

Article

Comparative Insights into Mechanical and Tribological Properties of Zr/Al-Modified TiN/TiCN Multilayer Coatings

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Abstract

The development of multilayer coatings based on titanium carbides and nitrides remains one of the most active areas in materials science, owing to their ability to markedly enhance wear resistance and extend the service life of machine components. Particular interest is currently focused on tailoring conventional TiN/TiCN architectures through alloying metal additions. In this study, the tribological and mechanical performance of aluminum- and zirconium-doped TiN/TiCN multilayer coatings deposited by direct-current magnetron sputtering onto 41Cr4 steel was investigated. The morphology, elemental distribution, and phase constitution of the multilayer coatings were examined. It is shown that increasing the number of bilayers from two to four in TiN/TiCN-based multilayer coatings leads to improved tribomechanical characteristics. It was determined that zirconium provides a more pronounced beneficial effect than aluminum. The four-bilayer TiZrN/TiZrCN coating simultaneously exhibited the lowest coefficient of friction (0.11) and wear rate ($10^{-6} \text{ mm}^3 \text{ m}^{-1} \text{ N}^{-1}$) at a hardness of 16.4 GPa.

Keywords: multilayer coating; magnetron sputtering; coefficient of friction; nanohardness; wear resistance



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1. Introduction

Wear and corrosion of the surfaces of machine parts and components remain major challenges across many sectors of the high-technology industry. In service, such surfaces are continually exposed to adverse mechanical loading and chemically aggressive environments, which places stringent demands on the hardness, wear resistance, and corrosion resistance of the near-surface layer [1–3]. Accordingly, enhancing the mechanical and tribological performance of frictional assemblies remains a pressing task.

To address wear and corrosion, a wide range of technological solutions has been pursued using physical, chemical, and hybrid surface-engineering approaches [4,5]. One particularly effective direction involves surface modification via the deposition of hard, protective, wear-resistant coatings [6,7]. Applying these coatings can improve the mechanical response, chemical stability, and corrosion behavior of the treated surface by combining high hardness with sufficient toughness and durability with strong adhesion

to the substrate. Among the most widely used routes for producing wear-resistant coatings are chemical vapor deposition (CVD) and physical vapor deposition (PVD). Owing to their high performance and comparatively low cost, PVD coatings are considered a promising alternative to CVD for broader industrial implementation [8,9]. Among PVD techniques, magnetron sputtering (MS) is frequently employed to deposit a wide variety of hard tribological coating systems designed for enhanced wear resistance. MS offers a low impurity level and enables straightforward control of the deposition rate [10]. Depending on the sputtering conditions, coatings based on metal nitrides and carbides can deliver excellent mechanical and tribological performances, reflecting their outstanding physicochemical properties [8,11,12]. Nevertheless, escalating industrial requirements for machine components continue to drive the development of new coatings with further improved characteristics.

Research on TiN- and TiCN-based multilayer coatings (MLCs) deposited by magnetron sputtering (MS) has attracted considerable scientific attention in recent years, as evidenced by the growing number of publications and experimental studies in this area [8,13–18]. The multilayer TiN/TiCN architecture is particularly appealing because it combines TiN, which provides strong adhesion, with TiCN, which offers higher nanohardness and wear resistance. For instance, Lyu Y. and co-authors [19] examined how the TiN/TiCN layer microstructure affects Ti/TiN/TiCN films when the TiN/TiCN deposition-time ratio is varied from 28.57 to 200%. They reported an adhesion strength of 18.6 N and residual stresses of 140 MPa at a deposition-time ratio of 50%. In [20], a 3 μm TiN/TiCN multilayer coating (0.8 μm TiN and 2.2 μm TiCN) deposited on plasma-nitrided Ph15-5 steel markedly improved its wear resistance. In [21], the authors described 23.5 μm TiN/TiCN multilayer coatings produced by direct-current magnetron sputtering (DCMS). The inner TiCN layers exhibited a nanocomposite structure, whereas the TiN layers were characterized by a nanocolumnar morphology. Adhesion and hardness tests revealed high values, reaching 29 GPa and 21.4 GPa, respectively.

Modifying TiN/TiCN multilayer systems through the incorporation of metallic elements is also a practical route to improving their functional performance [22–25]. The available literature reported that modified TiN/TiCN MLCs achieved, either by introducing additional interlayers or by alloying the base nitride layers, improvements to their service-related properties. In particular, the authors of [22] showed that the wear resistance of TiAlN-based coatings can be improved by inserting ductile TiAl interlayers. Among the architectures evaluated by the authors, the best performance was obtained for a coating comprising $\text{Ti}_{0.45}\text{Al}_{0.55}\text{N}$ layers with a thickness of 0.6 μm and $\text{Ti}_{0.45}\text{Al}_{0.55}$ interlayers of 0.2 μm . J.C. Caicedo and colleagues [25] investigated the structure and mechanical properties of TiCN/TiNbCN multilayer coatings deposited by MS, analyzing the influence of the bilayer number and period (from 1.5 μm down to 15 nm) on nanohardness and elastic modulus. In [26], the microstructure and mechanical properties of Ti/TiAlN/TiAlCN multilayer coatings were studied. The coatings exhibited a reduced coefficient of friction (CoF) relative to Al_2O_3 ceramics and higher hardness compared with similar uncoated materials. Scratch testing indicated strong interlayer adhesion. The authors of [27] presented a systematic comparative assessment of residual stresses, tribomechanical properties, and wear resistance in mono- and multilayer TiAlN and TiAlCN coatings deposited by MS and HiPIMS, demonstrating the decisive role of carbon content and multilayer architecture in governing the stress state and tribological response of the coatings. Wei et al. [28] investigated the effect of the N_2/Ar flow ratio on the microstructure and properties of nano-multilayer TiZrN/TiN coatings deposited by HiPIMS in hybrid mode. They demonstrated that the optimal N_2/Ar ratio yielded a maximum hardness of 27.15 GPa, a stable coefficient of friction of ~ 0.8 , a reduced wear rate, and high corrosion resistance. In [29], nanocomposite

multilayer TiZrN coatings (compared with TaZrN) were deposited by RF/DC magnetron sputtering on AISI 4140 steel. These coatings exhibited excellent tribological performance under high contact loads, confirming the potential of TiZrN multilayers for protecting components operating under severe friction and wear conditions.

Despite the substantial body of work examining how alloying and layer thickness affect the structure and properties of TiN/TiCN multilayer coatings, this research direction remains relatively young and is still insufficiently explored. The literature reveals extensive studies on Al-containing TiN/TiCN systems; however, publications addressing the incorporation of zirconium into TiN/TiCN multilayer architectures are scarce, underscoring both the novelty and the promise of this approach.

The present study focuses on the mechanical and tribological behavior of coatings with varied bilayer thickness while maintaining the same overall TiN/TiCN coating thickness, as well as on the effect of zirconium and aluminum modification. To this end, TiN/TiCN, TiAlN/TiAlCN, and TiZrN/TiZrCN multilayer coatings were deposited on 41Cr4 steel by DCMS. The elemental and phase composition, structure, and the mechanical and tribological properties of the coatings were systematically investigated.

2. Materials and Methods

2.1. Substrate Preparation and Coating Deposition

TiN/TiCN multilayer coatings, both in the as-deposited (undoped) state and modified with aluminum or zirconium, were deposited by DCMS in a high-vacuum deposition system. A 99 mm diameter VT1-0 titanium target (equivalent to Grade 2) was used. The substrates included 41Cr4 steel (Severstal, Cherepovets, Russia), p-type single-crystal silicon Si (100) (SW GmbH, Schramberg, Germany), and A99-grade aluminum foil (Eurofoil Luxembourg S.A., Dudelange, Luxembourg). The steel substrates were used for tribological testing, silicon wafers for cross-sectional imaging of the coatings, and aluminum foil to obtain coating powder for X-ray diffraction analysis. Prior to deposition, 58 mm diameter steel substrates were ground sequentially using abrasive papers with grit sizes P120, P180, P320, P600, P1000, P1200, and P2000, and then polished with diamond paste to a surface roughness of $R_a \approx 8\text{--}10$ nm, followed by ultrasonic cleaning in acetone. The prepared substrates were mounted in the process chamber on a 200 mm diameter substrate holder. The target-to-substrate distance was 300 mm.

Initially, the chamber was evacuated to a base pressure of 5×10^{-3} Pa using the pumping system. The substrates were then ion-cleaned in an ultra-high-purity argon plasma (99.999%) at a pressure of 0.3 Pa, with a plasma current of 30 mA and an accelerating voltage of 2.5 kV for 20 min. For this purpose, an APEL-IS-21CELL ion source (Applied Electronics, Tomsk, Russia) was employed. In the next step, the cleaned substrates were positioned opposite an APEL-MRE100 magnetron (Applied Electronics, Tomsk, Russia) for the deposition of multilayer coatings.

A titanium adhesion interlayer (400 nm) was deposited first to improve the coating–steel bonding for all samples. The multilayer coatings were deposited at a working pressure of 0.45 Pa in an atmosphere of argon and high-purity reactive gases (N_2 99.999% and C_2H_2 99.999%). During deposition, the following sputtering parameters were maintained: substrate bias of -100 V, plasma current of 2 A, discharge voltage of 550–650 V, and deposition time of 284 min. During deposition, the argon flow rate was maintained constant at 1.3 L/h, while the flow rates of the reactive gases N_2 and C_2H_2 were set at 0.08 L/h and 0.14 L/h, respectively. TiN and TiCN layers were formed by the sequential sputtering of titanium in Ar/ N_2 and Ar/ N_2 / C_2H_2 gas mixtures, respectively. The flow rates of inert and reactive gases were regulated using PPT-12 mass flow controllers (Eltochpribor, Moscow,

Russia). Zirconium and aluminum were introduced by attaching additional Al and Zr pieces to the surface of the titanium target.

To investigate the structure and properties of multilayer nitride and carbonitride coatings, TiN/TiCN, TiAlN/TiAlCN, and TiZrN/TiZrCN systems were deposited by DCMS. Each coating system was produced in two configurations: with two bilayers (2BL) and with four bilayers (4BL), enabling a direct assessment of how the number of repeating layers influences microstructure development and property evolution. The schematic illustrations in Figure 1 depict the sequence of alternating layers and highlight the multilayer design concept.

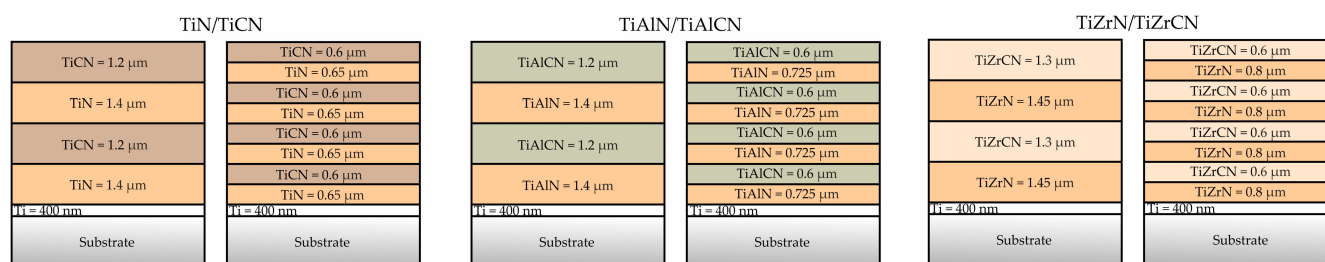


Figure 1. Schematic representations of the deposited multilayer coatings.

2.2. Coating Characterization Methods

The surface morphology and microstructure were examined using a scanning electron microscope (SEM), JXA-8230 (JEOL, Tokyo, Japan), equipped with an energy-dispersive X-ray spectroscopy (EDS) system for elemental analysis. The surface imaging of all coatings was carried out in the backscattered-electron (BSE) mode at an accelerating voltage of 20 kV. The coating composition was analyzed over a $100 \times 100 \mu\text{m}^2$ area at $\times 200$ magnification at several locations on each coating; the reported values represent the averaged elemental contents.

The surface roughness of the coatings was measured using a Model 130 profilometer (Proton, Moscow, Russia). Roughness measurements were performed in accordance with ISO 1302 [30]. For each specimen, 10 traces with a track length of 5 mm were recorded and the results were averaged. The scanning speed was 0.5 mm/s.

The phase composition of the coatings was determined by X-ray diffraction (XRD) using Cu-K α 1 radiation ($\lambda \approx 1.540598 \text{ \AA}$) on a D8 Advance diffractometer (Bruker, Ettlingen, Germany). Data were collected at a scanning rate of 0.1–1 degree/min over a 2θ range from 4 to 90 degrees with a step size of 0.01 degrees, at 35 kV and 20 mA. Diffraction patterns were recorded in Bragg–Brentano geometry. Phase identification was performed using the PDF-2 database.

The nanohardness and elastic modulus of the coatings were determined using the nanoindentation method with the FISCHERScope HM2000 S measurement system (Helmut Fischer, Sindelfingen, Germany). Measurements were conducted in accordance with the international standard DIN EN ISO 14577 [31]. The primary data processing was performed using the WIN-HCU software (version 7.1). The tests were conducted under a load of 40 mN using a four-sided Vickers diamond pyramid with an angle of 136° on the plane. The hardness measurements were performed with the following parameters: indenter approach speed of $2 \mu\text{m/s}$, load accuracy of 0.4 mg, displacement accuracy of 0.1 nm, and a 5 s creep time at maximum load. The data presented in the study are averaged from 10 indentations, taking into account the standard deviation. The indenter penetration depth into the coating was 0.4–0.5 μm .

The wear rate (WR) and coefficient of friction (CoF) of the coatings were investigated using a ball-on-disk tribometer, TRB³ (CSM Instruments, Peseux, Switzerland), at room

temperature under dry sliding conditions. The testing conditions adhered to the international standards DIN 50324 [31]. A 6 mm diameter ball made of 100Cr6 steel was employed as the counterbody, owing to its widespread use stemming from well-established and thoroughly characterized properties, including high hardness, excellent wear resistance, and uniform microstructure. This material pair (hard wear-resistant coating/steel) provides the most representative simulation of real-world tribological contacts encountered in mechanical engineering applications, where metal-to-metal or coating-to-steel interactions predominate. The tests were conducted with a normal load of 3 N, a track radius of 5 mm, a sliding speed of 1 cm/s, and a total of 3000 friction cycles. The CoF was recorded in real time, while the wear-track width was measured using a Surtronic S-100 profilometer (Taylor Hobson, London, UK).

3. Results and Discussion

3.1. Structure and Composition of Coatings

The surface morphology of the TiN/TiCN, TiAlN/TiAlCN, and TiZrN/TiZrCN systems did not exhibit significant differences. The surface is characterized by a homogeneous structure without noticeable defects, cracks, or macroscopic pores, indicating uniform deposition and good coating quality at the macro level. Figure 2 shows a schematic representation of the structure and cross-sectional SEM images of TiN/TiCN-2BL and TiZrN/TiZrCN-4BL multilayer coatings as an example. In the case of the TiN/TiCN-2BL coating, the total coating thickness is 5.6 μm , including a titanium sublayer of 400 nm that ensures adhesion to the steel substrate. The layers of TiN (1.4 μm) and TiCN (1.2 μm) alternate sequentially, forming two complete bilayers with uniform thickness and clear interface boundaries. In the TiZrN/TiZrCN-4BL coating, the total thickness reaches 6.0 μm . Each bilayer consists of alternating layers of TiZrN ($\approx 0.8 \mu\text{m}$) and TiZrCN ($\approx 0.6 \mu\text{m}$), confirming the stable formation of four repeating layer pairs. The thickness of the bilayers in the other systems was approximately the same as the coatings mentioned above, with minor deviations. Table 1 summarizes the surface roughness and layer thicknesses of all deposited multilayer coatings.

To analyze the elemental composition of the obtained multilayer coatings, more than 10 random positions on the coating surface were selected. The averaged composition results are shown in Table 2. The energy-dispersive X-ray spectroscopy results indicate that the Ti content in all coatings is in the range of 33–39 at.%. The TiN/TiCN coatings have a slightly higher titanium content compared with the modified coatings, as the presence of zirconium and aluminum reduces the titanium content. In the TiAlN/TiAlCN system, a significant amount of aluminum is observed, which increases as the number of bilayers increases, from 7.7 at.% in the two-layer sample to 15 at.% in the four-layer sample. Simultaneously, a decrease in nitrogen content (from 26.1 to 18.4 at.%) is observed, which may indicate element redistribution during deposition and the formation of more complex phases, such as TiAlCN. For the TiZrN/TiZrCN coatings, zirconium content is found to be in the range of 5–6 at.%, confirming the successful incorporation of Zr into the multilayer structure. In the other cases, the nitrogen and carbon content slightly fluctuates in the range of ≈ 25 –27 at.% and ≈ 28 –34 at.%, respectively. In all deposited coatings, an increase in the number of bilayers resulted in a rise in oxygen content from 3.0 to 4.2 at.%, which may be attributed to the larger interfacial area. These interfaces exhibit enhanced reactivity and promote the trapping of residual oxygen from the vacuum chamber. However, this oxygen content remains at the background level and exerts no noticeable adverse effect on the mechanical and tribological properties of the coatings [32,33].

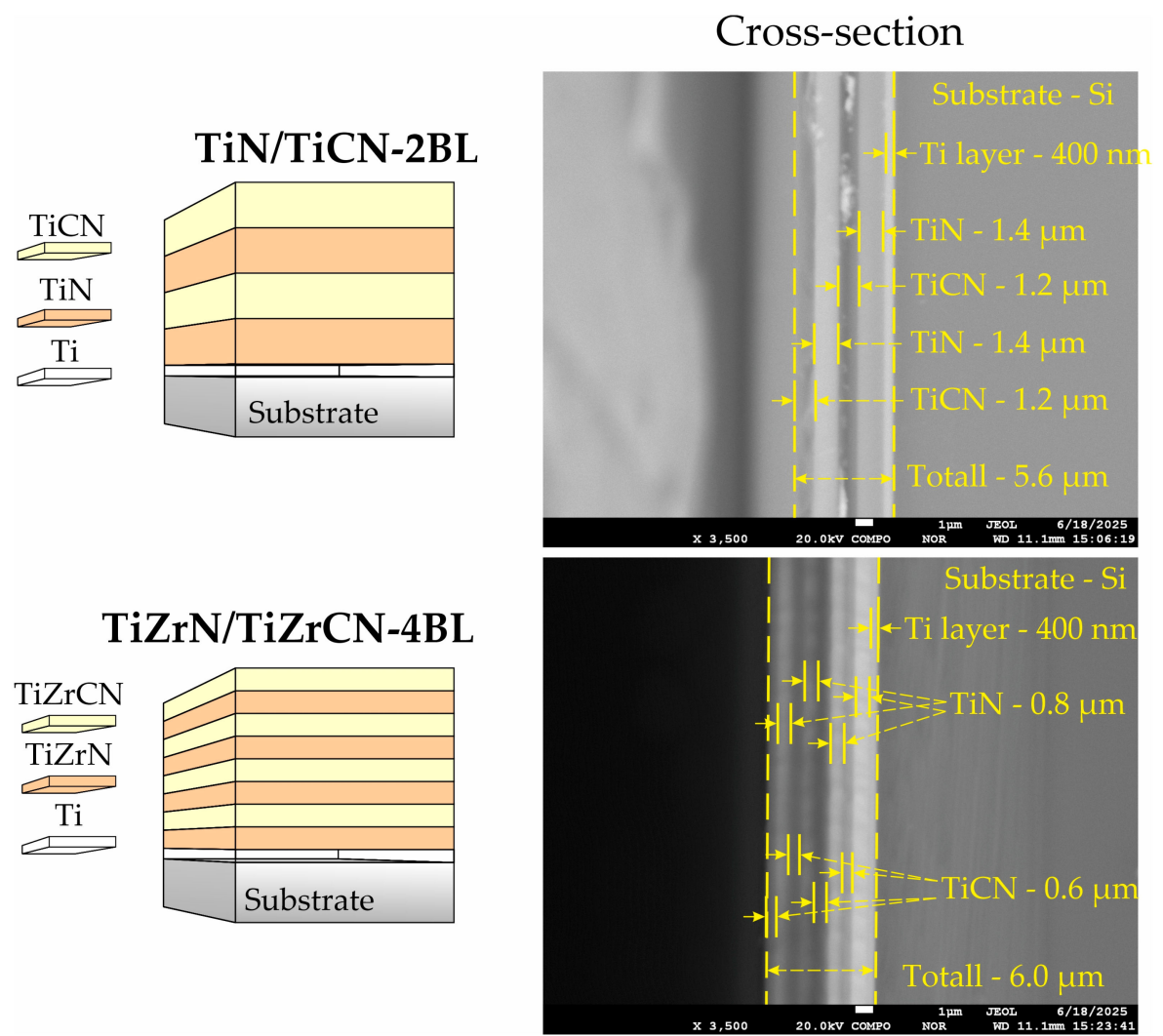


Figure 2. Thickness of layers on cross-sections of multilayer coatings.

Table 1. Layer thickness, roughness, and deposition rate of multilayer coatings in the TiN/TiCN, TiAlN/TiAlCN, and TiZrN/TiZrCN systems and substrates.

Multilayer Coatings	Total Thickness, μm	Thickness of the Layers, μm	The Average Roughness (Ra), nm	Deposition Rate, nm/min
Steel 41Cr4	–	–	10	–
TiN/TiCN-2BL	5.6	TiN – 1.4, TiCN – 1.2	17	19.7
TiN/TiCN-4BL	5.4	TiN – 0.65, TiCN – 0.6	18	19
TiN/TiAlCN-2BL	5.6	TiN – 1.4, TiCN – 1.2	24	19.7
TiN/TiAlCN-4BL	5.7	TiN – 0.72, TiCN – 0.6	30	20
TiN/TiZrCN-2BL	5.9	TiN – 1.45, TiCN – 1.3	26	20.7
TiN/TiZrCN-4BL	6.0	TiN – 0.8, TiCN – 0.6	17	21

Table 2. Elemental composition (at.%) of the TiN/TiCN, TiAlN/TiAlCN and TiZrN/TiZrCN multilayer coatings determined by EDS.

Multilayer Coatings	Elemental Composition, at.%						(C + N)/(Sum of Metals)
	Ti	Zr	Al	C	N	O	
TiN/TiCN-2BL	39.5	–	–	34.1	24.9	1.5	1.5
TiN/TiCN-4BL	37.9	–	–	30.5	27.0	4.6	1.5
TiN/TiAlCN-2BL	32.5	–	7.7	30.8	26.1	2.9	1.4
TiN/TiAlCN-4BL	33.0	–	15.0	29.4	18.4	4.2	1
TiN/TiZrCN-2BL	37.1	6.1	–	29.3	25.5	2	1.2
TiN/TiZrCN-4BL	33.7	5.5	–	30.6	26.8	3.4	1.4

In all deposited coatings, an increase in the number of bilayers is accompanied by a rise in the oxygen content, which may be related to an increase in the area of interfacial boundaries and their greater susceptibility to oxidation. The stoichiometric composition for the TiN/TiCN system, represented by the (C + N)/(sum of metals) ratio, was 1.5. With the addition of aluminum and zirconium, this ratio decreases from 1.4 to 1. It is known that the (C + N)/(sum of metals) ratio should approach 1 [10], but slightly deviated coatings have also shown good results in the literature [34,35].

Thus, varying the number of bilayers and introducing alloying elements (Zr, Al) significantly alters the chemical composition of the coatings. These changes affect the phase formation and may potentially influence the mechanical and tribological properties of the investigated multilayer systems.

X-ray diffraction (XRD) analysis of the deposited multilayer coatings was performed to investigate the impact of the modifying elements, zirconium and aluminum, on the phase composition of TiN/TiCN coatings. Figure 3 (bottom part) shows that for the TiN/TiCN coating, the main phases are TiCN and TiN, with five peaks corresponding to the planes (111), (200), (220), (311), and (222). The high intensity of the TiN (200) and TiCN (200) peaks indicates the preferred growth orientation of the coatings along the (200) plane. After the addition of Al and Zr to the TiN/TiCN multilayer system, there was a significant decrease in the intensity of the (200) peak and an increase in the intensity of the (111) peaks, suggesting a change in the preferred orientation from (200) to (111). Additionally, new diffraction peaks corresponding to phases such as TiZrCN, ZrN, TiCN, AlTiN, TiN, (TiZr)C₂, and Ti₃AlC₂ were observed. For the TiAlN/TiAlCN coatings, interpretation of the X-ray diffraction patterns requires consideration that no dedicated PDF-2 card is currently available for the TiAlCN phase (or the (Ti,Al)(C,N) solid solution). Therefore, phase identification was performed using structurally and crystallographically analogous phases with a face-centered cubic NaCl-type (B1) structure, such as TiN, AlTiN, or TiCN. This approach is validated by the formation of a continuous (Ti,Al)(C,N) solid solution that retains the B1 structure. The result is consistent with the data reported in [36,37]. Additional confirmation is provided by the EDS data. Depending on the number of bilayers in the same coating, the phase composition did not show significant changes.

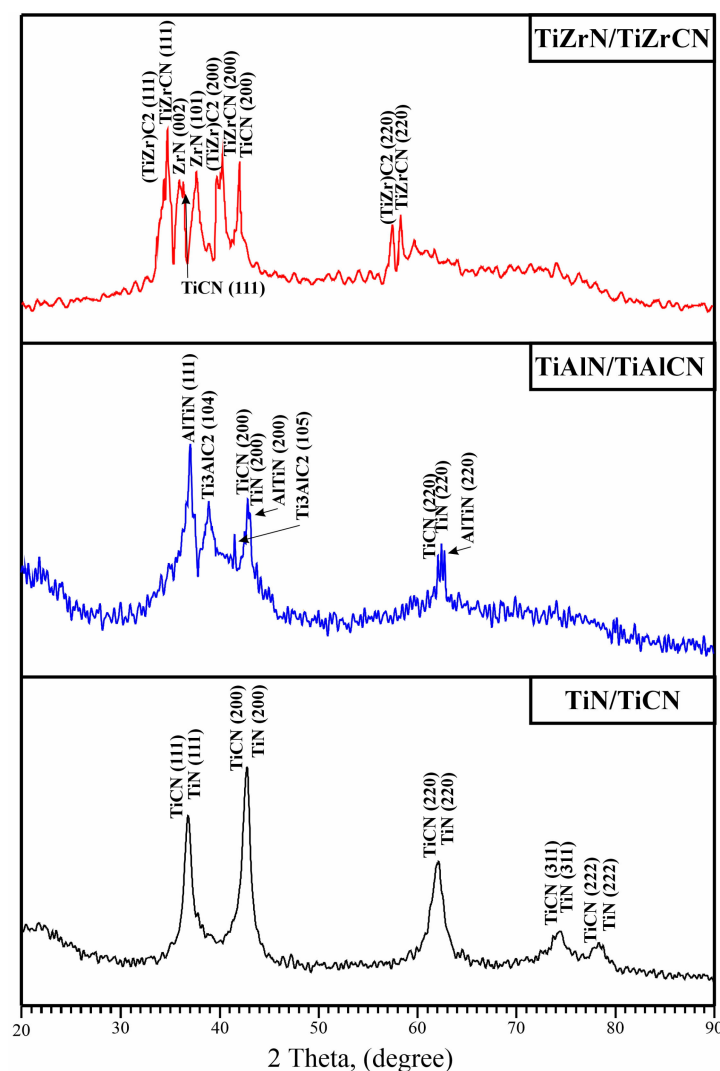


Figure 3. Diffractograms of deposited multilayer coatings.

3.2. Mechanical and Tribological Properties of Coatings

Figure 4 presents the graphical representation of mechanical properties, including nanohardness (H) and elastic modulus (E) (Figure 4a), the ratio of H/E and H^3/E^2 (Figure 4b), and the mechanical efficiency map (Figure 4c) for all the obtained coatings and the substrate material. From Figure 4a, it can be seen that the MLCs increase the nanohardness of the treated surface compared with the steel substrate material. For example, the nanohardness of steel (5.4 GPa) increases by approximately three times when the TiZrN/TiZrCN coating with four bilayers is applied (16.4 GPa). Furthermore, hardness analysis shows that MLCs with four bilayers exhibit a slightly higher nanohardness compared with those deposited with two bilayers. One reason for this is the increase in interface density, which hinders dislocation movement and deformation. This interlayer strengthening effect is consistent with previous studies [11,38–40].

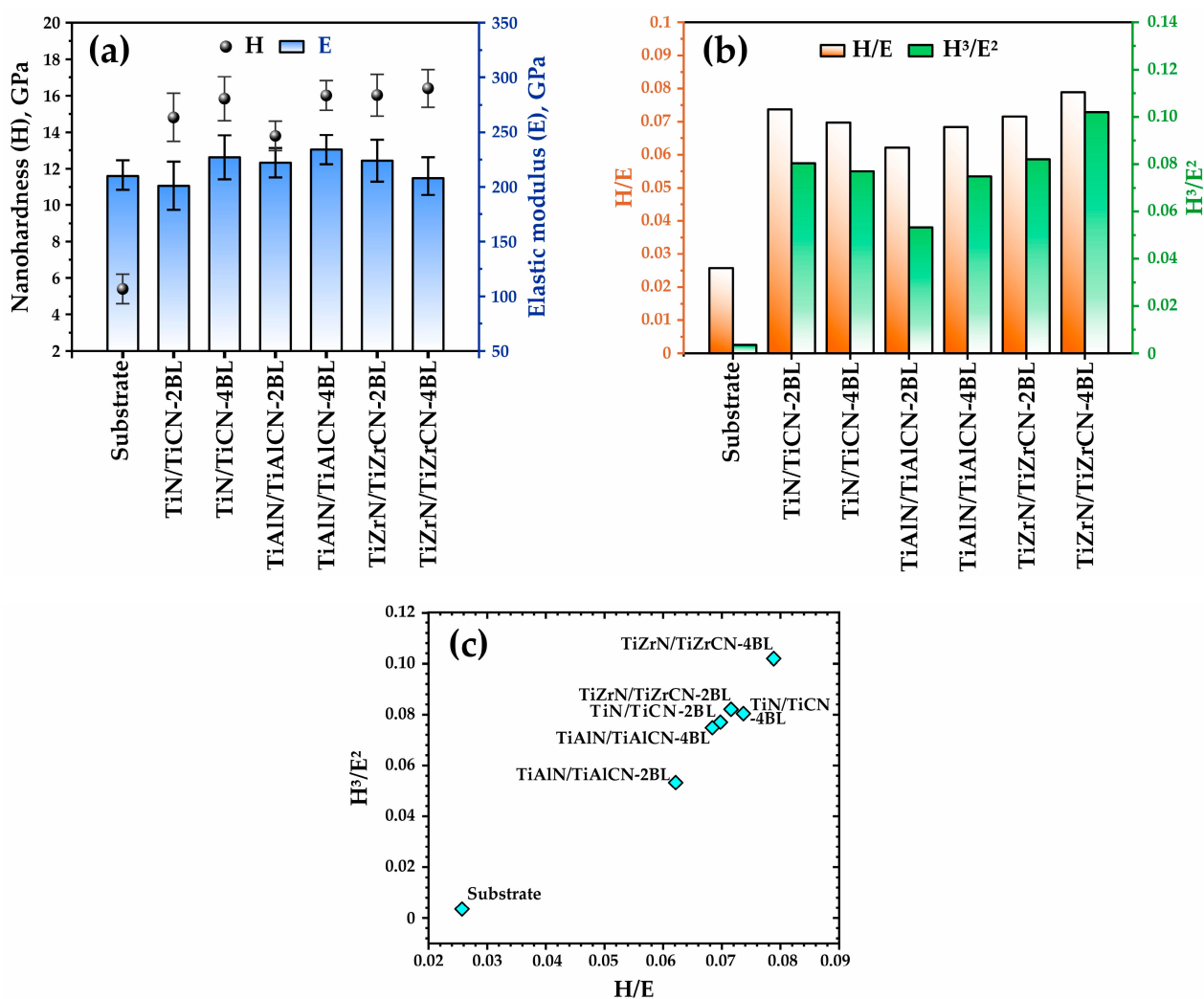


Figure 4. Mechanical characteristics of deposited multilayer coatings and substrate: (a) Nanohardness and elastic modulus; (b) values H/E and H^3/E^2 ; (c) H/E – H^3/E^2 diagram.

Figure 4b shows the calculated ratios of nanohardness to elastic modulus, which can be considered an indicator of good resistance to mechanical degradation and failure [41,42]. The results indicate that the TiZrN/TiZrCN system exhibits a high H/E ratio among the deposited MLCs, suggesting the ability to elastically absorb contact loads without accumulating plastic damage and crack formation. It was characterized by a hardness-to-elastic modulus ratio of $H/E = 0.08$ and a plastic deformation resistance parameter of $H^3/E^2 = 0.102$ GPa. These results are consistent with the literature data on nitride coatings. Thus, Kim et al. [43] reported $H/E \approx 0.087$ and lower H^3/E^2 values (<0.10) even after additional carbon doping. Industrial TiZrN coatings [44] exhibit higher H/E values at optimized substrate bias; however, the H^3/E^2 value of 0.102 GPa achieved in the present work remains competitive. In contrast, low H/E and H^3/E^2 values were exhibited by TiAlN/TiAlCN coatings. This may be associated with the high aluminum content in the coatings.

The mechanical efficiency map (Figure 4c) allows for the evaluation of the mechanical effectiveness of the coatings and highlights the deposition conditions that provide an optimal balance between elastic deformation and resistance to plastic flow. Coatings with optimized H/E and H^3/E^2 values are characterized by increased stability and toughness, which reduces the likelihood of premature failure under mechanical loading [42,45,46]. The map also highlights the TiZrN/TiZrCN-4BL MLC, which shows a high position in

the $H/E-H^3/E^2$ diagram among the investigated MLCs. The results of the mechanical efficiency map for most of the coatings correlate with and are confirmed by wear tests.

Figure 5 presents the CoF and wear rate (WR) of the deposited multilayer coatings and the substrate. The average CoF results show that the MLCs reduce the average CoF of the substrate from 0.42 to a minimum of 0.11. For TiN/TiCN and TiZrN/TiZrCN coatings, the CoF decreases with an increase in the number of bilayers from two to four. In contrast, a slight increase in the CoF is observed in the TiAlN/TiAlCN system. This behavior may be attributed to several factors. One of them is the elevated aluminum content (15 at.%) in the TiAlN/TiAlCN coatings. Although the influence of aluminum on the tribological properties of nitride coatings under dry friction is evaluated ambiguously in the literature [47,48], its contribution cannot be excluded in the present case. Additionally, surface tribo-oxidation can increase the coefficient of friction due to the formation of abrasive oxide particles and an increase in the local roughness of the contact zone [47,49]. Another equally probable factor is the difference in coating roughness: even a slight increase in R_a can markedly influence the frictional response under dry sliding.

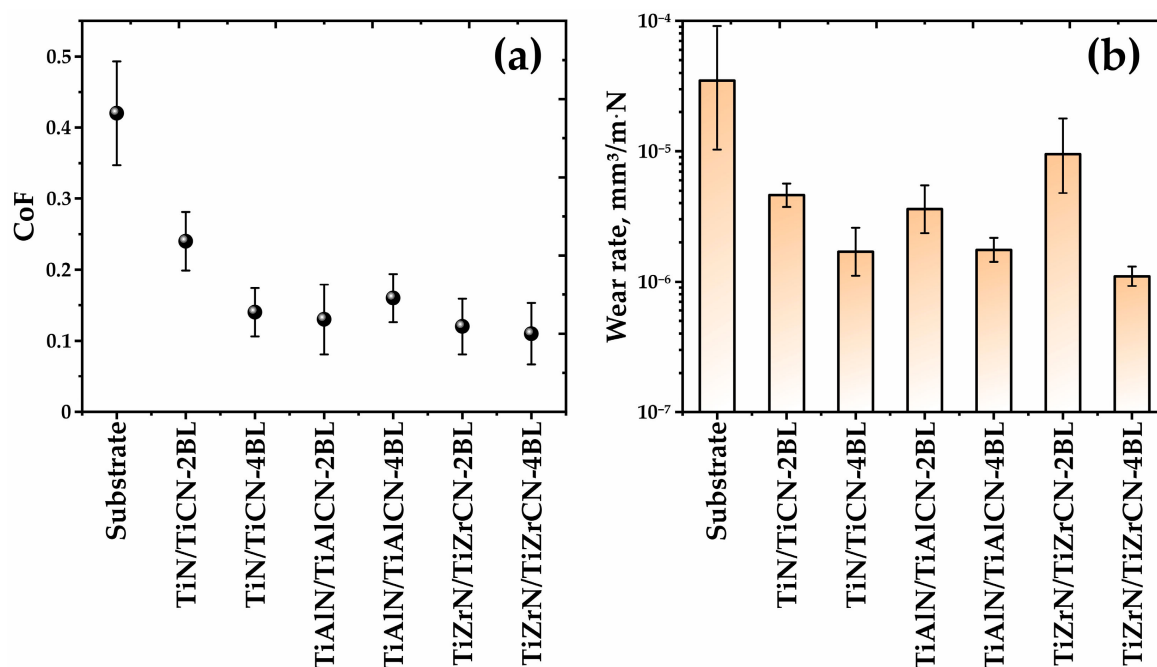


Figure 5. Tribological characteristics of deposited multilayer coatings and substrate: (a) Coefficient of friction of all coatings; (b) wear rate of all coatings.

In general, the deposited MLCs exhibited stable low CoF values. Notably, the increase in the number of bilayers to four positively affects the wear rate, as shown in Figure 5b. This confirms the role of interfacial boundaries as barriers to dislocation movement and crack propagation, as well as the formation of a more uniform and dense coating structure [50,51]. The TiZrN/TiZrCN-4BL coating, modified with zirconium, demonstrates the optimal low WR, showing both the minimum CoF (0.11) and wear rate ($10^{-6} \text{ mm}^3/(\text{m} \cdot \text{N})$), indicating the synergistic effect of multilayer architecture and alloying.

Thus, optimizing the bilayer thickness and introducing modifying elements such as aluminum and zirconium allows the control of the combination of mechanical and tribological properties. Taking into account the layer composition, structure, and properties of the obtained coatings, the highest wear resistance is achieved with the TiZrN/TiZrCN multilayer coatings with four bilayers, which can be considered promising protective systems for machine and component parts operating under conditions of increased friction and wear.

SEM micrographs in Figure 6 show the wear tracks formed on the four-bilayer coatings after ball-on-disk tribotesting under dry sliding conditions. EDS analysis was performed directly inside the highlighted regions of the tracks. The TiZrN/TiZrCN-4BL coating is characterized by a substantially smaller wear-track width (59.6 μm) compared with 79.3 μm for TiAlN/TiAlCN-4BL, which directly confirms its superior wear resistance and the low wear rate noted earlier. The EDS data additionally reveal significantly lower oxygen pickup inside the TiZrN/TiZrCN track (5.1 at.%) than in the Al-containing counterpart (13.34 at.%), indicating effective suppression of tribo-oxidation and a higher chemical stability of the Zr-based multilayer system. Both tracks exhibit a smooth morphology featuring only shallow parallel grooves and completely lack signs of cracking, spallation, or deep plowing; this morphology corresponds to mild abrasive wear accompanied by limited adhesive material transfer from the counterpart ball and minimal formation of oxide debris. The asymmetric distribution of the five shallow tribogrooves observed on the TiAlN/TiAlCN-4BL wear track (left image, Figure 6) arises from localized non-uniform contact between the counterbody and the coating during tribotesting, a phenomenon commonly encountered during the initial stages of wear in multilayered coatings under conditions of uneven load distribution or micro-asperities present on the counterface. In contrast, such asymmetry is absent in the TiZrN/TiZrCN-4BL coating due to its superior hardness and enhanced resistance to abrasive micro-cutting, resulting in the formation of a significantly more uniform wear track. Such behavior is fully consistent with the high resistance to plastic deformation ($H^3/E^2 = 0.102 \text{ GPa}$) and the low steady-state coefficient of friction (0.11) of the TiZrN/TiZrCN coating.

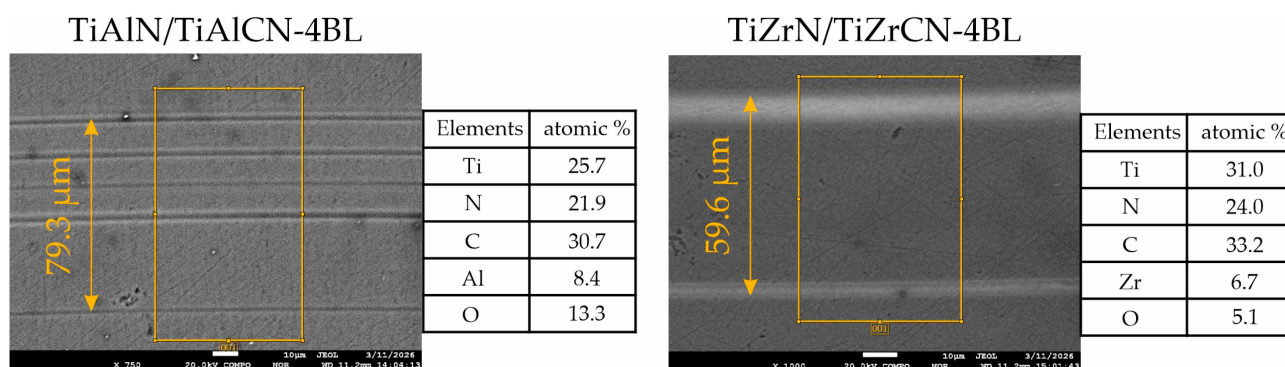


Figure 6. SEM image of the worn surface after tribological testing of coatings modified with aluminum and zirconium.

4. Conclusions

A comparative analysis of the mechanical and tribological properties of TiN/TiCN multilayer coatings modified with Zr and Al, with varying bilayer numbers at constant total thickness, was conducted in this study. Varying the number of bilayers and introducing alloying elements significantly alters the chemical composition of the multilayer coatings. It was shown that increasing the number of bilayers from two to four in TiN/TiCN-based multilayer coatings lead to improved tribomechanical properties, which were attributed to the increased interface density and the implementation of interlayer hardening. It was established that the introduction of zirconium had a more pronounced positive effect compared with aluminum. Considering the layer composition, structure, and properties of the obtained coatings, the best combination of properties was demonstrated by the TiZrN/TiZrCN-4BL coating, which exhibited maximum wear resistance, the lowest coefficient of friction (0.11), and the least wear rate ($10^{-6} \text{ mm}^3/(\text{m}\cdot\text{N})$). The obtained results can be applied in the design of TiN- and TiCN-based multilayer coatings for the wear protection of components used in a wide range of applications.

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Abbreviations

The following abbreviations are used in this manuscript:

MLCs	Multilayer coatings
2BL	Two bilayers
4BL	Four bilayers
DCMS	Direct-current magnetron sputtering
CoF	Coefficient of friction
WR	Wear rate

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