Temperature and Water Vapor Pressure Effects on the Friction Coefficient of Hydrogenated Diamondlike Carbon Films

Microtribological measurements of a hydrogenated diamondlike carbon film in controlled gaseous environments show that water vapor plays a significant role in the friction coefficient. These experiments reveal an initial high friction transient behavior that does not reoccur even after extended periods of exposure to low partial pressures of H$_2$O and O$_2$. Experiments varying both water vapor pressure and sample temperature show trends of a decreasing friction coefficient as a function of both the decreasing water vapor pressure and the increasing substrate temperature. These trends are examined with regard to first order gas-surface interactions. Model fits give activation energies on the order of 40 kJ/mol, which is consistent with water vapor desorption. [DOI: 10.1115/1.3139047]

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**Title and Subtitle**

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and was measured using a thermocouple that was adhered onto the sample surface. The pin and counterface samples were borosilicate glass that were coated with NFC; the pins had a 7.78 mm radius of curvature. The initial surface roughnesses were approximately $R_a = 3.2$ nm, as measured by a scanning white-light interferometer, and the film thicknesses were on the order of a micrometer.

3 Results and Discussion

An initial run-in experiment in the argon environment was performed on the as-deposited NFC coatings. The applied normal load ($F_n$) was 100 mN, the track length ($L$) was 0.6 mm, and the sliding speed ($V$) was 18 mm/s. Under the 100 mN load, the Hertzian track width was approximately 50 μm. As shown in Fig. 2, it took over 2000 cycles ($N$) of high friction ($\mu \sim 0.5$) sliding before running-in to a low friction coefficient condition. The energy ($U$) dissipated during the run-in period can be estimated by $U = 2\mu F_n L N$, and approximately 120 mJ of energy was dissipated during this regime. Previously, neutron reflectivity demonstrated that the as-deposited NFC films are composed of two layers with an approximately 30 Å thick higher density surface layer over the bulk [12]. In this argon environment the wear of the films was very low, and post-test analysis of the wear tracks and wear scars revealed that the wear was below our ability to report quantitative wear rates using scanning white-light interferometry.

A series of experiments were run on the same wear track without breaking the dry argon environment in order to assess whether or not a similar high friction layer could reform in the testing environment. The contact was separated randomly by orders of magnitude from 1 min to 10,000 min. After this aging of the samples, the transient friction behavior of the films was again examined using a “standard” test that consisted of 1000 cycles at 5 mm/s, under 3 mN of load, over a 0.6 mm track. Plots of the friction coefficient trends after the periods of dwell for each standard test are shown in Fig. 3. It was clear that regardless of dwell time the high friction run-in behavior did not return. For these experiments the initial friction coefficient value began at approximately $\mu = 0.13$, which is close to the highest steady-state friction coefficient for a self-mated NFC pair seen by Heimberg et al. [6].

In another experiment, water vapor was added to the chamber without increasing the oxygen partial pressure above 20 ppm. An experiment was run where the environment started as dry argon, the friction coefficient was allowed to run-in to a low value, and then the amount of water vapor was ramped up and back down to see how the friction coefficient responded to these changes in relative humidity (RH) (this is plotted in Fig. 4). This experiment clearly demonstrated that water vapor is a species that adversely affects the friction coefficient. It is also clear that even at ~32% RH the high initial friction coefficient ($\mu \sim 0.5$) seen in Fig. 2 was not observed, and the highest friction coefficient is similar to the starting friction coefficient values found during the exposure experiments shown in Fig. 3.

A series of experiments varying both the chamber water vapor pressure and the counterface surface temperature was designed and executed with the hope to correlate trends in friction coefficient to water adsorption and desorption kinetics. A single self-mated NFC coated pin and counterface sample were used for the entire matrix of experiments, and the experiments were all performed in the same wear track. The experimental matrix for this series consisted of four individual experiments. During each ex-

Fig. 1 Schematic of the contact region of the low contact pressure tribometer

Fig. 2 Initial run-in of two as-deposited self-mated NFC samples in a dry argon environment

Fig. 3 Friction coefficients for repeated sliding at the same location after separating the surface for specified periods of time in a dry argon environment

Fig. 4 Friction coefficients over a single experiment ramping the water vapor concentration while holding the oxygen partial pressure below 20 ppm. Under a contact load of 200 mN and a sliding speed of 4 mm/s.
Fig. 5 Experimental results of friction coefficient ($\mu$) as a function of counterface surface temperature and water vapor pressure

The surface coverage changes in water vapor pressure ($P$) and counterface temperature ($T$) can be examined using Langmuir’s model of surface adsorption and desorption [13]; we assume that the sticking coefficient is unity. Table 1 outlines the modeling parameters. The Langmuir model gives the change in surface coverage as a function of time assuming an adsorption rate ($K_aP$) over the nascent portion of the surface ($1-\theta$) minus the desorption rate ($K_d\theta$), as given by Eq. (2)

$$\frac{d\theta}{dt} = K_aP(1-\theta) - K_d\theta$$

Assuming an initial coverage of $\theta_0$, Eq. (2) can be solved to give the coverage as a function of the rates of adsorption, desorption, and time ($t$); this is given in Eq. (3). A steady-state this expression is simplified to Eq. (4)

$$\theta = \frac{K_aP}{K_aP + K_d} + \left(1 - \frac{K_aP}{K_aP + K_d}\right)e^{-(K_aP + K_d)t}$$

$$\theta_{SS} = \frac{K_aP}{K_aP + K_d}$$

The expression for the adsorption rate coefficient ($K_a$) is given by Eq. (5) [13,14]. In this expression, the adsorption rate coefficient is a function of the molecular impingement rate ($I$), the surface site density ($n_0$), and the pressure ($P$). The adsorption rate coefficient can also be expressed as a function of the site density ($n_0$), molecular mass ($m$), the Boltzmann constant ($k$), and the temperature ($T$)

$$K_a = \frac{I}{n_0P} = \frac{1}{n_0(2\pi mkT)^{1/2}}$$

Here all parameters are estimated. The site density ($n_0$) is estimated as $1.3 \times 10^{19}$ sites/m$^2$ and $2.99 \times 10^{-26}$ kg is used as the molecular mass of water. The Boltzmann constant is defined as $1.3807 \times 10^{-23}$ J/K. The appropriate temperature is assumed to be the chamber temperature, which was held constant at 303 K. This gives $K_a = 2838$ Pa$^{-1}$ s$^{-1}$.

The desorption rate is given in Eq. (6) [13,14], and is defined as the inverse of the average staying time ($\tau_0$) of a molecule on the surface. The desorption rate is a function of the time between molecular escape attempts ($\tau_0$), the activation energy ($E_a$), the Boltzmann constant, and the temperature.

$$K_d = \frac{1}{\tau_0} = \frac{1}{\tau_0} e^{(-E_a/kT)}$$

4 Modeling/Discussion

Comparisons of friction coefficient to a fractional coverage ($\theta$) of a contaminant on the exposed surface of the counterface are common in vapor and gas phase lubrication studies. Here the coverage on the pin sample, which is always in contact, was assumed to be zero. In order to estimate an equivalent coverage for a given condition, the friction coefficient was assumed to follow a linear model [10,11], as shown in Eq. (7)

$$\theta = \frac{(\mu - \mu_0)}{(\mu_1 - \mu_0)}$$

In Eq. (1), $\mu_0$ is the friction coefficient of a clean surface, and $\mu_1$ is the friction coefficient of a fully saturated surface. Friction coefficient values for the nascent (clean) and fully covered surfaces from previous modeling efforts were reported to be $\mu_0 = 0.006$ and $\mu_1 = 0.12$, respectively [10,11].

The surface coverage changes in water vapor pressure ($P$) and counterface temperature ($T$) can be examined using Langmuir’s model of surface adsorption and desorption [13]; we assume that the sticking coefficient is unity. Table 1 outlines the modeling parameters. The Langmuir model gives the change in surface coverage as a function of time assuming an adsorption rate ($K_aP$) over the nascent portion of the surface ($1-\theta$) minus the desorption rate ($K_d\theta$), as given by Eq. (2)

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$$\theta = \frac{K_aP}{K_aP + K_d} + \left(1 - \frac{K_aP}{K_aP + K_d}\right)e^{-(K_aP + K_d)t}$$

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$$K_d = \frac{1}{\tau_0} = \frac{1}{\tau_0} e^{(-E_a/kT)}$$

The important temperature for the desorption process is the counterface surface temperature, which was controlled during the experiments.

Figure 6(a) shows the fit of Eq. (4) to the data plotted in Fig. 5. A least-squares regression optimization returns attempt times of $\tau_0 = 2.5 \times 10^{-15}$ s and an activation energy of $E_a = 46.5$ kJ/mol. The inverse of the crystal lattice vibrational frequency may be used to estimate of the time between molecular surface escape attempts [13], and gives values on the order of $\tau_0 = 1 \times 10^{-13}$ s. It turns out that the fits are not particularly sensitive to attempt times of this order of magnitude. If the activation energy is treated as a free parameter, the fits improve slightly (Fig. 6(b)) and give values of activation energy between 40–50 kJ/mol. These activation energies are comparable to other investigations of water desorption that report activation energies on the order of 40 kJ/mol [15,16].

While water vapor is a clearly shown to be a contributing factor to the tribological performance of these self-mated highly-
hydrogenated diamondlike carbon films, this adsorption model has a major deficiency in time scale. The transient behaviors predicted by this model have time constants on the order of nanoseconds not minutes (see Figs. 3 and 4). This may be partially explained by studies of water molecules adsorbing and desorbing on a hydrogen terminated diamond surface using X-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS) [17]. This XPS and HREELS study suggested that physisorbed water is the dominant mechanism on hydrogen terminated diamond surfaces. Other hypotheses involve the formation of water layers on the surfaces, and if data are plotted as friction coefficient versus the surface relative humidity (Fig. 7), there is a trend of decreasing friction coefficient versus relative humidity, but the data do not collapse onto a single curve. Based on these experiments, superlow friction appears to be limited to local relative humidities below 1–2%. The details of water’s interactions with carbon films and its impacts on friction coefficient remain an open research question.

5 Conclusions
Low friction coefficients were achieved under microtribological (low contact pressure) sliding contacts of self-mated NFC. An initial high friction film was shown to take over 2000 repeated passes prior to providing low friction. Experiments varying the exposure time between contacts from 1 min to 10,000 min showed nearly identical transient behavior in friction coefficient.

Water vapor was shown to cause a high friction coefficient response, and though recoverable, the time constants were on the order of thousands of seconds. Temperature and water vapor experiments showed trends of decreasing friction coefficient with combinations of decreasing water vapor pressure and increasing substrate temperature.

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References