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The Role of Water in Modifying Friction within MoS_2 Sliding Interfaces

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ABSTRACT To explore the environmental dependence of friction for solid lubricants containing molybdenum disulfide (MoS_2), we have investigated friction on the basal plane of single-crystal MoS_2 with atomic force microscopy (AFM) as a function of relative humidity (RH) and tip composition. For both a bare Si_3N_4 tip and a MoS_2-coated tip, changes in interfacial friction are observed with increasing relative humidity, however, with markedly different behaviors. For sliding contacts involving bare Si_3N_4 tips, the friction coefficient is observed to increase with increasing RH, from 0% to the point of water saturation. For Si_3N_4 tips precoated with MoS_2 particles, friction appears to be relatively insensitive to increasing RH in the range of 0−40%. However, above 40% RH, a drastic increase in friction is observed and is accompanied by evidence for interfacial wear provided in images of the basal plane following the friction measurements. A comparison to the tribological properties of the basal plane of highly oriented pyrolytic graphite (HOPG) using identical probe tips highlights the unique character of self-mated MoS_2 interfaces.

KEYWORDS: molybdenum disulfide • water • highly oriented pyrolytic graphite • relative humidity • friction • atomic force microscopy

1. INTRODUCTION

Molybdenum disulfide (MoS_2) and graphite are two widely used solid lubricants. Both solids are of lamellar structure, with single-crystal specimens easily cleaved along the basal plane. In the past, their low friction has been attributed to the potential for shear at such weakly bonded interfaces. Although they afford operation in the absence of conventional liquid lubricants, the frictional characteristics of these solids have exhibited a clear dependence on environment. For example, early research demonstrated that graphite is a very poor lubricant in vacuum (1−3), thus precluding its use in many space-based applications. It has been proposed that the low friction of graphite arises as a result of adsorbed layers of condensable vapors, such as water or other ambient gases, within the sliding interface (1−3). Subsequent studies have refined this picture, highlighting the role of water adsorption specfically at defect and edge plane sites (4, 5). In contrast to this behavior, MoS_2, despite its similar lamellar structure, exhibits an entirely different environmental dependence with respect to its frictional properties. Applications involving MoS_2 as a solid lubricant have routinely exhibited an increase in interfacial friction upon exposure to ambient conditions, specifically those comprised of high humidity, while observing low friction in vacuum environments (6−9).

The environmental dependence of the frictional properties of MoS_2 have been reported for decades—the myriad of results and proposals regarding the origin of such effects are beyond the scope of the present report. Nonetheless, uncertainties regarding the molecular origin of the increase in friction with increasing relative humidity persist. In reviewing prior work, several general themes emerge. (i) As described above, the frictional properties of interfaces lubricated with MoS_2 are highly sensitive to partial pressures of water (7−11). (ii) The extent of environmental sensitivity has been observed to depend on the structural character of the MoS_2 coatings, which is often a function of the deposition procedure/protocol (12−16). (iii) The combination of MoS_2 with other elements or compounds offers a potential pathway to improving/altering the inherent environmental dependence (17−25). (iv) High rates of interfacial wear are observed under conditions (environment, structure, composition) producing high interfacial friction (26). With these themes in mind, the frictional properties of the basal plane of single-crystal MoS_2 have been investigated with atomic force microscopy (AFM), aiming to reduce the potential complexity of solid lubricant coatings and gain insight into the specific mechanism by which friction is influenced. These measurements have been performed as a function of relative humidity (RH) and tip composition, employing both a bare Si_3N_4 tip and a MoS_2-coated tip. On the basis of a comparison of the frictional properties of MoS_2 to those of highly oriented pyrolytic graphite (HOPG), measured under identical conditions, the high sensitivity of self-mated MoS_2 interfaces to the adsorption of water points to the specific role of water within the sliding contact.

2. EXPERIMENTAL SECTION

Experiments employed an ambient AFM controlled by RHK AFM electronics and software. The AFM was operated in a bell jar, allowing for the systematic control of relative humidity. Adjusting the relative flows of dry N_2 and a second N_2 stream passed through a water bubbler provided an easy method of varying RH within the bell jar. In general, the reported frictional properties have been measured as a function of both increasing and decreasing RH, with little observed hysteresis. RH was

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monitored throughout the course of the experiments by means of an Omega HX92 humidity transducer with a reported range of 3–95% RH and accuracy of 2.5%. All experiments were conducted at 25 °C. The experiments employed Si_3N_4 AFM tips (Veeco Company) possessing a nominal tip radius of 20 nm as determined by imaging a topographic standard. The normal force constant of the cantilever has been taken as the manufacturer's reported value of 0.58 N/m. The lateral force of the cantilever has been calibrated by previously documented methods (27–29), entailing the analysis of forces measured on the facets of a reconstructed $SrTiO_3$ (305) surface. Basal planes of MoS_2 were prepared by cleavage from a mineralogical sample whose composition was verified by X-ray photoelectron spectroscopy. Basal planes of HOPG were prepared through the Scotch tape peel method.

To explore the role of the counterface composition on the frictional response of MoS_2 to humidity, we modified Si_3N_4 AFM tips through the adsorption of MoS_2 powder (Acros, purity >98.5%). This was accomplished by first depositing a thin layer of MoS_2 powder on a clean silicon wafer. Afterward, because of van der Waals force between the probe tip and the MoS_2 powder, small MoS_2 flakes could be transferred to the Si_3N_4 tip through repeated scanning of a small fixed region. The transfer of MoS_2 flakes/particles was evidenced via the following observations. First, the magnitude of both friction and adhesion forces for a given tip on a basal plane standard were observed to measurably change following introduction of the MoS_2 particles. Second, upon scanning a region of the MoS_2 basal plane at high loads, single-layer MoS_2 flakes (0.6 nm in thickness) were transferred from the modified tip to the substrate.

Friction forces were measured on the atomic scale by cyclical scanning of a 100 nm line at a speed of 100 ms/line. Interfacial friction was measured as a function of applied load by application of a single, triangular voltage ramp to the z-piezo during the course of 256 line scans. The average kinetic friction force at a specific load was obtained as one-half of the integrated area bound by the forward and backward lateral force traces.

3. RESULTS

Si_3N_4–MoS_2 Interfaces. Figure 1 displays the friction and adhesion properties of an interface formed through the contact of the basal plane of single-crystal MoS_2 and a bare Si_3N_4 tip, measured for relative humidity conditions ranging from the lower detection limit (<3%) to the point of water saturation. In Figure 1a, the kinetic friction encountered during a 100 nm line scan of the MoS_2 surface, averaged over the length of the scan as well as scan direction, is plotted versus applied normal load for a select number of humidity conditions. Here, negative normal loads correspond to realms of tip–sample adhesion. The data sets acquired in this manner are fit to a line, subsequently defined as a microscopic coefficient of friction. These procedures have been repeated at multiple locations across the MoS_2 surface, producing the multiple friction coefficient values shown in Figure 1b for discrete values of relative humidity. The magnitude of error associated with the fit of the friction-load data was ∼5% for most RH conditions and locations. For all of Figure 1, the error associated with the measurement of RH is taken to be small and constant and is therefore not displayed. The data portray a systematic increase in friction with increasing RH. A composite view of multiple data sets suggests the possibility for different rates of change in friction in the ranges <3–40%, 40–80%, and 80% saturation RH (Figure 1b), but the trends are weak at best. Overall,

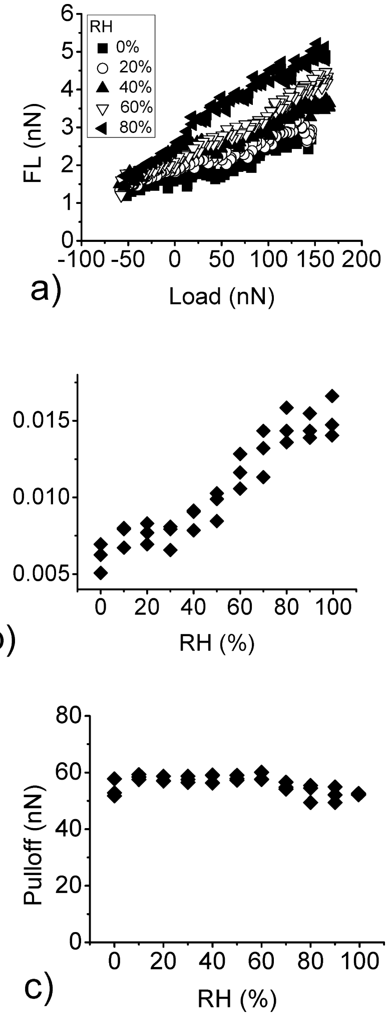

FIGURE 1. (a) Friction measured on the basal plane of MoS_2 with a bare Si_3N_4 tip as a function of applied load and relative humidity. Negative loads correspond to conditions of interfacial adhesion. (b) Friction coefficients (μ), defined as the slope of the friction-load plots in (a), are plotted as a function of relative humidity. The spread in data for specific humidity values reflects the variation in values determined on different regions of the sample. (c) Pulloff forces, reflecting adhesion between the tip and sample, exhibit little dependence on relative humidity for this interface. Experimental uncertainties associated with these measurements correspond to 10% (lateral force), 5% (normal force), and <3% (RH).

a 2.5-fold increase is observed over the range of humidity conditions. The adhesion data of Figure 1c, simultaneously measured to the friction data, clearly demonstrate that the changes in friction arise in the absence of any substantial changes in the adhesive character of the interface. As described above, these tribological properties were entirely repeatable for conditions of both increasing and decreasing RH. Furthermore, following each series of friction measurements, the previously scanned area was imaged and was found to be free from any morphological changes to the basal plane or the presence of any wear debris.

MoS_2–MoS_2 Interfaces. In the AFM friction measurements described above, the absence of wear scars or debris, together with the highly reproducible nature of the results, strongly suggest that the experiments on the single-crystal substrates have been performed without transfer of MoS_2 to the AFM tip. To further verify this claim and explore the

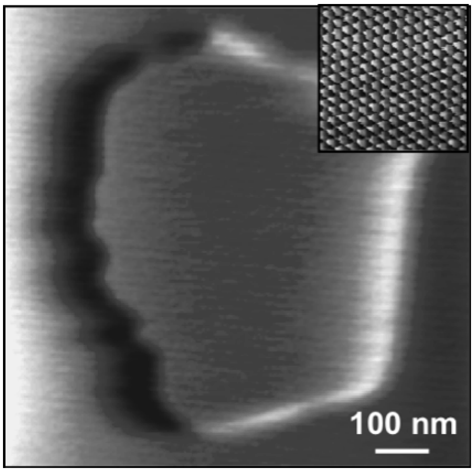

FIGURE 2. Pretreatment of a Si_3N_4 probe tip with MoS_2 powder provides a means of altering the composition of the sliding interface. Scanning at high loads (~200 nN) at 50% RH on occasion results in the transfer of material from the probe tip to the substrate. The height (0.6 nm) and stick−slip lattice resolution (inset, 5 nm ×5 nm) of the flake demonstrates the presence of MoS_2 on the probe tip.

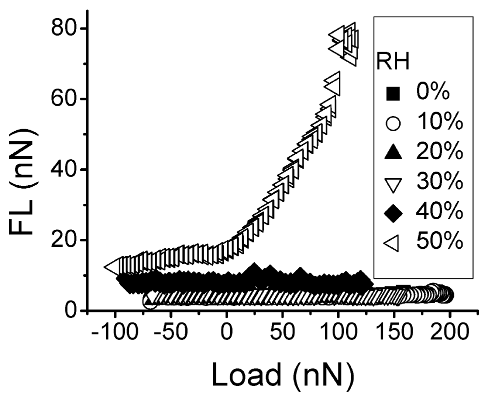

FIGURE 3. Friction measured as a function of applied load between the basal plane of MoS_2 and s Si_3N_4 tip pretreated with MoS_2 demonstrates a drastic dependence on relative humidity, with a sudden transition appearing between 40 and 50% RH. Experimental uncertainties associated with these measurements correspond to 10% (lateral force), 5% (normal force), and <3% (RH).

details of the interface undergoing shear, we have used Si_3N_4 probe tips purposefully pretreated with MoS_2 powder in repeating the experiments described above. Although the exact details of the MoS_2 at the end of the probe tip are not known, evidence of a molybdenum sulfide terminated tip is found in the nature of flakes transferred from the tip to the substrate while scanning under high loads (Figure 2) and the repeatability of control experiments described below. For the contact of such a tip with the basal plane of MoS_2, Figure 3 provides the plot of the average kinetic friction versus applied load for a range of humidity conditions. From the lower detection limit of RH to ~30%, the results obtained closely mirror those obtained with a bare Si_3N_4 tip, with only a slight increase in friction coefficient. By 40% RH, an increase in both adhesion, as seen by the data extending to more negative loads, and friction is observed. At this humidity, although the friction coefficient remains low, the absolute magnitude of friction forces encountered increases by a factor of 2 as compared to data collected with a bare tip. Further increasing the RH to ~50% produces an even

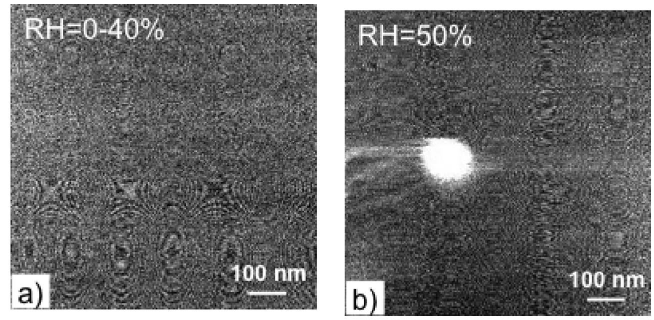

FIGURE 4. Friction images collected on the basal plane of MoS_2 (a) before and (b) after localized friction measurements at 50% RH demonstrate the presence of wear debris resulting from interfacial sliding at high humidity for the case of the MoS_2-coated tip.

higher adhesion force now accompanied by a complex friction response. For total loads (adhesive + applied) up to ~100 nN, a modest increase in friction coefficient, again defined as the slope of the friction-load plot, is observed. Beyond this load condition, a drastic increase in friction coefficient is detected. Such a complex frictional response can often be associated with a compositional or structural change of the shearing interface, i.e., the onset of interfacial wear. Topographic imaging of the regions in which these friction results were obtained provided additional confirmation of this assertion. For measurements conducted with the MoS_2 tips at RH up to ~40%, no changes in the surface are detected. However, following measurements performed at 50% RH, deposits were consistently encountered in the region of the friction measurements. It is specifically noted that the new features always appeared above the surface with no associated changes in the substrate, thus pointing to the likely transfer of MoS_2 from the tip to the sample under these conditions. Figure 4 displays lateral force images acquired (a) after friction measurements performed at low RH and (b) following measurements at 50% RH. Only for ~50% RH is a change detected through the appearance of a region exhibiting friction higher than that of the neighboring terrace regions. These features are understood to be wear debris generated while sliding at an elevated humidity. Further investigation of these features revealed that they could be swept from the field of view at higher loads, leaving no evidence of damage in that region of the substrate.

MoS_2−HOPG Interfaces. To further explore the role of interfacial composition in determining the tribological properties of MoS_2, the same MoS_2 pretreated tip was used to measure the frictional properties of HOPG as a function of relative humidity. Figure 5 compares the frictional properties of the basal planes of HOPG and MoS_2 in contact with a MoS_2 terminated tip. In Figure 5a, frictional data from the HOPG surface under conditions of 40 and 90% RH are representative of the entire humidity range explored for previous samples (see Figure 1a). The friction force values are exceptionally low, but above the detection limit of the instrument, and demonstrate the relative insensitivity of this interfacial pair to the presence of water.

The possibility of a tip change involving the complete removal of MoS_2 during the measurements on HOPG was excluded by subsequently repeating friction measurements

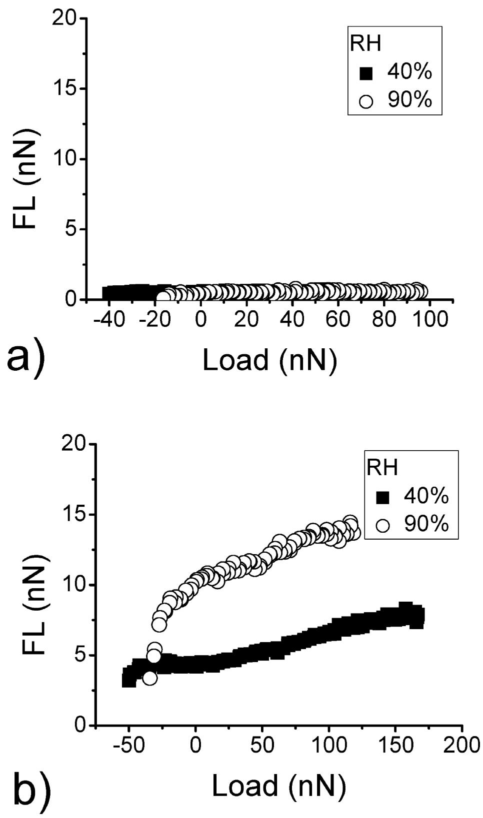

FIGURE 5. Friction between an MoS_2 pretreated Si_3N_4 tip and the basal plane of (a) graphite and (b) MoS_2 measured under two elevated humidity conditions. The identical tip was used in the measurements on both surfaces, with the observed effects being both reproducible and independent of the sequence of measurement. The friction-load behavior observed at 90% RH on MoS_2 and the extent of interfacial adhesion is noted to be lower than that observed at 50% (Figure 3), further indicating the complex role of water in modifying tribological properties of the self-mated interface. Experimental uncertainties associated with these measurements correspond to 10% (lateral force), 5% (normal force), and <3%(RH).

with the MoS_2 terminated tip on the MoS_2 substrate (Figure 5b). These data follow the results previously described, portraying increased friction above 40% RH. At 40% RH, the friction data quantitatively agree with those reported above (note the scale differences between Figures 2 and 5b). By 90% RH, the condensation of water at the sliding interface has reduced interfacial adhesion with respect to values measured at 40 and 50% RH, yet friction remains high, resembling the lower load friction data measured at 50% RH before the transition ascribed to interfacial wear. The frictional properties under 90% RH, at higher loads where wear would be expected, or the explicit dependence of wear on humidity were not explored in any greater detail.

4. DISCUSSION

It is widely recognized that MoS_2, when employed as a solid lubricant, exhibits a strong environmental dependence. The data presented above have been measured on a length and force scale allowing insight into the origins of this behavior. Comparative measurements of the friction properties of MoS_2 as a function of counterface and relative humidity highlight a unique interaction between adsorbed water and sliding interfaces entailing MoS_2.

Measurements conducted on the basal plane of MoS_2 with a Si_3N_4 probe tip as the counterface demonstrate an increase in friction with increasing humidity, but the net increase by a factor of 2.5 over the entire humidity range can be classified as moderate. Even at its highest value, the friction coefficient does not exceed a value of 0.02. Furthermore, no evidence of wear has been found at any point during the evaluation of this interface. A number of careful studies have considered the influence of water condensation with increasing humidity on friction measurements performed with microscopic probe tips (30−35). A host of behaviors has been observed and work remains to fully understand the relative contributions of tip geometry, tip composition, and interfacial energy to the environmental dependence. Here, an increase in friction with increasing humidity is consistent with the greater presence of adsorbed water at the higher humidities; however, the exact location of these species is not revealed by these measurements. In the absence of significant changes in adhesion across the humidity range, it appears that water is serving to directly modify the shear strength of the interface as opposed to shift the effective load scale, which occurs with changes in adhesion. It should be noted that experiments conducted with the identical tip on the basal plane of HOPG (data not shown) demonstrated no change in friction over the entire humidity range. This comparison underscores a unique interaction of water with the MoS_2 surface and suggests that the results presented here do not merely originate from capillary condensation around the AFM tip.

In applications entailing lubricant coatings containing MoS_2, the transfer of MoS_2 from one part of a frictional pair to the other is commonly observed and likely unavoidable. In fact, such a behavior is widely regarded as one of the critical pathways by which low friction is obtained with this material. With this in mind, the influence of humidity on an interface composed of two surfaces of MoS_2 was explored. Although a detailed chemical analysis of the exact flake(s) located at the end of the probe tip has not been possible, the high quality of the starting powder, the change in friction character upon its introduction, and the repeatability of the control experiments described above all point to having successfully created such an interface. The data of Figure 3 clearly demonstrate a stark contrast in friction behavior as compared to that of the MoS_2−Si_3N_4 interface. Here, a period of relative insensitivity to water is observed over the range <3−30% RH before the onset of a tremendous increase in friction occurs at between 40 and 50% RH. Recalling that no change in frictional behavior occurred with this tip on HOPG over the entire humidity range (Figure 5a), and that results similar to those of Figure 3 were found following the HOPG measurement (Figure 5b), the interaction of water between planes of MoS_2 must be considered as one origin of the environmental dependence. The increase in adhesion portrayed in the friction data of Figure 3, concomitant with the increase in friction, suggests a bridging role of the water. Unfortunately, the proximity of such events, either along the basal plane or at the edge sites of MoS_2 particles is not

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accessible by scanning probe microscopy—such topics are presently being investigated with other techniques.

Finally, the measurements presented herein underscore the relationship between the strong environmental dependence of many MoS_2 containing coatings/applications to interfacial wear. As detailed through AFM imaging of local sites of friction measurements at high humidity, material transfer is routinely observed under conditions of high friction. For a lamellar material with relatively weak interplane bonding, the introduction of a pathway to wear associated with the adsorption of an atmospheric species clearly points to a short or shortened lifetime of the intended application.

5. CONCLUSION

Friction on single-crystal MoS_2 has been investigated with AFM as a function of relative humidity, using both a bare Si_3N_4 tip and a MoS_2-coated tip. In both cases, the friction shows an increase with increasing relative humidity. For the bare Si_3N_4 tip, a modest increase is observed in the absence of changes in interfacial adhesion or the occurrence of interfacial wear. For the MoS_2-coated tip, a sharp rise in friction is detected near 50% RH and is accompanied by an increase in adhesion and the onset of wear. Through comparisons to results obtained on HOPG using identical probe tips where little evidence of an environmental dependence is found, water is seen to have a high affinity for bridging between two MoS_2 planes, in turn drastically altering the tribological properties of this material at higher humidities. As with previous studies, the results presented here suggest that caution should be exercised when employing solid lubricants containing MoS_2 in applications involving exposure to water vapor. Under such conditions, such lubricants can be anticipated to exhibit an increase in both friction and wear, significantly limiting the tribological performance of the application.

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