

Dealloying-induced surface porosity for enhancing tribological properties of Ag-DLC films under starved lubrication

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Abstract: Surface porous architectures serving as micro-oil reservoirs offer a promising adaptive self-lubrication strategy for critical engine components under starved lubrication conditions, especially during frequent start-stop cycles. However, the controlled fabrication of such structures on DLC surfaces and their tribological behavior under representative oil-starved conditions remain insufficiently explored. Herein, we propose a novel strategy that exploits the inherent thermodynamic incompatibility and self-migration behavior of Ag in the carbon matrix as a natural advantage. A simple dealloying method was employed to construct surface porous structure on Ag-DLC films via the selective removal of Ag particles, aiming to improve tribological properties under starved lubrication. Results reveal that the size and density of porous structure is regulated by the Ag target current during deposition. Notably, the introduced porous structure significantly mitigates abnormal wear at the friction interface while maintaining a low and stable friction coefficient under starved lubrication. The porous structure acts as micro-oil reservoirs, and it effectively replenishes the boundary lubricating film via load/thermal stimuli induced oil release. Mechanisms attribute to the synergistic effects of replenished the boundary lubricating film, reduced real contact area, and graphitized transfer films. These findings provide a foundation for designing intelligent adaptive DLC-based lubrication systems capable of autonomous oil replenishment under intermittent lubrication regimes.

Keywords: Ag-DLC films; Dealloying process; Surface porous structure; Starved lubrication.

1. Introduction

The solid-liquid composite lubrication system, consisting of diamond-like carbon (DLC) films and lubricating oil, has become one of the key technologies for enhancing the tribological performance of mechanical components, particularly in critical parts such as piston rings, cylinder liners, and bearings [1-6]. This system effectively combines the high hardness and low friction coefficient of the DLC films with the excellent heat dissipation and continuous lubrication capabilities of liquid lubricants, significantly reducing wear and extending service life. However, the outstanding performance of the composite system highly relies on the formation and continuity of the lubricating oil film at the friction interface [7-10]. Under practical operating conditions, especially during the frequent start-stop engine cycles, components often operate in a starved lubrication state, making it difficult to form a stable lubricating oil film. The direct contact between the friction pairs increases the risk of abnormal wear and premature failure of the DLC films, potentially leading to irreversible damage to the entire powertrain system [2, 11-14]. Therefore, it is an urgent core issue to enhance the adaptive lubrication capability of the DLC film surfaces under starved lubrication.

Constructing micro-nano porous structures on the material surface to function as “micro-oil reservoirs” is one of effective strategies to address the above challenges under starved lubrication, which garners significant attention [15-17]. These structures can actively adsorb and retain lubricating oil via capillary action, releasing it controllably to the friction interface under external stimuli (such as heat, pressure, or centrifugal force) in starved lubrication conditions. This mechanism enables self-lubrication and maintains a low friction state [18-20]. Among the preparation techniques for porous structures [21-27], the dealloying process, characterized by the

selective corrosion/removal of certain elemental phases from a composite material, exhibits unique advantages due to its ability to precisely control porosity and pore size [28, 29]. For instance, Bouts et al. [30] successfully prepared a nanoporous carbon film with a spongy-like morphology by selectively etching copper/carbon nano-composite films (nc-Cu/C) using nitric acid. Hatada et al. [31] developed a two-step method to prepare nanostructured surfaces on diamond-like carbon (DLC) films: first, a zinc-containing DLC film was prepared via plasma source ion implantation combined with magnetron sputtering, and then surface zinc particles were selectively dissolved in nitric acid, leaving behind a nanoporous surface. Jin et al. [15] deposited a DLC/micro-arc oxidation (MAO) composite coating with a porous surface, and found that the porous structure acts as a reservoir of lubricating oil and wear debris to replenish the liquid lubrication film and improve abrasive wear, thereby optimizing the tribological performance. Especially, silver-doped DLC (Ag-DLC) films represent an ideal material platform for preparing porous structure via the de-alloying process. On one hand, Ag incorporation helps alleviate the high internal stress of the DLC film and enhances the film-substrate adhesion [32]; on the other hand, due to the thermodynamic immiscibility between Ag and the carbon matrix, Ag tends to exist in the form of nanoparticles, which provides a foundation for subsequently building surface porous via selective etching [33]. Although the preparation and properties of Ag-DLC films have been widely investigated, existing studies have predominantly focused on their antibacterial characteristics, tribological performance under sufficient lubrication, or the solid lubricating effect of Ag [19, 34, 35]. To date, the deliberate design of porous structures on Ag-DLC films via dealloying, along with a systematic investigation of their lubrication behavior and underlying mechanisms under representative oil-starved conditions (during engine start-stop operations), remains a largely unexplored research frontier.

Therefore, this research aims to construct porous structures on the surface of Ag-DLC films with different Ag contents via a dealloying process, and investigate the tribological behavior under starved lubrication, emphasizing the friction and wear mechanisms. The related results are expected to provide novel design insights and a solid experimental foundation for developing a new generation of intelligent adaptive lubricating systems.

2. Experimental details

2.1 Dealloying treatment of Ag-DLC films

Ag-DLC films were deposited on 304 stainless steel substrates using unbalanced magnetron sputtering technology, and the specific process and deposition parameters have been reported in our previous work [36]. Considering the self-migration behavior of Ag, the prepared Ag-DLC films were stored at room temperature for 30 days. As shown in **Figure 1**, the as-deposited films were immersed in a concentrated nitric acid solution (concentration 65.0-68.0 wt%) [37] at 65°C for 30 minutes. Subsequently, the treated film surfaces were further washed using deionized water, and dried in N₂ atmosphere for 3 hours, ultimately yielding films with surface porous. According to the Ag target current (0, 0.3, 0.6, and 0.9 A) for depositing the Ag-DLC films, the treated films were designated as S1, S2, S3, and S4, respectively.

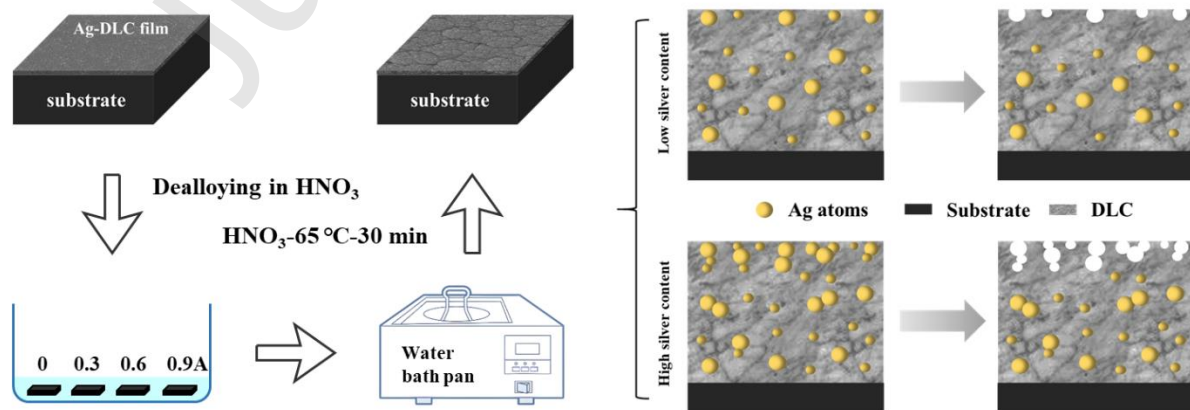


Figure.1 Schematic diagram of dealloying process

2.2 Microstructure characterization and mechanical property tests

The phase analysis of the films before and after dealloying treatment was conducted using an X-ray diffractometer (XRD, D8 ADVANCE, Bruker AXS), with a scanning range of 2θ from 20° to 80° and a scanning rate of 0.02 s/step. A Raman spectrometer (inVia Raman Microscope, RENISHAW, UK) with a laser wavelength of 532 nm and X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Scientific, USA) were utilized to characterize the microstructure of the Ag-DLC films after dealloying, and to investigate the impact of acid etching on the microstructure of the Ag-DLC films. Field emission scanning electron microscopy (FESEM, MIRA3, TESCAN, Czech Republic) was employed to obtain the surface and cross-sectional morphology of the films, and energy dispersive spectroscopy (XFlash 6130, BRUKER, Germany) was used for line scan analysis of the cross-section. Atomic force microscopy (AFM, Dimension ICON, BRUKER, Germany) was used to acquire the surface morphology and surface roughness of the films. The wettability of the film surface was characterized by a contact angle measurement instrument (JC2000D, POWEREACH, China).

The mechanical properties of the Ag-DLC films after dealloying were tested using a nanoindentation tester (TTX-NHT2, Anton Paar, Austria). The test was conducted in a constant depth mode, with the maximum indentation depth being approximately 10% of the film thickness to minimize the influence of the substrate on the mechanical property measurements. The loading/unloading rates were set at 501 nm/min, and the hold time was 10 seconds. Based on the load-depth curve, the elastic recovery rate of the Ag-DLC films was calculated using **Equation 1**:

$$ER\% = \frac{d_{max} - d_{res}}{d_{max}} \times 100\% \quad (1)$$

where d_{max} denotes the maximum penetration depth, and d_{res} represents the permanent plastic

deformation depth. The adhesive strength between the deposited films and the 304 stainless steel substrate was evaluated using a scratch tester (RST3, Anton Paar, Austria) with a scratch length of 5 mm, an initial load of 1 N, a maximum load of 30 N, and a loading/unloading rate of 29 N/min.

2.3 Tribological tests

The tribological behavior of the treated films under both oil lubrication conditions and starved lubrication conditions were assessed using a CSM tribometer (TRN 0204015, Anton Paar, Switzerland). Polyalphaolefin (PAO6) was employed as the lubricating oil in the experiments. The starved lubrication state was achieved by a standardized two-step procedure: the coated specimens were first fully immersed in PAO6 base oil for 8 h to allow complete saturation of the surface and any porous features, and then vertically suspended for 6 h to drain the excess oil by gravity. After this treatment, no visible bulk oil remained on the surface; only a thin adsorbed oil layer was retained, primarily by capillary forces within the porous structures and by physisorption, without any external oil supply during the subsequent sliding test. The friction tests were conducted under a reciprocating mode with a total amplitude of 5 mm, a load of 5 N (corresponding to a Hertzian contact pressure in the range of 0.36 to 1.14 GPa), a frequency of 5 Hz, and a total duration of 20000 cycles (200 m). A GCr15 ball with a diameter of 6 mm was used as the counterpart. The tests were performed in an ambient environment at 21 ± 2.5 °C and $25\% \pm 5\%$ RH. The wear rates of the treated films and the counterpart were calculated using the Archard wear equation (**Equation 2**) [38, 39], and the wear volume of the counterpart was determined using **Equation 3**:

$$K = \frac{V}{F \times D} = \frac{S \times l}{F \times D} \quad (2)$$

$$V_{ball} = \frac{\pi \times [2R^3 - (2R^2 + r^2)\sqrt{R^2 - r^2}]}{3} \quad (3)$$

where K ($\text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$) represents the wear rate of the treated films, F (N) is the applied normal

load, V (mm^3) is the wear volume, D (m) is the total distance of the friction test, S (mm^2) is the cross-sectional area of the wear track, l (mm) is the full amplitude of the reciprocating friction, and R/r (mm) is the radius of the counterpart/wear scar. The cross-sectional area of the wear track was measured using a 3D profilometer (MicroXAM-800, KLA-Tencor, USA), which also provided a 3D surface topography of the treated films. To further understand the differences in tribological behavior, the evolution in the morphology, structure, and material transfer (composition) at friction interface was characterized by an optical microscope (Axio Lab.A1, ZEISS, Germany), Raman spectroscopy, and an FESEM equipped with energy dispersive spectroscopy.

3. Results and discussion

3.1 Microstructure of the treated films

Figures 2a and **b** give the surface morphology and 3D topography of the treated films, respectively. In contrast to samples S2-S4 (the treated Ag-DLC films), sample S1 (the pure DLC film) displays a uniform and dense surface with a typical cluster-like (droplet-like) morphology, exhibiting nanoscale smoothness ($R_a = 4.25$ nm). Moreover, it also presents a uniform, compact cross-sectional structure without any signs of delamination (see **Figure 2c**). For the treated Ag-DLC systems (S2-S4), the surface exhibits larger cluster structures with distinct porous structures (20-200 nm) present between the clusters. As the Ag target current increases during Ag-DLC deposition, the porous structure on the treated film surface becomes more pronounced, manifested by an increase in both pore density and size, and the surface roughness rises correspondingly. These findings further confirm the successful preparation of DLC films with surface porosity via the dealloying method. The formation of the porous structure is closely related to the diffusion channels generated by the self-migration behavior of Ag. Specifically, the low compatibility between Ag

and the carbon matrix in DLC films promotes the formation of nanoclusters or isolated Ag phases. To reduce the system energy, Ag tends to undergo spontaneous migration and agglomeration via interlayer diffusion [40]. The diffusion of Ag atoms inevitably creates channels within the carbon matrix, which leave pores of varying sizes on the surface after acid treatment. Moreover, the dealloying process causes only minimal damage to the carbon matrix [41], allowing the overall clustered surface morphology of the film to be largely preserved.

EDS line-scan profiles of Ag (see **Figure 2c**) provide further evidence for the formation and size evolution of the porous structures. For sample S2, the distribution of Ag across the interface shows an initial increase followed by a decrease, indicating that dealloying is confined mainly to the surface region. This is because the Ag content is relatively low, and the dense DLC structure not only hinders Ag diffusion but also acts as an effective barrier against nitric acid, thereby limiting the dealloying effect to the surface layer. In contrast, for samples S3 and S4, the Ag distribution suggests a greater treatment depth. This is particularly evident in sample S4, where the Ag signal remains nearly constant along the interface. The higher Ag content in these films leads to extensive diffusion channels throughout the carbon matrix, enabling the dealloying process to penetrate the entire film thickness. As a result, the treatment depth is maximized, corresponding to the highest density and largest size of the resulting porous structures.

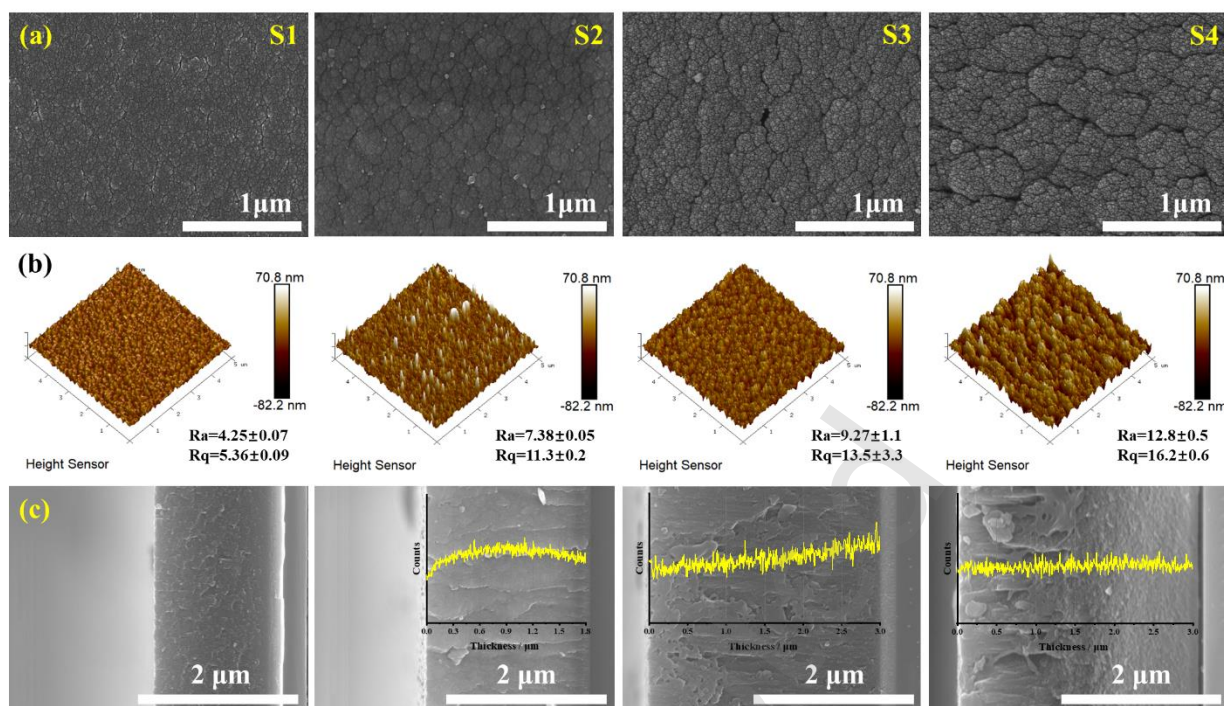


Figure.2 Morphology characteristics of the treated films. (a) Surface morphology; (b) 3D topography and corresponding surface roughness; (c) Cross-sectional morphology and EDS line-scan profile of Ag element.

As observed in **Figure 3a**, the Raman spectra exhibit a gradual increase in separation between the D band and G band from sample S1 to S4, indicating a transition of the carbon structure towards graphite structure. Further fitting [42] results (see **Figures 3b-c**), including the G peak positions, the full width at half maximum of the G peak (FWHM_G), and the intensity ratio of the D peak to the G peak (I_D/I_G), exhibit a similar trend consistent with that observed prior to dealloying in our earlier work [36]. The structure remains predominantly influenced by the Ag target current used during Ag-DLC deposition, with the carbon structure becoming more ordered with the target current. Notably, compared to the film before dealloying [36], the treated films present a slight increase in the I_D/I_G ratio and a decrease in the FWHM_G , indicating that dealloying treatment induces a certain degree of graphitization (or enhanced structure ordering) on the film surface [43].

From the XPS survey and the Ag content as illustrated in **Figures 3d-e**, the treated films are

primarily composed of C, O, and Ag, with C constituting the majority of the elemental composition. Notably, the Ag content displays a gradually decreasing trend (**Figure 3e**) from sample S1 to S4, reflecting the formation of a porous structure via the dealloying process. Normally, as a surface-sensitive technique, XPS primarily detects the elemental composition within the top few nanometers of a sample. Due to the high initial Ag content in samples S3 and S4 (especially S4), the self-migration of Ag created extensive diffusion channels throughout the film. This enabled efficient removal of Ag during dealloying, thereby resulting in the lowest Ag content and the formation of a porous surface structure. Taking the sample S3 as an example (**Figure 3f**), the C 1s spectrum of the film was fitted into four Lorentzian-Gaussian (20%/80%) peaks: C=C bond located at 284.6 ± 0.1 eV, C-C bond at 285.3 ± 0.1 eV, C-O bond at 286.5 ± 0.1 eV, and C=O bond at 288 ± 0.1 eV[44]. Results indicate that the variation in the $sp^2/(sp^2+sp^3)$ ratios as shown in **Figure 3g** further supports the Raman results. **Figure 3h** presents the XRD patterns of the films before and after dealloying. Characteristic diffraction peaks are observed at 38.1° , 44.3° , 64.4° , and 77.5° , corresponding to the (111), (200), (220), and (311) crystal planes of the Ag crystalline phase, respectively. Another distinct set of characteristic diffraction peaks at 43.6° , 50.8° , and 74.7° correspond to the (111), (200), and (220) crystal planes of the FeCrNi crystalline phase, respectively. The weakening and disappearance (especially in S4) of the Ag diffraction peaks provide additional evidence for the earlier conclusion.

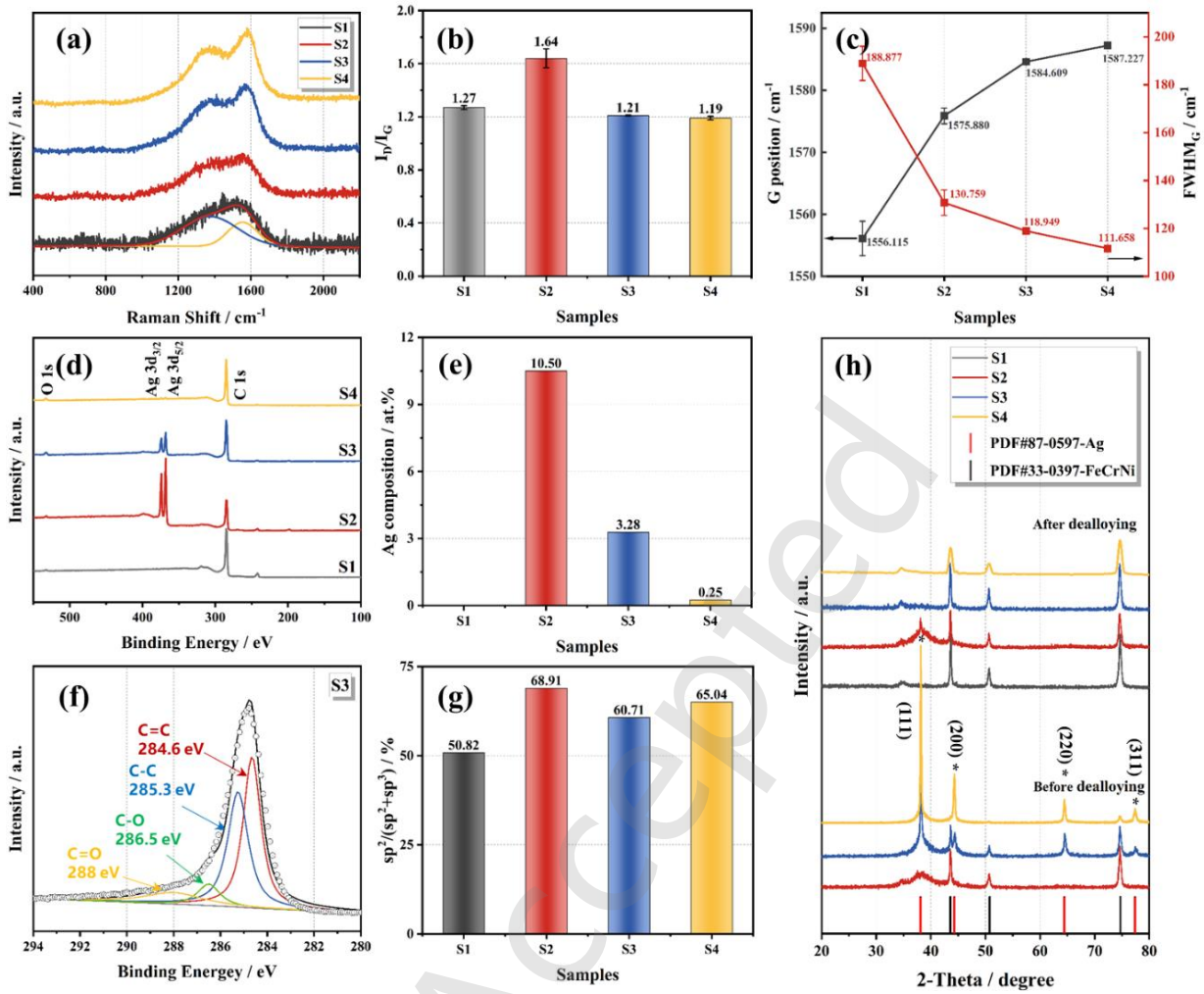


Figure 3 Microstructure of the treated films. (a-c) Raman spectra and the fitting results; (d) XPS survey; (e) Ag content obtained from XPS; (f) C1s spectrum of sample S3 and the deconvoluted results; (g) $sp^2/(sp^2+sp^3)$ ratio; (h) XRD patterns before and after dealloying treatment.

3.2 Mechanical properties of the treated films

Figure 4 presents the load-depth curves and key mechanical properties of the treated films. The Ag target current used during deposition remains the dominant factor influencing the mechanical properties of the treated films. Compared with Sample S1, Sample S2 shows improved mechanical properties including hardness, elastic modulus, elastic recovery ratio, H/E , and H^3/E^2 ratio), whereas Samples S3 and S4 exhibit a significant decline, which is attributed to the disruption of carbon matrix continuity caused by excessive Ag doping. Furthermore, the mechanical properties

of the treated films display a slight decrease compared to their state before dealloying treatment [36], which is attributed to the graphitization transition and the induced structural discontinuity resulting from the dealloying process.

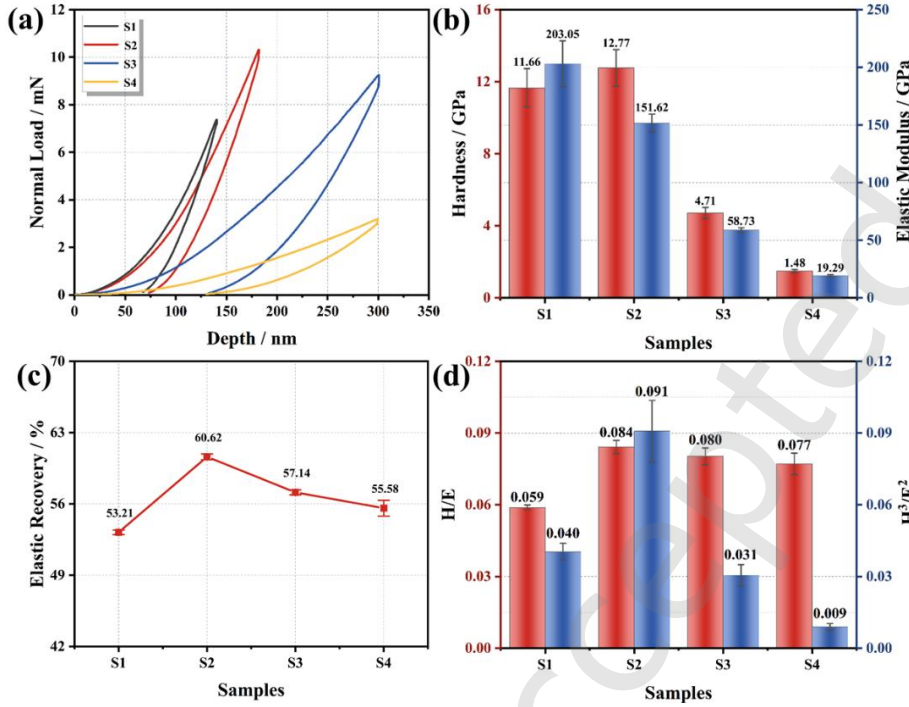


Figure 4 Load-depth curves (a), hardness and elastic modulus (b), elastic recovery rate (c), and H/E and H^3/E^2 ratios (d) of the treated films.

Figure 5 presents the scratch images of the films deposited on 304 stainless steel substrates together with the corresponding critical loads. The red, orange, and blue dashed lines denote the initial delamination point (Lc1), the continuous delamination point (Lc2), and the final failure point (Lc3), respectively. As the Ag target current increases, the Lc3 of the treated films exhibits a trend of first increasing and then decreasing. Specifically, sample S2 delivers the best adhesion performance: its Lc3 exceeds 30 N, and the interval between Lc2 and Lc3 is the widest, reflecting the highest bond strength and toughness. Sample S3 shows a pronounced decline, with Lc3 dropping to approximately 14.2 N. For sample S4, the substrate is exposed virtually from the onset of scratching, indicating extremely poor adhesion. These results demonstrate that, although

Ag-DLC films with the high Ag content develop a distinct porous structure after dealloying, the concurrently increased dealloying depth severely weakens the film–substrate adhesion, which is unfavorable for long-term service durability.

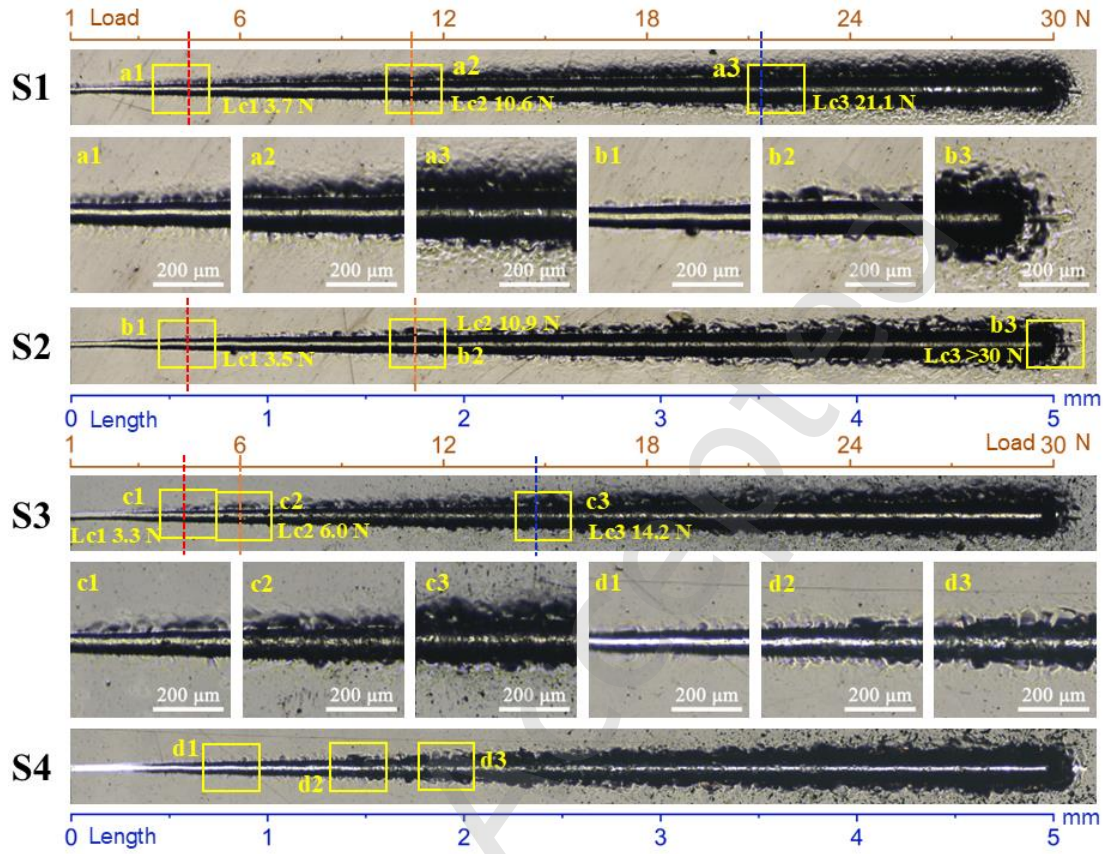


Figure 5 Scratch images and corresponding magnified views of the treated films

3.3 Tribological behaviors of the treated films

The friction coefficient curves of the films under both oil lubrication and starved lubrication conditions are displayed in **Figures 6a-b**. Compared to the oil lubrication condition, the friction curves of Sample S1 under starved lubrication condition exhibit a relatively distinct running-in phase. In contrast, Samples S2 and S3 exhibit stable friction coefficient curves under both service conditions, indicating the effectiveness of the surface porous structure in improving the friction coefficient under starved lubrication. Notably, the friction coefficient curve of Sample S4 rises sharply at approximately 100 cycles (friction failure), which is attributed to its inferior mechanical

properties (**Figure 4**) and poor film-substrate adhesion resulting from the greater dealloying depth (**Figures 2 and 5**). The average friction coefficients and wear rates of the treated films and the counterpart are presented in **Figures 6c-e**. The friction coefficients of the treated films show similar trends under both oil lubrication and starved lubrication conditions. Compared to Sample S1, the friction coefficients of Samples S2 and S3 decrease by approximately 20% (**Figure 6c**) and remain stable under both lubrication regimes, whereas the friction coefficient of Sample S1 increases significantly under starved lubrication. In contrast, the variation in wear rate differs from that of the friction coefficient. Under oil lubrication conditions, the wear rates of the three samples remain largely constant, which is attributed to the protective effect of the lubricating oil film. Under starved lubrication, however, the wear rates show a gradually decreasing trend (**Figure 6d**), with that of Sample S3 reaching as low as $9.26 \times 10^{-8} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$. Furthermore, the wear of the counterpart is also a critical factor determining the service life of the tribological system. In this study, the wear results of the GCr15 counterpart further confirm the beneficial effect of the surface porous structure. Compared to Sample S1, the wear rate of the counterpart sliding against S3 is reduced by more than an order of magnitude (**Figure 6e**). Especially, under starved lubrication, the wear rates of the counterparts (S2 and S3) increase only slightly compared to those under oil lubrication, and their increments are substantially lower than the wear increase observed for the counterpart sliding against Sample S1. Specifically, S2 and S3 maintain nearly the same friction coefficients (0.079/0.078) and wear rates ($9.52 \times 10^{-8}/9.26 \times 10^{-8} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$) under starved lubrication as under oil lubrication, whereas S1 shows an ~28% increase in wear rate and a rise in friction coefficient from 0.091 to 0.107, demonstrating the adaptive lubrication enabled by the porous structure. In summary, the design of a surface porous structure not only effectively mitigates abnormal wear at

the friction interface of DLC films under starved lubrication but also helps maintain a low and stable coefficient of friction. The underlying lubrication mechanisms will be discussed in detail in the following section.

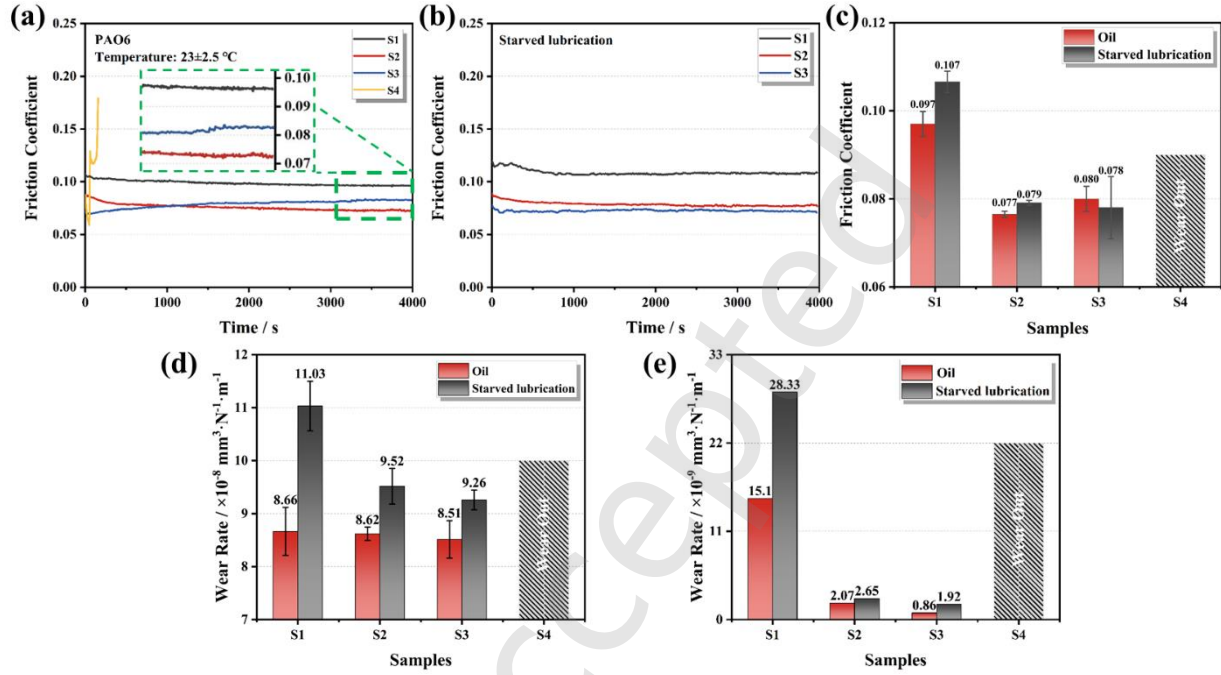


Figure 6 Tribological performance of the treated films under oil lubrication and starved lubrication conditions.

(a-b) Friction coefficient curves; (c) Average friction coefficient, (d-e) Wear rates of the treated films and GCr15 counterpart.

3.4 Tribological interface analysis

To understand the difference in tribological properties of the treated films, the morphological characteristics at friction interface of the treated films under both oil lubrication and starved lubrication conditions are illustrated in **Figure 7**. Under both oil lubrication and starved lubrication conditions, the friction interfaces exhibit relatively similar surface profile characteristics. For Sample S1, distinct and relatively deep ploughing grooves are observed inside the wear tracks and on the wear scar surfaces, accompanied by severe plastic deformation along the track edges. Almost

no material transfer is detected on the wear scar surface (particularly evident under oil lubrication conditions), indicating that the wear process of Sample S1 is primarily dominated by abrasive wear. In contrast, the number and depth of ploughing grooves and the plastic deformation at the wear track edges are significantly improved for Samples S2 and S3. Especially for Sample S3, ploughing grooves are nearly absent on the friction interface, and the material transfer is observed on the wear scar surface. This suggests that the surface porous structure effectively mitigates abrasive wear by entrapping wear debris. Meanwhile, the reduction in plastic deformation at the track edges is mainly attributed to the contribution of the lubricating oil film. Based on the Hamrock-Dawson equation [45, 46] (), the minimum thickness of the lubricating oil film ($H_{\min}$) in the contact region was calculated, and the lubrication regime was determined by the specific film thickness λ , as shown in **Figures 7g-h** and **Table S1 of Supplementary Data**. Under oil lubrication conditions, the λ values for the four samples range from 0.62 to 0.67, all falling within the boundary lubrication regime (**Figure 7h**). As shown in **Figure 7g**, the $H_{\min}$ gradually increases from 13.89 nm for Sample S1 to 16.52 nm for Sample S4. A thicker boundary lubrication film helps reduce both plastic deformation at the wear track edges and abrasive wear. Furthermore, under boundary lubrication, the lubricant cannot completely separate the film from the counterpart; therefore, the tribological behavior is also closely related to the surface roughness of the film [39, 47-49]. The rough, porous surface reduces the actual contact area, which is beneficial for lowering friction. Under starved lubrication conditions, the friction process of Sample S1 involves almost no lubricant, making the contact condition close to dry sliding and resulting in relatively severe wear. The classical Hamrock-Dawson equation presumes a fully flooded contact and is therefore not applicable under starved lubrication. For Samples S2-S3, however, the surface porous structure combined with high

oil affinity (**Figure 7i**) allows a portion of the lubricant to be retained even after prolonged static periods. This stored oil is released under mechanical stimulation during friction, enabling the DLC films to maintain a wear rate comparable to that under oil lubrication conditions even under starved lubrication.

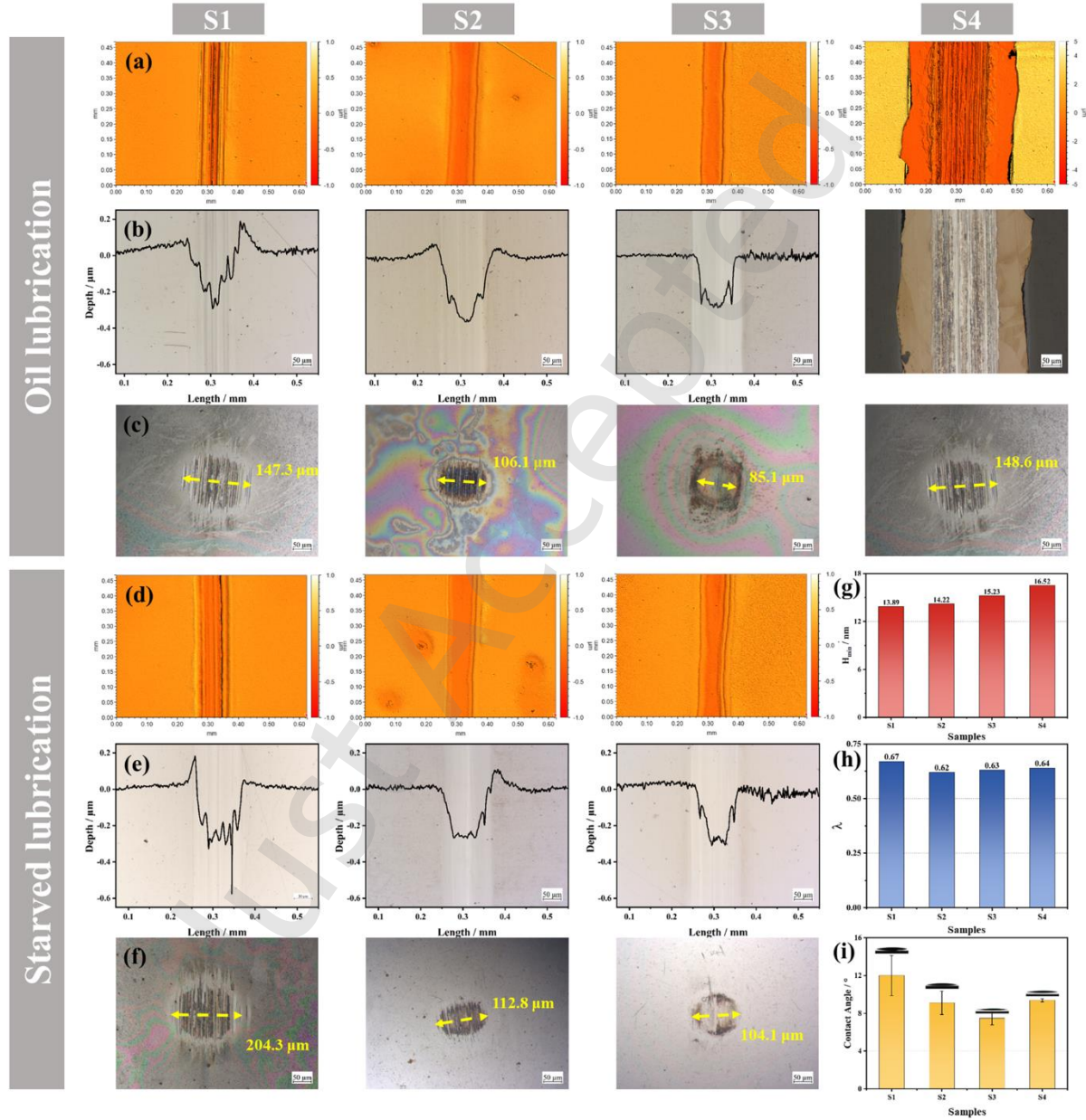


Figure 7 Interfacial characteristics of the treated films under oil lubrication and starved lubrication conditions.

(a, d) 3D topography of the wear tracks; (b, e) Optical images and surface profiles of the wear tracks; (c, f) Optical images of wear scars; (g) Minimum oil film thickness; (h) λ ; (i) Surface contact angle of PAO6 oil.

The structural evolution and composition of friction interface were further characterized under both oil lubrication and starved lubrication conditions, as displayed in **Figure 8**. Compared to the treated films before sliding, the I_D/I_G ratio inside the wear tracks shows varying degrees of increase, indicating that a certain degree of graphitization transformation occurred at the friction interface, which is beneficial for reducing the friction coefficient. Notably, under starved lubrication conditions, the I_D/I_G ratio of Sample S1 exhibited the most significant change before and after sliding, indirectly reflecting severe insufficiency of the lubricating oil film in this system, which leads to intense graphitization at the friction interface. Although the graphitization structure is conducive to form a low-shear sliding interface, it is essentially a process of material consumption and thus exacerbates wear. In contrast, the structure inside the wear track of Sample S3 remains almost unchanged before and after sliding, attributed to the protective effect of the lubricating oil film. **Figures 8c-h** present the C elemental mapping and Raman spectra of wear scars; the corresponding Fe and O maps are provided in **Fig. S1 of Supplementary Data**. Quantitative elemental compositions under oil and starved lubrication are summarized in **Tables S2 and S3**. The transfer films are dominated by C and Fe, with low O and negligible Ag, confirming the dominant role of the carbon transfer film. For Sample S1, no clearly defined carbon transfer film is observed; only a small amount of carbon is unevenly distributed inside the ploughing grooves, which is attributed to severe abrasive wear that disrupts the formation and retention of a surface carbon transfer film. In contrast, Samples S2 and S3, especially Sample S3, show the formation of a distinct and more uniformly distributed carbon transfer film on the wear scar surface. The variation in their I_D/I_G ratios follows the same trend as that observed inside the wear tracks. **The moderate dealloying-induced graphitization (Figure 3) is distinct from the pronounced friction-induced**

graphitization inside the wear tracks (**Figure 8**). Although S2 shows the highest I_D/I_G ratio (**Figures 8d and g**), its friction coefficient is nearly the same as that of S3, indicating the degree of interfacial graphitization is not the sole influencing factor. An additional contribution comes from the surface porous structure, which reduces the real contact area [39, 47-49] between the treated films and GCr15 counterpart, thereby synergistically improving the friction coefficient of the system. Moreover, the superior oil retention capability of the Sample S3 surface leads to the best tribological performance under starved lubrication conditions. It should be noted that a characteristic peak of PAO oil appears around 1440 cm^{-1} (**Figures 8f and g**), assigned to the deformation vibration of methyl ($-\text{CH}_3-$) groups. This signal originates from the interference of the adsorbed oil layer on the film surface [50].

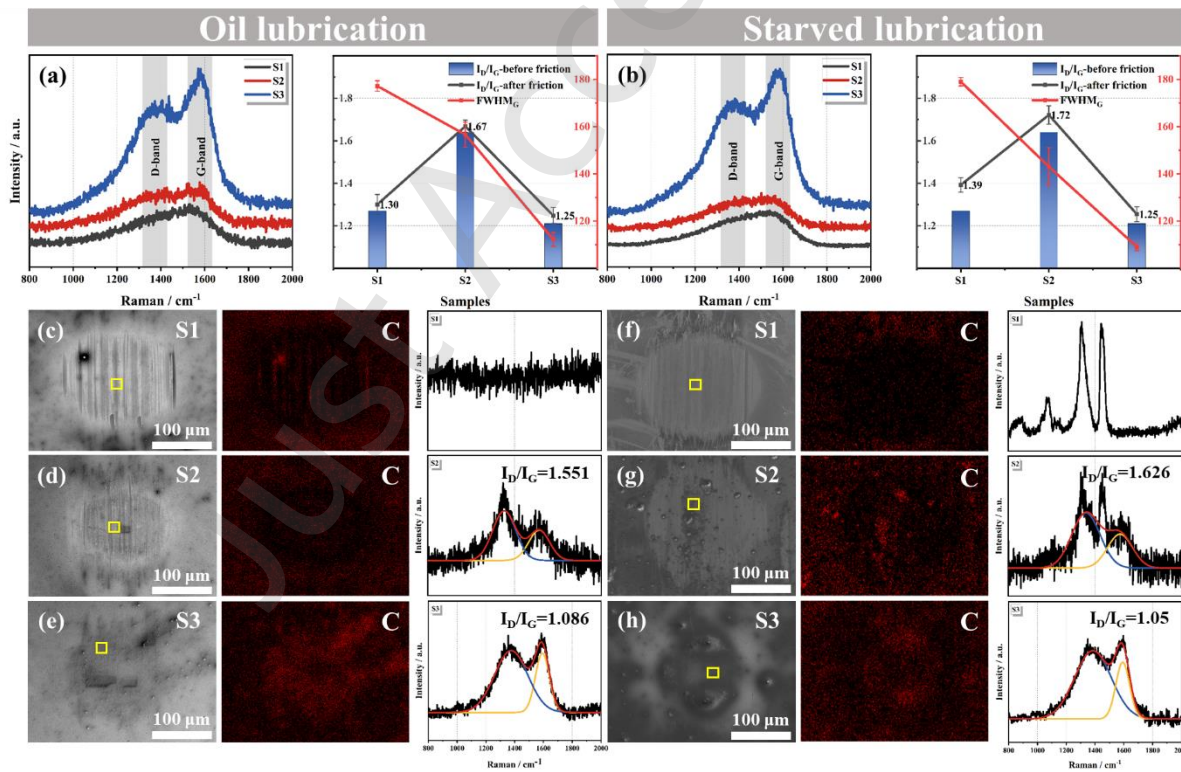


Figure 8 The structural evolution and composition of friction interface of the treated films under oil lubrication and starved lubrication conditions. (a-b) Raman spectra and fitted results inside the wear tracks; (c-h) EDS elemental mapping and Raman results of wear scars.

To further decouple the contributions of the surface porous structure and the solid lubrication of residual Ag, a comparison with the tribological performance of the original (untreated) Ag-DLC films under identical conditions would be ideal. However, Ag exists in its elemental form in the DLC matrix (**Figure 3h**) and is thermodynamically unstable, prone to self-migration and enrichment during friction, which continuously alters the interfacial Ag content and chemical state, thus complicating the interpretation. In our previous work [36], the untreated S1-S4 films exhibited steady-state friction coefficients in the range of 0.10-0.12 under the same oil lubrication conditions, comparable to those of the de-alloyed S2 and S3 samples, suggesting that residual Ag is not the dominant factor controlling the steady-state friction coefficient. Combined with the negligible residual Ag content (e.g., 3.28 at.% for S3) and the absence of Ag on the wear scars (**Figure 8**), the marked improvement in the performance of Sample S3 under starved lubrication further confirms that the “micro-oil reservoir” effect of the porous structure, rather than solid lubrication by Ag, is the primary mechanism. We acknowledge that the lack of direct tribological data for untreated Ag-DLC films under identical starved lubrication conditions represents a limitation of this study, and the present conclusions regarding the relative contributions of Ag and the porous structure rely on indirect experimental evidence.

In summary, the tribological performance of the treated films under both oil lubrication and starved lubrication conditions significantly depends on the surface porous structures, and the corresponding lubrication mechanism schematic is illustrated in **Figure 9**. Under oil lubrication conditions, the treated films and the lubricant together form a solid-liquid synergistic lubrication system (boundary lubrication regime). The protective effect of the boundary lubricating film and the intrinsic mechanical properties of the films result in only a minor influence of the porous

structure on the film wear rate (**Figures 9a** and **c**). However, the porous structure significantly alleviates abrasive wear, plastic deformation of the film, and the wear rate of the counterpart by entrapping wear debris (**Figure 9c**). The friction coefficient of the system is collectively determined by the distribution of the transfer film, the graphitization degree at the friction interface, and the real contact area between the film and the counterpart. Under starved lubrication conditions, the smooth and dense surface of the intrinsic DLC film (S1) cannot actively adsorb or retain lubricating oil, causing the friction process to approach a dry sliding state (corresponding to high friction coefficients and wear rates). In contrast, the film systems with surface porous structures (S2-S3) exhibit good oil affinity, enabling them to actively adsorb and store lubricant. Under starved lubrication, the stored oil can be released to the friction interface under external stimuli such as load and thermal effects (**Figure 9d**), thereby replenishing the boundary lubricating film. Together with the graphitized transfer film, this mechanism effectively mitigates the high friction coefficient and abnormal wear observed in the intrinsic DLC system (Sample S1, **Figure 9b**) under starved lubrication conditions. For sample S4, the premature failure originates from poor film-substrate adhesion and degraded mechanical integrity caused by the excessive dealloying depth, as evidenced by the scratch critical loads (**Figure 5**) and deep Ag removal shown by cross-sectional EDS line scans (**Figure 2c**).

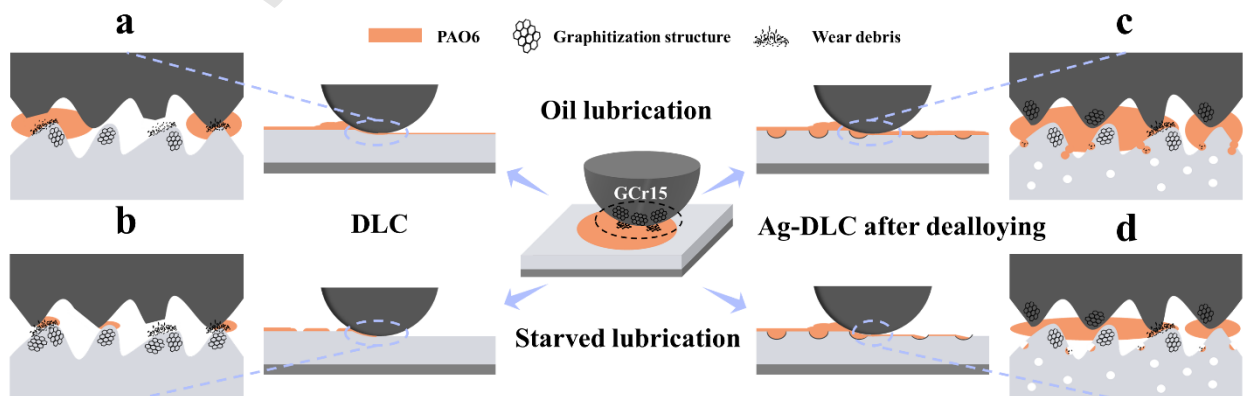


Figure 9 Friction mechanism diagram of the treated films under oil lubrication and starved lubrication conditions

4. Conclusions

This work successfully constructed porous structures on Ag-DLC films via a novel dealloying approach to enhance the tribological properties under starved lubrication, focusing on their tribological behaviors and the corresponding underlying lubrication mechanism. The main conclusions are as follows:

- Dealloying successfully fabricates 20-200 nm porous structures on Ag-DLC films. Pore density and size increase with the Ag target current, attributed to Ag self-migration induced diffusion channels. After dealloying, the carbon matrix exhibits a graphitization trend, and the mechanical properties first improve (S2) then deteriorate (S3/S4) due to excessive Ag-induced carbon matrix disruption.
- The design of a surface porous structure significantly mitigates abnormal wear at the friction interface of DLC films under starved lubrication, characterized by an ~20% reduction in friction coefficient, a lower wear rate ($9.26 \times 10^{-8} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$), and a reduction of more than an order of magnitude in the wear rate of GCr15 counterparts. In contrast, the dense DLC film (S1) suffers from severe wear and high friction due to insufficient lubrication, approaching a dry sliding state.
- Under starved lubrication, porous structures exhibit high oil affinity, enabling active oil storage and controlled release under load/thermal stimuli to replenish the boundary lubricating film. They also reduce real contact area and trap wear debris, synergizing with

friction-induced graphitized transfer films to improve the tribological performance. The findings offer new insights for developing a new generation of intelligent adaptive lubricating systems.

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