Friction in full view

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The authors report the direct observation of a single asperity tungsten tip sliding on graphite by in situ transmission electron microscopy (TEM) nanomanipulation. The *in situ* TEM studies have confirmed that graphitic flakes transfer to a sliding tungsten probe, validating proposed friction mechanisms explaining the unique tribological properties of graphite. Wear of graphite was observed, typically removing sheets of graphite on the order of ten basal planes in thickness. Consistency between wear flake thickness and interfacial dislocation standoff distances is discussed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2456192]

Experiments in tribology have long suffered from the inability to directly observe what takes place at a sliding interface—the classic buried interface problem. Sliding single asperities have been studied in great detail since the arrival and maturation of atomic force microscopy techniques. Although these techniques have identified many friction phenomena on the nanoscale, many of their interpretive pitfalls result from indirect or *ex situ* characterization of contact surfaces. It is for this reason that instruments are being developed that can simultaneously collect chemical or structural information from the interface during a friction experiment. Examples of this include *in situ* raman spectroscopy,[1,2] x-ray photoelectron spectroscopy,[3] and electron microscopy[4] tribometers. The present study addresses the issue of nanoscale friction on graphite, by directly observing the behavior of a single asperity probe sliding against an electron transparent sample in the transmission electron microscope (TEM).

Atomic scale friction phenomena including stick-slip,[5] superlubricity,[6–8] anisotropy,[6] and velocity dependence[9] have been demonstrated by use of scanning probe techniques. Mate *et al.*[5] showed that a scanning tungsten probe gave atomic scale features when sliding across the basal plane of a graphite surface at forces below 10^{-4} N. Later studies showed atomic stick-slip behavior on different substrates, including mica,[10] Cu,[11] NaF,[12] and diamond.[13] Hirano *et al.* demonstrated that for a larger micron-sized contacts between flat mica samples, the friction force varies strongly with the in-plane orientational misfit between surfaces.[14] The friction force was observed to change by a factor of four and displayed periodicity consistent with that of the hexagonal symmetry of the mica lattice. Dienwiebel *et al.*[6,7] have shown that this is also the case at very low loads between a tungsten tip and graphite surfaces. Extraordinarily low friction forces of 15 ± 15 pN at normal loads between −24 and 30 nN were measured at incommensurate contacts. For commensurate contact geometries, friction was observed to increase by an order of magnitude. In addition to misorientation anisotropy, sliding direction anisotropy was observed and consistent with a Tomlinson model simulation. The proposed underlying physical mechanism was that a small graphite flake from the substrate attached itself to the scanning tungsten probe during sliding creating a graphite-graphite sliding interface and resulted in low friction forces. Despite efforts to perform a postmortem TEM analysis, the authors were unable to confirm the presence of a graphite flake on the scanning probe. It is the purpose of the present investigation to directly observe via *in situ* TEM the graphite-tungsten sliding interface and characterize any structure-friction relationships.

Highly ordered pyrolytic graphite (HOPG) TEM samples were prepared by a sequential cleaving process to optical translucency. The samples were placed on standard copper TEM grids (200 mesh) for mounting onto the *in situ* stage. Scanning probes were fabricated from 0.25 mm tungsten wire using a standard electropolishing technique in a 1*N* NaOH solution biased between 0.1 and 4 V ac. Tip diameters were polished down to a minimum of 2 nm, with most typical radii in the 20–50 nm range.

A simplified schematic of the side-entry holder is shown in Fig. 1. The tungsten probe is horizontally mounted so that it is orthogonal to the electron beam (−*X*). The HOPG sample on a Cu grid is mounted at 45° to the horizontal, enabling simultaneous exposure and characterization by both the electron beam and the scanning probe.

The HS100 STM-holder™ holder (TM) stage used in this study was developed by Nanofactory Instruments (Göteborg, Sweden), and designed for use with a Tecnai F20ST TEM (200 kV, Schottky FEG). It is capable of course and fine three-dimensional control, with piezoresolutions of 0.2 Å in *XY* and 0.025 Å in *Z*. Coarse motion control gives wide ranges of motion: ±1–2 mm in *XY* and ±1 mm in *Z*. In addition to nanomechanical control, the stage is capable of

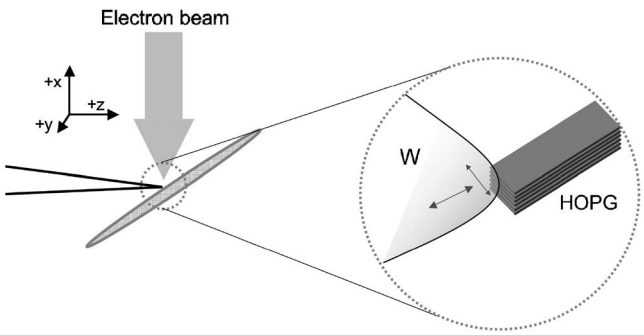

FIG. 1. STM-TEM holder schematic. Nanomanipulation allows for microstructural characterization during sliding and indentation.

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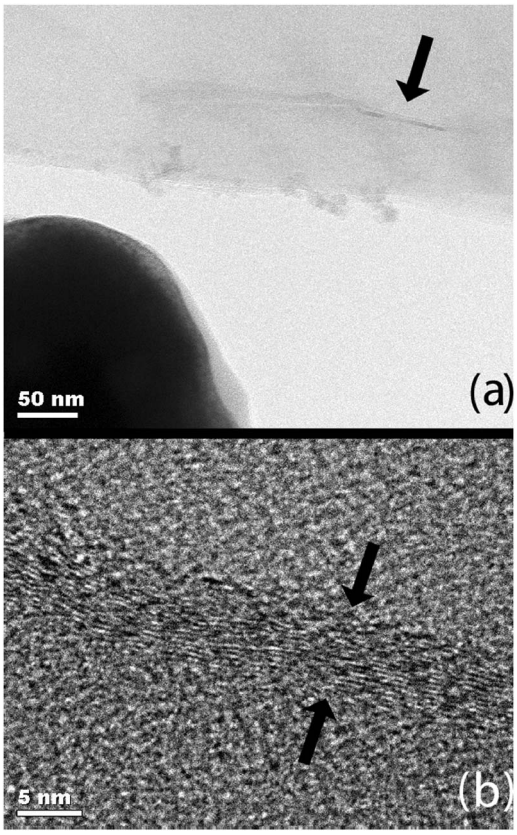

FIG. 2. Bright field (a) and high resolution (b) images of the wear track after 100 passes with the tungsten probe.

electrical characterization and acquiring scanning tunneling topographs. Several practical considerations arise during operation, particularly in the process of aligning the tip with the sample. First, the axes of the TEM and scanning probe are never perfectly matched implying that motion in Z (approaching sample) will inevitably yield some XY displacement. This is monitored on a coarse scale by modulating the tilt about the Z axis while positioning the tip in order to reduce wobble in the image, assuming the eucentric height is fixed. A finer approach requires measuring the objective lens focus setting and comparing with the Gaussian focus conditions for the scanning probe.

The initial approach with the tungsten probe contacted the sample near its edge. An unavoidable consequence of the tilted sample geometry causes slippage away from the sample edge so that the sliding interface is slightly shadowed by the scanning tip. This occurs when the compliant thin sample bends in response to an applied load by the probe. Increasing the load bends the graphite film by 200 nm (in plan view along Z), and subsequent passes with the slider (100 times) showed evidence of extended wear debris a few nanometers in width, as seen in Fig. 2. Several wear particles generated by sliding are observed near the edge of the sample. Selected area diffraction patterns have confirmed that their composition is polycrystalline graphite.

Upon closer inspection of the wear tracks as seen in Fig. 2, ordered graphitic planes were observed in the range of 5–35 basal plane spacings (2–10 nm). The planes are not all continuous, clearly showing local defects and bending. The observation of graphite planes in Fig. 2 indicates that sliding took place directly adjacent to them, causing the sliding tip to remove material from the HOPG surface subsequently pushing material to the side of the contact region. Graphite flakes are left in the tip's wake, of which a number are oriented parallel to the electron beam.

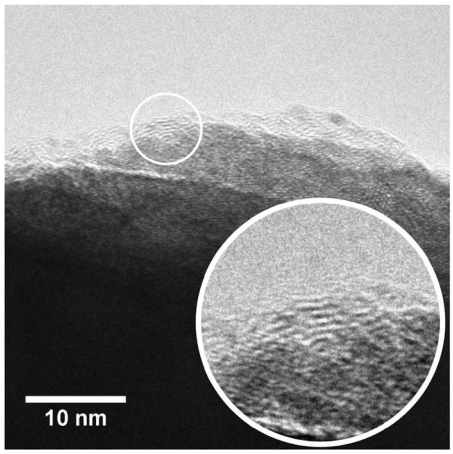

FIG. 3. Bright field TEM image of the tungsten probe showing graphitic layers that have transferred from sample to tip.

Immediately after sliding, the tungsten probe was inspected for evidence of material transfer, as predicted by Dienwiebel *et al.* Figure 3 shows evidence that graphitic material is present on the surface of the tungsten slider. These features were neither seen before sliding nor significantly long afterwards (>5 min), since beam damage is significant for small amounts of perpendicularly oriented graphite at 200 kV. A line scan along the planes as seen in the inset to Fig. 3 measures the planar spacing at 3.5 Å, in agreement with the known graphite basal spacing of 3.36 Å. The thickness of the attached graphite flake is seven basal spacings or 2.45 nm. This observation confirms that wear takes place by strong adhesion and transfer to the tungsten sliding probe. This establishes a graphite-graphite sliding interface, demonstrating the mechanism responsible for the lubricious properties of graphite.

The results here show direct evidence that crystallographic structure influences the tribological behavior of graphite. Moreover, defect structure may have an even more direct role, for it is the motion of dislocations throughout a material, be it at an interface or in the bulk, that is, the principal mechanism for deformation in materials. It is well established that for heterogeneous interfaces consisting of two materials with differing shear moduli, interfacial dislocations will be displaced by some standoff distance into the softer material.[15,16] in the original studies on metal-ceramic interfaces ($Nb-Al_2O_3$), a standoff distance of 1.9 (110) spacings was calculated and experimentally observed to be 4 (110) spacings.[17] For interfaces with a large shear modulus mismatch and a small crystallographic mismatch, it is not unreasonable to expect the equilibrium position of dislocations to be found greater than 20 planar spacings from the interface in the softer material.[15] Following Kamat's analysis for screw dislocations by inputting shear moduli for tungsten and graphite, we arrive at a standoff distance estimate of 15 nm (44 planar spacings). This is consistent with the observed thickness of wear flakes observed in the TEM images in this study. Once a graphite flake has been worn and attached to the tungsten probe, the graphite-graphite interface will exhibit no significant dislocation standoff, as the sliding interface is becomes the dislocation plane. A more detailed

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dislocation analysis would be interesting to apply to a variety of sliding interfaces.

In this letter we have reported the direct observation of a single asperity tribological interface of tungsten and graphite by *in situ* TEM. Landmark atomic scale friction experiments have drawn conclusions about the sliding behavior of these materials, notably the observation of atomic scale stick slip, friction anisotropy, and superlubricity. Our *in situ* TEM work has confirmed the transfer of graphite to a tungsten probe after sliding—direct evidence that validates the proposed friction mechanism of graphite-graphite sliding phenomena. Wear of HOPG was typically observed to occur by the removal of sheets on the order of ten basal planes in thickness. We believe the role of dislocations—their structure and dynamic behavior at interfaces—is largely uncharacterized in the field of tribology. We hope that the application of similar *in situ* techniques in combination with more complete models will build on this basic understanding.

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