

Achieving low friction and wear in superhard TiC_x coatings on GCr15 steel via ti-induced graphitization and TiO_2 stabilization

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Abstract

Ti-based carbon coatings are promising for low-friction and wear-resistant applications, but their performance on steel substrates is often limited by poor adhesion, high residual stress, and unstable tribological behavior under ambient conditions. In this work, TiC_x coatings were deposited on GCr15 bearing steel using a hybrid strategy combining magnetic filtered cathodic arc ion sputtering and magnetron sputtering. Dense Cr/CrN/CrTiN/TiCN graded interlayers ensured strong adhesion and a smooth

mechanical transition to the substrate, while the TiC_x top layer was tuned via the carbon target DC current. The TiC_x -1 coating, deposited at 4 A, exhibits an exceptional hardness of 43 GPa and a low friction coefficient of ~ 0.18 , demonstrating a superior combination of elastic-plastic properties and wear resistance. Structural analyses reveal that increasing DC current promotes sp^2 carbon formation and graphitization, while Ti incorporation facilitates TiC reinforcement and the in-situ generation of TiO_2 during sliding. Tribological tests, Raman and FIB-HRTEM observations confirm that friction and wear are dominated by the formation of a stable graphitized transfer film supported by TiO_2 , which reduces shear stress and stabilizes the sliding interface. However, excessive carbon enrichment at higher currents destabilizes the transfer film and degrades mechanical integrity, leading to higher friction and wear. These results highlight the synergistic roles of interfacial architecture, carbon bonding evolution, and Ti-assisted tribochemistry in governing the tribological performance of TiC_x coatings. This study provides a novel design strategy and fundamental insights for developing superhard, low-friction coatings for steel components under ambient conditions.

Keywords: TiC_x coatings; Metal transition Layer; Ultra-hard; Magnetic filtered cathodic arc

1 Introduction

The development of high-performance tribological coatings is essential for enhancing energy efficiency and ensuring reliable operation in advanced mechanical systems. Carbon-based coatings have attracted significant attention as protective coatings due to their high intrinsic hardness, low friction coefficients, and excellent resistance to wear and surface damage [1,2]. These coatings encompass a broad range of material systems, from amorphous carbon networks to engineered composite structures with tunable bonding states and microstructures [3]. However, despite these advantages, their practical applications remain constrained. In particular, their tribological performance is highly sensitive to environmental conditions, especially

humidity, and their high internal stresses often deteriorate film-substrate adhesion [1,4].

To address these limitations, elemental doping strategies, such as the incorporation of Si or metallic species, have been widely adopted. These approaches effectively improve humidity tolerance and reduce residual stress in carbon-based coatings [3,5]. In addition, the integration of advanced deposition techniques with multilayer architectures and surface-engineering strategies has been demonstrated to significantly enhance coating adhesion and tribological performance under demanding service conditions [6]. For instance, Si doping reduces the environmental sensitivity of diamond-like carbon (DLC) coatings, an effect mainly attributed to the formation of Si-OH passivation layers and curved graphene nanostructures, which together enable stable low-friction behavior under humid environments [7-9]. By contrast, Ti doping effectively mitigates the high intrinsic stress and poor adhesion commonly observed in carbon-based coatings. This improvement arises from the formation of a TiC/a-C nanocomposite structures, which in turn enhance mechanical strength and wear resistance [10,11]. Moreover, with the assistance of advanced deposition technologies, high-performance Ti-doped ta-C coatings can be reliably fabricated, further expanding their tribological applicability [12].

Building upon these advances, titanium carbide (TiC_x) coatings emerge as a particularly versatile class of coatings, exhibiting exceptional nanohardness, reaching values of up to 24.6 GPa, and therefore providing excellent resistance to abrasive wear [13]. Moreover, this material system shows strong potential for the development of ultra-hard surfaces, for example, ternary TiBN coatings have been reported to achieve

hardness values as high as 65 GPa [14]. In addition to their high mechanical strength, TiC_x-based coatings display an adaptive tribological response. Specifically, carbon-rich compositions can undergo shear-induced graphitization during sliding, which promotes the formation of self-lubricating transfer films at the contact interface [11]. Consequently, the synergy between superior mechanical properties and adaptive lubrication behavior renders TiC_x-based coatings promising candidates for demanding industrial tribological applications [15]. However, simultaneously achieving ultra-high hardness (>40 GPa) and a low friction coefficient (<0.2) in TiC_x coatings, particularly under ambient conditions, remains a significant challenge and represents a key advancement targeted in the present work.

In this study, TiC_x coatings with systematically varied carbon contents were deposited on GCr15 substrates using a magnetic-filtered cathodic arc ion sputtering technique. To ensure stable coating growth and enhance coating-substrate adhesion, a multilayer architecture was employed, consisting of a metallic Cr interlayer, followed by CrN, CrTiN, and TiCN nitride transition layers. By precisely regulating the carbon stoichiometry and engineering the interfacial structure, the resulting TiC_x coatings achieved an outstanding combination of superhardness (43 GPa) and a low friction coefficient (~0.18), demonstrating performance advantages over many conventional DLC coatings. This work establishes a new design paradigm for high-performance ceramic-like coatings and provides critical insights into the development of next-generation solid lubricating materials capable of reliable operation under extreme service conditions.

2. Experimental setup

2.1. Deposition of multilayer coatings

TiC_x coatings were deposited on GCr15 substrates using a self-developed multifunctional integrated magnetron sputtering (MS) system, the system was equipped with three target sources, namely Cr, Ti, and graphite (Φ 100 mm $\times$ 675 mm), and supplied with high-purity Ar gas (99.99%). Prior to deposition, the GCr15 steel substrates were ultrasonically cleaned in petroleum ether and ethanol for 20 min each. Subsequently, the substrates were dried with nitrogen gas and mounted on the sample holder in the deposition chamber. The chamber was evacuated to a base pressure of 5.0×10^{-3} Pa by sequential operation of the mechanical and turbomolecular pumps. As illustrated in **Fig. 1(a)** and summarized in **Table 1**, Ar was then introduced to maintain a working pressure of 0.5 Pa. An Ar glow-discharge cleaning process was performed at a bias voltage of -800 V and a pressure of 0.5 Pa for 30 min to effectively remove surface contaminants and native oxides from the substrates. The coatings were deposited sequentially. First, a Cr transition layer was deposited using a cathodic vacuum arc Cr source operated at 160 A. Subsequently, high-purity N₂ (99.99%) was introduced into the chamber to form a CrN transition layer. The third layer, CrTiN, was deposited by simultaneously operating the Cr and Ti arc sources at 160 A. Thereafter, the Cr source was switched off, and a TiCN layer was deposited using the Ti arc source at 160 A in combination with the central cylindrical graphite target operated at a DC current of 4 A. Each transition layer was deposited for 1 h. Finally, the multilayer TiC_x functional coatings were synthesized on the GCr15 substrates by operating the Ti arc

source at 120 A, while the graphite target was powered at DC currents of 4 A, 6 A, and 10 A to obtain TiC_x coatings with different carbon contents.

In the following discussion, the samples are designated as TiC_x -1, TiC_x -2, and TiC_x -3. These labels correspond to multilayer carbide coatings deposited at graphite target DC currents of 4 A, 6 A, and 10 A, respectively.

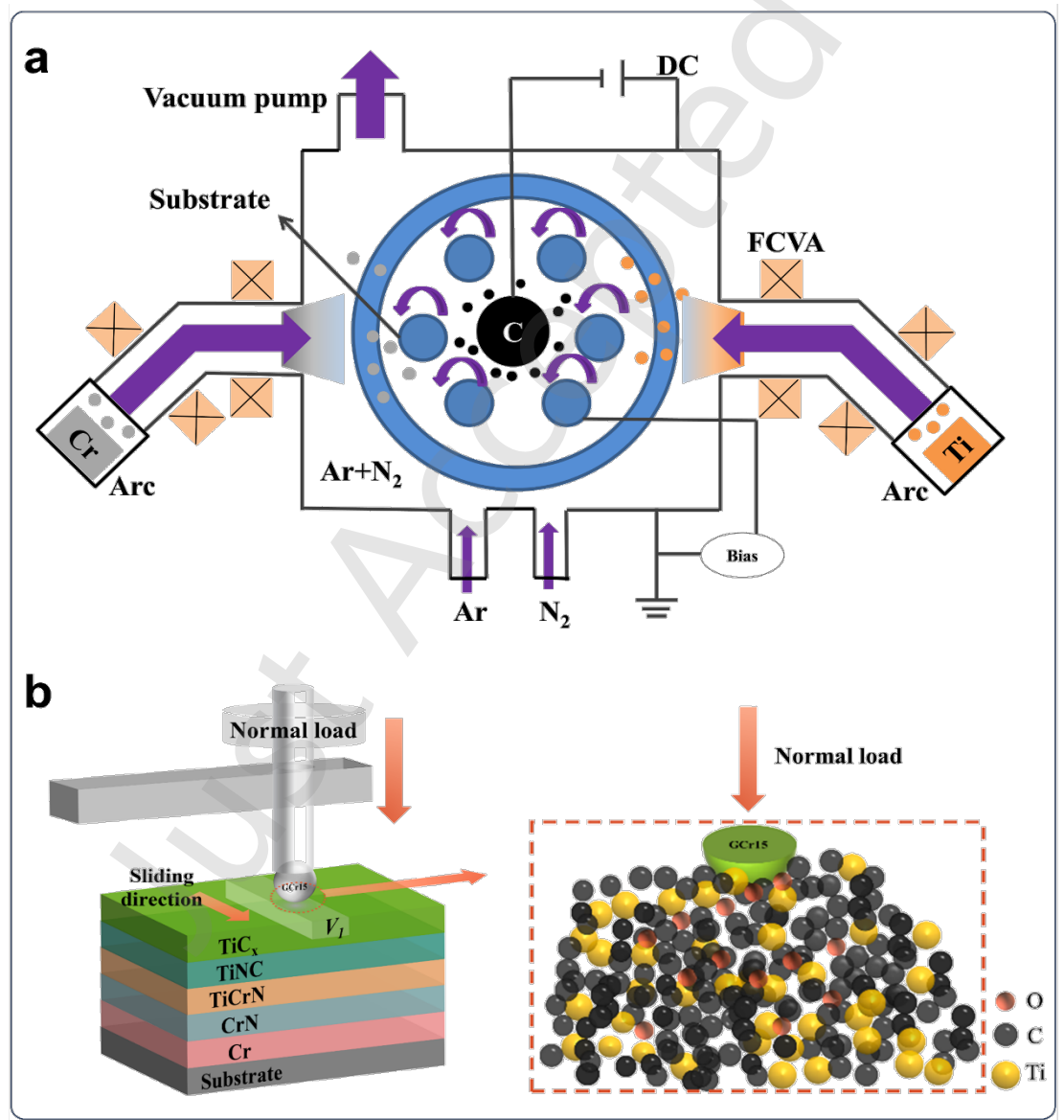


Fig. 1. (a) Schematic illustration of the multifunctional integrated magnetron sputtering (MS) system; (b) Schematic representation of the tribological test configuration.

Table 1. Deposition parameters for Cr/CrN/CrTiN/TiNC/TiC_x multilayer coatings prepared at different DC currents (4 A, 6 A, and 10 A).

Layer	Bias voltage (v)	Chromium target current (A)	Titanium target current (A)	Graphite target current (A)	Ar flow rate (sccm)	N ₂ flow rate (sccm)	Deposition Time (min)
Cr	75	160	0	0	100	0	60
CrN	75	160	0	0	100	50	60
CrTiN	75	160	160	0	100	50	60
TiCN	75	0	160	4	100	50	60
TiC	50	0	120	4/6/10	100	0	60

2.2. Characterization of coatings

The thickness and cross-sectional morphology of the TiC_x coatings were characterized by scanning electron microscopy (SEM, Apreo S, FEI, USA). The element composition and chemical bonding states were analyzed using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo-Fisher, USA). The bonding structure of the coatings, as well as the micro-Raman signals from counterface wear scars, were collected using a confocal micro-Raman spectrometer (LabRAM Evolution, HORIBA Jobin Yvon, France) equipped with a 532 nm laser. In addition, nanoscale tribolayers transferred from the TiC_x coatings to the counterfaces were extracted by focused ion beam milling (FIB-SEM, Helios 600, FEI, USA). These lamellae were subsequently examined by high-resolution transmission electron microscopy (HRTEM, TECNAL G2 STWIN F20, FEI, USA). The surface roughness and wear-track profiles of the coatings were further evaluated using three-dimensional (3D) optical profilometry (KLA-Tencor, USA).

2.3. Mechanical and tribological tests

The mechanical properties of the coatings were evaluated using a

nanindentation hardness tester (NHT3, Anton Paar, Germany). The measured parameters included hardness (H) and elastic modulus (E). A Berkovich diamond indenter was employed. the maximum indentation depth was limited to one-tenth of the coating thickness to minimize substrate effects. Five indentation points were selected on each sample, and their average values were reported as the final result.

Adhesion performance was evaluated using a standard scratch tester equipped with a conical diamond stylus with a spherical tip. For coatings deposited on GCr15 substrates, the stylus was drawn along a 5 mm scratch track while the normal load increased linearly from 0 to 80 N at a constant loading rate of 40 N/min.

Friction and wear tests were conducted using a ball-on-disc reciprocating tribometer (CSM, TRB3, Switzerland). The reciprocating stroke was set to 5 mm, and the sliding frequency was 5 Hz, with a total test duration of 1800 s. The maximum linear sliding speed reached 7.85 cm/s. All tests were performed in ambient air (30% RH) under a normal load of 5 N, using a GCr15 steel ball (Φ 6mm) as the counterface. Wear volumes were measured by three-dimensional (3D) profilometry, and the wear rates (W_r) of the coatings were calculated as follows:

$$W_r = V_1 / (F_N \times L) = (s \times l) / (F_N \times L) \quad (1)$$

where the V_1 is the wear volume of coatings (mm^3), s is the cross-sectional area of the wear track (mm^2) calculated by software, l is the wear-track length (mm), F_N is the applied normal load (N), and L is the total sliding distance (m). The wear scars on the GCr15 steel balls were examined using an optical microscope (Olympus BX51), and the wear volume of the ball scar (W_v) was calculated as follows:

$$W_v = \frac{\pi}{6} \left(r - \sqrt{r^2 - \frac{d^2}{4}} \right) \left(\frac{3d^2}{4} + r^2 - \frac{d^2}{4} \right) \quad (2)$$

where d is the wear scar diameter, and r is the radius of the GCr15 ball (3 mm). A Schematic diagram of the tribological test configuration is shown in **Fig. 1(b)**.

3. Results and discussion

3.1 Chemical composition and microstructure of the multilayer coatings

Raman spectroscopy is an effective, non-destructive tool for characterizing the detailed bonding structure of carbide coatings [16]. The Raman spectra of TiC_x coatings deposited on GCr15 substrates were deconvoluted into six peaks using Gaussian fitting, as shown in **Fig. 2(a)**. All coatings exhibit four characteristic TiC Raman bands, the two acoustic modes (TA and LA, 150-300 cm⁻¹) arise from vibrations of the heavy Ti ions, whereas the two optical modes (TO and LO, 400-650 cm⁻¹) are attributed to vibrations of the lighter C ions [17-19]. In addition, all coatings (except for TiC_{x-1}) display characteristic D peaks near 1350 cm⁻¹ and the G peaks near 1560 cm⁻¹. These correspond to the ring-breathing modes of sp²-hybridized carbon atoms (D peak) and the stretching vibration modes of all ring-like and chain-like sp²-C structures (G peak), respectively [20,21]. The microstructural characteristics of TiC_x coatings can thus be elucidated through analysis of Raman peak positions and intensities. The fitted data are summarized in **Fig. 2(a,m)** and **Table 2**. The intensity of the TiC Raman peaks progressively decreases with increasing DC current, and the most intense peak shifts toward lower wavenumbers. This behavior indicates a degradation in crystallinity, consistent with previous reports [17,22]. The TiC_{x-1} coating shows no pronounced D (~1360 cm⁻¹, disorder) and G (~1560 cm⁻¹, graphitic) bands, indicating the absence of

an amorphous carbon phase. This is likely due to the predominant combination of Ti and C atoms, leading to the formation of TiC ceramics, this is consistent with previous works [22,23]. As shown in **Fig. 2(m)**, the I_D/I_G ratio of the as-deposited coatings increases monotonically with increasing DC current, while the G peak position also shifts to higher wavenumbers. Generally, an increase in the I_D/I_G ratio and an upshift of the G peak indicate a higher content of sp^2 -C structures within TiC_x coatings. This structural transformation results in reduced coating hardness and enhanced graphitization.

This phenomenon can be attributed to the incorporation of Ti and C, which modifies the bonding configuration of the coating. Ti, as a strong carbide-forming element, readily forms thermodynamically stable metal carbides within the coating matrix. During co-deposition, Ti tends to aggregate into metal clusters and carbide nanoparticles, which in turn promotes an increase in the sp^2 -C content. Such structural modifications are likely responsible for the observed reduction in coating hardness. In summary, the simultaneous incorporation of Ti and C plays a decisive role in determining the composition and bonding states of the coating.

The cluster size of sp^2 -C (L_a), as listed in table 1, increases monotonically with increasing DC current. This trend is typically associated with enhanced graphitization of the TiC_x coatings, indicating a higher sp^2 -C content accompanied by a reduction in the sp^3 -C cluster size [24,25]. The calculation method for the sp^2 -C clusters is as follows:

$$I_D/I_G = C'(\lambda)L_a^2 \quad (3)$$

Where $C'(532) = 0.00625$ when $\lambda = 532$ nm [26].

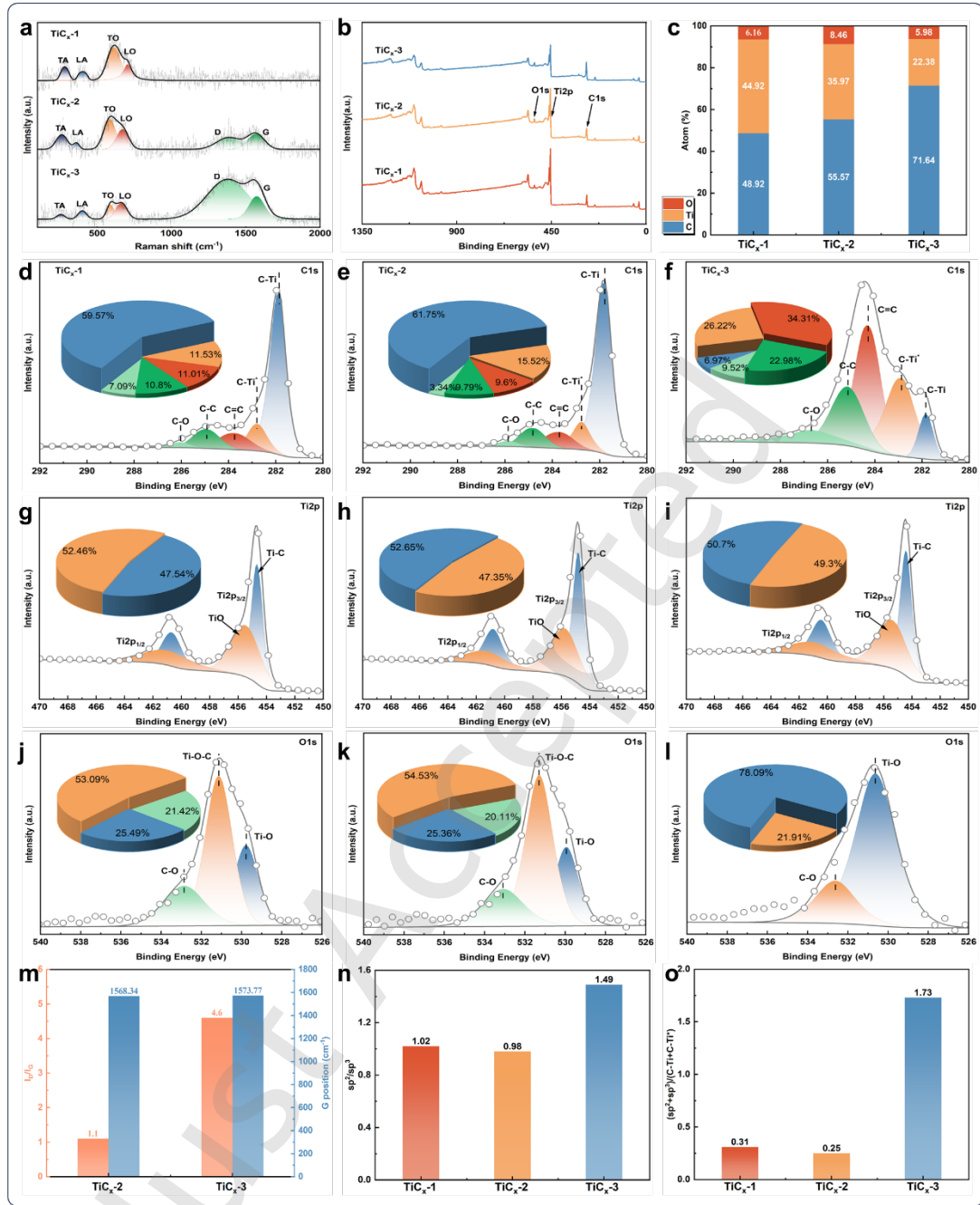


Fig. 2. (a) Raman spectra (b) XPS survey spectra, (c) element composition. High-resolution spectra of (d-f) C1s, (g-i) Ti2p, and (j-l) O1s for TiC_x coatings, (m) I_D/I_G ratio and G-peak position. (n-o) Bonding structure parameters derived from XPS fitting.

Table 2. Gaussian fitting parameters of Raman spectra for the TiC_x coatings

sample	TA	LA	TO	LO	D position (cm ⁻¹)	G Position (cm ⁻¹)	D peak area	G peak area	I _D /I _G	G peak FWHM (cm ⁻¹)	La
TiC _x -1	282.89	402.54	614.38	704.60	/	/	/	/	/	/	/
TiC _x -2	262.90	362.44	585.47	670.77	1385.70	1568.34	2876.06	2613.18	1.10	134.55	13.27

TiC _x -3	256.58	401.22	590.94	663.65	1379.32	1573.77	39748.56	8633.25	4.60	124.03	27.13
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Fig. 2 (b) presents the XPS survey spectra obtained after 60s of Ar ion etching at 2000 eV. The chemical compositions and atomic ratios of the TiC_x coatings derived from the survey spectra are summarized in **Fig. 2 (c)**. With increasing DC current, the carbon content increases from 48.92 at.% to 71.64 at.%, whereas the Ti content decreases accordingly. Meanwhile, the oxygen content remains nearly constant ($\approx 6-8$ at.%), and its presence is mainly attributed to incomplete vacuum conditions in the chamber, leading to oxidation during deposition, consequently, a small amount of TiO_x species is formed within the coatings. **Fig. 2(d-f)** present the high-resolution C1s spectrum. The spectra were deconvoluted into five components using Gaussian–Lorentzian fitting. These peaks correspond to C-O (286.2 ± 0.3 eV), C-C (285.0 ± 0.2 eV), C=C (283.9 ± 0.3 eV), C-Ti* (282.8 ± 0.1 eV) and C-Ti (281.8 ± 0.1 eV) bonds, respectively. No significant changes in the bonding types were observed for TiC_x coatings deposited under different DC currents. However, the relative fractions of these bonds vary significantly.

The fitting results indicate that the fractions of C=C and C-C bonds initially decrease and then increase with increasing DC current. In contrast, the C-Ti fraction shows an opposite trend, showing an initial increase followed by a decrease. As shown in **Fig. 2(n,o)**, the ratios of sp^2/sp^3 and $(sp^2+sp^3)/(C-Ti+C-Ti^*)$ display the same evolution, namely a decrease at low DC current followed by an increase at higher current. At low DC current, the spectra are dominated by C-Ti bonding, indicating that the coating structure is mainly composed of TiC_x phases. However, with increasing

current, the contribution of the amorphous carbon phase becomes progressively stronger. This trend is consistent with the Raman analysis and indicates enhanced graphitization of the carbon phase. This behavior can be attributed to the increased carbon content and the catalytic effect of Ti. On the one hand, higher DC current intensifies ion bombardment during deposition and promotes carbon incorporation into the TiC_x coating. The increased ion energy enables deeper carbon penetration into the coating matrix, resulting in higher fractions of both $\text{sp}^3\text{-C}$ and $\text{sp}^2\text{-C}$. On the other hand, Ti incorporation induces local rearrangement of carbon atoms, which favors the formation of C-Ti bonds. Such structural rearrangement further promotes the clustering of $\text{sp}^2\text{-C}$ and gradually leads to the development of more ordered carbon-layer structures.

Additional information can be obtained from the Ti2p and O1s spectra (**Fig. 2(g–l)**). The Ti2p spectra can be fitted with two components located at ~ 454.6 eV and ~ 455.5 eV, corresponding to Ti-C and Ti-O bonds, respectively. This result indicates that Ti mainly exists in the form of TiC_x and TiO_x within the coatings. Moreover, the relative fractions of Ti-C and Ti-O remain comparable for all coatings, suggesting that the Ti oxidation state does not change significantly with DC current. In contrast, the O1s spectra exhibit a noticeable evolution in bonding configuration. For the TiC_{x-1} and TiC_{x-2} coatings, three components centered at ~ 529.8 eV, ~ 531.1 eV, and ~ 532.8 eV are observed, which are assigned to Ti-O, Ti-O-C, and C-O bonds, respectively. The dominant Ti-O-C component suggests the presence of oxygen associated with interfacial structures between TiC_x phases and the carbon matrix. However, for the

TiC_x-3 coating the Ti-O-C component disappears, whereas the Ti-O contribution becomes dominant. This change indicates that increasing carbon content alters the coating structure. Specifically, the structure evolves from a TiC_x-rich nanocomposite toward a carbon-rich matrix containing dispersed TiC_x/TiO_x phases. Consequently, the TiC_x/C interfacial bonding decreases, and oxygen preferentially forms TiO_x species rather than Ti-O-C bridging bonds.

Fig. 3 presents the chemical composition and cross-sectional microstructure of the TiC_x coatings, the coating deposited on GCr15 steel substrates were sectioned by wire cutting, and the cross sections were subsequently polished to a mirror finish prior to observation. As shown in the SEM images in **Fig. 3(a-c)**, the coating thickness increases with increasing DC current, indicating an enhanced deposition rate under intensified ion bombardment. Moreover, the coatings deposited at different DC currents (4 A, 6 A, and 10 A) exhibit relatively dense cross-sectional morphologies, no distinct interfaces are observed between the transition layers, and no cracks are detected at the Cr interlayer/GCr15 substrate interface. These features indicate strong interfacial adhesion between the coatings and the substrate, which can be attribute to the high ion flux and ion energy during deposition. Meanwhile, the cross-sectional EDS mappings show well-defined elemental distributions, providing clear evidence for the multilayer architecture.

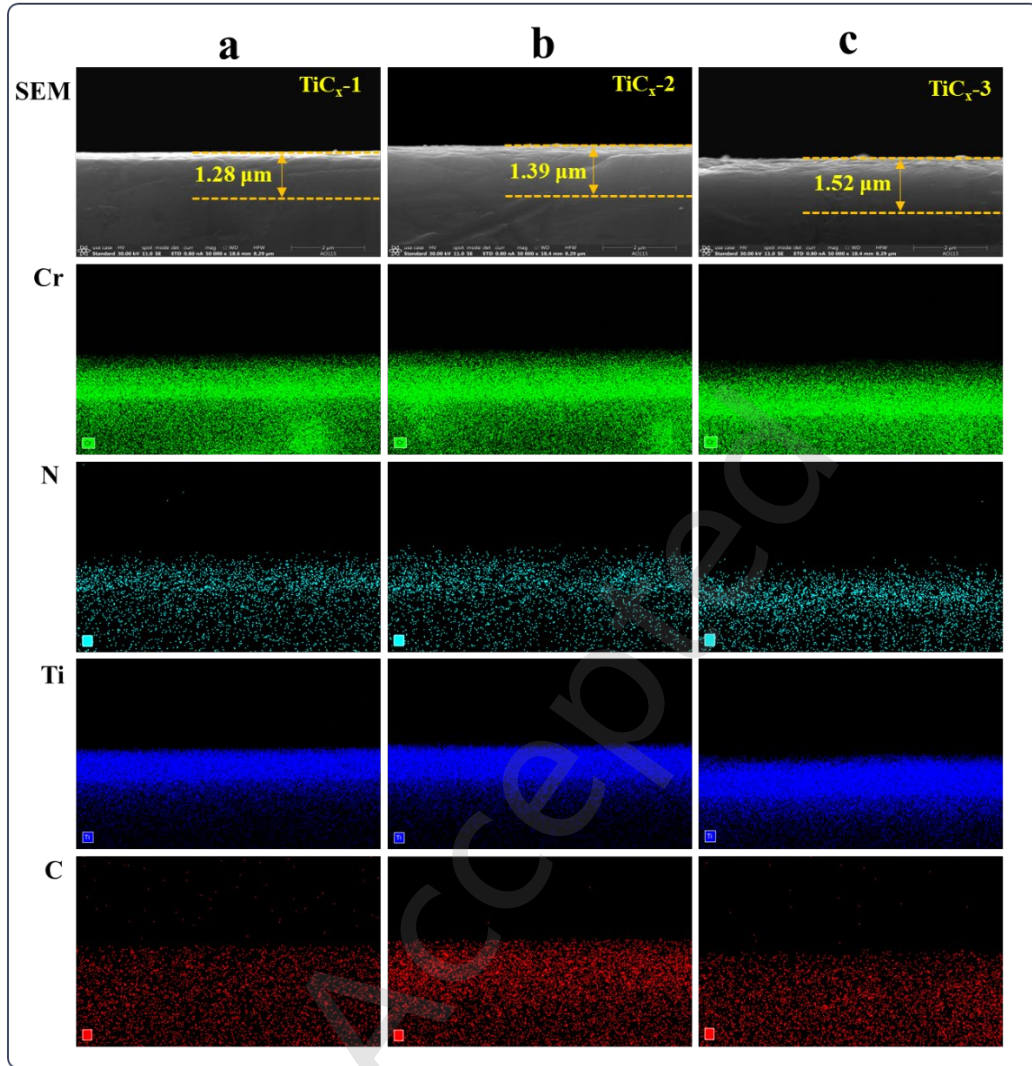


Fig. 3. (a) Cross-sectional morphology and corresponding EDS elemental mapping of TiC_x -1 coating; (b) cross-sectional morphology and corresponding EDS elemental mapping of TiC_x -2 coating; (c) cross-sectional morphology and corresponding EDS elemental mapping of TiC_x -3 coating.

3.2. Mechanical and tribological properties

Fig. 4(a-c) shows the surface morphologies of the as-fabricated TiC_x coatings prepared at different DC currents. All samples exhibit smooth and dense surfaces, with only minor height fluctuations. The surface roughness shows a clear dependence on the DC current. As summarized in **Fig. 4(j)**, the roughness increases monotonically with

increasing DC current. Nevertheless, even at higher currents, the coatings retain compact surface morphologies without observable surface defects.

Nanoindentation tests were performed to evaluate the mechanical properties of the TiC_x coatings, the corresponding load-displacement curves, obtained at a maximum indentation depth of 100 nm, are shown in **Fig. 4(d-f)**. A pronounced dependence of elastic recovery on DC current is observed. Among the three samples, the TiC_x -2 coating exhibits the highest elastic recovery, indicating superior elastic deformation capability. The TiC_x -1 coating shows a comparable but slightly lower recovery. By contrast, the TiC_x -3 coating displays the largest residual indentation depth, which suggests a reduced resistance to plastic deformation.

The quantitative mechanical properties, including hardness (H), elastic module (E), and the derived ratios H/E and H^3/E^2 , are summarized in **Fig. 4 (k,l)**. the TiC_x -1, TiC_x -2, and TiC_x -3 coatings exhibit hardness values of 42.79, 44.70, and 25.88 GPa, respectively. The corresponding elastic modulus values are 371.80, 390.21, and 318.39 GPa. All mechanical parameters exhibit a non-monotonic dependence on DC current. With increasing current, both hardness and elastic modulus initially increase and then decrease at higher current levels. A similar trend is observed for the H/E and H^3/E^2 ratios. Notably, the TiC_x -2 coating achieves the highest H/E and H^3/E^2 values, which are widely regarded as indicators of resistance to elastic strain to failure and plastic deformation. In contrast, the TiC_x -3 coating shows lowest values, reflecting inferior mechanical performance. The mechanical properties of the TiC_x -1 coating are comparable to those of TiC_x -2 but are slightly lower, consistent with the load-

displacement curve analysis.

It is worth noting that the hardness values obtained in this work are significantly higher than those reported for conventional TiC coatings. Typically, TiC coatings exhibit hardness values below 30 GPa, with average values of approximately 25 GPa under various deposition conditions [27-29]. This comparison clearly demonstrates the effectiveness of the present deposition strategy in enhancing the mechanical performance of TiC_x coatings.

Scratch test results further reveal a systematic evolution of interfacial adhesion strength with DC current. The critical load for adhesive failure (L_{c2}) increases monotonically from 43.75 N for the TiC_x-1 coating to 58.11 N for the TiC_x-3 coating, indicating a continuous enhancement of coating-substrate adhesion with increasing carbon target current.

Overall, the TiC_x-2 coating achieves an optimized balance between carbon-induced elastic compliance and TiC load-bearing capacity. Its superior elastic recovery, together with the highest H/E and H^3/E^2 ratios, indicates enhanced resistance to plastic deformation and improved mechanical reliability. In contrast, excessive carbon incorporation at high DC current in the TiC_x-3 coating leads to pronounced degradation of mechanical properties. This behavior can be attributed to the evolution of the bonding structure within the coatings. At moderate ion energies, the formation of strong Ti–C bonds and sp^3 -hybridized carbon structures is promoted. This facilitates the development of dense TiC nanophases or composite networks, resulting in effective dispersion strengthening. However, further increases in ion energy favor excessive

carbon enrichment and the formation of sp^2 -C, this weakens Ti-C bonding and promotes graphitization, which ultimately reduces hardness and elastic modulus. This interpretation is consistent with the Raman spectroscopic observations. Therefore, the TiC_x -2 coating exhibits superior mechanical performance, which is essential for improving wear resistance and impact tolerance in tribological applications.

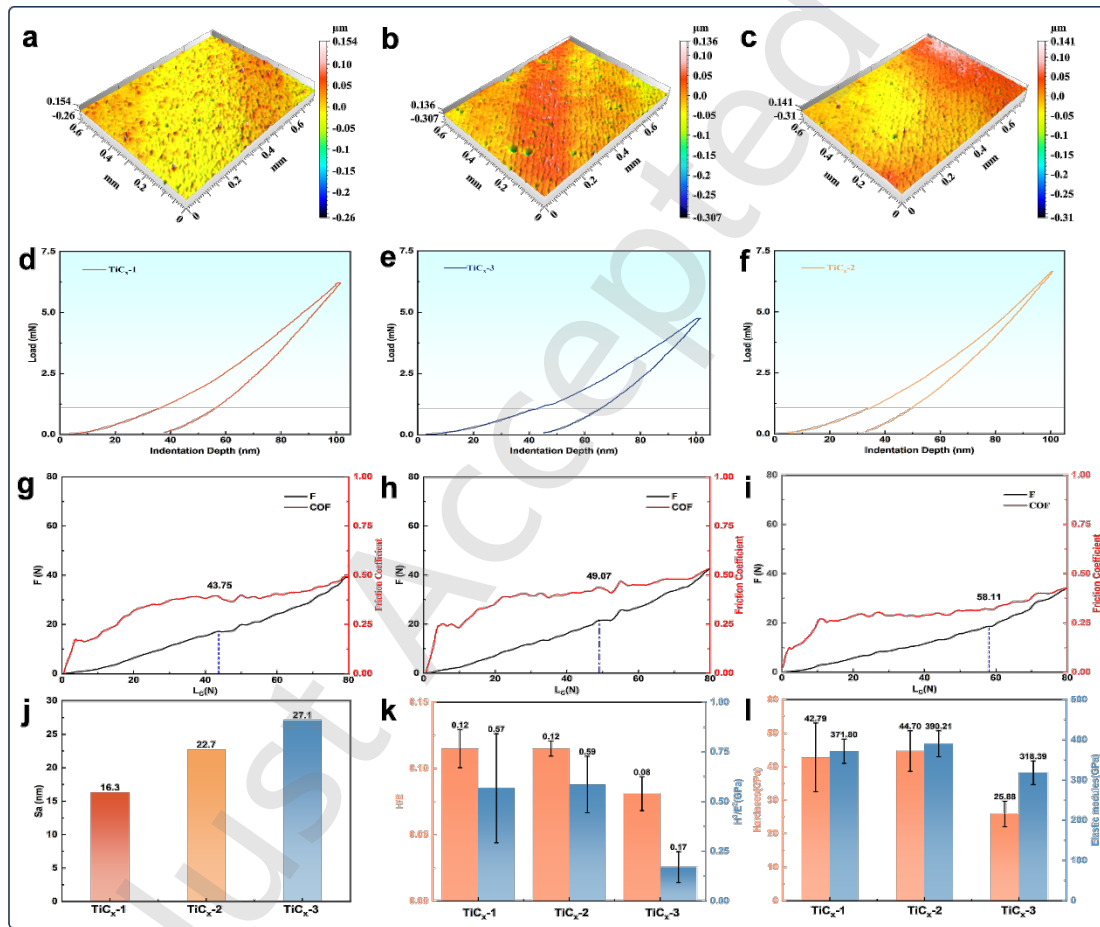


Fig. 4. Surface morphology and mechanical properties of TiC_x coatings deposited at different DC currents: (a-c) 3D surface topography; (d-f) nanoindentation load-displacement curves; (g-i) critical loads obtained from scratch tests; (j) surface roughness; (k) hardness and elastic modulus; (l) H/E and H^3/E^2 ratios.

3.3. Tribological performance of TiC_x coating

Fig. 5(a-c) show the friction coefficient (COF) curves of TiC_x coatings deposited

at different DC currents during sliding against GCr15 steel balls. The COF increases systematically with increasing DC current. The TiC_x-1 coating deposited at 4 A exhibits the lowest and most stable COF throughout the test, indicating favorable frictional behavior and a stable tribological interface. The TiC_x-2 coating deposited at 6 A shows a low and relatively stable COF, which can be attributed to the formation of a transfer film. In contrast, the TiC_x-3 coating deposited at 10 A displays a significantly higher COF with pronounced fluctuations, indicating unstable sliding conditions and intensified interfacial interactions.

Fig. 5(d-f) present the cross-sectional profiles of the wear tracks. The wear severity increases progressively with DC current. The TiC_x-1 and TiC_x-2 coatings exhibit relatively narrow wear tracks with clear ploughing grooves, which are characteristic of mild abrasive wear. In contrast, the TiC_x-3 coating shows the widest wear track without distinct ploughing features, indicating extensive material removal and severe wear damage. The 3D wear track profiles shown in **Fig. 5(g-i)** provide a more intuitive visualization of the wear morphology and are consistent with the cross-sectional results. Correspondingly, **Fig. 5(j-l)** display the 3D profiles of the wear scars on the counterpart balls, revealing a gradual enlargement of the real contact area with increasing DC current. Noticeable debris accumulation is observed on the wear scars of the TiC_x-2 and TiC_x-3 samples, with more severe agglomeration in the TiC_x-3 case. In contrast, no obvious debris accumulation is detected for the TiC_x-1 coating. The optical microscopy images in **Fig. 5(m)** further confirms these observations. Both the wear track width on the coatings and the wear scar diameter on the balls increase with

DC current, indicating an expansion of the contact area during sliding. Pronounced debris accumulation on the wear scars of the TiC_x-2 and TiC_x-3 samples is evident, which is in good agreement with the 3D morphological analysis.

Quantitative wear results are summarized in **Fig. 5(n, o)**. The wear rate of the TiC_x coatings increases monotonically with DC current. Similarly, the wear volume of the GCr15 balls increases with DC current. These results indicate that the TiC_x-1 and TiC_x-2 coating exhibit good wear resistance, whereas the TiC_x-3 coating shows inferior wear performance. The friction and wear behaviors are closely related to the structural and mechanical characteristics of the TiC_x coatings. Raman and XPS analyses reveal that increasing DC current leads to a higher sp²/sp³ ratio and enhanced graphitization, accompanied by a gradual reduction in Ti-C bonding. At lower DC currents, moderate ion bombardment promotes the formation of TiC nanophases embedded in a dense amorphous carbon matrix with relatively high sp³ content. Together with the higher hardness measured by nanoindentation, these coatings exhibit a reduced real contact area and enhanced resistance to plastic deformation, as a result, a low and stable COF is maintained. Meanwhile, a limited amount of sp²-bonded carbon provides graphite-like lubricity, which further stabilizes the tribological interface.

Overall, the TiC_x-1 coating deposited at 4 A exhibits the most favorable tribological performance. It is characterized by a low and stable friction coefficient, mild wear morphology, and reduced wear of both the coating and the counterpart ball. In contrast, the TiC_x-3 coating deposited at 10 A suffers from unstable friction behavior and severe wear damage. This degradation can be attributed to excessive graphitization,

reduced mechanical integrity, and increased surface roughness. These results demonstrate that a moderate DC current enables an optimized balance among microstructure, mechanical properties, and tribological performance in TiC_x coatings.

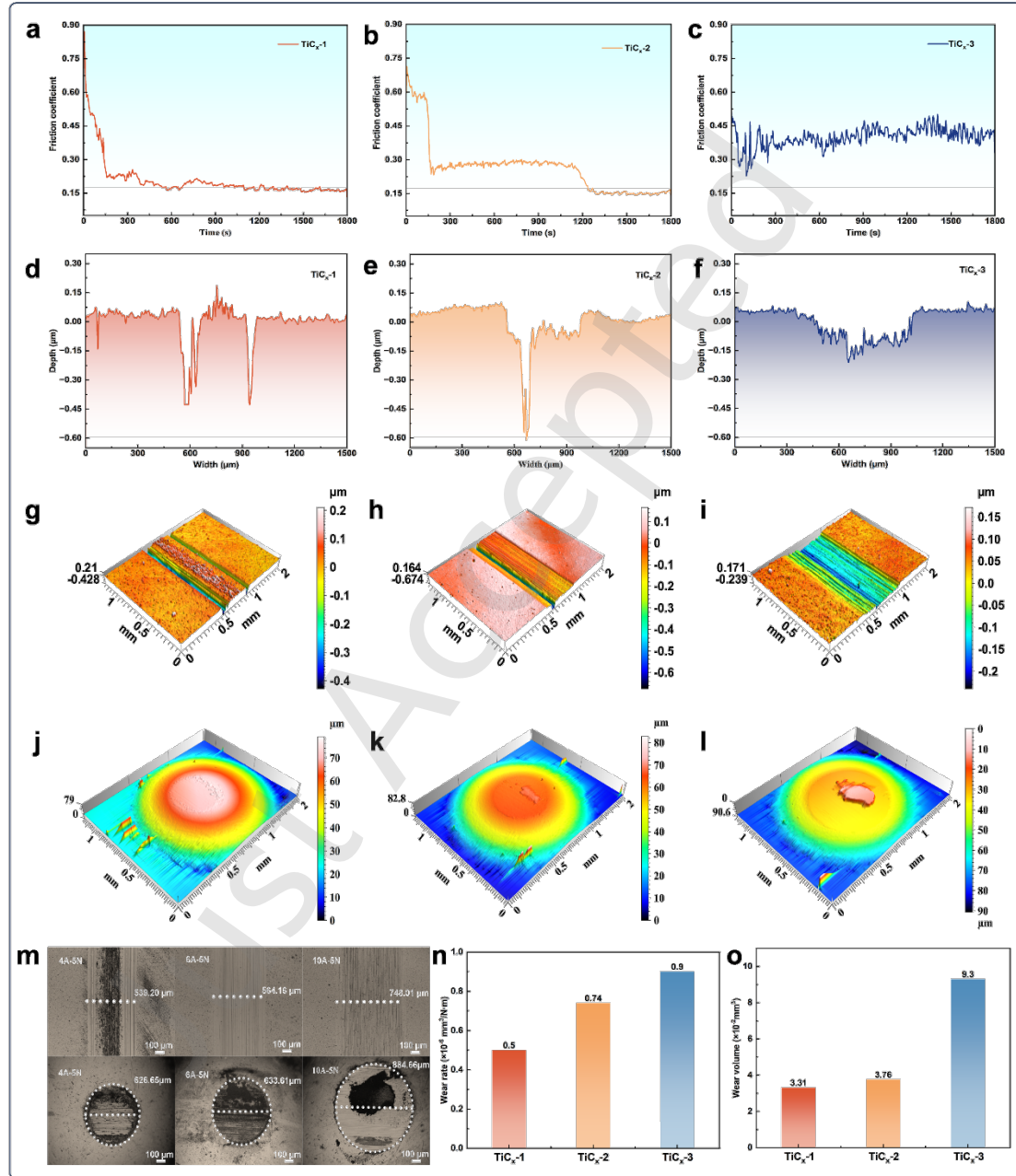


Fig. 5. (a-c) Friction coefficient curves of TiC_x coatings deposited at different DC currents; (d-f) cross-sectional wear depth profiles of the wear tracks; (g-i) 3D profile of wear tracks, (j-l) 3D profile of wear scars on the GCr15 balls; (m) optical microscopy images of the wear tracks and corresponding wear scars; (n) wear rates of the TiC_x coatings; and (o) wear volumes of the GCr15

balls after sliding against TiC_x-coated GCr15 substrates.

3.4. Friction mechanism of TiC_x coatings at ambient environment

To further elucidate the lubrication mechanism of TiC_x coatings under ambient conditions, the friction pairs was examined in detail. Raman spectra obtained from wear scars after a 30 min sliding test are shown in **Fig. 6(a)**. The Raman signals of the transfer films formed on the GCr15 balls were deconvoluted into three characteristic bands in the range of 1000-2000 cm⁻¹, corresponding to the T peak (~1080 cm⁻¹), the D peak (~1360 cm⁻¹), and the G peak (~1590 cm⁻¹). The T peak is associated with vibrational modes of sp³-bonded carbon. the quantitative fitting results are summarized in **Table 3**. Under a normal load of 5 N, a consistent decrease in the I_D/I_G ratio is observed for the transfer films on the GCr15 ball surfaces, indicating a reduced degree of graphitization after sliding. **Figs 6(b)** and **6(c)** correlate the friction coefficient with the I_D/I_G ratios of the pristine coatings and the transfer films, respectively. Notably, opposite trends are observed for these two cases. For the TiC_x coatings, a higher degree of graphitization corresponds to a higher friction coefficient. In contrast, for the transfer films on the counterface, a higher I_D/I_G ratio, reflecting a more developed sp²-dominated carbon structure, correlates with a lower friction coefficient. These results demonstrate that the friction behavior is not solely determined by the initial coating structure, but is predominantly governed by the structure of the tribo-induced transfer film.

Among the three samples, the transfer film formed during sliding against the TiC_x-1 coating exhibits the highest I_D/I_G ratio, followed by TiC_x-2, whereas TiC_x-3 shows the lowest value. This trend suggests a gradual decrease in the graphitization degree of the

transfer film with decreasing Ti content, which is consistent with the corresponding increase in friction coefficient observed during sliding. Therefore, the graphitization degree of the transfer film can be regarded as a key factor governing friction reduction. During sliding, Ti-C bonds in the TiC_x-1 coating are more prone to rupture, releasing Ti species that promote the reorganization of carbon into more ordered sp² structures at the sliding interface. Meanwhile, these Ti species can react with oxygen from the ambient environment to form TiO₂. The generated TiO₂ is proposed to act as a mechanically stable supporting phase, which protects the graphitized carbon structure from severe mechanical damage during sliding[30]. In contrast, the lower Ti content in the TiC_x-3 coating is insufficient to provide such interfacial support. As a results, the transfer film becomes less stable, leading to a higher and more fluctuating friction coefficient. **Fig. 6(d, e)** illustrate the relationships between I_D/I_G and wear rate, revealing trends similar to those observed for friction behavior. A higher I_D/I_G ratio in the TiC_x coatings corresponds to a higher wear rate, whereas a higher I_D/I_G ratio in the transfer films corresponds to a lower wear rate. This observation further confirms that a highly graphitized and stable transfer film plays a dominant role in reducing both friction and wear.

From a mechanical perspective, **Fig. 6(f, g)** show the correlations between the H/E and H³/E² ratios and the wear rate. Both parameters exhibit a non-monotonic dependence, increasing initially and then decreasing with DC current. The TiC_x-1 and TiC_x-2 coatings display relatively higher H/E and H³/E² values, indicating superior elastic strain tolerance and fracture resistance. These characteristics effectively

suppress plastic deformation and crack propagation during sliding, thereby resulting in lower wear rates. In contrast, the TiC_x-3 coating exhibits the lowest H/E and H³/E² values and consequently the poorest wear resistance, which is consistent with the tribological results. **Fig. 6(h)** summarizes the relationship between friction coefficient and wear rate. The TiC_x-1 coating exhibits both lowest friction coefficient and the lowest wear rate, whereas the TiC_x-3 coating shows the highest values for both parameters. The comprehensive performance of the coatings is further illustrated by the radar chart in **Fig. 6(i)**, which integrates hardness, elastic modulus, wear rate, ball wear volume, and friction coefficient. Among the three samples, TiC_x-1 demonstrates the best overall performance, followed by TiC_x-2, while TiC_x-3 exhibits the weakest comprehensive performance.

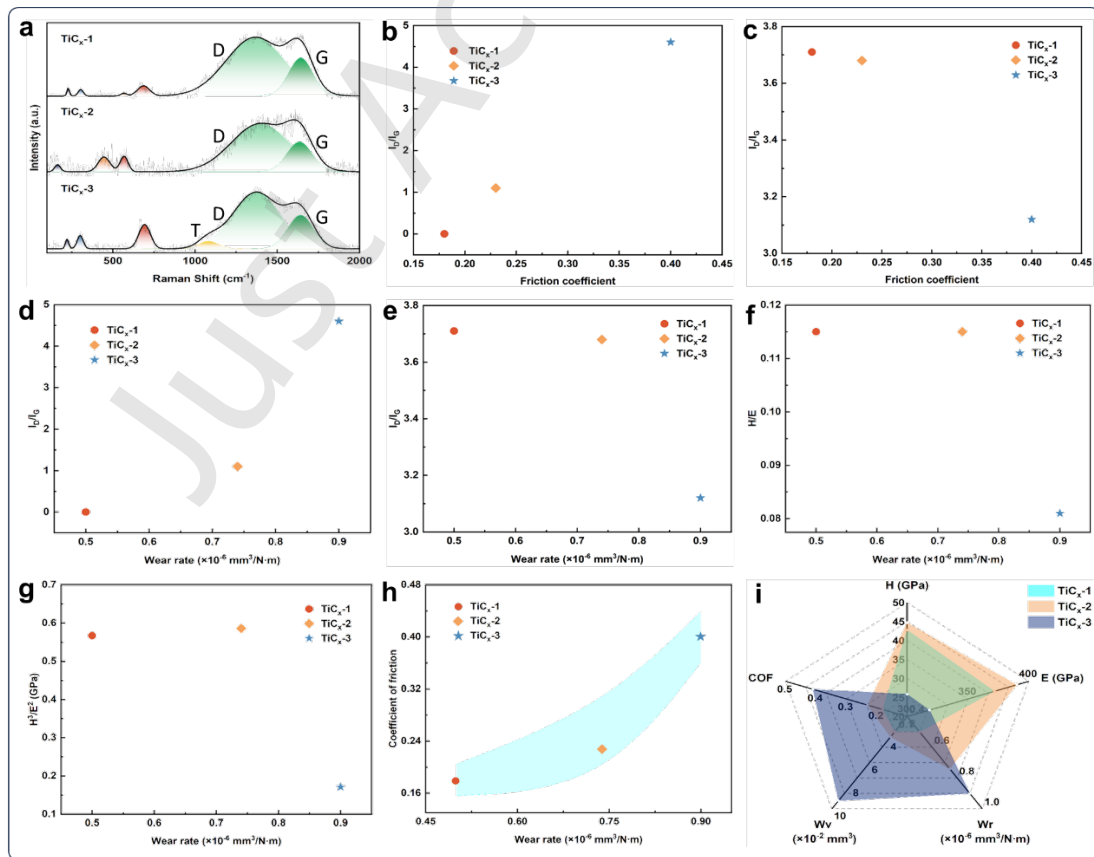


Fig. 6. (a) Raman spectra of wear scars; (b) correlation between the I_D/I_G ratio of TiC_x coatings

and the friction coefficient; (c) correlation between the I_D/I_G ratio of wear scars and the friction coefficient; (d) correlation between the I_D/I_G ratio of TiC_x coatings and the wear rate; (e) correlation between the I_D/I_G ratio of wear scars and the wear rate; (f) correlation between the H/E ratio and the wear rate; (g) correlation between the H^3/E^2 ratio and the wear rate; (h) correlation between the friction coefficient and the wear rate; and (i) radar chart summarizing the key mechanical and tribological parameters.

Overall, the tribological behavior of TiC_x coatings is governed by the synergistic effects of Ti-induced graphitized transfer film formation, TiO_2 -assisted interfacial stabilization, and optimized elastic-plastic mechanical properties. Among the investigated samples, the TiC_{x-1} coating achieves the most favorable balance between interfacial chemistry, structural evolution, and mechanical response. As a result, it exhibits the lowest friction coefficient and the best overall tribological performance under ambient conditions.

Table 3. Gaussian fitting parameters of the Raman spectra for the transfer coatings formed on the GCr15 ball surfaces.

sample	D position (cm^{-1})	G position (cm^{-1})	D peak area	G peak area	I_D/I_G	La
4A	1366.88	1642.36	574750.78	154780.27	3.71	24.36
6A	1397.23	1635.04	97753.58	26562.83	3.68	24.27
10A	1372.26	1641.39	356562.60	114190.54	3.12	22.34

To further clarify the lubrication and wear mechanisms of the TiC_x coatings, focused ion beam high-resolution transmission electron microscopy (FIB-HRTEM) analyses was conducted on the transfer films formed on the GCr15 balls after sliding

against the TiC_x-1 and TiC_x-3 coatings, as illustrated in **Fig. 7** and **8**. **Fig. 7** presents the bright-field (BF) TEM images together with corresponding EDS analyses of the transfer films. As illustrated schematically, the cross-sectional structure can be divided into three distinct regions: a top Pt protective layer, a middle transfer-film layer, and the GCr15 steel substrate. For the TiC_x-1 sample (**Fig. 7(a)**), the transfer film is relatively thin, with a thickness of about 40 nm. Discrete TiC particles are embedded within the transfer layer, and shallowly distributed TiO₂ nanoparticles are also observed. The corresponding EDS elemental maps (**Fig. 7(b)**) show high contents of Fe and O, whereas Ti and C are present at lower levels. Ti is mainly concentrated in the middle region of the transfer film, while carbon tends to distribute around oxide-rich areas. The nearly overlapping distributions of Fe and O indicate the formation of iron oxides through tribochemical oxidation during sliding. In contrast, the transfer film formed against the TiC_x-3 coating (**Fig. 7(c)**) is significantly thicker, reaching approximately 195 nm. Here, TiC nanoparticles are more uniformly dispersed within the transfer layer, while TiO₂ is only sparsely observed near the Pt protective layer and is barely distinguishable elsewhere. The EDS results reveal the highest oxygen content among the detected elements, together with relatively low Ti and C contents. Ti is homogeneously distributed throughout the transfer film, whereas Fe and O again exhibit similar spatial distributions, confirming that oxidation reactions dominate at the sliding interface. Compared with the TiC_x-1 coating, the limited amount of TiO₂ in the TiC_x-3 case appears insufficient to suppress continuous oxidation during sliding. As a result, the progressive formation of iron oxides destabilizes the sp²-C structure at the

interface, leading to pronounced friction fluctuations and continuous thickening of the transfer film.

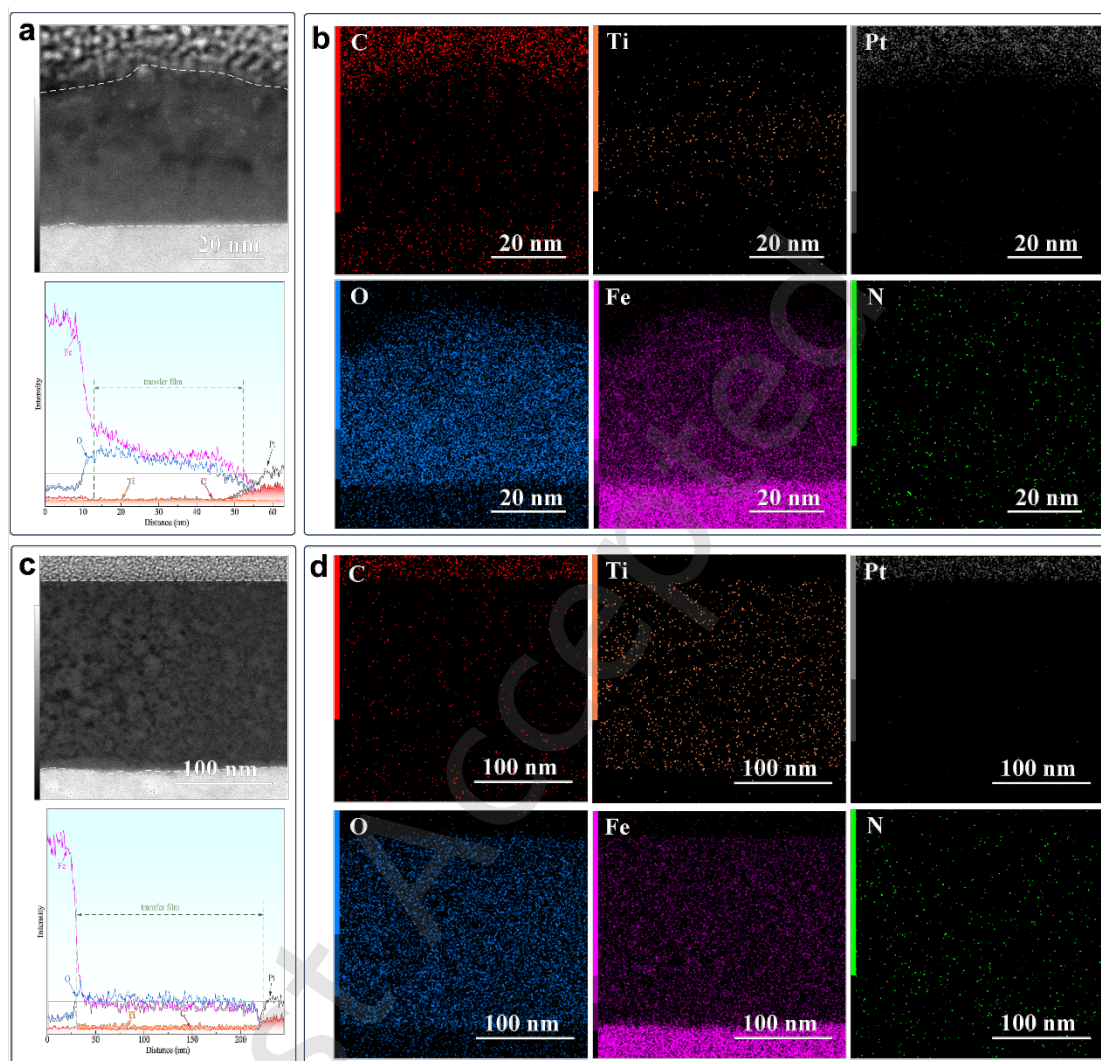


Fig. 7. HRTEM images and corresponding EDS analyses of transfer films formed on GCr15 balls after sliding against (a, b) TiCx-1 and (c, d) TiCx-3 coatings.

Further insights into the microstructural characteristics of the transfer films were obtained by HRTEM, as shown in Fig. 8. For the transfer film derived from the TiCx-1 coating (**Fig. 8 (a,b)**), the near-surface region is mainly composed of crystalline brookite TiO₂, whereas the region adjacent to the substrate is dominated by γ -Fe₂O₃. The remaining regions are largely amorphous iron oxides. The presence of TiO₂ within

the transfer film is considered to provide mechanical support and structural stabilization, thereby protecting the graphitized sp^2 -carbon network from severe mechanical disruption during sliding. In contrast, the transfer film formed against the TiC_x -3 coating (**Fig. 8(c, d)**) is dominated by γ - Fe_2O_3 crystals in both the near-surface and near-substrate regions, with the remaining phase being largely amorphous oxides. Only trace amounts of TiO_2 are detected, which are insufficient to provide effective structural reinforcement. This microstructural feature is consistent with the inferior tribological stability observed for the TiC_x -3 coating.

Overall, the favorable lubricating behavior of TiC_x coatings in ambient air can be attributed to the multifunctional role of Ti during sliding. Ti facilitates the formation of a graphitized transfer layer through Ti-C bond rupture and subsequent carbon reorganization. Meanwhile, Ti reacts with oxygen to generate TiO_2 within the transfer film. The TiO_2 phase provides a mechanically stable supporting framework, while graphitized carbon tends to surround the oxide phases. Together, they form a low-shear-strength lubricating layer. In addition, Ti incorporation promotes the formation of hard TiC phases within the coating. This enhances coating hardness and reduces counterball wear, thereby improving overall wear resistance.

Consequently, the TiC_x coatings operate under a mixed lubrication regime governed by the synergistic effects of tribo-induced graphitized transfer film formation, tribochemical oxidation reactions, and optimized mechanical properties of the coating system. As shown in **Fig. 9(a, b)** and **Table 4**, compared with previously reported works, the TiC_x -1 coating demonstrates a competitively low friction coefficient and a favorable

overall tribological performance under ambient conditions [27-29,31,32]. Unlike the humidity-sensitive lubrication of pure carbon films or the Si-OH passivation mechanism in Si-doped DLCs [7-9], the in-situ formed TiO_2 in our TiC_x coatings establishes a humidity-insensitive, mechanically robust Ti-O network. This network effectively stabilizes the graphitized carbon transfer film and mitigates its oxidation into high-shear iron oxides, thereby ensuring low and stable friction in ambient air (30% RH). A schematic illustration of the proposed lubrication and wear mechanism is summarized in Fig. 9(c).

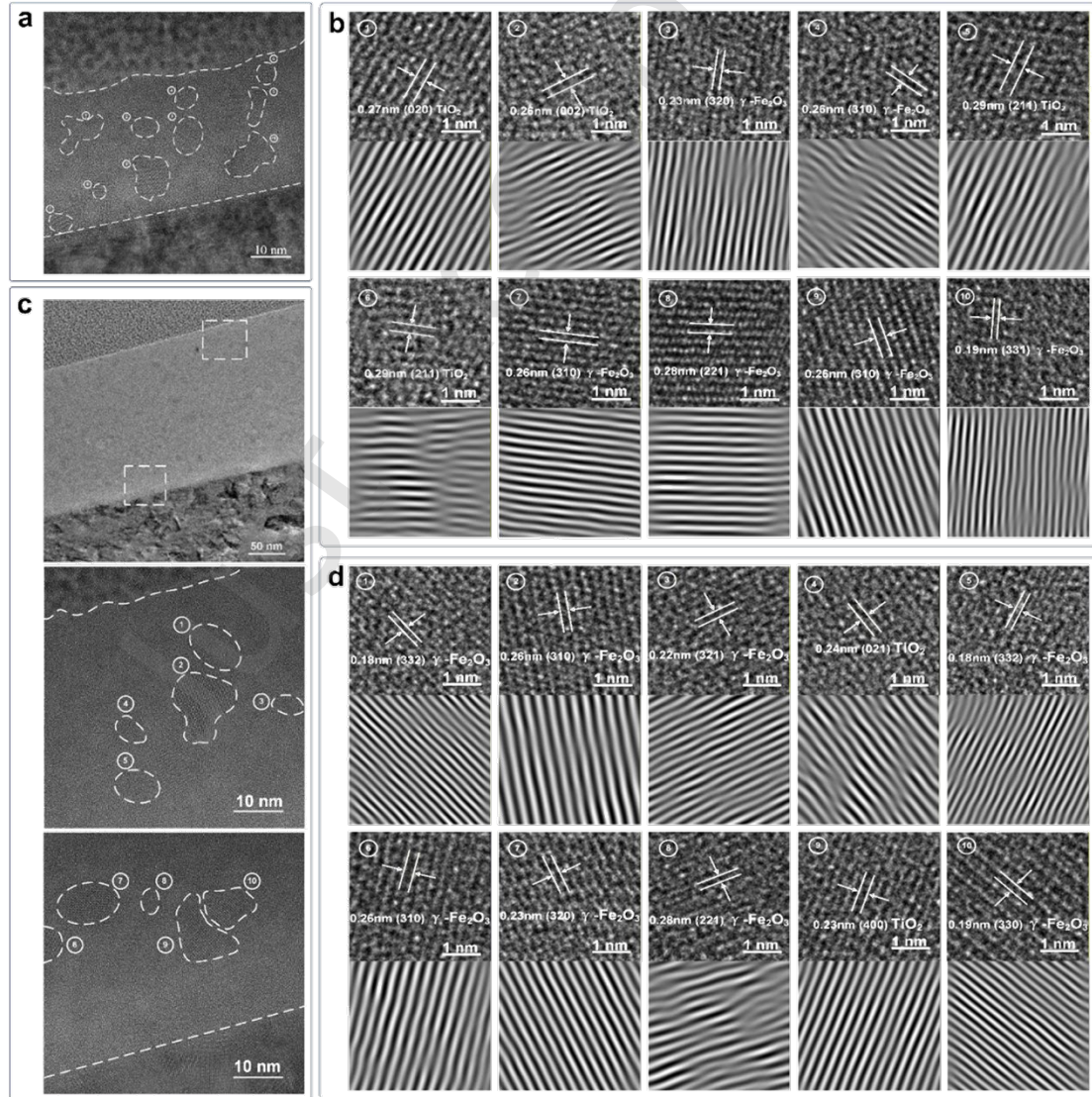


Fig. 8. HRTEM analysis of transfer films formed on GCr15 balls after sliding against TiC_x

coatings: (a) Overview HRTEM image of the transfer film generated from the TiC_x-1 coating; (b) HRTEM image of the selected region in (a), together with the corresponding inverse fast Fourier transform (IFFT) image; (c) Overview HRTEM image of the transfer film generated from the TiC_x-3 coating; and (d) HRTEM image of the selected region in (c), together with the corresponding inverse fast Fourier transform (IFFT) image.

Table 4. Comparison of deposition conditions and tribological properties of TiC_x coatings reported in the literature.

Material	COF	Wear rate ($\times 10^{-6}$ mm ³ /N·m)	Hardness (GPa)	Deposition method	Refs
TiC _x	0.3	10	24	UBMS	[28]
TiC _x	0.22	5.1	28	pDCMS	[27]
TiC _x	0.22	0.86	36	MS	[29]
TiC _x	0.18	0.4	29.4	SPS	[31]
TiC _x	0.19	0.7	29.4	SPS	[32]

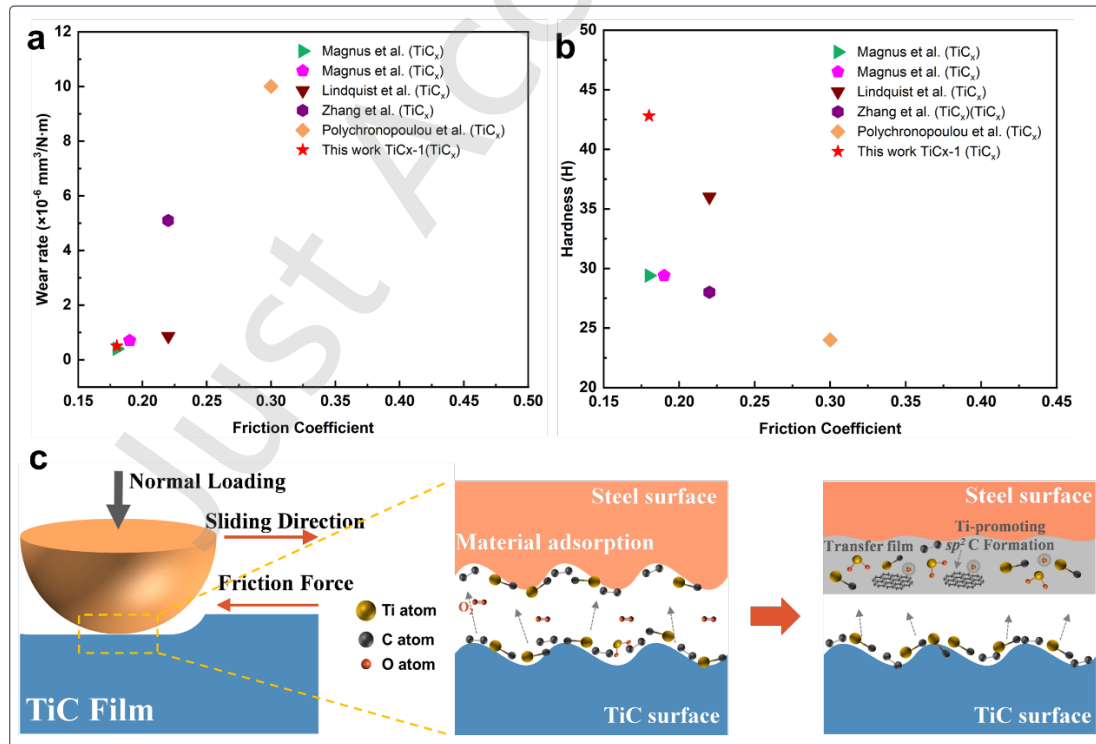


Fig. 9. Correlations between the friction coefficient and wear rate (a) as well as hardness (b); (c) Lubrication mechanism of multilayer TiC_x coating.

4. Conclusion

In this work, TiC_x coatings with tunable carbon content were fabricated on GCr15

bearing steel using a hybrid deposition strategy combining magnetic filtered cathodic arc ion sputtering and magnetron sputtering. Dense Cr/CrN/CrTiN/TiCN graded interlayers ensured strong adhesion and a smooth mechanical transition from the steel substrate to the TiC_x top layer, providing a robust structural foundation for tribological performance.

The results reveal that increasing the carbon target DC current drives a gradual transition from TiC-dominated bonding to carbon-rich structures with higher sp² content. Moderate carbon incorporation promotes the formation of a dense nc-TiC/a-C nanocomposite structure, which optimizes hardness, elastic strain tolerance, and load-bearing capability.

Tribological tests under ambient conditions demonstrate that friction and wear behavior are governed by the coupled effects of coating mechanical properties and the structure of the tribo-induced transfer films. The TiC_x-1 coating deposited at a DC current of 4 A exhibits the most favorable performance, achieving high hardness (~43 GPa), a low friction coefficient (~0.18), and excellent wear resistance.

More importantly, Raman spectroscopy and FIB-HRTEM analyses reveal that tribological performance is primarily controlled by the structure and stability of the transfer film. Ti promotes carbon reorganization and facilitates the formation of a graphitized sp²-rich transfer layer with low shear strength, while the simultaneous formation of TiO₂ provides mechanical support and interfacial stabilization. The synergistic coexistence of graphitized carbon and TiO₂ establishes a stable mixed-lubrication regime under ambient conditions.

Overall, this work clarifies the coupled roles of graded interfacial architecture, carbon bonding evolution, and Ti-assisted transfer-film formation in regulating the tribological behavior of TiC_x coatings. These findings provide practical guidance for designing high-hardness, low-friction carbide-based coatings for advanced engineering applications.

CRedit authorship contribution statement

XXX: Writing – review & editing, Methodology, Investigation, Validation. **XXX:** Methodology, Software, Formal analysis, Data curation. **XXX:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Project administration, Conceptualization. **XXX:** Resources, Investigation, Visualization. **XXX:** Project administration, Validation, Resources. **XXX:** Supervision, Funding acquisition, Writing – review & editing, Investigation.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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