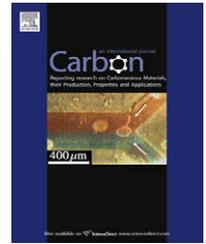


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# In situ TEM studies of tribo-induced bonding modifications in near-frictionless carbon films

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## ARTICLE INFO

### Article history:

Received 29 May 2009

Accepted 25 August 2009

Available online 29 August 2009

## ABSTRACT

Direct in situ TEM evidence is presented for a mechanically-induced increase in  $sp^2$  bond content in the tribolayers formed on near-frictionless carbon (NFC) films. An in situ TEM nanomanipulation holder is used to perform sliding experiments between a nano-sized tungsten probe and electron transparent NFC samples. Electron energy loss spectra (EELS) were acquired between sliding events to show an incremental increase in the  $1s-\pi$  peak, suggesting that a graphitization-like process occurs which can lead to a change in the tribological performance of a variety of hard carbon films. Presently, this behavior is only observed for one of the two varieties of NFC, while supporting TEM imaging evidence is in qualitative agreement with macroscopic friction and wear behavior.

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## 1. Introduction

In this paper, we report the results of *in situ* tribology experiments performed on hard amorphous carbon films within a transmission electron microscope (TEM). This emerging technique allows us to characterize a sliding interface directly, with the aim of ruling out any postmortem or macroscopic effects that would otherwise obscure the interpretation of nanotribological results [1]. Of the many allotropes of carbon, diamond-like carbon (DLC) refers to a class of metastable disordered carbon with significant  $sp^3$  hybridization [2]. DLC typically combines high hardness and strength with chemical inertness, electrical insulation, optical transparency, and low static and kinetic friction, although these properties may be significantly affected by small changes in the deposition source and environmental conditions. These materials have found extensive use as protective coatings in a number of device applications including automotive gears, magnetic

storage disks, biological implants and micro-electromechanical (MEMS) devices [3].

Erdemir et al. have developed a technique of plasma-enhanced chemical vapor deposition (PECVD) to grow ultra-low friction hydrogenated films in a plasma of a 3-1 hydrogen–methane mixture, which have been shown to reach friction coefficients as low as 0.001 in dry inert environments, and are referred to as “near-frictionless carbon” or simply NFC [4]. However, it is well known that not all DLC films have such attractive tribological properties. In fact, DLC materials probably have the largest range of wear and friction coefficients among solid lubricants [5]. Ranges of friction coefficients have been reported in the literature from  $\mu = 0.001$  to  $>0.5$ . To explain this variation, it has been shown that humidity, hydrogen content and oxygen partial pressure have a significant effect on friction and wear rates [6,7], where friction may vary by orders of magnitude over modest changes in relative humidity or  $H_2O$  partial pressure under vacuum [8,9]. Hydrogen-free DLC films tend to show low friction in humid

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doi:10.1016/j.carbon.2009.08.036

environments, while hydrogenated films only possess this property in dry or inert environments. The behavior of the latter has been attributed to the hydrogen termination layer and its resistance to tribo-chemical reactions on the surface of NFC [7]. To further stabilize friction behavior, the doping of DLC films with S, Fe, Si or Ti has been shown to maintain low friction in dry and humid environments [10,11].

The presence of third bodies or transfer layers are an influential component in determining the friction properties of DLC [12,13]. It has been demonstrated that graphitized transfer layers maintain low and stable friction forces in humid environments [14], mimicking the lubricious behavior of graphite. Furthermore, Liu et al. have shown that graphitized debris particles appear on the surfaces of worn DLC contacts, as verified by TEM and Raman analysis [15]. The accompanying reduction and stabilization of friction forces corresponded to the formation of this graphitized transfer layer in ambient conditions. Since graphite lubricates moderately well in humid environments, and hydrogenated DLC films generally show extremely low friction in dry environments, the complex interplay between the formation and wear of transfer layers is central to the study and understanding of self-lubricating carbon surfaces.

In order to form a more complete understanding of the tribo-chemical and structural changes and to unambiguously correlate these with tribological behavior, it is essential to approach the problem with *in situ* techniques. For this reason, we have chosen to reproduce DLC sliding conditions within the TEM while searching for direct evidence of mechanically-induced formation of a carbon rich transfer layer.

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## 2. Experimental procedures

### 2.1. Sample preparation

Diamond-like carbon TEM samples were prepared using a plasma-enhanced chemical vapor deposition (PECVD) technique. A capacitively coupled r.f. discharge plasma was used to deposit films on a substrate at 30 mTorr with a bias of  $-500$  V; the first film, called NFC6, was produced with a gas mixture of 25% CH<sub>4</sub> and 75% H<sub>2</sub>. This ratio of methane to carbon has been shown to possess lower wear rates and friction forces than other mixtures [4]. A 30 nm bond layer of Si was deposited in order to improve adhesion to the Cu grid, since DLC films often suffer from delamination problems. Following this, the carbon film was deposited at room temperature onto a copper TEM grid to a thickness of approximately 100 nm. The second sample, NFC7, was fabricated using the same technique, only the gas precursor was pure methane in this case. NFC7 exhibits less favorable tribological performance (higher friction and wear) than NFC6, as determined by macroscopic pin-on-disk experiments [4]. After deposition, small amounts of the film remained attached to the carbon grid, not extending across the grid square, but remaining localized near the edges of the grid. In other words, the sample was not a traditional suspended film, spanning the grid square distance. This was beneficial for two reasons: it enabled a more localized and repeatable contact area to be maintained, and it improved the local rigidity of the film.

### 2.2. Tribological experiments

The sliding element was fabricated via standard electro-polishing techniques (0–5 V AC) from 0.25 mm polycrystalline tungsten (99.995%) wire in a 2 N NaOH solution to a radius of curvature on the order of 10 nm.

A HS100 STM-Holder™ (Nanofactory Instruments, Göteborg, Sweden), designed for operation with a 200 kV Schottky Field Emission TEM, was used to carry out *in situ* sliding experiments. Specimen-level vacuum was kept in the mid- $10^{-7}$  Torr range during the experiments, and a liquid nitrogen cooled anti-contamination finger was used all times to keep contamination to a minimum. By combining this with minimal e-beam exposure (low magnification) over the duration of the experiment (on the order of minutes), we are confident that no significant contamination was present. Also, the edges of the specimen and sliding probe were frequently monitored for contamination growth. The nanomanipulation holder is configured to accept standard 3 mm TEM grids at a 30° incline to the horizontal. A probe is inserted, which can be spatially controlled in three dimensions by piezo elements and is capable of standard STM measurements. Its piezo resolution is 0.2 Å in XY and 0.025 Å in Z, while coarse motion control yields a range of  $\pm 1$ –2 mm in XY and  $\pm 1$  mm in Z. Additional details regarding the *in situ* TEM holder configuration for sliding experiments may be found in [16].

By maneuvering the tip in a controlled way toward the sample, gentle contact with the sample was established and sliding was performed along a track length of a few hundred nanometers. The sliding velocity was approximately 1  $\mu$ m/s, and EELS spectra were collected after every 50–100 passes. We were not able to directly measure or quantify the magnitude of the normal force applied to the samples during the tests. All loads were made comparable by maintaining a similar degree of deflection and deformation of the scanning probe.

### 2.3. Electron energy loss spectroscopy

A post-column Gatan image filter was employed to perform energy loss spectroscopic measurements. Each loss spectrum was acquired from a region of approximately 100 nm in length (inset, Fig. 1), corresponding to the sliding track area.

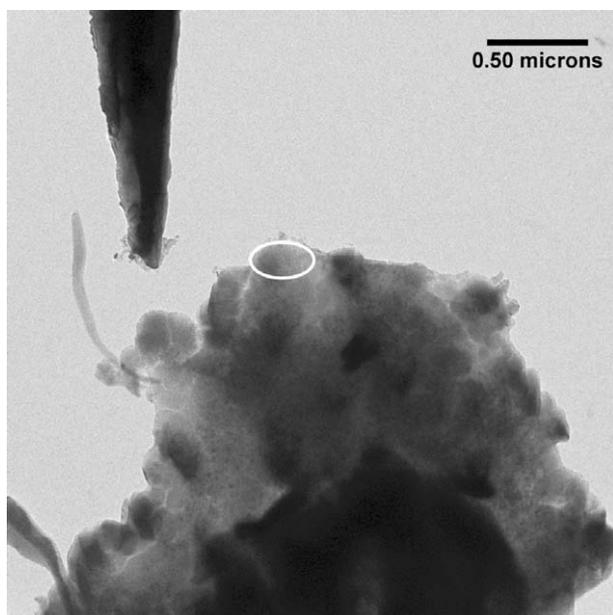
### 2.4. Transmission electron microscopy

TEM bright field images were captured before and after sliding to record the microstructure of the sample. The partial pressure of H<sub>2</sub>O in the TEM column was not recorded, but a liquid nitrogen cold trap was in use to minimize water condensation on the sample and improve the local (high) vacuum.

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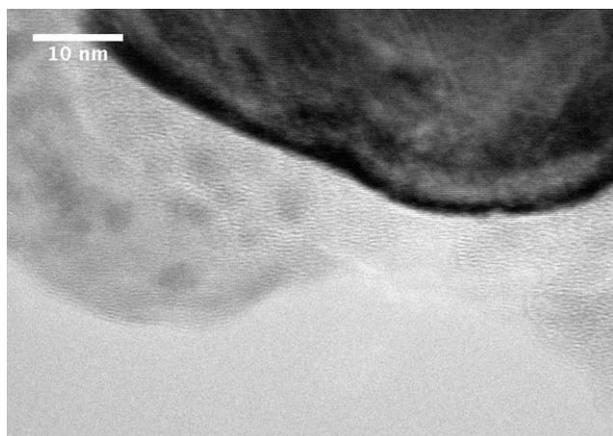
## 3. Results and discussion

Previous work has investigated the relationship between graphitization and frictional behavior in DLC [14] where it was found that the steady-state coefficient of friction was due to wear-induced graphitization. Both sliding velocity



**Fig. 1** – Bright field TEM image of NFC6. The white circle shows the sliding region after 200 passes.

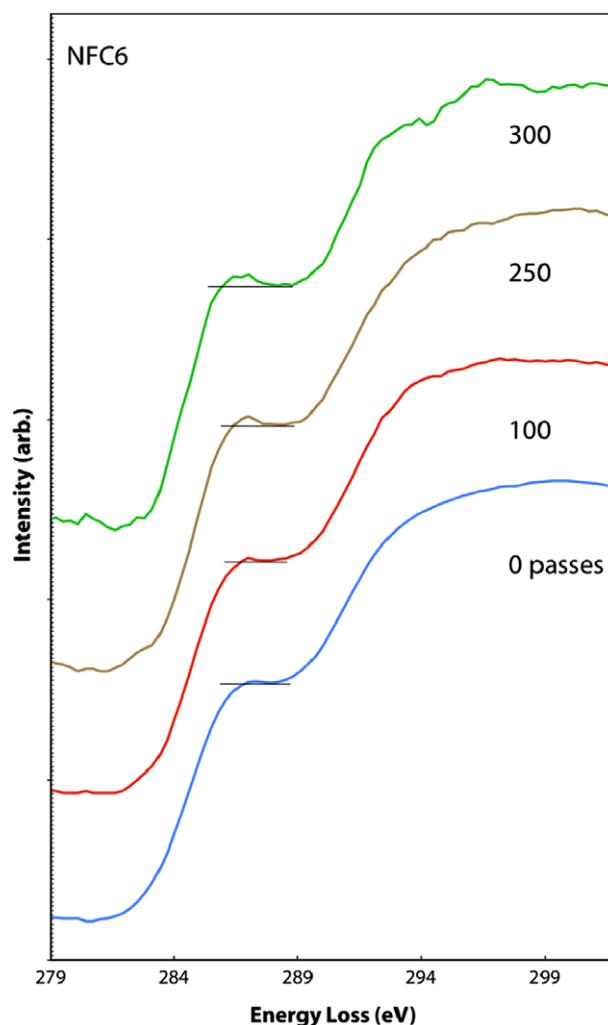
and loading level were shown to have a significant influence on the graphitization process. The work was carried out by conducting friction and wear tests *ex situ* and then loading the worn sample and debris into a TEM for examination. By that method the surfaces are subject to atmospheric conditions, which may have a great effect (e.g. humidity, capillary forces). For the *in situ* work conducted presently the effect of loading and sliding is observed under high vacuum. Fig. 1 shows a bright field image of the NFC6 sample and the tungsten probe between sliding events. The material observed near the end of the tip after sliding appears to be carbon wear debris and is shown in Fig. 2. We arrive at this conclusion because the film debris attached to the tip appears both significantly brighter than the tungsten tip and nearly identical in structure to the standalone NFC film. The source of the carbon is likely to be a combination of material worn from



**Fig. 2** – Bright field TEM micrograph of carbon film material (from NFC6) attached to the W tip after sliding.

contamination layers built up due to the electron beam as well as worn material from the carbon sample.

In the EELS spectra depicted in Fig. 3, a pre-edge resonance is found at 285.4 eV due to transitions from the C 1s orbital to the unoccupied  $\pi^*$  orbitals originating from  $sp^2$  sites and  $sp$  sites if they are present. The broad band observed in the range 288–310 eV is present as a result of overlapping C 1s  $\rightarrow \sigma^*$  transitions at the  $sp$ ,  $sp^2$ , and  $sp^3$  sites of the DLC films. A pre-edge resonance at 285.4 eV is not visible in the spectrum of diamond as it consists only of  $sp^3$  sites so this peak is considered a good indicator of  $sp^2$  content. EELS spectra captured from the NFC6 sample within the region highlighted in Fig. 1 after each set of 100 sliding passes show an increasing 1s- $\pi$  peak trend (Fig. 3) with the amount of sliding. This suggests that a transformation towards a more graphitic material is taking place; possibly an ordered graphitized carbon layer was formed by the mechanical excitation of the film due to the sliding. High resolution imaging, however, failed to unambiguously identify individual graphitic features in the sliding region of interest on the sample. This does not eliminate the



**Fig. 3** – 1s near edge carbon peaks detected by EELS for NFC6 after 0, 100, 250, and 300 sliding passes with a 20 nm tungsten scanning probe. Horizontal lines added at the  $\pi$ -peak for visual clarity.

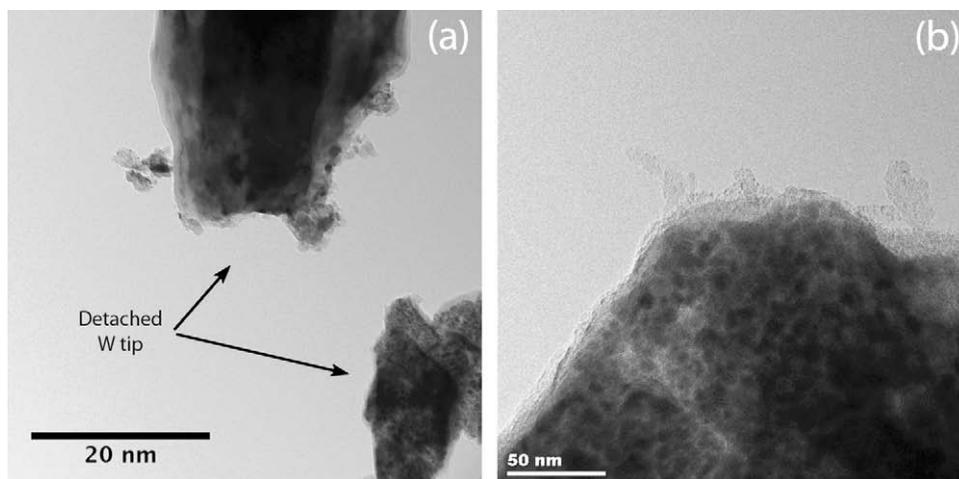


Fig. 4 – Fractured tungsten tip (a) after sliding on NFC7 (b).

possibility of the presence of graphitic carbon, since, if produced and deposited on the sample, graphitic particles would most likely exist in small quantities and lie in unfavorable orientations for imaging purposes. Excessive sliding (400–500 passes) on NFC6 caused the sample to detach from the copper grid substrate, placing an upper limit on the amount of sliding.

Neither imaging nor EELS analysis showed any indication of a relative increase in the  $\pi^*$  peak after sliding on the NFC7 sample. However, significantly more wear debris was produced, for equal amounts of sliding. As shown in Fig. 4, the end of the tungsten tip was fractured and broken off after only 200 sliding passes under the same conditions as for NFC6. This behavior is qualitatively consistent with the macroscopic observation of NFC7 exhibiting higher friction and wear rates than NFC6 [4]; the results shown in [4] give the wear rate of NFC7 to be more than an order of magnitude higher than that of NFC6. For NFC7 the wear rate is  $9 \times 10^{-9} \text{ mm}^3/\text{Nm}$  and for NFC6,  $4.6 \times 10^{-10} \text{ mm}^3/\text{Nm}$ ; the corresponding coefficients of friction are 0.015 and 0.003 in dry nitrogen. As there is no evidence of a graphitic transfer layer in NFC7 this suggests that the formation of an  $\text{sp}^2$  rich transfer layer is related to the observed wear behavior under the conditions within the microscope. The cause of this behavior involves a complex process involving tribo-chemical reactions, mechanical excitation and frictional heating in combination with different structures pertaining to NFC6 and NFC7 as elucidated by fluctuation electron microscopy (FEM) [17]. FEM showed that the films with the highest friction coefficient, i.e. NFC7 had a very distinct layer structure with discernable differences between the local bonding and the medium-range order in the surface in comparison with the bulk of the film. Compared to NFC6, FEM determined that NFC7 films had more  $\text{sp}^3$  carbon bonding on the surface and were more structured in the medium-range. NFC6 was found to be more homogeneous, which was attributed to the increased amount of hydrogen flux in the plasma. The structural differences between the two films are also a factor in the respective relative increase and decrease in  $\text{sp}^2$  bonding sites in NFC6 and NFC7 films.

#### 4. Conclusions

In this study, low friction diamond-like amorphous carbon films were analyzed by *in situ* TEM to determine bonding and structural behavior under tribological loading. Two films were subjected to sliding by a single asperity tungsten probe during simultaneous observation within the TEM. EELS measurements captured incrementally after each series of sliding passes showed successive increases in the  $1s$ - $\pi$  carbon peak ratio for NFC6 (75%  $\text{CH}_4$ -25%  $\text{H}_2$ ) as seen previously on a macroscopic scale [18]. Conversely, no variations in the peak intensities were observed for NFC7 (100%  $\text{CH}_4$ ). These *in situ* results suggest that an increase in local relative  $\text{sp}^2$  bonding, consistent with graphitization effects, are present at tribolayers formed at the sliding interface of tungsten and NFC6 by local mechanical excitation. Qualitatively, it was found that the NFC7 film wore more rapidly than NFC6 as evidenced by significantly higher amounts of debris adhering to the tungsten tip; this result is in agreement with macroscopic observations on identical film compositions [4]. This result is consistent with the understanding that the superior lubricity properties of NFC6 as compared to NFC7 is a function of the higher hydrogen content of NFC6 films. By establishing a nanoscale sliding interface within the TEM and performing real-time imaging and spectroscopy of a moving contact, we have demonstrated the power and flexibility of *in situ* nanomanipulation techniques to analyze structure–property relationships at nanotribological interfaces and offered strong evidence that the formation of a graphitic layer is the frictional controlling mechanism in these films.

#### Acknowledgements

This work was supported by the National Science Foundation on Grant No. DGE-0114429, the Air Force Office of Scientific Research on Grant No. 49620-03-1-0092, Office of Energy Efficiency and Renewable Energy, Freedom Car and Vehicle Technologies Program, under Contract No. DE-AC02-06CH11357, and was carried out in the Electron Microscopy Center at

Argonne National Laboratory, which is supported by the DOE Office of Science under Contract No. W-31-109-Eng-38.

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