

## Article

# Micro and Macro-Tribology Behavior of a Hierarchical Architecture of a Multilayer TaN/Ta Hard Coating

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**Abstract:** The micro- and macro-tribological behaviors of a novel hierarchical TaN/Ta coating deposited on Ti6Al4V biomedical alloy by direct current magnetron sputtering were analyzed in the present work. This analysis was associated with the morphological, structural, and mechanical properties, as well as the roughness changes during and after the tribological tests. The wear track of the coating after the macro-tribology tests was evaluated by Raman spectroscopy in order to detect the compounds formed as a result of the tribo-reactions that occurred during the tests. Micro- and macro-tribology behaviors showed a significant wear rate reduction of the hierarchical coating in comparison to the Ti6Al4V substrate. For the case of the micro-tribology tests, this reduction was attributed to the high hardness of the coating (31.4 GPa); however, this hardness caused a considerable increment in the friction coefficient. On the other hand, the macro-tribology performance was associated with the hardness and the ability of the hierarchical architecture to prevent the propagation of cracks. Moreover, the friction coefficient increased considerably at the end of the test; this increment was associated with the tantalum oxides in the wear track detected by Raman spectroscopy.

**Keywords:** micro-tribology; macro-tribology; hierarchical architecture; hard coating; Raman spectroscopy

## 1. Introduction

Tantalum (Ta) and tantalum nitride (TaN) coatings are widely used in industrial applications for high temperature and wear protection due to their biocompatibility and excellent corrosion resistance. They are also promising multifunctional materials in the area of biomedical implants [1,2]. These coatings in a single-layer configuration suffer from low ductility and compressive or tensile stresses that under a mechanical load can promote cracks, leading to coating failure [3,4]. To overcome these problems, some researchers have proposed multilayer configurations improving thereby the toughness, friction, and hardness [5–9]. Although a multilayer configuration has better performance in terms of load-bearing capacity and cracking reduction than single-layer coatings, the stress gradient within

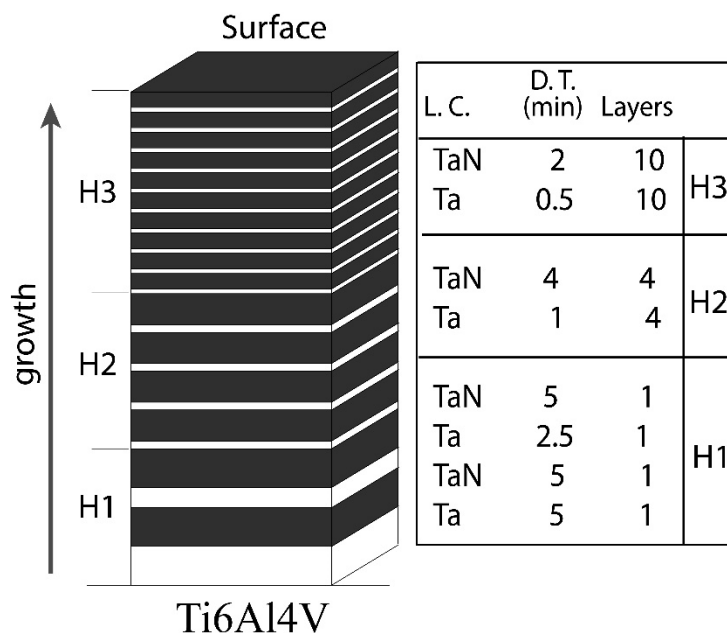
layers constituting the coatings and at substrate interface still remains as a weakness, limiting their applications. Among multilayer configurations, there are some known as hierarchical or graded, consisting of a gradual reduction of the period size ( $\Lambda$ ) from the coating–substrate interface to the surface [6]. Such configurations can increase the hardness by means of the Hall–Petch effect, since the grain size decreases with the period size [10–13], and they can also improve the adhesion between the coating and the substrate if the layer anchored to the substrate is thick and ductile, and the top layer is hard and thin, mimicking an exoskeletal microstructure [14]. Multilayer coatings have shown a significant reduction of abrasive, fretting, and adhesive wear, which are the more common wear mechanisms in biomedical applications [7]. Since Ta and TaN are desirable biomedical wear resistance coatings for applications such as hip and knee prosthesis, it is important to consider the tribocorrosive wear. One of the main problems of coating/substrate systems working in a tribocorrosive environment are defects such as cracks, pin-holes, and holes that can produce pitting corrosion on the metallic layers and the substrate. This usually conduces to the formation of debris that eventually increases wear, leading to ions release from the substrate [15–17]. It is important to mention that the multilayer configuration principle not only applies to the improvement of the mechanical properties, it is also used for other applications such as energy harvesting by thermoelectric devices and heat barriers [18–23], where the interfaces between each layer and the differences of the physical properties of the layers play an important role.

Many publications have focused on increasing the wear resistance of the biomedical alloys by the growth of ceramic monolayers of TaN or TaN/Ta multilayers, but none of them have used hierarchical configurations [24–27]. Furthermore, the micro-tribology studies about this type of coatings are limited [28]. In this paper, we present the micro- and macro-scale tribological behavior of Ti6Al4V substrate with a novel hierarchical multilayer TaN/Ta coating deposited by direct current (DC) magnetron sputtering. The investigation deals with the effects of the hierarchical architecture on the micro- and macro-tribological behaviors.

## 2. Materials and Methods

The design of the hierarchical configuration Hier-TaN/Ta coating shown in Figure 1, based on our previous published research on WC/WCN/W multilayers [10], roughly mimics the armor of some beetles and mollusks [29]. The outermost zone H3 is the hardest to protect against external aggression (penetration and wear), the middle region H2 works as a transition to avoid abrupt changes that can lead to delamination, and the zone H1 provides toughening by dissipating the mechanical energy, and it also increases the adhesion of the multilayer with the substrate.

The coating was deposited by unbalanced reactive DC magnetron sputtering (DCMS) from a Ta target of 50.8 mm diameter located at 60 mm from two kinds of substrates (Ti6Al4V and Si wafer) in a vacuum chamber with a base pressure of less than  $2.27 \times 10^{-3}$  Pa. During the sputtering process, the substrates were maintained at approximately 300 °C temperature ( $T_s$ ) and a negative bias of 60V DC. The crystalline structure of the coatings was assessed by X-ray diffraction (XRD) experiments using a Panalytical Empyrean diffractometer (Almelo, The Netherlands), with  $\text{CuK}\alpha$  radiation (step 0.026°) following the Bragg–Brentano geometry. The morphology and the thickness of each coating were evaluated by cross-sectional images from brittle fractured samples deposited simultaneously on Si (100) by using a FESEM (Field Emission Scanning Electronic Microscope) Tescan MIRA 3LMU (Brno, Czech Republic) system. In addition, the thicknesses were also verified with a contact profilometer Veeco Dektak 150 (Plainview, NY, USA).



**Figure 1.** Schematic drawing of the deposition time used for each layer of the TaN/Ta coating, L.C (layer composition), D.T (deposition time).

The mechanical properties of the TaN/Ta coating and Ti6Al4V substrate were determined by using a nanoindenter FISHERSCOPE HM2000 (Sindelfingen, Germany). Seven nanoindentation tests on the surface of each sample were performed at 6.5 mN load with a Vickers type diamond tip (Sindelfingen, Germany) to obtain load–displacement curves; the hardness (H) and elastic modulus (E) were evaluated from the unloaded portion by using the Oliver and Pharr method [30]. Each nanoindentation was made in three steps: first, the load was increased linearly from 0 to 6.5 mN in 20 s; then, the load was kept constant at the maximum load for 5 s, and finally, the tip was unloaded to 0 mN in 20 s. The tip displacement during the second step was used to calculate the creep after software thermal drift correction. The micro-tribological behavior was studied by a reciprocal friction-wear test in a controlled environment of approximately 20 °C and a relative humidity of approximately 40% using a Triboindenter TI-950 from Hysitron (Eden Prairie, MI, USA). A 5 mN load was applied to a diamond conical probe of 2 µm diameter moving in a stroke length of 5 µm to evaluate the wear of the track on the surface coating and substrate. The speed of the probe was set at 1 µm/s in an experiment that takes 712 s. Details and applications of the wear test method are described in [31,32]. Macro-tribological evaluations of the substrate and the hierarchical configuration were made by using a tribometer CETR-UMT2 (Center for Tribology, Campbell, CA, USA) with a reciprocating ball-on-plate configuration in relative humidity (RH) of approximately 48% at room temperature (approximately 25 °C). The tests were done with a reciprocal sliding movement of 10 mm stroke length at a frequency of 1 Hz, with an applied load of 3 N during 30 min, using a 10 mm alumina ball (Al<sub>2</sub>O<sub>3</sub>) as a counterpart. After the macro-tribology test, the wear tracks and debris generated in the tests were analyzed by Raman spectroscopy with a Thermo Scientific DXR confocal Raman microscope (Waltham, MA, USA) applying a wavelength of 532 nm. Furthermore, the cross-sectional area of wear scars was measured by contact profilometry (Veeco Dektak 150, Plainview, NY, USA).

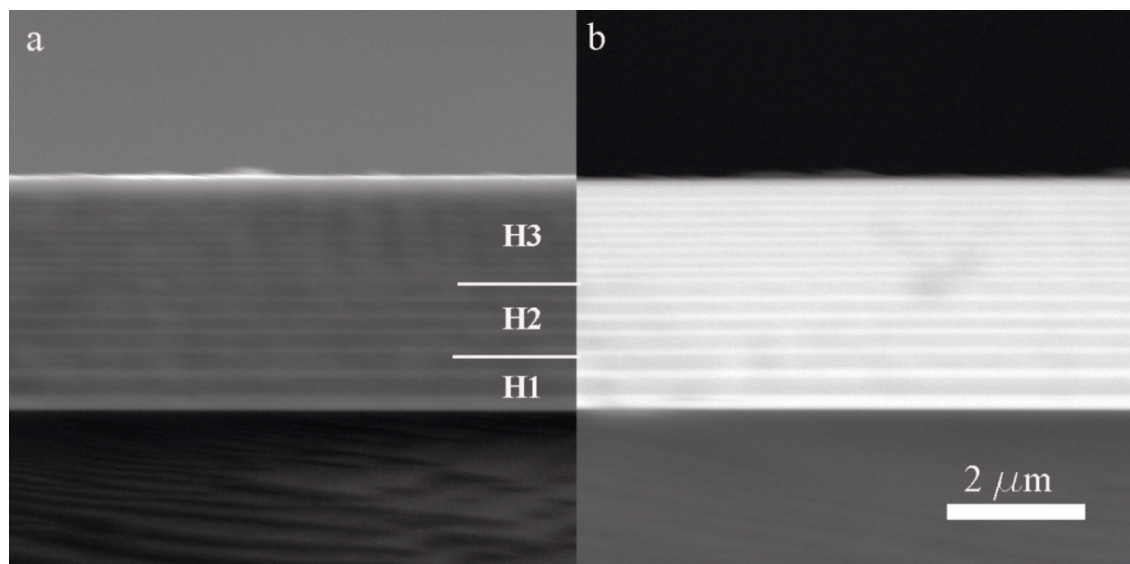
### 3. Results and Discussion

#### 3.1. Morphological, Structural, and Mechanical Characterization

Secondary electron and electron backscattering images (Figure 2a,b, respectively) allow the quantification of thickness and number of layers of the hierarchical configuration design in Figure 1.

Furthermore, no evidence of columnar growth is found, owing to the high number of layers that increased the interfaces and reduced this type of growth [10]. The total thickness of the coating was approximately  $3.49\text{ }\mu\text{m}$ , and the thickness of sections H1, H2, and H3 were approximately  $0.79$ ,  $1.10$ , and  $1.6\text{ }\mu\text{m}$ , respectively (Figure 2a,b). Figure 3 shows the diffraction pattern of the coating Hier-TaN/Ta and the substrate, where it is possible to identify the hexagonal phase ( $\epsilon$ -TaN, PDF# 01-089-5198) and cubic phase ( $\delta$ -TaN, PDF# 01-089-5196) of TaN. These are in good agreement with those previously reported in [33]. The lack of Ta peaks could have been caused by the small thickness periods of the Ta layers at the layers close to the surface that do not give enough contribution to the diffraction signal. Furthermore, the first two thick layers of Ta deposited on the substrate (see H1 in Figure 2b) are too far from the surface sample, generating a small contribution to the diffraction signal, which is also masked by the diffraction signal of the Ti6Al4V alloy.

A more detailed analysis revealed that the diffraction peak of the hexagonal  $\epsilon$ -TaN at  $2\theta \approx 34.9^\circ$  in the nitride Hier-TaN/Ta coating had a slight shift to larger angles, suggesting possible tensional stress into the layers with this  $\epsilon$ -TaN phase. However, the cubic  $\delta$ -TaN peaks are shifted to lower angles, indicating compressive stresses for the layers that contain this phase. Such compressive stresses act on the atomic planes perpendicular to the surface substrate, reducing the distance between them and increasing the distance between the crystallographic planes parallel to the surface substrate; thus, the diffraction pattern suffered this slight modification. Furthermore, it is clear that the  $\delta$ -TaN phase presented more diffraction peaks in comparison to the  $\epsilon$ -TaN phase that only diffracted at  $2\theta \approx 34.9^\circ$ , indicating that most of the layers have a  $\delta$ -TaN phase. Therefore, it is possible to suggest that most layers of the coating had compressive stresses that improve the adhesion at the coating/substrate interface and could have reduced the internal tensional stresses of the entire coating, producing a relaxation effect that helps obtain more efficient dissipation energy. Furthermore, the crystallite size for the  $\delta$ -TaN phase was evaluated by the Scherrer equation using the peak located at  $2\theta \approx 59^\circ$ , where there was no influence of diffractions peaks from the substrate on the full width at half maximum. A value of approximately  $3.6\text{ nm}$  was obtained, which is in agreement with the observed values in other publications where a reduction of the period size reduces the grain size [10,13,34–36].



**Figure 2.** FESEM images of the cross-section of the HIER-TaN/N sample. (a) Secondary electron image, where three periodicity sections are marked. (b) Electron backscattering images where the visualization of all the layers is easier.

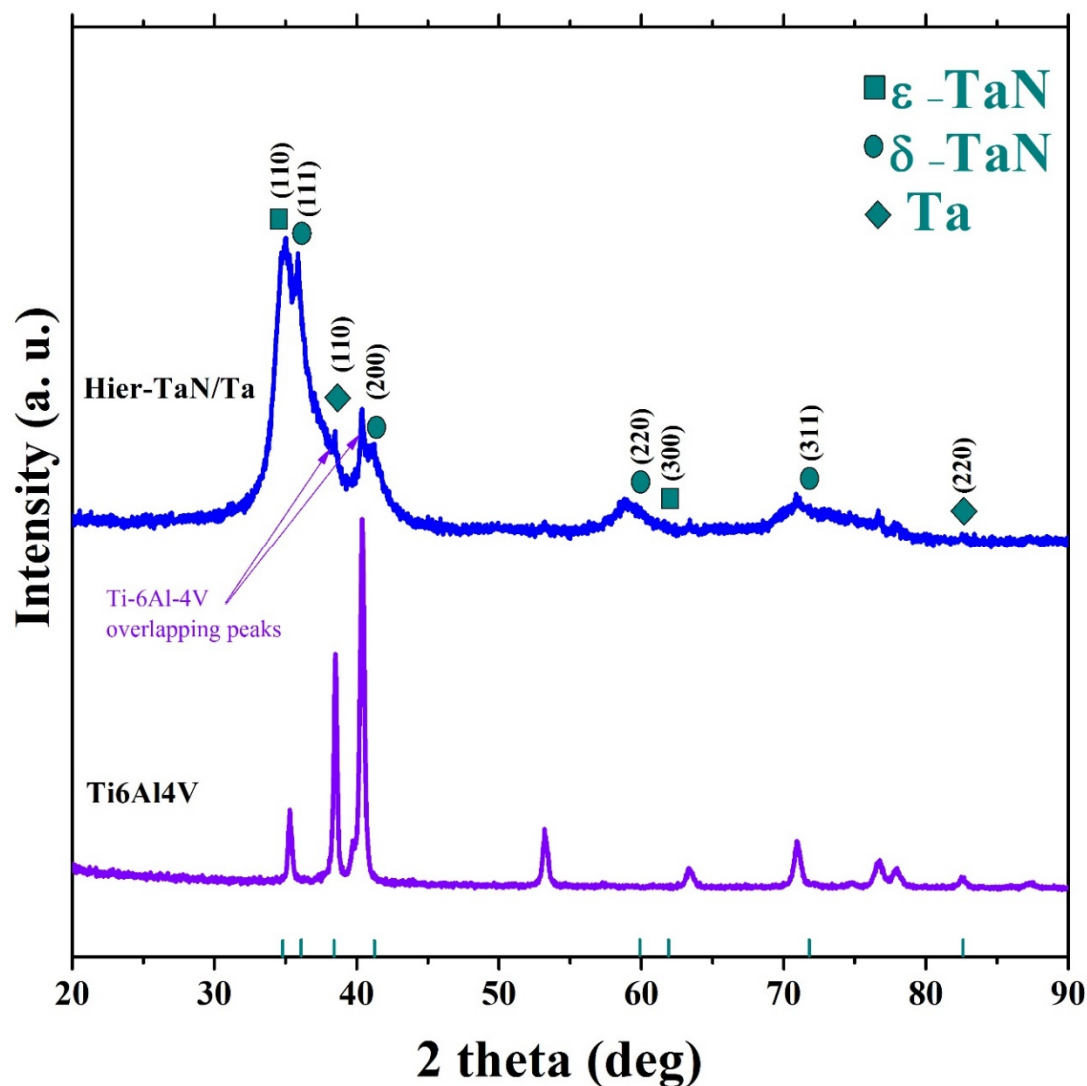
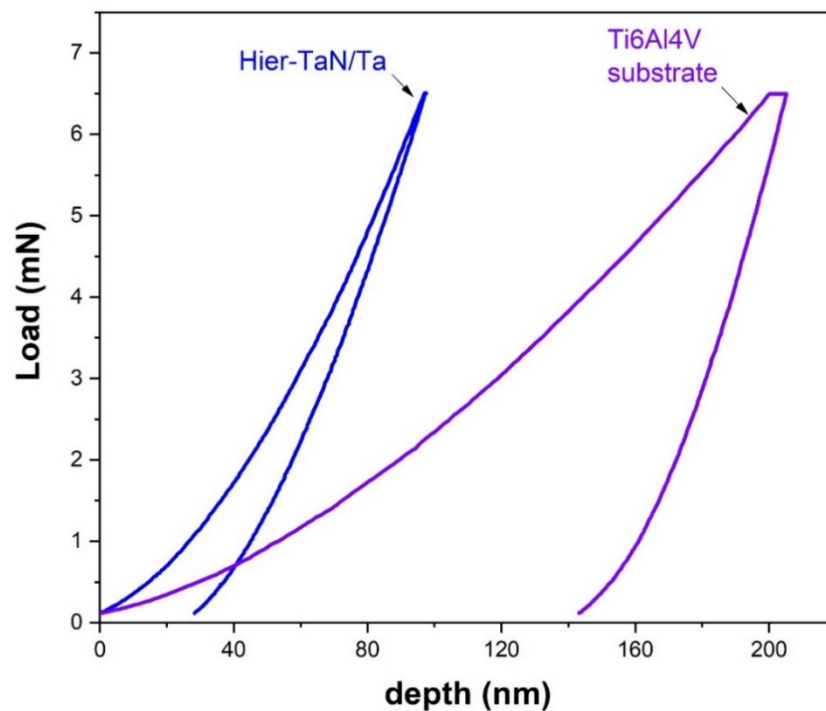


Figure 3. XRD patterns of the Hier-TaN-Ta coating and Ti6Al4V substrate.

Figure 4 shows the load–displacement curves obtained from the nanoindentation tests of the hierarchical coating and substrate. It has been assumed by many researchers that the maximum penetration depth in nanoindentation should be less than 10% of the coating thickness, which in our case is 3.49  $\mu\text{m}$ . According to this rule (known also as the Bückle’s rule), we could have used a maximum penetration of 349 nm. However, this “rule” is not always valid, as it has been discussed in [37]. In our experiments, we have used the graphitic method explained in the ISO 14577 Standard Part 4 [38], where the maximum penetration depth is chosen in the penetration range where the hardness stays approximately constant. The mechanical response is summarized in Table 1. The high hardness of the Hier-TaN-Ta coating (31.4 GPa) is probably due to both the nitrided layers [4,39] and also to the reduction of the grain size in the layers of H3 giving the Hall–Petch effect [40]. Additionally, the increase in the number of layers also reduces the creep in comparison to the substrate (see Table 1) through an annihilation process that was described by Wang and Misra [41] and promotes toughening mechanisms [42].



**Figure 4.** Load–displacement curves for the Hier-TaN/Ta coating and Ti6Al4V substrate.

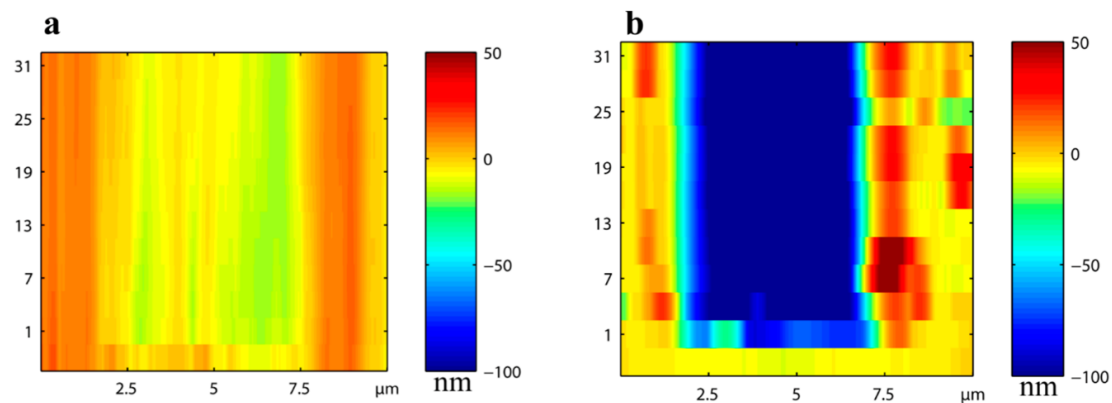
**Table 1.** Mechanical properties obtained from the nanoindentation tests.

| Samples           | Hardness, H (GPa) | Reduced Elastic Modulus, $E_r$ (GPa) | Elastic Recovery (%) | Creep (nm/s) |
|-------------------|-------------------|--------------------------------------|----------------------|--------------|
| Hier-TaN/Ta       | $31.4 \pm 2.8$    | $310 \pm 20$                         | 64.8                 | 0.2          |
| Ti6Al4V substrate | $5.3 \pm 1.9$     | $152 \pm 12$                         | 27.3                 | 5.9          |

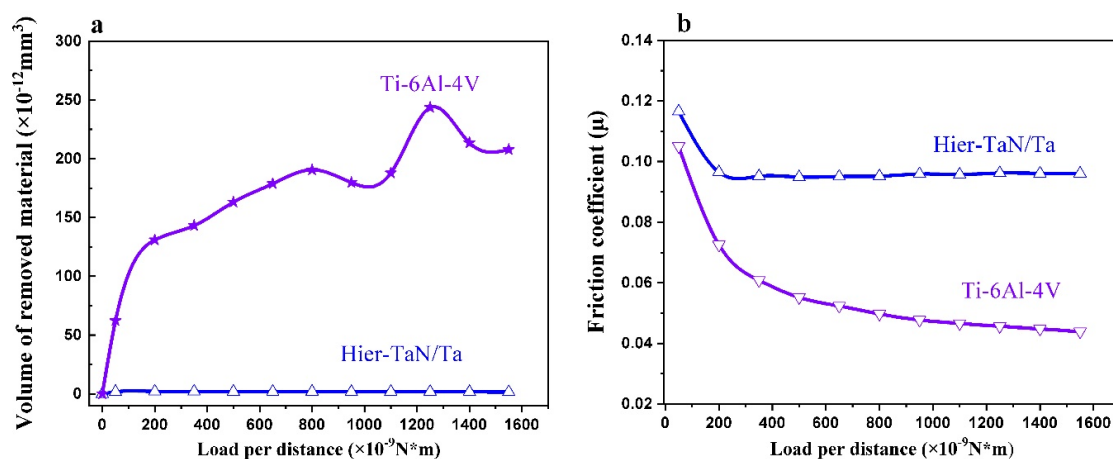
### 3.2. Micro and Macro-Tribological Behavior

There are no standards explaining how to make a microtribological test [43]. A new methodology to study the friction and wear behavior of coatings at the microscale was introduced in 2015 [31]. In our experiments, we have used similar loads to those suggested in that publication which allows understanding the mechanical contact of a single asperity on the tribological behavior of the substrate and the TaN/Ta hierarchical coating architecture.

Figure 5a,b show the wear evolution maps for the Hier-TaN/Ta coating and Ti6Al4V substrate respectively obtained from the micro-tribology tests. We can observe significant wear track differences, revealing an outstanding wear resistance of the coating compared to the substrate. Figure 6a,b show the quantitative evolution of the volume of removed material ( $\text{mm}^3$ ) and friction coefficient (CoF), respectively. The Hier-TaN/Ta coating displays a notable reduction of wear in comparison to the substrate ( $1.6$  and  $207 \times 10^{-12} \text{ mm}^3$  for Hier-TaN/Ta and Ti6Al4V substrate, respectively). Furthermore, the wear evolution and removed material were constant throughout the traveled distance, showing no increment in the depth penetration as the test progresses. On the other hand, wear was increasing as the traveled load per distance increased for the case of the substrate, which leads to a deeper wear track after the micro-tribology test; see Figures 5b and 6a.

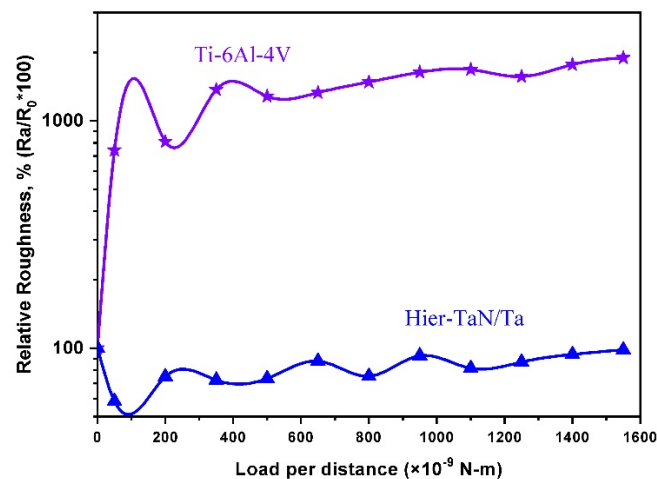


**Figure 5.** Wear evolution maps for (a) Hier-TaN/Ta coating, and (b) Ti6Al4V substrate. The Y-axis indicates the number of cycles to produce wear, the X-axis is the width of the wear track, and the bar scale represents the wear depth in nanometers.



**Figure 6.** (a) Volume of removed material and (b) friction coefficient of Ti-6Al-4V and Hier-TaN/Ta coating.

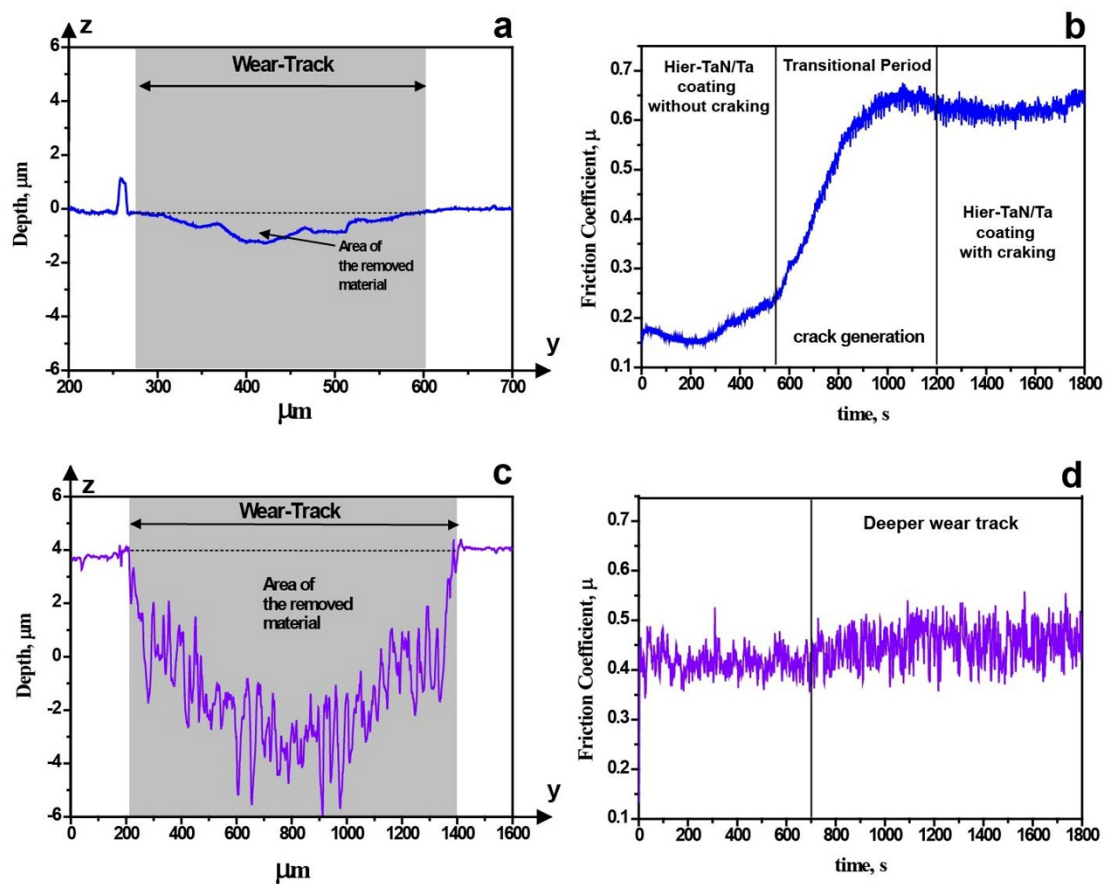
Regarding the friction coefficient, the Ti6Al4V substrate displays lower values compared to the Hier-TaN/Ta coating: 0.044 and 0.088 respectively, see Figure 6b. This behavior can be attributed to the elevated hardness of the coating surface, the valley and hills with low plastic deformation, and the high rigidity that increased the lateral forces of the Triboindenter tip, increasing the friction coefficient. The lower CoF values of the substrate was attributed mainly to the low surface hardness, where the high ductility of the substrate surface generated low resistance to the Triboindenter tip movement and significantly decreased the lateral forces. This friction explanation can be corroborated using the relative roughness parameter,  $R(\%)$ , of the trench.  $R(\%) = 100 \cdot R_a / R_0$ , where  $R_0$  is the average roughness of the track before the first experiment and  $R_a$  is the average trench roughness. The  $R_0$  values were 3 nm and 1 nm for the Ti6Al4V substrate and Hier-TaN/Ta coating, respectively. These results are plotted in Figure 7; the relative roughness values of the coating remained close to 100%, which means that the roughness variation was minimal in comparison to the virgin surface roughness of the wear track before the test (also see Figure 5a). On the other hand, for the case of the Ti6Al4V substrate, the relative roughness values were above 1000%, indicating a considerable roughness modification in comparison to the initial roughness of the virgin surface, showing a high degree of ductility. This friction interpretation is based on the microscopic surface roughness and surface hardness, which are the main considerations for this analysis. However, it is worth considering debris or third-body particles as shown in the micro-tribology investigation of Broitman et al. [44]. Furthermore, different tribo-chemical reactions generated by the interaction of the surface–tip need to be considered.



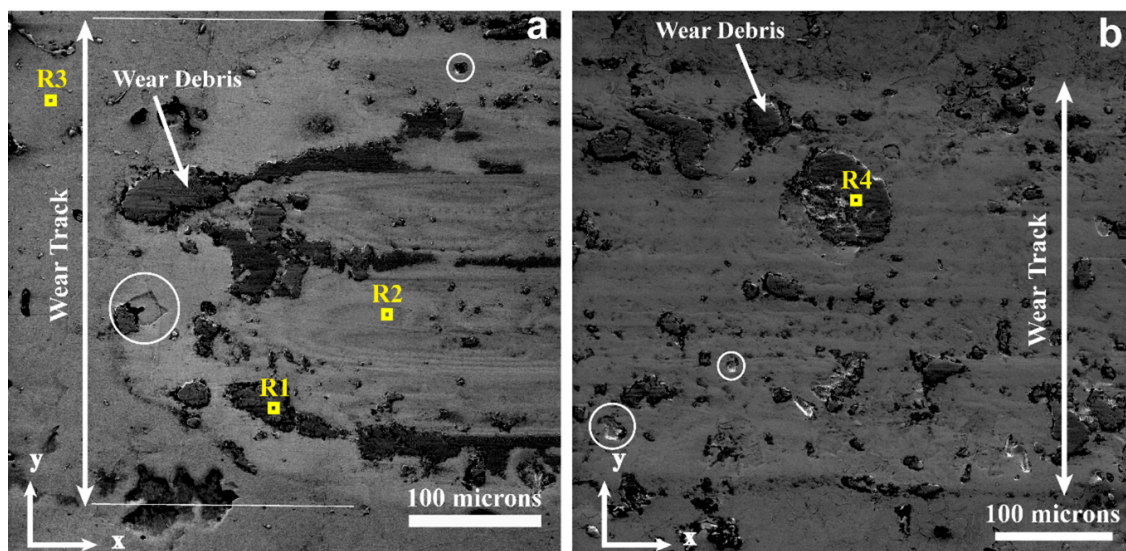
**Figure 7.** Relative roughness as a function of load per distance traveled obtained on the Ti6Al4V substrate and Hier-TaN/Ta coating. Values close to 100% indicate a low roughness modification in comparison to the virgin surface before the tribological test.

Present results indicate that wear is closely related to the coating and substrate hardness for this type of test at the micro-level. The high resistance to wear of the Hier-TaN/Ta coating can be attributed to its high hardness value (31.4 GPa). Similar behavior was seen in our previous work at the micro-scale level for WC/WCN/W coatings [10]. Therefore, the increment of hardness with the number of interfaces of TaN/Ta in a multilayer configuration was one of the main factors for the low wear seen in the Hier-TaN/Ta coating. The direct effects of the hierarchical architecture on the results after micro-tribology tests were limited only to the H3 level, see Figure 2a, since the maximum penetration wear on the Hier-TaN/Ta coating was around approximately 25 nm, see Figure 5a. However, there could be some indirect effects from the H2 and H1 levels, such as the reduction of tensional stresses in the H3 level. Nevertheless, this hardness caused another unwanted effect such as the increment of friction, which was provoked by the hills and valleys on the surface that were difficult to deform, generating the increment of the friction force and CoF values as mentioned above.

In our macro-tribological experiments, the initial maximum Hertzian contact pressures are approximately 580 MPa for the substrate and approximately 930 MPa for the coating. Our chosen conditions represent a severe condition in terms of contact pressure for materials used in the artificial hip and knees, as the experimental values reported for the implanted knees and hips range between 13 and 25 MPa [15]. The macro-tribology wear tracks and the evolution of the friction coefficient (CoF) of the hierarchical coating and substrate are shown in Figure 8. The wear rate of the Hier-TaN/Ta coating was found to be considerably lower in comparison to the substrate ( $2.1 \times 10^{-3} \text{ mm}^3$  and  $51 \times 10^{-3} \text{ mm}^3$  respectively), in a similar way to the micro-tribology tests, see Table 2. This wear reduction at the macro-scale of the hierarchical coating can also be correlated to its high hardness (31.4 GPa). The FE-SEM images in Figure 9 show the wear track after the macro-tribology test of the Hier-TaN/Ta coating. The white circles in these images indicate cracking, showing a brittle behavior on the surface of the coating. Nevertheless, the wear profile of the coating shows no evidence of cracks or fractures that reach the substrate, since the maximum depth showed was around  $1.30 \mu\text{m}$ ; see Figure 8a. This limited cracking could have been generated by the hierarchical configuration of the coating, since it is to expect that layers in the H2 and H1 levels (below the surface, see Figure 2a) had a lower elastic modulus than the layers near the surface coating (layers in the H3 level), and they suffered a higher degree of plastic deformation that increased the contact area, generating a reduction of internal stresses that can stop the cracks before they reach the substrate, avoiding a catastrophic rupture of the coating and demonstrating the functionality of the H1 and H2 levels to stop or limit cracks into the hierarchical configuration.



**Figure 8.** Typical wear track profile obtained by the macro-tribology tests for (a) Hier-TaN/Ta coating and (c) Ti6Al4V substrate. Friction coefficient obtained during the macro-tribology test; (b) Hier-TaN/Ta coating and (d) Ti6Al4V substrate.



**Figure 9.** FE-SEM images of the wear track generated from the macro-tribology tests of the Hier-TaN/Ta coating, the white circles and yellow squares indicate limited cracking and points where the Raman spectra were obtained respectively; (a) left border; and (b) center of the wear track after the macro-tribology test.

**Table 2.** Summary of the main results obtained from the micro and macro-tribological tests of the coatings and substrate. \* CoF (friction coefficient) obtained until the 540 s without cracking.

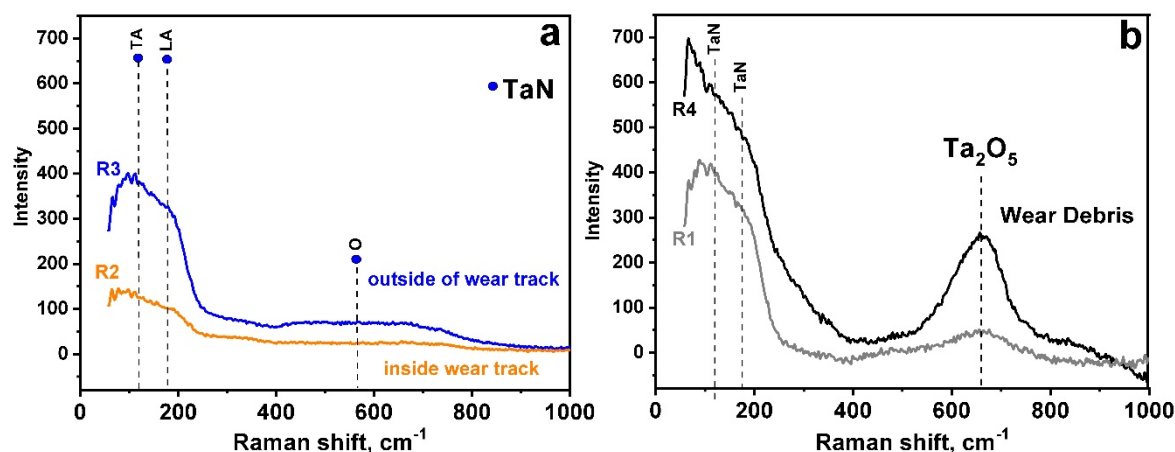
| Sample      | Micro<br>Wear Volume<br>$\times 10^{-12} \text{ mm}^3$ | Macro<br>Wear Volume<br>$\times 10^{-3} \text{ mm}^3$ | Micro<br>CoF | Macro<br>CoF |
|-------------|--------------------------------------------------------|-------------------------------------------------------|--------------|--------------|
| Hier-TaN/Ta | 1.6                                                    | 2.1                                                   | 0.088        | *0.18        |
| Ti6Al4V     | 207                                                    | 51                                                    | 0.044        | 0.44         |

In the case of the friction coefficient evaluation, the substrate showed an average CoF of 0.44 for the entire test. However, two behaviors from the CoF graph are shown, see Figure 8d; the average CoF until approximately 700 s was slightly lower: 0.42. After this point, the CoF increased slightly due to the increment of the wear track depth, generating the sinking of the tribometer ball, and therefore increasing the lateral force and CoF. For the case of Hier-TaN/Ta coating, the friction behavior was more complex; the CoF graph showed three different behaviors, as shown in Figure 8b. The first one showed up at the beginning of the test, with a CoF value of 0.18 until 540 s and was the CoF of the surface Hier-TaN/Ta coating without cracking. After this point, the CoF behavior passed into a transition period until approximately 1200 s, where the apparition of cracks and debris increased the friction coefficient considerably. After 1200 s, the CoF of the coating remained without significant changes with an average CoF of 0.62, which is a value that is higher than the substrate that could have been provoked by the surface cracking, hard debris such as oxides, and the roughness increment.

Figure 10 shows the Raman spectra of the yellow square points shown on the surface of the Hier-TaN/Ta coating from Figure 9. The R3 point was located outside of the wear track (see Figure 9a), showing a typical TaN Raman spectrum (see Figure 10a). This result is in agreement with the TaN (001) Raman spectrum research of M. Stoehr et al. [45], which was obtained with a wavelength of 488 nm that is close to the 532 nm used in this research. The R2 point is located at the center of the wear track (see Figure 9a), where the max wear depth reach approximately  $1.30 \mu\text{m}$  as mentioned above. Therefore, it is expected that at this point, the surface corresponds to a TaN layer due to its higher hardness in comparison to the layers of Ta. This can be corroborated with the TaN Raman spectrum obtained at this point, which was similar to the R3 spectrum, but with a significant reduction of the intensity. This reduction is attributed to a possible combination of Ta and TaN material where the metallic components reduced and interfere with the Raman signal. Besides, at this point, after the macro-tribology tests, the surface suffers energy alterations and breaks of the Ta-N bonds energies that can reduce the vibrations that produce the Raman signal. The Raman spectra shown in Figure 10a shows two primary bands corresponding to the first-order acoustic band (A) between  $50$  and  $200 \text{ cm}^{-1}$  and the first-order optical band (O) between  $400$  and  $750 \text{ cm}^{-1}$ . The two peaks shown at approximately  $120$  and  $180 \text{ cm}^{-1}$  correspond to the first-order transverse acoustic (TA) and longitudinal acoustic (LA) modes respectively according to M. Stoehr et al. [45]. Furthermore, according to this cited research, the presence of strong first-order peaks and the lack of second-order acoustic peaks indicate the presence of point defects and/or lattice disorder in stoichiometric TaN samples [45]. This can be corroborated in our investigation, since the Raman spectra shown in Figure 10a had strong first-order acoustic peaks and no evidence of second-order peaks, and the TaN/Ta coating presented typical defects generated by the DC magnetron sputtering process and by the multilayer configuration; see Figure 2.

Figure 10b shows the Raman spectra of the wear debris and tribo-layer generated during the macro-tribology test corresponding to the R1 and R4 points; see Figure 9. Here, the first-order acoustic peaks showed in the previous analysis are shown (see Figure 10a), which correspond to the TaN peaks. However, it is possible to identify the apparition of a strong peak at approximately  $660 \text{ cm}^{-1}$  that corresponds to the tantalum oxide,  $\text{Ta}_2\text{O}_5$ . This Raman spectrum is in accordance with the investigation of Chen et al. [46], corroborating the formation of oxides between the TaN surface and the alumina ball during the reciprocating movement provoked by the brittle behavior of the surface coating. Therefore, these tantalum oxides could increase the friction coefficient even more and generate abrasive wear, since

the oxides were content into the debris that acted as hard erosive particles. Furthermore, the intensity differences between the R1 and R4 spectra can be attributed to the Hertzian pressure differences on the wear track, since it is well known that the max pressure is located at the center of the track, and it decreases near the border. Therefore, the formation of tantalum oxides increased with the Hertzian pressure. In the case of the R1 spectrum, this obtained a lower intensity at the point that is located near the border of the wear track, and the R4 spectrum showed higher intensity values at point R4, which is near the center of the wear track; see Figure 9a,b.



**Figure 10.** (a) Raman spectra of the Hier-TaN/Ta surface inside and outside of the wear track; (b) spectra of the wear debris generated after the macro-tribology tests; see Figure 9.

#### 4. Conclusions

We design and deposit a novel hierarchical architecture for a TaN/Ta multilayer coating using DC magnetron sputtering for the deposition process. The morphology of the section transversal showed a correct implementation of the hierarchical architecture due to the extraordinary versatility of this deposition process, besides, such morphology showed low columnar growth, which is the typical disadvantage for the DC magnetron sputtering processes. It was shown that the use of these types of architectures reduces the grain size and the columnar growth. The structural characterization showed cubic and hexagonal TaN phases into the hierarchical coating layers. Furthermore, a slight shift to lower angles of the cubic phase peaks indicating qualitatively a reduction of internal stresses in the layers with the cubic phase. The nanoindentation characterization showed an extraordinary hardness of the hierarchical coating (31.4 GPa). This hardness was attributed to the formation of a ceramic TaN layer with the introduction of nitrogen into the vacuum chamber and by the reduction of the grain size in the layers near of the surface or into the H3 level by the Hall–Petch effect.

The micro-tribology tests revealed that hardness is closely related to the wear rate at this microscopic level, and the wear rates of the hierarchical coating were reduced significantly in comparison to the Ti6Al4V, where the wear was practically null. Therefore, the reliability of this coating configuration to micro-tribology applications was demonstrated. In the case of the macro-tribology tests, the analysis of the entire hierarchical architecture was possible. The wear was significantly reduced in comparison to the Ti6Al4V substrate, which was probably due to the high hardness and the ability of the hierarchical coating to stop or limit the cracks. The friction coefficient behavior and the FE-SEM images of the wear track showed that the material is still brittle, but without cracks that reach the substrate. Therefore, the hierarchical architecture successfully limited the material brittle behavior, avoiding a catastrophic coating rupture. Furthermore, the Raman analysis of the wear track showed the formation of tantalum oxides in the debris on the wear track; this debris could have increased the friction coefficient and generated abrasive wear that probably contributed to the increase of the material brittle behavior mainly toward the end of the test.

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