

Article

Wear Resistance and Electrochemical Corrosion Behavior of Ti-6Al-4V Alloy by Plasma Nitriding

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Highlights

What are the main findings?

- Plasma nitriding formed a continuous 2.77 μm nitrided layer on Ti-6Al-4V alloy.
- Surface hardness increased from 317.60 HV to 548.77 HV after nitriding.
- Wear rate decreased by 98.6% despite an increased friction coefficient.
- The nitrided sample showed lower corrosion current and higher impedance in NaCl.

What are the implications of the main findings?

- The nitrided layer improves load-bearing capacity during sliding wear.
- Plasma nitriding shifts severe adhesive-abrasive wear to mild abrasive wear.
- Surface hardening suppresses deep ploughing, adhesive tearing, and delamination.
- Plasma nitriding provides a practical route to protect Ti-6Al-4V alloy surfaces.

Abstract

Ti-6Al-4V alloy exhibits excellent comprehensive mechanical properties and good corrosion resistance; however, its relatively low surface hardness and insufficient wear resistance limit its further applications in sliding contact and corrosive environments. In this study, plasma nitriding at 750 °C was employed to modify the surface of Ti-6Al-4V alloy, and the effects of plasma nitriding treatment on microstructural evolution, wear resistance, and electrochemical corrosion behavior were systematically investigated. The results indicate that a continuous nitrided layer with a thickness of approximately 2.77 μm was formed on the surface of Ti-6Al-4V alloy. The surface hardness increased from 317.60 HV for the untreated sample to 548.77 HV after plasma nitriding. Compared with the untreated sample, the average friction coefficient of the nitrided sample increased from 0.328 to 0.497; however, the maximum wear depth decreased significantly from 73.91 μm to 0.60 μm , and the wear rate decreased from $30.73 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ to $0.43 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$, corresponding to a reduction of approximately 98.6%. Wear morphology analysis shows that severe ploughing grooves, adhesive tearing, and localized spalling dominated the wear mechanism of the untreated sample. In contrast, the nitrided sample exhibited significantly mitigated wear, characterized mainly by shallow grooves, slight debris accumulation, and minor localized delamination. Electrochemical measurements demonstrate that the nitrided sample exhibits a lower corrosion current density and higher impedance in NaCl solution, indicating that the nitrided layer effectively enhances the electrochemical stability of Ti-6Al-4V alloy. The improved wear and corrosion resistance of the plasma nitrided



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samples can be primarily attributed to the high hardness and effective surface protection provided by the continuous nitrided layer.

Keywords: Ti-6Al-4V alloy; plasma nitriding; wear resistance; electrochemical corrosion

1. Introduction

Titanium alloys have been widely used in aerospace, marine engineering, biomedical applications, and other critical fields, owing to their low density, high specific strength, excellent corrosion resistance, and good high-temperature mechanical properties. However, their further applications are still facing increasing challenges [1–3]. One of the main limitations lies in their relatively low surface hardness (typically around 300–400 HV) and poor wear resistance. Under sliding contact conditions, titanium alloys are prone to adhesive wear, abrasive wear, and fretting wear, which often lead to premature failure of components and restrict their use in more demanding service environments. In marine engineering applications, although titanium alloys show excellent resistance to general corrosion, they are still susceptible to crevice corrosion under harsh conditions such as high temperature, high acidity, and high chloride ion concentration. In addition, poor wear resistance can further accelerate localized corrosion damage [4–6]. Therefore, improving surface hardness, wear resistance, corrosion resistance, and fatigue performance of titanium alloys without compromising their excellent bulk properties has become a key bottleneck restricting their wider engineering applications.

Conventional surface modification techniques, such as electroplating, thermal spraying, and chemical vapor deposition (CVD), often face limitations, including inadequate coating-substrate adhesion, complex processing procedures, and considerable environmental burdens [7–9]. In contrast, plasma nitriding activates the titanium alloy surface through ion bombardment. It facilitates the adsorption, reaction, and inward diffusion of nitrogen-containing species, thereby producing a modified near-surface structure comprising a nitride compound layer and an underlying nitrogen diffusion zone. Consequently, plasma nitriding has emerged as an effective technique for enhancing the surface hardness, wear resistance, and corrosion resistance of Ti-6Al-4V alloys [10]. Nevertheless, the formation and evolution of the nitrided layer are not governed by any single processing parameter; rather, they are controlled by the coupled processes of surface nitrogen supply, nitride formation, and nitrogen diffusion into the substrate.

The nitriding temperature and holding time jointly control surface reactions and nitrogen diffusion during plasma nitriding. Increasing the treatment temperature enhances nitrogen diffusivity and accelerates the formation of Ti-N phases, whereas extending the holding time promotes the continued thickening of the compound layer and the inward development of the nitrogen diffusion zone. Ongtrakulkij et al. [11] reported that prolonging the treatment time at 750 and 800 °C increased both the compound-layer thickness and the hardened-layer depth, while simultaneously affecting the surface roughness and residual-stress state. Almeida et al. [12] identified TiN and Ti₂N phases after nitriding at 690 °C for 4 h; however, the resulting modified layer remained relatively thin, further demonstrating the coupled influence of temperature and holding time on nitrided-layer growth. At relatively low temperatures, longer treatment durations are generally required to compensate for the limited diffusion kinetics of nitrogen. By contrast, excessively high temperatures or prolonged treatment may cause excessive growth or coarsening of the compound layer, increased brittleness, and thermally induced microstructural changes

in the substrate. Therefore, the temperature–time regime must be carefully optimized to balance nitrided-layer growth, surface integrity, and the thermal stability of the substrate.

The effects of nitriding temperature and holding time are further modulated by the treatment atmosphere, gas flow rate, chamber pressure, and discharge characteristics. Gas composition determines the surface nitrogen potential and the population of reactive species, whereas chamber pressure and discharge conditions govern particle transport, ion bombardment intensity, and surface activation. Badr et al. [13] demonstrated that variations in the N_2/O_2 ratio, treatment temperature, and holding time significantly affected the microstructure and corrosion behavior of the modified layer. Shen et al. [14] further showed that gas composition strongly influences the thickness, phase constitution, wear resistance, and corrosion resistance of the Ti-N layer. Li et al. [15] reported that increasing the nitrogen supply does not necessarily improve the nitriding response; rather, a relatively uniform hardened layer can be obtained only when the surface nitriding reactions are appropriately balanced with the inward diffusion of nitrogen. Dwivedi et al. [16] also observed distinct electrochemical responses of nitrided layers in NaCl solution, Hank's solution, and artificial saliva, indicating that process-induced variations in layer structure can substantially affect the stability and corrosion performance of the nitrided surface in different corrosive environments.

In addition to the treatment parameters, the substrate microstructure and initial surface condition also play critical roles in the formation and evolution of the nitrided layer. The native oxide film on titanium alloy surfaces acts as a barrier to nitrogen adsorption and inward diffusion. However, ion bombardment, mechanical surface treatment, and surface nanocrystallization can remove or disrupt this oxide film while introducing a high density of dislocations, grain boundaries, and surface defects, thereby facilitating nitrogen uptake and diffusion. Sun et al. [17] and Yao et al. [18] demonstrated that surface nanocrystallization pretreatment promotes nitrided-layer formation and improves the mechanical integrity and fretting wear resistance of the modified surface. Through a comparative investigation of different titanium alloys, Rossi et al. [19] further showed that the phase constitution and initial microstructure of the substrate strongly affect the microstructure, morphology, and micro-abrasive wear behavior of the resulting nitrided layer. Tkachuk et al. [20] employed a multistage nitriding process to better coordinate surface nitride formation with the inward diffusion of nitrogen, thereby further improving the wear and corrosion resistance of Ti-6Al-4V under physiologically relevant conditions.

For precision titanium-alloy components, plasma nitriding should provide adequate surface hardness and wear resistance while limiting excessive thermal exposure that may adversely affect dimensional accuracy. Therefore, a comparatively moderate nitriding temperature is desirable to balance nitrided-layer formation, surface hardening, and dimensional stability. Based on these considerations, Ti-6Al-4V alloy was plasma-nitrided at 750 °C for 15 h in this study. The cross-sectional morphology and phase constitution of the nitrided layer were characterized, and its effects on surface hardness, friction and wear behavior, and electrochemical corrosion performance were evaluated. The results provide experimental support for the application and further optimization of plasma nitriding treatments for Ti-6Al-4V alloy.

2. Experimental

2.1. Materials and Methods

Commercial Ti-6Al-4V alloy was used as the substrate material, and its chemical composition is listed in Table 1. The alloy is mainly composed of Ti, with Al and V as the principal alloying elements, along with small amounts of Fe, O, and N. Al acts as an

α -phase stabilizer, while V serves as a β -phase stabilizer. Accordingly, Ti-6Al-4V alloy exhibits a typical $\alpha + \beta$ dual-phase microstructure.

Table 1. Chemical composition of Ti-6Al-4V alloy (wt.%).

Element	Ti	Al	V	Fe	O	N
Content	Balance	6.1	4.0	0.16	0.18	0.01

Ti-6Al-4V alloy was cut into block specimens with dimensions of 50 mm $\times$ 10 mm $\times$ 5 mm by wire electrical discharge machining (WEDM). To minimize the influence of the initial surface condition on nitrided layer formation and tribological behavior, all specimens were sequentially subjected to mechanical grinding, polishing, and ultrasonic cleaning prior to treatment. The cleaning process involved successive rinsing with absolute ethanol and deionized water to remove surface contaminants such as oil residues, wear debris, and other impurities, followed by drying with hot air. A schematic illustration of the plasma nitriding setup used in this study is shown in Figure 1. Before plasma nitriding, the chamber was evacuated to a vacuum state, and ion bombardment was applied to activate the specimen surface, thereby reducing the effects of surface contamination and the native oxide film on nitrogen diffusion. Plasma nitriding was then carried out at 750 °C in a pure NH_3 atmosphere, with the chamber pressure maintained at 300 Pa and a holding time of 15 h. After treatment, the specimens were furnace-cooled to room temperature. According to the processing condition, the untreated Ti-6Al-4V alloy was designated as AR, while the sample subjected to plasma nitriding at 750 °C was denoted as PN750.

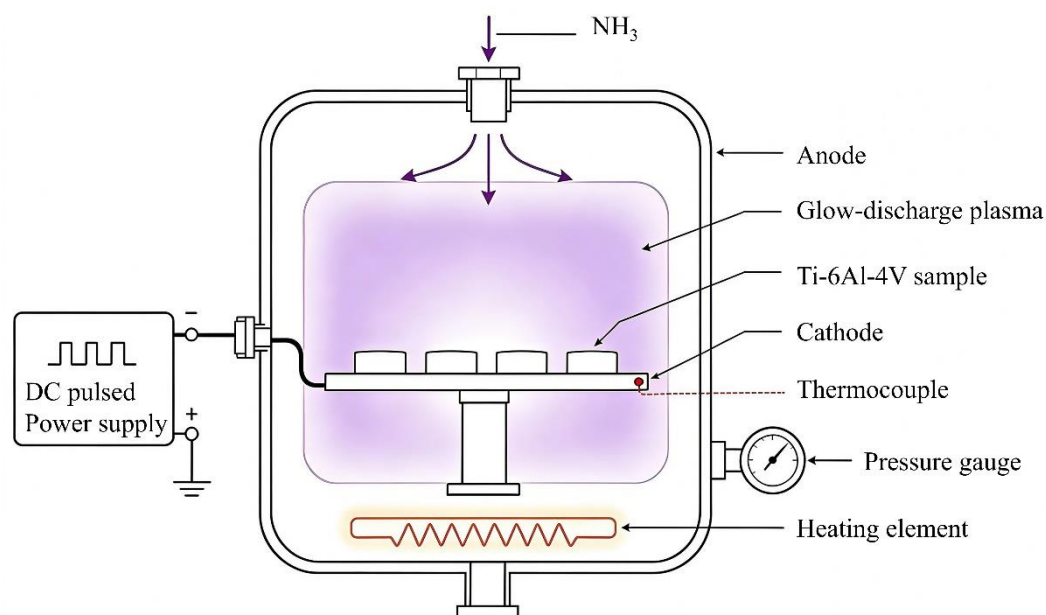


Figure 1. Schematic diagram of the plasma nitriding setup.

2.2. Microstructural Characterization

The cross-sectional morphology and worn surface of the samples were examined using a field emission scanning electron microscope (FE-SEM, Sigma 300, Carl Zeiss AG, Oberkochen, Germany) at an accelerating voltage of 15 kV. Cross-sectional specimens were mounted, ground, and polished prior to observation to evaluate the thickness, continuity, and interfacial bonding state of the nitrided layer. After friction and wear tests, the wear tracks of both AR and PN750 samples were characterized by SEM to compare the corresponding wear damage features. In addition, energy-dispersive X-ray spectroscopy

(EDS) attached to the SEM was employed to perform elemental mapping of the wear track regions, providing the distribution of elements such as Ti, N, O, and Si. The phase composition of the nitrided layer was analyzed by X-ray diffraction (XRD, DX-2700BH, Dandong Haoyuan Instrument Co., Ltd., Dandong, China) using Cu K α radiation. The diffraction patterns were recorded over a 2 θ range of 30–80° at a scanning rate of 2°/min.

2.3. Mechanical and Tribological Property Tests

The surface hardness of the AR and PN750 samples was measured using a Vickers hardness tester (200HVS-5, Shanghai Hualong Test Instruments Corporation, Shanghai, China). A load of 0.5 kgf was applied with a dwell time of 10 s. To minimize the influence of local microstructural heterogeneity and measurement uncertainty, five different locations were randomly selected on each sample, and the average value was reported as the final hardness. Reciprocating sliding wear tests were conducted on a multifunctional tribometer (MS-M9000, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China). A Si₃N₄ ceramic ball with a diameter of 6 mm was used as the counterface. The normal load was set to 15 N, with a reciprocating frequency of 5 Hz, a stroke length of 5 mm, and a total test duration of 15 min. The friction coefficient was continuously recorded during the tests to compare the frictional response of different samples under identical sliding conditions. After wear testing, a 3D surface profilometer (S neox 3D confocal interferometric microscope, Sensofar Metrology, Barcelona, Spain) was used to measure the wear track profile and wear volume, combined with SEM observation of the worn surfaces. The wear rate K was calculated according to Equation (1):

$$K = \frac{V}{F \times L} \quad (1)$$

where V is the wear volume (mm³), F is the applied normal load (N), and L is the total sliding distance (m).

2.4. Electrochemical Measurements

To investigate the effect of plasma nitriding on the corrosion resistance of Ti-6Al-4V alloy, electrochemical tests including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were carried out in 3.5 wt.% and 5.0 wt.% NaCl solutions. A conventional three-electrode system was employed, with the titanium alloy specimen serving as the working electrode, a platinum sheet as the counter electrode, and an Ag/AgCl electrode as the reference electrode. All measurements were performed using an electrochemical workstation (CS310H, Corrtest Instruments Co., Ltd., Wuhan, China). The exposed area of the working electrode was approximately 1 cm². Prior to measurements, open-circuit potential (OCP) monitoring was conducted for 1800 s to ensure system stabilization. EIS measurements were then performed at the stabilized OCP using a 5 mV AC perturbation over a frequency range from 100 kHz to 10 mHz. The obtained EIS data were fitted using an equivalent circuit (EC) model with ZView software (version 3.1). Subsequently, potentiodynamic polarization tests were carried out within a potential range of −0.8 to 1.8 V at a scan rate of 3 mV/s [21]. The corrosion current density (I_{corr}), corrosion potential (E_{corr}), and corrosion rate (CR) were determined using the Tafel extrapolation method [22]. The corrosion rate (CR) was calculated using Equation (2):

$$CR = \frac{k \times I_{\text{corr}} \times E.W.}{d} \quad (2)$$

When the corrosion rate is defined by the constant $k = 3.27 \times 10^{-3}$ mm·year^{−1}, I_{corr} represents the corrosion current density, d is the density of the alloy (the density of

Ti-6Al-4V alloy is 4.45 g/cm³), and E.W. is the equivalent weight of the titanium alloy (gram-equivalent), which is determined using Equation (3):

$$E.W. = \frac{1}{\sum \left| \frac{n_i \times f_i}{\omega_i} \right|} \quad (3)$$

Here, f_i is the mass fraction of the i -th element, ω_i is the atomic mass of the i -th element, and n_i is the valence of the i -th element.

3. Results and Discussion

3.1. Cross-Sectional Morphology and Phase Composition of the Nitrided Layer

Figure 2 shows the cross-sectional SEM morphology of the PN750 sample. After plasma nitriding at 750 °C, a continuous surface-modified layer with a thickness of approximately 2.77 µm was formed on the Ti-6Al-4V alloy. The modified layer was relatively uniform along the specimen surface. No obvious gaps at the layer/substrate interface, through-thickness cracks, or large-scale delamination were observed, indicating good morphological continuity and integrity.

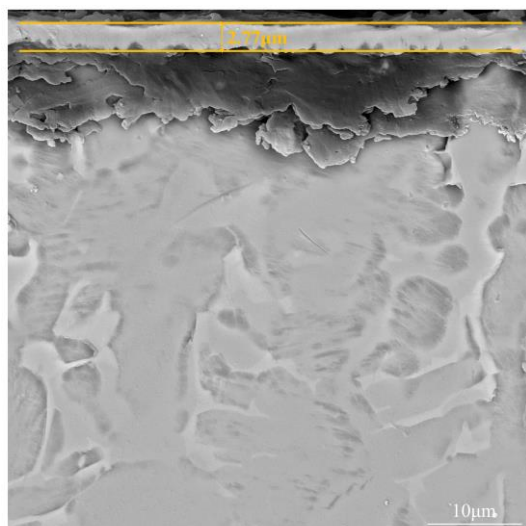


Figure 2. Cross-sectional SEM morphology of the nitrided layer in the PN750 sample.

Figure 3 presents the XRD patterns of the AR and PN750 specimens. The diffraction peaks of the AR specimen primarily correspond to α -Ti, indicating that the diffraction response of the untreated Ti-6Al-4V alloy is mainly attributed to the α -Ti matrix. After plasma nitriding at 750 °C, the PN750 specimen not only retains the characteristic peaks of α -Ti but also exhibits additional characteristic diffraction peaks corresponding to TiN and Ti₂N, demonstrating that active nitrogen reacts with Ti during the nitriding process and forms a nitrogen compound layer on the alloy surface.

Lavrys et al. [23] reported that gas nitriding of Grade 2 titanium at 750 °C produced an approximately 3 µm-thick Ti₂N compound layer with an underlying diffusion zone, whereas the formation of TiN became more pronounced at 900 °C. In comparison, both TiN and Ti₂N were detected in the present Ti-6Al-4V alloy after plasma nitriding at 750 °C. This difference may be related to the different substrate compositions and nitriding conditions, including the nitriding atmosphere, pressure, and plasma activation. Nevertheless, both studies demonstrate the formation of Ti-N compound phases and a hardened near-surface region after nitriding treatment.

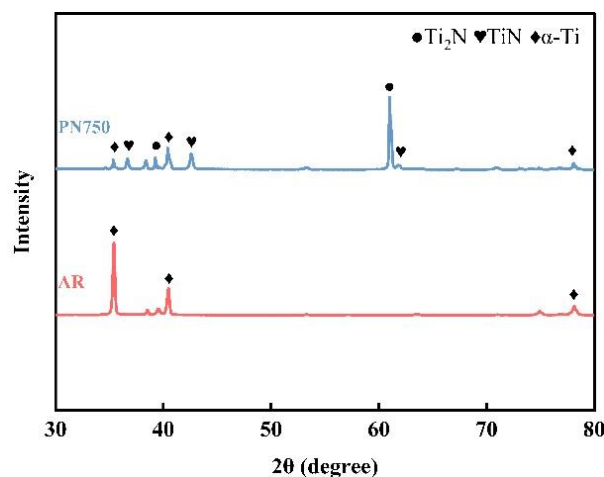


Figure 3. XRD patterns of the AR and PN750 specimens.

3.2. Hardness and Tribological Behavior

Figure 4 shows the surface microhardness of the AR and PN750 specimens. The average hardness increased from 317.60 HV for the AR specimen to 548.77 HV for the PN750 specimen after plasma nitriding at 750 °C. In the present study, the hardness results are used to evaluate the surface-hardening response achieved under the selected nitriding condition and to provide mechanical context for the subsequent tribological analysis.

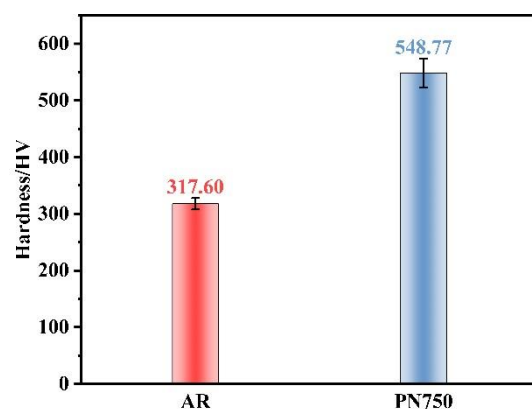


Figure 4. Surface microhardness of the AR and PN750 specimens.

Figure 5a shows the friction coefficient curves of the AR/Si₃N₄ and PN750/Si₃N₄ contact pairs under a normal load of 15 N. The friction coefficient of the AR/Si₃N₄ contact pair increased rapidly during the initial running-in stage and subsequently reached a relatively stable stage with noticeable fluctuations, with an average value of approximately 0.328. In comparison, the PN750/Si₃N₄ contact pair exhibited a higher average friction coefficient of approximately 0.497, which remained within the range of 0.48–0.54 after a short running-in period. Figure 5b presents the cross-sectional profiles of the wear tracks. The AR sample exhibited a broad and deep groove-like wear profile, with a maximum wear depth of 73.91 μm. In contrast, the PN750 sample showed a nearly flat wear profile with only slight fluctuations, and its maximum wear depth was approximately 0.60 μm, representing a reduction of approximately 99.2% compared with the AR sample. As shown in Figure 5c, the wear rate decreased from $30.73 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ for the AR sample to $0.43 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ for the PN750 sample, corresponding to a reduction of approximately 98.6%. Although the PN750/Si₃N₄ contact pair exhibited a higher average friction coefficient, the PN750 sample showed substantially lower wear depth and wear rate than the AR sample. These results indicate that, under the present test conditions, the

higher friction coefficient was not accompanied by greater material loss. Therefore, the friction coefficient and wear loss represent distinct aspects of the tribological response and should be evaluated separately.

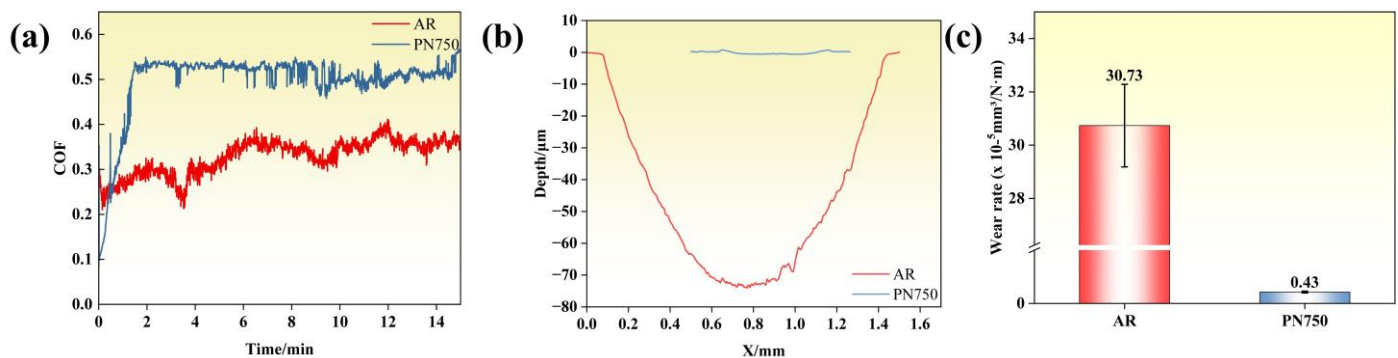


Figure 5. Friction and wear behavior of AR and PN750 samples under a 15 N load: (a) friction coefficient curves; (b) cross-sectional profiles of wear tracks; (c) wear rate.

3.3. Three-Dimensional Wear-Track Morphology and Worn-Surface Characteristics

Figure 6 shows the three-dimensional morphologies of the wear tracks on the AR and PN750 samples. The AR sample exhibited a broad and deep wear track with pronounced topographic variations, consistent with its relatively large wear depth and wear rate. In comparison, the PN750 sample showed a substantially narrower and shallower wear track, with only limited variations in surface height. The maximum wear depth of the PN750 sample was approximately 0.60 μm, which was lower than the apparent nitrided-layer thickness of approximately 2.77 μm determined from the cross-sectional SEM image in Section 3.1. This dimensional comparison suggests that the measured wear penetration remained within the apparent thickness of the nitrided surface layer and that a substantial portion of the nitrogen-containing surface material was retained after the wear test.

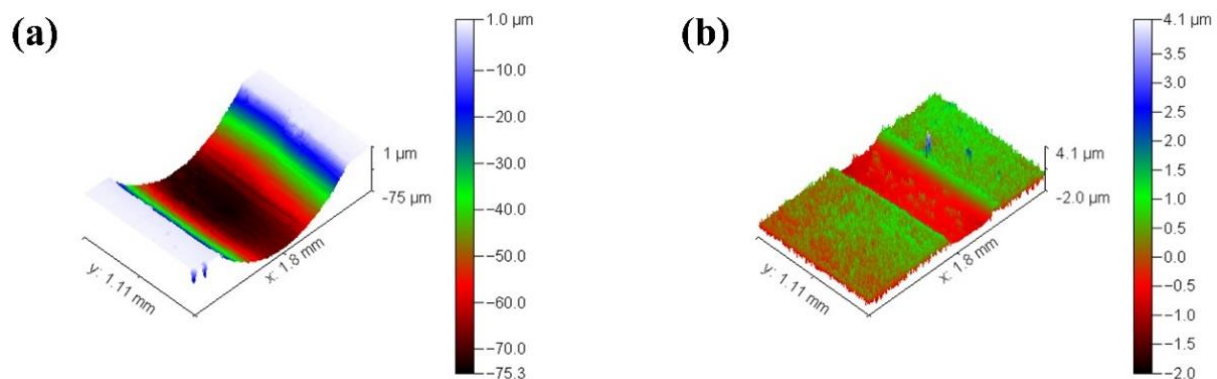


Figure 6. Three-dimensional wear track morphology of AR and PN750 samples (a) AR; (b) PN750.

Figure 7 presents the SEM morphologies and corresponding EDS elemental maps of the wear tracks on the AR and PN750 samples. The wear track on the AR sample was approximately 1.23 mm wide. At higher magnification, pronounced grooves extending parallel to the sliding direction, accumulated wear debris, and locally detached regions were observed within the worn area. These features are consistent with the broad and deep wear profile and the relatively high wear rate of the AR sample. In comparison, the wear-track width of the PN750 sample was approximately 428.25 μm, representing a reduction of approximately 65.2% relative to the AR sample. Its worn surface was mainly characterized by shallower grooves, limited debris accumulation, and small locally spalled regions. The pronounced deep grooves and relatively extensive material detachment observed on the

AR sample were not evident on the PN750 sample. These morphological differences are consistent with the substantially reduced wear depth and wear rate after plasma nitriding. The EDS results showed that the worn regions of both samples were dominated by Ti and O signals, together with a weak Si signal, whereas a distinct N signal was detected only in the worn region of the PN750 sample. The retained N signal, combined with the relatively small wear depth of the PN750 sample, is consistent with the presence of nitrogen-containing modified material within the analysed worn region after testing. The O content measured in the PN750 wear track was somewhat higher than that in the AR wear track, indicating a greater presence of oxygen-containing species on the worn surface. However, their specific chemical states cannot be identified from EDS results alone. Because Si_3N_4 was used as the counterbody, the weak Si signals detected in both wear tracks may be associated with a small amount of Si-containing debris or limited material transfer at the sliding interface. Overall, the PN750 sample exhibited a smaller wear-track width and depth, together with less pronounced grooves, debris accumulation, and localized material detachment. These morphological and compositional observations are consistent with its substantially lower wear rate, indicating that plasma nitriding improved the resistance of the Ti-6Al-4V alloy to worn-surface damage and material removal under the present test conditions.

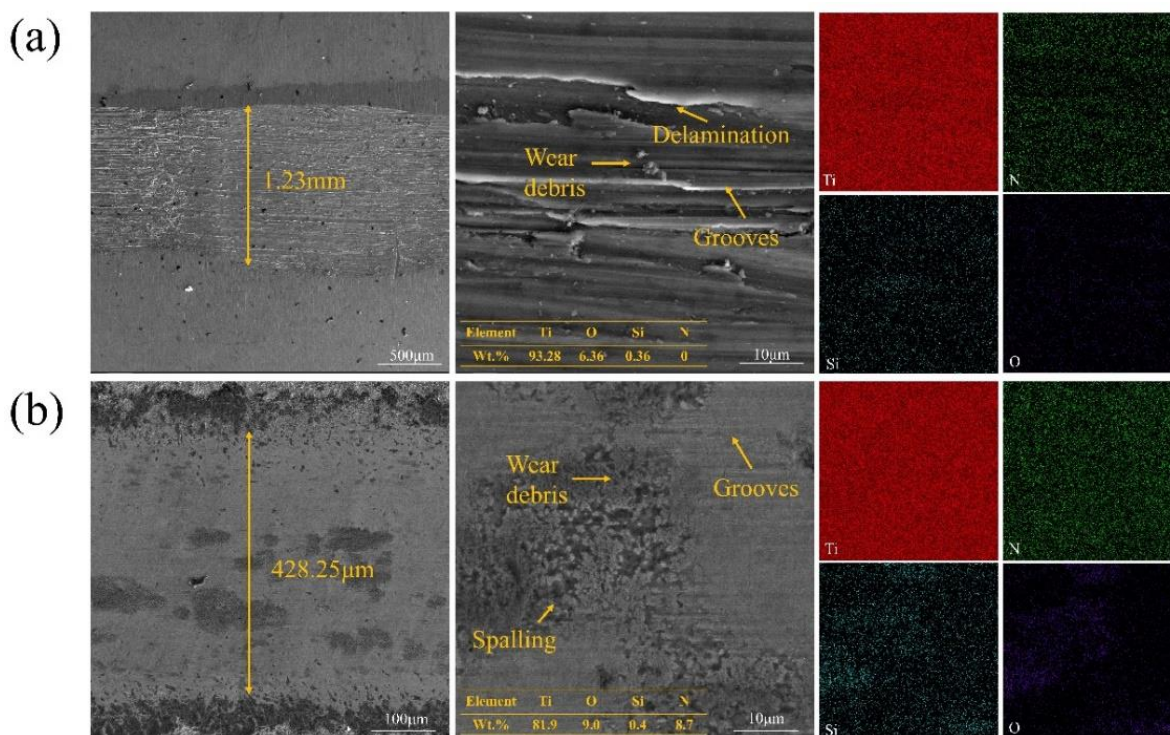


Figure 7. SEM morphologies and EDS elemental mapping of wear tracks after friction and wear tests: (a) AR; (b) PN750.

3.4. Electrochemical Behavior Analysis

Figure 8 presents the potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) fitting results of the AR and the PN750 in 3.5 wt.% and 5.0 wt.% NaCl solutions. Tables 2 and 3 summarize the electrochemical parameters obtained from the polarization curves and EIS fitting results, respectively.

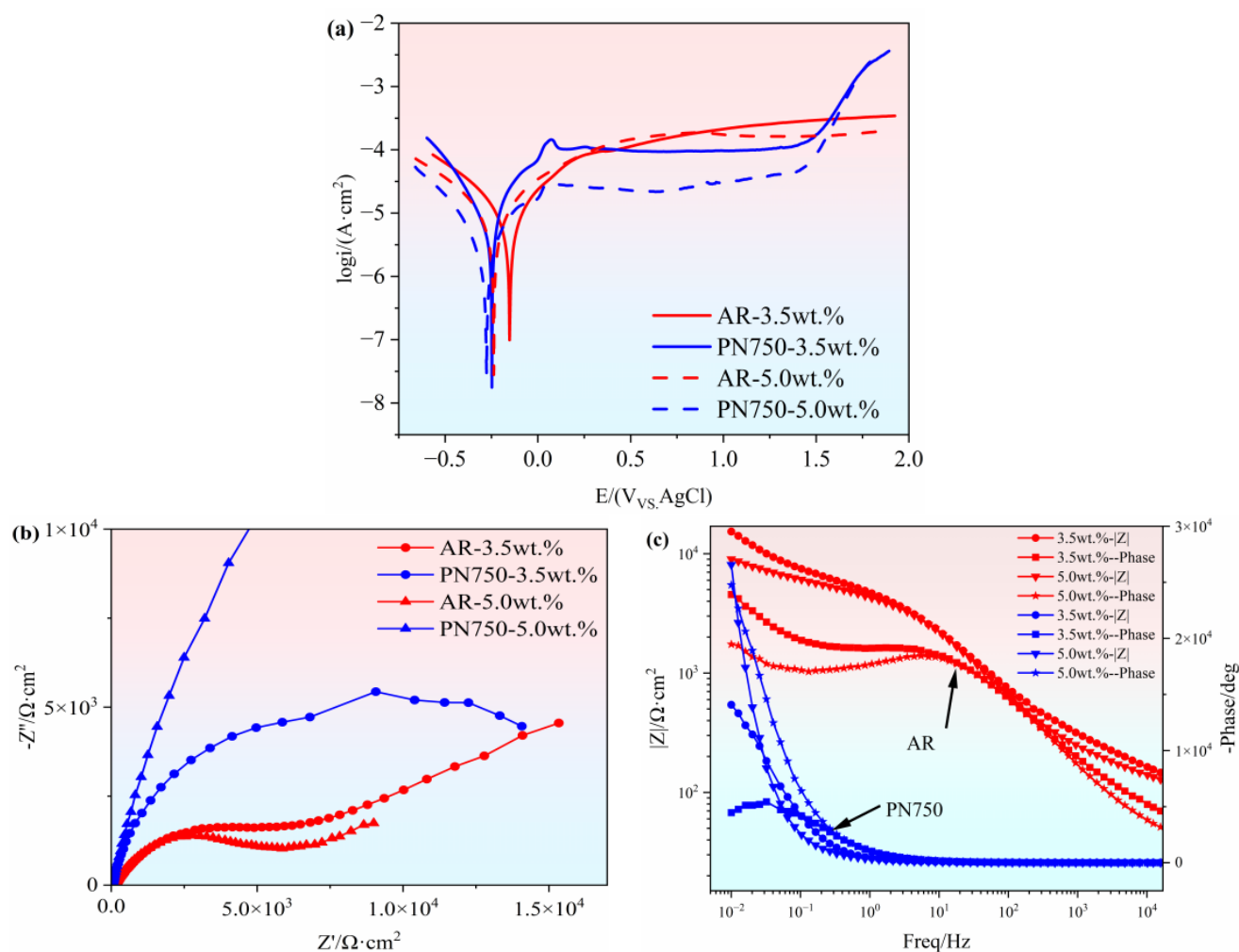


Figure 8. Potentiodynamic polarization curves and electrochemical impedance spectra: (a) polarization curves; (b) Nyquist plots; (c) Bode plots.

Table 2. Electrochemical corrosion parameters.

Sample	NaCl/wt. %	E_{cor}/mV	$I_{cor} (\mu A/cm^2)$	Corrosion Rate (mm/year)
AR	3.5	−152.04	0.017091	0.20049
PN750	3.5	−247.67	0.011722	0.13752
AR	5.0	−237.29	0.016680	0.19567
PN750	5.0	−277.49	0.0028104	0.032969

Table 3. EIS fitting parameters.

Sample	NaCl/wt. %	$R_s/\Omega \cdot cm^2$	$CPE1/\Omega^{-1}cm^{-2}s^n$	$Rp1/\Omega \cdot cm^2$	$CPE2/\Omega^{-1}cm^{-2}s^n$	$Rp2/\Omega \cdot cm^2$	$\chi^2 (\times 10^{-3})$
AR	3.5	67.66	4.75×10^{-5}	9940	2.12×10^{-3}	4800	1.22
PN750	3.5	5.819	7.99×10^{-3}	14,300	1.20×10^{-4}	14,737	2.51
AR	5.0	84.42	3.06×10^{-5}	6268	2.01×10^{-3}	3900	1.18
PN750	5.0	4.941	2.30×10^{-3}	1042	2.15×10^{-4}	56,879	0.59

From Table 2, in 3.5 wt.% NaCl solution, the corrosion current densities of the AR and PN750 samples are $0.017091 \mu A \cdot cm^{-2}$ and $0.011722 \mu A \cdot cm^{-2}$, respectively. After plasma nitriding, the corrosion current density decreases by approximately 31%, corresponding to

a reduction in corrosion rate from $0.20049 \text{ mm} \cdot \text{year}^{-1}$ to $0.13752 \text{ mm} \cdot \text{year}^{-1}$, indicating that the nitrided layer can, to some extent, retard the corrosion of the substrate. When the NaCl concentration increases to 5.0 wt.%, the corrosion current density of the AR sample is $0.01668 \mu\text{A} \cdot \text{cm}^{-2}$, whereas that of the PN750 sample decreases significantly to $0.0028104 \mu\text{A} \cdot \text{cm}^{-2}$, representing a reduction of over 83%. The corresponding corrosion rate decreases from $0.1956 \text{ mm} \cdot \text{year}^{-1}$ to $0.032969 \text{ mm} \cdot \text{year}^{-1}$. Compared with the 3.5 wt.% NaCl solution, the protective effect of the nitrided layer becomes more pronounced in the higher chloride concentration environment, demonstrating improved corrosion resistance. The potentiodynamic polarization curves show that all samples exhibit a relatively wide passive region, indicating the good self-passivation behavior of Ti-6Al-4V alloy. Compared with the AR sample, the PN750 sample shows a significantly lower passive current density, suggesting that its passive film is more effective in suppressing metal dissolution. In addition, at higher anodic potentials, the nitrided sample exhibits a more gradual increase in current density, indicating a stronger resistance of the surface film to Cl^- attack [24].

Figure 8b,c presents the Nyquist and Bode plots of the different samples in NaCl solutions, respectively, and the corresponding fitting results are listed in Table 3. All Nyquist plots exhibit depressed capacitive semicircles, indicating that the corrosion process is predominantly controlled by charge transfer reactions [25]. Compared with the AR sample, the PN750 sample shows a markedly larger capacitive arc radius, suggesting an increased interfacial charge transfer resistance and an effectively suppressed corrosion process. In 3.5 wt.% NaCl solution, the total polarization resistance increases from $14,740 \Omega \cdot \text{cm}^2$ to $29,037 \Omega \cdot \text{cm}^2$ after nitriding. In 5.0 wt.% NaCl solution, the total polarization resistance further increases to $57,921 \Omega \cdot \text{cm}^2$, which is approximately 5.7 times higher than that of the AR sample ($10,168 \Omega \cdot \text{cm}^2$). The Bode plots are consistent with the Nyquist results. The PN750 sample exhibits a higher impedance modulus in the low-frequency region, indicating a stronger barrier effect of the surface film against the penetration of corrosive species. In addition, its phase angle shows a wider peak range and approaches an ideal capacitive response, suggesting a more intact and stable surface film structure [26].

Based on the polarization and EIS results, plasma nitriding significantly improves the corrosion resistance of Ti-6Al-4V alloy in NaCl solutions, with a more pronounced effect in 5.0 wt.% NaCl. This improvement is mainly attributed to the nitrided layer, which possesses high chemical stability and reduces the diffusion rate of Cl^- toward the substrate. Meanwhile, the nitrided layer promotes the formation of a more compact TiO_2 passive film, enhancing its stability and repassivation ability. When localized attack by Cl^- occurs, the nitrided layer can effectively delay further penetration of corrosive species into the substrate, thereby mitigating the initiation and propagation of localized corrosion [27].

4. Conclusions

Plasma nitriding at 750°C was applied to modify the surface of Ti-6Al-4V alloy, and its effects on surface hardness, tribological behavior, and electrochemical corrosion behavior were systematically investigated. Based on the results of cross-sectional morphology, hardness measurements, wear tests, and electrochemical evaluations, the following conclusions can be drawn:

- (1) After plasma nitriding at 750°C , a continuous nitrided layer with a thickness of approximately $2.77 \mu\text{m}$ was formed on the surface of Ti-6Al-4V alloy. The layer remains generally intact, and no obvious through-thickness cracks or large-scale delamination are observed, indicating good structural integrity and strong interfacial bonding under the present processing conditions.
- (2) Plasma nitriding significantly improves the surface hardness of Ti-6Al-4V alloy. The hardness of the untreated AR sample is 317.60 HV, while that of the PN750 sample

increases to 548.77 HV, corresponding to an improvement of approximately 72.8%. The increase in hardness is mainly attributed to the diffusion of nitrogen atoms into the near-surface region and the formation of a nitrogen-enriched strengthening layer, which enhances the surface's resistance to localized plastic deformation.

- (3) Plasma nitriding significantly improves the wear resistance of Ti-6Al-4V alloy. Although the average friction coefficient of the PN750 sample increases from 0.328 for the AR sample to 0.497, the maximum wear depth decreases from 73.91 μm to 0.60 μm . The wear rate decreases from $30.73 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ to $0.43 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$, corresponding to a reduction of approximately 98.6%. This indicates that the improvement in wear resistance is not achieved by reducing the friction coefficient, but mainly by enhancing surface hardness and load-bearing capacity, thereby suppressing severe material removal.
- (4) Plasma nitriding markedly alters the wear mechanism of Ti-6Al-4V alloy. The AR sample exhibits pronounced deep ploughing grooves, adhesive tearing, localized delamination, and debris accumulation, with severe abrasive wear and adhesive wear as the dominant mechanisms. In contrast, the PN750 sample shows a much shallower wear track, mainly characterized by shallow grooves, slight debris accumulation, and minor localized spallation. Since the wear depth of the PN750 sample is significantly lower than the thickness of the nitrided layer, the wear damage is mainly confined within the modified layer, and the dominant wear mechanism shifts to mild abrasive wear, accompanied by localized oxidative wear and debris compaction.
- (5) Electrochemical measurements indicate that plasma nitriding at 750 °C improves the corrosion resistance of Ti-6Al-4V alloy in NaCl solution. Compared with the AR sample, the PN750 sample shows a lower corrosion current density. Meanwhile, the larger capacitive arc radius in the Nyquist plots and the increased interfacial impedance suggest that the nitrided layer enhances the barrier effect against corrosive media and suppresses the corrosion reaction process. Therefore, plasma nitriding at 750 °C is an effective surface modification technique for simultaneously improving the wear resistance and electrochemical stability of Ti-6Al-4V alloy.

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