

Article

Tribological Properties of MoN/TiN Multilayer Coatings Prepared via High-Power Impulse Magnetron Sputtering

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Abstract

To address the limitations of single-layer nitride coatings, such as poor load adaptability and low long-term durability, MoN/TiN multilayer coatings were prepared via high-power impulse magnetron sputtering (HiPIMS). HiPIMS produces highly ionized plasmas that enable intense ion bombardment, yielding nitride films with enhanced mechanical strength, durability, and thermal stability versus conventional methods. The multilayer coating demonstrated a low coefficient of friction (COF, ~0.4) and wear rate ($1.31 \times 10^{-7} \text{ mm}^3/[\text{N}\cdot\text{m}]$). In contrast, both TiN and MoN coatings failed at 5 N and 10 N loads, respectively. Under increasing loads, the multilayer coating maintained stable wear rates ($1.84\text{--}3.06 \times 10^{-7} \text{ mm}^3/[\text{N}\cdot\text{m}]$) below 20 N, and ultimately failed at 25 N. Furthermore, the MoN layer contributes to COF reduction. Grazing-incidence X-ray diffraction analysis confirmed the enhanced crystallographic stability of the multilayer coating, thereby revealing a dominant (111) orientation. The multilayer architecture suppresses crack propagation while effectively balancing hardness and toughness, offering a promising design for extreme-load applications.

Keywords: MoN/TiN multilayer coating; wear performance; toughness; hardness



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1. Introduction

Transition metal nitride (TMN) coatings, such as TiN and MoN, are well known for their excellent hardness, wear resistance, and thermal stability; thus, these are ideal candidates for protective coatings in mechanical and tribological applications [1–4]. However, TMN monolithic coatings frequently exhibit limitations in balancing hardness and toughness, leading to premature failure under high-load or prolonged friction conditions [5,6]. To overcome these limitations, elemental doping has been widely adopted. For instance, Al additions in TiN can considerably enhance coating hardness [7]. Codoping TiN coatings with Al, Cr, Si, and Y has been shown to further improve the thermal stability and mechanical performance [8].

Furthermore, multilayer and composite designs have also been demonstrated as effective approaches for enhancing the mechanical and tribological properties of TMN coatings [9,10]. For instance, alternating hard and ductile layers in multilayer coatings can effectively suppress crack propagation and improve wear resistance [11–13]. Multilayer architectures exhibit considerable improvements in hardness, toughness, wear resistance, and oxidation resistance compared with monolithic coatings composed of individual components. For example, TiN/CrN multilayers exhibit approximately 5 GPa higher hardness values than single-layer TiN, as reported by Sala et al. [14]. Optimized CrN/AlN coatings demonstrate high hardness (42 GPa) combined with a low friction coefficient (0.35), according to Lin et al. [15]. Rizzo et al. found that TiAlN/AlN-n coatings show improved high-temperature wear resistance, with a wear rate of $1.35 \times 10^{-5} \text{ mm}^3/(\text{N}\cdot\text{m})$ at 400 °C, representing an 85% reduction compared to TiAlN coatings under identical conditions [16].

Moreover, incorporating MoN-based phases into hard matrices enhances mechanical properties, such as hardness (up to 28.8 GPa) and wear resistance (COF, as low as ~0.3), and provides effective lubrication by forming MoO₃ tribolayers [17–19]. Despite these advantages, further optimization of MoN-based coatings for extreme-load applications remains challenging, particularly the balance of hardness, toughness, and interfacial stability to achieve high performance under demanding conditions. For example, CrN/MoN coatings deposited by arc-PVD achieved a friction coefficient of 0.586 and wear rate of $13.45 \times 10^{-7} \text{ mm}^3/(\text{N}\cdot\text{m})$, though this method typically produces high residual stresses and droplet defects [20].

Conventional ionized-physical vapor deposition (PVD) techniques, such as pulsed laser deposition or cathodic arc evaporation, frequently fail to fulfill the growing demands for density and surface quality. Nordin et al. reported that MoN/TiN coatings made by a hybrid PVD process (ion plating and magnetron sputtering) showed reduced practical adhesion due to high compressive residual stress, along with a wear rate of approximately $1.3 \times 10^{-4} \text{ mm}^3/(\text{N}\cdot\text{m})$ and a hardness of ~28 GPa [21]. In addition, MoN/TiN coatings have been fabricated using alternative deposition methods including unbalanced magnetron sputtering and arc evaporation [22–24]. For instance, Wang et al. deposited TiN/MoN coatings on HSS drill bits using closed-field unbalanced magnetron sputtering, achieving a hardness of 31.2 GPa [25]. However, these methods exhibit drawbacks such as high residual stress and surface defects, stemming from the inherent technical limitations of arc evaporation and magnetron sputtering, including droplet formation [26].

Conversely, the high-power impulse magnetron sputtering (HiPIMS) technology has widespread application owing to its advanced functionalities [27]. This method utilizes highly ionized plasma to precisely control microstructural formation, facilitating tailored coating properties [28]. HiPIMS is particularly effective for optimizing critical characteristics, including hardness, elastic modulus, and residual stress. Synchronized HiPIMS enables precise pulse timing control to maximize ion energy impact and optimize substrate interactions, significantly enhancing coating structural integrity. The technology distinguishes itself by generating highly ionized plasmas that facilitate intense ion bombardment, leading to nitride films with better mechanical strength and enhanced thermal stability compared to conventional deposition methods [26]. Further, this method produces coatings featuring well-controlled microstructures and minimal defects through unique plasma conditions, while simultaneously reducing the coefficient of friction and improving tribological performance [28].

Herein, a Ti interlayer, a gradient TiN transition layer, and MoN/TiN multilayer coatings were successively deposited on the substrate using HiPIMS technology. TiN monolithic and MoN monolithic coatings were prepared as control groups for comparison. Furthermore, the tribological performance of these coatings was systematically evaluated under varying loads and sliding conditions. Compared with the TiN and MoN monolithic coatings, the MoN/TiN multilayer coating exhibited improved tribological properties, demonstrating their potential for advanced tribological applications.

2. Preparation and Characterization

2.1. Sample Preparation

The MoN/TiN multilayer coating was prepared via HiPIMS composite deposition using an ion-arc/magnetron sputtering composite coating machine (Beijing Powertech Technology Co., Ltd., Beijing, China; SP-0806ASI). Pure Ti (99.9% purity) and Mo (99.9% purity) targets were employed for HiPIMS, and Ar (99.9% purity) was used as the working gas. Si wafers ($10 \times 10 \times 0.5 \text{ mm}^3$) were used for morphology and structural characterizations, and WC–Co carbide substrates (YG8; $12 \times 12 \times 4 \text{ mm}^3$), which exhibited a coefficient of friction of ~ 0.52 and wear rate of $\sim 4.55 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ under 5 N at 2 Hz, were employed for mechanical testing.

Before deposition, the vacuum chamber temperature was increased to 300°C , and the system was pumped down to a base pressure of 5×10^{-3} Pascals (Pa). Subsequently, Ar gas (99.9%, 50 sccm) was injected into the chamber, and the substrate surface was etched using Ti plasma for 5 min to remove contaminants, enhancing adhesion between the coating and substrate. Etching was performed at an arc current of 60 A, a bias voltage of -800 V , and an Ar pressure of 0.3 Pa. Then, the Ar flow rate was increased until the pressure reached 0.8 Pa, and a Ti layer was deposited as a transition layer using HiPIMS with a current of 100 A and a voltage of 50 V. The gradient layer of TiN was achieved by adjusting the N_2 gas flow rate (0–30 sccm). The Ti and TiN transition layers exhibited a total thickness of $\sim 0.4 \mu\text{m}$. Finally, 50 alternating layers of MoN/TiN were deposited with a target current of 100 A (60 s per layer), completing the MoN/TiN multilayer coating. The multilayer coating exhibited a $\sim 40 \text{ nm}$ bilayer period ($\sim 10 \text{ nm}$ TiN and $\sim 30 \text{ nm}$ MoN layers) and $\sim 0.92 \mu\text{m}$ total thickness.

2.2. Morphological and Structural Characterization of Coatings

The surface morphologies of the coatings were observed using scanning electron microscopy (SEM; S4800, Hitachi, Tokyo, Japan). The phase structures of the MoN/TiN multilayer coating were analyzed via grazing-incidence X-ray diffraction (GIXRD; Smart-Lab, Rigaku Corporation, Tokyo, Japan) using Cu radiation (9 kV; 150 mA; wavelength: $1.54059 \text{ \AA}$). The GIXRD analysis was conducted in the grazing mode at an incidence angle of 1° , employing a scanning speed of $5^\circ/\text{min}$ and a scanning range of 20° – 85° .

2.3. Mechanical Properties of Coatings

A nanoindenter (Nano Test Vantage, Micro Materials, Wrexham, UK) was used to measure the hardness (H) and elastic modulus (E) of the MoN/TiN multilayer coating. Dynamic nanoindentation tests were performed using a Berkovich diamond indenter, maintaining the indentation load below a maximum of 15 mN. Loading and unloading times were 30 s, resulting in equal loading and unloading rates. A holding time of 30 s was applied at the peak load.

Friction and wear behavior analyses were conducted using a reciprocating friction and wear testing machine (MFT-5000, Rtec Instruments, San Jose, CA, USA) at room temperature ($\sim 25^\circ\text{C}$) and a relative humidity of $\sim 60\%$ for 1800 s. A 6 mm diameter Si_3N_4 ball served as the counter body for the tribotest, and the tests were performed using a sliding distance of 5 mm per stroke and a frequency of 2 Hz.

Wear traces were examined via white-light interferometry (Lambda, Rtec Instruments, San Jose, CA, USA), and the wear rate (W) was calculated using the following equation [29]:

$$W = V/(FL), \quad (1)$$

where V , F , and L represent the volume loss of the coating, applied load, and total sliding distance, respectively. The volume loss was determined using the Mountains Map Imaging Topography included with the testing machine.

The Vickers indentation (HMV-2, SHIMADZU, Kyoto, Japan) was used to evaluate the fracture toughness (K_{Ic}) of the coatings by the equation as follows [30]:

$$K_{Ic} = \delta \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right), \quad (2)$$

where H and E are the hardness and elastic modulus, respectively. P is the applied load. c is the radial crack length measured from the indentation center. δ is the empirical coefficient ($\delta = 0.0169$ for Vickers indenter).

Adhesion between the coating and substrate was assessed using a Rockwell tester utilizing a force of 60 kgf and a loading time of 25 s. The indenter effect was observed using an optical microscope, and the adhesion quality was interpreted following the VDI 3198 standard [31].

3. Results and Discussion

3.1. Coating Morphologies

Figure 1 depicts the SEM images of the TiN monolithic, MoN monolithic, and MoN/TiN multilayer coatings. The thicknesses of the TiN, MoN, and MoN/TiN coatings were approximately 1.1, 1.4, and 1.3 μm , respectively.

The MoN coating possessed finer but less uniform particles than the TiN and MoN/TiN coatings. Conversely, the TiN and MoN/TiN multilayer coatings had larger and more homogeneous particle distributions, and the MoN/TiN multilayer coating exhibited a more compact structure and a flatter, smoother surface. The improved uniformity of the MoN/TiN multilayer coating was attributed to its multilayer structure, in which alternating TiN and MoN layers create periodic interfaces, further disrupting columnar grain growth and promoting homogeneous particle distribution [14,25,32]. The cross-sectional images reveal prominent columnar grain structures in the TiN and MoN coatings (Figure 1), which are characteristic of PVD processes. In contrast, the MoN/TiN multilayer coating had a dense microstructure featuring refined columnar grains. This refinement resulted from the multilayer architecture, in which alternating layers interrupted columnar growth and reduced structural defects [14]. Moreover, the high ionization efficiency of HiPIMS enhanced adhesion and layer uniformity, contributing to the dense and fine-grained structure of the coating [28,33–35].

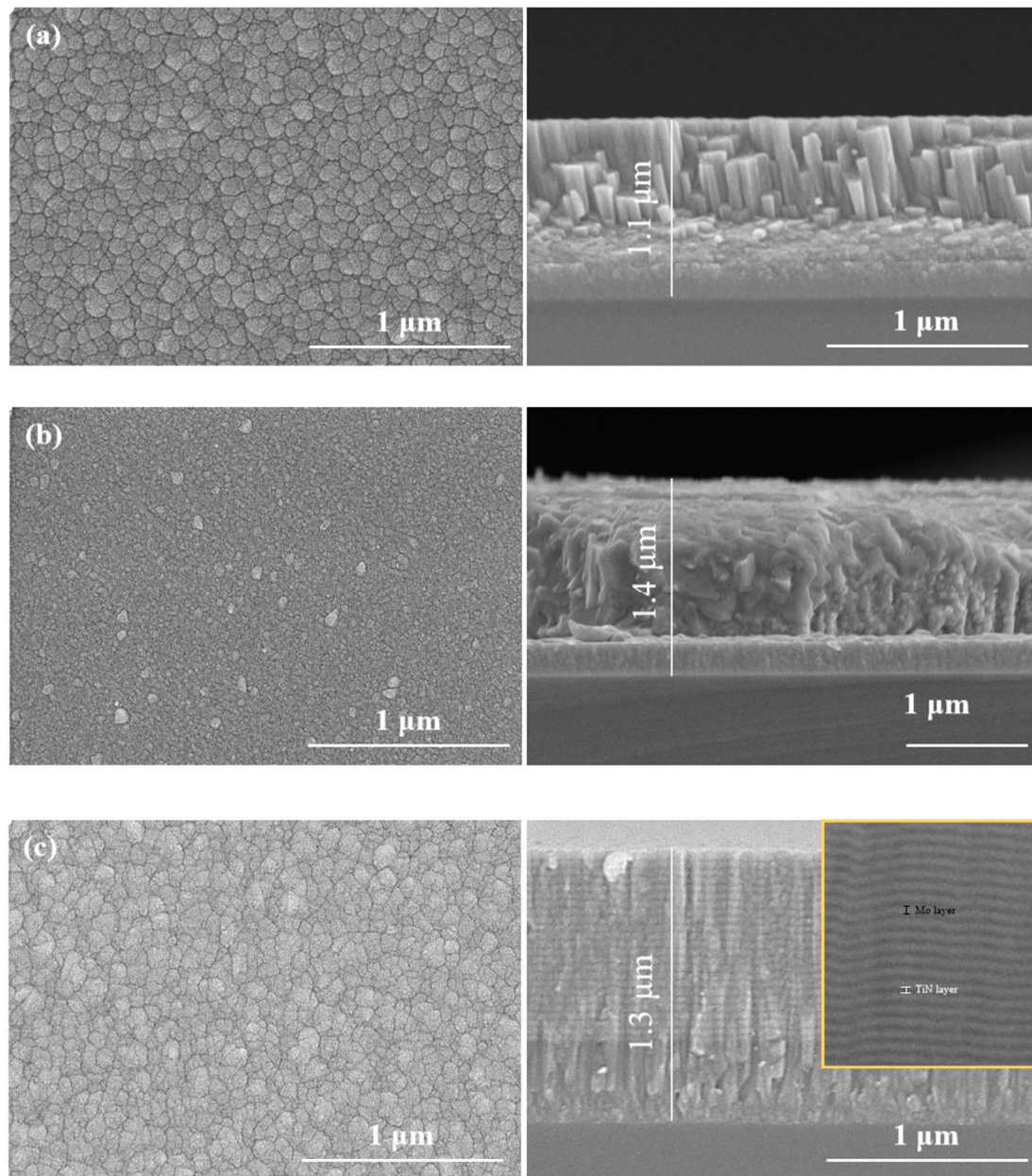


Figure 1. SEM images exhibiting the surface morphologies (**left**) and cross-section (**right**) of (a) TiN, (b) MoN, and (c) MoN/TiN coatings.

3.2. Phase Structure of Coatings

The XRD patterns of the TiN monolithic, MoN monolithic, and MoN/TiN multilayer coatings are shown in Figure 2. The XRD pattern of the TiN coating confirmed the presence of a face-centered cubic TiN phase. Distinct diffraction peaks observed at 36.6° , 42.6° , 61.7° , 74.0° , and 77.9° could be indexed to the (111), (200), (220), (311), and (222) crystallographic planes of TiN, respectively. This pattern demonstrated that the TiN coating comprised grains with multiple crystallographic orientations, among which the (111), (200), and (220) planes were dominant [36]. The well-defined sharp peaks further indicated the high crystallinity of the deposited TiN coating [37]. The XRD patterns of the MoN and MoN/TiN coatings exhibited a face-centered cubic (FCC) NaCl-type structure, as evidenced by the appearance of (111), (200), (220), (311), and (222) diffraction peaks. In general, the MoN_x thin films exhibited diffraction peaks characteristic of an (FCC) NaCl-type structure, with

nearly identical peak positions, corresponding to the (111), (200), (220), (311), and (222) planes of the cubic structure [38].

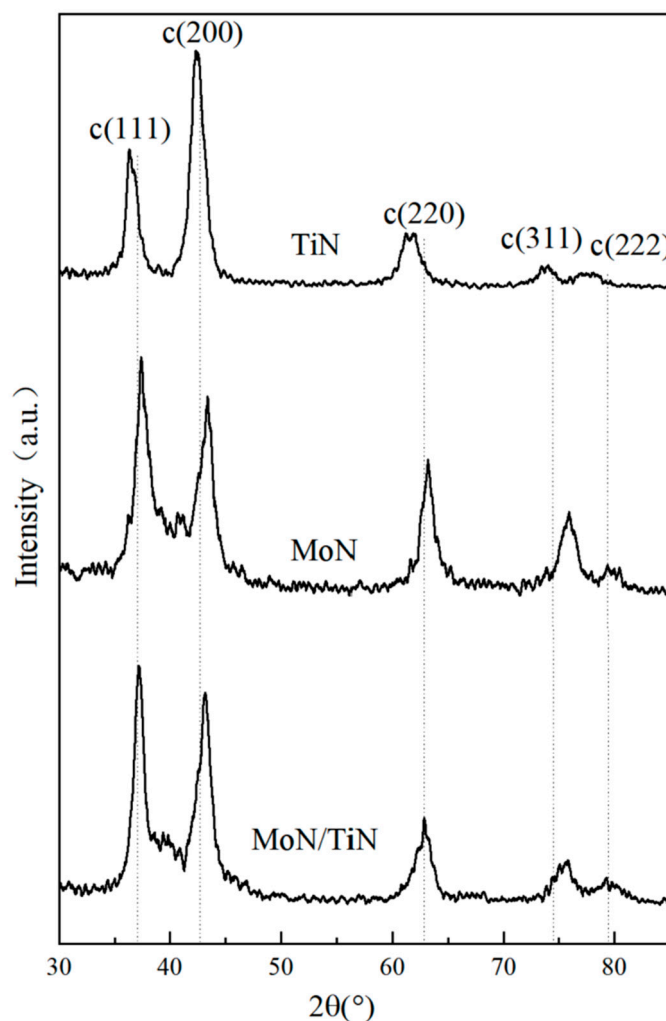


Figure 2. GIXRD patterns of the TiN, MoN, MoN/TiN coatings.

The suppression of columnar grain growth due to the multilayer structure (Figure 1c) promoted a dense atomic packing along the (111) planes, as evidenced by the dominant (111) orientation in the XRD patterns (Figure 2). The transition from (200)-oriented TiN to (111)-oriented MoN/TiN indicated that the layered architecture alters the energy-minimization pathway during crystallization [25,39]. As reported by Shen, the (111) planes are closest-packed in the (FCC) Mo_2N structure accompanied by the lowest surface energy [40].

The TiN coating depicted a dominant (200) preferred orientation—typical for TiN films owing to their lower surface energy in this crystallographic plane [39]. Conversely, the MoN and MoN/TiN multilayer coatings exhibited a dominant (111) preferred orientation, indicating the modification of the growth mechanism due to MoN incorporation and multilayer confinement [25,41].

The peak positions in the MoN/TiN multilayer coating patterns were intermediate to those in the TiN and MoN patterns because of the compositional gradients and interfacial strain within the multilayer structure [41]. The dominant (111) orientation in MoN/TiN was particularly crucial because the higher atomic packing density and lower surface energy of the (111) orientation than those of the (200) orientation directly improved the hardness and wear resistance [42]. The (111) preferred orientation, in synergy with alternating MoN/TiN

layers, enhanced the resistance to plastic deformation by restricting the dislocation motion along the close-packed planes [25,42].

3.3. Hardness and Toughness of Coatings

Figure 3 presents the SEM images of the Vickers indentations under a load of 3000 mN. Table 1 lists the hardness, elastic modulus, and K_{IC} values of the coatings, with the K_{IC} values illustrating the fracture toughness of the TiN, MoN, and MoN/TiN multilayer coatings. Although affected by the substrate, Vickers indentation provided a semiquantitative evaluation of the fracture toughness of ceramic coatings [43]. All the coatings demonstrated typical radial cracks under this load. Among the analyzed coatings, the MoN/TiN multilayer coating depicted the highest fracture toughness ($K_{IC} = 1.64 \text{ MPa}\cdot\text{m}^{1/2}$), whereas the MoN coating displayed the longest diagonal crack length with the lowest fracture toughness ($K_{IC} = 1.08 \text{ MPa}\cdot\text{m}^{1/2}$).

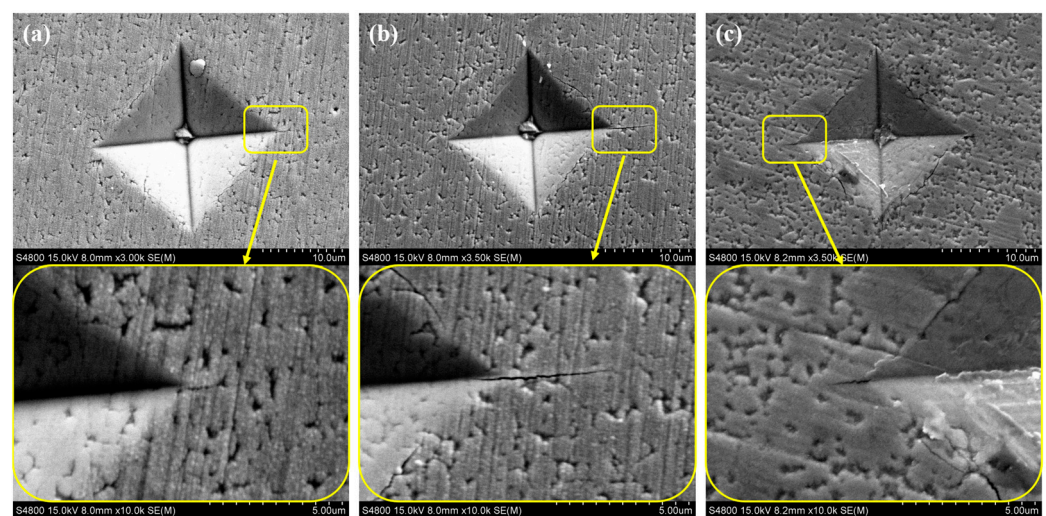


Figure 3. SEM images of Vickers indentations on WC–Co carbide substrates under a load of 3000 mN for (a) TiN, (b) MoN, and (c) MoN/TiN coatings.

Table 1. Mechanical properties of the coatings: hardness (H), elastic modulus (E), H/E ratio, H^3/E^2 ratio, and fracture toughness (K_{IC}).

Coating	Preparation Technology	Hardness (GPa)	Elastic Modulus (GPa)	H/E	H^3/E^2	K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)
TiN	HiPIMS	19.73 ± 2.26	357.97 ± 24.4	0.05511	0.05993	1.49
MoN	HiPIMS	23.98 ± 1.94	349.46 ± 16.1	0.06862	0.11296	1.08
MoN/TiN	HiPIMS	32.34 ± 1.74	461.12 ± 67.0	0.07014	0.15911	1.64

Table 1 shows that the MoN/TiN multilayer coating demonstrated the highest hardness (32.34 GPa), surpassing the MoN (23.98 GPa) and TiN (19.73 GPa) coatings. The improved hardness of the MoN/TiN multilayer coating was consistent with the characteristics reported for TiN/TiC multilayers [1], in which the interfaces suppress the dislocation motion via the Hall–Petch mechanism. The SEM images revealing the multilayer structure (Figure 1), and XRD analysis (Figure 2) further validate the interfacial strengthening. The high hardness of the multilayer coating may improve its wear resistance, which is critical for the friction performance. Additionally, among the analyzed coatings, the MoN/TiN multilayer coating exhibited the highest H/E and H^3/E^2 values, suggesting its better wear resistance and toughness than the single-component coatings.

In Table 1, the H^3/E^2 ratio of the MoN coating is higher than that of TiN, and the MoN/TiN multilayer coating has the highest H^3/E^2 ratio. Reportedly, the H^3/E^2 ratio is correlated with coating toughness [44,45]. While discrepancies exist between H^3/E^2 ratios and K_{IC} values when evaluating the fracture toughness of TiN and MoN coatings, both metrics consistently demonstrate the better toughness of MoN/TiN multilayer coatings. The observed differences in TiN and MoN coatings may originate from the Vickers indentation methods, which are significantly influenced by the substrate. Since nanoindentation-derived hardness and elastic modulus values obtained at shallow penetration depths predominantly reflect the intrinsic mechanical properties of coatings, they effectively minimize substrate influence [9]. Therefore, the H^3/E^2 ratio is more indicative of the crack resistance of the coatings than the performance of the coating–substrate system under high contact loads [46].

The generation and propagation of cracks in multilayer coatings during cutting operations comprise a complex process, primarily initiated at microdefects and subsequently influenced by multiple factors, such as the sublayer thickness, interfacial shear stresses, and interactions between coating microdefects [47,48]. The crack propagation behavior of the multilayer coating is analyzed for the single-crack case, and the improved crack resistance and toughness of the multilayer coating are primarily attributed to the interfacial crack-deflection mechanisms [49]. From Figure 4, the monolithic coatings exhibited direct crack propagation from the surface to the substrate. Liu et al. reported that in monolithic coatings, cracks propagate easily from the surface to the substrate [49]. Comparatively, the multilayer coating demonstrated enhanced performance via interfacial crack-deflection mechanisms [50]. The alternating soft layers served as shear bands that relieved the interfacial stresses and simultaneously reduced the tensile stresses in the adjacent hard layers, absorbing the impact energy [51]. Moreover, the multiple interfaces facilitated energy dissipation via crack splitting and deflection, effectively preventing crack penetration toward the substrate. Moreover, the multiple interfaces facilitated energy dissipation via crack deflection while the inherent higher toughness of MoN/TiN coatings further enhanced this energy absorption mechanism, collectively reducing crack driving forces and effectively preventing crack penetration toward the substrate, thereby contributing to the better fracture toughness of the multilayer structure [52].

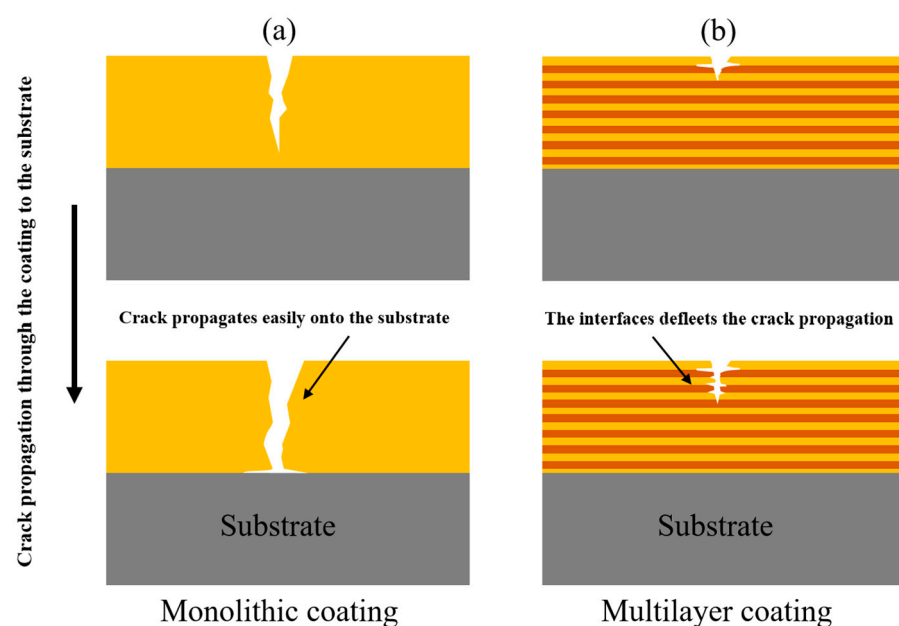


Figure 4. Schematic of the cracking behavior of (a) monolithic and (b) multilayer coatings.

In conclusion, the MoN/TiN multilayer coating exhibited better hardness and fracture toughness than the monolithic ones, as evidenced by the shorter radial cracks under indentation, suggesting a higher crack resistance of the multilayer structure.

3.4. Coating Adhesions

Figure 5 presents the adhesion strength of the TiN, MoN, and MoN/TiN multilayer coatings evaluated using Rockwell-C hardness indentations. The MoN/TiN multilayer coating depicted slightly higher adhesion strength than the TiN and MoN coatings. This difference can be attributed to the variations in the interfacial bonding characteristics of the coatings [42].

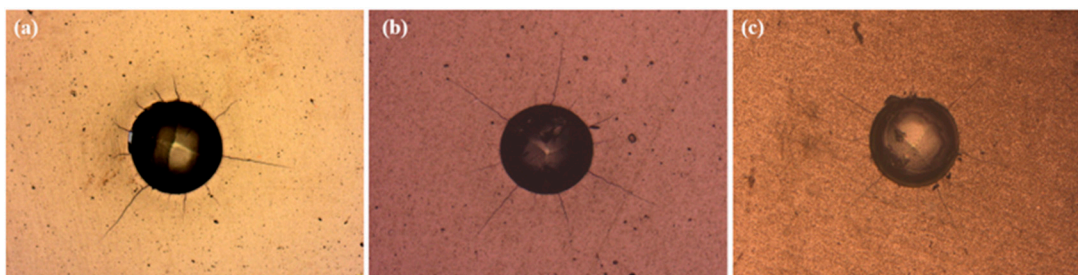


Figure 5. Optical microscopy images of Rockwell-C hardness indentations on (a) TiN, (b) MoN, and (c) MoN/TiN coatings.

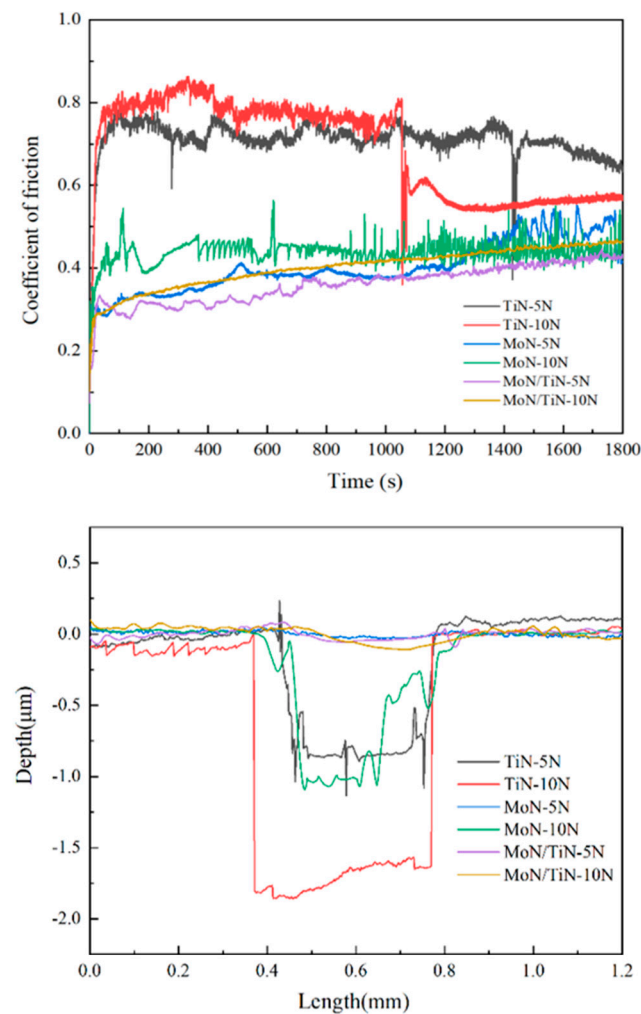
The better adhesion of the MoN/TiN multilayer coating than that of the other coatings was plausibly because of the synergistic effect of MoN and TiN, which enhanced the interfacial compatibility and reduced stress concentration at the coating–substrate interface. This was further supported by the higher hardness (32.34 GPa) and optimal H/E and H^3/E^2 values of the multilayer coating, indicating improved elasticity, toughness, and resistance to crack propagation [42].

In conclusion, the MoN/TiN multilayer coating exhibited better adhesion than the MoN monolithic coating, indicating that the multilayer structure enhances adhesion between the coating and substrate.

3.5. Tribological Properties of Coatings

The coefficient of friction, wear profile, and wear rate of the TiN, MoN, and MoN/TiN multilayer coating samples obtained through friction and wear tests using the same frequency and duration (2 Hz and 1800 s) are depicted in Figure 6. Figures 7 and 8 display the morphology of the wear traces and elemental distribution maps of the TiN and MoN coating samples under the loads of 5 and 10 N, respectively.

The TiN coating samples exhibited unstable fluctuations in the coefficient of friction (COF), ranging from ~0.7 to 0.8, under a load of 5 N. Under a load of 10 N, the COF considerably changed after 1050 s of sliding, decreasing from ~0.8 to ~0.5. Combined with the wear profile and elemental distribution map in Figure 7, the TiN coating is completely worn. Conversely, the MoN coating samples demonstrated higher stability and a lower COF (~0.4) under both loads. However, the COF of the MoN coating samples under 10 N was higher and more unstable than that under 5 N. The MoN/TiN multilayer coating samples exhibited the lowest COF (~0.3–0.34), and their COF under 5 N was lower than that under 10 N.



Coating	Wear rate-	Wear rate-
	5N2Hz (mm ³ /[N·m])	10N2Hz (mm ³ /[N·m])
TiN	Failed	Failed
MoN	5.27×10^{-7}	Failed
MoN/TiN	1.31×10^{-7}	1.33×10^{-7}

Figure 6. Coefficient of friction, wear profile, and wear rate of the coating samples under 5 and 10 N.

The wear rates of the MoN and MoN/TiN multilayer coating samples were 5.27×10^{-7} and 1.31×10^{-7} mm³/(N·m), respectively, under a 5 N load (with the TiN coating having failed). At a 10 N load, the wear rates of the MoN/TiN multilayer coating samples were 1.33×10^{-7} mm³/(N·m), while the MoN coating had failed. Among the analyzed coatings, both TiN and MoN coating samples failed under 5 N and 10 N loads, respectively. The MoN/TiN multilayer coating samples maintained excellent wear resistance under both loads, demonstrating superior wear performance compared with the TiN and MoN coating samples under the tested conditions.

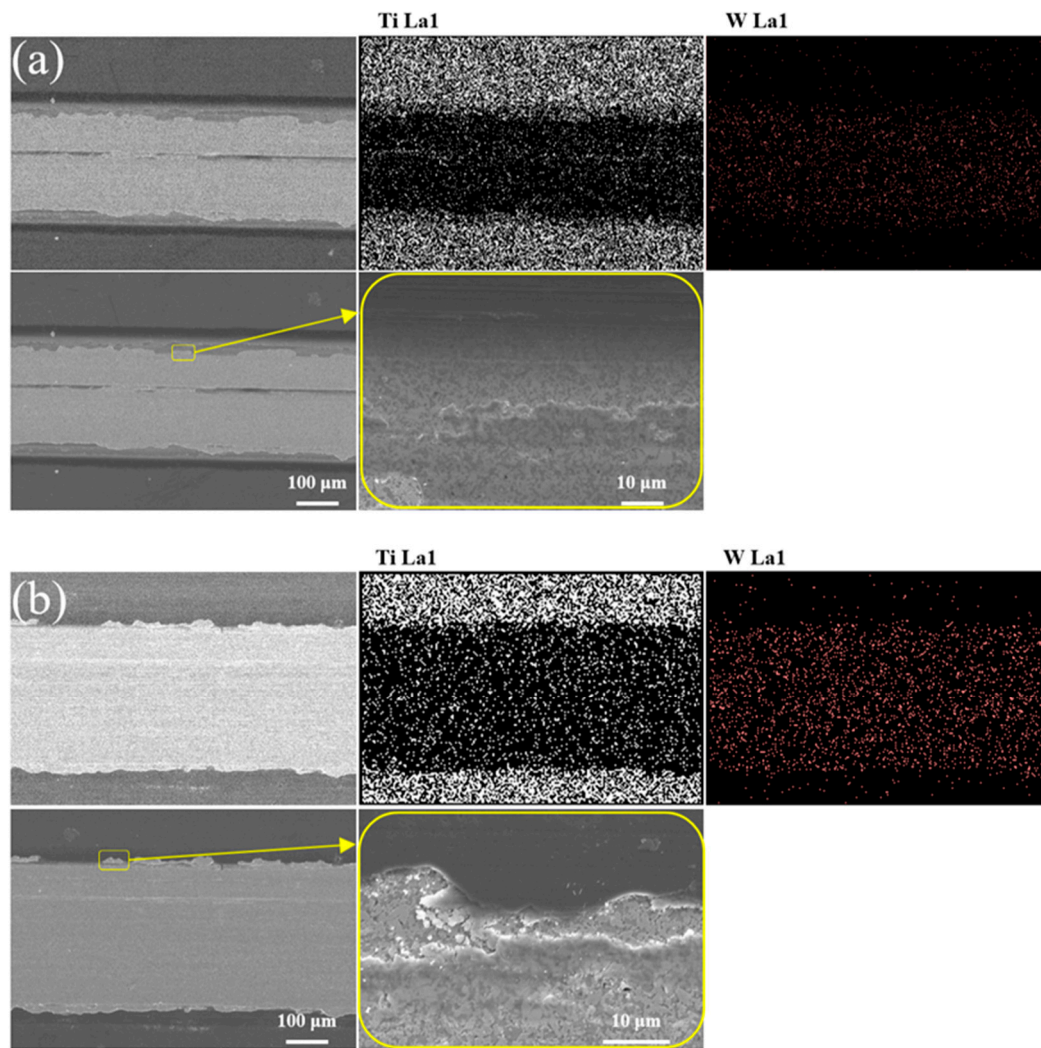


Figure 7. Morphology of the wear trace and the Ti and W element distribution map of the TiN coating samples under the loads of (a) 5 and (b) 10 N.

Under a load of 5 N, the TiN coating samples exhibited severe wear and a prominent W elemental signature (Figure 7a), indicating coating removal and substrate exposure. The wear track displayed a furrow-like morphology, and fatigue wear was initiated at the center and propagated to the edges. Under a load of 10 N, the wear track considerably widened, and the W elemental signature intensified (Figure 7b), further confirming the substrate exposure. A notable increase in film flaking was observed inside the wear marks, where the coating was detached and extensively delaminated. Deep grooves and severe fatigue wear were observed throughout the track, demonstrating that high loads considerably accelerate the failure of the TiN coating.

The lower wear resistance of the TiN coating samples under the loads of 5 and 10 N can be attributed to their lower hardness and less favorable H/E and H^3/E^2 ratios than the MoN/TiN multilayer coating samples [53]. Additionally, the dominant (200) crystallographic orientation of the TiN coating determined via the XRD analysis may contribute to the higher residual stress and inferior interfacial bonding, leading to its lower wear performance. Conversely, the MoN/TiN multilayer coating samples, featuring better hardness, optimal H/E and H^3/E^2 ratios, and (111) orientation, demonstrated considerably higher wear resistance under the same conditions.

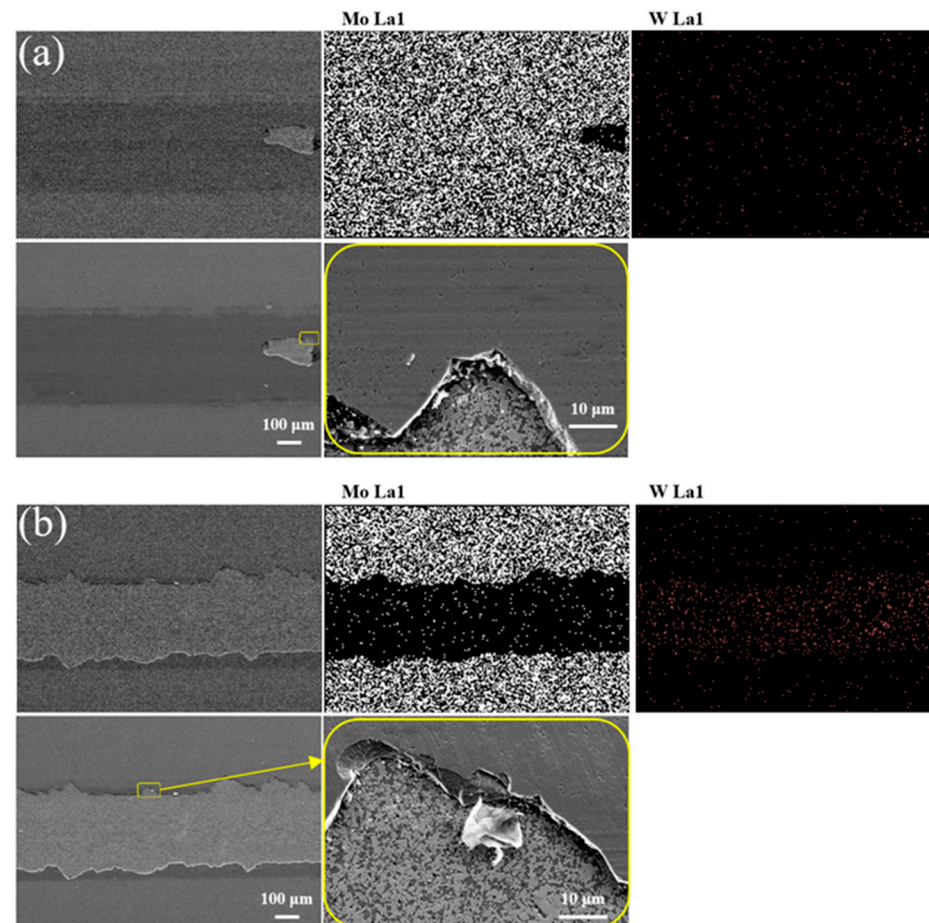


Figure 8. Morphology of the wear trace and the Mo and W element distribution map of the MoN coating samples under the loads of (a) 5 and (b) 10 N.

Under a load of 5 N, the MoN coating samples exhibited minor abrasive wear, and the W element content was substantial (Figure 8a), indicating that the coating remained mostly intact. However, slight spalling was observed, suggesting the onset of localized wear. Conversely, under a load of 10 N, the wear track of the MoN coating samples was considerably wider than that under 5 N, and severe fatigue wear was evident. The elemental distribution map (Figure 8b) revealed the presence of the W element, confirming the exposure of the substrate material because of coating failure.

Under lower loads (5 N), the wear of the MoN coating samples was primarily dominated by abrasive wear, and the coating demonstrated good wear resistance. However, under higher loads (10 N), adhesive wear was the dominant mechanism, leading to localized adhesion and tearing, further resulting in extensive coating delamination. Therefore, the MoN coating samples performed well under low loads; however, they exhibited insufficient resistance to adhesive wear under high loads, ultimately leading to failure.

The limited performance of the MoN coating samples under high loads can be attributed to their adhesion strength and toughness, which are critical factors in preventing coating delamination and wear. These results emphasize the need for the optimization of the mechanical properties of the coating, particularly under high-load conditions, to enhance its durability and wear resistance.

Figure 9 presents the coefficient of friction, wear profile, and wear rate of the MoN/TiN multilayer coating samples determined through the friction and wear tests at a constant frequency and duration (2 Hz and 1800 s). The elemental distribution maps and

wear trace morphology of the multilayer coating under different loads are displayed in Figures 10 and 11, respectively.

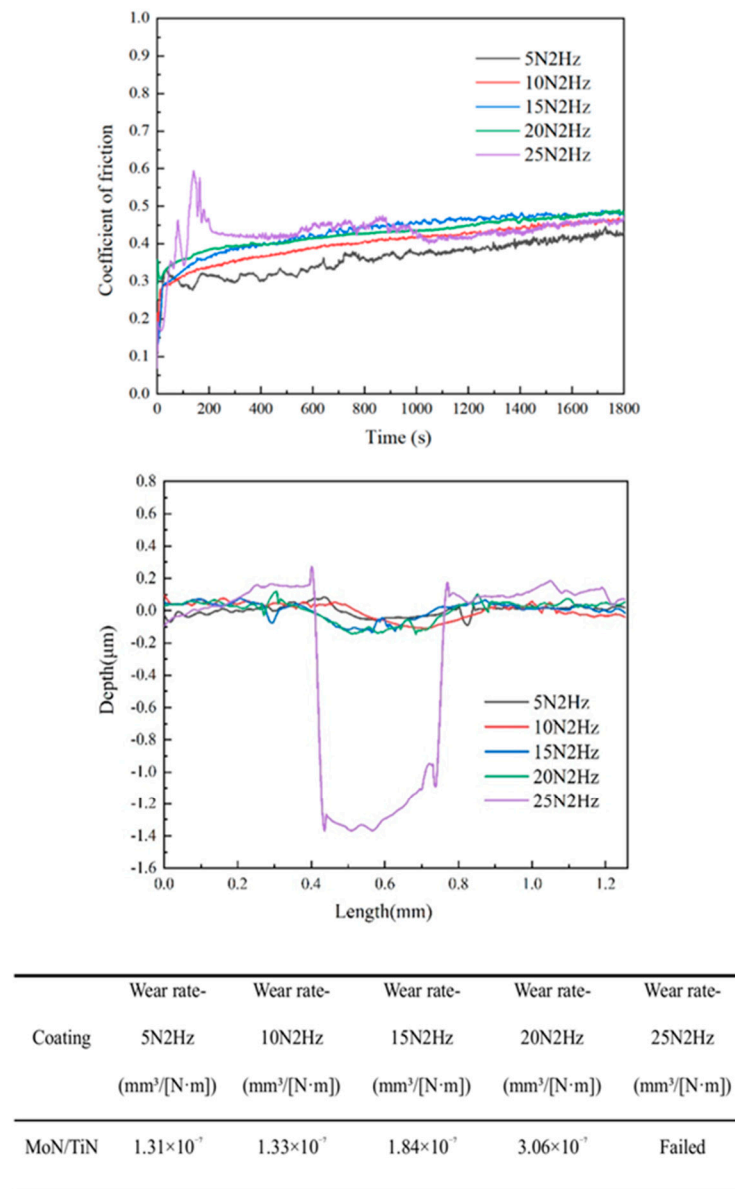


Figure 9. Coefficient of friction, wear profile, and wear rate of the MoN/TiN multilayer coating samples under different loads.

With increasing load, the COF of the MoN/TiN multilayer coating samples slightly increased and subsequently stabilized at a low range of ~0.3–0.45 after 1800 s of sliding under the loads of 5, 10, 15, and 20 N. However, under 25 N, the COF considerably increased during the first 200 s and then gradually decreased, owing to inadequate lubrication and higher surface roughness at the contact interface between the friction pair and coating, leading to a higher friction resistance [54,55]. This unstable behavior temporarily disrupted the friction process before the COF stabilized at ~0.45.

The wear rate of the MoN/TiN multilayer coating samples gradually increased with increasing load from 5 to 20 N. However, it sharply increased to $25.08 \times 10^{-7} \text{ mm}^3/(\text{N} \cdot \text{m})$ under 25 N, indicating severe wear. This was further supported by the W elemental signature (Figure 10e), which confirmed the substrate exposure owing to coating failure.

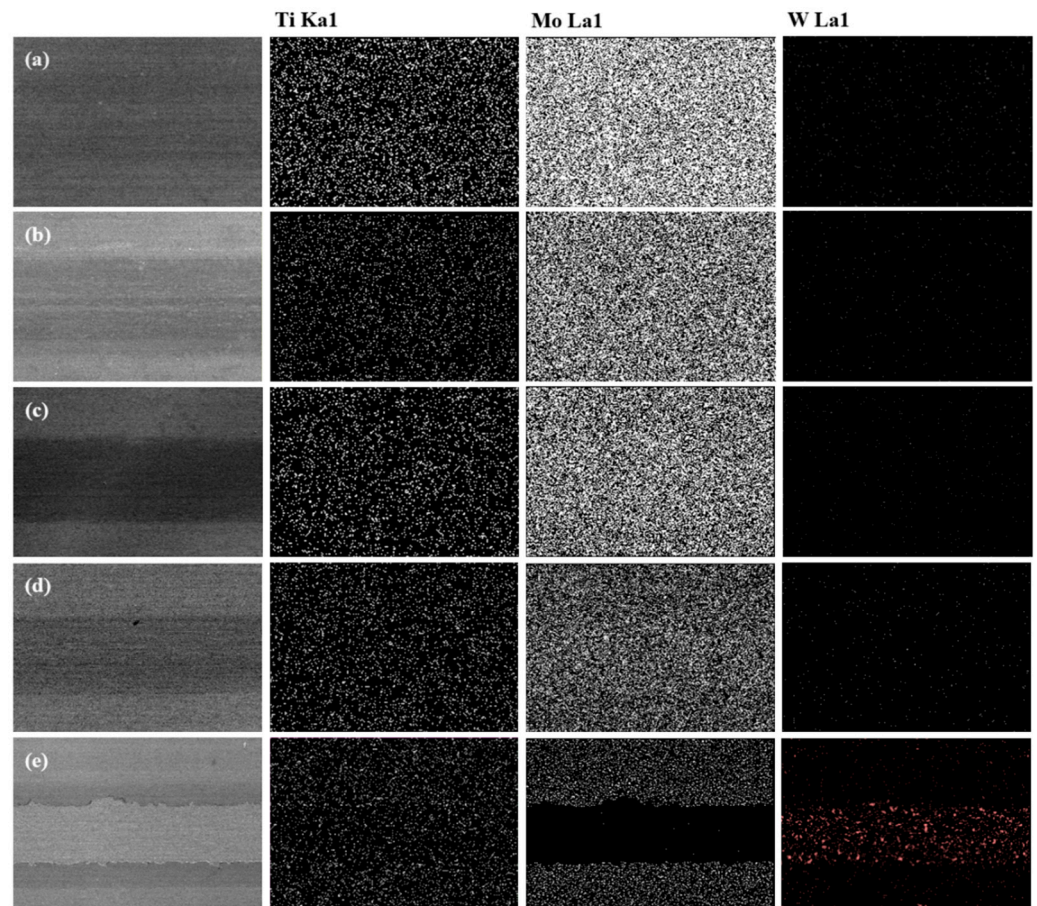


Figure 10. Ti, Mo, and W element distribution map of the MoN/TiN multilayer coating samples under different loads: (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 N.

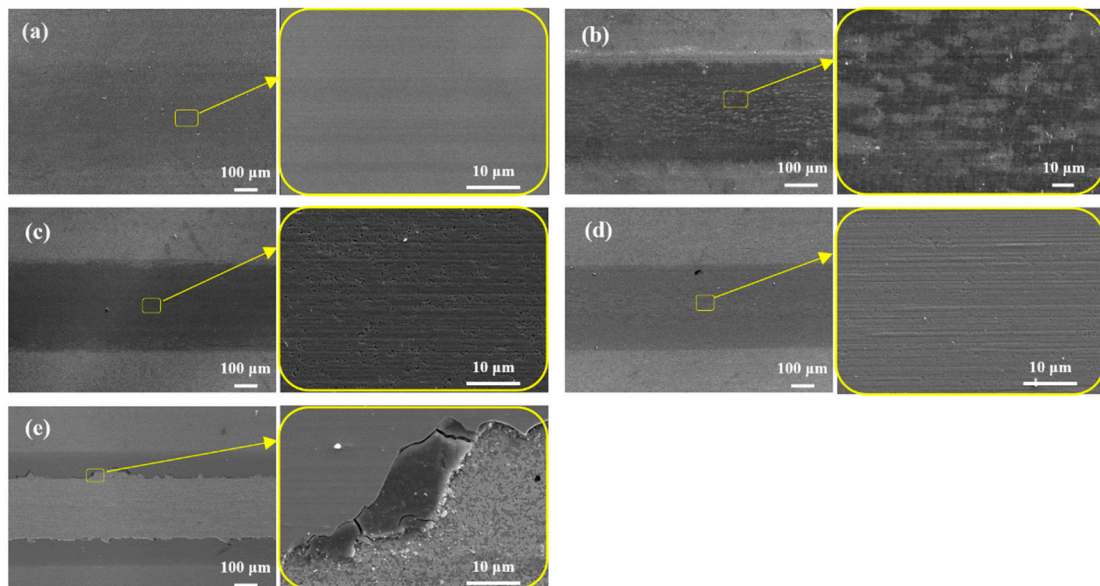


Figure 11. Morphology of the wear trace of the MoN/TiN multilayer coating samples under different loads: (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 N.

Wear trace analysis (Figure 11) revealed that the width and depth of the traces increased with increasing loads. Under 5 N, the traces were narrow and shallow, whereas under 25 N, furrow formation was observed, along with fatigue wear characteristics. Despite the severe wear under 25 N, the MoN/TiN multilayer coating samples demonstrated

better wear resistance than the TiN and MoN coating samples under similar conditions (Figures 7 and 8).

At 5–10 N, the wear traces consistently exhibited a narrow and shallow morphology comprising furrow features, indicating abrasive wear as the dominant wear mechanism [56]. Under 25 N, the coating samples demonstrated extensive delamination and fatigue wear, resulting in coating failure.

The stable and low COF of the MoN/TiN multilayer coating samples under loads up to 20 N results from the dense microstructure and good toughness of the coating, thereby contributing to enhanced load-bearing capacity and reduced friction [49,57].

The multilayer structure of the MoN/TiN coating is crucial in wear resistance. The alternating TiN and MoN layers disrupt columnar grain growth and provide multiple interfaces that hinder crack propagation, enhancing the toughness and wear performance of the multilayer coating [1,10]. Figure 12 illustrates the friction mechanism of the TiN, MoN, and MoN/TiN multilayer coatings. The TiN coating initially underwent small particle shedding, creating wear tracks resembling furrows (Figure 7), in which abrasive wear is the dominant mechanism. With the continuous progression of the test, widespread coating shedding occurs, ultimately causing coating failure. The MoN coating developed cracks during wear owing to inadequate adhesion strength. These cracks extended to the substrate (Figure 8), thereby leading to adhesive wear and extensive coating shedding, which substantially increased the wear rate. For the MoN/TiN multilayer coating, although cracks were formed during wear, the layered structure successfully hindered crack propagation, thereby preventing crack growth toward the substrate and the subsequent extensive coating shedding. This explains the higher performance of the MoN/TiN multilayer coating than that of the TiN and MoN coatings, which lack the aforementioned structural advantages.

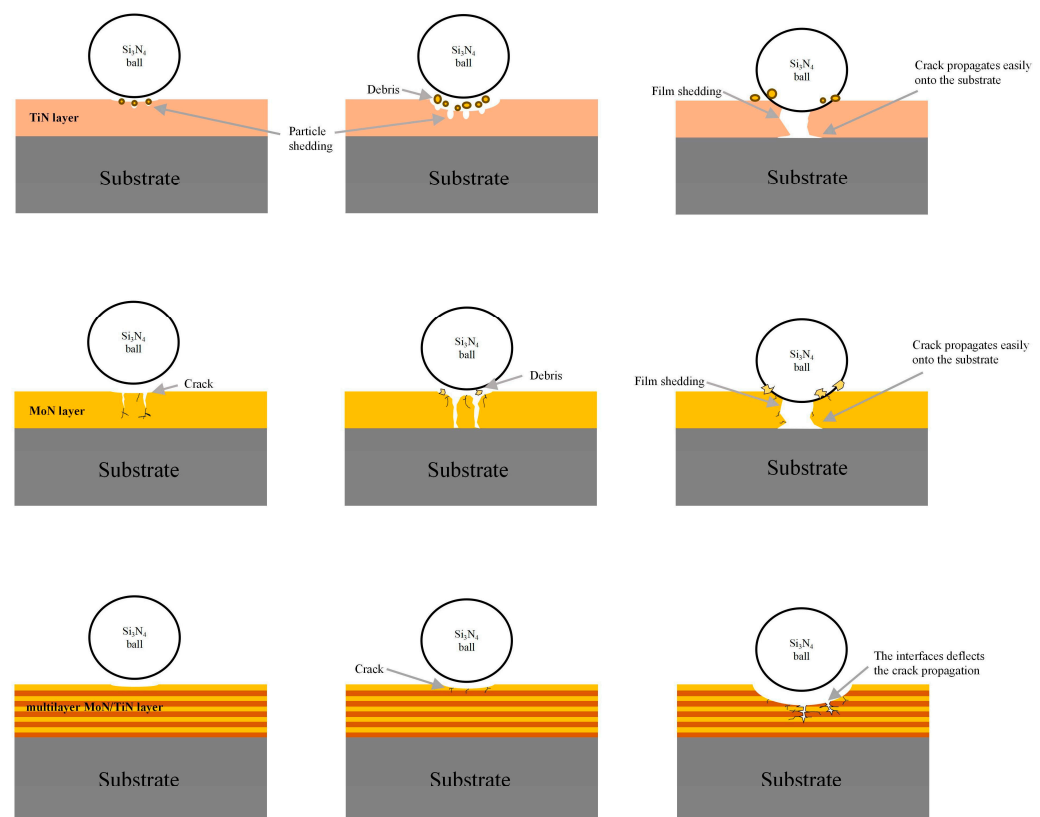


Figure 12. Schematic of the friction mechanism of the coatings.

In conclusion, the MoN/TiN multilayer coating exhibited high wear resistance and low COF under loads up to 20 N.

4. Conclusions

This study systematically investigated the tribological properties of the MoN/TiN multilayer coating, considering the TiN and MoN monolithic coatings as experimental controls. The MoN/TiN multilayer coating demonstrated enhanced mechanical properties and wear resistance, which was supported by the following key findings:

1. SEM analysis revealed that the alternating MoN/TiN multilayer architecture led to a dense microstructure through columnar growth disruption, considerably reducing the number of structural defects. The refined grain structure and multiple interfaces effectively deflected crack propagation, enhancing the fracture toughness of the MoN/TiN coating compared with that of the monolithic coatings.
2. The nanoindentation results demonstrated that the MoN/TiN multilayer coating achieved an optimal balance between hardness and toughness via the multilayer architecture. The multilayer interface structure that effectively suppressed dislocation motion considerably improved the hardness of the MoN/TiN coating by 64% and 35% compared with the corresponding values of the TiN and MoN monolithic coatings, respectively, and achieved an H^3/E^2 ratio of 0.159.
3. Friction and wear tests revealed that the MoN/TiN multilayer coating samples maintained a low and stable COF (~0.3–0.45) under loads up to 20 N, demonstrating wear rates ($3.06 \times 10^{-7} \text{ mm}^3/[\text{N}\cdot\text{m}]$) considerably lower than those of the TiN and MoN monolithic coating samples. Although the MoN/TiN multilayer coating samples were subjected to substrate exposure under a load of 25 N, their critical load capacity remarkably exceeded those of the TiN (5 N) and MoN (10 N) monolithic coating samples. The multilayer structure effectively hindered crack propagation, preventing crack growth toward the substrate and coating delamination, which enhanced the tribological performance of the MoN/TiN multilayer coating samples.

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