

Article

A Comparative Study of Microstructure and Tribological Properties of Electroless Ni-P, Ni-W-P, and Ni-Ce-P Coatings on 6061 Aluminum Alloy: The Role of Heat Treatment

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Highlights

What are the main findings?

- Ce refines microstructure into dense nodules; W induces solid-solution strengthening.
- All coatings achieve peak hardness at 350 °C due to Ni₃P precipitation.
- Wear resistance shows a non-monotonic relationship with heat treatment temperature.

What are the implications of the main findings?

- 350 °C/1 h is identified as the optimal heat treatment regime.
- The Ni-Ce-P coating is recommended for high-wear lightweight applications.
- Achieving optimal wear requires synergistic hardness and toughness.

Abstract

This study conducts a systematic comparison of binary Ni-P, ternary Ni-W-P, and ternary Ni-Ce-P electroless coatings on 6061-T6 aluminum alloy, focusing on the effects of post-plating heat treatment at 300, 350, and 400 °C. The originality of this work lies in its direct comparison of W and Ce doping under identical conditions and its identification of a critical brittle transition that decouples hardness from wear resistance. All coatings achieved peak hardness at 350 °C, with Ni-W-P reaching approximately 1691 ± 45 HV_{0.1} due to Ni₃P precipitation and solid-solution strengthening. However, a key finding is the severe embrittlement of the Ni-P coating at 300 °C, where its wear rate increased by over 50 times despite a hardness increase. Treatment at 400 °C degraded wear performance across all systems, likely due to precipitate coarsening and substrate over-aging. The best overall performance within the tested window was achieved with the Ni-Ce-P coating heat-treated at 350 °C for 1 h, which exhibited a fine nodular structure and reduced the wear rate by 98.9% compared to the bare substrate. These results highlight the importance of balancing hardness and toughness, identifying an optimized processing window for enhancing the tribological performance of lightweight aluminum components.

Keywords: 6061 aluminum alloy; Ni-based electroless plating; heat treatment

Academic Editor: Kevin Plucknett

Received: 25 January 2026

Revised: 30 January 2026

Accepted: 3 February 2026

Published: 4 February 2026

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1. Introduction

Aluminum alloys, distinguished by their high strength-to-weight ratio, excellent thermal and electrical conductivity, and superior corrosion resistance, have become indispensable lightweight structural materials in modern aerospace, automotive, and electronic industries [1–4]. Among these, the 6xxx series (Al-Mg-Si), represented by 6061-T6, is ubiquitous. However, the tribological application of aluminum alloys is severely restricted by their low surface hardness and high coefficient of friction. Under relative motion, these alloys are prone to severe adhesive wear, galling, and seizure, leading to premature component failure [5–8]. Therefore, the development of high-efficiency surface modification technologies to enhance surface hardness and wear resistance while preserving the bulk properties of the aluminum substrate remains a focal point in materials science research [9].

Among various surface treatment technologies—including anodizing, physical vapor deposition (PVD), and thermal spraying—electroless plating (autocatalytic plating) stands out for its unique ability to produce functional coatings with uniform thickness, high density, and excellent adhesion on workpieces with complex geometries [10–12]. Specifically, binary Ni-P alloy coatings have been the industry standard, offering amorphous or microcrystalline structures that provide outstanding corrosion resistance and non-magnetic characteristics. However, traditional binary Ni-P coatings face performance bottlenecks when addressing extreme operating conditions, such as high-load friction, high-temperature oxidation, and severe abrasive environments. The hardness of as-plated Ni-P (typically 500–600 HV) is often insufficient for demanding tribological applications without post-treatment.

To overcome these limitations, recent research has pivoted towards the construction of ternary or multi-element electroless plating systems by introducing a third component, typically a refractory metal (e.g., W, Mo) or a rare earth element (e.g., Ce, La). The addition of Tungsten (W) forms a Ni-W-P ternary alloy, where W atoms enter the Ni lattice to form a solid solution [13]. This not only enhances hardness through lattice distortion but also improves the thermal stability of the coating, pushing the crystallization temperature higher and retaining amorphous properties in hotter environments [14]. Conversely, the incorporation of Cerium (Ce), a rare earth element, introduces a different strengthening mechanism. Ce atoms, due to their large atomic radius, tend to segregate at grain boundaries and active growth sites. They act as surfactants, lowering the surface energy required for nucleation and thereby promoting a finer, denser grain structure (Hall–Petch strengthening) [15].

While the benefits of doping are recognized, the optimization of post-deposition heat treatment for these ternary systems on aluminum substrates remains a complex and under-investigated challenge. Heat treatment is essential to transform the metastable as-plated structure into a hard, stable crystalline state (precipitating Ni₃P). However, this process involves a delicate trade-off.

Coating Evolution: Low temperatures (<300 °C) may not induce sufficient precipitation hardening, while excessive temperatures (>400 °C) can lead to grain coarsening, precipitate agglomeration (Ostwald ripening), and micro-cracking due to volume shrinkage.

Substrate Stability: Crucially, precipitation-hardened aluminum alloys like 6061-T6 are sensitive to temperature. The T6 temper involves aging at ~160–175 °C. Subjecting the substrate to coating heat treatments at 300–400 °C can lead to severe over-aging, dissolving or coarsening the strengthening Mg₂Si precipitates in the aluminum matrix. This softening of the substrate creates a “hard coating on soft substrate” scenario, often referred to as the “eggshell effect,” where the coating fails due to lack of substrate support under load [13–16].

The existing literature often focuses on maximizing coating hardness in isolation, neglecting the holistic response of the coating–substrate system and the non-monotonic evolution of wear resistance [13,16]. While the benefits of individual doping elements are known, there is a lack of systematic comparative studies that directly evaluate the behavior of Ni-W-P and Ni-Ce-P coatings on aluminum alloy substrates under identical heat treatment conditions, particularly in the critical medium temperature range (300–400 °C) where substrate properties can be compromised [17,18].

Based on this background, this study selects the 6061-T6 aluminum alloy as the substrate to prepare binary Ni-P, ternary Ni-W-P, and ternary Ni-Ce-P electroless coatings. The study focuses on investigating the effects of heat treatment temperature (300 °C, 350 °C, 400 °C) on the microscopic morphology, phase transformation kinetics, microhardness, and tribological behavior. The aim is to reveal the distinct mechanisms by which W and Ce modify the crystallization and wear response, and to define an optimized process window that balances coating hardness with substrate integrity.

2. Materials and Methods

2.1. Sample Preparation

A commercial 6061-T6 aluminum alloy was selected as the substrate material. Its chemical composition is presented in Table 1. The aluminum alloy was machined into disk specimens with a diameter of 30 mm and a thickness of 5 mm. To ensure uniform handling during the plating process, a small hole was drilled and tapped on the edge of each specimen for suspension.

Table 1. Chemical composition of 6061-T6 aluminum alloy (wt.%).

Element	Mg	Si	Cu	Cr	Al
Content	0.8	0.5	0.25	0.22	Bal.

Pre-treatment is critical for aluminum plating due to its high affinity for oxygen. The specimens underwent a rigorous multi-step process:

Solvent Degreasing: Ultrasonic cleaning in acetone for 10 min to remove organic oils.

Alkaline Cleaning: Soak in 50 g/L Na₂CO₃ + 15 g/L Na₃PO₄ solution (60 °C) for 5 min to remove surface oil and natural oxide film.

Acid Etching: Activation in 50% HNO₃ for 30 s to remove initial oxide layers.

Double Zincate Treatment: After the initial zinc immersion (ZnO 100 g/L + NaOH 500 g/L), the zinc layer is removed with 50% HNO₃, followed by a second zinc immersion. This step forms a dense, thin, and uniform zinc layer on the aluminum surface, preventing further oxidation and serving as a catalytic active center for subsequent nickel deposition.

2.2. Electroless Plating Process

Three different electroless plating baths were prepared to deposit the respective coatings. The base electrolyte was an acidic hypophosphite system. The detailed compositions of the baths are listed in Table 2. The plating conditions were maintained at a temperature of 90 ± 2 °C and a pH of 4.5–4.8. The loading capacity was kept at 1 dm². The deposition time was adjusted to achieve a uniform coating thickness of approximately 25 µm for all samples.

Table 2. Compositions of the electroless plating baths.

Component	Bath A (Ni-P)	Bath B (Ni-W-P)	Bath C (Ni-Ce-P)
NiSO ₄ ·6H ₂ O (g/L)	30	30	30
NaH ₂ PO ₂ ·H ₂ O (g/L)	25	25	25

Lactic Acid (mL/L)	20	20	20
NH ₄ Cl (g/L)	10	10	10
Na ₂ WO ₄ ·2H ₂ O (g/L)	-	18	-
Sodium Citrate (g/L)	-	20	-
Ce(NO ₃) ₃ ·6H ₂ O (mg/L)	-	-	50

2.3. Heat Treatment Process

Post-deposition heat treatment was conducted in a box-type resistance furnace (Shanghai Heheng Instrument Equipment Co., Ltd., Shanghai, China) under a protective Nitrogen (N₂) atmosphere to prevent surface oxidation/discoloration.

The coated samples were heated to three target temperatures: 300 °C, 350 °C, and 400 °C.

Duration: The holding time was fixed at 1 h.

Ramp/Cooling: A heating rate of 10 °C/min was used, followed by furnace cooling to room temperature to minimize thermal shock residual stresses.

2.4. Structural Characterization and Mechanical Property Testing

Scanning Electron Microscopy (SEM, Verios G4, FEI, Lausanne, Switzerland) was employed to observe the surface and cross-sectional morphology of the coatings under different heat treatment conditions, analyzing grain morphology and defect distribution. An X-ray Diffractometer (Bruker, Billerica, MA, USA, D8, Cu K α radiation, 40 kV, 40 mA) was used to test the phase composition and crystal structure evolution of the coatings, with a scanning range (2 θ) of 20°–90° and a step size of 0.02°.

Vickers microhardness testing was conducted using an HV-1000 hardness tester (Shanghai Yanrun Micro-Vickers Hardness Tester Factory, Shanghai, China). A load of 100 g (HV_{0.1}) was applied to the sample surface with a dwell time of 10 s. Five random points were selected on each sample for testing, and the average value was calculated.

Friction and wear tests were performed using a ball-on-disk tribometer (MS-HT1000, Lanzhou Huahui Instrument Technology Co., Ltd., Lanzhou, China) at room temperature under dry sliding conditions. A 6 mm diameter ZrO₂ ceramic ball was used as the counterface. The test parameters were selected based on common practice for evaluating hard coatings on aluminum alloys [15,16]: a normal load of 10 N, a sliding speed of 200 rpm (equivalent to a linear velocity of 0.105 m/s at a 5 mm wear track radius), and a total sliding time of 30 min. Real-time friction coefficient curves were recorded throughout the tests. To ensure data reliability, all wear tests were performed three times for each condition, and the average values are reported. After testing, the samples were ultrasonically cleaned in acetone to remove loose debris. The wear volume was calculated from the mass loss, which was measured using an analytical balance with a precision of 0.01 mg. The wear rate (W) was then calculated using the formula: $W = \Delta m / (q \times F \times L)$, where Δm is the mass loss, q is the density of the coating (approximated as 7.9 g/cm³ for Ni-P, 8.1 g/cm³ for Ni-W-P, and 7.9 g/cm³ for Ni-Ce-P), F is the normal load, and L is the total sliding distance. The morphology of the wear tracks and debris was observed via SEM to analyze the wear mechanisms.

3. Results

3.1. Microstructural Morphology Before and After Heat Treatment

Figure 1 exhibits the typical SEM surface morphologies of the three Ni-based coatings on 6061 aluminum alloy. Figure 2 shows the EDS results of three Ni-based coatings without heat treatment. In the non-heat-treated state, the Ni-P coating presents a continuous,

dense, cellular grain accumulation structure. The grain size is approximately 5–8 μm , arranged uniformly and tightly, with almost no visible macroscopic pores or cracks. This “cellular” structure is a typical characteristic of high-phosphorus Ni-P electroless coatings, formed by the nucleation of multiple fine crystallites in the initial deposition stage, followed by outward growth and mutual coverage of these cells to form quasi-spherical clusters. Additionally, the co-deposition of phosphorus hinders Ni grain growth, resulting in a partially amorphous structure that enhances overall density.

The Ni-Ce-P coating surface consists of a dense accumulation of numerous fine “nodular” (bread-loaf-like) particles. The grain size is significantly smaller than that of the Ni-P coating, making the coating finer and more uniform. This indicates that trace amounts of Ce element significantly refined the coating grains and improved deposition uniformity.

In contrast, the Ni-W-P coating surface presents an ordered “banded” (strip-like) structure. Fine grains are arranged along the direction of the substrate’s polishing texture, forming parallel “queues,” with clear interfaces visible between the bands. This preferred orientation strip morphology may be related to the distribution mode of tungsten in the plating solution: under specific conditions, the addition of W alters the nucleation and growth process of Ni-P, causing the deposit to periodically form lamellar or layered structures; furthermore, pre-treatment scratches on the substrate surface serve as “templates” for the ordered arrangement of nuclei. Overall, the addition of W and Ce did not introduce obvious defects but rather increased the coating density and refined the microstructure.

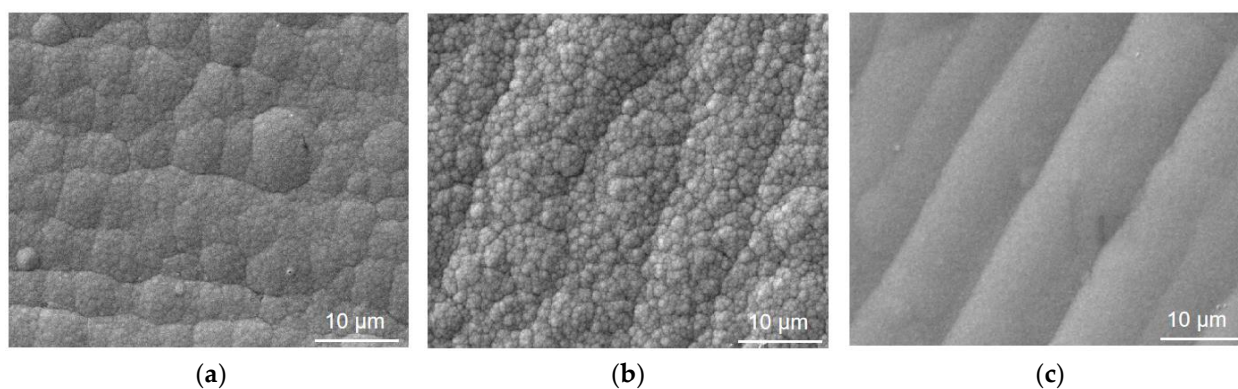


Figure 1. Three electroless plating morphologies without heat treatment: (a) Ni-P; (b) Ni-Ce-P; (c) Ni-W-P.

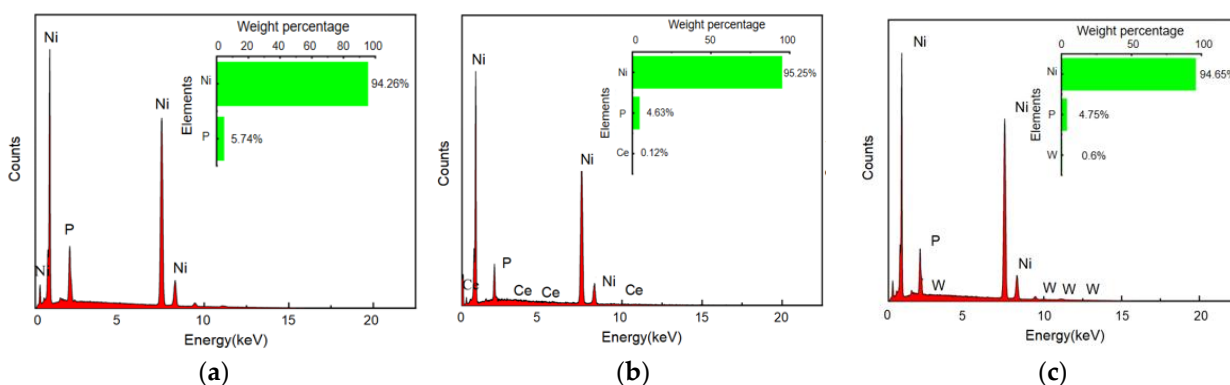


Figure 2. EDS of three electroless plating morphologies without heat treatment: (a) Ni-P; (b) Ni-Ce-P; (c) Ni-W-P.

Figure 3 compares the SEM surface morphologies of the coatings under different heat treatment temperatures. For the Ni-P coating, heat treatment at 300 °C caused slight expansion of the original cellular grains and thinning of grain boundaries. While local porosity increased slightly, the overall surface became flatter and denser, maintaining continuous coverage. This suggests that low-temperature treatment promoted stress relaxation and atomic diffusion in the Ni matrix, causing the originally distinct cell boundaries to blur and fuse. Upon increasing the temperature to 350 °C, Ni-P grains continued to grow, with some fine grains merging into larger aggregates; however, the surface remained uniform and smooth without obvious cracks or large pores. At this stage, the coating achieved peak density and hardness. Further heating to 400 °C caused the cellular structure to become loose, with a significantly increased number of pores and cracks appearing. This indicates that high temperatures promoted significant grain coarsening and the release of greater internal stress, ultimately leading to the deterioration of the coating's overall microstructure.

For the Ni-Ce-P coating, at 300 °C, only slight grain growth occurred, with most fine grains retaining their original size while fusing. At 350 °C, grains grew further, tending to form regular polygonal morphologies. The surface became smoother and denser, with no obvious holes or cracks observed. This indicates that moderate heat treatment promoted the transformation of the Ni-Ce-P structure towards a more uniform and dense state, maintaining good compactness while significantly enhancing hardness. However, at 400 °C, obvious cracks and holes began to appear on the surface, and grain size increased significantly: the excessively high temperature counteracted the beneficial grain-refining effect of the Ce element, and thermal stress exacerbated coating cracking.

In contrast, the Ni-W-P coating underwent more drastic structural evolution during heat treatment. At 300 °C, the banded structure began to disperse, and Ni grains showed a tendency to aggregate and grow; the interfaces between bands gradually blurred, and preferred orientation weakened. After 350 °C treatment, the banded structure almost completely disappeared. The surface roughness increased significantly, and visible cracks and holes appeared. This suggests that the Ni-W-P coating underwent significant recrystallization and stress release processes at medium-to-high temperatures, with micro-cracks easily initiating at grain boundaries. This is likely attributable to the high crystallization tendency and internal stress concentration of the initial amorphous structure of the Ni-W-P coating [17]. Furthermore, the presence of W may lead to thermal expansion coefficient mismatch or the precipitation of brittle phases, resulting in crack defects at relatively lower temperatures. Simultaneously, W solid solution in the Ni matrix significantly alters crystallization kinetics and thermal stability, promoting the precipitation of Ni(W) solid solution and Ni₃P strengthening phases [18].

The evolution of surface roughness with heat treatment temperature is summarized in Table 3. For all coatings, the roughness initially decreases at 300 °C due to surface relaxation and then increases at higher temperatures, especially at 400 °C, which is consistent with the observed grain coarsening and defect formation.

Table 3. Surface roughness (R_a , μm) of the coatings after heat treatment.

Temperature	Ni-P	Ni-Ce-P	Ni-W-P
As-deposited	0.12 ± 0.02	0.08 ± 0.01	0.15 ± 0.03
300 °C	0.10 ± 0.02	0.07 ± 0.01	0.13 ± 0.02
350 °C	0.14 ± 0.03	0.11 ± 0.02	0.18 ± 0.04
400 °C	0.25 ± 0.05	0.19 ± 0.04	0.28 ± 0.06

In summary, the influence of heat treatment at different temperatures on the microstructure manifests as initially promoting densification and stress release, followed by inducing grain coarsening and increased defects. This pattern aligns with literature reports.

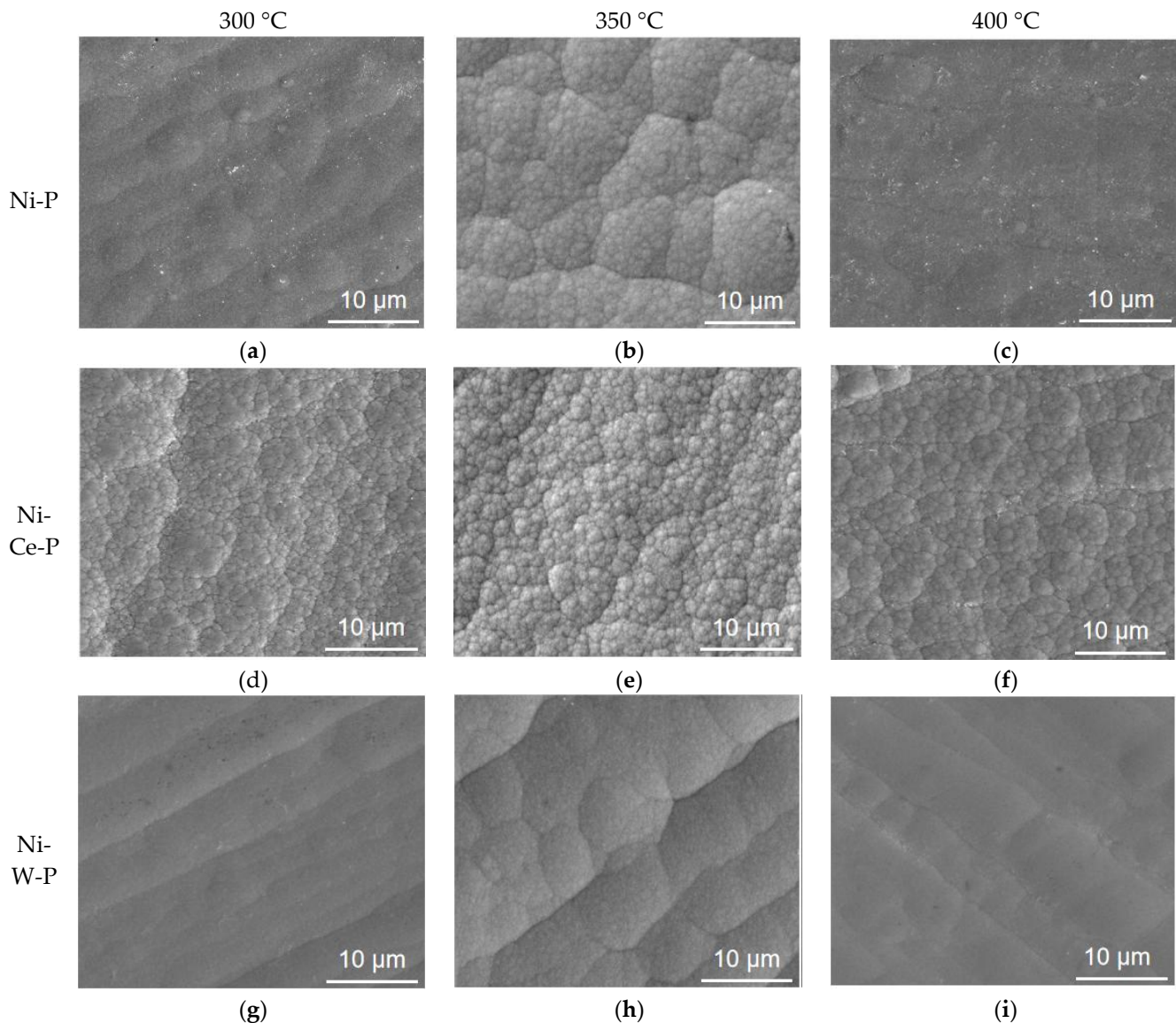


Figure 3. SEM Morphology of the Coating Surface at Different Heat Treatment Temperature.

3.2. Effect of Heat Treatment on Phase Transformation

Figure 4 shows the XRD patterns of the coatings under different heat treatment conditions. For the Ni-P coating, the as-deposited XRD spectrum shows only a broadened diffuse peak around $2\theta = 44^\circ$, with no obvious crystalline peaks, indicating the coating is primarily composed of an amorphous phase and a small amount of nanocrystalline Ni. This is consistent with the amorphous + microcrystalline mixed structure of typical medium-phosphorus Ni-P coatings. After 300 °C treatment, the sharpness of the broad diffraction peak increased slightly, accompanied by the appearance of several weak crystalline peaks, confirming partial crystallization and the initial precipitation of fine crystalline phases; however, diffraction peaks remained broad and low intensity due to limited precipitate content. This stage may involve the formation of metastable nickel phosphides. When the temperature rose to 350 °C, characteristic diffraction peaks for Ni_3P and Ni_5P_3 became clearly visible, and the Ni phase peaks intensified significantly. This indicates the massive precipitation of the stable hard phase Ni_3P , transforming the coating from an

amorphous matrix to a crystalline structure of Ni + Ni₃P. At 400 °C, the intensity of Ni₃P peaks continued to increase and sharpen, confirming that the coating was nearly fully crystallized. However, despite the higher Ni₃P content, the hardness did not exceed the peak at 350 °C, suggesting that excessive coarsening of Ni₃P particles and defects generated by high-temperature treatment weakened the precipitation strengthening effect.

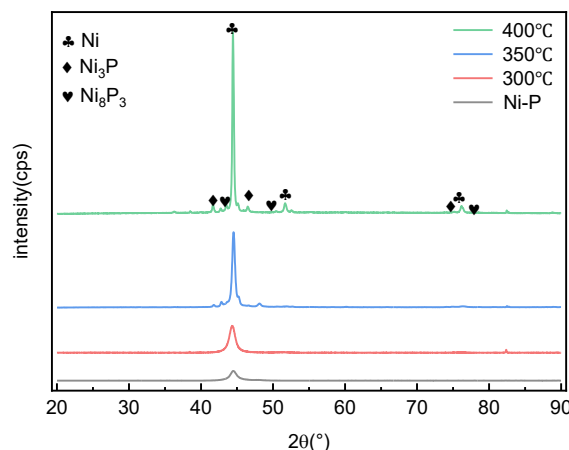


Figure 4. XRD of Ni-P electroless plating layer after heat treatment.

The phase transformation behaviors of Ni-Ce-P and Ni-W-P coatings (Figure 5) were similar to Ni-P but with distinct differences. For Ni-Ce-P, the as-deposited state also presented an amorphous/microcrystalline structure. As the temperature increased from 300 °C to 400 °C, the amorphous diffuse scattering peak gradually weakened, and crystalline peaks strengthened. After treatment at 350 °C and above, Ni and Ni₃P peaks were clearly detected. Notably, the introduction of Ce exhibited an inhibitory effect on Ni₃P precipitation. Literature indicates that rare earth elements can improve the thermal stability of Ni-P coatings, raising the Ni₃P precipitation temperature. In this experiment, the limited hardness increase of Ni-Ce-P at 300 °C confirms Ce's retarding effect on crystallization; however, at 350 °C, massive Ni₃P precipitation occurred, completing the strengthening transformation.

For the Ni-W-P coating, XRD results showed a phase evolution highly similar to Ni-P: from 300 to 400 °C, the amorphous broad peak sharpened, and Ni/Ni₃P peak intensities increased, indicating continuous transformation to a crystalline state. No new W-related diffraction peaks appeared, suggesting W mainly existed as a solid solution in the Ni matrix or Ni₃P phase. Literature confirms that small W additions to Ni-P typically do not form Ni-W intermetallics but dissolve in the Ni lattice.

In summary, heat treatment promotes the transformation of all three coatings from amorphous/microcrystalline to crystalline Ni solid solution + Ni₃P hard phase. Compared to pure Ni-P, W and Ce incorporation delayed Ni₃P precipitation: Ni-Ce-P showed a lag in crystallization peak temperature, while Ni-W-P required higher temperatures for complete crystallization. However, between 350 and 400 °C, all coatings eventually formed Ni₃P, differing only slightly in the temperature of peak precipitation. This indicates that Ce atoms increased the undercooling required for Ni₃P nucleation, while W influenced the diffusion rates of Ni/P atoms, without altering the final precipitate type.

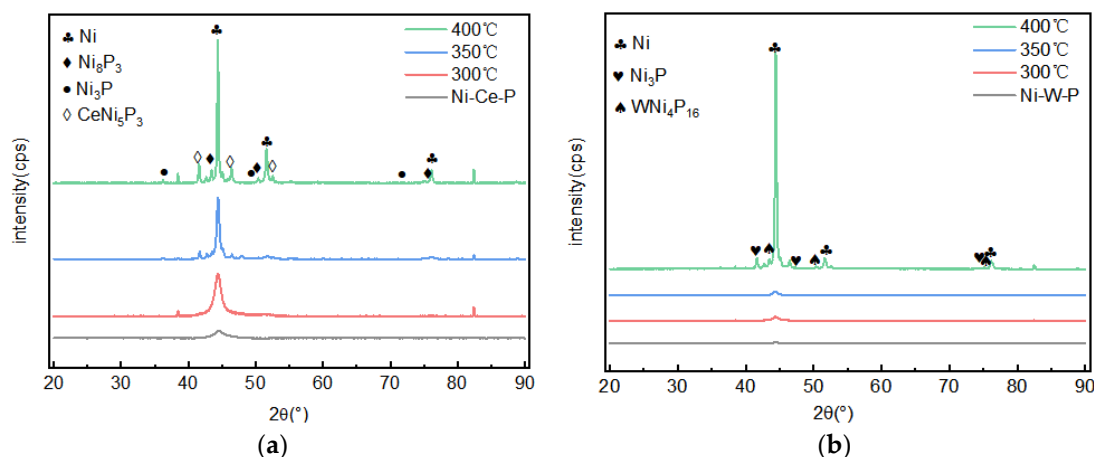


Figure 5. XRD of electroless plating layer after heat treatment: (a) Ni-Ce-P; (b) Ni-W-P.

3.3. Effect of Heat Treatment on Microhardness

Figure 6 illustrates the Vickers hardness changes of the three coatings under different heat treatment conditions. The hardness of all three coatings in the non-heat-treated state was significantly higher than that of the 6061 aluminum alloy substrate. Specifically, the hardness of the Ni-P coating was approximately 539 HV_{0.1}, Ni-W-P was approximately 714 HV_{0.1}, and Ni-Ce-P reached the highest at 789 HV_{0.1}. This indicates that electroless plating formed a high-hardness Ni-P solid solution coating on the aluminum surface, significantly improving surface hardness compared to the soft aluminum substrate. The hardness of Ni-W-P and Ni-Ce-P coatings was higher than that of Ni-P because the addition of alloying elements introduced extra strengthening effects: W served as a solid solution strengthening element to increase the hardness of the Ni matrix, while Ce enhanced the hardening effect through grain refinement and possible dispersion strengthening.

After heat treatment, the hardness of all three coatings significantly increased. All coatings reached peak hardness at 350 °C: Ni-P hardness increased from 539 HV_{0.1} to approximately 1538 HV_{0.1} (an increase of about 1.85 times); Ni-W-P increased from 714 HV_{0.1} to 1691 HV_{0.1} (an increase of about 1.37 times); Ni-Ce-P increased from 789 HV_{0.1} to 1685 HV_{0.1} (an increase of about 1.13 times). At 350 °C, the hardness of the Ni-W-P coating was slightly higher than that of the Ni-Ce-P coating, with both reaching the highest hardness level of approximately 1690 HV_{0.1}. This may be because the Ni-W-P coating had a higher initial degree of crystallinity, and at 350 °C, the Ni₃P hard phase precipitated massively and dispersed uniformly, causing hardness to rise rapidly; while the Ni-Ce-P coating had the highest initial hardness, its Ni₃P precipitation slightly lagged, resulting in a relatively smaller hardness increase.

The primary mechanism of hardness strengthening lies in the precipitation of the Ni₃P hard phase during heat treatment. At approximately 350 °C, the coating undergoes a transformation process of “amorphous Ni-P matrix → metastable nickel phosphides → stable Ni + Ni₃P crystalline phases.” Ni₃P precipitates as fine particles from the amorphous matrix and is uniformly distributed within the coating. On one hand, these high-hardness particles effectively hinder dislocation movement, increasing the yield strength of the matrix; on the other hand, the hardness of Ni₃P itself is extremely high, and its massive precipitation naturally increases the overall hardness of the coating. Additionally, lattice distortion during crystallization also provides certain solid solution strengthening. Therefore, the heat-treated Ni-based coatings possess both solid solution strengthening and precipitation strengthening mechanisms, making the hardness far superior to the original as-deposited level.

It is worth noting that the effect of different heat treatment temperatures on hardness exhibits an “over-aging” phenomenon. As seen in Figure 6, after heat treatment at 300 °C, the coating hardness only increased slightly: Ni-P increased by about 0.85 times, Ni-Ce-P by about 0.45 times, and Ni-W-P by about 0.52 times, indicating that only a small amount of Ni₃P and metastable phases precipitated at this time, with limited strengthening effect; however, hardness jumped to the peak value when the temperature rose to 350 °C. When the temperature continued to rise to 400 °C, the hardness actually decreased compared to 350 °C: Ni-P decreased by about 14.3%, Ni-Ce-P decreased by about 8.6%, and Ni-W-P decreased by about 21.8%. Although the hardness after 400 °C treatment was still far higher than the untreated state, it had clearly fallen back from the peak. The reasons for the decrease in hardness may be two-fold: on one hand, high temperature promoted the further growth and aggregation of Ni₃P particles, reducing the precipitation strengthening effect [19]; on the other hand, defects such as cracks and pores appearing in the coating at 400 °C reduced the actual load-bearing area of the coating, leading to a decrease in macroscopic hardness [20]. Therefore, medium-temperature heat treatment around 350 °C is the optimal hardening condition for Ni-based coatings on 6061-T6 alloy, consistent with the recommended heat treatment temperature range of 345–400 °C in the literature [21,22]. Under this condition, the highest coating hardness and optimal microstructural state can be obtained.

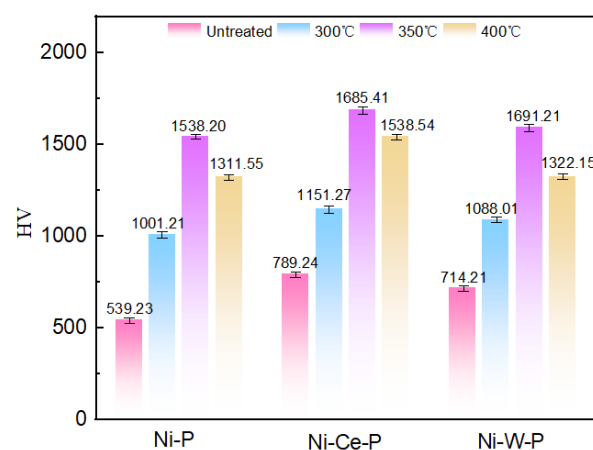


Figure 6. Hardness of electroless plating after heat treatment.

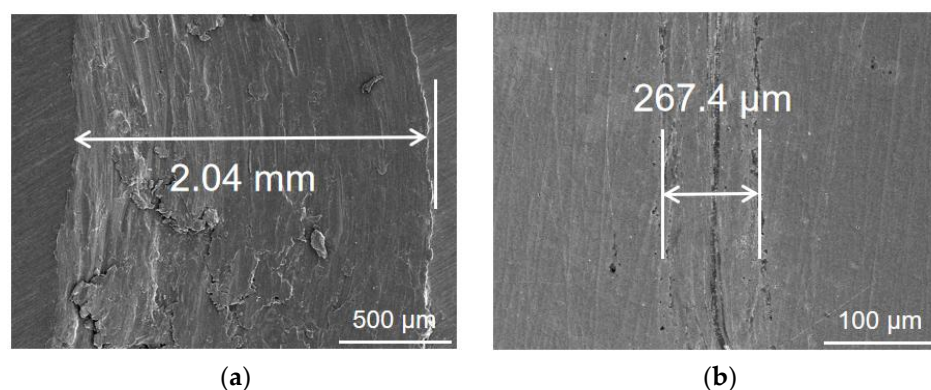
3.4. Effect of Heat Treatment on Wear Resistance and Mechanism

Table 4 summarizes the wear rate test results for the substrate and the as-deposited coatings. The wear rate of the 6061 aluminum alloy substrate was approximately 1.03×10^{-5} g/(N·m). All coatings significantly improved wear resistance. The wear rate of the Ni-P coating was 1.65×10^{-6} g/(N·m), a reduction of about 84.0%. The Ni-W-P coating showed a wear rate of 2.66×10^{-7} g/(N·m), a reduction of 97.4%. The Ni-Ce-P coating exhibited the best performance, with the lowest wear rate of 1.12×10^{-7} g/(N·m), a reduction of 98.9% compared to the substrate. It is evident that Ni-based electroless coatings greatly improved the wear resistance of the aluminum alloy surface, with Ni-Ce-P coating showing the best effect, followed by Ni-W-P, and Ni-P being relatively weaker. This trend is highly correlated with the initial hardness of each coating; the Ni-Ce-P coating with the highest hardness had the best wear resistance, while the Ni-P coating with the lowest hardness had relatively weaker wear resistance. However, it must be emphasized that even the Ni-P coating with the lowest hardness reduced the wear rate by over 80% compared to the unplated aluminum substrate, indicating that electroless plating significantly improved the wear resistance of the aluminum alloy.

Table 4. Wear rate of substrate and after different electroless plating treatments.

Technology	Matrix	Ni-P	Ni-Ce-P	Ni-W-P
Rate of Wear g/(N·m)	1.034×10^{-5}	1.65×10^{-6}	1.12×10^{-7}	2.66×10^{-7}

SEM observation of the wear scar morphology further revealed differences in wear mechanisms (Figure 7). The unplated 6061 aluminum alloy surface showed deep plowing grooves about 2.1 mm wide and a large amount of massive debris after wear, typically characteristic of abrasive wear; while the wear scar width of the Ni-P plated sample was only about 281 μm , with shallower surface scratches and significantly reduced debris size. The wear scar width of the Ni-Ce-P coating was about 436 μm , and Ni-W-P was about 577 μm (wear scar width relates to coating hardness and microstructure, discussed later). Overall, the wear scar width of the coated samples was far smaller than the substrate, and the surface was relatively smooth without wide plowing grooves, producing mainly fine debris rather than large chunks of material. This indicates that the coatings mainly experienced slight surface abrasion during friction, rather than severe cutting on the substrate. The aluminum substrate, due to low hardness, allowed the grinding ball to penetrate deep into the material and grind out a large amount of plastic chips during friction, dominated by abrasive wear; whereas the hardened Ni-based coatings were harder, preventing deep penetration by the grinding ball, causing only microscopic scratches on the surface, accompanied by a small amount of adhesive transfer. Therefore, the wear mechanism of Ni-based coatings manifested as a “abrasive wear + adhesive wear” composite mode. The Ce and W elements added to the coating further improved wear behavior. The addition of Ce and W refined coating grains and increased hardness, reducing the depth of abrasive scratching; simultaneously, the presence of rare earth and transition metals may have altered the oxidation and tribochemical characteristics of the coating surface, reducing the tendency for severe adhesion. Consequently, regarding wear scar morphology, neither Ni-Ce-P nor Ni-W-P coatings showed large-area material peeling, and their debris was mainly in the form of fine particles. This characteristic is directly related to the higher hardness and more uniform, dense microstructure of these two coatings compared to the Ni-P coating.



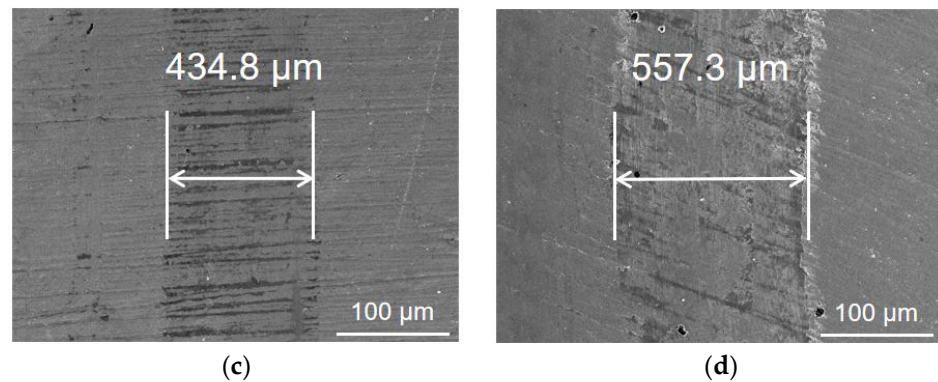


Figure 7. 6061 aluminum alloy and different electroless plating scratch width: (a) 6061 aluminum alloy; (b) Ni-P; (c) Ni-Ce-P; (d) Ni-W-P.

Heat treatment had a very significant effect on the wear resistance of the coatings, but it presented a non-monotonic trend of “deterioration–improvement–deterioration”. The changes in wear rate of the coatings are shown in Table 5, and the microscopic morphology of wear scars is shown in Figure 8.

Ni-P: The wear rate was 1.79×10^{-6} g/(N·m) without heat treatment; after heat treatment at 300 °C, it surged to 9.53×10^{-5} g/(N·m), an increase of about 53 times, indicating significant deterioration in wear resistance; when the temperature was raised to 350 °C, the wear rate dropped to 5.14×10^{-6} g/(N·m), a reduction of about 94.6% compared to 300 °C, approaching the level of the untreated sample. Clearly, 350 °C heat treatment drastically improved the poor wear resistance at 300 °C. This is because at 300 °C, the coating only partially crystallized, precipitating some hard and brittle Ni_3P and metastable phases while the matrix still retained a large amount of ductile Ni solid solution, causing the coating to have insufficient toughness despite increased hardness. During friction, it was prone to large-area peeling into coarse fragments, leading to a surge in wear volume. SEM observation confirmed that the wear scar of the Ni-P coating heat-treated at 300 °C had obvious peeling pits and large detached fragments, verifying the deteriorated wear phenomenon caused by coating embrittlement. After raising the heat treatment temperature to 350 °C, the wear rate of the Ni-P coating significantly decreased to 5.14×10^{-6} g/(N·m), almost recovering to the level of the unheated sample; at this time, the coating structure was more uniform and stable, with Ni_3P hard phases fully precipitated and uniformly distributed. Hardness increased significantly while retaining certain toughness, enabling the coating to effectively resist abrasive plowing without overall peeling. Wear scar examination showed that the Ni-P coating treated at 350 °C only left fine scratches without obvious peeling pits, indicating a good balance between hardness and toughness. However, when the temperature further rose to 400 °C, the wear rate of the Ni-P coating rose again to 2.23×10^{-5} g/(N·m), an increase of about 11 times compared to the untreated state. Although the hardness of the coating at 400 °C was slightly lower than at 350 °C, the main problem was that grain coarsening and cracks caused by high temperature reduced the overall strength of the coating. Once subjected to friction load, material was easily peeled off along the crack propagation. Therefore, the wear resistance of the Ni-P coating deteriorated significantly at 400 °C.

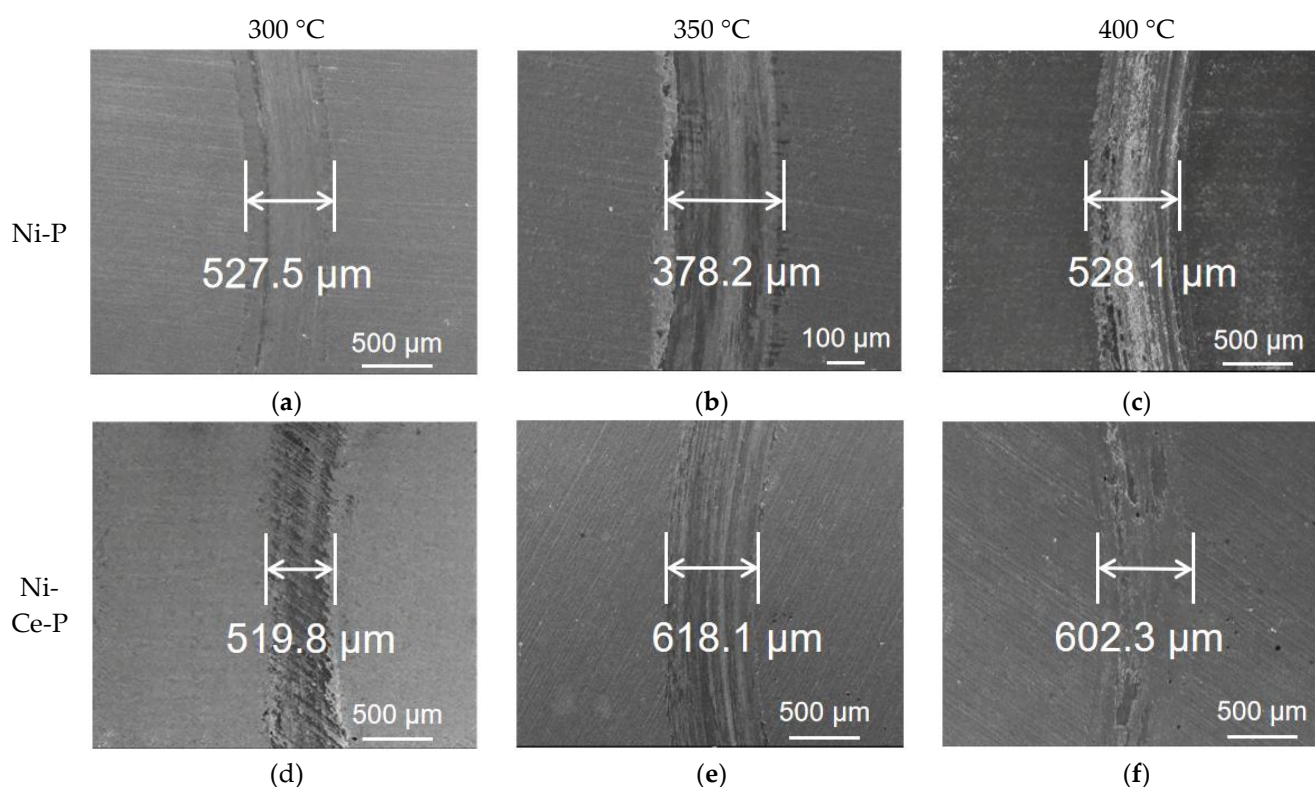
Ni-Ce-P: This coating showed a different trend. The wear rate was lowest when untreated (1.10×10^{-7} g/(N·m)), but rose sharply to 4.87×10^{-6} g/(N·m) after 300 °C heat treatment (an increase of about 42 times), dropped to 2.68×10^{-6} g/(N·m) at 350 °C (about 23 times), and further slightly dropped to 2.27×10^{-6} g/(N·m) at 400 °C (about 20 times). That is, the wear resistance of the Ni-Ce-P coating recovered to some extent at high temperatures, but even with 400 °C heat treatment, its wear rate was still far higher than the untreated state. This may be related to the inhibition of Ni_3P precipitation by the Ce element.

The Ni-Ce-P coating did not increase much in hardness at 300 °C but had already become brittle, thus wear resistance decreased drastically; whereas at 400 °C, the Ni₃P phase fully precipitated, and the coating hardness was close to 2.1 times that of the untreated state, and the structure remained relatively fine (compared to the coarsening degree of Ni-P and Ni-W-P), so the wear rate decreased relative to 350 °C.

Ni-W-P: The wear resistance change of the Ni-W-P coating was similar to Ni-P but with a smaller amplitude. At 300 °C, its wear rate rose from 2.70×10^{-7} g/(N·m) to 6.49×10^{-7} g/(N·m), dropped to 5.14×10^{-7} g/(N·m) at 350 °C, and rose to 9.37×10^{-7} g/(N·m) at 400 °C. Thus, the optimal wear resistance of the Ni-W-P coating appeared at 350 °C heat treatment. Although the wear rate was slightly higher than the untreated state, it was significantly better than at 300 °C and 400 °C. Compared with Ni-P, the deterioration of wear resistance of the Ni-W-P coating at 300 °C was smaller, because its original structure was more crystalline, and the addition of W improved the thermal stability of the coating, resulting in fewer brittle defects generated at low temperatures. However, at 400 °C, wear resistance declined again due to grain growth and cracks.

Table 5. Wear rates after different electroless plating heat treatments.

Technology	Heat Treatment Process	Rate of Wear
Ni-P	300 °C	9.53×10^{-5}
	350 °C	5.14×10^{-6}
	400 °C	2.23×10^{-5}
Ni-Ce-P	300 °C	4.87×10^{-6}
	350 °C	2.68×10^{-6}
	400 °C	2.27×10^{-6}
Ni-W-P	300 °C	6.49×10^{-7}
	350 °C	5.14×10^{-7}
	400 °C	9.37×10^{-7}



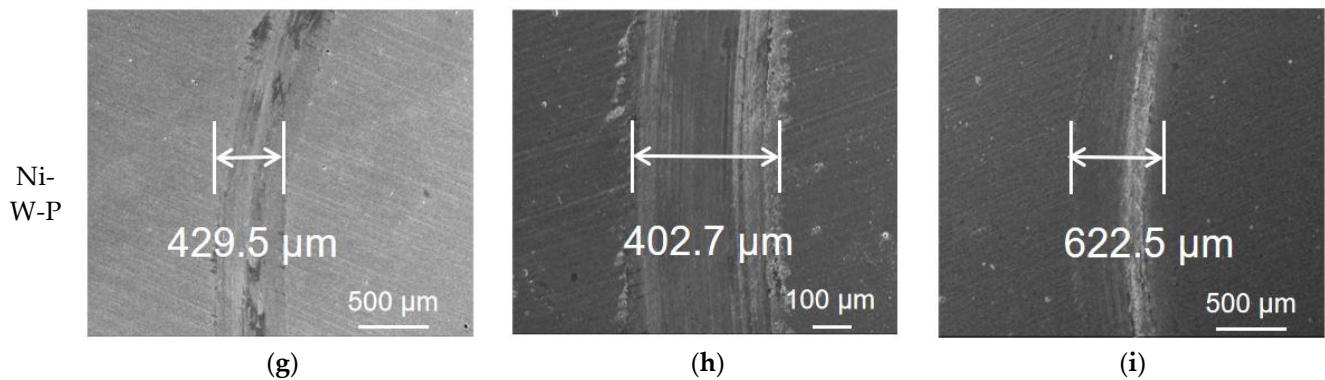


Figure 8. SEM of abrasion marks after different electroless plating heat treatment.

Figure 9 shows the real-time friction coefficient curves for the coatings heat-treated at the optimal temperature of 350 °C. The Ni-Ce-P coating exhibited the lowest and most stable friction coefficient (≈ 0.45), followed by Ni-W-P (≈ 0.52) and Ni-P (≈ 0.56). The lower friction coefficient of the Ni-Ce-P coating can be attributed to its fine-grained, dense structure, which promotes the formation of a stable tribo-layer and reduces adhesive interactions. The higher friction coefficients of the other coatings correspond to their relatively rougher surfaces and different wear mechanisms.

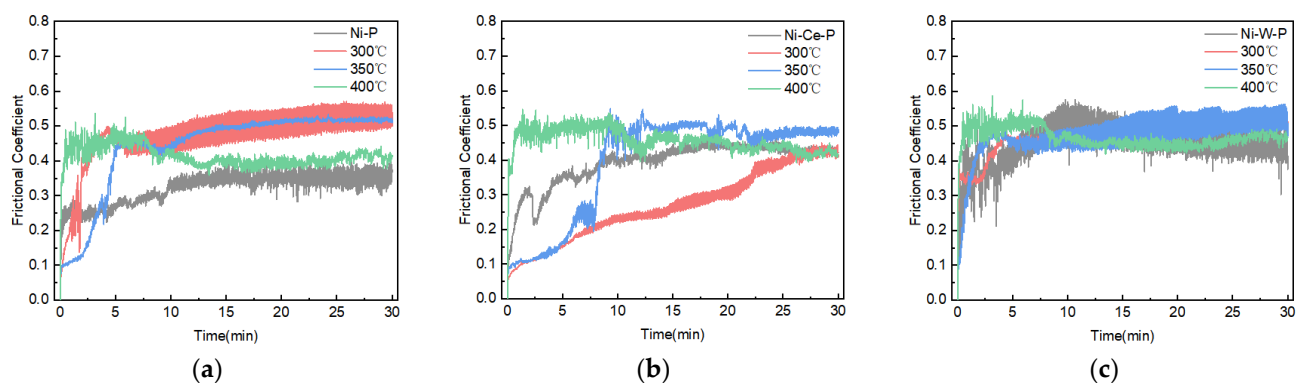


Figure 9. Friction coefficient curves of the coatings heat-treated at 350 °C: (a) Ni-P; (b) Ni-Ce-P; (c) Ni-W-P.

The above results indicate that the relationship between coating hardness improvement and wear resistance is not a simple linear one; wear resistance depends on the synergistic optimization of hardness and toughness. In the initial stage of hardness increase, if the coating toughness is insufficient to withstand the wear load, brittle peeling will primarily occur, leading to increased wear volume; when hardness reaches a specific threshold and the microstructure tends to be stable, the coating can effectively resist abrasive cutting while suppressing macroscopic peeling, at which point the wear volume reaches a minimum; however, continued temperature increase or prolonged holding time induces micro-cracks, after which the coating easily peels along crack propagation, causing the wear volume to rise again. It can be seen that there is an optimized temperature range for the heat treatment process to achieve synergistic control of high hardness and stable structure. In this study, this optimized temperature range is approximately 350 °C. It is worth noting that even under conditions where heat treatment parameters were mismatched leading to decreased wear resistance, the overall wear resistance of the heat-treated coatings was still significantly superior to that of the aluminum alloy substrate.

4. Discussion

4.1. Mechanisms of Microstructural Modification by W and Ce

The distinct surface morphologies observed in the as-plated coatings can be attributed to the different modification mechanisms of the doped elements, a finding consistent with previous studies [13,15]. The “nodular” refinement in the Ni-Ce-P coating (Figure 1b) validates the role of Cerium as a surface-active element. As illustrated in Figure 10, Ce atoms, due to their large atomic radius, tend to segregate at grain boundaries, reducing surface energy and inhibiting grain growth, which promotes a finer, denser nucleation density. This grain refinement is a well-documented effect of rare earth additions in Ni-P systems [15]. In contrast, the “banded” structure of the Ni-W-P coating (Figure 1c) is less common but can be attributed to the influence of tungsten on deposition kinetics. The competitive adsorption between tungstate and nickel ions can lead to layered or anisotropic growth, especially on a substrate with oriented polishing marks [14]. The homogenization of this structure at 350 °C confirms the diffusion of W into the Ni lattice, forming a more uniform solid solution.

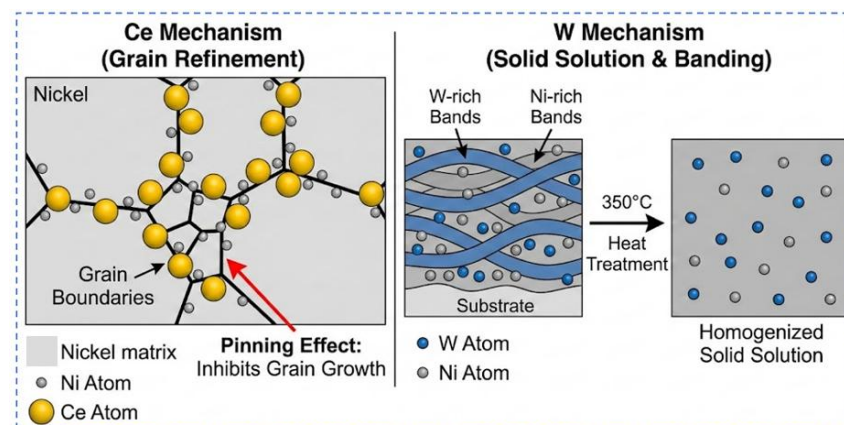


Figure 10. Schematic illustration of the microstructural modification mechanisms.

4.2. Phase Transformation Kinetics and Precipitation Hardening

The evolution of hardness across all three coating systems follows a classic precipitation hardening curve, peaking at 350 °C (Figure 6). This behavior is fundamentally driven by the transformation of the as-deposited amorphous/nanocrystalline matrix into a crystalline Ni structure reinforced by dispersed Ni₃P precipitates, as illustrated in the schematic in Figure 11. The peak hardness values obtained (up to 1691 HV_{0.1}) are in the high range but comparable to those reported by other researchers for optimally heat-treated Ni-W-P and Ni-P coatings [16,19]. However, the doping elements exert a kinetic influence on this transformation. The XRD results indicate that Ce retards the crystallization process, as evidenced by the lower hardness gain at 300 °C compared to Ni-P. This suggests that Ce atoms, by segregating to boundaries, hinder the diffusion paths required for Ni and P atoms to aggregate and form precipitates, thereby stabilizing the amorphous phase at lower temperatures. Conversely, W induces solid solution strengthening within the Ni matrix. Even though no specific W-precipitates (like Ni₄W) were identified, the lattice distortion caused by W atoms, combined with Ni₃P precipitation, allows the Ni-W-P system to achieve the highest peak hardness at 350 °C.

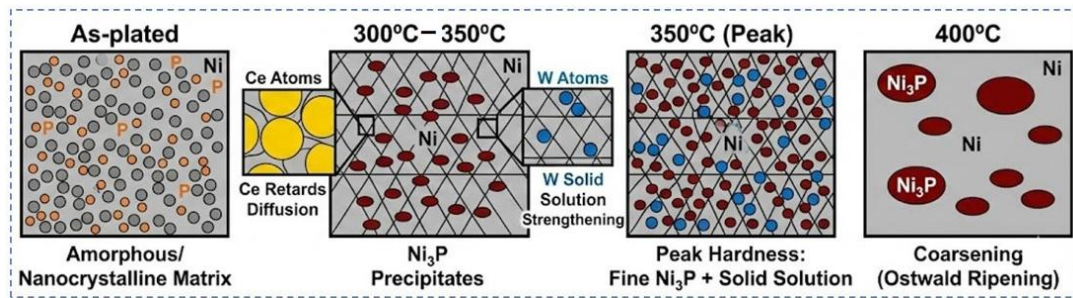


Figure 11. Diagram showing the phase transformation and precipitation hardening mechanism.

4.3. The Non-Linear Relationship Between Hardness and Wear Resistance

A critical finding of this study is the decoupling of hardness and wear resistance, particularly evident in the Ni-P coating treated at 300 °C. As illustrated in Figure 12, while hardness increased, the wear rate catastrophically increased by over 50 times (Table 5). This anomaly can be explained by the “brittle transition” phenomenon. At 300 °C, the coating undergoes partial crystallization, where hard, brittle Ni_3P phases nucleate within a matrix that retains high internal stress [17]. This creates a microstructure that is hard but lacks the toughness to accommodate shear stresses during sliding. Consequently, the wear mechanism shifts from mild abrasion to severe brittle fracture and delamination, as confirmed by the large peeling pits observed in the wear track (Figure 8a). This non-linear relationship is a crucial consideration often overlooked in studies that focus solely on maximizing hardness. The optimal performance achieved at 350 °C represents a synergy between hardness and toughness. At this temperature, the coatings are fully crystallized with a uniform distribution of Ni_3P precipitates, and the internal stresses from deposition have been relieved. The Ni-Ce-P coating exhibits the best performance because its refined grain structure limits the propagation of micro-cracks during friction, allowing it to withstand high loads without the brittle failure seen in binary Ni-P.

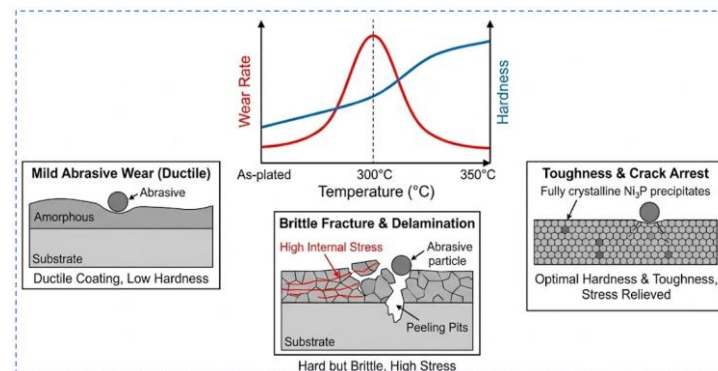


Figure 12. Illustration of the non-linear relationship between hardness and wear rate.

4.4. Optimization of the Heat Treatment Regime

The deterioration of properties at 400 °C highlights the upper limit of the process window, with the underlying mechanisms summarized in Figure 13. The observed decrease in hardness and wear resistance is attributed to two primary factors. First, high temperatures induce Ostwald ripening of the Ni_3P precipitates, leading to coarser, less effective strengthening [19]. Second, and critically for this substrate, significant over-aging of the 6061-T6 aluminum alloy occurs. While not directly measured in this study, it is well-established that exposure to 400 °C will dissolve the strengthening precipitates in the alloy, drastically reducing its hardness and load-bearing capacity [13,16]. This creates a classic “eggshell” effect, where the hard coating collapses under load due to the deformation of

the softened substrate, leading to catastrophic failure. Therefore, heat treatment at 350 °C for 1 h is identified as the optimal regime. It maximizes the precipitation hardening of the coating while mitigating the severe grain coarsening and substrate over-aging associated with higher temperatures. Under these optimized conditions, the Ni-Ce-P ternary system proves to be a superior candidate for lightweight engineering applications, offering a tribological life significantly extending that of the bare aluminum alloy.

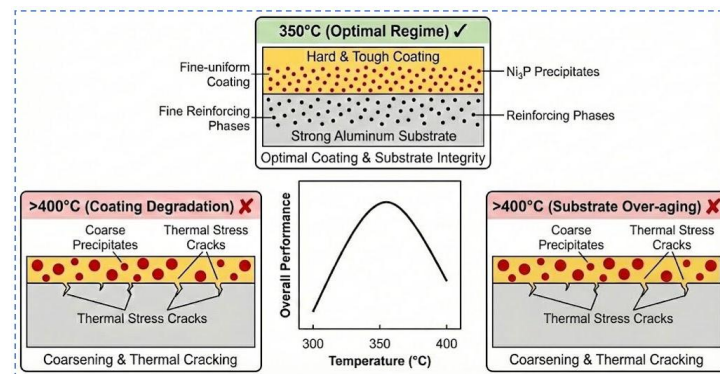


Figure 13. Diagram summarizing the optimization of the heat treatment regime.

5. Conclusions

This comparative study investigated the influence of heat treatment on the microstructure and tribological properties of Ni-P, Ni-W-P, and Ni-Ce-P coatings on 6061-T6 aluminum alloy. The main conclusions are as follows:

1. Doping with Ce refines the as-deposited microstructure into fine nodules, while W addition results in a banded structure and provides solid solution strengthening, leading to higher as-deposited hardness compared to the binary Ni-P coating.
2. Heat treatment at 350 °C for 1 h provides the best combination of properties for all three coating systems within the tested temperature range. This treatment leads to the precipitation of the Ni₃P hard phase, with peak hardness values reaching up to $1691 \pm 45 \text{ HV}_{0.1}$ for the Ni-W-P coating.
3. A critical non-linear relationship between hardness and wear resistance was identified. Treatment at 300 °C induced a brittle transition, especially in the Ni-P coating, causing a catastrophic increase in wear rate despite an increase in hardness. Treatment at 400 °C resulted in decreased hardness and wear resistance due to precipitate coarsening and substrate over-aging.
4. Under the optimal heat treatment condition (350 °C), the Ni-Ce-P coating exhibited the best overall tribological performance, with the lowest wear rate ($1.12 \times 10^{-7} \text{ g/(N}\cdot\text{m)}$) and the lowest friction coefficient (≈ 0.45). This is attributed to its combination of high hardness and a fine, tough microstructure.

This study was limited to a single heat treatment duration (1 h) and did not include direct measurement of the substrate's mechanical properties after heat treatment. Future work could explore the effect of holding time and directly quantify the extent of substrate over-aging to further refine the processing window.

Author Contributions: Conceptualization, K.X.; methodology, J.N.; validation, T.L.; writing—original draft preparation, K.X.; writing—review and editing, J.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Scientific Research Program Funded by the Education Department of Shaanxi Provincial Government (Program No. 25JK0540).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within this article.

Conflicts of Interest: No authors have patent applications, equity interests, or consulting roles related to the subject matter of this work. The research was independently designed, executed, and analyzed, with all data and conclusions reported accurately and transparently.

References

1. El Garchani, F.E.; Lgaz, H.; Kaya, S.; Lee, H.S.; Ibrahim, S.M.; Chafiq, M.; Ko, Y.G.; Kabiri, M.R. Effects of heat treatment on the corrosion behavior and mechanical properties of aluminum alloy 2024. *J. Mater. Res. Technol.* **2023**, *25*, 1355–1363.
2. Zhu, D. Effects of Activation Methods on the Preparation and Properties of High-Phosphorus Ni-P Coatings via Chemical Deposition on Aluminum Alloy Surfaces. Master's Thesis, Changchun University of Technology, Changchun, China, 2024.
3. Rahimi, A.; Sarraf, S.; Soltanieh, M. Nickel electroplating of 6061-T6 aluminum alloy using anodizing process as the pretreatment. *J. Mater. Res. Technol.* **2023**, *27*, 5701–5708.
4. Davoodi, F.; Ashrafizadeh, F.; Atapour, M.; Akbari-Kharaji, E.; Mokhtari, R. Anticorrosion performance of TiN coating with electroless nickel-phosphorus interlayer on Al 6061 alloy. *Mater. Chem. Phys.* **2023**, *296*, 127170.
5. Tao, H.W.; Cai, Q.F.; Chen, M.; Zhang, W.C.; Cao, G.; Zhang, H. Effect of heat treatment on the microstructure and corrosion performance of 2219 Al alloy cold sprayed coatings. *Corros. Sci.* **2024**, *241*, 112526.
6. Yu, X.; Jiang, R.; Gao, Y.; Li, Y.P.; Gong, W.B.; Li, X.S.; Lü, W. Microstructure and wear-resistant behaviors of Al₂O₃-TiO₂ reinforced Ni-based composite coating plasma-sprayed on 6061 aluminum alloy. *Surf. Coat. Technol.* **2024**, *487*, 131032.
7. Chen, C.A.; Jian, S.Y.; Lu, C.H.; Lee, C.Y.; Aktug, S.L.; Ger, M.D. Evaluation of microstructural effects on corrosion behavior of AZ31B magnesium alloy with a MAO coating and electroless Ni-P plating. *J. Mater. Res. Technol.* **2020**, *9*, 13902–13913.
8. Mihoob, M.M.; Albarody, T.M.B.; Ahmad, F.; Alnarabiji, M.S. Optimizing the Thermal Spray Parameters for Producing High-Performance Mo/ZrB₂ Metal Matrix Composites Using the Taguchi Method. *Coatings* **2023**, *13*, 1620.
9. Luo, H.; Leitch, M.; Behnamian, Y.; Ma, Y.S.; Zeng, H.B.; Luo, J.L. Development of electroless Ni-P/nano-WC composite coatings and investigation on its properties. *Surf. Coat. Technol.* **2015**, *277*, 99–106.
10. Tasci, S.; Özden, R.C.; Anik, M. Corrosion and Wear Characteristics of Electroless Ni-P, Ni-P-W and Composite Ni-P-W/Al₂O₃ Coatings on AZ91 Sheet. *Met. Mater. Int.* **2019**, *25*, 313–323.
11. Gao, J.; Cui, K.F.; Li, S.Q.; Zhong, L.; Dai, J.X.; Yang, Z.G.; Qiang, R.M. A New Process of Chemical Plating Ni-P Electromagnetic Induction Heating Activation on the Surface of Aluminium Alloy Base Material. *Coatings* **2024**, *14*, 1221.
12. Wang, B.; Li, J.W.; Xie, Z.H.; Wang, G.J.; Yu, G. High corrosion and wear resistant electroless Ni-P gradient coatings on aviation aluminum alloy parts. *Int. J. Miner. Metall. Mater.* **2024**, *31*, 155–164.
13. Kumar, V.; Mandal, B.B.; Das, S.; Oraon, B.; Mukherjee, S. Tailoring electroless Ni-W-P polyalloy coatings: Unveiling the synergistic impact of cerium addition and annealing on surface functional properties. *Surf. Coat. Technol.* **2024**, *485*, 130874.
14. Ren, L.; Cheng, Y.H.; Yang, J.Y.; Wang, Q.G. Study on Heat Transfer Performance and Anti-Fouling Mechanism of Ternary Ni-W-P Coating. *Appl. Sci.* **2020**, *10*, 3905.
15. Badiheghdam, M.; Khoie, S.M.M.; Khast, F.; Khosrowshahi, M.S. Mechanical Properties and Electrochemical Behavior of Electroless Ni-P-AlN Nanocomposite Coating. *Met. Mater. Int.* **2022**, *28*, 1372–1385.
16. Biswas, A.; Das, S.K.; Sahoo, P. Investigation of the tribological behavior of electroless Ni-W-P coating pre and post phase transformation regime. *Mater. Res. Express* **2019**, *6*, 0965c1.
17. Balaraju, J.N.; Kalavati; Manikandanath, N.T.; Grips, V.K.W. Phase transformation behavior of nanocrystalline Ni-W-P alloys containing various W and P contents. *Surf. Coat. Technol.* **2012**, *206*, 2682–2689.
18. Zhao, G.L.; Wang, R.H.; Liu, S.S.; Wang, T.; Wu, D.T.; Zhang, Y.G.; Chen, J.; Zou, Y. Microstructure analysis of element W in improving the Ni-P deposit thermal stability. *J. Mater. Res. Technol.* **2020**, *9*, 5474–5486.
19. Safavi, M.S.; Rasooli, A. Ni-P-TiO₂ nanocomposite coatings with uniformly dispersed Ni₃Ti intermetallics: Effects of current density and post heat treatment. *Surf. Coat. Technol.* **2019**, *372*, 252–259.
20. Jia, Y.; Lai, J.P.; Yu, J.X.; Qi, H.M.; Zhang, Y.F.; He, H.T. Tribological Behaviors of Electroless Nickel-Boron Coating on Titanium Alloy Surface. *Chin. J. Mech. Eng.* **2024**, *37*, 13.

21. Li, S.Z.; Yu, J.H.; Zheng, Y.; Qin, Y.S.; Zhao, L.J.; Feng, L.; Liu, Y.Y.; Bai, J.Y.; Cui, Q.X.; Zhang, L.G.; et al. Effect of vacuum and air heat treatments on the properties of the electroless Ni-P coating on magnesium alloy. *Mater. Res. Express* **2025**, *12*, 066506.
22. León-Patiño, C.A.; García-Guerra, J.; Aguilar-Reyes, E.A. Tribological characterization of heat-treated Ni-P and Ni-P-Al₂O₃ composite coatings by reciprocating sliding tests. *Wear* **2019**, *426*, 330–340.

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