

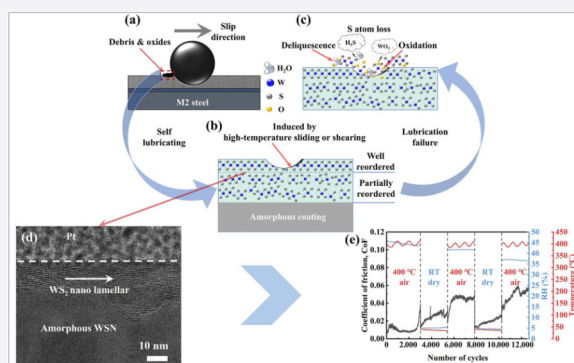
Temperature-insensitive ultralow lubrication of sputtered WSN coatings: Insights into constant, ramping, and cycling temperatures from room to 400 °C

Zhonghao Liu¹, Jiahui Qi², Shang Li¹, Xuanpu Dong¹, W. Mark Rainforth², Yutao Pei³, Ying Chen⁴, Xiangli Zhong⁴, Mingwen Bai⁵, Jeff Th. M. De Hosson⁶, Huatang Cao¹✉

✉ Cite this article: Liu ZH, Qi JH, Li S, et al. *Friction* 2026, **14**(4): 9441138. <https://doi.org/10.26599/FRICT.2025.9441138>

ABSTRACT: This study introduces a breakthrough in self-lubricating WS₂-nitrogen (WSN) coatings engineered for demanding applications across industries requiring adaptive durability and high performance. Deposited via nonequilibrium reactive magnetron sputtering in N₂-containing atmospheres, the WSN coatings demonstrate exceptional tribological behavior across a range of extreme conditions, including constantly discrete high temperatures, ramping temperatures either during heating or cooling and wide temperature cycling from room temperature to 400 °C. The WSN coatings exhibit an extremely low coefficient of friction (CoF = 0.02) up to 400 °C, with high thermal stability and superior triboproperty. Moreover, the coatings possess favorable tribo-reversibility under 400 °C ↔ room temperature cycles. Transmission electron microscopy analysis verified the self-lubricating, tribologically reversible, and ultralow lubrication mechanisms of the WSN coatings. However, under high-temperature tribosliding, the WS₂ layer still dynamically forms a self-organized, layered interface structure that continuously adapts to sliding conditions, ultimately enabling sustained superlubricity and tribological reversibility. Oxidation during high-temperature tribosliding actually has only a minor degrading effect on friction provided that the coatings retain sufficient sulfur to predominantly form WS₂ lubricant agents. This study provides novel insights into the development of advanced tribocoatings exhibiting adaptive ultralubrication under various temperature conditions.

KEYWORDS: tungsten disulfide; magnetron sputtering; nanocomposite coating; tribology; adaptive lubrication; cyclic temperatures



1 Introduction

The key function of solid lubricants is to attain ultralow friction and high wear resistance, as well as stability, reversibility in variable environments, and prolonged service life where liquid lubrications are discouraged [1, 2]. Workpieces are frequently subjected to irregular or cyclic environmental changes under certain service conditions. For example, the solid lubrication of aerospace equipment faces challenges such as limited service life, poor stability, temperature sensitivity, and irreversible tribological properties. These issues are particularly severe during spacecraft round trips between the ground (high temperature, humidity) and

space (low or even negative temperatures, vacuum conditions, and atomic oxygen). Under such extreme conditions, current solid lubricant coatings are prone to failure and cannot meet stable low-friction and high wear resistance requirements [3–5]. In particular, environmentally self-adaptive solid lubricating coatings with sustained ultralow lubricity under multiple special temperature conditions (e.g., discrete high temperatures, continuously ramping temperatures either in heating or cooling and wide-temperature range cycles) are urgently needed for high-end precision devices.

Although certain studies have achieved tribo-reversibility in solid lubricant coatings currently used in multiple-temperature

¹ State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China. ² Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, UK. ³ Engineering and Technology Institute Groningen, University of Groningen, Nijenborgh 4, 9747AG, the Netherlands. ⁴ Henry Royce Institute, Department of Materials, University of Manchester, Manchester M13 9PL, UK. ⁵ School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, UK. ⁶ Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG Groningen, the Netherlands.

✉ Corresponding author. E-mail: caoht@hust.edu.cn

Received: February 6, 2025; Revised: May 20, 2025; Accepted: June 22, 2025

© The Author(s) 2026. This is an open access article under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0, <http://creativecommons.org/licenses/by/4.0/>).

environments, the coefficient of friction (CoF) mostly remains extraordinarily high and unstable. When the coating returns from high temperatures to room temperature (RT), its lubrication rapidly fails, indicating a loss of tribo-reversibility. For example, a lubricating coating consisting of a yttria-stabilized zirconia (YSZ) oxide matrix can effectively lubricate at 500 °C (CoF < 0.4). However, lubrication rapidly fails at RT (CoF > 0.8). While tribo-reversibility under temperature cycling can be accomplished through the construction of a nanocomposite multilayer structure, the CoF tends to be excessively high (CoF > 0.4) [6]. The TiC/a-C coating maintains thermal stability when annealed at 350 °C, but it fails to provide lubrication at only 210 °C with a continuously increasing ramping temperature [7]. The MoCN–Ag and NiMoAl–Ag–WS₂ coatings are effective for continuous friction applications over a temperature range of 25–700 °C. However, the incompatibility of lubrication due to complex tribological byproducts at different high-temperature ranges causes large CoF fluctuations and discontinuities [8, 9]. A recent SiN_x ceramic phase was introduced to construct a Mo₂N–Ag–SiN_x multilayer composite coating, effectively balancing diffusion control of the lubricating phase with the development of tribolayers. This composite coating demonstrates tribo-reversibility over temperature cycles from RT to 500 °C; however, the CoF remains relatively high (> ~0.4), limiting its potential applications for ultralow lubrication engineering demands [10, 11].

WS₂ is a two-dimensional layered substance that is composed of a layer of tungsten atoms sandwiched between two layers of sulfur atoms. The layers are held together by weak van der Waals forces, while the atoms within each layer are connected by covalent bonds. This unique structure enables the layers to slide effortlessly, thereby delivering exceptional lubrication potentials. As a result, WS₂ is extensively employed in aerospace, automotive, and industrial equipment because of its excellent lubricating properties [12, 13]. However, WS₂ coatings react easily with atmospheric oxygen and moisture, consequently degrading their low friction potentials in extreme environments such as humid and oxygen [3]. In addition, their low hardness and load-bearing capacity could further limit their applications due to high probabilities of premature mechanical failure. However, the hardness of pure WS₂ is quite low (< 0.5 GPa), which is susceptible to easy wear loss and oxidation failure (WS₂ → WO₃) in humid and high-temperature environments, resulting in failure of lubricating functionalities [14, 15]. The aforementioned factors restrict the application of WS₂ solid lubricating coatings under extreme conditions, such as high-temperature changes and a wide temperature range of cycles.

Previous studies have shown that alloying WS₂ with certain metals (Ti, Cr, Ag, and Au [16–19]) and nonmetals (C and N [20, 21]) could improve the load-bearing capacity, increase the hardness, and increase the oxidation resistance. Studies on the doping of WS₂ have revealed that alloying can effectively improve the coating hardness and overcome the susceptibility to oxidation at high temperatures and under humid conditions [22–24]. Among them, the doping of metal elements has certain drawbacks: some hard metal doping may cause metal particles to precipitate on the surface of the coating, making it more challenging for lubricating tribofilms to form [17]. The oxidation resistance of the coating is not effectively enhanced by metallic elements because of potential oxidation factors [25].

The nonmetallic elements in WS₂ coatings are generally doped with elements such as C and N, which results in the formation of an amorphous matrix and effectively inhibits the formation and growth of columnar structures in the coating. Therefore, the coating, which has a typical mixture of amorphous and

nanocrystalline structures while achieving good compactness and high hardness, is preferably conducive to achieving good lubrication of the coating in high-temperature and humid environments [26–28]. Cao et al. [15] introduced C by magnetron sputtering to prepare a WS₂–carbon (WSC) coating. During continuous heating from 100 to 500 °C, the WS₂ lubricating phase fully exerted its primary lubricating performance, demonstrating temperature insensitivity and tribo-reversibility throughout the thermal cycles. A study on the N-doped WS₂ coating revealed that the WSN coating prepared by reactive sputtering had a relatively high hardness (up to 8.0 GPa) and a CoF as low as 0.02 at 200 °C compared with those of the pure WS₂ coating [27]. The analysis of the structure of the WSN coating revealed that its excellent tribological performance is due mainly to the formation of WS₂ tribofilms, which are arranged along the sliding direction both inside and on the surface of the amorphous coating, and these tribofilms play a critical role in providing lubrication [16]. However, there are few studies on the tribological mechanisms of WSN coatings under harsh service conditions across various environments, particularly regarding continuously stable lubrication and tribo-reversibility as a function of temperature. The existing research is insufficient to satisfy the current demands for continuously stable lubrication and tribo-reversibility of solid lubricant coatings in aerospace industries, which are characterized by the abovementioned harsh service conditions.

It has been well established [27, 28] that the gas atmosphere during sputtering deposition influences the microstructure and mechanical properties of WS₂-based tribological coatings. However, previous studies have not scrutinized the tribological mechanisms of WS₂ coatings under various deposition atmospheres in harsh environments. The current study introduces nitrogen as the reactive gas in nonequilibrium magnetron sputtering to prepare WSN coatings under different nitrogen flow rates and then evaluates their tribological properties under various testing conditions, including discrete, continuously ramping temperatures either during heating or cooling and cycles over a wide temperature range. This study aims to investigate the microstructure, composition, stoichiometry, and triboperformance of WSN coatings with tunable N contents, highlighting the superior self-lubricating and tribologically reversible mechanisms of WSN solid lubricating coatings under constant, continuously ramping temperatures either in heating or cooling cycles or wide temperature cycles between RT and 400 °C. This study provides a promising strategy for advanced tribocoatings engineered for temperature-demanding applications across industries requiring adaptive durability and high performance.

2 Experimental

2.1 Preparation of the WSN coatings

WSN thin coatings were deposited via a closed-field unbalanced magnetron sputtering system (TEER UDP400/4, Teer Coatings Limited, UK) in different atmospheres (10 sccm Ar/5 sccm N₂ and 15 sccm Ar/10 sccm N₂), designated WSN5 and WSN10, respectively. Single-crystal silicon (100) wafers and M₂ high-speed steel were used as substrates for characterizing the microstructure of the coatings and high-temperature tribological properties, respectively. The sputtering targets were arranged vertically on the chamber wall, and the substrates were vertically mounted on a rotating substrate holder. The rotational speed of the holder was 3 r/min, and the target-to-substrate distance was 290 mm. The substrates were ultrasonically cleaned in acetone prior to Ar plasma etching for 20 min at a negative bias voltage of 400 V (pulsed DC mode at 250 kHz, 87.5% duty cycle). Two WS₂ targets

were sputtered with 0.5 A pulsed DC power source (150 kHz with a 62.5% duty cycle) in Ar-N plasma to deposit WSN nanocomposite coatings. A Cr intermediate layer with a thickness of approximately 300 nm was first deposited to enhance the interfacial adhesion between the coatings and the substrates. The sputtering deposition time was 2 h, yielding a coating thickness of approximately 1–1.5 μm . During deposition, no extra heat was applied.

2.2 Characterization of the WSN coatings

The surface morphologies and microstructures of the coatings were analyzed by a scanning electron microscope (SEM; TESCAN Mira, TESCAN, Czech Republic) and a high-resolution transmission electron microscope (HR-TEM; Talos F200X, FEI, USA; Tecnai F30, FEI, USA). Focused ion beam microscopes (FIB; Helios 660, FEI, USA; Quanta 3D, FEI, USA) were employed to slice electron-transparent transmission electron microscopy (TEM) lamella at the center of the wear track under the indicated tribological testing conditions. The coating composition was determined via an energy dispersive X-ray spectroscopy (EDS; Octane Silicon Drift Detector, EDAX, USA) via SEM at an accelerating voltage of 20 kV. The elemental composition and chemical valence states of the WSN coating were analyzed via an X-ray photoelectron spectroscopy (XPS; AXIS-ULTRA DLD-600 W, Kratos Analytical, UK). During the measurement, the pressure in the analysis chamber was maintained below 1×10^{-8} Pa. To minimize interference from surface oxides and adsorbed contaminants, the sample surface was etched with Ar⁺ plasma bombardment for 10 min prior to XPS analysis. Raman spectra of the wear tracks were acquired with an instrument (InVia, Renishaw, UK) equipped with a HeNe laser (532 nm) at approximately 2 mW in the range of 200–2,000 cm^{-1} for qualitative analysis of the coating phase. The hardness and elastic modulus of the WSN coatings were measured with a nano indenter (Nano Indenter® G200, KLA Instruments, USA) instrument equipped with a diamond Berkovich tip. The

indentation depth was fixed at 100 nm, i.e., approximately 10% of the coating thickness, to avoid the influence of the substrate. The tribological properties of the coating under various temperatures and humid-dry environments were analyzed via a UMT TriboLab (Bruker, UK) with a precise temperature-controlled unit. Tribotests were conducted under different temperature conditions (discrete constantly stable temperatures at 100, 200, and 400 °C; ramping temperatures included both continuously heating from 100 to 400 °C and cooling from 400 to 100 °C and further 400 °C $\leftrightarrow$ 100 °C temperature cycles) and a humidity chamber (dry air of 5% relative humidity (RH), humid air of 35%–45% RH). The chamber was equipped with a humidity controller that allowed precise adjustment of the RH by mixing dry and humidified air streams via a reciprocating configuration. Note that the temperature cyclic tribotests were conducted in situ on the same wear track of the sample to verify the triboreversibility of the coating potential. Given the extended time required for cooling to RT, this study considers 100 °C as a representative low-temperature condition, as in Ref. [29]. The tests utilized 100Cr6 steel balls with a diameter of 6 mm as counter bodies, which were subjected to a sliding speed of 10 cm/s and a normal load of 5 N (the initial Hertz contact pressure was approximately 0.75 GPa). All the samples were subjected to tribological tests at different temperatures and humidities, which were precisely adjusted by the integrated regulator through the UMT TriboLab control software. The wear test of all the samples was repeated twice, for a total of 3,000–10,000 cycles. The wear rate (W_R) calculation is expressed as $k = SL/FI$, where S is the wear cross-sectional area, L is the wear track length (10 mm), F is the load (5 N), and I is the friction distance (60 m).

3 Results and discussion

3.1 Tribological properties

Different temperature conditions were used to conduct tribotests

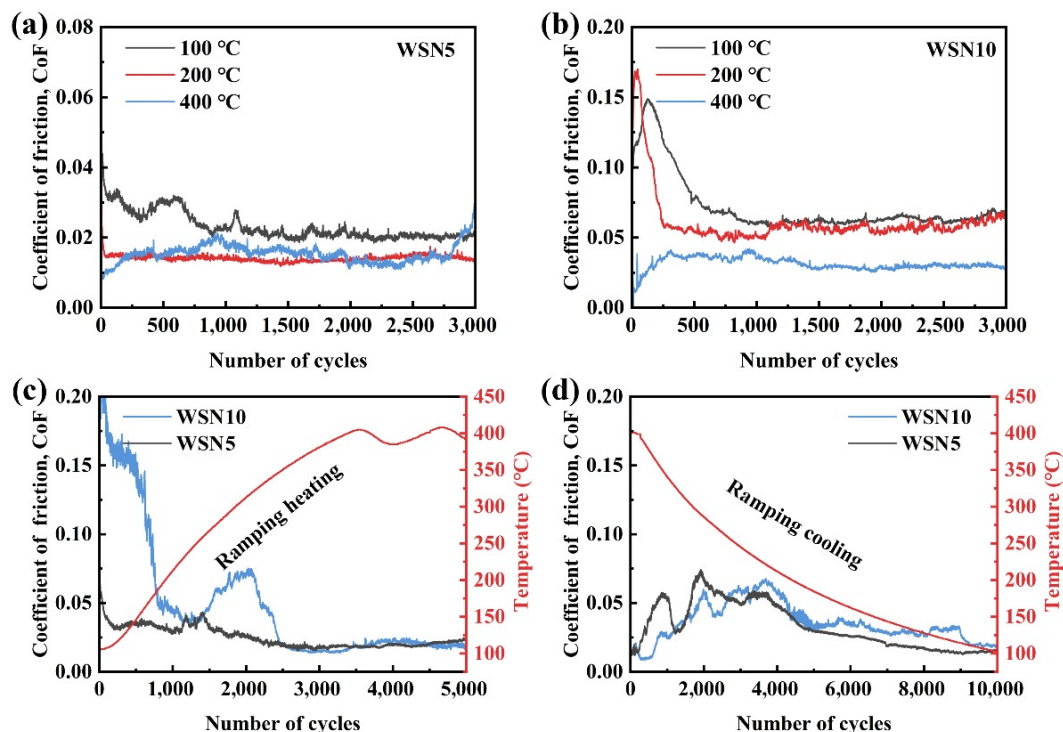


Fig. 1 CoFs of WSN coatings under various conditions: (a) WSN5 and (b) WSN10 coatings tribotested at 100, 200, and 400 °C, respectively; WSN5 and WSN10 coatings tribotested at (c) 100 to 400 °C continuously heated and (d) 400 to 100 °C continuously cooled. The red curves in (c) and (d) represent the dynamic temperature.

on the WSN5 and WSN10 coatings. Figure 1(a) shows the instant CoF of the WSN5 coating at constant temperatures of 100, 200, and 400 °C. Careful observations show that the CoF of the WSN5 coating remains relatively stable and low. Especially at 200 and 400 °C, the coating has an ultralow CoF (approximately 0.02). The CoF of the coating at 100 °C is slightly higher, approximately 0.022. This may be because water molecules absorbed on the coating have not completely evaporated at 100 °C, as the CoF of the WS₂-based coating tends to be high (approximately 0.2–0.3) in humid/moisture environments [30]. The CoFs of the WSN10 coatings at 100, 200, and 400 °C are depicted in Fig. 1(b). At relatively low temperatures of 100 and 200 °C, the CoFs of the coating first fluctuate greatly and then stabilize after 1,500 cycles. Although it appears to become stable later, the average CoF is relatively higher (> 0.05) than that of the WSN5 coating (< 0.04). When the temperature reached 400 °C, the CoF coating decreased and became more stable (< 0.03). By observing the CoF trends of the WSN5 and WSN10 coatings at 100, 200, and 400 °C, it is evident that the WSN coating has a lower CoF at relatively high temperatures (400 °C). The WSN5 coating, which has a lower nitrogen flow, demonstrates greater thermal stability and superior tribological properties than the pure WS₂ coating previously reported in Ref. [31].

To further investigate the impact of temperature on the CoF of the WSN coatings, the CoF of the WSN coatings was tested under conditions of continuous heating and cooling. Figure 1(c) depicts the temperature dependence of the CoF of the WSN5 and WSN10 coatings under continuous heating from 100 to 400 °C. This demonstrates that as the temperature increases, the CoF of the WSN5 coating remains extremely stable and low. However, the CoF of the WSN10 coating fluctuates moderately during the initial stages, stabilizes after 2,500 cycles, and eventually becomes comparable to the CoF of the WSN5 coating. In contrast, Fig. 1(d) depicts the situation of continuously cooling from 400 to 100 °C. The CoFs of the WSN5 and WSN10 coatings tend to fluctuate approximately 0.05 as the temperature decreases; compared with the continuously ramping heating, the tribo-performance is more unstable. The initial high-temperature (400 °C) oxidation byproducts of continuously ramping cooling may be more temperature sensitive, which results in greater CoF instability.

To further investigate the temperature dependence of the tribological properties of the WSN coating, the CoFs of the WSN5 and WSN10 coatings were tested in environmental temperature cycles from 400 °C air (35%–45% RH) to RT dry air (5% RH), as shown in Fig. 2. The results show that during the first cycle in the 400 °C air environment, the CoF of the WSN coating remained relatively stable and was less than 0.02. After switching to the dry environment at RT, the CoF tended to increase but remained relatively low (< 0.03). During subsequent cycles, the CoF

remained relatively high in the 400 °C air environment. However, after switching back to the RT dry environment, the CoF decreased immediately, favorably achieving a reversible CoF from 0.04 to 0.02. Both WSN5 and WSN10 coatings demonstrate exceptional triboreversibility under temperature and humidity cycles with relatively low CoFs (< 0.06), as verified in Figs. 2(a) and 2(b), consequently meeting the requirements for reliably stable lubrication in space applications with CoFs generally below 0.1 [32].

To further compare the effects of humidity on the tribological behavior of the WSN coatings, tribotests were conducted in both RT dry and RT humid air environments. Figure 3(a) shows that the WSN5 coating maintained a low CoF in the dry environment at RT (average CoF of 0.021). However, as the humidity increased to 35% RH, the CoF initially rose significantly above 0.15, briefly dropping below 0.1 somewhere approximately 3,500 cycles before the coating started to fail at approximately 4,000 cycles, as the CoF suddenly increased to 0.5–0.6, indicating coating failure due to dry sliding as a result of direct metal contact [30]. This aligns with the view that WS₂ coatings are prone to deliquescence failure in humid environments [18, 33]. Similarly, Fig. 3(b) shows that while WSN10 starts with a high CoF of approximately 0.20, it still maintains a relatively low CoF (approximately 0.05) in the RT dry environment for up to 5,000 cycles, although its tribological performance is inferior to that of the WSN5 coating. After 1,500 cycles in an RT humid air environment, the WSN10 coating experiences an instant increase in CoF (approximately 0.5), indicating that lubrication essentially starts to fail. These results demonstrate that while higher humidity undermines the tribological properties of WSN coatings, the tribological performance of WSN coatings in high-temperature atmospheric environments remains relatively exceptional, despite the presence of oxygen during tribotests.

3.2 Analysis of worn surfaces

To further study the self-lubricating and tribologically reversible properties of the WSN coating, the micromorphologies of the coating surface and wear tracks were characterized. Figures 4(a) and 4(b) depict the morphologies of the original WSN5 and WSN10 coatings, respectively. Compared with the pure WS₂ surface morphologies reported in previous studies [34–36], the WSN5 coating appears denser with lower porosity and exhibits a typical cauliflower structure. The cauliflower structure helps to disperse frictional forces and mitigate local stress concentrations by increasing the number of microscale protrusions and depressions on the surface to reduce the contact area and consequently improve the wear resistance. Additionally, this structure contributes to the densification of the coating surface,

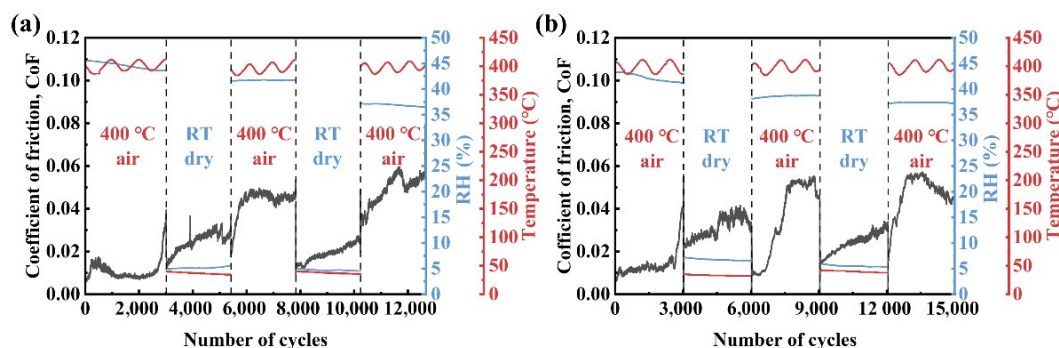


Fig. 2 CoFs of (a) WSN5 and (b) WSN10 coatings tribotested under 400 °C air and RT dry environment switching cycles. Note that the black, red, and blue lines represent the CoF, temperature, and humidity, respectively.

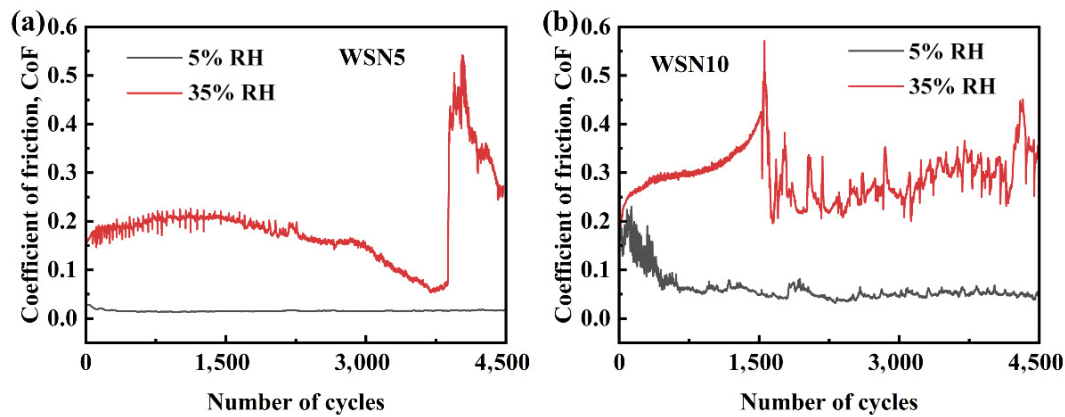


Fig. 3 CoFs of the WSN5 and WSN10 coatings at different humidities (5 RH% and 35 RH%) under RT conditions: (a) WSN5 and (b) WSN10.

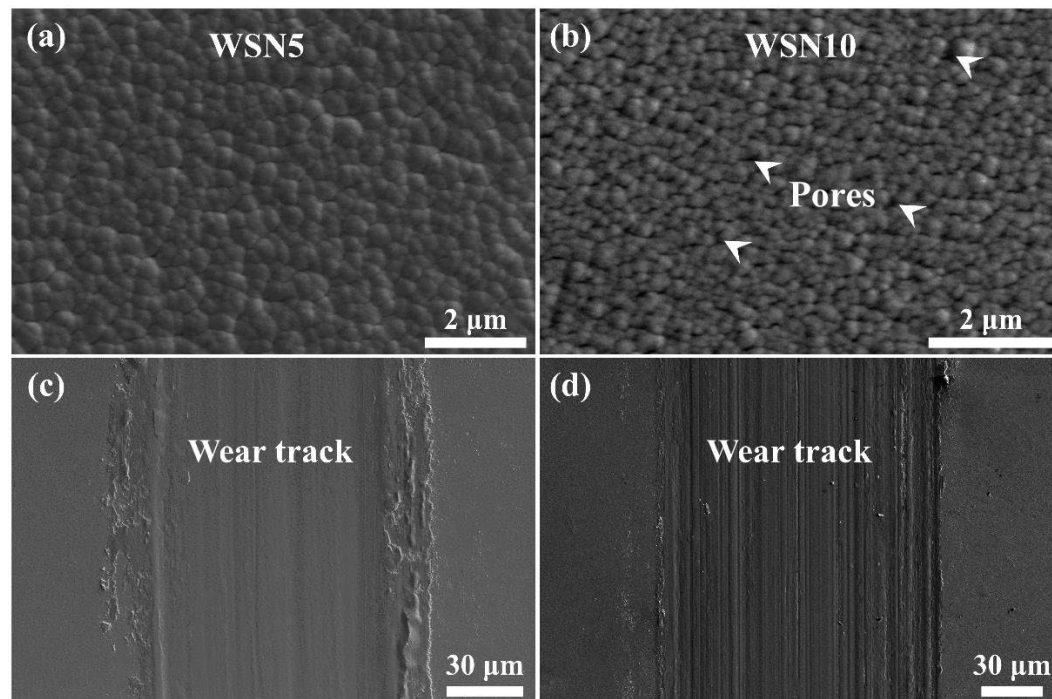


Fig. 4 Surface morphologies and wear tracks of the (a, c) WSN5 and (b, d) WSN10 coatings.

increases the surface hardness, and effectively resists wear. This indicates that the addition of nitrogen improved the compactness of the coating. The introduction of N atoms during the sputtering process alters the thermodynamic and kinetic conditions of WS_2 crystal growth, potentially changing the local energy and atomic interactions during lattice formation. This can inhibit the growth rate of columnar crystals in the coating, leading to denser and more uniform growth of the coating [37]. Figure 4(b) shows the surface morphologies of the WSN10 coating. When the nitrogen flow rate increases further and more N atoms are introduced, it may lead to lattice defects, further compromising the compactness of the coating and resulting in noticeable pores. The wear track morphologies of the WSN5 and WSN10 coatings after wear testing under the same conditions are shown in Figs. 4(c) and 4(d), respectively. Comparisons of the wear tracks revealed that the WSN5 coating has smoother and shallower wear tracks due to its greater compactness, whereas the WSN10 coating has deeper and rougher wear tracks. This difference in wear track morphology reflects a key factor contributing to the superior triboperformance of the WSN5 coating compared with the WSN10 coating.

To further examine the elemental composition and chemical valence states of the as-deposited WSN coating, XPS analysis was performed on the coating surface, as shown in Fig. 5. In the W 4f spectrum, the WSN5 coating exhibited peaks corresponding to WS_2 and WO_3 at binding energies of 32.01, 34.35, and 36.55 eV, respectively, as shown in Fig. 5(a). The WSN10 coating also exhibited characteristic peaks corresponding to WS_2 and WO_3 at binding energies of 32.65, 34.51, 36.65, and 40.25 eV, as shown in Fig. 5(d). However, the peaks associated with WO_3 have a notably higher relative intensity, indicating an increased oxygen content, which is probably related to the structural characteristics of the coating. As illustrated in Fig. 4(b), the loose and porous surface morphology of the WSN10 coating facilitates oxygen penetration, thereby promoting oxidation. In the S 2p spectrum, the WSN5 coating exhibited fitted peaks corresponding to WS_2 at binding energies of 162.46 and 163.42 eV, as shown in Fig. 5(b). In contrast, the WSN10 coating presents an additional peak corresponding to SO_4^{2-} at a binding energy of 167.60 eV, as shown in Fig. 5(e), which is indicative of a higher degree of oxidation in the coating [20]. In the N 1s spectrum, the WSN5 coating exhibited a single characteristic peak at a binding energy of

400.10 eV, corresponding to the presence of W–N bonds, as shown in Fig. 5(c), confirming the successful incorporation of N. In contrast, the WSN10 coating exhibited strong double peaks corresponding to W–N bonds at binding energies of 398.70 eV and 400.46 eV, as shown in Fig. 5(f), indicating increased N incorporation, which was attributed to the increased nitrogen flow rate employed during the coating deposition process.

As shown in Fig. 4, the WSN5 coating produced with a lower nitrogen flow rate exhibited a denser surface structure and shallower wear tracks, indicating improved hardness and wear resistance. To characterize the hardness and wear resistance of the WSN coatings, Fig. 6 presents the hardness (H), elastic modulus (E), H/E ratio, and H^3/E^2 values for the WSN5 and WSN10 coatings. As shown in Fig. 6(a), the WSN5 coating has a hardness of 4.76 GPa, whereas the hardness of WSN10 is 4.39 GPa, which is closely related to its denser structure. Furthermore, the hardness of the WSN coating is significantly greater than that of the pure WS_2 coating, which is reported to be less than 0.5 GPa [35]. However, its elastic modulus is lower at 71.3 GPa than it is at 76.5 GPa for WSN10. This reduction is primarily due to the high-

density grain boundaries inherent in its dense structure, which introduce additional stress concentration areas, increasing the likelihood of microslipping and grain boundaries sliding around these boundaries [20]. For WSN coatings, a high H/E ratio is generally regarded as a reliable indicator of improved wear resistance, whereas a high H^3/E^2 ratio is associated with enhanced resistance to plastic deformation in the coating. The H/E and H^3/E^2 ratios of the WSN5 coating are higher than those of the WSN10 coating, as shown in Fig. 6(b), indicating that the WSN5 coating offers better wear resistance and enhanced resistance to plastic deformation.

To investigate the tribological behavior of the WSN coatings as a function of temperature, the wear tracks formed at different test temperatures were analyzed. Figure 7 shows the 3D confocal morphologies of the WSN coating wear track as the test temperature changed. The wear tracks of the WSN5 coatings at 100 °C (Fig. 7(a)) and 200 °C (Fig. 7(c)) are relatively narrow, shallow in depth, and correspondingly exhibit a low wear rate. When the temperature increases to 400 °C (Fig. 7(e)), the wear track becomes deeper, and more wear debris appears at the edges,

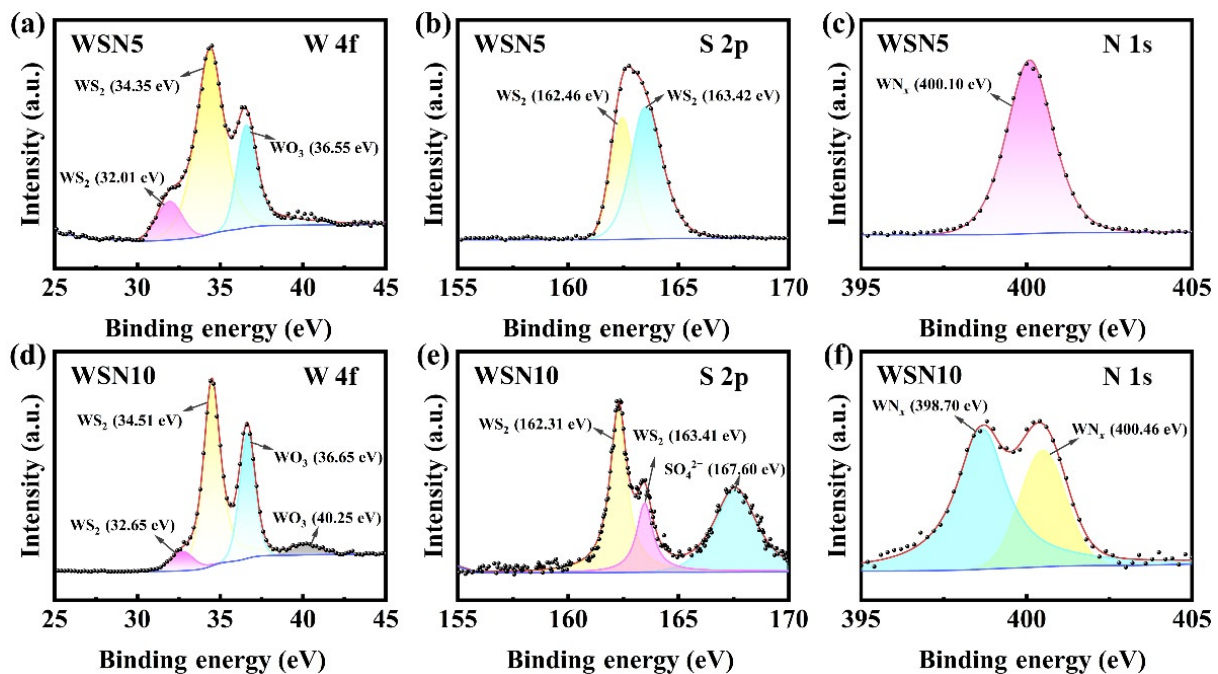


Fig. 5 XPS spectra of (a) W 4f, (b) S 2p, and (c) N 1s for the WSN 5 coating and (d) W 4f, (e) S 2p, and (f) N 1s for the WSN 10 coating.

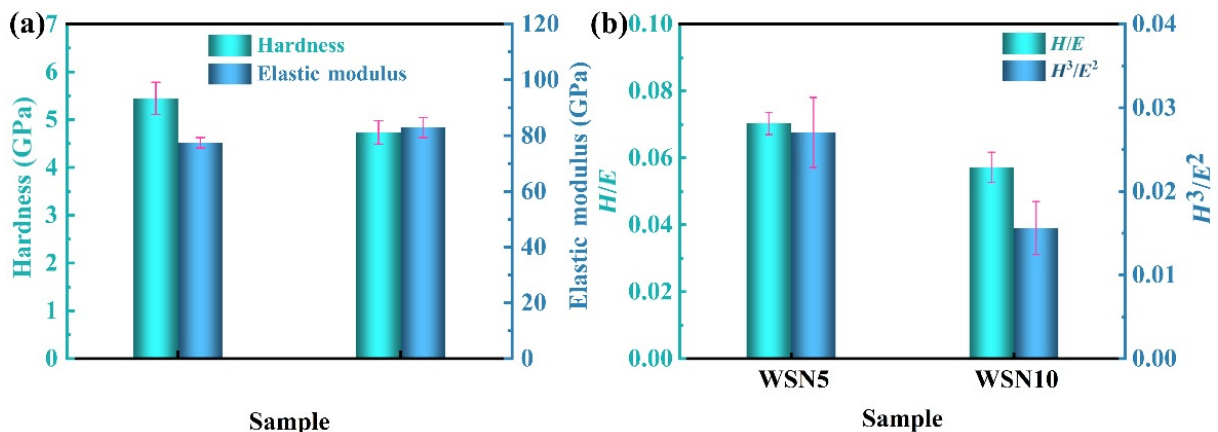


Fig. 6 (a) Hardness, elastic modulus and (b) H/E and H^3/E^2 ratios of the WSN coatings.

indicating relatively severe wear. The higher wear rate of the WSN5 coating at 400 °C is due mainly to the generation of more lamellar lubricating WS_2 phases under high-temperature friction. Shear slip is more likely to occur during friction, resulting in increased wear debris. The wear debris fills the wear track and is retransformed into new lubricant agents [21]. This is also the main reason for ultralow friction at high temperatures. Under the same test conditions of 100 °C (Fig. 7(b)), 200 °C (Fig. 7(d)), and 400 °C (Fig. 7(f)), the wear tracks of the WSN10 coating are relatively wider and significantly deeper. This is mainly because the WSN10 coating has more pores, leading to poor compactness. Although high-temperature-induced shear slip contributes to a lower CoF in high-temperature environments (Fig. 1(b)), the lower compactness of the WSN10 coating makes its lubricating functional phases easier to remove, thereby negatively affecting its tribological properties compared with those of the WSN5 coating.

The cross-sections of the wear tracks were extracted from 3D confocal micrographs and are shown in Fig. 7, and the cross-sectional wear areas from the three measurements are provided in Table 1. A comparison of the cross-sectional wear areas of the WSN5 (Fig. 7(g)) and WSN10 (Fig. 7(h)) coatings under testing conditions of 100, 200, and 400 °C clearly reveals that the cross-sectional wear area of the WSN10 coating is significantly wider than that of the WSN5 coating. Additionally, high temperatures

further exacerbate the wear of the coatings. Figure 7(i) shows W_R from the wear test results at 100, 200, and 400 °C. The wear rate of the same coating increases with temperature. The wear rate of the WSN5 coating at 200 °C was as low as $1.45 \times 10^{-7} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$. Notably, a wear rate of $1 \times 10^{-7} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ represents an average removal rate of less than one atomic layer per cm under a normal load of 5 N. This exceptionally low wear and CoF (< 0.02) may meet the application requirements for aerospace self-lubricating wear-resistant coatings, specifically, a wear rate $< 10^{-6} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ and CoF < 0.1 , indicating significant application prospects in the aerospace industry [32]. The higher wear rate and lower CoF at high temperatures may be attributed to the wear debris generated by high-temperature friction filling the wear tracks and acting as a lubricating agent, thereby enabling the WSN coating to achieve ultralow lubrication performance at high temperatures [20].

As mentioned previously, the WSN coating is susceptible to deliquescence failure in an RT air environment with relatively high humidity. The confocal micrographs and surface morphologies of the wear tracks of the WSN5 (Figs. 8(a) and 8(c)) and WSN10 (Figs. 8(b) and 8(d)) coatings under RT humid air are shown in Fig. 8. Figures 8(a) and 8(c) show that after the WSN5 coating is worn in a humid air environment, noticeable cracks appear in the coating. In contrast, the WSN10 coating shows significant degradation in the same environment, with

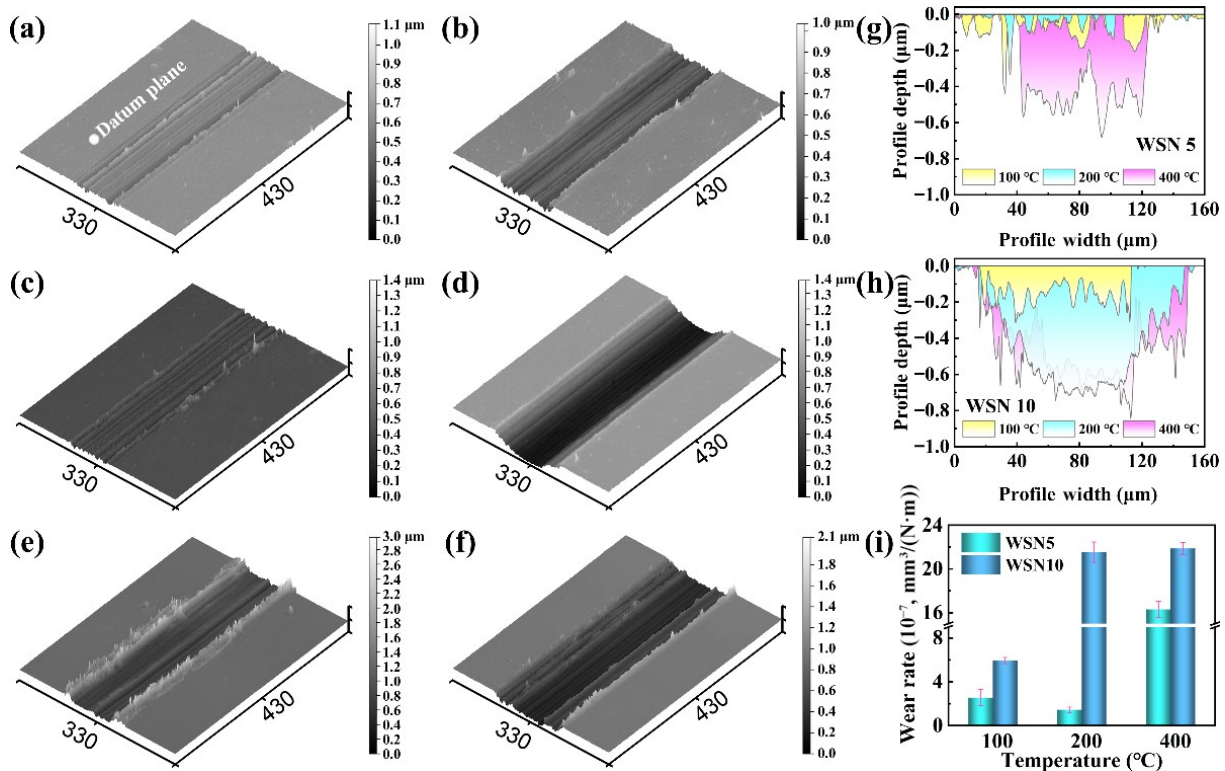


Fig. 7 Confocal micrographs ($330 \mu\text{m} \times 430 \mu\text{m}$) showing 3D views of the wear tracks as a function of temperature: (a) 100 °C, (c) 200 °C, and (e) 400 °C WSN5 coating; (b) 100 °C, (d) 200 °C, and (f) 400 °C WSN10 coating. Cross-sectional wear tracks of (g) WSN5 and (h) WSN10 coatings under various discrete testing temperatures of 100, 200, and 400 °C, respectively. (i) Wear rates of WSN5 and WSN10 coatings under testing conditions of 100, 200, and 400 °C.

Table 1 Wear cross-sectional area of the WSN coating at different tribotest temperatures

Temperature (°C)	100 °C		200 °C		400 °C	
Sample No.	WSN5	WSN10	WSN5	WSN10	WSN5	WSN10
Wear cross-sectional area (10^{-6} mm^2)	10.21	17.33	3.55	67.71	51.14	67.25
	5.87	17.45	4.46	62.97	46.69	65.99
	6.86	18.82	5.01	63.24	48.62	63.87

deeper wear tracks visible in Figs. 8(b) and 8(d). The coating is damaged, and the substrate is exposed, which aligns with the instant failure of the coating observed in Fig. 3(b).

To further investigate the phase evolution of the WSN coatings before and after wear, Raman spectroscopy was conducted on both the as-deposited coatings and the corresponding wear tracks. Figures 9(a) and 9(d) present the Raman spectra of the original WSN5 and WSN10 coatings, respectively. The original coatings do not exhibit distinct peaks corresponding to WS_2 phases. Instead, an E_1g characteristic peak attributed to WO_3 appears near 809 cm^{-1} , indicating partial oxidation of the coatings. The WO_3 peak is more pronounced in the WSN10 coating, suggesting a

higher degree of oxidation, which is consistent with the results of the XPS analysis. Owing to the limited crystallinity of the as-deposited WS_2 , the characteristic Raman-active signals are either extremely weak or absent. As a result, no peaks corresponding to WS_2 are observed in the Raman spectrum of the as-deposited film. In contrast, as shown in Fig. 5, the XPS analysis confirmed the presence of W-S bonds, indicating the existence of WS_2 in the amorphous film. Raman spectroscopy analysis was performed on the center part of the wear tracks to further investigate the tribological mechanism of the WSN coating. Figures 9(b) and 9(c) show the Raman spectra of the WSN5 and WSN10 coatings on the wear tracks at 100, 200, and 400 °C. The Raman spectra reveal

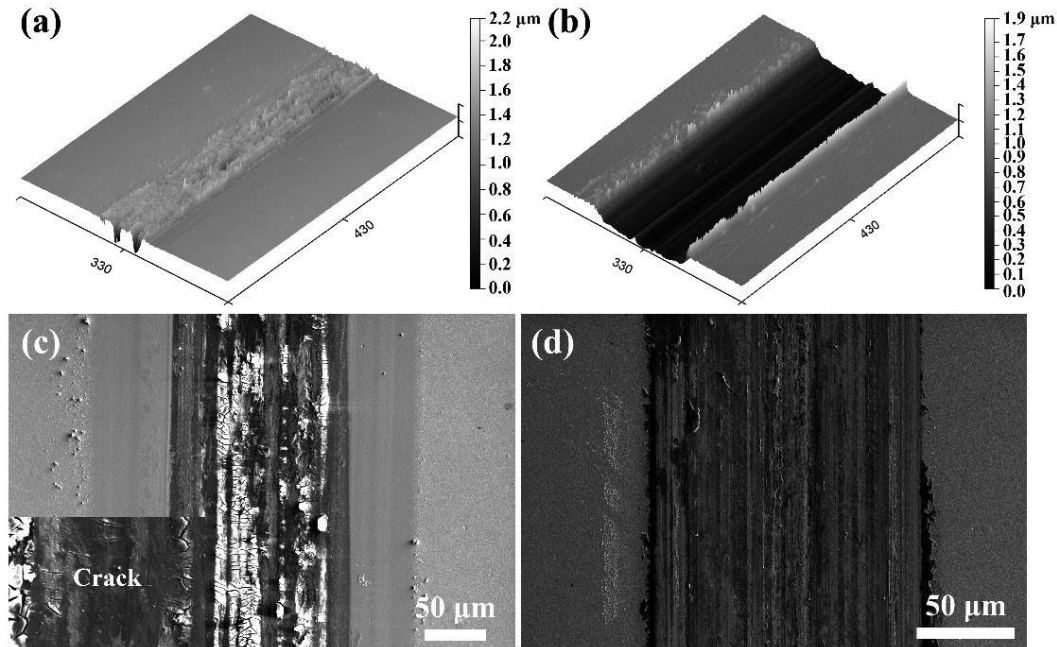


Fig. 8 Confocal micrographs and surface morphologies of the wear tracks of the (a, c) WSN5, and (b, d) WSN10 coatings under RT humid air.

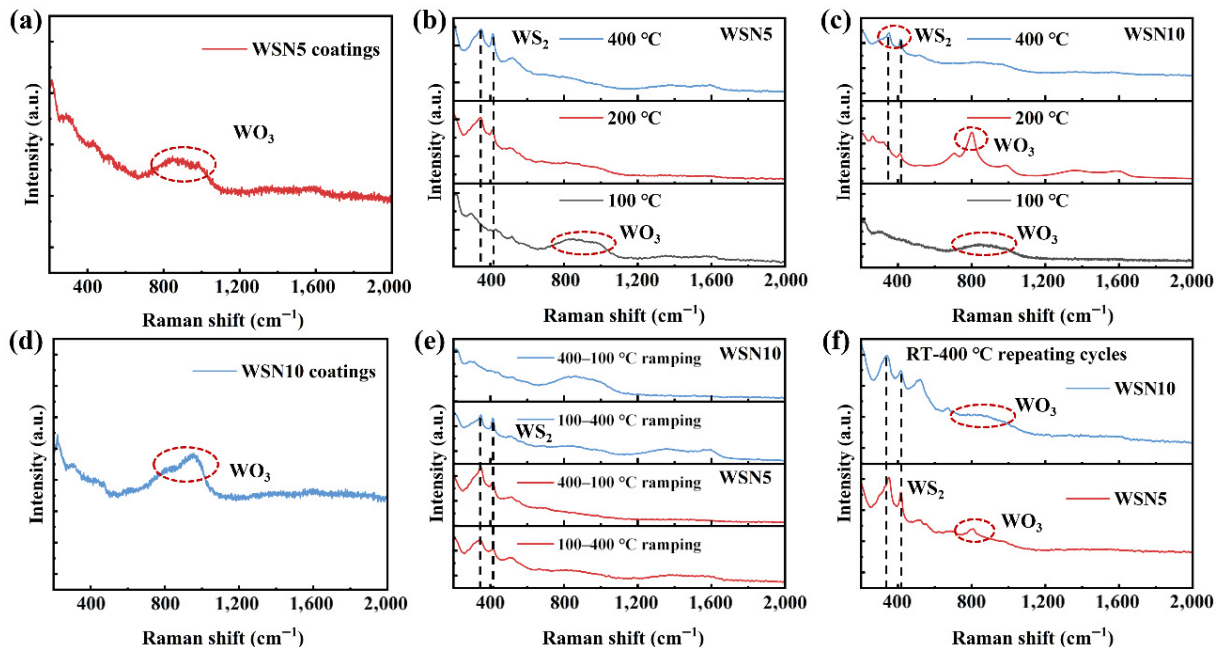


Fig. 9 Raman spectroscopy of WSN coatings: original (a) WSN5 and (d) WSN10 coatings; wear tested (b) WSN5 and (c) WSN10 coatings under 100, 200, and 400 °C, respectively. (e) Wear tested of WSN coatings under 100 °C continuously ramped heating to 400 °C and 400 °C continuously ramped cooling to 100 °C. (f) Wear tested of WSN coatings under 400 °C air and RT dry environmental cycles.

that the wear tracks of the WSN5 coating, depicted in Fig. 9(b), are Raman-active in the 350–420 cm^{-1} region at relatively high temperatures (200 and 400 $^{\circ}\text{C}$), corresponding to the $\text{E}_{2\text{g}}$ (approximately 355 cm^{-1}) and $\text{A}_{1\text{g}}$ (421 cm^{-1}) peaks, characteristic of hexagonal WS_2 . This peak is not apparent at 100 $^{\circ}\text{C}$; instead, a peaking trend appears at approximately 800 cm^{-1} , corresponding to the $\text{E}_{1\text{g}}$ (809 cm^{-1}) peak of WO_3 . These results indicate that the WS_2 lubricating phases induced by high-temperature friction are primarily responsible for the excellent tribo-performance of the WSN coating at 400 $^{\circ}\text{C}$. At 100 $^{\circ}\text{C}$, the water molecules within the coating have not yet completely evaporated, and the tribological process produces WO_3 , a degrading lubricating phase compared with WS_2 . However, as the temperature increases, the oxides of WO_3 are gradually removed by sliding the counterpart ball [15]. Figure 9(c) shows that at high temperatures of 200 and 400 $^{\circ}\text{C}$, the WS_2 lubricating phases are also generated at the wear tracks of the WSN10 coating, but the peak intensity corresponding to WS_2 tends to be significantly weaker. At 200 $^{\circ}\text{C}$, a strong peak of WO_3 simultaneously appears, indicating a significant oxidation phenomenon. However, at 400 $^{\circ}\text{C}$, WO_3 oxides are dynamically removed during high-temperature sliding and shearing. This convincingly explains why the CoF of WSN10 is relatively high and less stable at 200 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$. The Raman spectra of the wear tracks for the WSN5 and WSN10 coatings under continuous temperature ramping either during heating or cooling and a wide range of temperature cycles are shown in Figs. 9(e) and 9(f). WS_2 peaks are observed in both the heating and cooling cycles for WSN5, whereas they appear only during the heating process for WSN10. This explains the superior performance of the WSN5 coating under continuous ramping, either during heating or cooling, and the wide temperature range of cycles.

The exceptional triboperformance is primarily due to the *in situ* formation of WS_2 lubricating phases. Although WO_3 , an oxide, is also generated, it has less impact, as it still serves as a degrading but still effective lubricant. However, the low compactness of the WSN10 coating allows the newly formed WS_2 lubricating phase to be easily worn away during the friction and wear process, as shown in Fig. 9(e), where no WS_2 phase was detected at the wear tracks under continuously ramping cooling from 400 to 100 $^{\circ}\text{C}$. This results in a significant loss of S atoms, decreasing the amount of chemical elements crucially required for the formation of WS_2 phases and ultimately leading to unstable and degraded lubrication [13].

3.3 High-temperature self-lubricating mechanism

As previously stated, WSN5 coatings with sufficient N content exhibit exceptional tribological properties at high temperature (400 $^{\circ}\text{C}$), maintaining stable, ultralow CoFs in switchable environments of high-temperature, humid, and dry air conditions, thereby achieving consistent ultralow friction with tribo-reversibility. Raman spectroscopy analysis confirmed that the formation of a new WS_2 phase during tribosliding is the key to achieving outstanding triboperformance and triboreversibility.

The wear track of the coating was sliced via FIB-cut and subsequently analyzed via HR-TEM to further validate the mechanism underlying the friction-induced generation of a new WS_2 phase. Figure 10(a) shows the cross-section of a TEM slice from the wear track of the WSN5 coating at 400 $^{\circ}\text{C}$. The cross-sectional TEM image reveals the uniform thickness, dense structure, and typical columnar crystal growth of the coating. A thin tribofilm generated by frictional slip is visible on the surface. Figure 10(b) further provides a close-up view of area b in the tribofilm, which presents a variable thickness of several to 40 nm.

HR-TEM analysis was performed on the top (area c) and middle (area d) of the tribofilm.

Figure 10(c) shows an HR-TEM image of the top of the tribofilm. The base of the WSN coating maintains its amorphous structure. After high-temperature triboslides at 400 $^{\circ}\text{C}$, WS_2 nanolamellae and nanocrystalline WO_3 formed on the top and within the amorphous substrate. During sliding, many WS_2 nanolamellae with a (002) basal orientation progressively form and move in the sliding direction toward the top of the tribofilm. These lamellar WS_2 , with weak van der Waals forces between the layers, undergo shear slip, providing excellent lubrication. Below the WS_2 -rich layers, some WO_3 nanocrystals are present, but these are gradually removed during sliding. As a result, the oxidation of transition metal dichalcogenide (TMD)-based nanocomposite coatings during high-temperature tribosliding tends not to be a significant concern, as previously proposed [1, 15]. Although the WS_2 coating may oxidize to form WO_3 during the friction process, this oxide is continuously removed when its counterpart slides. Instead, lamellar WS_2 lubricating phases dynamically form at the tribointerface. However, the lubrication performance significantly degrades in the absence of S atoms as a consequence of a lack of elements for the formation of WS_2 , which is the predominant lubricant agent leading to ultralow lubrication (CoF: 0.02). Figure 10(d) shows the HR-TEM image of the middle portion of the tribofilm, where numerous WS_2 nanolamellae are generated within the tribofilm, reorient along the (002) direction of frictional slip, and gradually ascend toward the tribofilm top area. A moderate amount of nanocrystalline WO_3 is also present, as identified by the polycrystalline diffraction rings. However, the presence of these nanocrystals offers negligible resistance to the climbing of WS_2 nanolamellae, thereby allowing the WSN5 coating to maintain outstanding triboperformance at high temperatures [19].

Figure 11(a) shows the cross-section of a TEM slice cut from the wear track of the WSN10 coating at 400 $^{\circ}\text{C}$. Compared with the WSN5 coating, the tribofilm of the WSN10 coating after high-temperature tribosliding at 400 $^{\circ}\text{C}$ is looser, more porous, and less compact. Figure 11(b) provides a close-up view of area b in the tribofilm, which has a variable thickness ranging from several to 150 nm. HR-TEM analysis of the top (area c) of the tribofilm is shown in Fig. 11(c). After high-temperature triboslides at 400 $^{\circ}\text{C}$, WS_2 nanolamellae and nanocrystalline WO_3 formed within the amorphous substrate of the WSN10 coating. However, compared with that of the WSN5 coating, the CoF of WSN10 is relatively higher during high-temperature tribosliding, as shown in Figs. 1(a) and 1(b). This is primarily attributed to its loose and thick tribofilm. The failure mechanism of the WSN10 coating is discussed in detail in Section 3.4.

To verify the formation and movement mechanism of the WS_2 nanolamellae, FIB slices and TEM analysis were conducted at various temperatures on the wear tracks and away from the wear track of the WSN5 coating. Figures 12(a) and 12(b) show HR-TEM images of a FIB cut away from the wear track at RT and 400 $^{\circ}\text{C}$, respectively. At RT, the as-deposited WSN5 coating exhibited a typical disordered amorphous structure, with no ordered crystals (also confirmed by the amorphous diffraction ring in the inset selected area electron diffraction (SAED) image in Fig. 12(a)). However, after testing at 400 $^{\circ}\text{C}$, scattered and dispersed WS_2 lamellae appear within the amorphous matrix, indicating that high temperature could reversely promote WS_2 crystal formation.

Figure 12(c) shows an HR-TEM image of a longitudinal section of the wear track after testing at 400 $^{\circ}\text{C}$, where frictional slip has occurred. Unlike the scattered and disordered WS_2 crystal units in the as-deposited WSN5 coating (away from the wear track), the

WS₂ elements in the longitudinal section of the wear track are reoriented by frictional slip to form a layered WS₂ structure with exceptional lubricating properties. Frictional slip plays a crucial role in the reorientation of WS₂. Under the combined influence of slipping and high temperature, amorphous, short, scattered WS₂ units reconnect to form a continuous WS₂ nanolayered structure via the dislocation climbing mechanism [38–40]. In conclusion, the dynamic generation and reorientation of the WS₂ phase

induced by frictional slip and high temperature are key mechanisms enabling WSN coatings to achieve self-lubrication at high temperatures and maintain tribo-reversibility in cyclic temperature environments.

3.4 Failure mechanism

The above describes the self-lubricating and tribologically reversible mechanisms of WSN coatings at elevated temperatures

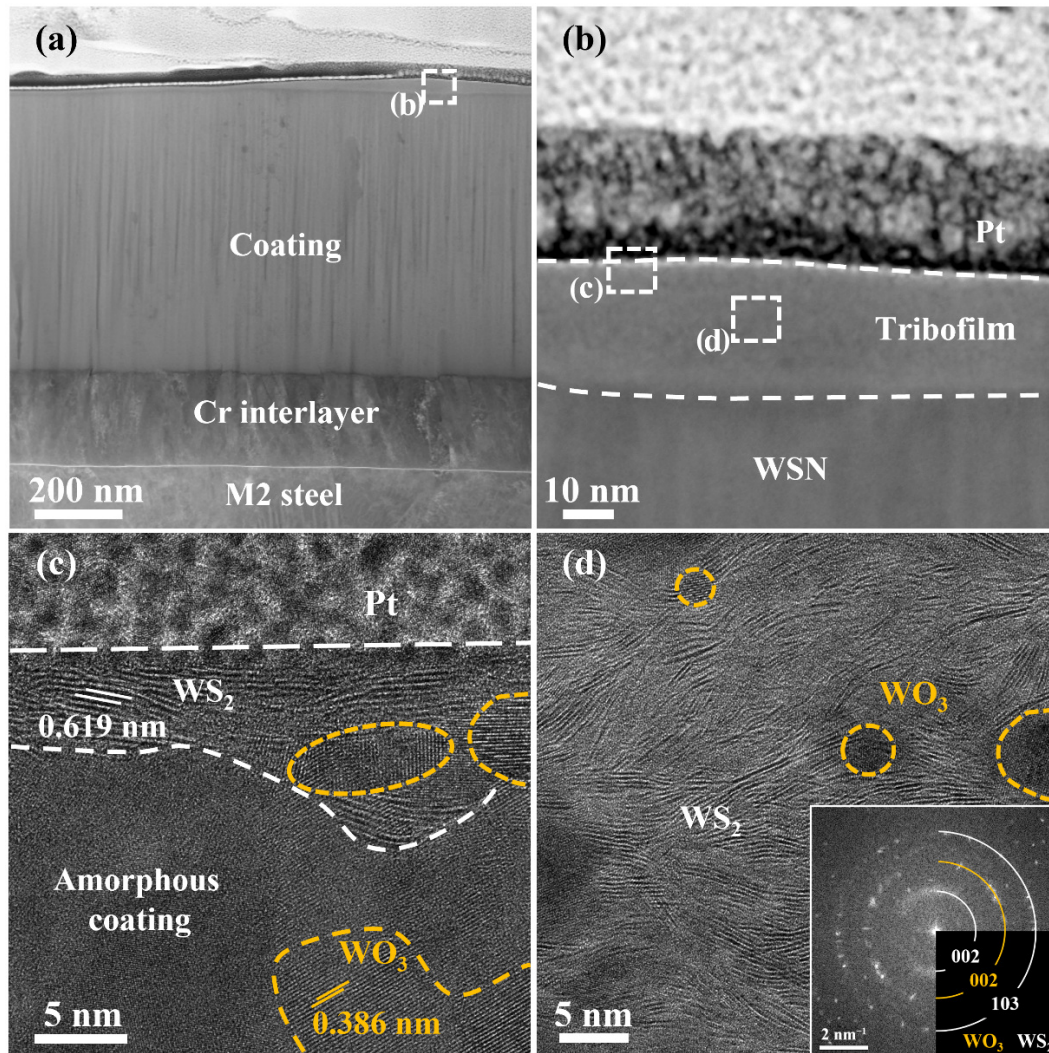


Fig. 10 Cross-sectional STEM image of a TEM slice cut with a FIB at the wear tracks of the (a) WSN5 coating at 400 °C, (b) local close-up image of the tribofilm at the top of the coating, (c) HR-TEM images of the top, and (d) intermediate portion of the tribofilm.

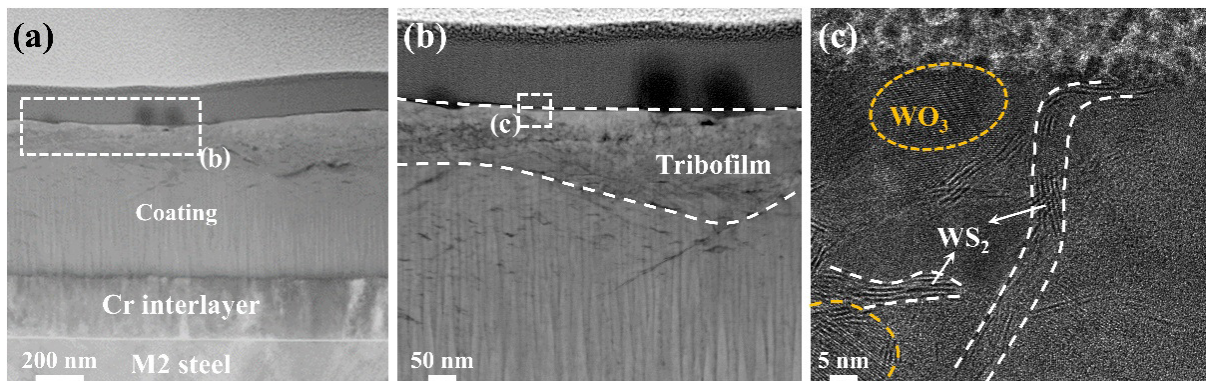


Fig. 11 (a) Cross-sectional STEM image of a TEM slice with an FIB cut at the wear tracks of the WSN10 coating at 400 °C. (b) Local close-up image of the tribofilm at the top of the coating. (c) HR-TEM images of the top portion of the tribofilm.

and under friction induction. However, the relatively poor and unstable tribo-performance of the WSN10 coating at high temperatures necessitates a detailed analysis of its failure mechanism. Figure 13(a) shows a cross-sectional STEM image of a TEM slice taken along the wear tracks of the WSN10 coating at 400 °C. Sliding at high temperature results in the formation of a thick tribofilm (60–140 nm) on the surface of the WSN10 coating, which is noticeably cracked and uneven compared with the intact tribofilm of the WSN5 coating. Spots 1 and 2 correspond to positions within the coating and tribofilm, respectively.

Figure 13(b) presents the STEM-EDS analysis and corresponding elemental contents of these two locations. The diagram shows that the S content in spot 1 (inside the coating) is significantly greater than that in spot 2 (after high-temperature friction), where the oxygen content is also exceedingly low. Spot 1 has a sulfur-to-tungsten atomic (S/W) ratio of 1.08, whereas Spot 2 has a S/W ratio of only 0.06. The S/W ratio, as the primary parameter for the sulfur content within the reaction coating, is significantly associated with the formation of lubricating phases. Under the influence of frictional slip shear, the generation of sulfur-containing lubricating phases, such as WS₂ nanolamellae,

provides effective lubrication during the friction process. If the sulfur content in the coating decreases, the formation of these lubricating phases is inhibited, leading to a reduction in lubrication performance, which subsequently results in an increase in CoF and increased wear [15]. The scanning transmission electron microscopy-energy-dispersive X-ray spectroscopy (STEM-EDS) mappings in Figs. 13(c)–13(f) reveal the distributions of W, S, N, and O, revealing an evident lack of S and an enrichment of O in the tribofilm regions. The introduction of excess N may cause a substitution reaction with S atoms, disrupting the integrity of the WS₂ structure. This loose state allows S atoms to escape during the tribological process, consequently reducing the coating lubrication effectiveness because of insufficient S to form WS₂ lubricating agents.

The self-lubrication and failure mechanisms of the WSN coating are illustrated in Fig. 14(a). The debris and oxidation products produced during the high-temperature tribological process are dynamically removed during mutual sliding. During this process, a portion of WS₂ is ordered within the amorphous matrix of the WSN coating through atomic release and orientation resetting (Fig. 10(c)). Under the dislocation climbing

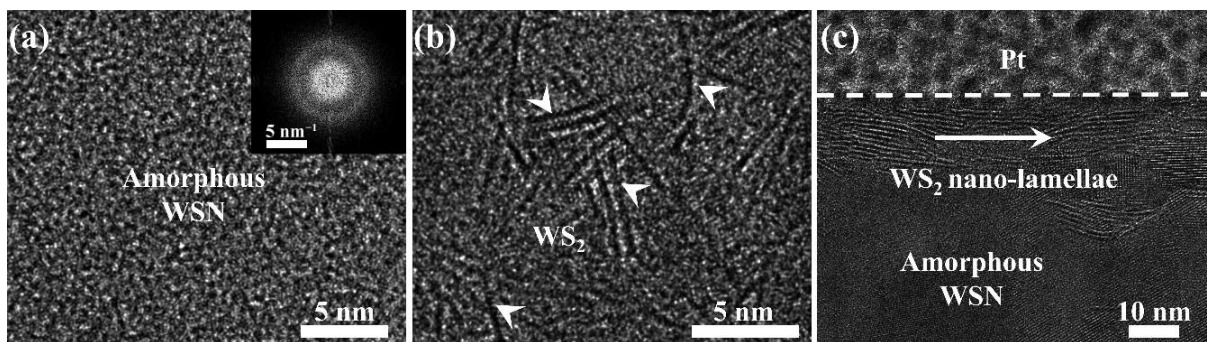


Fig. 12 Cross-sectional HR-TEM images of the WSN5 coating surface and wear tracks at various temperatures: (a) RT and (b) 400 °C for the as-deposited WSN5 coating (away from the wear track). (c) Longitudinal section of the wear track after testing at 400 °C.

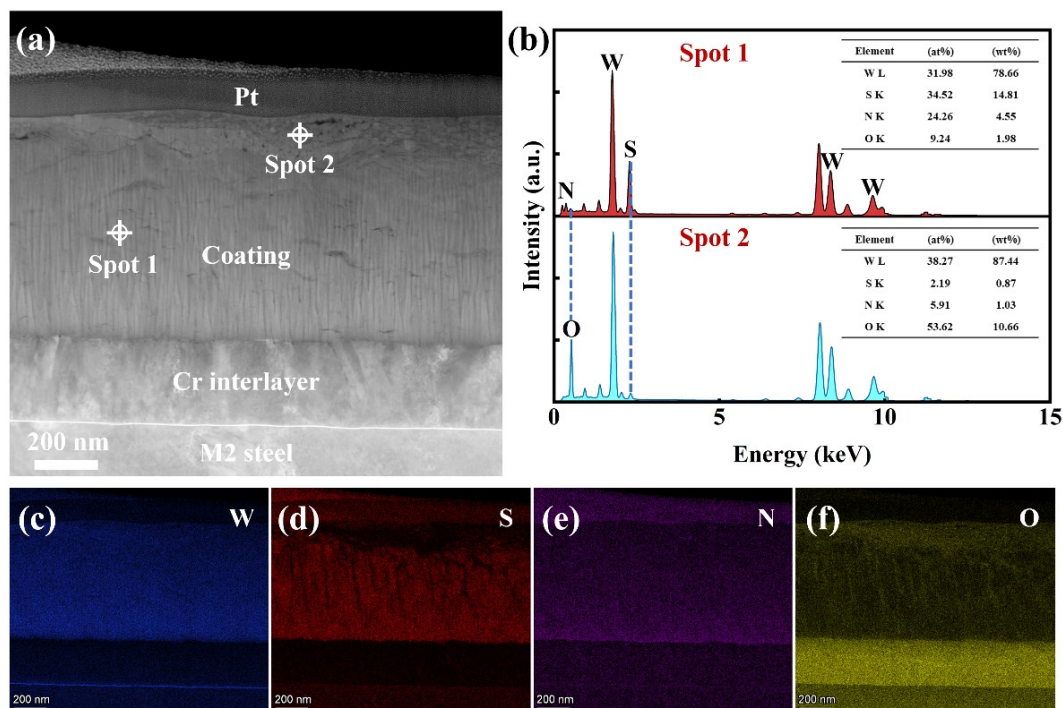


Fig. 13 (a) Cross-sectional STEM image of a TEM slice via FIB-cut at the wear tracks of the WSN10 coating at 400 °C. (b) STEM-EDS results of Spots 1 and 2 and their elemental compositions. (c)–(e) STEM-EDS elemental mappings of the cross-sectional area in (a).

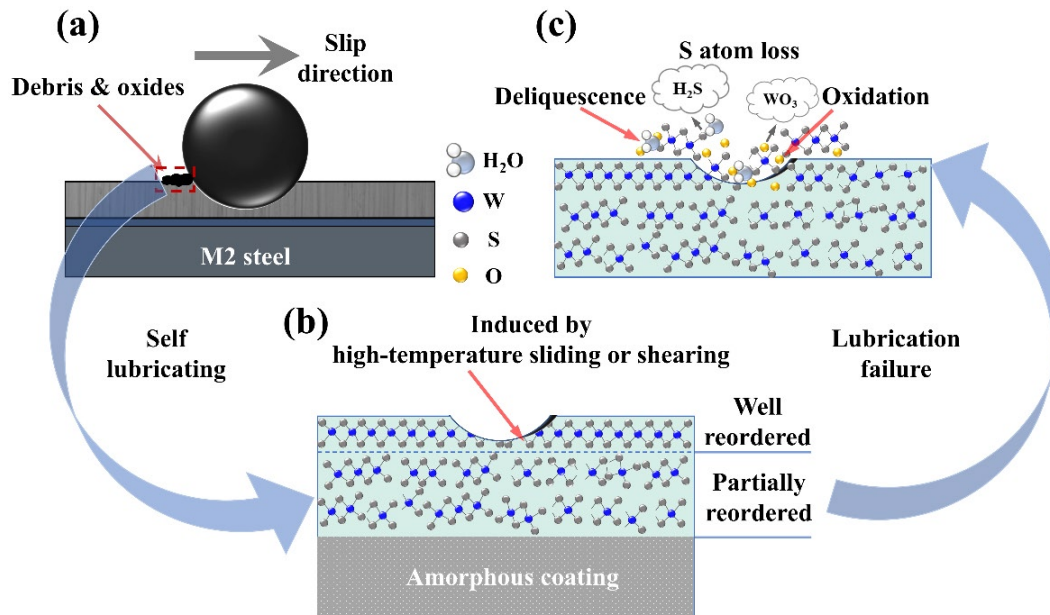


Fig. 14 Schematic of the self-lubrication and lubrication failure mechanisms of the WSN coating at high temperatures: (a) debris and oxidation products are dynamically removed; (b) W and S atoms are released from the amorphous WSN coating, and the atomic reorientation (002) of WS₂ is well achieved; (c) coating deliquescence and oxidation result in lubrication failure.

mechanism, these ordered WS₂ layers gradually connect and grow along the sliding direction, enabling self-lubrication of the coating (Fig. 14(b)). However, when the production rate of the WS₂ lubricating phase due to sliding or shearing is lower than the loss rate of S atoms caused by deliquescence and oxidation, lubrication failure starts to occur (Fig. 14(c)). At this point, severe oxidation and lattice defects from excess N atoms prevent the rapid formation of the WS₂ lubricating layer [41]. The tribofilm surface mainly consists of loose oxides instead, which are then quickly removed by sliding, and because the newly formed WS₂ crystal units do not have time to connect into WS₂ nanolamellae, the lubrication performance is drastically degraded accordingly [42, 43].

4 Conclusions

This study presents a novel WSN self-lubricating coating with unique advantages over traditional solid lubricating coatings. The coating is adaptive for applications involving environmentally switchable changes (temperature in particular) and demonstrates excellent thermal stability and ultralow lubrication performance, especially under high temperatures and variable environmental conditions, whether in dry or humid air. The main conclusions are summarized as follows:

(1) The self-lubricating, temperature-insensitive WSN coating maintains an extremely low CoF (0.02) at high temperatures (400 °C). It also shows stable tribo-performance under continuous temperature ramping, including either dynamic ramping heating or cooling. In addition, it retains a relatively stable and low CoF during environmentally switching cycles between 400 °C air and RT dry conditions, confirming the successful tribo-reversibility of the coating.

(2) When the nitrogen flow rate is low, the WSN5 coating has a denser and more uniform structure, resulting in a higher hardness (4.76 GPa) and improved H/E and H^2/E^2 ratios, which contributes to its excellent tribological properties. In contrast, a high nitrogen flow rate leads to a looser and more porous structure in the WSN10 coating, characterized by a lower hardness and H/E and

H^2/E^2 ratios, resulting in poor wear resistance and reduced resistance to plastic deformation.

(3) The wear rate of the WSN coating increases with increasing temperature. At high temperatures, the increased wear rate produces more wear debris and oxides. Although this wear debris initially has a lubricating performance, it is easily deliquescent in the air environment, consequently leading to coating failure.

(4) The mechanism by which WSNs achieve self-lubrication and a tribological reversal during RT ↔ high-temperature cycles involves high-temperature friction, which induces atomic release and orientation resetting to generate WS₂ crystal units.

(5) High-temperature tribosiding-induced oxidation does not necessarily impair the frictional triboperformance of the coating, while the loss of sulfur atoms tends to primarily account for lubrication failure in WSN coatings. This occurred because when the generation rate of the WS₂ lubricating phase is lower than the formation rate of WO₃ oxides, loose oxides are easily removed, which subsequently exacerbates lubrication failure.

CRedit authorship contribution statement

Zhonghao Liu: Conceptualization, Formal analysis, Investigation, Data curation, Writing—original draft. Jiahui Qi: Investigation, Data curation, Writing—review & editing. S. Li: Formal analysis, Software. Xuanpu Dong: Conceptualization, Resources, Writing—review & editing. W. Mark Rainforth: Data curation, Methodology. Yutao Pei: Methodology, Writing—review & editing. Ying Chen: Investigation, Writing—review & editing. Xiangli Zhong: Investigation, Validation. Mingwen Bai: Conceptualization, Writing—review & editing. Jeff Th. M. De Hosson: Conceptualization, Methodology, Writing—review & editing. Huatang Cao: Writing—review & editing, Resources, Supervision, Project administration, Funding acquisition.

Acknowledgements

This work was financially supported by startup funding from the Huazhong University of Science and Technology, China, and the Liaoning Key Laboratory of Aeroengine Materials Tribology (No.

LKLAMTF202503). The authors thank Dr. Wei Zhang for assisting in the preparation of WSN coatings at the University of Groningen, the Netherlands. The authors would like to thank the Analytical & Testing Center of Huazhong University of Science and Technology for support with the material characterizations and tests.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

References

- [1] Liu Y Z, Han J H, Xu S S, Jung Y C, Kim D E. Dual *in-situ* observation of tribochemical and morphological evolution of single-layer WS₂ and multi-layer WS₂/C coatings. *Friction* **12**(7): 1580–1598 (2024)
- [2] Manu K M S, Raag L A, Rajan T P D, Pai B C, Petley V, Verma S N. Self-lubricating bidirectional carbon fiber reinforced smart aluminum composites by squeeze infiltration process. *J Mater Sci Technol* **35**(11): 2559–2569 (2019)
- [3] Donnet C, Erdemir A. Historical developments and new trends in tribological and solid lubricant coatings. *Surf Coat Tech* **180**: 76–84 (2004)
- [4] Roberts E W. Space tribology: Its role in spacecraft mechanisms. *J Phys D Appl Phys* **45**(50): 503001 (2012)
- [5] Holmberg K, Erdemir A. Influence of tribology on global energy consumption, costs and emissions. *Friction* **5**(3): 263–284 (2017)
- [6] Muratore C, Hu J J, Voevodin A A. Tribological coatings for lubrication over multiple thermal cycles. *Surf Coat Tech* **203**(8): 957–962 (2009)
- [7] Pei Y T, Galvan D, De Hosson J T M. Tribological behavior and thermal stability of TiC/a-C: H nanocomposite coatings. *J Vac Sci Technol A* **24**(4): 1448–1453 (2006)
- [8] Bondarev A V, Kiryukhantsev-Korneev P V, Sidorenko D A, Shtansky D V. A new insight into hard low friction MoCN–Ag coatings intended for applications in wide temperature range. *Mater Design* **93**: 63–72 (2016)
- [9] Singh A K, Atheaya D, Tyagi R, Ranjan V. High temperature friction and wear of atmospheric plasma spray deposited NiMoAl–Ag–WS₂ composite coatings. *Surf Coat Tech* **455**: 129225 (2023)
- [10] Ju H B, Zhou R, Luan J, Yu L H, Xu J H, Zuo B, Yang J F, Geng Y X, Zhao L J, Fernandes F. Multilayer Mo₂N–Ag/SiN_x films for demanding applications: Morphology, structure and temperature-cycling tribological properties. *Mater Design* **223**: 111128 (2022)
- [11] Luan J, Kong F L, Evaristo M, Fernandes F, Zhou Y Z, Cavaleiro A, Ju H B. Design and magnetron sputtering of nanomultilayered W₂N/Ag–SiN_x films: Microstructural insights and optimized self-lubricant properties from room temperature to 500 °C. *Ceram Int* **50**(20): 39226–39234 (2024)
- [12] Wang Q C, Chen M H, Shan Z M, Sui C G, Zhang L, Zhu S L, Wang F H. Comparative study of mechanical and wear behavior of Cu/WS₂ composites fabricated by spark plasma sintering and hot pressing. *J Mater Sci Technol* **33**(11): 1416–1423 (2017)
- [13] Zhang Y P, Li P P, Ji L, Liu X H, Wan H Q, Chen L, Li H X, Jin Z L. Tribological properties of MoS₂ coating for ultra-long wear-life and low coefficient of friction combined with additive g-C₃N₄ in air. *Friction* **9**(4): 789–801 (2021)
- [14] Li H, Wang J H, Gao S, Chen Q, Peng L M, Liu K H, Wei X L. Superlubricity between MoS₂ monolayers. *Adv Mater* **29**(27): 1701474–1701479 (2017)
- [15] Cao H T, Momand J, Syari'ati A, Wen F, Rudolf P, Xiao P, De Hosson J T M, Pei Y T. Temperature-adaptive ultralubricity of a WS₂/a-C nanocomposite coating: Performance from room temperature up to 500 °C. *ACS Appl Mater Inter* **13**(24): 28843–28854 (2021)
- [16] Banerjee T, Chattopadhyay A K. Structural, mechanical and tribological properties of WS₂–Ti composite coating with and without hard under layer of TiN. *Surf Coat Tech* **258**: 849–860 (2014)
- [17] Lu X L, Yan M M, Yan Z, Chen W Y, Sui X D, Hao J Y, Liu W M. Exploring the atmospheric tribological properties of MoS₂–(Cr, Nb, Ti, Al, V) composite coatings by high throughput preparation method. *Tribol Int* **156**: 106844 (2021)
- [18] Zhang X, Zhang K, Kang X, Zhang L. Friction maps and wear maps of Ag/MoS₂/WS₂ nanocomposite with different sliding speed and normal force. *Tribol Int* **164**: 107228 (2021)
- [19] Gao X M, Hu M, Fu Y L, Weng L J, Liu W M, Sun J Y. MoS₂–Au/Au multilayer lubrication film with better resistance to space environment. *J Alloys Compd* **815**: 152483 (2020)
- [20] Zhu J N, Zeng Q F, Zhang B, Yan C, He W J. Elevated-temperature super-lubrication performance analysis of dispersion-strengthened WSN coatings: Experimental research and first-principles calculation. *Surf Coat Tech* **406**: 126651 (2021)
- [21] Cao H T, Wen F, De Hosson J T M, Pei Y T. On the self-repair of WS₂/a-C tribocoating. *Adv Mater Interfaces* **7**: 1900938 (2020)
- [22] Cao H T, De Hosson J T M, Pei Y T. Self-healing of a pre-notched WS₂/a-C coating. *Mater Res Lett* **7**(3): 103–109 (2019)
- [23] Li Z, Meng F S, Ding H H, Wang W J, Liu Q Y. Preparation and tribological properties of carbon-coated WS₂ nanosheets. *Materials* **12**(17): 2835 (2019)
- [24] Li S P, Sun H Y, Qin X D, Li H, Zhao Q. Tribological and dry drilling performance of WS₂/Cr–AlCrN coatings. *J Adv Mech Des Syst* **15**(1): JAMDSM0004 (2021)
- [25] Ding X Z, Zeng X T, He X Y, Chen Z. Tribological properties of Cr- and Ti-doped MoS₂ composite coatings under different humidity atmosphere. *Surf Coat Tech* **205**(1): 224–231 (2010)
- [26] Cao H T, Wen F, De Hosson J T M, Pei Y T. Instant WS₂ platelets reorientation of self-adaptive WS₂/a-C tribocoating. *Mater Lett* **229**: 64–67 (2018)
- [27] Yaqub T B, Al-Rjoub A, Cavaleiro A, Fernandes F. Exploring the industrial implementation of W–S–N coatings: A detailed study of the synthesis, compositional, structural, mechanical and multi-environment lubrication properties. *J Mater Res Technol* **18**: 547–563 (2022)
- [28] Yaqub T B, Yaqoob K, Mukhtar A, Fernandes F, Bondarev A, Ferreira F, Al-Rjoub A, Cavaleiro A. Vacuum tribological properties of W–S–N coatings synthesized by direct current magnetron sputtering. *Coatings* **12**(11): 1646 (2022)
- [29] Wang B, Gao K, Chang Q Y, Berman D, Tian Y. Magnesium silicate hydroxide–MoS₂–Sb₂O₃ coating nanomaterials for high-temperature superlubricity. *ACS Appl Nano Mater* **4**(7): 7097–7106 (2021)
- [30] Singh S, Saggi I S, Chen K W, Xuan Z X, Swihart M T, Sharma S. Humidity-tolerant room-temperature selective dual sensing and discrimination of NH₃ and NO using a WS₂/MWCNT composite. *ACS Appl Mater Inter* **14**(35): 40382–40395 (2022)
- [31] Wang G Q, Song J F, Zhao G, Ding Q J, Yin T Q, Wang H X. Tribological performance prediction of WS₂ coating under different conditions by machine learning. *Wear* **532**: 205092 (2023)
- [32] Voevodin A A, Zabinski J S. Nanocomposite and nanostructured tribological materials for space applications. *Compos Sci Technol* **65**(5): 741–748 (2005)
- [33] Meng Y G, Xu J, Ma L R, Jin Z M, Prakash B, Ma T B, Wang W Z. A review of advances in tribology in 2020–2021. *Friction* **10**(10): 1443–1595 (2022)
- [34] Polcar T, Cavaleiro A. Review on self-lubricant transition metal dichalcogenide nanocomposite coatings alloyed with carbon. *Surf Coat Tech* **206**(4): 686–695 (2011)
- [35] Cao H T, De Hosson J T M, Pei Y T. Effect of carbon concentration and argon flow rate on the microstructure and triboperformance of magnetron sputtered WS₂/a-C coatings. *Surf Coat Tech* **332**: 142–152 (2017)
- [36] Hudec T, Izai V, Satrapinskyy L, Huminiuc T, Roch T, Gregor M, Grančič B, Mikula M, Polcar T. Structure, mechanical and tribological properties of MoSe₂ and Mo–Se–N solid lubricant coatings. *Surf Coat Tech* **405**: 126536 (2021)

- [37] Mutafov P, Evaristo M, Cavaleiro A, Polcar T. Structure, mechanical and tribological properties of self-lubricant W-S-N coatings. *Surf Coat Tech* **261**: 7–14 (2015)
- [38] Xu J, He T F, Chai L Q, Qiao L, Zhang X Q, Wang P, Liu W M. Selective-releasing-affected lubricant mechanism of a self-assembled MoS₂/Mo-S-C nanoperiod multilayer film sliding in diverse atmospheres. *Phys Chem Chem Phys* **19**(12): 8161–8173 (2017)
- [39] Gustavsson F, Bugnet M, Polcar T, Cavaleiro A, Jacobson S. A high-resolution TEM/EELS study of the effect of doping elements on the sliding mechanisms of sputtered WS₂ coatings. *Tribol T* **58**(1): 113–118 (2015)
- [40] Polcar T, Evaristo M, Colaço R, Silviu Sandu C, Cavaleiro A. Nanoscale triboactivity: The response of Mo-Se-C coatings to sliding. *Acta Mater* **56**(18): 5101–5111 (2008)
- [41] Voevodin A A, O'Neill J P, Zabinski J S. Nanocomposite tribological coatings for aerospace applications. *Surf Coat Tech* **116**: 36–45 (1999)
- [42] Zhu J N, Zeng Q F, Zhang B, Yan C, He W J, Lin N M. Improving the lubrication of WSNb nanocomposite coatings by the *in-situ* oxygen shielding effect at elevated temperatures: A combined study with density functional theory simulations. *P I Mech Eng J-J Eng* **237** (5): 1181–1196 (2023)
- [43] Javdošňák D, Musil J, Soukup Z, Haviar S, Čerstvý R, Houska J. Tribological properties and oxidation resistance of tungsten and tungsten nitride films at temperatures up to 500 °C. *Tribol Int* **132**: 211–220 (2019)



Zhonghao Liu is currently a Ph.D. candidate at the School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), China. His research focused mainly on the design, deposition, and performance optimization of functional protective coatings for tribological and piezoelectric applications.



Huatang Cao is a professor and Ph.D. supervisor at the School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), China. He was selected for both the National and Hubei Provincial High-Level Overseas Talent Programs. He received his Ph.D. degree from the University of Groningen, the Netherlands, in 2019 and worked as a postdoc researcher at the University of Manchester, UK, from 2019 to 2022. He joined the State Key Laboratory of Materials Processing and Die & Mold Technology at HUST in 2022. His research interests include functional protective coatings, metal surface modification, tribology, solid lubrication and physical metallurgy, such as metal solidification and additive manufacturing.