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Tribocorrosion Performance of TiAlN and AlTiN Coatings on Ti6Al4V in Artificial Saliva: Influence of Mechanical and Electrochemical Responses

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Abstract

The tribocorrosion performance of TiAlN and AlTiN coatings on Ti6Al4V was investigated in a near-neutral, chloride-containing artificial saliva electrolyte to assess the relationship between mechanical properties, tribological behavior, and electrochemical response. The coatings were deposited by cathodic arc evaporation and characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy, nanoindentation, scratch testing, friction measurements, open-circuit potential (OCP) monitoring, and wear-track analysis. Nanoindentation and scratch testing revealed superior mechanical performance for AlTiN, which exhibited higher hardness, H/E and H^3/E^2 ratios, and critical loads than TiAlN. Under tribocorrosion conditions, however, TiAlN exhibited the lowest measured wear rate despite its

lower mechanical performance. Both coatings reduced the coefficient of friction (COF) relative to uncoated Ti6Al4V, with AlTiN showing the lowest average COF against alumina ball, and TiAlN exhibiting a more stable friction coefficient response. The OCP transients revealed a smaller potential perturbation during sliding for TiAlN, indicating a lower degree of electrochemical activation under the investigated conditions. SEM/EDS analysis of the wear tracks also revealed differences in the distribution and retention of oxygen- and electrolyte-derived species on the coating surfaces. These observations suggest that the higher mechanical properties of AlTiN did not directly translate into improved resistance to tribocorrosion. The contrasting OCP responses and wear-track chemistry are consistent with differences in surface-film retention and electrochemical activation, although the specific chemical nature of the films was not established. Under the investigated artificial-saliva conditions, TiAlN provided the highest resistance to tribocorrosion-induced material loss among the tested systems.

Keywords: Titanium alloy, Ti6Al4V, tribocorrosion, TiAlN, thin films

1. Introduction

Ti6Al4V is widely used for biomedical components due to its high specific strength, excellent fracture toughness, good corrosion resistance, and overall biocompatibility [1–6]. However, its relatively poor resistance to mechanical wear remains a concern in applications involving repeated contact and sliding. In physiological and oral environments, mechanical wear occurs simultaneously with electrochemical reactions, producing tribocorrosion. This interaction can intensify material degradation beyond the level expected from wear and corrosion occurring separately [7–9].

In titanium alloys, tribocorrosion develops through the interaction between mechanical damage and electrochemical reactions at the sliding interface. Sliding removes or disrupts the surface oxide within the contact region, while the surrounding electrolyte promotes the restoration of the film. The damaged area may consequently behave as an anodic region relative to the intact surface, creating conditions for localized dissolution and corrosion-assisted wear. The final response depends not only on hardness or dry-sliding resistance, but also on the persistence and recovery of the protective surface layer [7,8,10,11].

Artificial saliva is commonly used as a laboratory electrolyte for evaluating materials intended for oral environments. Its near-neutral pH and ionic composition reproduce selected aspects of the oral environment, but the solution does not reproduce the full chemical and biological complexity of natural saliva [12–14]. In chloride-containing media, mechanical damage to the surface film may facilitate localized electrochemical activation. Phosphate- and oxygen-containing species may also participate in the formation or modification of surface products. These factors make film continuity and repassivation kinetics relevant variables in the interpretation of tribocorrosion results.

Several surface-engineering strategies have been explored to enhance the wear and corrosion resistance of Ti6Al4V, including diamond-like carbon films, TiN and CrN coatings, oxide layers, and TiAlN-based protective coatings [15–18]. Among these materials, TiAlN and AlTiN are particularly attractive because their mechanical and chemical properties can be modified by changing the relative aluminum and titanium contents. Increasing the Al/(Al+Ti) ratio generally improves hardness and resistance to plastic deformation within a specific compositional range, making Al-rich Ti(Al)N coatings attractive for dry-wear applications [19,20]. However, the effect of this compositional change under simultaneous sliding and electrochemical exposure remains insufficiently understood.

In particular, the distinction between Ti-rich TiAlN and Al-rich AlTiN may be important under tribocorrosion conditions. The coating composition can influence not only hardness, elastic strain tolerance, and adhesion, but also the nature, continuity, and mechanical stability of the surface film formed during sliding [21,22]. A Ti-rich coating may favor the formation of Ti-containing oxide species that contribute to the retention of a protective tribofilm. Conversely, the increased aluminum content in AlTiN may influence both the chemical composition and stability of the surface layer formed in aqueous media containing chloride ions [23]. Therefore, differences in coating composition should be evaluated in relation to both mechanical performance and electrochemical evolution during sliding.

Although TiAlN and AlTiN coatings have been widely investigated in machining and dry-wear applications, comparatively limited attention has been given to their tribocorrosion behavior on Ti6Al4V in artificial saliva. More specifically, it remains unclear whether the higher hardness and

improved mechanical-performance indicators commonly associated with Al-rich compositions also result in lower material loss when the coating is subjected to simultaneous mechanical loading and electrochemical activation.

The specific scientific gap addressed in this study is therefore the lack of a direct comparison between Ti-rich TiAlN and Al-rich AlTiN coatings in terms of how their composition affects tribofilm stability and tribocorrosion mechanisms in a chloride-containing artificial saliva. In particular, this study evaluates whether the coating with superior mechanical properties also provides the greatest resistance to tribocorrosion-induced material loss, or whether electrochemical activation and tribofilm stability become the dominant factors controlling performance.

Accordingly, the aim of this work is to compare the mechanical, tribological, and electrochemical responses of TiAlN- and AlTiN-coated Ti6Al4V under tribocorrosion conditions in artificial saliva. Nanoindentation and scratch testing are used to characterize the mechanical response and coating adhesion, while friction measurements, open-circuit-potential monitoring, wear-track topography, and SEM/EDS analyses are used to assess the coupled wear–corrosion behavior and the possible relationship between Ti/Al composition, tribofilm retention, and electrochemical activation.

2. Materials and Methods

Ti6Al4V alloy bars (Acnis do Brasil, Sorocaba, Brazil) were machined into disc specimens measuring 15 mm in diameter and 5 mm in thickness. Prior to coating deposition, the surfaces were sequentially ground with SiC abrasive papers of 320, 500, 800, and 1200 grit, followed by polishing with colloidal silica until a mirror-like surface was obtained ($R_a = 0.05 \mu\text{m}$). The specimens were then ultrasonically cleaned in acetone and dried in air.

Commercial TiAlN and AlTiN coatings were deposited on the polished Ti6Al4V substrates by cathodic arc physical vapor deposition (arc-PVD) at Oerlikon Balzers (São José dos Pinhais, Brazil). The coatings were produced according to the manufacturer's standard industrial deposition procedures. Because the process conditions were proprietary, the detailed deposition parameters were not available to the authors.

The surface morphology and chemical composition of the uncoated substrate and coated specimens were examined by scanning electron microscopy (SEM, Tescan Vega3) and energy-dispersive X-ray spectroscopy (EDS, Oxford X-act). Analyses were performed at an accelerating voltage of 10 kV, and three different regions were evaluated for each condition. The crystalline structure was investigated by X-ray diffraction (XRD, Shimadzu XRD7000). Measurements were performed in grazing-incidence geometry with an incidence angle of 2° , using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 30 mA. Diffraction patterns were collected over a 2θ range from 20° to 80° .

Mechanical properties were assessed by nanoindentation using the quasi-continuous stiffness measurement (QCSM) mode on a Zwick/Roell instrument. In this mode, the contact stiffness is recorded continuously during penetration, allowing the determination of depth-dependent hardness and indentation modulus at a single test location. During loading, the force was periodically held for 1–4 s, while a small sinusoidal oscillation was superimposed through the piezoelectric actuator. The oscillation amplitude and phase were measured using a lock-in filter, which improves sensitivity at low loads and shallow penetration depths. A calibrated Berkovich diamond indenter was used with a maximum load of 100 mN. Thirty-five indents were performed for each specimen, and the results are reported as the mean value $\pm$ standard deviation.

Coating adhesion was evaluated using a scratch tester (Anton-Paar, Revetest) equipped with a Rockwell diamond indenter (tip radius of $200 \text{ }\mu\text{m}$) under a progressively increasing load from 1 to 60 N. Tests were conducted over a scratch length of 3 mm at a sliding speed of 6 mm/s. After testing, the scratch tracks were examined by SEM to characterize the damage features and failure modes of the coatings.

Tribocorrosion behavior was investigated using a universal tribometer (Anton-Paar) in a ball-on-plate linear reciprocating configuration. A 6-mm alumina ball was used as the counter-body, and a normal load of 10 N was applied. Artificial saliva was used as the test electrolyte (150 mmol/L KCl, 1.5 mmol/L $\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 0.9 mmol/L $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, 0.1 mol/L tris(hydroxymethyl) aminomethane, and $0.05 \text{ }\mu\text{g/mL}$ NaF, adjusted to pH 7.0). The artificial saliva composition was selected from [24,25], with modifications intended to provide a chloride-containing, near-neutral electrolyte representative of the ionic environment relevant to oral tribocorrosion. Tests were

performed over a total sliding distance of 10 m, at a linear speed of 1 cm/s, with a 3 mm stroke length. Three tribological tests were conducted per sample, with the wear rate results reported as the average value.

The tribometer was coupled to a three-electrode electrochemical cell connected to a potentiostat. The coated Ti6Al4V sample served as the working electrode, a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The open-circuit potential (OCP) was continuously monitored throughout the test in order to follow the coupled tribological and electrochemical response during sliding. A schematic representation of the experimental arrangement is shown in Figure 1.

Wear track topography was characterized by white light interferometry (WLI, Filmetrics Profilm3D) to determine the wear volume after tribocorrosion tests. The wear rate (k) was calculated as the ratio between the worn volume (V) and the product of the applied normal load (F) and sliding distance (L), $k = V/F \cdot L$ [mm³/N.m].

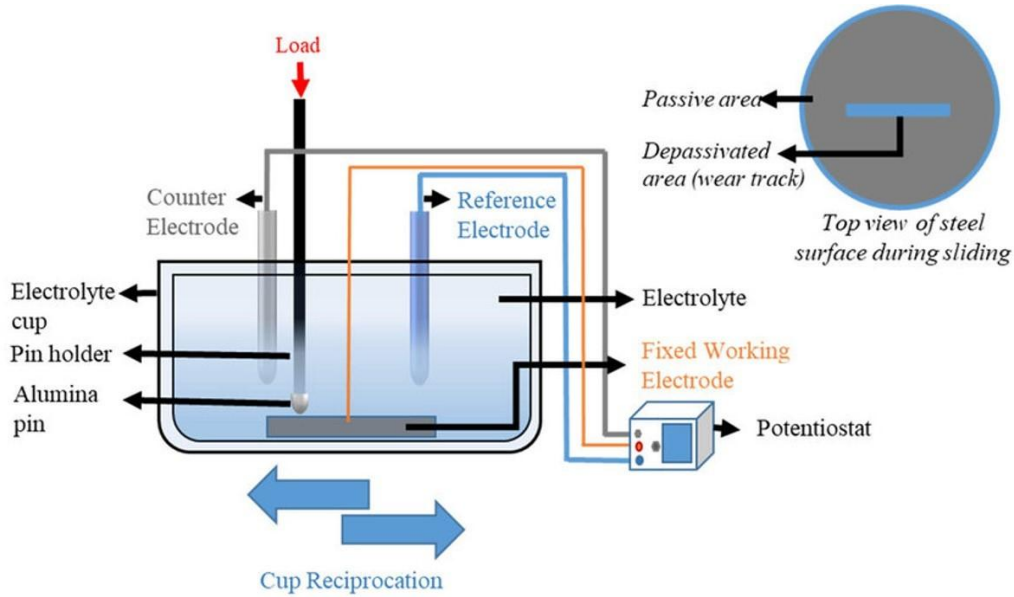


Figure 1. Schematic of the reciprocating tribocorrosion setup. A 6 mm alumina ball slides on the fixed coated specimen (working electrode) inside an electrolyte cup that reciprocates laterally. The electrochemical cell comprises a platinum counter electrode and an SCE reference electrode connected to a potentiostat for in situ monitoring (OCP). The inset illustrates the depassivated wear track surrounded by a passive surface region during sliding.

3. Results and Discussion

3.1 Thin-film Characterization

Surface and cross-sectional scanning electron microscopy (SEM) analyses of the TiAlN and AlTiN coatings deposited on Ti6Al4V by cathodic arc evaporation (CAE) revealed dense films with comparable morphology and thickness (TiAlN: $2.79 \pm 0.1 \mu\text{m}$; AlTiN: $2.71 \pm 0.5 \mu\text{m}$) (Figure 2). The surfaces of both coatings exhibited the presence of droplets, which are characteristic of the CAE process[26] and are associated with unreacted cathode-derived material (Figure 2a-b). Cross-sectional observations further showed that both coatings were compact and free from visible defects, indicating the formation of continuous and uniform layers over the substrate (Figure 2c-d).

The chemical compositions of the coatings were determined by energy-dispersive X-ray spectroscopy (EDS), and the results are summarized in Table 1. For the TiAlN coating, the measured composition was 47.6 wt% Ti (25.0 at%), 22.1 wt% Al (20.6 at%), and 30.1 wt% N (54.2 at%). In contrast, the AlTiN coating exhibited 35.9 wt% Ti (17.8 at%), 32.4 wt% Al (28.5 at%), and 31.6 wt% N (53.7 at%). These results are consistent with the nominal compositions of the coatings, with TiAlN presenting a higher titanium content and AlTiN showing a higher aluminum content [20]. For consistency, coating composition is discussed using the Al/(Al+Ti) atomic ratio, which was approximately 0.45 for TiAlN and 0.62 for AlTiN.

Table 1. EDS chemical composition (wt% and at%) of TiAlN and AlTiN coatings deposited on Ti6Al4V.

	Ti (wt%)	Al (wt%)	N (wt%)	Ti (at%)	Al (at%)	N (at%)	Al/(Al+Ti)
TiAlN	47.6	22.1	30.1	25.0	20.6	54.2	0.45
AlTiN	35.9	32.4	31.6	17.8	28.5	53.7	0.62

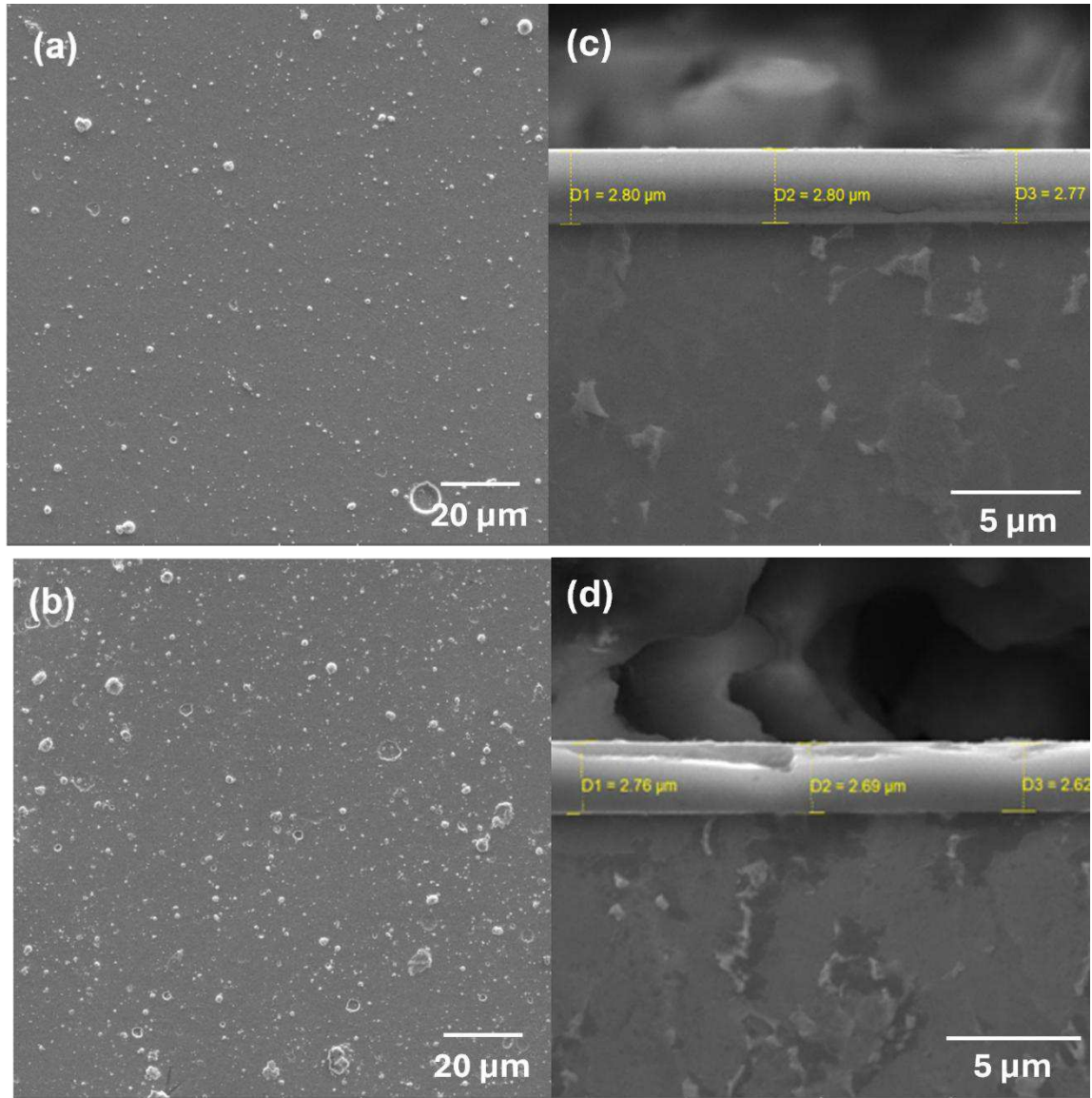


Figure 2. SEM surface morphology (left) and cross-sectional view (right) of (a-c) TiAlN and (b-d) AlTiN coatings deposited by cathodic arc evaporation on Ti6Al4V.

X-ray diffraction (XRD) patterns of the substrate and coatings are presented in Figure 3. The Ti6Al4V substrate (black curve) exhibited diffraction peaks corresponding to the α -Ti and β -Ti phases. Both the TiAlN (blue curve) and AlTiN (red curve) coatings displayed the characteristic diffraction pattern of the TiN-type face-centered cubic structure, with a pronounced preferred orientation along the (200) plane. The AlTiN coating exhibited broader and less intense diffraction peaks than TiAlN, particularly at higher 2θ values. The peak broadening may result from reduced

coherent crystallite size, increased microstrain, or a combination of both effects, which can be associated with the incorporation of a higher Al content into the FCC Ti(Al)N lattice. In addition, the increased Al content tends to decrease the lattice parameter [27,28], resulting in a shift of the diffraction peaks toward higher 2θ values. Thus, the observed changes in peak position and width are consistent with modifications of the Ti(Al)N lattice arising from the higher Al concentration, potentially involving both lattice contraction and increased structural disorder.

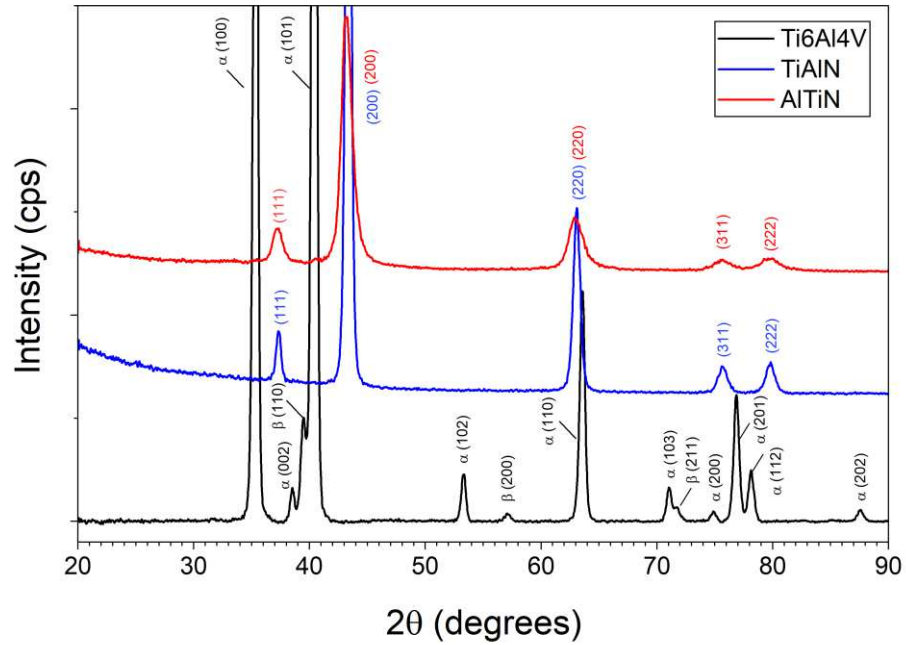


Figure 3. XRD patterns of the Ti6Al4V substrate (black) and coatings: TiAlN (blue) and AlTiN (red).

3.2 Mechanical properties by nanoindentation

Hardness and elastic modulus were obtained for both coatings using the Oliver-Pharr method [29]. Nanoindentation measurements (Figure 4a) revealed a pronounced increase in hardness for both coatings compared with the Ti6Al4V substrate. The AlTiN coating exhibited a hardness of approximately 31 GPa, in close agreement with values previously reported in the literature [27], whereas the substrate showed a hardness of about 4 GPa. This corresponds to an increase of nearly

eight times in hardness after deposition of the AlTiN coating. Among the coatings, AlTiN displayed higher hardness than TiAlN. This behavior is consistent with previous studies [20,27,30], which indicate that maximum hardness is achieved at an Al/(Al+Ti) ratio close to 0.6. The higher Al content also appears to promote a reduction in the lattice parameter, in agreement with the trend reported for increasing AlN fraction.

Both coatings exhibited substantially higher modulus values than the Ti6Al4V substrate, while the TiAlN and AlTiN curves remained very similar over the investigated penetration range (Figure 4b). For both coatings, the apparent elastic modulus decreased with increasing indentation depth, reflecting the progressive influence of the substrate on the measurement. To reduce this effect, the 10% rule was applied. Considering a coating thickness of approximately 2.5 μm , the modulus was therefore evaluated at a depth of 0.25 μm , yielding values of approximately 354 GPa for both coatings. At the reference depth of 0.25 μm , TiAlN presented a hardness of 28.9 GPa and an elastic modulus of 354 GPa, whereas AlTiN showed a hardness of 31.7 GPa and an elastic modulus of 351.8 GPa.

Based on these values, the parameters commonly used to assess potential tribological performance [31,32] were calculated. For TiAlN, the ratios were $H/E = 0.0816$ and $H^3/E^2 = 0.193$; for AlTiN, they were $H/E = 0.0901$ and $H^3/E^2 = 0.257$. The H/E ratio, which is associated with the ability to accommodate elastic strain, was approximately 10.4% higher for AlTiN. Likewise, the H^3/E^2 parameter, which is related to resistance to plastic deformation, was approximately 33.6% higher for AlTiN. Collectively, these results indicate that, at the same penetration depth, AlTiN shows higher elastic-strain tolerance and plastic-deformation resistance than TiAlN [33].

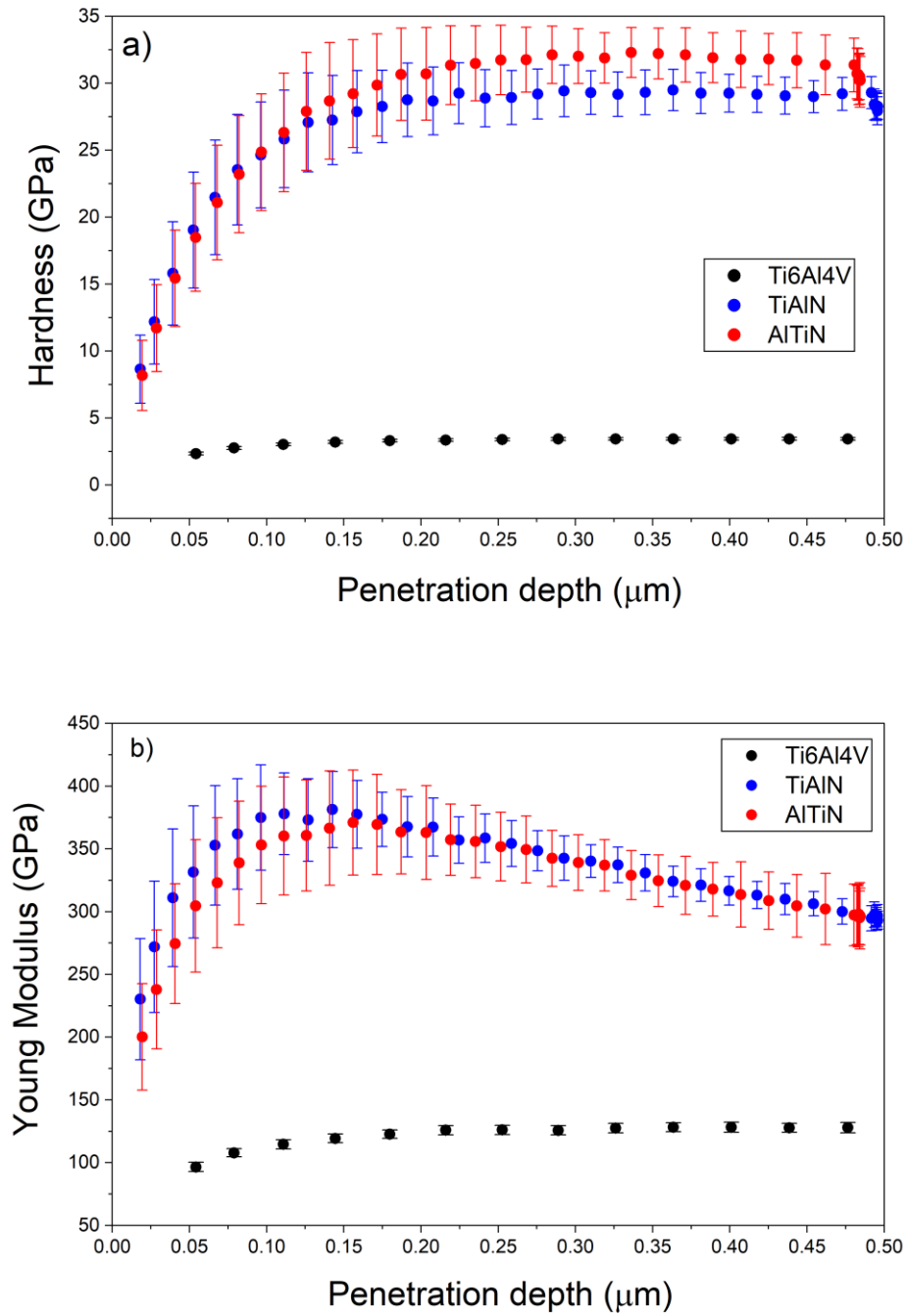


Figure 4. Depth-dependent mechanical properties from nanoindentation (QCSM mode). (a) Hardness and (b) Young's modulus as a function of penetration depth for Ti6Al4V (black), TiAlN (blue), and AlTiN (red). Error bars indicate standard deviation.

3.3 Adhesion to substrate

Scratch testing showed that both coatings underwent similar failure sequences (Figures 5 and 6). For TiAlN (Figure 5), the first critical load, $L_{c1} = 12$ N, corresponding to the onset of lateral cracking and therefore cohesive damage, was identified by correlating the SEM observations with the first change in the slope of the coefficient of friction (COF) curve. The second critical load, $L_{c2} = 28$ N, associated with the initiation of lateral delamination and thus adhesive failure, coincided with pronounced acoustic-emission (AE) events together with a second change in the COF slope. The third critical load, $L_{c3} = 37$ N, was defined as the onset of substrate exposure [38], as indicated by a further increase in the COF gradient and confirmed by SEM and optical microscopy. However, complete substrate exposure was only observed at loads of approximately 45 N.

For AlTiN (Figure 6), the failure progression was analogous. The corresponding critical loads were $L_{c1} = 16$ N for lateral cracking, $L_{c2} = 29$ N for lateral delamination, and $L_{c3} = 39$ N for the onset of substrate exposure. In this case, L_{c1} and L_{c2} were most clearly identified from the AE signal, whereas L_{c3} was more reliably determined by combining the evolution of the COF curve with the corresponding surface images.

Overall, AlTiN exhibited higher critical loads than TiAlN, indicating superior scratch resistance. This result is consistent with the mechanical property indicators measured at a penetration depth of 0.25 μm , where AlTiN presented higher values of H/E and H^3/E^2 than TiAlN. These findings reinforce that AlTiN provides a more favorable combination of elastic strain to failure (H/E) and resistance to plastic deformation or load-bearing capacity, which is reflected in its improved scratch performance [34].

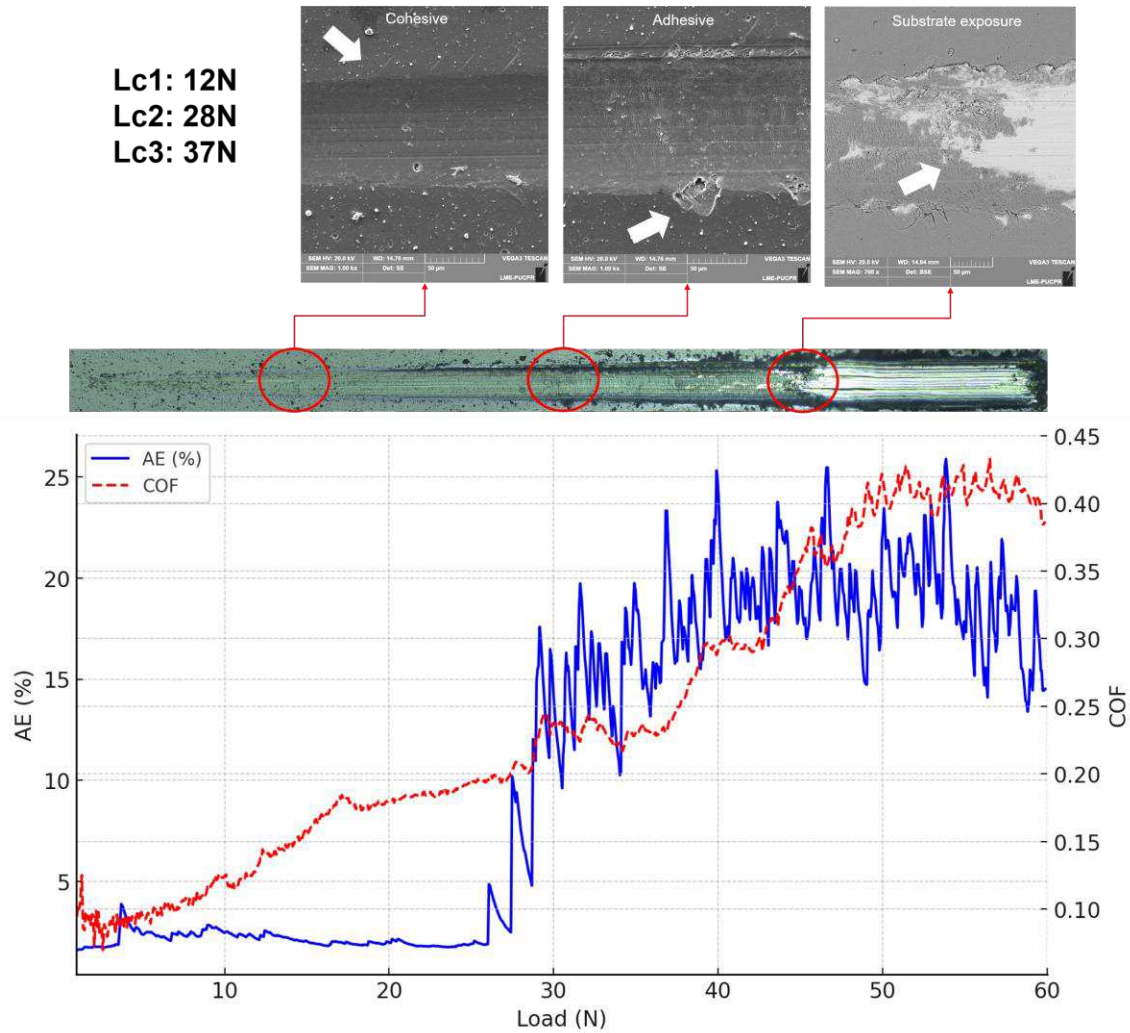


Figure 5. Scratch test results for the TiAlN coating. Top: SEM micrographs at the critical loads indicating (left to right) lateral cracking (cohesive), lateral delamination (adhesive), and onset of substrate exposure; critical loads: $L_{c1} = 12$ N, $L_{c2} = 28$ N, $L_{c3} = 37$ N. Middle: optical image of the full scratch track. Bottom: in situ acoustic emission (AE, left axis) and coefficient of friction (COF, right axis) versus normal load, used to correlate the events with the observed failure modes.

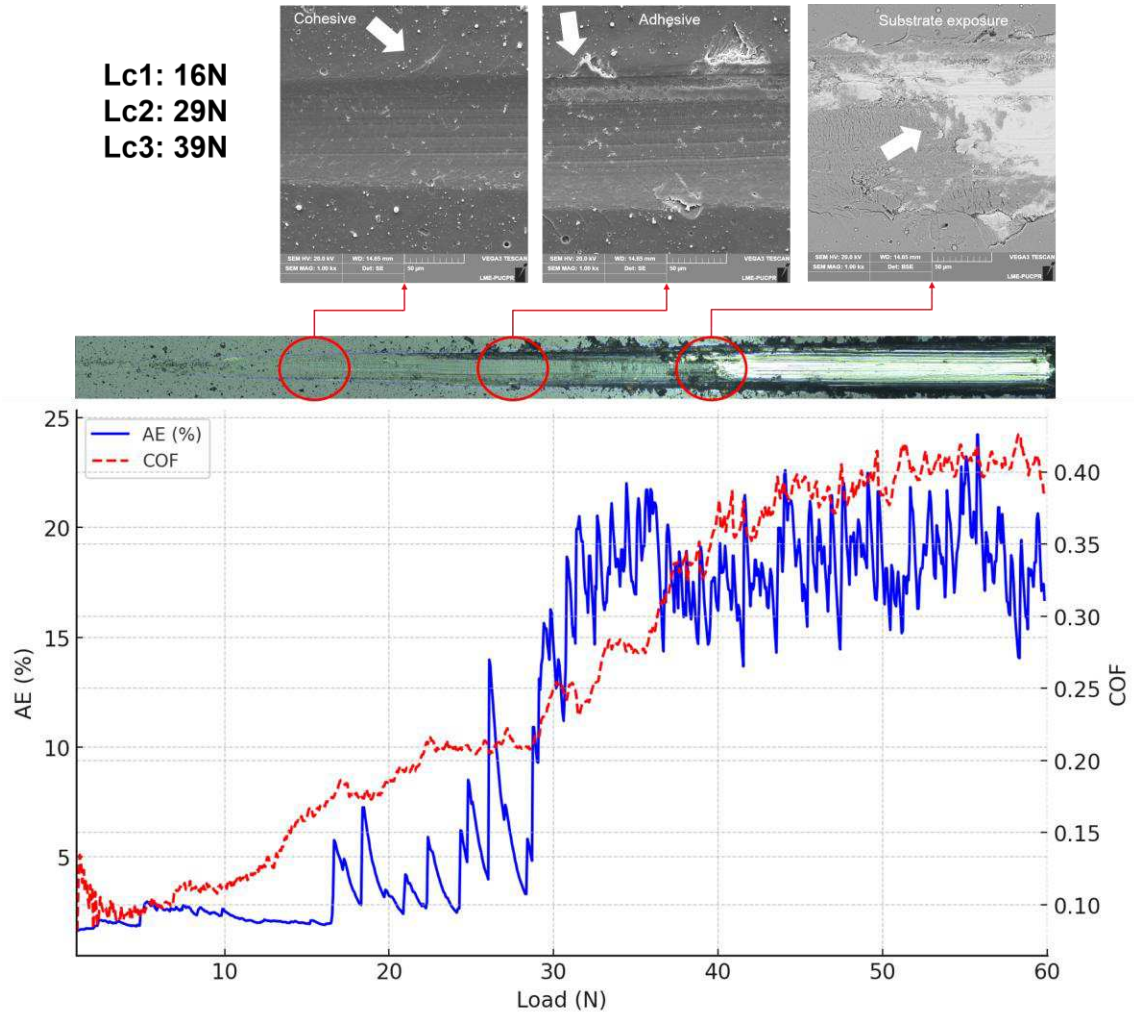


Figure 6. Scratch test results for the AlTiN coating. Top: SEM micrographs at the critical loads showing (left to right) lateral cracking (cohesive), lateral delamination (adhesive), and onset of substrate exposure; critical loads: $L_{c1} = 16$ N, $L_{c2} = 29$ N, $L_{c3} = 39$ N. Middle: optical image of the full scratch track. Bottom: in situ acoustic emission (AE, left axis) and coefficient of friction (COF, right axis) versus normal load, enabling correlation between the mechanical response and the observed failure modes.

3.4 Tribocorrosion test

As shown in Figure 7, the evolution of the coefficient of friction (COF) differed significantly among the three systems. The Ti6Al4V substrate exhibited the highest steady-state COF,

approximately 0.50-0.55, together with the largest fluctuation amplitude over the 10 m sliding distance. These oscillations are consistent with unstable formation and removal of third-body debris on passive metals under tribocorrosion conditions, where adhesive and oxidized patches intermittently nucleate, grow, and detach. This cyclic process promotes local stick-slip events, which temporarily increase or decrease both friction and the electrochemical response as these surface layers are formed and subsequently swept away [8,35,36].

In contrast, both nitride coatings slightly reduced the COF and markedly suppressed its variability. AlTiN produced the lowest COF throughout the test, whereas TiAlN showed the most stable friction trace, as evidenced by its narrower fluctuation band. This behavior agrees with previous studies showing that hard nitride coatings on Ti6Al4V, particularly within the TiN/TiAlN family, may promote the formation of denser and chemically more stable surface films while also smoothing the contact interface, thereby reducing friction scatter and mitigating wear-corrosion synergy [18,37,38].

The open-circuit potential (OCP) transients recorded before, during, and after sliding further highlighted distinct passivation responses among the tested surfaces (Figure 8). Before sliding, TiAlN exhibited the noblest potential (- 0.235 V), followed by AlTiN (- 0.408 V) and the uncoated substrate (- 0.502 V), indicating progressively more protective native or passive surface films. At the onset of sliding, all systems showed an abrupt drop in OCP, which is characteristic of mechanical depassivation caused by exposure of fresh, reactive material within the wear track [39]. The magnitude of this potential decrease followed the order Ti6Al4V $\gg$ AlTiN > TiAlN, reaching approximately -1.093 V for the substrate, -0.691 V for AlTiN, and -0.485 V for TiAlN. Within the triboelectrochemical framework, such cathodic shifts arise from the galvanic coupling established between the depassivated wear track, which acts as the anode, and the surrounding still-passive surface, which acts as the cathode, under OCP conditions. The greater the galvanic imbalance and the larger the fraction of activated surface within the wear track, the more negative the measured potential becomes [40,41]. Accordingly, the smaller OCP perturbation observed for TiAlN is consistent with a lower degree of electrochemical activation during sliding and may indicate that a larger fraction of the surface remained protected during tribocorrosion.

During sliding, the bare substrate maintained low and highly unstable OCP values, indicating a state dominated by continuous depassivation with repeated local repassivation events. These OCP oscillations reflect the dynamic competition between mechanical rupture and electrochemical reformation of the passive film within the wear track, a behavior commonly reported for titanium alloys and related materials under tribocorrosion conditions [35,39,42]. By contrast, the coated samples exhibited much steadier OCP curves. TiAlN, in particular, displayed a gradual potential drift during sliding rather than a nearly constant plateau. This behavior is consistent with a short-range galvanic coupling scenario in which depassivated regions coexist with still-passive microdomains inside the wear track. As these local anodic and cathodic domains continuously evolve through film rupture and partial restoration, a smooth potential trend is generated instead of abrupt electrochemical transitions [41,43]. The absence of a similarly pronounced drift in the other curves is consistent with differences in the spatial distribution and evolution of active and passive regions within the wear track. For TiAlN, the smaller potential perturbation may indicate that a greater fraction of the surface remained electrochemically protected during sliding. However, OCP behavior alone cannot determine whether this protection resulted from a persistent passive film, a mechanically retained tribofilm, or a combination of both.

The darker regions observed along the sliding direction (Figure 10) may correspond to chemically modified surface regions or tribofilm deposits. Their morphology and the local enrichment in O and electrolyte-derived elements are consistent with tribofilm formation. After sliding ceased, the OCP progressively recovered toward the pre-sliding values, indicating electrochemical recovery of the surface. AlTiN exhibited the fastest potential recovery, followed by TiAlN and Ti6Al4V, indicating a more rapid restoration of surface passivity. Rapid OCP recovery indicates faster restoration of the electrochemical condition of the surface after sliding. This recovery may involve repassivation, redistribution of surface species, or re-establishment of a mechanically disrupted oxide or nitride-containing layer, and therefore a lower corrosion tendency once the mechanical action is interrupted [44]. When considered together with the smaller OCP drop at sliding initiation, these recovery kinetics indicate that both coatings, and particularly AlTiN during the post-sliding stage, promote rapid restoration of passivity and thereby reduce the corrosion-related component of the wear-corrosion synergy.

Overall, the results indicate that both coatings improve tribocorrosion performance relative to the uncoated substrate, although through partially different mechanisms. On one hand, AlTiN lowers the COF more effectively and accelerates post-sliding repassivation. On the other hand, TiAlN provides greater electrochemical stability during sliding, as evidenced by its smaller OCP drop and more stable passive or tribofilm response. Thus, both coatings outperform the substrate under OCP tribocorrosion conditions by reducing the severity of mechanical depassivation and limiting galvanic driving forces within the wear track, features that are technologically important for minimizing material degradation in coupled wear–corrosion environments [45,46].

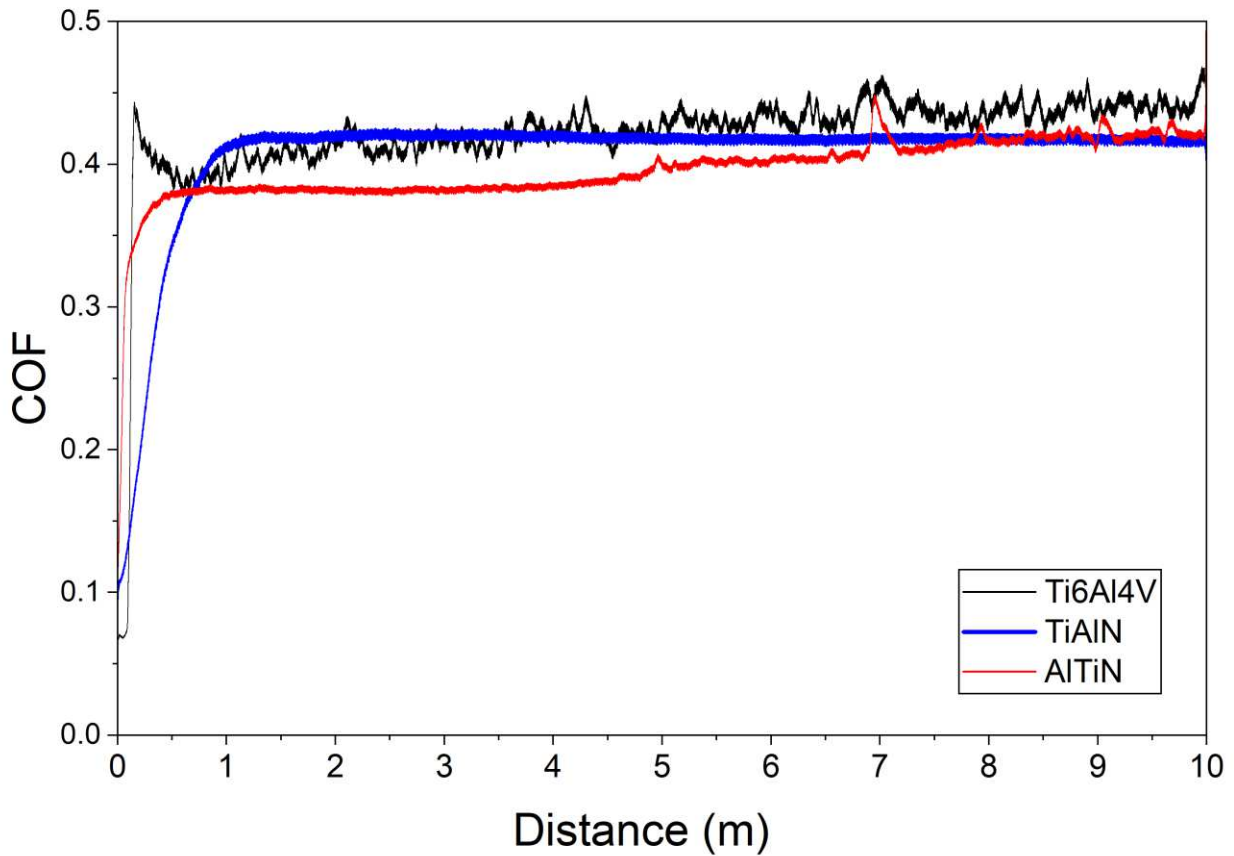


Figure 7. Representative coefficient of friction (COF) vs. sliding distance (0-10 m) in tribocorrosion.

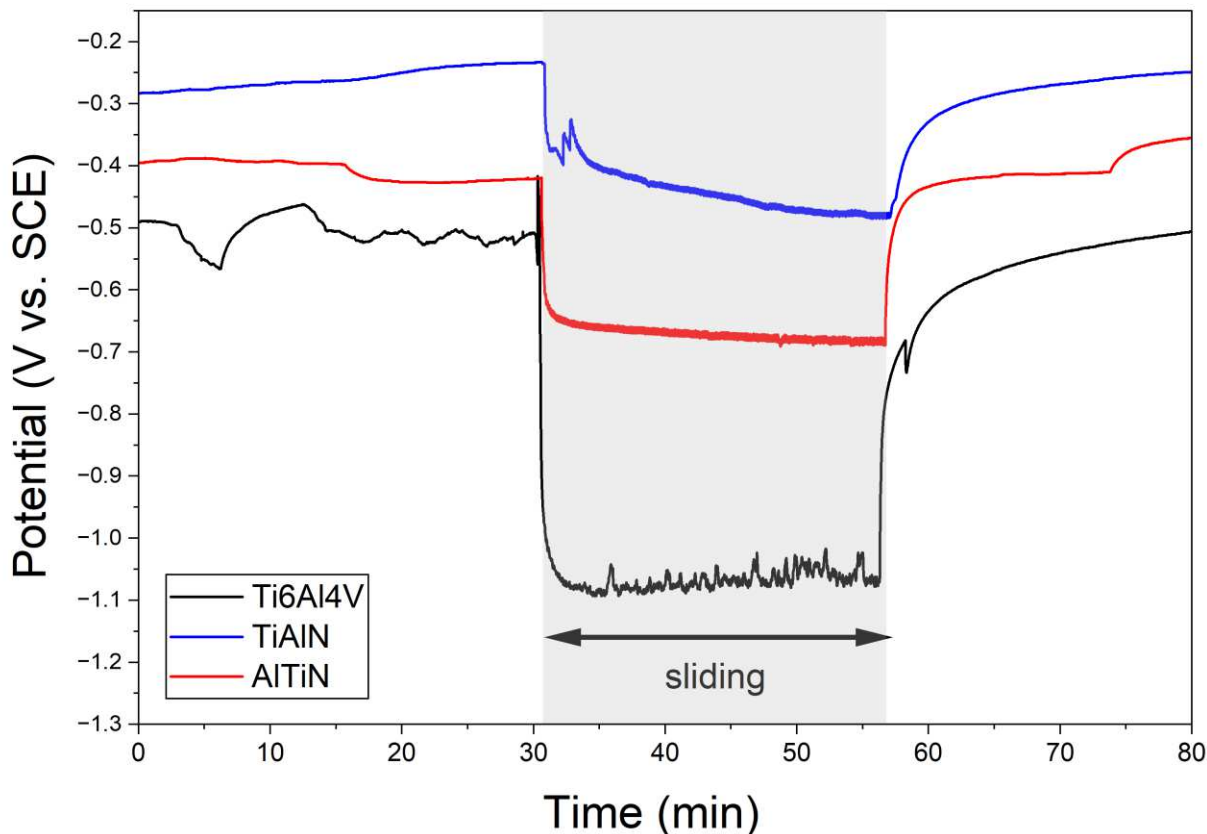


Figure 8. Representative open-circuit potential (OCP, E in V vs. SCE) vs. time during tribocorrosion in artificial saliva.

SEM and EDS analyses of the Ti6Al4V substrate wear track (Figure 9 and Table 2) revealed a deep and wide scar, in agreement with the high wear rate quantified from the WLI maps (Figure 12 and Table 5). From a morphological standpoint, the wear track displayed features typical of both abrasive and adhesive wear, including ploughing grooves and patches of adhered material. EDS measurements performed at points 1-4 within the track detected not only the principal substrate elements (Ti and Al), but also C, O, P, Na, K, and Cl, indicating incorporation of constituents from the artificial saliva into the mechanically mixed surface layer. The consistent presence of electrolyte-derived species at all analyzed locations suggests that the passive film covering the substrate was extensively disrupted during sliding, thereby promoting repeated depassivation and intensifying corrosion-assisted wear. These findings provide a mechanistic basis

for the large COF fluctuations, the pronounced OCP drops, and the highest overall wear rate observed for the uncoated Ti6Al4V substrate under tribocorrosion conditions.

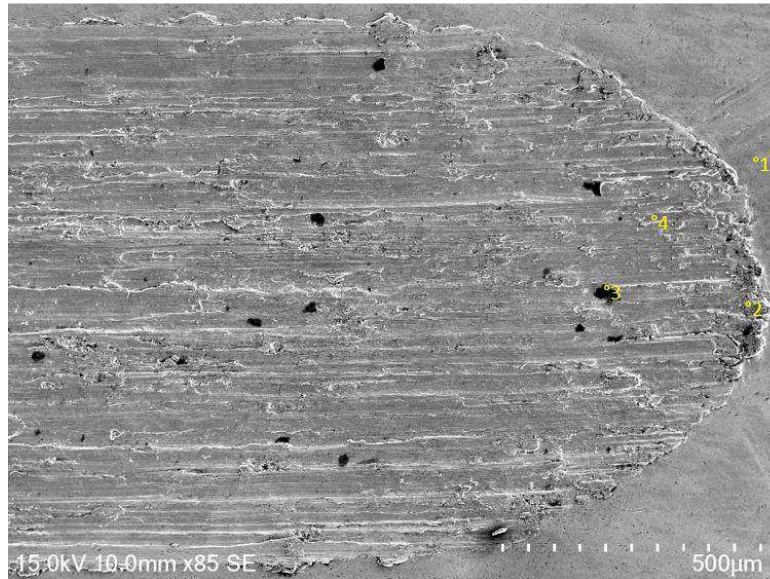


Figure 9. SEM surface morphology of the wear track after tribocorrosion testing of the Ti6Al4V substrate. EDS analyses were conducted at points 1–4; results are reported in Table 2.

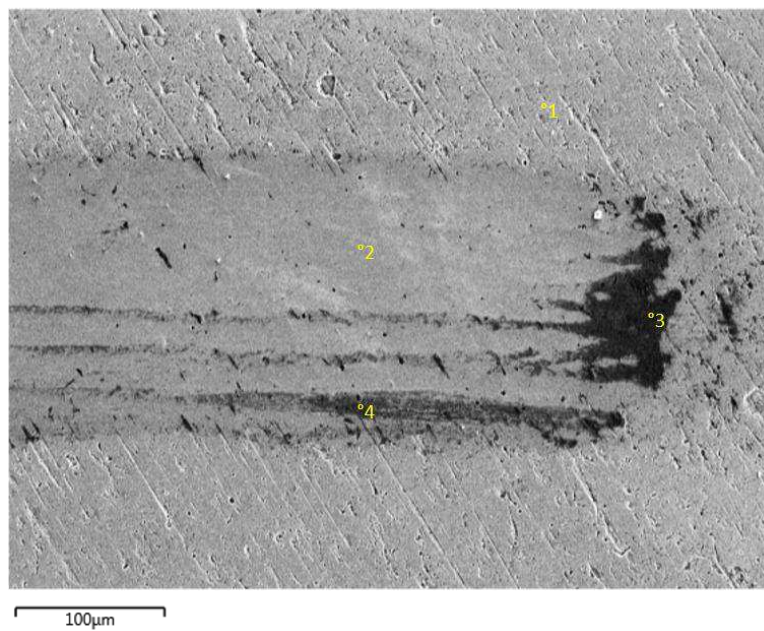


Figure 10. SEM surface morphology of the wear track after tribocorrosion testing of the TiAlN coating. EDS analyses were conducted at points 1-4; results are reported in Table 3.

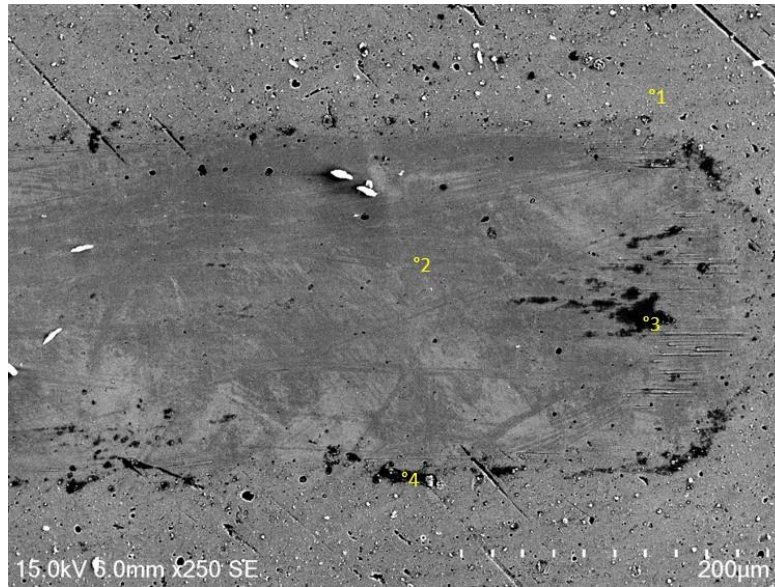


Figure 11. SEM surface morphology of the wear track after tribocorrosion testing of the AlTiN coating. EDS analyses were conducted at points 1-4; results are reported in Table 4.

Table 2. Ti6Al4V substrate EDS point analysis results (at.%).

Element	Point 1	Point 2	Point 3	Point 4
Ti	72.9	47.3	36.9	74.8
O	20.7	29.3	32.5	17.0
C	6.4	22.0	30.1	5.0
Al	—	0.7	—	2.8
Cl	—	0.5	0.3	0.4
Na	—	—	0.2	—

P	—	0.2	—	—
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SEM analysis of the TiAlN wear track (Figure 10 and Table 3) revealed a significantly narrower and shallower scar than that observed on the Ti6Al4V substrate, corroborating the reduced wear depth measured by WLI (Figure 12 and Table 5). EDS point analyses further clarified the chemical evolution within the track. At point 1, located outside the wear scar, the surface composition was dominated by Ti, Al, and N, consistent with the TiAlN coating, together with detectable carbon, most likely associated with the Tris-containing artificial saliva. Within the wear track (points 2–4), carbon remained present, indicating incorporation of saliva-derived species into the mechanically mixed surface layer. In addition, elements originating from the electrolyte (oxygen, phosphorus, sodium, potassium, and chlorine) were detected, with their highest concentrations at point 3, near the track extremity, suggesting localized accumulation of a tribofilm. The darker regions visible in the SEM micrographs appear as continuous streaks running along the sliding direction, extending from the beginning to the end of the wear track, although they do not cover their full width. This morphology is consistent with the formation of a partially continuous tribofilm. The presence of these oxide- and electrolyte-enriched regions likely contributes to stabilization of the passive film, thereby reducing direct metal-counterbody contact, mitigating corrosion-assisted wear, and providing a mechanistic basis for the low COF variability and small OCP perturbations observed for TiAlN during sliding. Overall, these findings indicate that, under tribocorrosion conditions in artificial saliva, TiAlN is able to sustain a chemically and mechanically resilient tribofilm along the wear track, which may contribute to its superior wear resistance relative to AlTiN and the uncoated substrate.

Table 3. TiAlN EDS point analysis results (at.%).

Element	Point 1	Point 2	Point 3	Point 4
N	43.1	42.8	19.0	32.1
Ti	28.6	29.1	21.8	24.8

Al	23.6	24.0	17.7	20.6
C	4.7	4.1	7.6	6.5
O	–	–	33.0	15.5
P	–	–	0.4	0.3
Na	–	–	0.2	–
K	–	–	0.1	–
Cl	–	–	0.1	–

In contrast, SEM/EDS analysis of the AlTiN wear track (Figure 11 and Table 4) revealed a markedly different tribochemical response. Although oxygen and electrolyte-derived elements such as P, K, and Na were detected, their distribution was highly localized at the track edges (points 3 and 4), with only limited presence in the central region of the scar. This distribution suggests that any tribofilm formed during sliding was largely removed by mechanical action, leaving only residual deposits near the track boundaries. Compared with TiAlN, which maintained tribofilm features along the track, AlTiN exhibited less effective passive film coverage, consistent with the larger OCP drop and more negative potential values recorded during sliding.

These differences may be related, at least in part, to the distinct chemical compositions of the coatings. The higher concentration of oxygen and electrolyte-derived elements within the TiAlN wear track suggests greater incorporation of an oxygen- and electrolyte-containing surface layer. Given the Ti-rich composition of the TiAlN coating, the formation of Ti-containing oxygen enriched surface films that are more resistant to attack by chloride-containing media is plausible. In contrast, the lower oxygen enrichment in the central region of the AlTiN wear track may indicate reduced film retention or greater removal during sliding. In artificial saliva, which contains a relatively high concentration of Cl^- together with Na^+ , K^+ , and phosphate species, the

stability and continuity of the tribofilm are critical for limiting galvanic coupling between depassivated and still-passive regions. Consequently, TiAlN appears to sustain a more chemically and mechanically resistant surface film capable of shielding the surface from aggressive ionic species, whereas the discontinuous film formed on AlTiN provides only partial protection, thereby explaining its intermediate wear rate, despite its higher H/E ratio. In addition, SEM observations of the terminal region of the AlTiN wear track revealed features characteristic of abrasive wear, including linear grooves and ploughed material, consistent with localized removal of the residual tribofilm during sliding.

Table 4. AlTiN point analysis results (at.%).

Element	Point 1	Point 2	Point 3	Point 4
N	41.9	42.4	13.5	12.4
Ti	20.4	20.6	15.1	13.3
Al	32.5	32.5	24.0	21.8
C	5.2	4.5	7.0	10.5
O	–	–	39.3	40.4
P	–	–	0.5	0.7
Na	–	–	0.2	0.3
K	–	–	0.1	0.3
Cl	–	–	0.3	0.3
Ca	–	–	–	0.1

The white-light interferometry (WLI) maps of the substrate, TiAlN, and AlTiN surfaces (Figure 12), along with the wear depth profiles shown in Figure 13, corroborate the wear-rate ranking presented in Table 5. The Ti6Al4V substrate exhibits the widest and deepest wear scar, whereas both nitride coatings markedly reduce surface damage. Among the coated samples, TiAlN produces a substantially shallower wear track than AlTiN. Quantitatively, the wear rate decreases from $4.281 \times 10^{-4} \text{ mm}^3/\text{N.m}$ on the substrate to $3.035 \times 10^{-6} \text{ mm}^3/\text{N.m}$ for AlTiN, reaching the lowest value of $1.288 \times 10^{-6} \text{ mm}^3/\text{N.m}$ for TiAlN.

When considered together with the mechanical properties, the tribocorrosion results reveal that the higher hardness and H/E and H^3/E^2 values of AlTiN did not translate into lower material loss. Despite its superior mechanical indicators, AlTiN exhibited a higher wear rate than TiAlN under the present tribocorrosion conditions. This discrepancy indicates that, in addition to mechanical resistance, electrochemical and tribochemical processes play an important role in determining the overall wear response

In agreement with the OCP transients discussed above, AlTiN experienced a larger depassivation shift at the onset of sliding and maintained a more negative potential during sliding than TiAlN, indicating stronger galvanic coupling between the active wear track and the surrounding passive regions. Such conditions intensify corrosion-assisted removal of the mechanically generated third body and accelerate total material loss [47]. By contrast, TiAlN maintained a more stable and resilient passive layer within the wear track, as evidenced by its smaller OCP drop and steadier electrochemical evolution. This behavior effectively suppressed the corrosion component of the wear-corrosion synergy, resulting in the lowest overall wear rate despite its slightly lower H/E value. Therefore, although previous studies have shown that increasing Al content can improve hardness and dry-wear resistance in TiAlN/AlTiN systems [48–50], the present results demonstrate that such trends cannot be directly extended to tribocorrosion conditions, where the stability and reparability of the passive film, and the associated galvanic interactions, become the dominant factors controlling wear. This effect is clearly illustrated here by the superior performance of TiAlN relative to AlTiN.

From a physiological perspective, it is also important to note that all tests were conducted in artificial saliva, a chloride-containing electrolyte at near-neutral pH designed to simulate the oral

environment. In such media, passive films on Ti-based materials are continuously challenged by the competing effects of chloride adsorption and penetration and surface hydroxylation, so that any mechanically induced depassivation within the wear track rapidly generates an electrochemical driving force for metal dissolution. Within this framework, the overall behavior observed in the present study becomes fully consistent. The larger OCP drop and slower recovery of the Ti6Al4V substrate indicate that the surface remained in a more persistent depassivated state during sliding; together with its higher and more unstable COF, this condition favored corrosion-assisted removal of third-body material and explains the highest wear rate.

Although AlTiN exhibited more favorable mechanical indicators for dry sliding, it underwent stronger galvanic coupling in artificial saliva during sliding, so that the corrosion component became dominant and its wear rate was not the lowest. In contrast, TiAlN combined a lower and more stable COF with smaller OCP excursions and faster repassivation, indicating the presence of a passive film better able to withstand chloride attack within the wear track. As a result, the corrosion contribution to the wear-corrosion synergy was minimized, and TiAlN showed the best overall wear performance among the tested systems. These electrolyte-specific effects highlight that rankings established under dry sliding cannot be directly extrapolated to body-fluid analogues. Under artificial saliva, the strength and reparability of the passive film in a near neutral chloride-containing environment become the rate-controlling factors, and in this respect TiAlN outperformed AlTiN in the present study.

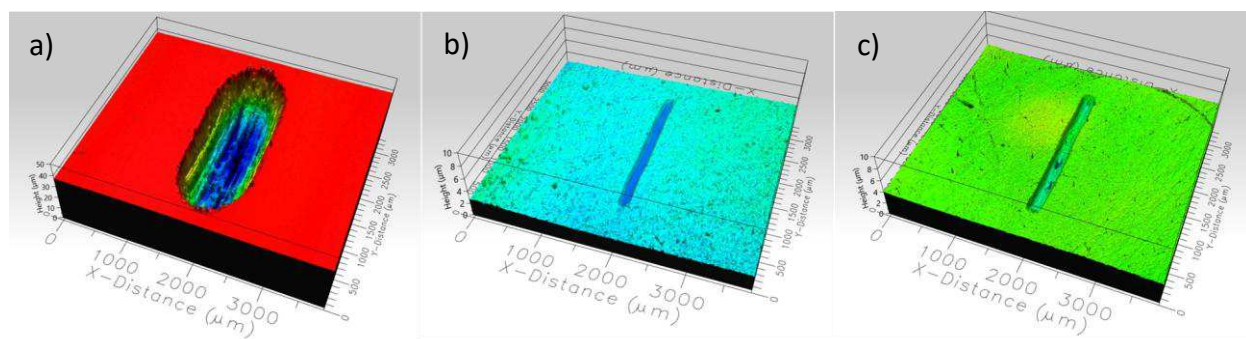


Figure 12. White-light interferometry (WLI) surface maps after tribocorrosion in artificial saliva. Left to right: a) Ti6Al4V substrate, b) TiAlN, c) AlTiN.

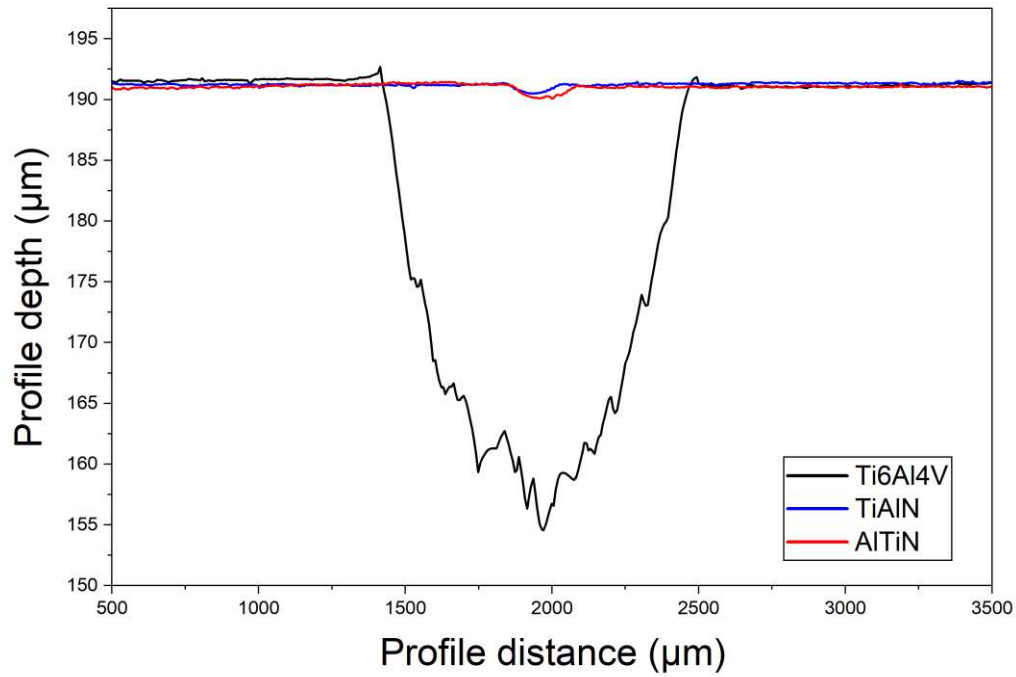


Figure 13. Representative wear depth profile after tribocorrosion test in artificial saliva.

Table 5. Average wear rate ($\text{mm}^3/\text{N}\cdot\text{m}$) obtained from tribocorrosion tests.

Sample	Wear rate ($\text{mm}^3/\text{N}\cdot\text{m}$)
Ti6Al4V	$4.281 \pm 0.452 \times 10^{-4}$
TiAlN	$1.288 \pm 0.074 \times 10^{-6}$
AlTiN	$3.035 \pm 0.301 \times 10^{-6}$

4. Conclusions

This study investigated the tribocorrosion behavior of Ti6Al4V coated with TiAlN and AlTiN thin films deposited by cathodic arc evaporation in a near-neutral, chloride-containing artificial saliva electrolyte. Nanoindentation revealed a clear mechanical advantage for AlTiN, which exhibited

higher hardness and higher H/E and H^3/E^2 ratios than TiAlN. Scratch testing supported this trend, with AlTiN showing higher critical loads for the identified damage and failure events.

Under tribocorrosion conditions, however, the superior mechanical properties of AlTiN did not result in the lowest material loss. Both coatings reduced and stabilized the coefficient of friction compared with uncoated Ti6Al4V. AlTiN exhibited the lowest average COF, whereas TiAlN showed the smaller fluctuation amplitude, indicating a more stable friction response. The OCP measurements further showed that sliding caused the largest potential drop for Ti6Al4V, an intermediate response for AlTiN, and the smallest perturbation for TiAlN. Following sliding, the electrochemical potential recovered more rapidly for AlTiN and TiAlN than for the uncoated substrate.

Despite its lower hardness and lower H/E and H^3/E^2 values, TiAlN exhibited the lowest measured tribocorrosion wear rate among the tested systems. The smaller OCP perturbation during sliding was observed for TiAlN, whereas AlTiN exhibited the fastest potential recovery after sliding. These differences suggest that TiAlN provided greater electrochemical stability during mechanical activation, while AlTiN promoted faster restoration of the measured open-circuit potential after the sliding stage. However, the present measurements do not establish whether this layer was a passive oxide, a tribochemical film, or a combination of surface products. Similarly, although AlTiN exhibited superior mechanical indicators, its higher tribocorrosion wear rate suggests that mechanical properties alone were insufficient to predict material loss under the investigated electrochemical sliding conditions.

Based on the measured wear rate, the performance ranking from highest to lowest tribocorrosion resistance was TiAlN, followed by AlTiN and the uncoated Ti6Al4V substrate. These results indicate that the tribocorrosion response of TiAlN and AlTiN depends on the combined effects of mechanical, tribological, and electrochemical processes, rather than on hardness or other mechanical descriptors alone. Within the limitations of the present experimental conditions, TiAlN provided the highest resistance to tribocorrosion-induced material loss among the tested systems.

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Authorship contribution

Conceptualization was led by LCF, RDT, and PS. Methodology was developed by TLG, BLP, LCF, and PS. Investigation and data curation were performed by TLG, BLP, and LHG. Software was managed by BLP. Formal analysis and validation were carried out by TLG, AL, BLP, LW, and PS. Visualization was handled by AL. Resources were provided by LCF, RC, RDT, and PS. Funding acquisition and overall supervision were overseen by PS. The original draft of the manuscript was written by TLG. Review and editing of the manuscript were performed by LW, RC, RDT, and PS. All authors read and approved the final manuscript.

Declaration of competing interest

All the Authors declare no conflicts of interests.

Data availability

Data will be made available on request.

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