>10</td>
<td>4.7 ± 0.9</td>
<td>4.8 ± 0.6</td>
<td>0.728</td>
</tr>
<tr>
<td>G2 (Amalgam)</td>
<td>10</td>
<td>5.0 ± 0.6</td>
<td>5.5 ± 0.8</td>
<td>0.118</td>
</tr>
<tr>
<td>G3</td>
<td></td>
<td>Ti-6Al-4V</td>
<td>4.7 ± 0.4</td>
<td>4.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amalgam</td>
<td>4.7 ± 0.4</td>
<td>7 ± 2</td>
</tr>
</tbody>
</table>

| p-value †† | 0.426 | 0.019 * |

* is the usual indication of what is statistically significant.

Figure 3. Distribution of Ra and Rz variation (micrometers) of all samples from T0 to T1 clustered by type of solution.

Ti6-Al-4V samples of G1 presented almost null Rz variation regardless of the electrolyte solution (Figure 3). However, Ti6-Al-4V samples of G3 presented a slight increase in Rz in artificial saliva, whereas there was a reduction in the maximum height of the profile for Ti6-Al-4V samples of G3 tested in fluoridated saliva.
3.4. Volume of the Wear Tracks

The mean volumes of the wear tracks of each group are shown in Table 3.

Table 3. Volume loss associated with the wear tracks measured by profilometry, mm$^3$. † $p$-value for the artificial saliva and fluoridated saliva comparison within each group (Mann–Whitney test); ‡ $p$-value for the group comparison in each of the immersion solutions (artificial saliva and fluoridated saliva (Kruskal–Wallis test and all pairwise post hoc comparisons with Bonferroni correction; similar superscript letters indicate groups that differ at the 0.05 level).

<table>
<thead>
<tr>
<th>Group</th>
<th>Material</th>
<th>Wear Volume in Artificial Saliva Mean ± SD</th>
<th>Wear Volume in Fluoridated Saliva Mean ± SD</th>
<th>$p$-Value †</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>TiAlV</td>
<td>0.0753 ± 0.0152 $^{abc}$</td>
<td>0.0655 ± 0.0233 $^{abc}$</td>
<td>0.315</td>
</tr>
<tr>
<td>G2</td>
<td>Amalgam</td>
<td>0.0061 ± 0.0097 $^{ab}$</td>
<td>0.0050 ± 0.0092 $^{ab}$</td>
<td>0.190</td>
</tr>
<tr>
<td>G3</td>
<td>TiAlV</td>
<td>0.0740 ± 0.0116 $^{bd}$</td>
<td>0.0730 ± 0.0097 $^{bd}$</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td>G3</td>
<td>Amalgam</td>
<td>0.0100 ± 0.0081 $^{cd}$</td>
<td>0.0020 ± 0.0011 $^{cd}$</td>
<td>0.151</td>
</tr>
</tbody>
</table>

$p$-value ‡

Three-way ANOVA was unable to detect a three-way interaction between material, type of electrolyte solution, and cylinder combination in the volume of the wear track: F(1, 52) = 1.05, $p = 0.311$. Also, no two-way interactions were identified between any pair of variables ($p > 0.05$ for all interactions). Therefore only the variable “material” shows a statistically significant main effect (F(1, 52) = 310.68, $p < 0.001$), with higher wear track volumes equal to 0.07 mm$^3$ (95% CI: [0.06–0.07]).

The absence of simple main effects for electrolyte solution and any type of interactions indicated that there were no statistically significant differences between samples of the same material in different electrolyte solutions, i.e., Ti-6Al-4V in artificial saliva presented comparable volume loss to Ti-6Al-4V in fluoridated artificial saliva ($p = 0.315$) and a similar situation occurred with amalgam in artificial and fluoridated artificial saliva ($p = 0.190$). The simultaneous presence of two different materials had no impact on the volume of the wear track for both Ti-6Al-4V and amalgam ($p > 0.05$ and $p = 0.151$, respectively).

3.5. SEM Observation of the Wear Tracks

Representative images of the scanning electron microscopy observation of different samples after the wearing tests are shown in Figures 4–10.

Figure 4. SEM images of an amalgam sample tested with Ti-6Al-4V in artificial saliva: (a) 350× and (b) 1500×.
In Figure 4, amalgam samples tested simultaneously with Ti-6Al-4V (G3) in artificial saliva show visible tips, material deposit on the bottom, and extensive ploughing. The wear tracks demonstrate a strong abrasive action of the alumina ball.

Figure 5. SEM images of an amalgam sample tested with Ti-6Al-4V in fluoridated saliva: (a) 75× and (b) 1000×.

Figure 6. SEM images of a Ti-6Al-4V tested with amalgam in artificial saliva: (a) 750× and (b) 1000×.

Figure 7. SEM image of a Ti-6Al-4V tested with amalgam in artificial saliva at 3500×. Notice the micro-crack identified in the sliding track.
In Figure 4, amalgam samples tested simultaneously with Ti-6Al-4V (G3) in AS show uniform wear tracks, without significant material destruction. However, some pores are visible, as detailed in Figure 4b. When these two materials are tested simultaneously in FS, it is possible to observe cylindrical particles deposited on the surface of the amalgam samples (Figure 5b), even though no significant destruction can be reported for the wear tracks. From the analysis of micrographs of Ti-6Al-4V (Figure 6), we can conclude that...
wear causes significant surface destruction, occasionally with micro-cracks in the bottom of the track perpendicular to the sliding direction (Figure 7). It is also possible to observe the accumulation of debris particles in front of the counter body (Figure 6a) as well as the formation of a lamellae structure on the periphery of the wear tracks (Figure 6b). The crumbling material that drags in front of the counter body works as a third body and sometimes facilitates wear as a lubricant.

When these two materials are simultaneously tested in fluoridated saliva, the Ti-6Al-4V samples (Figure 8) show visible tips, material deposit on the bottom of the wear track, and extensive ploughing.

The wear tracks of amalgam samples (G2) tested in artificial saliva and fluoridated saliva are presented in Figure 9a,b, respectively. The wear tracks of these samples show neither morphological differences nor material pullout, although it is possible to see on the surface the same cylindrical particles that are observed in Figure 5b. Ti-6Al-4V samples of G1 tested in artificial saliva shown in Figure 10a present material deformation aligned in lamellae, small microfractures in a repetitive process, extensive ploughing, large deformation, and very strong abrasion, but no great crumbling. The dragged material shapes a track and not the counter body.

Micrographs of Ti-6Al-4V samples of G2 tested in fluoridated saliva (Figure 10b) reveal a spallation and extensive ploughing on the wear track, demonstrating a strong abrasive wear action of the alumina ball.

4. Discussion

Dental alloy corrosion measured by electrochemical methods has been extensively tested in recent years; however, in our literature review, we found that there is a gap in tribological studies for Ti-6Al-4V. Having in mind that there are many patients who have different metal alloys in the oral cavity and corrosion rate, in general, strongly affected by mechanical processes such as wear, a sliding device has been developed that makes it possible to simulate the coexistence of two alloys but also subject them to the action of forces when immersed in an electrolyte solution. In previous studies, it has been reported that galvanic corrosion occurs in amalgam alloys in contact with Ti implants [28]. Bumgardner and Johansson [29] have also found that coupling those two dental alloys may undergo the release of saliva of potentially toxic corrosion products. Although the use of amalgam has fallen into disuse, we still find many patients with teeth restored with this material. So, in the present study, the wearing of two different metallic alloys, amalgam and Ti-6Al-4V, submerged in a wet medium, with and without fluoride, was evaluated.

The main results obtained in this study indicate that, in artificial saliva, there is no significant difference in the average mass loss of the Ti-6Al-4V samples, either when tested alone or together with amalgam. However, fluoridation of the moist environment leads to an increase in mass loss in all the Ti-6Al-4V samples. This can be explained by the delamination of the oxide film on the surface of the Ti-6Al-4V samples due to the presence of fluoride ions [18]. It is important to note that when Ti-6Al-4V is tested simultaneously with amalgam samples, mass loss is twice that of Ti-6Al-4V tested alone.

Even though in this study mass loss was considered a surrogate variable for the wear assessment, other variables like surface roughness and volume of the wear track were assessed. According to DeLong, the volume is the preferred parameter for measuring the wear effect [30].

We obtained the wear volume by measuring the wear crater by profilometry, taking a measurement that crosses the wear track, and multiplying this value by the length of the wear track. Here we were unable to find differences between the wear crater of Ti-6Al-4V samples regardless of the presence of the amalgam or the type of electrolyte solution. Nevertheless, Ti-6Al-4V has, on average, 0.07 mm$^3$ higher volume loss than amalgam. This result is in agreement with those reported by Atar [31], who studied the sliding wear performance of Ti-6Al-4V, 316 stainless steel, and CoCr isolated in dry conditions. They demonstrated that the Ti6-Al-4V has poor wear resistance, as justified by the low shear
strength of titanium and its high tendency to scuff off the HCC structure, contrariwise dental amalgam is known for its high resistance to occlusal wear. We have found that no correlation between volume wear mass losses were found. The reason for this may be the high heterogeneity of the craters, as can be seen from SEM images, which leads to different volumes of wear paths.

With regard to the SEM images, in Ti-6Al-4V, extensive shear deformation and signals of abrasive wear were observed. We have also found some areas of particle detachments and delaminated wear compatible with adhesive wear. Our results are in line with the studies published by Atar, Fu et al., and Meddah et al. [31–33], even though the conditions of these studies are different. In the Ti-6Al-4V samples, the wear mechanism is formed with the worn material accumulating in the areas surrounding the wear track and, in particular, in front of the counter body, acting as a third body that increases surface degradation.

From the results obtained, we verified that there was extensive carving in the wear tracks as well as a delamination mechanism in the Ti-6Al-4V samples, which was corroborated by some other studies [33,34] that report that despite the high resistance of titanium to corrosion, it is little wear resistant. Among the damage mechanisms seen in Ti-6Al-4V, micro-cracks observed in the wear track act as crack initiation sites, which may coalesce and lead to premature fatigue.

In the amalgam samples, we observed grooves parallel to the sliding direction, compatible with the abrasive wear mechanism. It is also possible to observe cylindrical particles that we believe correspond to oxides; according to Landolt et al. [35], during the sliding contact, metallic wear particles are torn from the first body, and these particles create a metallic third body. Some may undergo electrochemical oxidation, leading to the formation of solid oxides, so it would be of interest in future investigations to analyze the surface chemical structure of these particles. Additionally, as previously described, when we tested the two alloys simultaneously, in a fluoridated medium, the mass of amalgam samples increased, which leads us to suppose that some debris and oxides released from the Ti-6Al-4V are deposited in amalgam samples.

While for all the amalgam samples, the roughness parameters analyzed (Ra and Rz) increased in both media; in the Ti-6Al-4V alloy, when tested simultaneously with amalgam, the Rz value in artificial saliva and the Ra value in fluoridated saliva slightly increased, with a contrasting decrease in the value of Rz. These results may be explained through the development of galvanic currents and by the release and deposition of oxides resulting from this phenomenon, as well as by the wear to which they were subjected.

Regarding Vickers hardness, we consider that it is stable with the loads used, since it does not suffer large variations, for both alloys.

The hardness of the metal alloy must be sufficient to resist occlusal forces without wearing down the opposing teeth. According to El-Bediwi et al. [36], alloys with a Vickers hardness <125 kg/mm² are susceptible to wear, while with a hardness greater than 340 kg/mm², there is a risk of wearing down the opposing teeth. Based on the results obtained, both Ti-6Al-4V and amalgam have surface hardness within this range of values.

According to Archard’s Law, the volume of loss material should be proportional to load and sliding distance and inversely proportional to the hardness value of the material [37]. Martin et al. [38] investigated the tribocorrosion behavior of Ti-6Al-4V and established a connection between a lower hardness and high mechanical wear.

In the present study, it was not possible to correlate the hardness of Ti-6Al-4V and wear, which is consistent with the findings of Chan et al. [39]; although the surface hardness of Ti-6Al-4V was higher than that of amalgam, mechanical wear was more pronounced.

It should be noted that in this tribological study, due to equipment limitations, the applied load was lower than that recommended by Heintze for this type of simulation. The author states that the applied load should be between 20 and 120 N, which is similar to that of the biting force in molars [7]. Nevertheless, 15 N was the load chosen by some other authors [40–42], and under 15 N load, severe material damage of the Ti-6Al-4V samples was observed, being higher than that of the amalgam samples.
Due to the large difference in galvanic potentials between amalgam and Ti-6Al-4V, it is reasonable that the amalgam suffers greater galvanic corrosion than the more noble alloy, Ti-6Al-4V. As would be expected, in artificial saliva, the Ti-6Al-4V sample does not suffer alterations when tested simultaneously with amalgam. However, this premise does not happen in the presence of fluoride; in this medium, Ti-6Al-4V suffers a greater loss of mass and a decrease in Rz, which makes us suppose that there is a synergistic effect between fluoride and amalgam.

5. Conclusions

Based on the data presented and discussed, we can conclude that the surface roughness and mass losses obtained for both alloys are in close agreement with the SEM analysis. It can also be concluded that, in artificial saliva when Ti-6Al-4V and amalgam are simultaneously present, no significant changes in the physical parameters of the former are found. However, in a fluoridated medium, there is a higher mass loss in Ti-6Al-4V, and on the contrary, amalgam samples do not suffer any mass variation. In these conditions, the surface roughness (Rz) of Ti-6Al-4V reduces whereas its counterpart amalgam increases significantly. In fact, apparently, Ti-6Al-4V alloy seems to suffer the synergistic action of fluoride and amalgam. Fluor-containing substances should be avoided over Ti-6Al-4V alloys placed in areas of mechanical wear, especially if dental amalgam is also present.


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References


37. Archard, J.F. Contact and Rubbing of Flat Surfaces. J. Appl. Phys. 1953, 24, 981–988. [CrossRef]

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