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ORIGINAL PAPER

Thermally Activated Friction

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Abstract The temperature dependence of the kinetic friction between a highly oriented pyrolytic graphite surface and a silicon nitride probe tip has been evaluated through atomic force microscopy measurements performed under an ultra-high vacuum environment over the temperature range 140–750 K. As temperature increases from 140 to 400 K a sharp decrease in friction is observed. A relatively weaker dependence on temperature is observed in the friction measured between 400 and 750 K. Collectively, these results obtained from a fundamental interface are consistent with an activated mechanism of energy dissipation during sliding.

Keywords Friction mechanisms · Graphite · AFM

Introduction

The relative motion of two bodies in contact involves a number of forces acting across the interface and influencing the nature of sliding and wear. Of these, frictional forces play a central role and are known to depend on many factors including composition, topography, third bodies (adsorbates, lubricants), velocity, and temperature. Of particular interest here, large variations in friction are routinely experienced in practical applications as operation conditions diverge from room temperature in both cryogenic and elevated temperature directions. Previously, macroscopic testing of solid lubricants performed at temperatures below ambient have been frequently conducted in submerged environments; the state-of-the-art is less than optimal [1, 2]. Attempts to operate pin-on-disk tribometers under cryogenic gas boil off have provided friction coefficient data down to ~77 K under He [3, 4] and N_2 [2] gas streams. Contamination with water has been a particular concern for these studies; 1 ppb of H_20 in the gas stream is the equilibrium vapor pressure above ice at approximately 160 K. Over the temperature range from 150 to 450 K macroscopic pin-on-disk tests with polytetrafluoroethylene (PTFE) films have shown a friction coefficient response that was characteristic of a thermally activated Arrhenius behavior [2]. In separate experiments, employing a cryostat with a tilting slider-block tribometer using steel pins on PTFE, steel pins on sapphire, and sapphire on sapphire, no discernable temperature dependence from 4 to 300 K was observed, although wear was apparent in these systems [5].

Fundamental studies of the origin of frictional forces and their dependence on environmental conditions must seek to account for the simultaneous contribution of individual influences (composition, velocity, temperature, etc.) or seek to eliminate their contribution. Such studies will be facilitated through the assessment of systems in which interfacial sliding occurs between clean, model surfaces, and for contacts of known area and location. The discussions of friction coefficients based on a thermally activated sliding interface are likely not appropriate for systems experiencing gross wear and material deformation. This report documents measurements of kinetic friction measured between a silicon nitride probe tip and a highly oriented pyrolytic graphite surface, where the potential influence of interfacial wear has been excluded through imaging of the contact region and the high reproducibility

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of the measured data sets. The frictional properties of graphite surfaces have been the subject of previous microscopic studies, many of these highlighting the atomic nature of the interfacial contact and the energy dissipation mechanisms active for graphite interfaces [6–8]. The present report focuses on the significant increase in friction experienced at graphite interfaces at cryogenic temperatures.

The fundamental nature of atomic-scale friction has been investigated previously in terms of its velocity and temperature dependence, employing both theoretical and experimental approaches [9–13]. These investigations have addressed friction for a range of conditions related to both the properties of the sliding pair and the nature of the characterization approach, and have reported a range of results. Although exploring varied temperature conditions, these studies of interfacial friction have focused primarily on the velocity dependence of friction as a means to assessing the origin of frictional energy losses.

Krylov et al. recently conducted theoretical investigations of friction for the contact of a microscopic probe tip and a well-characterized substrate across a full range of surface corrugations, temperatures, and scanning velocities [11]. In their work, friction is predicted to exhibit an exponential temperature dependence of the form $F_{\mathrm{L}} \sim \exp(U_0/k_{\mathrm{B}}T)$, where U_0 is defined as the surface barrier amplitude, k_{B} Boltzman's constant, and T the support temperature. Although the explicit form of the derived equation was predicted to depend collectively on the magnitude of the velocity, temperature, and the surface potential, the model was based on reversible activated jumps between potential energy wells associated with the local lattice corrugation. Under conditions of constant velocity and all other variables being fixed, the model suggests that friction will decrease with increasing temperature at interfaces involving meaningful surface corrugations. To date, these findings have lacked experimental corroboration—a recent vacuum AFM study entailing friction measurements of the interfacial sliding of a silicon-silicon contact (native oxides present) documented a temperature dependence of dynamic friction in the temperature range 50–300 K [13], however the data was not characterized with respect to a specific functional form.

In this article, the temperature dependence of frictional forces *at fixed velocities* has been measured with atomic force microscopy (AFM) for the contact of atomically flat (as determined from AFM images), highly oriented pyrolytic graphite (HOPG) surfaces, and a silicon nitride probe tip under ultrahigh vacuum conditions ($<2 \times 10^{-10}$ torr). This approach has allowed the elimination of topographic effects other than local atomic corrugations—HOPG is easily cleaved producing atomically flat surfaces extending over several microns, well beyond the area of interrogation of these microscopic measurements. In addition, the approach has sought to reduce chemical contributions, as HOPG is relatively inert with respect to interactions with the AFM tip surfaces. Finally, measurements performed under ultrahigh vacuum (UHV) conditions have allowed the assessment of frictional forces at cryogenic temperatures apart from the influence of adsorbed species. In this article, we report variable-temperature friction results obtained on HOPG over the temperature range of 140–750 K, which exhibit a thermally activated behavior.

Experimental

The measurements reported here were performed using a variable temperature AFM employing a beam deflection detection scheme and equipped with cooling and heating facilities providing access to the temperature range 25–750 K (Omicron Nanotechnolgy) [14]. The microscope was mounted in an ion pumped UHV chamber with a base pressure of $<2 \times 10^{-10}$ torr. A remote liquid nitrogen bath thermally coupled to the substrate produced temperatures from 140 to 300 K. From 300 to 750 K, a pyrolytic boron nitride heater mounted behind the sample holder supplied heat to the substrate. Due to the large difference in mass between the tip and sample, and the timeframe of the measurements, the tip is assumed to be in thermal equilibrium with the substrate. The HOPG sample was cleaved ex situ, immediately introduced to the vacuum chamber, and annealed to 400 K for a sufficient time to eliminate outgassing. The friction measurements employed a Si_3N_4 cantilever (Digital Instruments) possessing a normal force constant of ~0.58 N/m and a nominal tip radius of ~20 nm. In the reported friction values, zero normal force has been defined as the force acting on the cantilever at its equilibrium deflection when away from the substrate. The friction experiments employed a scanning velocity of 600 nm/s over a distance of 100 nm. In all measurements, the tip was scanned with respect to a fixed sample location and was located within 5% of the zero offset location of the scanning piezo. Friction measurements employed a low-gain feedback of the tip displacement, systematically modified by an external voltage ramp used to explore variable normal loads. Individual friction loops comprised of lateral force measurements (F_{L}) as a function of sample location (x) were collected in a line-scan mode in which the tip was translated orthogonally to the long dimension of the cantilever (see Fig. 1), a process also repeated as a function of temperature. The low friction forces in the high temperature limit were estimated to be on the order of 1 nN, based on the expected lateral force constant [15]; however the data is presented in arbitrary units to avoid

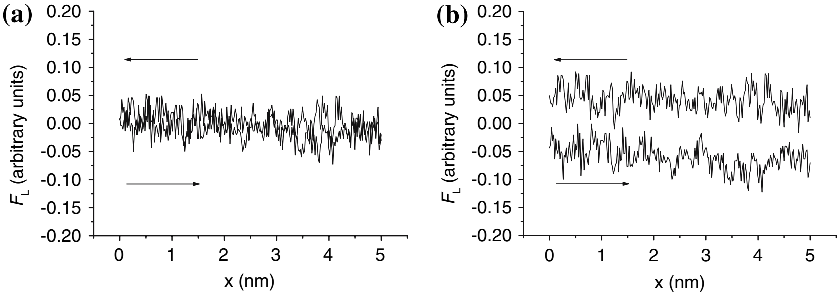

Fig. 1 (**a**) An individual friction loop measured for the contact of a silicon nitride probe tip and HOPG at 300 K and 0 nN applied load. The overlapping nature of the data measured for opposite scan directions along the same line is indicative of the low friction measured for this interface. (**b**) When the frictional traces are artificially offset, evidence for the stick-slip motion at the interface is apparent. Friction force values are reported in arbitrary units; an assessment of these values is provided in the experimental section.

erroneous comparisons to other data sets employing different probes and measurement conditions.

Frictional properties were further characterized through friction loops measured as a function of load in the regime of 0–20 nN applied load. The slopes of the linear plots of lateral force versus normal force have been ascribed to a microscopic friction coefficient (μ). For each reported value of lateral force or friction coefficient, the tip-substrate contact has been allowed to reach thermal equilibrium. Values of lateral force or friction coefficient are reported as normalized values (f/f_0 or μ/μ_0), with respect to values measured at 280 K.

Results and Discussion

Figure 1a displays a representative friction loop measured for the contact of the Si_3N_4 probe tip and the HOPG surface at a surface temperature of 300 K and an applied load of 0 nN. In this plot, lateral force is plotted versus sample displacement for a single reciprocal cycle of sliding in one dimension. From this measurement, the average kinetic friction is calculated as ½ of the difference of the average friction experienced when sliding in the different directions. It is apparent from Fig. 1b, where the different traces have been artificially offset, that non-zero friction events consistent with the stick-slip motion of the tip occur, although the average is very close to zero. It is also clear that the ability to resolve frictional differences under these conditions becomes limited by the inherent fluctuations in lateral force experienced by the tip during motion across the surface. Nonetheless, as temperature was decreased or load increased in the experiments described below, non-zero values of the average kinetic friction were detected and were used to characterize the temperature dependence of the friction properties of graphite.

Figure 2a displays the atomic-scale friction experienced between an HOPG surface and a Si_3N_4 probe tip at an applied external load of 0 nN over the temperature range of 140–750 K. The data represent the lateral force experienced while sliding, averaged over sample location and sliding direction. An abrupt decrease in lateral force is experienced over the temperature range of 140–300 K; above 300 K, the lateral forces remain low with variations on the order of the statistical spread in measured values. An Arrhenius analysis of the temperature-dependent data is presented in Fig. 2b, in which the natural log of the normalized friction is plotted versus 1/T. The slope of a linear fit of this plot for data collected below 280 K yields an effective activation energy in the form of a surface potential barrier (U_0) of ~0.1 eV (~10.8 kJ/mol) (deviations from a linear behavior above 280 K reflect the very low values of friction with respect to the resolvable limit of friction differences). In comparison, prior AFM investigations of a cleaved NaCl(100) surface under UHV conditions reported a barrier height of 0.25 eV at an applied normal load of 0.44 nN [9]. Based on the analysis of Fig. 2b, a 0.1 eV activation energy is used to plot the function $F_L \sim \exp(U_0/k_B T)$ (solid line). Values for a prefactor could be calculated from information of the sliding velocity and surface periodicity; however, previous discussions of prefactor values have highlighted the potential uncertainty in the meaning of such a value arising from the unknown mass of the probe tip (or relevant portion of the tip involved in the sliding interaction). Attempts to fit the data of Fig. 2a with different prefactor terms, including those entailing additional temperature terms such as in Ref. [11], demonstrated that the temperature dependent behavior observed here is predominantly captured in the exponential term ($\exp(U_0/k_B T)$). Varying prefactor terms yielded only modest changes in the calculated potential barrier or fit of the data in the extreme temperature limits.

An analogous set of measurements was conducted, in which the microscopic friction coefficient was measured for the contact of HOPG and a silicon nitride probe tip as a

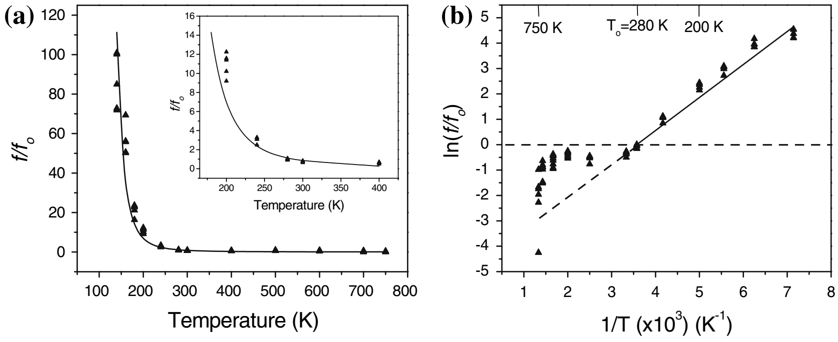

Fig. 2 (**a**) Discreet friction forces averaged over sliding distance and direction, normalized to the value measured at 280 K, measured on HOPG at 0 nN applied load as a function of surface temperature. (**b**) An Arrhenius analysis of the friction data over the temperature range 140–280 K (solid line) produces a surface potential (activation energy) of ~0.1 eV. The horizontal dashed line in (b) represents the friction value used for normalization—friction values higher than this line were measured at lower temperatures. Friction values measured at higher temperatures remained low with average values approaching the resolvable detection limit. The inset in (a) illustrates the high quality of fit in the intermediate temperature range 280–400 K. The solid line in (a) represents a plot of the function $f/f_0 \sim \exp(U_0/k_\mathrm{B}T)$, employing the potential of 0.1 eV determined from the analysis presented in (b).

function of temperature. Figure 3a displays the temperature dependence of the normalized friction coefficient for the range 140–750 K. Again, the uncalibrated microscopic friction coefficients have been normalized with respect to the value measured at 280 K. Similar to the temperature dependence of the average sliding friction forces, friction coefficients decrease exponentially with temperature increasing from 140 K to 280 K. Figure 3b presents the Arrhenius analysis of the friction coefficient data, with the fit and slope analysis conducted over the temperature range 140–280 K. This analysis, consistent with a thermally activated sliding mechanism, produces an activation energy (U_0) of ~0.1 eV. The agreement between values of activation energy determined from the two separate approaches demonstrates that the observed thermal behavior originates from the activated motion of the tip across an energetically corrugated surface. Specifically, the agreement confirms that the reported temperature dependence is not dominated by variations in the mechanics of the microscopic contact as a function of temperature. This claim is substantiated by the absence of significant changes in the pull-off force (adhesion) measured between the same probe tip and surface as a function of temperature (Fig. 4, where pull-off force is reported as a negative force). The large scatter in tip-sample adhesion values at the lowest temperature reflects an instability in the tip-sample contact at this temperature that is not presently understood. At all other temperatures, over which significant changes in friction were observed, little change in the adhesion force is detected.

This report of the temperature dependence of friction documents an energetically activated mechanism for the

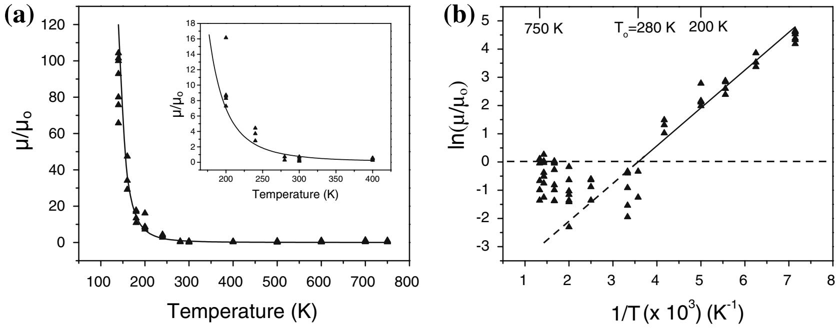

Fig. 3 (**a**) Friction coefficients, normalized to the value measured at 280 K, measured for the contact of a Si_3N_4 probe tip sliding on HOPG as a function of temperature. These data have been determined from measurements of the load dependence of friction, distinct from the procedures employed in collecting the data presented in Fig. 2 (see ''Experimental'' Section). (**b**) An Arrhenius plot of the normalized friction coefficient data, producing a straight line (solid line) for the data in (a) from 140 to 280 K, suggests the contribution of an activated sliding mechanism to the energy dissipation process over this temperature range with an activation energy of ~0.1 eV. As in Fig. 2, the horizontal line in (b) represents the normalizing coefficient of friction value measured at 280 K. Above this temperature, very low values of coefficients of friction, as for absolute friction measurements, were recorded. The solid line in (a) and its inset corresponds to a plot of $f/f_0 \sim \exp(U_0/k_\mathrm{B}T)$, where U_0 is taken to be 0.1 eV

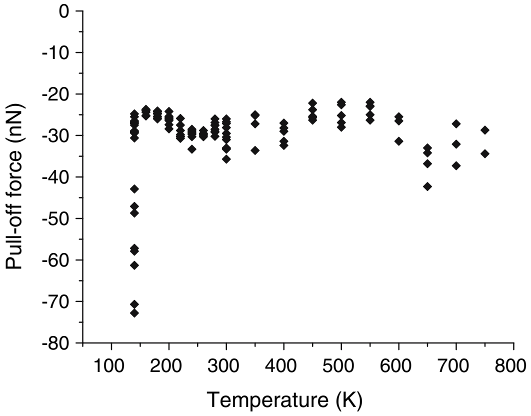

Fig. 4 The temperature dependence of interfacial adhesion is reflected in the values of the pull-off force experienced during normal force-displacement measurements of the same tip-substrate interface. Multiple data points plotted at individual temperatures represent the statistical spread in the measured forces. The weak temperature dependence of pull-off forces excludes adhesion as a dominant influence in the reported temperature behavior of friction

sliding of microscopic contacts. The results have been obtained at a well-defined atomically flat interface of known surface corrugation, for which chemical reactions under the conditions investigated are unlikely. Furthermore, the fundamental measurements have been conducted in the absence of adsorbates capable of significantly altering the frictional interaction at cryogenic temperatures; isothermal temperature programed desorption measurements of water have demonstrated that water layers (including the last layer) are not stable on a graphite surface above a temperature of 142 K [16]. Although frictional forces are known to depend on a variety of system properties, the results presented here clearly document a strong temperature dependence at cryogenic temperatures for this highly idealized interface. The relatively weaker temperature dependence of friction observed above room temperature for graphite likely originates from the thermal motion of surface atoms (increased local vibrations) at these temperatures and a blurring of local potentials responsible for the activated behavior evident at low temperatures.

Summary

A thermally activated sliding mechanism related to the origin of friction forces at the interface has been measured for the contact of an AFM probe tip and a crystalline graphite surface. The activation energy for the interfacial sliding, in the absence of wear, of a Si_3N_4 tip on HOPG is ~0.1 eV in the temperature range of 140–750 K, characteristic of a weakly interacting system and the widely recognized low-friction properties of graphite at ambient temperatures.

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