

Direct Observation of Tribochimically Assisted Wear on Diamond-Like Carbon Thin Films

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Received: 28 March 2012 / Accepted: 14 November 2012 / Published online: 1 December 2012
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Abstract Friction represents a major energy wastage, with typical estimates in the range of 2–5 % of the GDP of developed countries; 15 % of the energy losses in a new automobile engine are due to friction (Uchida et al. *J. Cryst. Growth* 114:565–568, 1991). While the macroscopic laws of friction have been known for centuries, the exact nanoscale processes taking place are less clear. It is established that friction involves small asperities sliding on a locally flat surface, but the exact mechanisms of slip as well as energy dissipation are still unclear and sometimes controversial. In many ways even less is known about chemical reactions occurring during sliding, what is called tribochemistry. We report here direct *in situ* observation at the nanoscale of tribochemically assisted wear for a tungsten tip sliding on diamond-like carbon films in wet hydrogen, nitrogen and compare these to similar experiments in vacuum. Differences in the wear directly indicate passivation of the films in hydrogen and accelerated wear in wet nitrogen. The results are surprisingly similar to what

one would expect at the macroscale, indicating that in many respects there is little difference between the processes taking place across many length scales.

Keywords Nanotribology · Friction mechanisms · Wear mechanisms · Corrosive wear · Solid lubrication mechanisms · TEM · EELS

1 Introduction

Carbon in various forms is one of the most common solid lubricants, and graphite has been manufactured and used for this purpose for over a century. More recently, diamond and diamond-like carbon (DLC) films have been of increasing interest in part because of their desirable tribological properties when used as coatings. DLC is a metastable amorphous combination of sp^2 and sp^3 hybridized carbon, often hydrogenated during deposition. The composition varies with deposition method—chemical vapor deposition, sputtering, and ion beam methods can all be used—but the resulting thin film is chemically inert, due in part to hydrogen's passivating effect on dangling bonds [1]. In vacuum or an inert gas environment both friction and wear are normally very low. Macroscale studies have shown the graphitization of DLC films [2, 3] as well as the formation of tribolayers [4, 5] while *in situ* experiments at the nanoscale indicate a partial transformation of sp^3 bonded carbon to more graphitic sp^2 bonding [6, 7].

Tribological wear is a complex phenomenon, and can occur in a multitude of ways. It is further complicated by its strong dependence on the operating environment, which changes the chemical atmosphere in which the sliding takes place. The interdependence of mechanical and chemical factors to affect tribological behavior is known as tribochemistry

Electronic supplementary material The online version of this article (doi:[10.1007/s11249-012-0074-x](https://doi.org/10.1007/s11249-012-0074-x)) contains supplementary material, which is available to authorized users.

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or mechanochemistry, and significant work has been dedicated to this topic in general, and specifically in the case of DLC.

In addition to studies that examine the macroscale effects of different gas environments [4, 8–19], there have been nanoscale studies that look at small scale tribochemical wear both experimentally [20–24] and using simulation [25]. Other work uses spectroscopy or other methods to determine the thermodynamical and chemical reactions that occur during sliding [26–34].

However, to date there is a gap in our understanding connecting the monolayer level to tribochemical wear at the nanoscale and linking this to macroscopic results. We aim in this study to observe the sliding contact *in situ* and more directly at the nanoscale, which will allow us to make more definitive statements regarding the origins of DLC friction and wear behavior at this sort of tribological contact and shed light on the nature of tribochemical reactions in general.

In order to fully understand the myriad mechanisms responsible for the variation in tribological performance, we used an experimental setup that simulates a single-asperity contact. We make the sliding contact as delicately as possible in order to limit the mechanisms at work and ease analysis. Using chemical and structural measurement techniques in an environmental transmission electron microscope (ETEM) and an *in situ* sample holder, we studied the fundamental tribochemical science of these films during a sliding experiment in real time. The experiments were performed in both wet N₂ and H₂ gas, and the resulting micrographs, videos, and electron energy loss spectra show the structural and chemical evolution of the surface structure as a function of time and sliding duration.

2 Experimental Method

Electron transparent “N3FC” DLC films were deposited by magnetron sputtering onto NaCl crystal, and subsequently floated off in water and supported on a copper TEM grid coated with a lacey carbon film. Grids were attached to a Nanofactory HS-100 STM-TEM sample holder by conductive epoxy to a gold wire. See Ref. [7] for further details of the *in situ* sample holder operation. Transmission electron micrographs, videos, and electron energy loss spectra were obtained using an FEI Titan 80-300 ETEM at Brookhaven National Laboratory. Sliding experiments were performed at 300 kV under 0.15 torr N₂, 0.15 torr H₂, and 1.5 torr H₂ gas, as well as corresponding non-sliding time series to measure the effect of the electron beam alone. The probe tips were tungsten wire, electrochemically etched in NaOH with radius of curvature approximately 100 nm. The stroke length and tip velocity varied, but were on the order of 1 μm and 2 μm/s, respectively.

Estimations of the volume of worn material were done by assuming the measured intensity of the film is linearly proportional to its thickness. This is a good approximation for materials where diffraction is so weak that mass and thickness dominate the contrast. Because our samples are largely amorphous and homogenous, relating micrograph brightness to thickness is a valid approach.

Every wear track with significant enough area to be outlined in two dimensions was highlighted manually and the average intensity in that region compared to the average intensities in vacuum and a nearby unscratched area of the film to determine the volume of material removed: the surface area given by the outline and the depth given by where the average pixel brightness fell between the vacuum and unscratched film values. Essentially, knowing the thickness of the film from EELS, the vacuum and unscratched film values yield the slope of the brightness–thickness linear relation, and from there we can calculate the thickness of any given brightness value.

Wear particles that remained on the sample were also highlighted using a brightness threshold, and the estimation of volume was made using the thickness contrast of the particles in linear relation to the film thickness determined by EELS. The sample area was kept constant by virtue of the delicate sliding motion which did not physically cause the sample to move, and by use of landmarks to ensure that the examined areas remained the same.

The ratio of sp² to sp³ carbon bonding over the course of the experiment was measured by integrating normalized, background-subtracted EELS spectra. The carbon K-edge σ* contribution, corresponding to sp³ bonds, can be distinguished from the π* edge which corresponds to sp² bonding. The proportional rate of change over the course of the experiment is measured to avoid inaccuracies with absolute measurement. The energy shifts of nitrogen and oxygen features were measured with respect to the carbon K-edge. In addition, the spectra were fit using Gaussian functions to distinguish between energy-loss features at close to the same energy.

3 Results and Discussion

The results in wet N₂ show classic wear behavior as shown in Fig. 1, an energy-filtered micrograph of the film mid-experiment. An energy-filtered video is provided as part of the supplemental material (V1), where the lighter regions are interpreted as thickness contrast—regions where material has worn away. Even though this is taking place at the nanoscale, the reduction in the total thickness indicated by the “brighter” regions is very similar to what one observes for wear tracks at the macroscopic scale; one could increase the scale bar by a factor of 1,000–10,000 in which case the

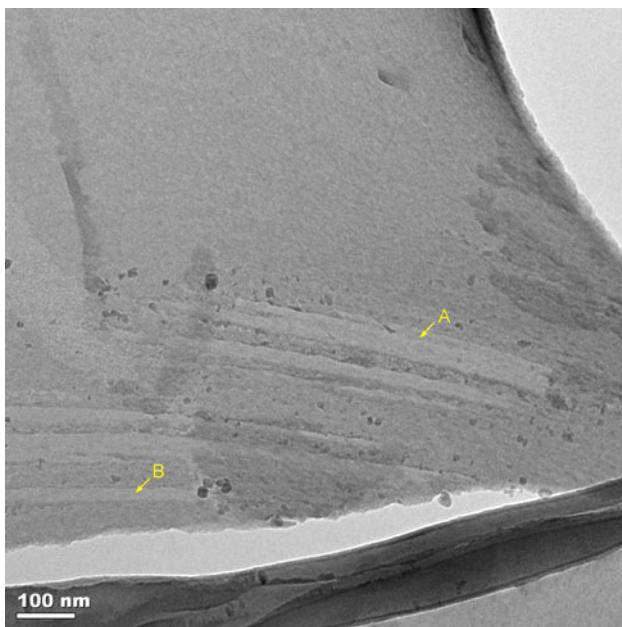


Fig. 1 An energy-filtered (zero-loss) micrograph showing the surface of the DLC film during a wet N_2 sliding experiment after 20 sliding passes. Arrows indicate lighter regions, which we interpret as thinner due to the amorphous nature of the film. As *A* and *B* have different background brightness levels, separate calculations were done in each part of the micrograph in order to determine the estimated volume lost

results would look similar to typical SEM images of wear tracks.

Electron energy-loss data as shown in Fig. 2 clearly shows a strong oxygen edge at ~ 525 eV which is unsurprising considering a known 10^{-5} torr water vapor impurity in the environmental system. The presence of chemisorbed oxygen species on the film surface implies their likely involvement in tribochemical wear. Consistent with this, there is little to no wear debris, indicating that the wear tracks are forming volatile species as would be expected if the tribochemical reactions taking place formed molecules such as carbon monoxide. Using the brightness of the micrographs, we can estimate the wear rate from chemical processes as a function of the number of sliding passes as shown in Fig. 3. By contrast, there was a much slower general etching of the DLC film in regions where sliding was not taking place (see Supplemental material).

These results can be compared to those in wet H_2 (see Fig. 4 and the video V2 in the Supplemental material) where there are no significant wear tracks. Despite the presence of chemisorbed oxygen, the amount of wear observed in these tests was too small to be measured. We can also compare the results with sliding in vacuum [7] where there are no significant wear scars or wear debris—see Supplemental Fig. 1.

Finally, we can measure the rate of the carbon $sp^3 \rightarrow sp^2$ phase transition induced by sliding, and compare it to previous

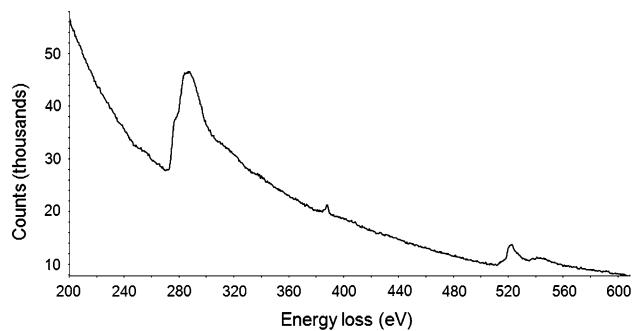


Fig. 2 EELS spectrum after 110 sliding passes in wet N_2 showing the relative prevalence of chemisorbed oxygen to nitrogen. From *left* to *right*, the carbon, nitrogen, and oxygen K-edges can be seen. Quantification suggests a two- to four-fold increase in the relative amount of oxygen compared to nitrogen present in the sampled volume over the course of a sliding experiment

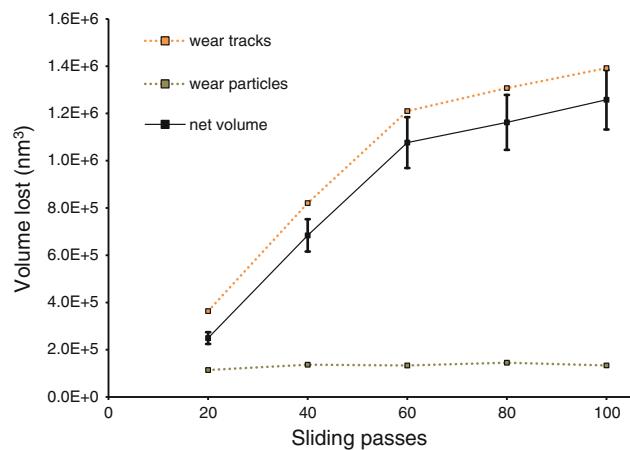


Fig. 3 Estimated volume loss in both the observed wear tracks and the wear particles. During sliding in wet N_2 , the estimated volume of wear particles remains relatively constant, although the average particle size increases over the course of the experiment. The estimated volume of material removed from the wear tracks continues to increase until the film curls up at 120 sliding passes and measurement becomes too difficult. Because the delineation of the edges of wear tracks was done by hand, a human error of 20 % is shown

work [7]. We find that the rate is substantially increased in wet sliding tests as shown in Table 1. During sliding in wet N_2 , we also observe the ratio of adsorbed oxygen to nitrogen to increase by 2–4 times over the course of the experiment—see Supplemental Fig. 4.

For completeness, we note that electrons can etch carbon in the presence of water vapor [35], probably involving electron-activation of the water–gas shift reaction [26, 36]. While this was also taking place during observation, the rate of etching was much slower than the wear directly due to sliding of the tip over the surface. At this scale, the thermal contribution from the electron beam is minimal,

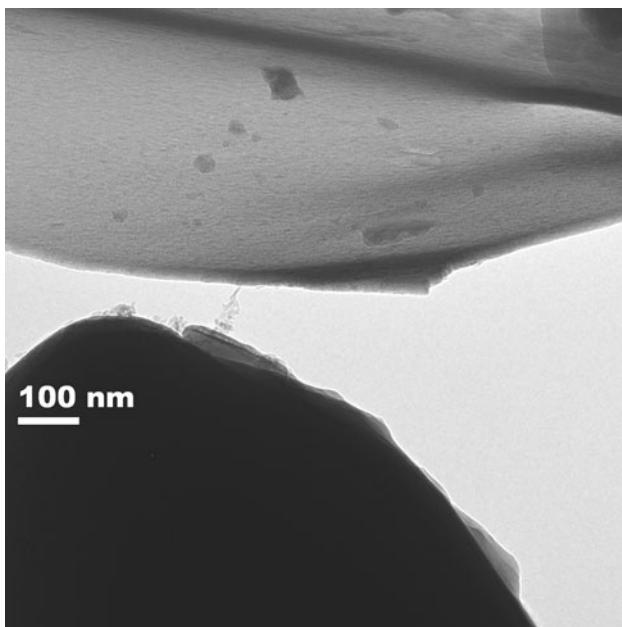


Fig. 4 Micrograph of a wet H₂ sliding experiment. No significant wear tracks are observed at the conclusion of the test, although some light markings are visible

Table 1 Comparison of the percentage increase of the carbon π/σ bonding ratio over the course of the experiment. Our results confirm the acceleration of graphitization in a gas environment and also highlight a pressure dependence

Experiment	Percentage change of carbon π/σ bonding ratio	Number of sliding passes or minutes
Vacuum baseline	−10.8 %	30 min
Vacuum sliding	+10.3 %	1,500 passes
0.15 torr wet H ₂ baseline	−8.2 %	40 min
0.15 torr wet H ₂ sliding	+35.4 %	125 passes
1.5 torr wet H ₂ baseline	−28.4 %	12 min
1.5 torr wet H ₂ sliding	+66.8 %	175 passes
0.15 torr wet N ₂ baseline	−2.7 %	35 min
0.15 torr wet N ₂ sliding	+5.1 %	150 passes

and therefore the localized character of the wear suggests that thermal processes are not involved.

To understand the results, we will first focus on the tribochemical wear in wet N₂. The observation of wear tracks where the tip passes indicates that sliding produces chemically activated atoms which then react with either gas-phase water or, more likely, chemisorbed oxygen or hydroxyl species in the immediate vicinity. We note that a sliding interface is intrinsically similar to a sliding fracture zone, and there is strong evidence that fracture can lead to highly activated species which are capable of emitting X-rays [37] or creating oxygen vacancies at the surface of

strontium titanate [38]. In effect, if we consider the trailing edge of the tip after it passes there will be carbon radicals present which will be very reactive. The absence of wear tracks in wet H₂ experiments indicate that highly active carbon radicals at the trailing edge of the tip are passivated in a nonvolatile manner, almost certainly due to chemisorption of hydrogen. Despite the presence of water vapor, the lower bond-dissociation energy of H₂ and the high activity of H⁺ support the observed dominance of passivation over tribochemical wear reactions in these tests, an effect which has been observed at the macroscale [1].

Electron energy loss spectra show the chemical involvement of nitrogen species as well (see Supplemental Fig. 3). Considering the relative strength of the nitrogen bond when compared to oxygen or hydrogen, the low quantity of chemisorbed nitrogen is not surprising. Still, some interactions are observed, making up a component of the corrosive wear that proceeds at a much slower rate than oxidation. The measured increase of adsorbed oxygen compared to nitrogen suggests that the mechanically induced oxidation processes are not limited to the film surface, and there is some incorporation of oxygen into the solid phase [7, 39–42].

The enhanced formation of sp² carbon in a wet environment compared to dry also points to tribochemical reactions, but here having a secondary effect. Even in an amorphous structure, the more thermodynamically stable in-plane sp² bonding is expected to react slower with oxygen/hydroxide than sp³-hybridized carbon or radicals which may be present immediately after sliding.

4 Conclusions

What should be apparent is that the results are surprisingly similar to what one would expect for mesoscale experiments, with much higher tribochemical wear in the presence of water and clearly indicate that tribochemical processes are only taking place in the immediate vicinity of a sliding interface. There is little difference between the processes taking place across many length scales, beyond the obvious effects due to multiple asperity contacts at the mesoscale and different rate terms that are predictable based on differences in contact areas. Tribochemical wear, and we suspect tribochemical reactions in general will show little nanoscale variation, with the obvious exception of possible secondary effects associated with the enhanced reactivity of nanoparticles which is well known in heterogeneous catalysis.

Acknowledgments This study was supported by the National Science Foundation on grant number CMMI-1030703. Additional support was provided by the U.S. Department of Energy, Office of

Energy Efficiency and Renewable Energy, Vehicle Technologies Program, under Contract No. DE-AC02-06CH11357. Research carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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