Running-in behavior of a H-DLC/Al₂O₃ pair at the nanoscale

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Abstract: Diamond-like carbon (DLC) film has been developed as an extremely effective lubricant to reduce energy dissipation; however, most films should undergo running-in to achieve a super-low friction state. In this study, the running-in behaviors of an H-DLC/Al₂O₃ pair were investigated through a controllable single-asperity contact study using an atomic force microscope. This study presents direct evidence that illustrates the role of transfer layer formation and oxide layer removal in the friction reduction during running-in. After 200 sliding cycles, a thin transfer layer was formed on the Al₂O₃ tip. Compared with a clean tip, this modified tip showed a significantly lower adhesion force and friction force on the original H-DLC film, which confirmed the contribution of the transfer layer formation in the friction reduction during running-in. It was also found that the friction coefficient of the H-DLC/Al₂O₃ pair decreased linearly as the oxygen concentration of the H-DLC substrate surface decreased. This phenomenon can be explained by a change in the contact surface from an oxygen termination with strong hydrogen bond interactions to a hydrogen termination with weak van der Waals interactions. These results provide new insights that quantitatively reveal the running-in mechanism at the nanoscale, which may help with the design optimization of DLC films for different environmental applications.

Keywords: hydrogenated diamond-like carbon (H-DLC) film; running-in; nanoscale; oxide film; transfer layer

1 Introduction

As an unavoidable phenomenon for most as-fabricated mechanical parts during the initial operation, running-in alters the performance of the moving components and plays a crucial role at all size scales, from macroscale engines down to dynamic nano-devices [1–8]. Diamond-like carbon (DLC) film is one of the most promising materials for reducing energy consumption and CO₂ emission since it is capable of achieving super-low friction for sliding parts [9–12]. Except for a few specially treated DLC films, such as those with a pre-existing highly graphitized surface [8, 13], most kinds of DLC films must initially

undergo a transition to lower the friction level. The high friction and severe wear during this running-in process may greatly hinder the development of additional applications of DLC films [14–16]. Therefore, it is important to achieve a scientific understanding of the contact and friction mechanisms that occur during the running-in of a DLC film from the nanoscale to the macroscale.

In previous running-in studies, tribological experiments on DLC films were usually performed at the macroscale and several mechanisms involving transfer layer formation, substrate graphitization [17–19], passivation theory [20–22], and native oxide removal [23–25] were proposed to explain the

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running-in behaviors. Normally, the decrease of friction during initial sliding cycles was found to strongly relate to the formation of the transfer layer at the contact surface [13–26]. However, since this process is also accompanied by complex changes, such as substrate graphitization and native oxide removal, it is difficult to confirm the role of transfer layer formation in the friction reduction during the running-in process [24]. The running-in of a DLC film depends not only on the friction products (i.e., transfer layer or graphitized material) but also on the native oxide layer of the pristine substrate surface [27]. For instance, the friction on the DLC surface decreased with the removal of the outermost oxide layer and the DLC sample with a thick oxide layer required a longer running-in period [24, 28]. The stronger bonds caused by the termination of oxygen atoms at the interface may be responsible for the higher friction of the oxide layer. In the presence of oxygen atoms, hydrogen bonds occur between the interfaces, and the bonding strength of each bond is about 0.21 eV. In contrast, after the removal of the native oxide layer, the van der Waals bonding strength is only about 0.08 eV per bond due to the hydrogen termination. However, the relationship between the oxygen concentration of a hydrogenated diamond-like carbon (H-DLC) substrate and friction is still unclear.

Previous tribological studies on the running-in behaviors of DLC films were normally performed at the macroscale. Under these conditions, the native oxide layer that might play a significant role in initial friction behavior was removed very fast. Furthermore, the contact states became more and more complicated (i.e., multi-asperity contact or three-body contact) along with surface wear [29, 30]. Thus, the evolution of DLC surface wear and its role in the decrease in friction is difficult to quantify at the macroscale, where the main contributions of surface graphitization, surface passivation, and native oxide removal to the friction reduction during the running-in process may be hidden in the complex interfacial behaviors. Here, the nanoscale running-in behaviors of a DLC film are investigated in a controllable single-asperity contact provided by an atomic force microscope (AFM). Direct evidence is presented to illustrate

the role of transfer layer formation and oxide layer removal in the friction reduction during running-in. A quantitative relationship between oxygen concentration and friction is proposed. The results provide new insights for the understanding of the running-in behaviors and will help for optimizing the design of DLC films for applications in different working environments.

2 Materials and methods

H-DLC films covering an atomically smooth silicon substrate were prepared by plasma-enhanced chemical vapor deposition. First, the silicon substrates were ultrasonically cleaned in ethanol for 30 min. Afterward, the silicon substrates were moved into a vacuum chamber ($\sim 10^{-4}$ Pa) and etched by Ar^+ ions under 5 Pa for 30 min to remove the existing oxides and surface contamination. Then, the H-DLC film was deposited as lubricating layers in a mixture of methane and hydrogen gases. Raman measurement detected two peaks, including the D peak at $\sim 1,445\text{ cm}^{-1}$ and the G peak at $\sim 1,560\text{ cm}^{-1}$ in the Raman spectra. The intensity ratio of these two peaks (I_D/I_G) was ~ 0.57 . The film thickness was characterized as ~ 870 nm based on the cross-section observation, which was several hundred times larger than the maximum wear depth in this study (Fig. S1 in the Electronic Supplementary Material (ESM)). Therefore, any effect from the silicon substrate on the tribological behaviors was ruled out. The H content of the used H-DLC films was estimated at around 16 at% based on the Raman spectrum of a pristine surface collected with a 514 nm argon ion laser (Fig. S2 in ESM). The root mean square roughness of the H-DLC film was measured as ~ 0.2 nm over a $500\text{ nm} \times 500\text{ nm}$ scanning area using an AFM with a sharp Si_3N_4 tip (radius $R = \sim 15$ nm). The surface oxide layer was analyzed using atomic emission spectroscopy (AES, ULVAC-PHI, Inc., Japan). Figure 1(b) shows the O_{KLL} auger intensity as a function of sputter depth, indicating the existence of a ~ 1.2 nm-thick oxide film on the pristine H-DLC surface.

The running-in tests of H-DLC films against the Al_2O_3 microsphere tips at room temperature ($\sim 25^\circ\text{C}$) were comparatively studied under vacuum ($< 10^{-3}$ Pa)

Fig. 1 (a) Schematic illustration showing a nanoscale friction test of H-DLC film against an Al_2O_3 microsphere attached to a silicon cantilever under vacuum ($< 10^{-3}$ Pa). (b) The oxygen content of the H-DLC film plotted as a function of sputter depth.

using an AFM (SPI3800N, Seiko Instruments Inc., Japan). Figure 1 shows that the AFM tests were conducted under a reciprocating-scanning mode with an applied normal load of $4 \mu\text{N}$ and a sliding speed of $4 \mu\text{m/s}$. The curvature radius of the Al_2O_3 tips (Navoscan, American) was $\sim 2.5 \mu\text{m}$ and the spring constant of the tip cantilever was $16 \pm 1 \text{ N/m}$. The friction forces were calculated based on the dissipative energy during running-in [31], and the friction values were calibrated based on the wedge calibration method (TGF11, MikroMasch, Germany) [32, 33]. After the sliding tests, the topographies of the wear tracks were characterized using a sharp Si_3N_4 tip with a soft cantilever ($\sim 0.1 \text{ N/m}$).

3 Experimental results

3.1 Running-in of the H-DLC film under vacuum

Figure 2 shows the variation of the friction coefficient during running-in under vacuum. The friction coefficient under vacuum decreased sharply to ~ 0.1 during

Fig. 2 Single-asperity friction behavior of an H-DLC film against an Al_2O_3 tip under vacuum ($< 10^{-3}$ Pa).

the first ~ 250 sliding cycles. Surprisingly, a further reduction in the friction coefficient occurred as the sliding cycle (n) further increased from $\sim 1,100$ to $\sim 1,500$. After that, the friction coefficient remained constant at approximately 0.05 through the sliding cycle 2,000.

3.2 Nanowear of an H-DLC film during the running-in process

Under vacuum conditions, the discriminable nano wear of the H-DLC film formed after five reciprocating sliding cycles during running-in (Fig. 3(a)). Figure 3(b) shows the corresponding wear depth and wear rate at various sliding stages. As the number of sliding cycles increased, the wear depth initially increased drastically. The increase rate of the wear depth went down after the initial cycles and the final wear depth was $\sim 1.4 \text{ nm}$ at 2,000 cycles. The corresponding wear rate (γ) was estimated by dividing the wear volume (v) with the applied load (F_n) and sliding distance (l): $\gamma = v/F_n l$, which decreased sharply at the initial ~ 250 sliding cycles and then leveled off (Fig. 3(b)). In comparison with the friction behaviors shown in Fig. 2, the decrease in wear rate was consistent with the first decrease in friction. Furthermore, the wear depth reached $\sim 1.2 \text{ nm}$ at $\sim 1,500$ cycles, which was close to the thickness of the native oxide layer (Fig. 1(b)). The native oxide layer wore out at this critical cycle and then the H-DLC substrate inside wear scar instead of the initial native oxide layer would contact the Al_2O_3 tip. The alignment of the oxide wear and the decrease in friction before $\sim 1,500$ sliding cycles (Figs. 2 and 3(b)) may imply that the further reduction in

Fig. 3 Nanowear of the H-DLC film during running-in under vacuum. (a) AFM images and the corresponding cross-section profiles of the wear traces on the H-DLC film formed after various sliding cycles. (b) Wear depth and wear rate plotted as a function of sliding cycles under vacuum.

friction is correlated to the change in the contact interface.

4 Discussion

4.1 Role of transfer film in the running-in process

The contact surface of the Al_2O_3 tip used in the running-in test was characterized through mapping using a sharp Si_3N_4 tip (radius $R \approx 15$ nm). Figure 4 shows the topographies of the Al_2O_3 tip before and after sliding 300 cycles under vacuum conditions. The comparison of cross-section profiles in Fig. 4(b) indicates that the tip damage is negligible, and an obvious transfer layer is formed during running-in. To reveal the effect of the transfer layer on the contact state, we measured the adhesion forces on the origin H-DLC surface using Al_2O_3 tips before and after modification with a transfer layer. Each adhesion measurement was conducted under the same environmental conditions as the sliding tests. Under vacuum conditions, the value of adhesion was ~ 650 nN on the origin H-DLC surface before the test, and it decreased to ~ 160 nN after 300 sliding cycles. The deposition of a transfer layer on the Al_2O_3 tip surface could reduce the actual contact area between the tip and the substrate surface. This condition may help reduce the adhesion force.

During running-in, the Al_2O_3 tip surface and the H-DLC substrate surface are both altered by wear. Under vacuum, the adhesion force measured by the modified tip was ~ 90 nN on the wear area, which further decreased by 40% compared with the value (~ 160 nN) measured on the origin H-DLC surface

Fig. 4 Characterization of the Al_2O_3 microsphere before and after running-in. (a) Morphologies of the Al_2O_3 microsphere before ($n = 0$, left) and after ($n = 300$, right) sliding for 300 cycles. (b) Comparison of the cross-section profiles of the Al_2O_3 microsphere before ($n = 0$) and after ($n = 300$) running-in.

(Fig. 5). The sharp decrease in friction during running-in resulted from the transfer layer formation on the Al_2O_3 sphere surface and the modification of the H-DLC surface (i.e., native oxide layer removal). Moreover, the friction force decreased dramatically because of the change in the AFM tip and the appearance of a transfer layer led to a simultaneous decline in friction and adhesion force.

4.2 Role of the oxide layer removal in the running-in process

The effect of the transfer layer on the friction force

Fig. 5 Adhesion and friction forces of the H-DLC/Al₂O₃ pair measured before sliding tests ($n = 0$, a new Al₂O₃ tip against the origin H-DLC surface) and after tip modification during running-in ($n = 300$, modified Al₂O₃ tip against origin H-DLC surface or wear area).

reduction during running-in was quantified under the following controlled conditions, as shown in Fig. 6. Firstly, a new Al₂O₃ tip was rubbed on an origin H-DLC surface until the friction force decreased to a constant value after running-in at 1,600 cycles. Then, the friction forces were measured alternating between the origin substrate (at 1,601 and 1,603 cycles) and wear area (at 1,602 and 1,604 cycles) using the modified tip (see the insets in Fig. 6). Here, the difference in friction measured by the new tip and the modified tip on an origin H-DLC surface should be purely attributed to the transfer layer formation. Figure 6 shows that the typical friction coefficient at the first sliding cycle was ~ 0.3 under

Fig. 6 During running-in (0–1,600 cycles), a clean Al₂O₃ tip slid against an H-DLC film until the friction coefficient was stable. After running-in, the friction forces were measured inside the wear trace (at 1,600, 1,602, and 1,604 cycles) and outside the wear trace (at 1,601 and 1,603 cycles) using the modified Al₂O₃ tip.

vacuum conditions, and the value measured with the modified tip decreased to ~ 0.15 on the origin H-DLC surface, which was approximately three times larger than that measured on the wear area (~ 0.05). Thus, the formation of a transfer layer leads to a partial decrease in friction, but the transfer layer is not the only reason for the decrease in friction; other factors promote the decrease in friction.

Due to the geometry of the wear track, the contact states of the Al₂O₃ tip inside and outside the wear trace were quite different. To eliminate the effect of contact area, the friction force on a pristine H-DLC surface was compared with a larger square of a worn surface; it was found that the friction force on the worn surface was only 50%–60% of that on the pristine H-DLC surface, as shown in Fig. S6 in the ESM. In other words, the friction force was decreased by 40%–50% after removal of the surface oxide layer, which is similar to the value ($\sim 50\%$) given in Fig. 6. These results indicate that the evolution of the contact area due to surface wearing has a limited influence on the variation of friction during the running-in process.

The results of the adhesion force (Fig. 5) and the friction force (Fig. 6) indicated that the modification of the Al₂O₃ tip and H-DLC surface resulted in the sharp decrease in friction under vacuum. Figure 7 shows a decrease in the amplitude of friction during running-in. The total reduction values at different sliding cycles were obtained and compared with the initial value measured on the origin H-DLC surface using a new tip. The contribution of the transfer layer formation to the reduced friction was estimated based on the friction coefficient between the origin substrate surface and the modified Al₂O₃ tip surface (Fig. 6). Afterward, the cause of the remaining decrease was mainly attributed to the substrate surface change.

During the running-in of the H-DLC film, either the graphitization of the strained material or the removal of the oxide layer may change the surface properties of the substrate [12]. However, Tambe and Bhushan [34] indicated that the graphitization of H-DLC film may not occur at low sliding speed ($< 400 \mu\text{m/s}$) in the nanoscale wear tests. Moreover, the graphitization of the H-DLC film was not detected when the sliding speed was $6 \times 10^4 \mu\text{m/s}$ in the

Fig. 7 Contributions of the transfer layer formation and oxide layer removal to the reduced friction. (a) The blue line is the friction coefficient value gathered from the experimental results and the orange line is the reduction due to the formation of a transfer layer. The solid part is determined by the position change experiments in Figs. 5 and 6. (b) Reduction of friction coefficient due to the removal of the oxide layer on the H-DLC film.

macroscopic experiment [35]. Considering that the maximum sliding speed in this study was 4 $\mu\text{m/s}$, the graphitization of the contact area may be negligible. To verify this, friction tests between an Al_2O_3 ball with a diameter of 3 mm and the same type of H-DLC were conducted under vacuum using a ball-on-disk tribometer (CSM Instruments SA, Switzerland). At a sliding velocity of 30 mm/s, the graphitization of the H-DLC film was not detected in the wear trace (Fig. S4 in the ESM). Therefore, when the Al_2O_3 tip slides on the worn surface, the decrease in friction force compared to that on a pristine H-DLC surface must be mainly attributed to the removal of the surface oxide layer, not the graphitization of the worn surface. This finding was supported by the alignment of the worn-out oxide layer and the further reduction of friction (Figs. 2 and 3).

To further understand the effect of oxide layer removal on the friction reduction, the oxygen content of the contact area was estimated by an alternative approach. First, the shape and size of the contact area were estimated by Hertz contact theory (Fig. 8(a)), and the oxygen concentration at different depths of the contact area was determined by the AES results in Fig. 1(b) (Fig. 8(b)). Then, the average oxygen content of the contact area was obtained by integrating the oxygen content of each point in the contact area. Figure 8(c) provides a comparison of the friction reduction due to the oxide layer removal and the evolution of the average oxygen content along with the depth. It was found that the friction

coefficient decreased linearly as the oxygen concentration decreased, namely as

$$f = 0.152 + 0.015 \times \text{Oxygen concentration (at\%)} \quad (1)$$

Their linear relationship (Fig. 8(d)) confirmed that the remaining component of the friction reduction may be a result of the removal of the native oxide layer on the H-DLC surface during running-in.

For H-DLC films, dangling carbon bonds are rare due to the presence of hydrogen atoms [36, 37]. The friction was mainly attributed to hydrogen termination and oxygen termination. Van der Waals interactions exist between the hydrogen-terminated DLC interfaces, whereas hydrogen bond interactions occur between oxygen terminated DLC interfaces. The secondary ion mass spectrometry (SIMS) results given by Eryilmaz and Erdemir [38] showed that there were almost no hydrogen atoms on the DLC surface, hence the main interfacial force was the H-bond (0.21 eV per bond) force caused by oxygen termination. Therefore, the friction coefficient of the initial stage could be estimated as

$$f_{\text{start}} \propto 0.21 \text{ eV} \times 10.2 \text{ at\% (oxygen content)} \quad (2)$$

Meanwhile, the abundant C_2H_2 groups in the wear trace [38, 39] indicated that when the oxide layer was completely removed, the oxygen termination was converted to hydrogen termination. Hence the interaction between the interfaces changed from H-bonds (0.21 eV) to van der Waals forces (0.08 eV) [40, 41], so the friction coefficient after running-in was estimated as

Fig. 8 (a, b) Schematic diagram of the oxygen content in the contact area. (c) Variation of the friction reduction and the average oxygen content of the H-DLC film with an increase in the number of sliding cycles. Here, the average oxygen content was obtained by integrating the oxygen content of each point in the contact area. (d) Friction reduction plotted as a function of the average oxygen content of the H-DLC film. The inset shows the transition from relatively strong hydrogen bonding to weaker van der Waals interactions.

$$f_{\text{end}} \propto 0.21 \text{ eV} \times 2 \text{ at\%} + 0.08 \text{ eV} \times 8.2 \text{ at\% (oxygen content)}. \quad (3)$$

The calculated friction coefficient decreased by 49.8% ($(f_{\text{start}} - f_{\text{end}}) / f_{\text{start}}$), which is close to the experimental value of 40% obtained from Fig. 8(b).

4.3 Running-in mechanism of the H-DLC under vacuum

Figure 9 schematically shows the running-in process of an H-DLC surface against an Al_2O_3 microsphere under vacuum. The H-DLC surface with a native oxide layer was mainly terminated with C–OH and C–O groups (Fig. S in the ESM) and the hydrogen bonds were extremely scarce in the outermost layer [25, 27, 39]. Hydrogen passivation can saturate the free σ -bonds on the sliding surface of the H-DLC film and result in low friction [20–22, 39, 42, 43]. Due to the lack of hydrogen bonds on the substrate surface, the strong interaction between the surface atoms of the native oxide layer and the new Al_2O_3 tip caused relatively high friction during the early running-in stage (Fig. 9(a)) [44]. With the continuous wear of the surface oxide layer, a transfer layer

formed on the Al_2O_3 tip surface, which effectively decreased the friction and nano wear of the H-DLC/ Al_2O_3 interface (Fig. 9(b)). First, transfer layers with low shear strength can lubricate sliding surfaces [26, 45] and may reduce the real contact area to some extent. Second, the hydrogen content of the H-DLC surface may increase along with the wear depth and the hydrogen passivation can decrease the interfacial bond interaction [38, 39]. This role would become more prevalent after the complete removal of the native oxide layer at ~1,500 sliding cycles. Through time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements, Eryilmaz and Erdemir [38] detected that hydrogen atoms could precipitate from the subsurface of a sliding region to form a hydrogen-rich layer on the H-DLC surface. This rich layer is absent in the hydrogen-deficient oxide layer. Therefore, the further reduction of friction under vacuum might result from the change in the contact interface due to the removal of the native oxide layer and the subsequent formation of a region passivated with a large number of hydrogen terminations on the exposed H-DLC substrate (Fig. 9(c)).

Fig. 9 Schematics illustrating the running-in process of an H-DLC film against an Al_2O_3 tip under vacuum. (a) Initial stage ($n = 0$, before wear): high friction due to the strong hydrogen bonds between a new Al_2O_3 tip and the oxide-covered H-DLC surface. (b) Intermediary stage ($n = 300-1,500$ cycles): low friction due to the transfer layer formation and partial oxide layer removal. (c) The final stage ($n > 1,500$ cycles, after running-in): lowest friction due to the weak van der Waals interactions between the modified tip and the exposed H-DLC substrate.

5 Conclusions

Using an AFM, the running-in process of an H-DLC/ Al_2O_3 pair at the nanoscale was investigated under vacuum. The main conclusions can be summarized as follows:

1) It is the combination of the formation of a transfer layer and the removal of the oxide layer that leads to the running-in behavior of the H-DLC/ Al_2O_3 pair at the nanoscale. Once formed in the initial stage, the transfer layer's contribution to friction reduction is constant.

2) Compared with a clean Al_2O_3 tip, the decrease of the friction coefficient ($0.3 \rightarrow 0.15$) between the modified Al_2O_3 tip and the original H-DLC film provides direct evidence for the contribution of the transfer layer. This could be attributed to the weak interaction between the H-DLC film and the transfer layer on the modified Al_2O_3 tip.

3) The friction coefficient of the H-DLC/ Al_2O_3 pair decreased linearly as the oxygen concentration of H-DLC substrate surface decreased. This can be explained by the change in the contact surface from oxygen termination with strong hydrogen bond interactions to hydrogen termination with weak van der Waals interactions.

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