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The tribological properties of low-friction hydrogenated diamond-like carbon measured in ultrahigh vacuum

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In this paper, we investigate the sliding friction and wear behavior of a hydrogenated diamond-like carbon (DLC) film in ultrahigh vacuum (UHV) and under partial pressures of water vapor, oxygen, nitrogen and hydrogen. The initial friction coefficient of the film in UHV was ~0.15, but decreased steadily to values as low as 0.03 after about 30 sliding passes. During longer duration tests, the friction coefficient increased again to values as high as ~0.15 and such an increase in friction coincided with hydrogen desorption from the contacting surfaces (as detected by a mass spectrometer). Heating DLC to temperatures higher than 360 K also caused desorption of hydrogen and a resulting marked increase in friction. The presence of molecular nitrogen, oxygen and hydrogen in the test chamber did not have any noticeable effect on friction, but the presence of thermally dissociated or ionized hydrogen within the close proximity of sliding surfaces had a beneficial effect by restoring the low friction behavior of the DLC films. The introduction of water vapor into test chamber had an adverse effect on friction. The results of this study confirm that hydrogen is key to low friction behavior of hydrogenated DLC films and that the presence of water molecules has an adverse effect on their friction behavior.

KEY WORDS: diamond-like carbon (DLC), friction coefficient, hydrogen, water, ultrahigh vacuum

1. Introduction

Diamond-like carbon (DLC) films have attracted much research attention because of their low interfacial friction coefficients and high wear resistance [1–10]. DLC's can be divided into two categories, hydrogenated and hydrogen-free DLCs, depending on their hydrogen content. It has been shown that the hydrogen content in DLC films plays a central role in their tribological properties [1–3]. Unfortunately, due to the variety of film formation methods and tribological test conditions, a general consensus on the role of hydrogen has not yet obtained. A great majority of the tribological studies on DLC films to date has been performed in air (at various levels of relative humidity), in other gases (such as nitrogen or argon), or under moderate vacuum [4–11]. In some of these studies, the adsorption of gaseous species onto DLC surfaces has been demonstrated to have a strong influence on friction [6–9] and in one of these [6], the time evolution of the friction coefficient of the DLC surfaces in the presence of water vapor was modeled using the Elovich equation. However, the number of tribological studies that involved ultrahigh vacuum (UHV) has remained very limited [2, 9, 12].

In the present study, the effect of gaseous species on the frictional behavior of hydrogenated DLC films was explored by carrying out model experiments in UHV. The sample was then pressurized to a certain extent to establish the effects of partial pressures of various gases, including water vapor, oxygen, nitrogen and hydrogen. While it has been demonstrated previously that high pressures of gas-phase molecular hydrogen ($P(H_2)$ ~7.5 Torr [9]) can prevent the loss of super-low friction in DLC films, clearly the dissociative sticking probability of hydrogen on carbon is likely to be extremely low. In order to facilitate hydrogen adsorption in UHV and to avoid this dissociative adsorption step, hydrogen or deuterium was predissociated in this work by using a heated tungsten filament.

2. Experimental

Experiments were carried out in a stainless steel, UHV chamber, which normally operates at base pressures of $\sim 2\times10^{-10}$ Torr following bakeout at ~420 K, which has been described in detail elsewhere [13]. In the experiments with DLC films, the chamber was baked at a substantially lower temperature (330 K) than normal for 36 h to avoid thermal damage to the sample during bakeout. It is demonstrated below that this temperature does not affect the DLC film and the chamber pressure was $\sim 1\times10^{-9}$ Torr after this low-temperature bakeout.

The vacuum chamber is equipped with a Dycor quadrupole mass spectrometer for temperature-programmed desorption (TPD) measurements and a single-

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pass, cylindrical-mirror analyzer for Auger analyses of the surface. The DLC film was deposited onto a steel plate (1 mm thick) and a K-type thermocouple was mounted to the back of the plate to allow the temperature to be monitored. The friction coefficient was measured using a tungsten carbide ball (6.35×10^{-3} m radius), also coated with DLC, mounted to the end of an arm where normal and lateral forces could be measured by strain gauges attached to thinned sections of the arm. These were calibrated by hanging weights from the arm and the lateral sensitivity was increased to be able to measure the low friction coefficients anticipated in this work [13]. Experiments were generally carried out using an applied load of 0.98 N, yielding a maximum Hertzian stress of 630 MPa, with a sliding speed of 8×10^{-3} m/s.

The DLC films used in this study were grown by a plasma-enhanced, chemical vapor deposition (PECVD) method on the highly polished surfaces of steel plates and tungsten carbide (WC) balls. The films were ~1 μm thick and were derived from a gas discharged plasma that contained 25% CH_4 and 74% H_2. In earlier studies, it was demonstrated that the DLC films grown in such plasmas provide superlow friction in an inert gas environment [4,5]. The procedure for forming DLC films on steel and WC substrates by the PECVD process first involved sputter cleaning the substrate in an argon plasma for 30 min by applying a 1200–1700 V bias. These substrates were then coated with a 50–70 nm-thick silicon bonding layer by switching to a sputtering mode and sputtering silicon from a target. Finally CH_4 and H_2 gases were introduced into the chamber and the deposition of DLC on the substrates was started. The gas pressure ranged from 10 to 13 mTorr and the radio frequency (RF) bias was maintained between 400 and 600 V during deposition. The substrates were not externally heated, but the temperature reached ~420 K during deposition (mainly because of electrical discharge and high-energy ion/atom bombardment). Further details of the deposition process can be found in Refs. 4 and 5.

3. Results

Shown in figure 1(a) is the trace of friction coefficient as a function of the number of passes, for sliding in both directions, of the tribopin over the DLC film surface. The friction coefficients measured in each direction were identical. This reveals that the initial friction coefficient is relatively high (~0.14), but decreases relatively rapidly with the number of passes so that it reaches a limiting value of ~0.04 after approximately 25 oscillations and decreases slowly thereafter to reach a limiting value of ~0.03. The friction coefficient maintains a constant value of ~0.03 for hundreds of passes. At this point, no damage is noted by eye on the surface so that sliding appears to proceed without macroscopic wear. As sliding continues over the same region of the film for over 500 oscillations, the friction coefficient increases rapidly once again (figure 1(b)) to reach a constant value of ~0.14–0.16. Such an increase in friction after a large number of passes in UHV has been noted previously [9]. Since the presence of hydrogen in the film is essential for achieving low friction, an attempt was made to rehydrogenate the sample by extended exposure to molecular hydrogen (1×10^{-7} Torr for 3 h). This had no effect on the friction coefficient. Since carbon is likely not to be sufficiently reactive to dissociatively adsorb molecular hydrogen, the hydrogen was predissociated using a heated tungsten filament (~1000 K) placed close to the sample where the exposure was identical to that used previously for molecular hydrogen (1×10^{-7} Torr for 3 h). The sample temperature was monitored during this procedure to ensure that the filament did not heat the sample. The resulting plot of friction coefficient collected while sliding over the same place as used to collect the data shown in figure 1, versus the number of passes, is

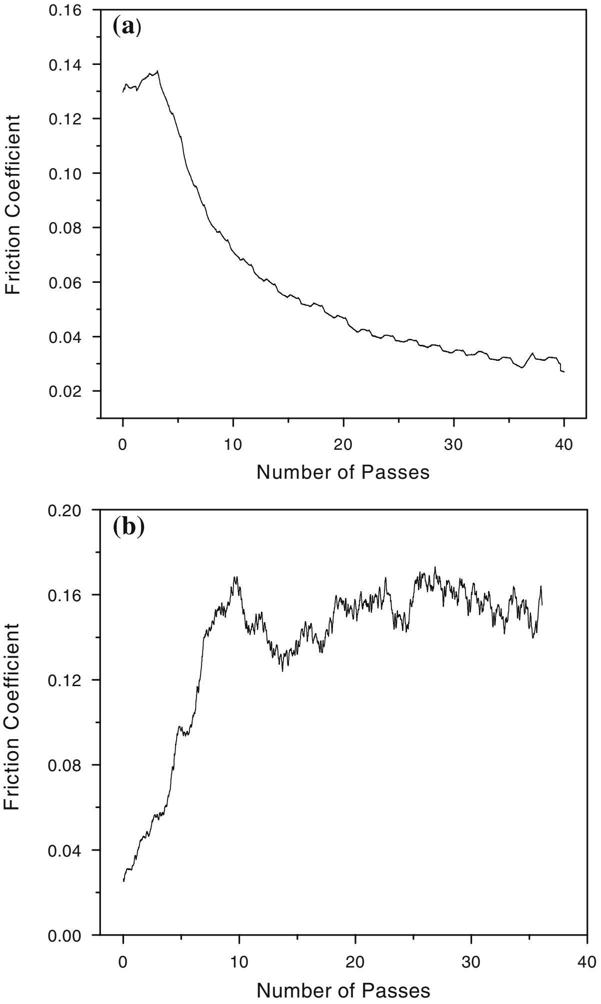

Figure 1. Plot of friction coefficient as a function of the number of passes for (a) the initial 40 passes for a hydrogenated DLC film in an ultrahigh vacuum chamber after baking at 330 K (for 36 h to yield a background pressure of 1×10^{-9} Torr) plotted versus the number of times slid and (b) after longer sliding showing the increase in friction coefficient.

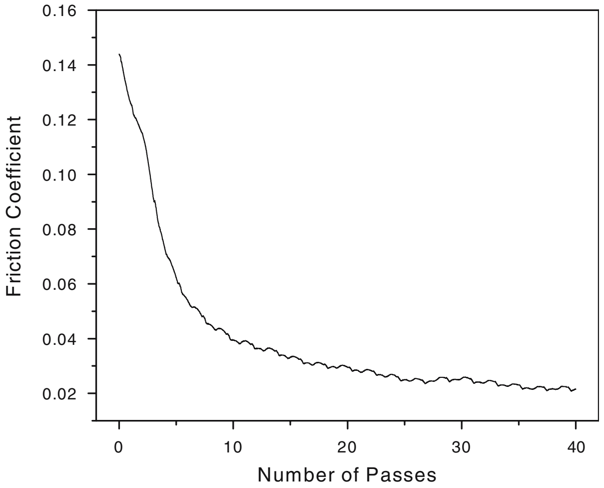

Figure 2. Plot of a friction coefficient versus the number of passes sliding over the same area as for the data shown in figure 1(b), after the friction coefficient has increased and after dosing the surface with 1×10^{-7} Torr of hydrogen for 3 h in the presence of a heated tungsten filament.

displayed in figure 2. This shows that initially the friction coefficient appears to be unaffected by hydrogen dosing since, during the first pass, the friction coefficient is still ~0.14. The friction coefficient however, decreases drastically after five passes to ~0.076 and more slowly thereafter, reaching a plateau value of ~0.02, similar to the corresponding plateau value found for the freshly inserted sample (figure 1). This confirms that the hydrogen content is critical to the frictional behavior and implies that hydrogen removal was responsible for the increase in friction noted in figure 1(b).

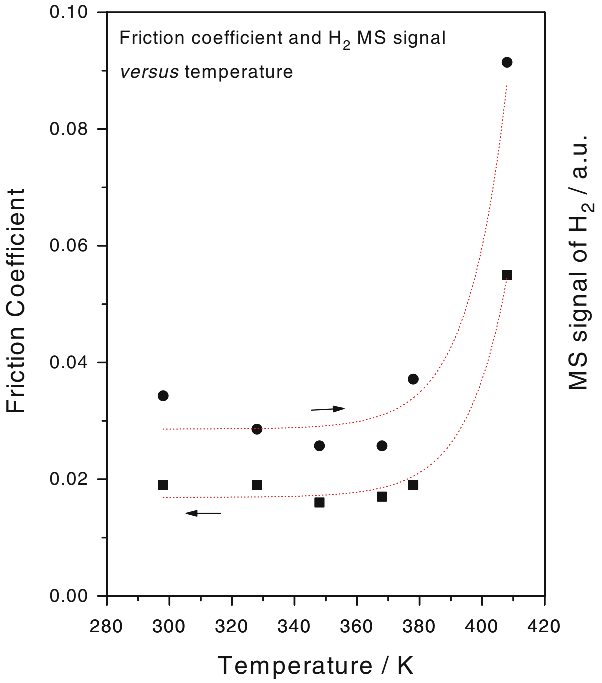

Figure 3. Plot of friction coefficient (■) versus annealing temperature after the sample had been heated *in vacuo* for 20 s. The friction coefficient was measured after allowing the sample to cool to 300 K. Shown also is the 2 amu (H_2) mass spectrometer intensity (●) measured while heating the sample.

In order to further test these ideas, the following experiment was carried out. The sample was heated *in vacuo* to various temperatures while monitoring the gases desorbing from the surface by mass spectroscopy. After heating, the sample was allowed to cool to 300 K and the limiting friction coefficient measured after sliding the pin in a reciprocating fashion 20 times on a fresh portion of the sample. Hydrogen was the only product detected in the gas phase during this procedure and the results are summarized in figure 3, which plots the friction coefficient (■) and the intensity of the 2-amu (hydrogen) signal (●) versus annealing temperature. No hydrogen evolution is detected below ~360 K, and the friction coefficient remains constant over this temperature range. This result confirms that initially baking the vacuum chamber at 330 K did not affect the properties of the film. Heating to ~420 K causes substantial hydrogen evolution and a concomitant increase in friction coefficient to ~0.06, after which the experiment was stopped in order to avoid excessive damage to the sample. The hydrogen-depleted sample was then dosed with deuterium (D_2) in the presence of a filament (1×10^{-7} Torr for 3 h). A similar experiment was carried out, by heating the sample to various temperatures for 20 s and monitoring the 2, 3 and 4 amu (H_2, HD and D_2 respectively) signals in the mass spectrometer, as well as measuring the friction coefficient. The results are displayed in figure 4 where figure 4(a) plots the friction coefficient, and figure 4(b) the intensities of the various masses, as a function of annealing temperature. These data show that rehydrogenating the sample reduces the friction coefficient confirming that the increase in friction coefficient found in figure 1(b) was due to the removal of hydrogen from the surface. These data show a similar behavior to that found in figure 3; the friction coefficient is unaffected by heating to ~360 K, but then increases above this temperature. In this case, the sample was heated to 425 K so that the friction coefficient increased even further to a limiting value of ~0.14, close to that for a sample initially introduced into the vacuum chamber (figure 1(a)), and after extended sliding (figure 1(b)). The increase in friction coefficient in figure 1(b) may therefore be ascribed to the removal of hydrogen during sliding, resulting in increased energy dissipation at the surface, and the appearance of some wear. This conjecture is confirmed by the observation that rehydrogenating the sample results in a decrease in friction (figure 2). This, however, does not explain the initial decrease in friction coefficient found for the sample after insertion into the vacuum chamber (figure 1(a)). One possible origin for this effect is that contaminants initially present on the surface are removed by rubbing, leading to a clean surface that exhibits low friction. Note that water adsorption has been shown to increase the friction

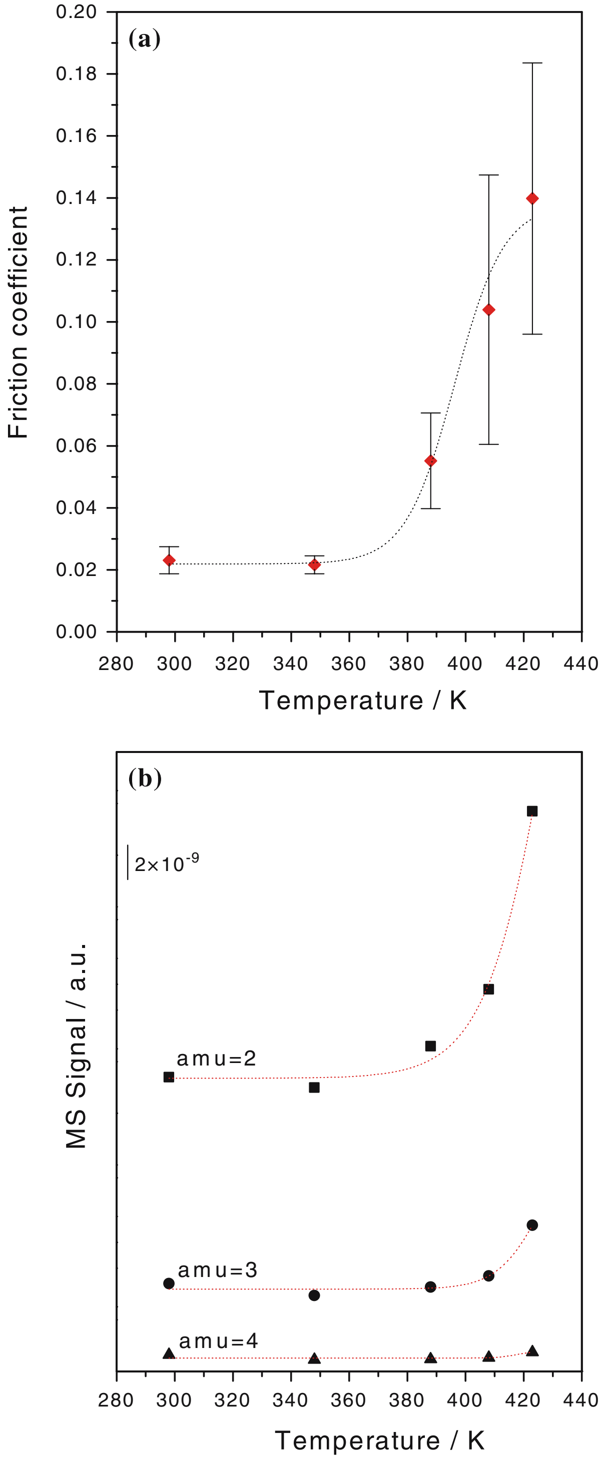

Figure 4. Plot of the friction coefficient (♦) versus annealing temperature (a) for a sample that had been previously heated to 420 K and then dosed with 1×10^{-7} Torr of deuterium for 3 h in the presence of a heated tungsten filament. Plot (b) shows the corresponding intensities of the 2, 3 and 4 amu signals measured while heating.

coefficient of DLC where limiting values of above 0.1 were found, close to the value of ~0.14 noted here [6]. Similar initial decreases in friction have been noted for DLC films measured in ultrahigh vacuum but it should be emphasized that the initial decrease is not due to the formation of a transfer film [9] in this case since both surfaces were coated with DLC. Since the sample can be heated *in vacuo* to ~420 K and the original low friction was regained by dosing with atomic hydrogen, this procedure was carried out to obtain a clean sample. Auger analysis of the sample after this treatment showed the presence of only carbon. This is consistent with the observation that no water desorption was detected mass spectroscopically during this treatment, and only hydrogen evolution was observed, confirming the absence of adsorbed oxygen or water. The resulting plot of friction coefficient as a function of the number of sliding cycles, measured on a fresh, previously untested part of the sample, is displayed in figure 5. This shows an initial very high friction coefficient of ~0.22. Clearly, just removing surface contaminants does not result in a low-friction film. Repeated sliding, however, does cause the friction coefficient to decrease to a limiting value of ~0.02. The reduction in friction with rubbing cannot therefore be ascribed to either removal of contaminants from the surface or the formation of a transfer film, but may be due to a restructuring or some other change of the surface during sliding. It can be expected that any such restructuring would eventually relax, leading to an increase in friction coefficient. In order to test this idea, a sample that had been cleaned by heating to 420 K *in vacuo*, the hydrogen then replenished, and that had been pretreated by sliding with 40 passes to reduce the friction coefficient to ~0.014, was subsequently slid in ultrahigh vacuum (with a background pressure of ~1×10^{-9} Torr) once every 15 min. The resulting plot of friction coefficient as a function of time is plotted in figure 6. This shows a significant increase in friction coefficient to ~0.022 after about 30 min. As shown by the data points taken after

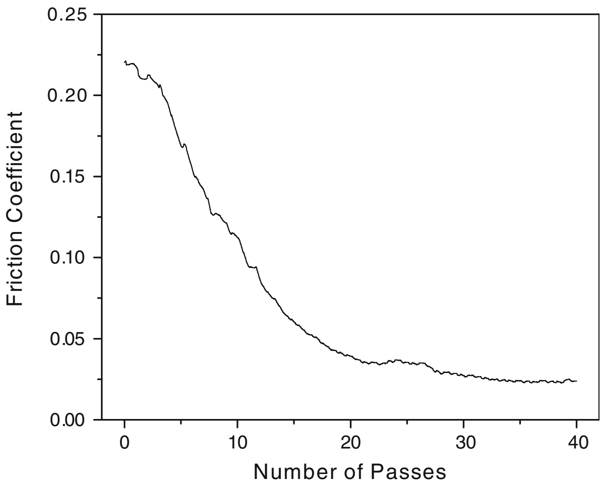

Figure 5. Plot of friction coefficient versus the number of passes for a sample that had been cleaned in ultrahigh vacuum by heating to 420 K and replenishing the sample with hydrogen by exposing to 1×10^{-7} Torr of hydrogen for 3 h in the presence of a heated tungsten filament.

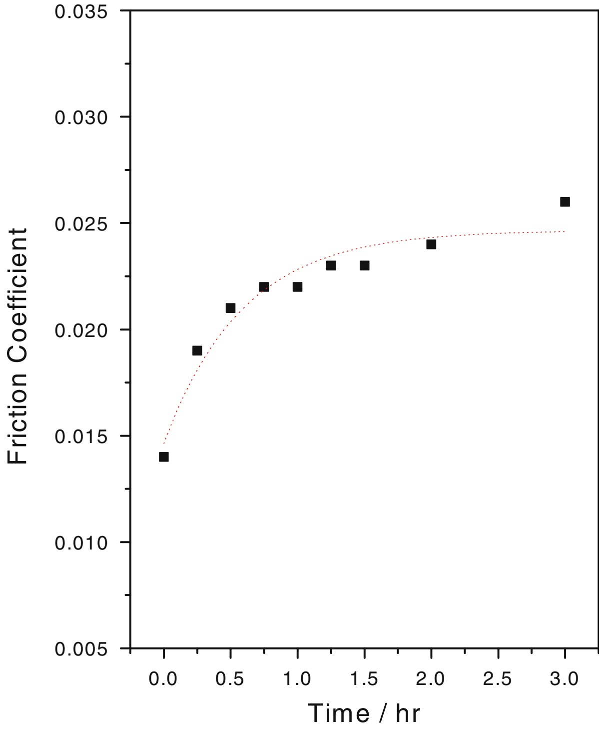

Figure 6. Plot of the friction coefficient versus time of the sample after 40 rubbing cycles as shown in figure 5, initially taken with a single pass at intervals of 15 min for the first 2 h and then at a one-hour interval.

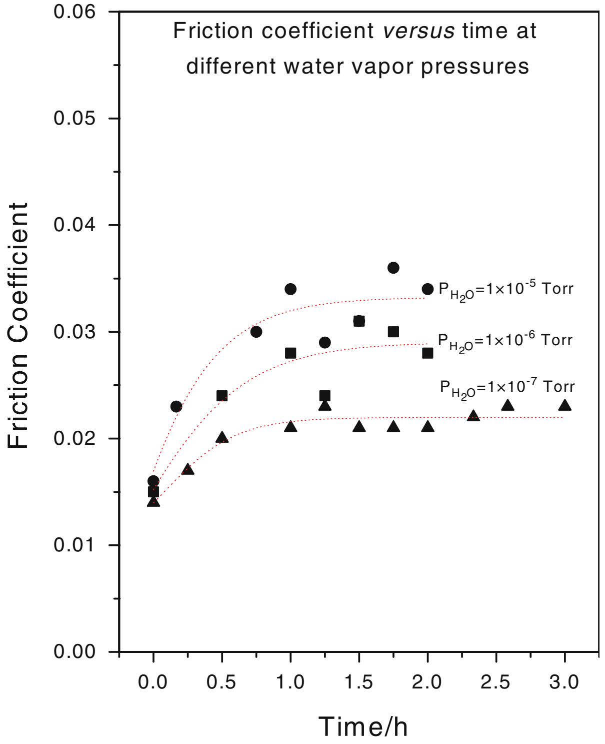

Figure 7. Plot of friction coefficient versus time taken every 15 min with a single pass in the presence of 1×10^{-7} (Δ), 1×10^{-6} (■) and 1×10^{-5} Torr (•) of water vapor.

2 and 3 h, longer delays between sliding result in higher friction coefficients reaching a limiting value of ~0.025. Since these effects may have been caused by the adsorption of background gases over the long times required to carry out these experiments, a similar experiment was carried out in the presence of a background of 1×10^{-7} Torr of water vapor (much higher than any background water vapor pressure in UHV). The resulting change in friction coefficient with time is displayed in figure 7 (▲). These data are very similar to those found in UHV (figure 6), indicating that water vapor has no effect on the variation in friction coefficient with time. However, it is interesting to note that increasing the water vapor pressure to 1×10^{-6} (■) and 1×10^{-5} Torr (•) does have a slight effect on the maximum value of friction coefficient. This suggests that the water vapor may aid any surface restructuring. Similar experiments were carried out using 1×10^{-5} Torr of oxygen, nitrogen and hydrogen and no additional changes in friction coefficient were noted. As noted previously, water appears to have a unique influence on the tribological behavior of DLC [14]. Following these experiments in the presence of 1×10^{-5} Torr of water vapor, the chamber was evacuated and the friction measured once the pressure had reached 1×10^{-9} Torr. All water is expected to desorb from the surface under these conditions and Auger analysis confirmed the absence of any oxygen on the sample. The friction coefficient was measured as a function of the number of passes in two ways, first, by sliding continuously, and second by sliding once at intervals of 15 min. The results are displayed in figure 8, which shows the initial increase in the presence of water vapor reproduced from figure 7 for comparison, along with the friction data collected following evacuation either by sliding continuously or by sliding every 15 min (■). Apparently,

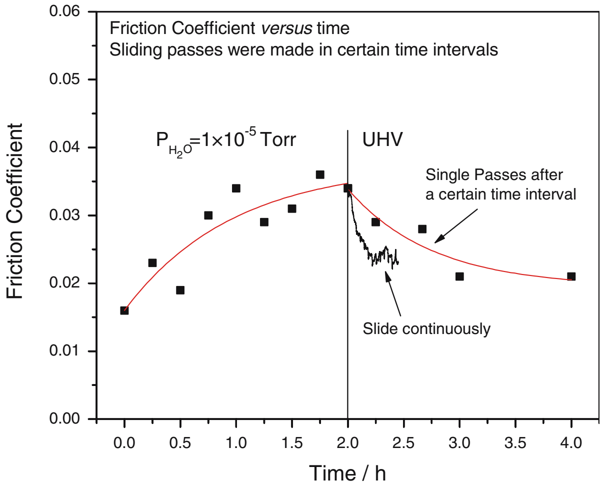

Figure 8. Plot of friction coefficient versus time taken every 15 min with single pass in the presence of 1×10^{-5} Torr of water vapor (■) and reproduces the data shown in figure 7. The chamber was evacuated to 1×10^{-9} Torr after 2 h and the friction coefficient was measured *in vacuo* either by repeated scanning (solid line) or by a single pass, initially every 15 min for an hour and then after 1 h.

the low final friction coefficient depends only on the number of times that the film has been slid and not on the time interval, further suggesting that it is a change in the structure of the film that causes the friction coefficient to decrease to its limiting value, rather than adsorption or reaction on the surface.

4. Discussion

The friction coefficient of hydrogenated, diamond-like carbon decreases with the number of sliding cycles (figures 1 and 2). It appears that this effect is not due to the contamination of the surface. This conclusion is arrived at first, since the effect is seen on surfaces that have been cleaned by heating to 420 K and rehydrogenated by atomic hydrogen (figure 5). Second, the friction coefficient rises once again when an interval is left between each pass (figure 6), where this effect is not due to the adsorption of background contaminants on the sample (figure 7). However, higher background pressures of water do cause an increase in friction coefficient (figure 7), although this effect does not appear to be directly due to the presence of water on the surface, rather due to a change in surface caused by water (figure 8). The most obvious explanation for these effects is that sliding causes a reorganization of the surface that results in a lowering of the friction coefficient and that this structural change relaxes as a function of time, but is accelerated by the presence of water vapor. This effect is fairly small at water vapor pressures up to 10^{-5} Torr (figure 7), but larger changes, causing the friction coefficient to increase up to 0.15, have been observed at higher water partial pressures [6]. No similar effects are found with oxygen, nitrogen or hydrogen implying a specific interaction between the water and hydrogenated carbon film. This is evidently not a surface oxidation reaction and indeed carbon oxidation by water to 300 K is extremely unlikely. It is possibly due to a weak hydrogen-bonding interaction between the water and the carbon of the films causing a structural change.

An increase in friction coefficient is also caused by the removal of hydrogen from the film, either thermally (figures 3 and 4) or tribologically (figure 1(b)). In this case, removal of hydrogen not only results in an increase in friction coefficient, but also in an increase in wear rate. The film can be rehydrogenated by exposure to atomic hydrogen or deuterium. The inclusion of deuterium in the film is confirmed by detecting some D_2 and HD when the sample is heated (figure 4). If the proportion of deuterium in the film is β, and it is assumed that the recombination of H and D is taken to be random, then the HD yield is proportional to 2β, and the yield of D_2 to β^2. Analysis of the relative yields found experimentally in figure 8(b) shows that $\beta \sim 0.17$ indicating that about 17% of the hydrogen has been replaced by deuterium implying that approximately this amount of hydrogen was removed on heating to ~420 K. It is not known whether the deuterium is uniformly distributed though the film or whether it is preferentially located near the surface, although it is more likely to be located predominantly near the surface. The friction coefficients of the hydrogenated and deuterated films are essentially identical (with values of ~0.02) indicating that the presence of deuterium does not affect the friction coefficient. The vibrational frequency of deuterium is substantially lower than that of hydrogen (by a factor of approximately 1.44) suggesting that dynamical factors do not affect friction.

The effect of hydrogen in maintaining low friction has been noted previously [9] and ascribed to the formation of a larger concentration of sp^3-hybridized carbon [15]. Similar effects have been noted for the friction of diamond [16]. The larger pressures of molecular hydrogen required to reduce the friction of DLC is presumably related to the low dissociative sticking probability of hydrogen on a carbon surface.

5. Conclusions

It is shown that depleting a low-friction DLC film of hydrogen by heating in ultrahigh vacuum results in an increase in friction coefficient. Low friction can be restored by replenishing the film with hydrogen thus confirming the importance of the presence of hydrogen in these films. This hydrogen removal and replacement strategy provides a method for ensuring that the surface of the sample is clean and indicates that the initial decrease in friction coefficient from values of ~0.14 to their low values of less than ~0.02 is not due to removal of contaminants from the surface. It is suggested that this effect is due to some surface change, possibly a restructuring, that is caused by the surfaces sliding together. This change appears to be reversed by the presence of water vapor, but not by molecular oxygen, nitrogen or hydrogen.

Acknowledgments

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