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Effect of Tribochemistry on Lubricity of DLC Films in Hydrogen

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ABSTRACT

This paper presents the results of a systematic study demonstrating how controlled or targeted tribochemistry can lead to super-low friction and wear in diamond-like carbon (DLC) films. Specifically, how hydrogen can lead to dramatic reductions in the friction and wear of hydrogen-free DLC films which otherwise experience high friction and severe wear losses. When sliding tests are performed with a hydrogen-free DLC film in an inert gas (like Ar), the friction coefficients were in the range of 0.4 to 0.7 and it wore out rather quickly. However, when the same tests were run under the 1333 Pa partial pressure of hydrogen, the friction coefficients were reduced by factors of more than 10 and the wear damage became very difficult to quantify. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) analyses provided strong chemical evidence that the sliding contact surfaces of these films underwent tribochemical reactions with hydrogen effectively passivating dangling bonds of surface carbon atoms, which is believed to be responsible for ultralow friction and wear. In an effort to rule out the possibility of contamination

and confirm the pivotal role of hydrogen in lubricity of DLC films, we ran similar tests with the same hydrogen-free DLC in deuterium (an isotope of hydrogen) and achieved essentially the same level of reduction in friction. TOF-SIMS clearly confirmed the formation of a deuterium-rich tribofilm on rubbing surfaces thus confirming the critical role of tribochemistry in super-low friction and wear of DLC.

Keywords: Diamond-like carbon, tribochemistry, test environment, lubrication mechanism, TOF-SIMS

1. INTRODUCTION

Despite huge scientific and technological advances in controlling friction and wear during the past century through developments of a myriad of novel materials, coatings, and lubricants, we still waste huge amounts of energy to overcome friction in many moving mechanical systems every day. For example, in a typical car, nearly one third of fuel's energy is spent to overcome friction and at a global scale, this amounts to more than 360 million tons of petroleum being consumed by friction in a year [1]. Greenhouse gas emissions coming from fossil fuel burning are suspected to cause climate change around the world. Accordingly, with increasing worldwide concerns over energy and environment, further reduction of friction in moving mechanical systems has lately become a strategic goal of many industrialized nations.

Among the numerous tribological coatings, diamond-like carbons (DLCs) are considered to have the greatest potential in reducing friction and wear related energy and material losses in moving mechanical systems [2-4]. Despite the fact that they have been around for more than half a century, their real potentials for large-scale industrial applications have not been realized until late 1990s [4]. Since then, interests in these coatings have intensified first in magnetic storage media, then in consumer products like razor blades, and finally, various transportation applications, like fuel injectors, tappets, piston pins and rings, etc. [4]. Ease of production using various deposition techniques such as chemical vapor deposition (CVD), physical vapor deposition (PVD), and pulsed laser deposition (PLD) at relatively low costs made DLC a mainstream tribological coating for many industrial applications.

DLC films can be derived from gaseous and liquid hydrocarbons or solid carbon precursors using plasma based PVD and/or CVD system. Depending on the type of precursors used during deposition, the resultant DLC films may consist of a combination of sp^2 and sp^3 bonded carbon atoms. Highly sp^3 -bonded DLC films are superhard (also known as tetragonal amorphous carbon, or ta-C coatings) and can provide high wear resistance and superior thermal stability. DLCs with high sp^2 -bonded carbon atoms are much softer and mostly deposited in a sputtering system. Both films are produced from solid carbon targets, and hence they contain very little or no hydrogen, (this is why they are also often referred to as hydrogen-free DLC films). If the precursor material is made of a hydrogen rich substance such as hydrocarbon gases or liquids, some of the hydrogens in the precursor are incorporated into the DLC films [2-4]. Depending on the amount of hydrogen, the mechanical and tribological properties of these films could be very different. This class of DLCs is often referred to as hydrogenated-DLC. When tested for their tribological performance, hydrogenated and hydrogen-free DLCs behave very differently in both dry and lubricated test environments [4-9]. Despite being much softer, hydrogenated DLCs can provide super-low friction and wear coefficients in inert test environments or in vacuum [8-10]. In contrast, hydrogen-free DLCs (especially the ones with high sp^3 -bonded carbon) are very hard and hence exhibit high wear resistance but their friction in vacuum could be rather high and unsteady. However, they can afford much lower friction to sliding surfaces in humid or liquid test environments (as well as under certain lubricated test conditions) [5-7,11-13].

In an effort to better understand such a disparity in frictional performance of hydrogenated versus hydrogen-free DLCs (as well as diamond films), many researchers have examined the nature and extent of tribochemical interactions occurring during sliding tests [5-15]. In general, they

confirmed the existence of very strong tribochemical interactions depending on the test condition and environment as well as the kinds of DLCs being tested [5-7]. For example, in inert gases or vacuum environments, friction coefficients of as low as 0.001 have been reported for highly hydrogenated DLC films [8,14], while under similar test conditions, 0.6 to more than 1 friction coefficients have been reported for hydrogen-free DLCs or diamond films [9,10,11,13,15].

Interestingly, the friction coefficients of hydrogen-free DLC films were found to come down to as low as 0.1 in humid test chambers and reach values less than 0.01 when tested in glycerol and/or glycerol mono-oleate containing lubricants [5,6]. Such a large disparity in friction and wear of DLC films is rather unusual (rarely observed or found in other materials). Most researchers have conceded that these differences are most likely associated with some intrinsic (film specific) and extrinsic (atmospheric or test condition specific) factors that dominate tribochemistry and hence shear rheology of DLCs at their contact interfaces [4-9].

As mentioned earlier, intrinsically, DLC films are primarily made of sp^2 and sp^3 bonded carbon atoms (with perhaps very little sp^1 bonded carbon as well) [2-4]. Depending on the deposition procedures and source materials or gases used, they may also contain large amounts of hydrogen and/or other alloying elements [2-4,14]. Keeping the tribological test conditions constant, such intrinsic factors alone were shown to have significant effects on their physical, mechanical and tribological properties [8-14]. Extrinsically, the chemical nature (i.e., presence or absence of reactive gaseous or liquid species) of test environments was found to be very influential in the friction and wear behaviors of DLC films [4-10,16-21]. In particular, reactive gases like hydrogen, oxygen, alcohol, and water molecules as well as oil and additive chemicals were found to chemically interact with the sliding surfaces of DLCs and hence lead to dramatic changes in their friction and

wear behaviors [6,7,10,13,17-22]. For films with high hydrogen content (i.e., above 30 at.%), inert gases or high vacuum were shown to be the most ideal test environments since friction coefficients of less than 0.01 were achieved in such environments [8,4,15]. However, the same films were found to exhibit 10 to 15 times higher friction in the presence of oxygen and/or moisture in the test chambers [10,11,22,23]. As for the hydrogen-free DLC films, an opposite effect is observed; specifically, in inert or vacuum-like test environments, these films showed the highest friction coefficients (i.e., as high as 1) and wore out very quickly [7,9,10,11,9,13]. When tested in oxygen and/or moist environments, their friction coefficients decreased to 0.1-0.35 levels [21,22]. The best overall frictional performance for these types of DLC films were attained in glycerol or glycerol-mono-oleate-containing base oils with reported friction coefficients of less than 0.01 [5,6]. It is conceivable that part of this low friction may have been due to highly viscous nature of glycerol. Overall, all DLC films are chemically made of carbon, but very minute differences in their physical states or structural chemistry and operating environments can make a huge positive or negative difference in their friction and wear behaviors.

In this paper, we attempted to further understand the effects of hydrogen on friction and wear of hydrogen-free DLC films. Specifically, using a vacuum tribometer and a TOF-SIMS instrument, we aimed at elucidating the extent and nature of tribochemical interactions that occur between sliding surfaces of hydrogen-free DLC films in the presence of Ar and H₂. In support of our findings from hydrogen environment, we also ran tests in deuterium (D₂) and observed similar effects. The knowledge gained from these studies will be crucial for better understanding of the fundamental tribochemical mechanisms involved in the friction and wear of such films. It will also

validate the accuracy of various lubrication mechanisms that have been proposed in the past for the superlow-friction and wear behaviors of DLC films.

2. EXPERIMENTAL PROCEDURES

Hydrogen-free DLC films used in this study were deposited on the highly polished surfaces (with less than 0.01 μm , RMS) of AISI M2 steel flats and 440C steel balls (9.5 mm in diameter) using a magnetron sputtering system whose details can be found in Ref. 23. The bulk Vickers hardness of ball and flat samples was ≈ 8 GPa and they were cleaned with acetone, and isopropanol alcohol in an ultrasonic bath prior to loading into the deposition chamber of the magnetron deposition system. To enhance their adhesion to substrates, a Cr bond layer (≈ 50 nm thick) was applied first. Subsequently, the hydrogen-free DLC films were produced on top of the Cr bond layer by sputtering carbon atoms from a solid graphite target. It is important to remind that these DLC films were not like tetragonal amorphous carbon (or ta-C) but rather similar to amorphous carbon (or a-C) with high proportion of sp^2 bonding. The total power to the graphite target was 3 KW (6.75 W/cm^2) during the sputtering process and a -35V pulsed bias (with the frequency of 250 KHz and 1600 ns reverse cycle) was used. The Ar flow rate was kept at 150 sccm during the carbon film deposition while the total pressure was 0.4 Pa. The total thickness of the carbon film was about 200 nm. The sputter deposition was performed at room temperature but due to the discharge of charged species and electrons, the temperature of the specimen holder reached $\approx 100^\circ\text{C}$. The surface roughness of the hydrogen-free DLC films was comparable to the original RMS roughness of the substrate steel; i.e., less than 0.01 μm , RMS.

The sliding friction and wear tests were performed in a high vacuum tribometer with a ball-on-disc contact geometry at room temperature and under 1333 Pa partial pressures of Ar, H₂, and deuterium gases. Ar is an inert, chemically insensitive gas; so it is not expected to interact with sliding surface or trigger tribochemistry like hydrogen and deuterium can do. Further details of this tribological test system and the procedures followed can be found elsewhere [22,23]. Briefly, the contact load applied on the ball holder ranged from 1 to 2 N (which would create peak Hertz pressures of $\approx$ 500 to 600 MPa, respectively), and the track diameter was around 10 mm. The sliding velocity was 0.63-0.95 cm/s. To measure the true friction coefficient of the DLC film itself, the DLC-coated balls were slid against the DLC-coated steel disks to establish a self-mated sliding contact.

TOF-SIMS of the sliding contact surfaces of DLC were carried out using a Physical Electronics PHI TRIFT III instrument. This analytical tool is very powerful and versatile in studying the chemical nature of very thin layers especially in imaging mode (i.e., down to a few atomic layers and ppb level concentrations are feasible) and hence is well-suited for the analysis of very thin or small tribochemical changes that may have occurred on sliding DLC surfaces [24]. It also possesses excellent mass resolutions, hence provides very reliable chemical and distributional (in both lateral and depth) information for a wide variety of species including lowest mass hydrogen which was one of the gases used during our tribological studies [25].

~~Principally, TOF-SIMS is based on the mass analysis of ionized species or clusters (called secondary ions) which are ejected by a stream of pulsed primary ions (such as Au⁺, Ga⁺, Cs⁺, O⁻, C₆₀⁺) from the interested area or spot on a solid surface [25]. The secondary ions ejected from the top surface are then accelerated to a mass analyzer which essentially rank arriving secondary ions~~

~~according to their flight or arrival time and hence masses. Lighter ion's (like H^+) flight time is the shortest, hence it arrives to the detector the fastest, while heavier ions take much longer and their arrival time could be much longer. In our case, the raw data streams of the sputter depth profiles of tribofilms encompass a full mass spectrum of every pixel in three-dimensional (3-D) space; hence, the TOF-SIMS images of the area of interest on a given surface can be re-constructed from the selected masses and/or in-depths to provide important tribochemical information that can help understand the fundamental mechanisms that are involved [20-24].~~

For the generation of TOF-SIMS spectra and images, we used a 22 keV- pulsed Au cluster ion source, and the beam current was between 500 pA and 2 nA. Cesium ions were used for sputtering of the contaminant layers from top surfaces. The sputtering area was kept two times larger than the analyzed area to prevent any artificial edge effects during data collection. The sputtering guns were operated at 2 kV and 1500 pA and the sputtering time was 1 s for each cycle. The mass range of secondary ions analyzed was from 1 to 300 amu, and the mass resolution $m/\Delta m$ was better than 2300 at mass 25.

3. RESULTS

To clearly demonstrate the pivotal role of hydrogen in frictional behavior of hydrogen-free DLC films, we started the sliding test in 1333 Pa of ultra-high purity Ar for a certain amount of time and then very quickly switched to 1333 Pa of hydrogen environment for the same wear track of the same sample. Sliding distance in Ar was limited to about 0.65 m or 100 s; mainly because, when tested longer, the film would have suffered significant wear. As can be seen in Figure 1, the

friction coefficient in Ar increases very quickly to about 0.7 after sliding for ≈ 0.4 m. We kept the test running until reaching 0.65 m sliding distance, then stopped the test and the Ar gas was purged very quickly until a vacuum level of 1.33×10^{-4} Pa was achieved. At this point, the test chamber was backfilled with H₂ gas until the same background pressure of 1333 Pa was attained and then the sliding experiment was resumed. As shown in Fig. 1, the friction coefficient of hydrogen-free DLC was very low to start with (i.e., 0.1) in the beginning but during further sliding passes, it decreased to ≈ 0.05 . This simple experiment demonstrates that the presence of hydrogen was indeed very effective in reducing the friction coefficient of hydrogen-free DLC film from about 0.7 to about 0.05.

In another test on the same test pair (but a different contact spot and wear track) in 1333 Pa hydrogen, we ran a continuous test from the start of the test (Figure 2). Initially, the friction was again high, i.e., 0.45, but during repeated sliding passes, it came down to some extremely low friction value (i.e., 0.01 to 0.03). The wear track formed on DLC coated flat side (Figure 3a) was examined by TOF-SIMS and the chemical hydrogen mapping of the analyzed portion of this wear track confirmed significantly high hydrogen concentration within the wear track as shown in Figure 3b. TOF-SIMS analysis of the region on ball side where sliding contact had occurred also revealed high concentration of hydrogen.

To eliminate potential parasitic contaminations from residual hydrogen sources in ambient and further substantiate the critical role of hydrogen in lubricity of DLC films, we performed the same test in deuterium, D₂ (an isotope of hydrogen). Figure 4 shows the frictional behavior of the hydrogen-free DLC film under 1333 Pa partial pressure of deuterium. Consistent with the H₂ test

cases, the friction coefficient was high (i.e., ≈ 0.4) initially and then decreased to about 0.03. This test result further confirmed the pivotal role of D_2 in frictional behavior of hydrogen-free DLC.

Figure 5 shows the deuterium TOF-SIMS images of the sliding wear track formed on the hydrogen-free DLC coated disk side after test in 1333 Pa of deuterium. It can be clearly seen that the sliding wear track became very rich in deuterium during the sliding test, suggesting that carbon atoms within the wear track had reacted with deuterium in the test chamber.

The friction test results in Figs. 1, 2 and 4 reveal a close correlation between the frictional behavior of tested DLC films and the formation of hydrogen- and deuterium-rich tribofilm on rubbing surfaces. Specifically, during tests in hydrogen, friction coefficients are very low (i.e., 0.05 or less, which amounts to a more than 90% reduction). Furthermore, if a similar test is run in 1333 Pa of deuterium, the steady-state friction coefficient again becomes quite low (0.03) and remains at this level for the duration of the sliding test.

4. DISCUSSION

The extent of adhesive interactions and hence friction of sliding DLC surfaces can be influenced by a combination of short- and long-range physical attractions (i.e., van der Waals forces, electrostatic attractions, capillary forces, etc.) and tribochemical interactions as discussed in Ref. 15. In our experiments, capillary forces due to water adsorption or accumulation in and around the contact spots can be ignored since the tests were run under ultra-dry conditions and in low pressure (i.e., 1333 Pa) of Ar, H_2 or deuterium gases with ultra-high purity. However, at the interface between DLC-coated ball and disk test pair, strong covalent interactions and relatively

weak van der Waals forces may have been present and most likely causing the very high friction of such DLC test pairs in dry Ar. Specifically, as shown in Fig 1, such a test pair exhibited more than 0.7 friction coefficient. Similarly, other investigators have also observed high friction on hydrogen-free DLC films when tested in vacuum or N₂ [10,11,13]. Note that initially, the friction coefficient of DLC coated ball against DLC coated disk was relatively low, i.e., ≈ 0.1 . This is most likely due to surface contaminants or physisorbed/chemisorbed layers left on the surface during exposure to air or cleaning procedure [17, 26]. In fact, as explained in Refs. 27-28, most DLC films will have a very thin (1-2 nm thick) relatively lower-density top layers which often descend on the top surface during the shutting-down period of the deposition process. Therefore, we believe that the extent and nature of the frictional interactions at the start of sliding tests (see Figs. 1, 2, 4) were primarily dominated by these layers.

As the top layer is worn out during the consecutive sliding passes in Ar, the friction coefficient increases steeply to 0.7 in the case of Ar as shown in Fig. 1. We believe that such an increase is most likely due to the increase in dangling bond interactions between the freshly created or exposed carbon atoms of the hydrogen-free DLC films on both sides of the sliding pair. Obviously, due to its inert nature, Ar gas is not able to react chemically with the sliding surfaces of DLC and hence passivate the reactive sites. In reality, the surface carbon atoms in these hydrogen-free DLC films are bonded to their immediate neighbors with very strong π - and σ -bonds. During mechanical rubbing action, it is possible that some of these bonds are broken and become available to establish strong covalent bonds with the atoms of the carbon film on opposite side and then generate strong adhesion and hence high friction as shown in Fig. 1. Therefore, the

high friction coefficient (i.e., 0.7) of DLC against itself in Ar is most likely due to transient chemical bond formation across the sliding carbon interface.

Note that friction coefficient begins to decrease slightly to 0.5 from its peak value of ~0.7 after about 0.4 m of sliding distance. This slight decrease in friction could have been due to the presence of small wear debris of DLC acting as a powdery graphitic solid lubricant. In earlier studies, we have confirmed that such a reduction in friction during the later stages of sliding experiments involving diamond and hydrogen-free DLC films was primarily triggered by the transformation of highly sp^3 -bonded DLC or diamond films to graphitic third body layers that are trapped at the sliding interface and acting as a solid lubricant [29,30].

As is obvious from Fig. 1, when the remainder of the sliding test is resumed in 1333 Pa of hydrogen gas, the friction coefficient is 0.1 to begin with and decreases steadily to 0.05 as sliding continues. Such a dramatic reduction in friction coefficient of the same hydrogen-free DLC film in the presence of hydrogen can be explained as follows. We believe that as in argon, dangling σ -bonds of surface carbon atoms may have also been present or created by mechanical rubbing action or frictional heating, but they are instantly passivated by hydrogen present in surrounding atmosphere. Even if some of the surface hydrogen may have been removed and the dangling bonds were re-exposed due to mechanical wear and/or frictional heating, they are re-passivated instantly by hydrogen gas from the environment. As a result, the friction coefficient of hydrogen-free DLC film remains very low (i.e., 0.05) in hydrogen gas. This finding is very consistent with the results presented in Fig. 2 which shows that when test is conducted in the presence of

hydrogen from the very beginning of test, after the initial run-in, the friction is reduced substantially confirming that regardless of hydrogen being introduced to the test chamber in the middle or from the beginning of the sliding test, it lowers friction of DLC to very low values. These findings are very consistent with earlier studies dealing with hydrogen-free and highly hydrogenated DLC films in Refs.20, 22, and 28.

As shown in Fig. 4, the friction coefficient of hydrogen-free DLC film is as low as 0.03 in deuterium environment. The deuterium TOF-SIMS image in Fig. 5 provides very clear chemical evidence that sliding wear track on DLC-coated disk side becomes very rich in deuterium. More specifically, this image suggests that during the sliding experiment, carbon atoms within the wear track react with deuterium in the surrounding environment, but no evidence of any such reaction is seen outside the wear track; hence this was a tribochemically induced phenomenon. Based on such observations, we may argue that just like in the case of hydrogen, the termination of dangling bonds on sliding DLC surfaces with deuterium is perhaps the most important mechanism for their low friction behavior. Since deuterium was readily available in the surrounding atmosphere, it was able to continuously replenish and terminate those dangling bonds that may have been re-generated by mechanical rubbing action or frictional heating. Carbon-hydrogen and carbon-deuterium bonds are chemically very strong and stable (i.e., it takes more than 700°C to initiate thermal desorption of hydrogen from carbon) [31]; hence they are not expected to be removed from the surface very easily. In short, the elimination of the strong covalent bond interactions (or dangling bonds) by hydrogen and/or deuterium at the sliding contact interfaces of hydrogen-free DLC films play important roles for the much lower friction of these DLC films in H₂ and deuterium. Overall, these experiments demonstrate that the presence (in the case of hydrogen and

deuterium) or absence (in the case of argon) of favorable tribochemical interactions on sliding DLC surfaces has a strong influence on the frictional behavior of hydrogen-free DLC films.

5. CONCLUSIONS

Based on the results of our tribological and TOF-SIMS studies, it can be concluded that the frictional behavior of hydrogen-free DLC films is strongly influenced by the presence of hydrogen and deuterium gases in test environment. Without them, the friction coefficients are much higher, i.e. about 0.4-0.7; with them, the friction coefficients are low, i.e., 0.01-0.05. TOF-SIMS analysis of sliding surfaces reveals high levels of hydrogen and/or deuterium within the wear tracks thus suggesting that the low-friction behavior of hydrogen-free DLC films is most likely the result of a tribochemical reaction between these gases and carbon atoms of DLC.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program, under Contract W-31-109-Eng-38 and in part by the Air Force Office of Scientific Research under Contract Number FA9550-08-1-0010 as well as NSF funding (CMMI-1131128). TOF-SIMS characterization studies were carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-91-ER45439.

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FIGURE CAPTIONS:

Figure 1. Frictional performance of hydrogen-free DLC film in first argon and then in hydrogen. Both ball and disk were coated with DLC, the partial pressures of argon and hydrogen during test was 1333 Pa. The contact load was 1 N (≈ 470 MPa Peak Hertz pressure), the sliding velocity was 0.7 cm/s.

Figure 2. Friction coefficient of a-C coating in 1333 Pa of hydrogen environment.

Figure 3. (a) Wear track formed on a-C coated flat side after test of Fig. 2 and (b) TOF-SIMS hydrogen map of the wear track showing higher concentration for hydrogen in and around this wear track.

Figure 4. Friction coefficient of hydrogen-free DLC in 1333 Pa deuterium gas. Both ball and disk were coated with DLC. The contact load was 2 N (≈ 600 MPa peak Hertz pressure), the sliding velocity was 0.9 cm/s.

Figure 5. Deuterium chemical image of the wear track formed on DLC-coated disk side during test in 1333 Pa deuterium.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.