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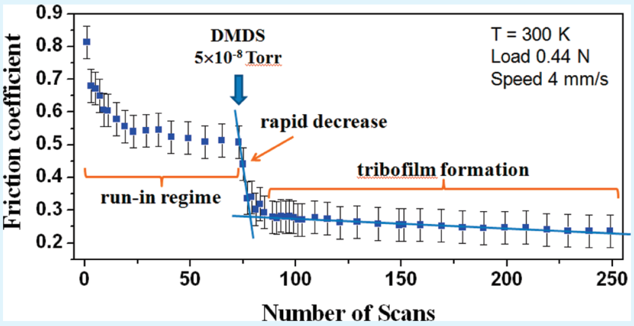
Low-Temperature, Shear-Induced Tribofilm Formation from Dimethyl Disulfide on Copper

Octavio J. Furlong,[†] Brendan P. Miller,[†] Peter Kotvis,[‡] and Wilfred. T. Tysoe*[,†]

[†]Department of Chemistry and Biochemistry, and Laboratory for Surface Studies, University of Wisconsin Milwaukee, Milwaukee, Wisconsin 53211, United States

[‡]Benz Oil, Inc., 2724 W. Hampton Avenue, Milwaukee, Wisconsin 53209, United States

ABSTRACT: The frictional properties of a sliding copper−copper interface exposed to dimethyl disulfide (DMDS) are measured in UHV under conditions at which the interfacial temperature rise is <1 K. A significant reduction in friction is found from the clean-surface values and sulfur is found on the surface and below the surface in the wear scar region by Auger spectroscopy. Because the interfacial temperature rise under the experimental conditions used to measure friction is very small, tribofilm formation is not thermally induced. The novel, low-temperature tribofilm formation observed here is ascribed to a shear-induced intermixing of the surface layer(s) with the subsurface region as suggested using previous molecular dynamics simulations. Although the tribofilm contains predominantly sulfur, a small amount of carbon is also found in the film.



KEYWORDS: copper, dimethyl disulfide, Auger spectroscopy, ultrahigh vacuum tribometer, friction, tribofilm

INTRODUCTION

It has previously been shown that under so-called extreme-pressure (EP) conditions (where interfacial temperatures can attain ∼1000 K), tribofilms are formed by an initial rapid thermal decomposition of the additives on the surface. This is due to the high interfacial temperatures present under EP conditions causing the lubricant additives to rapidly and completely thermally decompose on the surface.[1,2] The reaction kinetics are sufficiently rapid at such high temperatures that the nature of tribofilms formed under these conditions can often, but not invariably, be simply predicted using thermodynamics. On the other hand, some applications require lubrication of sliding metal−metal interfaces at much lower temperatures, where the tribofilm-formation mechanism described above does not occur. For example, lubrication of copper−copper sliding contacts is of significant importance in electric motors,[3−6] where the working conditions involve relatively low loads and low temperatures. It has recently been demonstrated that the sulfur in an adsorbed overlayer consisting of methyl thiolate species, formed from dimethyl disulfide (DMDS) on a copper surface at room temperature, is transported into the subsurface region of the copper by rubbing at relatively low loads.[7] This process was ascribed to an intermixing between the surface and subsurface regions caused by vortices that have been modeled using molecular dynamics (MD) simulations.[8−10] These results suggest that, as the surface layer is transported into the substrate, bare active surface sites can be regenerated, allowing subsequent surface reactions to occur. Therefore, it is anticipated that continually dosing the surface with dimethyl disulfide while rubbing will result in a continual transport of sulfur into the subsurface region to form a tribofilm. This effect is explored in the following. Such a tribofilm-formation mechanism is completely different from that occurring at high temperatures (for example, under EP conditions) because it is not thermally driven, but caused instead by shear at the metal−metal interface. In fact, sulfur present in the subsurface region of a copper surface thermally diffuses to the surface at relatively high temperatures because adsorbed sulfur is more thermodynamically stable than sulfur in the copper bulk.[11] Because tribofilm formation is an inherently kinetic phenomenon, which film formation mechanism dominates will depend on the conditions occurring at the tribological interface.

In addition, sulfur-containing molecules are used as lubricant additives for iron[12−25] and dialkyl disulfides have been used to probe the tribological chemistry on iron[26−28] where they react at the high interfacial temperatures to form a ferrous sulfide film. DMDS on copper is particularly suitable for exploring low-temperature tribofilm formation because it reacts below room temperature to form methyl thiolate species, with a concomitant scission of the S−S bond, which are stable up to ∼420 K.[11] Because the temperature rise in the contact under the experimental conditions used in this work is estimated to be less than 1 K,[29] any thermal effects caused by rubbing are negligible and the formation of a tribofilm must be ascribed solely to shear at the interface. The temperature rise was estimated from the maximum flash temperature under the conditions used for the experiment.

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This yielded a Peclet number of ∼1.5×10^{-3}, resulting in a calculated value of the maximum flash temperature for a circular contact of ∼1×10^{-2} K. This occurs because of the relatively low load and sliding speed, and the high thermal conductivity of copper.

EXPERIMENTAL SECTION

Experiments were carried out in a stainless-steel, ultrahigh vacuum (UHV) chamber operating at a base pressure of ∼2×10^{-10} Torr following bakeout, which has been described in detail elsewhere.[30] Briefly, the chamber was equipped with a UHV-compatible tribometer, which simultaneously measures normal forces, lateral forces and the contact resistance between the tip and substrate. All tribological measurements were made in reciprocating mode using a sliding speed of ∼4×10^{-3} m/s at a normal load of ∼0.44 N. The tribopin, (∼1.27×10^{-2} m diameter) was made from tungsten carbide containing some cobalt binder and could be heated by electron bombardment in vacuo in order to clean it. Measurement of the pin topology using atomic force microscopy (AFM) showed that it was substantially rougher than the polished metal substrates with an approximately Gaussian height distribution and a width at half height of ∼200 nm.[31] Experiments were performed by initially rubbing the tribopin against the clean copper sample until a constant friction coefficient was obtained. This formed a wear track on the surface (about 150 μm wide) and likely resulted in the transfer of copper to the tribopin so that friction results are for a sliding copper—copper interface. The chamber also contained a single-pass, cylindrical-mirror analyzer (CMA) for Auger analysis, and an argon ion bombardment source for sample cleaning.

A high-resolution electron gun with a channeltron secondary electron detector was also incorporated into the system, allowing the electron beam to be rastered over the surface thereby allowing scanning electron microscope (SEM) images of the wear scar to be collected. The electron gun could be configured to collect high-quality Auger spectra using the CMA with a peak-to-peak modulation amplitude of ∼4 V. A LabView script was written to control the voltage applied to the deflection plates on the electron gun while monitoring the output from the lock-in amplifier in order to collect Auger intensity profiles. This allowed for Auger line profiles across the wear scar to be obtained with a spatial resolution estimated to be ∼70 μm.[7] Finally, the chamber also included a quadrupole mass spectrometer for leak checking and for gauging sample purity.

The copper foil samples (Alfa Aesar, 99.99% pure, 1 mm thick) were polished to a mirror finish using 1 μm diamond paste and then rinsed with deionized water and degreased ultrasonically in acetone. The samples were attached to a steel plate to provide rigidity and mounted to a UHV-compatible sample manipulator. The sample could be resistively heated and the temperature monitored by means of a thermocouple mounted to the sample. Once in UHV, the copper foils were cleaned using a standard procedure which consisted of Argon ion bombardment (∼1 kV, ∼2 μA/cm^2) and annealing cycles up to ∼850 K, and the cleanliness of the samples was monitored using Auger spectroscopy. Prior to the tribological experiments, no impurities, in particular carbon and sulfur, were detected on the surface. This procedure also results in a surface that produces a square (1 × 1) low-energy electron diffraction pattern and is therefore well-ordered.[11]

The DMDS (Aldrich, 99.0% purity) was transferred to glass bottles and attached to the gas-handling systems of the vacuum chambers. The purity was monitored using mass spectroscopy and was dosed onto the surface by means of a 6 mm diameter tube directed toward the copper sample to minimize background contamination.

Tribological measurements using DMDS (5 wt.%) dissolved in a poly α-olefin were made using a pin and v-block apparatus with a copper pin and steel v-blocks as described elsewhere[32,33] where the friction coefficient is derived from a plot of the torque versus normal load. The rotation speed for these measurements was 290 rpm and the slope of the torque versus normal load was converted into a friction coefficient by multiplication of the slope of the plot by 117 m^{-1} to take account of the experimental geometry.[31,32]

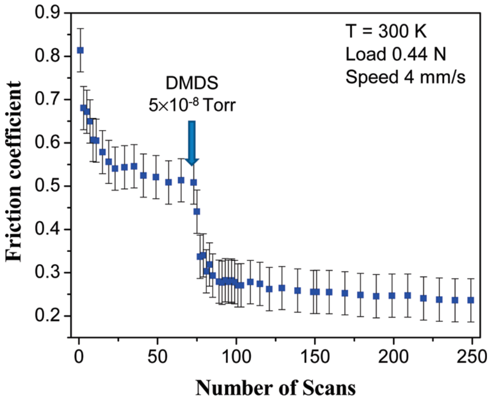

Figure 1. Plot of friction coefficient versus number of cycles measured in the ultrahigh vacuum tribometer at a sliding speed of 4×10^{-3} m/s and a normal load of 0.44 N. The clean surface was initially rubbed 70 times to reach a steady-state value of friction coefficient, and then dimethyl disulfide was introduced via a dosing tube at a background pressure of ∼5×10^{-8} Torr and the friction coefficient then recorded in the presence of gas-phase DMDS.

RESULTS

The tribological experiments were carried out using the following protocol. First, an initial 70 scans were made on the clean copper substrate without DMDS dosing to obtain an initially constant friction coefficient to ensure that any subsequent changes in friction were due to DMDS dosing. As shown in Figure 1, this resulted in a friction coefficient decrease from an initial value of ∼0.82 to ∼0.53 after rubbing 40 times, and remained essentially constant thereafter. Note that the friction coefficient is not displayed for all rubbing cycles for clarity. Control experiments show that, on a clean copper substrate, the friction coefficient remains constant at ∼0.53 for an extended number of rubbing cycles. Following the run-in period, the surface was saturated with DMDS by dosing in vacuo (at a background pressure of ∼2×10^{-8} Torr of DMDS for ∼10 min) to gauge the effect of having rubbed the surface on the sulfur coverage in the wear scar at a sample temperature of ∼300 K. Previous work has shown that thiolate species form on the surface under these conditions.[11] Figure 2 shows the resulting Auger profile collected across the wear scar after dosing with DMDS following the run-in period. The graph plots the peak-to-peak intensity of the S LMM Auger feature (∼152 eV kinetic energy) ratioed to that of the Cu LMM feature (at ∼920 eV kinetic energy), where the center of the wear scar is located at 200 μm. It can be seen that the sulfur signal increases within the wear scar compared to the unrubbed region, where the S/Cu Auger peak-to-peak ratio outside the wear scar is ∼0.45, whereas inside the wear scar it increases to ∼0.60. Complete Auger spectra collected within and outside the wear scar (shown as insets) confirm that the amount of sulfur inside the wear scar increases. Thus, having rubbed the clean surface allows more sulfur to adsorb onto the copper by about 33% with respect to the unrubbed region. Also, from this plot, the width of the wear track can be estimated to be ∼152 μm. Unfortunately, the methyl

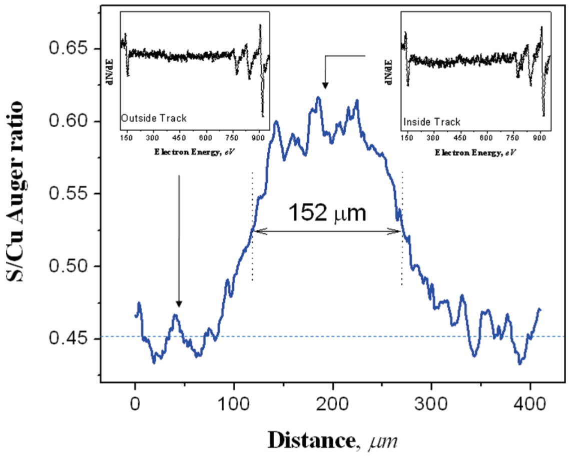

Figure 2. Ratio of the sulfur LMM Auger peak-to-peak amplitude to the copper LMM substrate signal along a line scan across a wear track that had been formed by rubbing the clean surface for 70 scans and then exposing to dimethyl disulfide to saturate the surface. Vertical lines are drawn to indicate the width of the wear track measured using scanning electron microscopy.

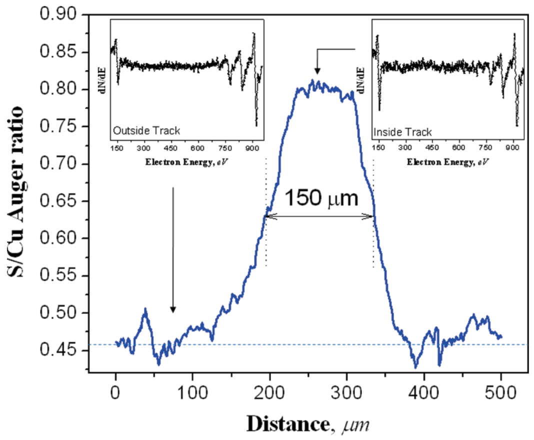

Figure 3. Ratio of the sulfur LMM Auger peak-to-peak amplitude to the copper LMM substrate signal along a line scan across a wear track that had been formed by rubbing the surface for 170 scans while exposing it to dimethyl disulfide via a dosing tube with a background pressure of ~5 × 10^{-8} Torr. Vertical lines are drawn to indicate the width of the wear track measured using scanning electron microscopy.

carbon (which would appear at ~272 eV kinetic energy) in the thiolate overlayer cannot be detected by Auger spectroscopy since it undergoes rapid electron-stimulated desorption of the methyl moiety via S—C bond cleavage,[34] while the sulfur signal is unaffected. The relative increase of the S signal indicates that the copper surface has undergone topographical changes during rubbing that enable it to adsorb more sulfur, but whether this has caused the thiolate species to decompose cannot be ascertained.

Following this, a second wear scar was created, the tribopin cleaned by electron-beam heating, and the run-in period was repeated for 70 scans. The surface was then dosed while rubbing at a background pressure of DMDS of ~5 × 10^{-8} Torr and the resulting friction coefficient was monitored. The resulting variation in the friction coefficient with number of scans is displayed in Figure 1.

A rapid initial decrease in the friction coefficient to ~0.28 was found after an additional ~10 scans after the run-in period while exposing the copper sample to a background pressure of ~5 × 10^{-8} Torr of DMDS while rubbing. This is followed by a much slower, but discernible decrease over the next 170 scans to a value of ~0.23 (see Figure 1). The sulfur Auger profile across the second wear scar after 100 scans is shown in Figure.3. The concentration of sulfur in the wear scar is again higher than outside as found in Figure 2, but repeated rubbing leads to an additional increase of the S/Cu ratio up to ~0.80. It can also be observed that the estimated width of the wear scar did not change after this procedure.

It has been found that rubbing a copper surface covered with a thiolate monolayer formed by DMDS adsorption causes shear-induced sulfur transport into the subsurface region.[7] In order to ascertain whether this has occurred in this case, an argon-ion bombardment depth profile was measured inside and outside the wear scar and the results are displayed in Figure 4. Essentially all sulfur is removed outside the wear scar in ~30 min by ion bombardment (■) (~1 kV, ~1 μA/cm^2) and the data are fit to an exponential decay, where the decay constant (to 1/e of the initial value) is 8 ± 2 min. The depth profile within the wear scar (●) shows a similar rapid decay (with a decay constant of 12 ± 2 min), but with a sulfur signal that persists deeper into the sample where the S/Cu Auger ratio reaches an asymptotic value of 0.14 ± 0.04. Using published Auger sensitivity factors for sulfur and copper,[35] where the sulfur signal is about three times more sensitive than the copper signal, indicates that the sulfur concentration in the subsurface region is ~5 mol %. This indicates that sulfur has penetrated into the subsurface region.

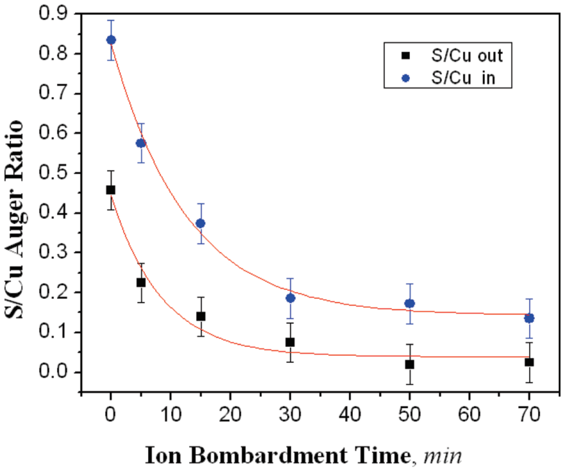

Figure 4. Depth profile obtained by monitoring the sulfur LMM Auger peak-to-peak amplitude ratioed to the copper LMM substrate signal as a function of ion bombardment time using an argon ion beam current density of 1 μA/cm^2 with a beam energy of 1 keV within (●) and outside (■) the wear track.

Because sulfur is more thermodynamically stable on the surface than in the bulk, this provides an alternative strategy to gauge whether sulfur has penetrated into the subsurface region, by removing all the surface sulfur by ion bombardment and then heating.[7] Thus, after completion of the experiments shown in Figure 1, the surface was ion bombarded to remove all of the sulfur. The resulting sulfur LMM and carbon KLL Auger signal profiles across the wear scar are plotted in the bottom traces in panels a and b in Figure 5, respectively. Note that the center of

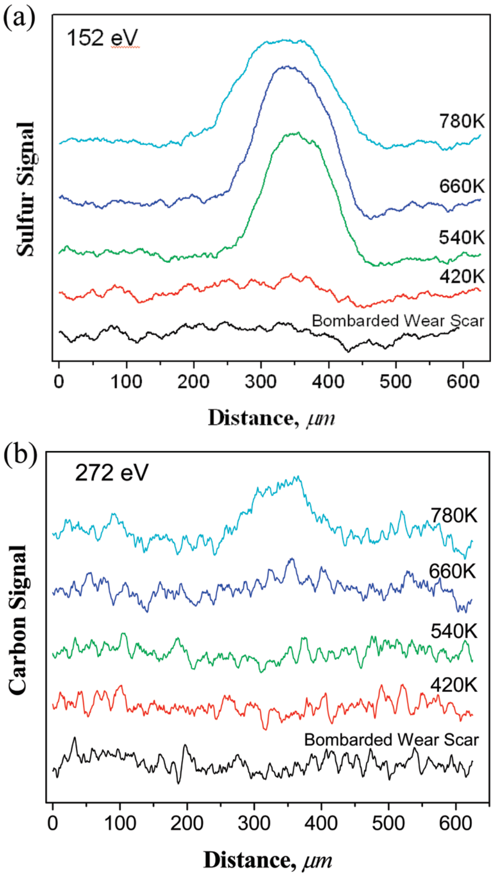

Figure 5. Peak to-peak amplitude of (a) the sulfur LMM Auger feature and (b) the carbon KLL transition along a line scan across a wear track that had been formed by rubbing the surface for 170 scans while exposing it to dimethyl disulfide via a dosing tube with a background pressure of $\sim 5 \times 10^{-8}$ Torr (Figure 2) and then ion bombarded until no sulfur was detected within or outside of the wear scar (~100 min) after annealing the sample to various temperatures. The annealing temperatures are indicated adjacent to the corresponding profile.

the wear scar is now located at 350 μm, and reveals that there is no sulfur or carbon on the surface after ion bombardment. The sample was then heated to various temperatures and the resulting sulfur LMM and carbon KLL Auger signal profiles across the wear scar are plotted in Figure 5 as a function of annealing temperature. Now both carbon and sulfur diffuse to the surface, where sulfur appears after heating to ~540 K (Figure 5a) and carbon at ~780 K (Figure 5b). Note that control experiments showed that no sulfur or carbon were detected in the unrubbed wear scar after heating. This indicates that, in addition to sulfur penetrating into the bulk of the sample, a small amount of carbon is formed by continually rubbing the surface and that this is also transported into the bulk. Removing the surface carbon and sulfur by ion bombardment and heating again to ~750 K causes only sulfur to reappear on the surface, and this process can be repeated numerous times, indicating that a substantial amount of sulfur has penetrated the surface (data not shown).

Finally, Figure 6 shows the results for torque versus load obtained using a pin and v-block apparatus[32,33] using 5 wt % DMDS dissolved in a poly α-olefin (PAO), where a friction coefficient of ~0.05 is obtained. Starting at the lowest load measured, the torque value at each load was then taken after a 60 s equilibration period during which it became relatively constant.

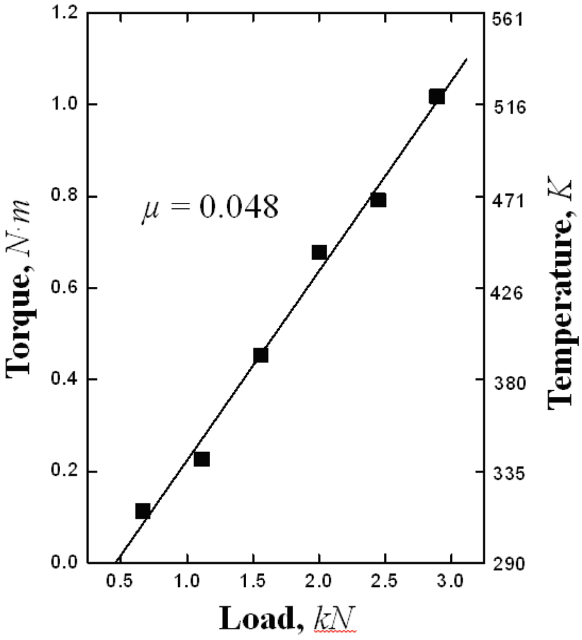

Figure 6. Torque measured during the rotation of a cylindrical copper pin between steel v-blocks at 290 rpm in a pin and v-block experiment versus direct pinching load on the pin.

This results in the transfer of copper to the steel v-blocks.[33] Because there are 290 complete rotations of the copper pin and two separate line contacts that it makes with each of the two diametrically opposed v-blocks pinching it, there are almost 1200 passes per minute for each contact point of the rotating pin with v-block surfaces. This is approximately 6 times the number of passes shown in Figure 1 for the tribopin sliding against the copper foil during its exposure to DMDS. Since plastic deformation contact conditions are obtained in both experiments, one would expect essentially the same friction coefficient for the same fully developed interfacial film; it appears that extrapolation of the curve in Figure 1 could reasonably be expected to yield a similar friction coefficient to that shown in Figure 6 for these very different ambient conditions. Nonetheless, one would expect a sulfur-containing film to separate the copper on copper tribopair in both cases.

DISCUSSION

The gas-phase reaction during rubbing between DMDS and a clean copper surface results in the formation of a tribofilm that causes a significant reduction in the friction coefficient with a rapid initial drop from ~0.53 to ~0.28 as the DMDS is introduced. As emphasized above, this reaction is not thermally initiated since the interfacial temperature rise is less than 1 K, while the thiolate species that forms at 300 K from DMDS are stable on the surface up to ~420 K.[11] Initially, rubbing a clean copper surface appears to increase its roughness so that more sulfur can be accommodated on the rubbed portion of the surface compared to the unrubbed part (Figure 2). Whether this is present as the thiolate species or it has undergone some decomposition on the rough surface cannot be ascertained since the carbon signal from the thiolate species cannot be detected using Auger spectroscopy.[34] Continuously rubbing the surface while exposing the contact to DMDS results in an increase in sulfur coverage in the wear scar (Figure 3) and a decrease in the friction coefficient.

A depth profile of the sulfur inside and outside the wear scar is shown in Figure 4. This reveals an initial rapid decrease in sulfur Auger signal both inside (●) and outside (■) the wear track during the first ~20 min of ion bombardment. This initial decrease in sulfur Auger signal is ascribed to the removal of the sulfur-containing overlayer since all of sulfur outside the wear scar (Figure 4 (■)) has been removed by ion bombardment. This indicates that no sulfur has thermally diffused into the bulk of the copper and suggests that the sulfur removed inside the wear scar during the first 20 min of ion bombardment is also due to the removal of surface sulfur. In contrast, the sulfur signal persists inside the wear track after at least 70 min of Argon ion bombardment, confirming that sulfur has penetrated into the subsurface region where the surface has been rubbed. Assuming that the time for the overlayer signal to decrease to 1/e of its initial value (~10 min) corresponds to the time taken to remove a monolayer, this implies that the sulfur has penetrated at least seven layers into the bulk of the copper.

It has been found previously that adsorbed sulfur is more thermodynamically stable than sulfur in the bulk.[11] This effect is exploited to more sensitively explore whether there is sulfur in the bulk of the copper after rubbing because any subsurface sulfur is expected to diffuse to the surface when the sample is heated to high enough temperatures. The results of this experiment are displayed in Figure 5. As the copper sample is heated to ~540 K, a relatively large sulfur signal appears (Figure 5a). Note that this is not due to sulfur diffusing from the unrubbed region surrounding the wear scar since this has all been removed by ion bombardment (Figure 4) and therefore must be ascribed to sulfur segregating to the surface from the subsurface region. This further confirms the presence of subsurface sulfur in the wear track. Heating to ~780 K also results in the appearance of carbon on the surface, again only in the wear track (Figure 5b), indicating that the subsurface region also contains some carbon from the initially adsorbed thiolate species formed from DMDS. The signal probably does not accurately reflect the amount of carbon in the subsurface region compared to sulfur since the carbon clearly diffuses more slowly than the sulfur, but it does indicate that sulfur predominates in the subsurface region beneath the wear scar. It is also likely that some of the carbon in the thiolate species is removed from the surface by shear of the methyl group due to rubbing.

As emphasized above, the transport of sulfur into the subsurface region is not thermally driven, first because the temperature rise under the conditions used in this experiment is negligible, and second, because sulfur is more thermodynamically stable on the surface than in the bulk.[11] This clearly shows that the tribofilm, which results in a significant reduction in the friction coefficient (Figure 1), is formed by shear at the interface. A plausible explanation for this phenomenon comes from molecular dynamics (MD) simulations of a metal—metal sliding interface,[8−10] where vortices are produced in the near-surface region causing the atoms in the layers near the surface to intermix. Therefore, atoms that are originally located on the surface are transported several layers into the subsurface region as suggested by the experiments described above. When only a thiolate monolayer is present on the surface, shear causes the thiolate species to be removed from the surface resulting in the appearance of subsurface sulfur as found here.[7] However, the surface sites exposed in this way are then available to adsorb additional thiolate species that cause more sulfur to be transported into the subsurface region to form a sulfur-containing tribofilm. Thus, the slow decrease in friction that follows the initial drop after exposing the surface to DMDS, as a function of the number of scans (Figure 1) is likely to be due to the slow, shear-induced accumulation of sulfur in the subsurface region. This trend can be extrapolated by using the higher rotation speeds available in the pin and v-block apparatus and should result in a lower friction coefficient. This idea is borne out by measuring the friction coefficient of 5 wt % DMDS dissolved in PAO for a copper—copper sliding interface in a pin and v-block apparatus, which yields a friction coefficient of ~0.05 (Figure 6). In this experiment, when the normal load is maintained below ~1.5 kN, previous calculations of the interfacial temperature in the pin and V-block apparatus, shown on the right-hand axis in Figure 6, reveal that the interfacial temperature was below ~400 K. Again, this is below the thiolate decomposition temperature,[11] suggesting that in this case, the tribofilm may also be produced by a shear-induced surface-to-bulk transport.

A key issue in the chemistry of tribofilm formation is that the film growth kinetics should be self-limiting. That is, the film should grow to some limiting value and not continue to react indefinitely with the substrate. In the case of films formed under EP conditions, this occurs since the film growth kinetics are dictated by the electric field that forms between the electronegative reactants on the surface and the metallic substrate, which lowers the activation energy for diffusion into the substrate in a Mott-Cabrera growth mechanism.[36,31] The electric field decreases as the film becomes thicker thereby limiting the thickness of the film that is formed. In the case of shear-induced film formation described here, the film thickness is limited by the depth to which intermixing occurs. In addition, since the intermixing occurs for metallic substrates, it may be that inorganic tribofilm formation eventually inhibits the vorticity found in the MD simulation for the metallic interface and will limit the thickness of the tribofilm. This is of great importance for applications that require good electrical contact within the sliding interface (e.g., copper brushes in electrical motors), because thicker films would tend to increase the interfacial resistance, thereby causing Ohmic heating of the current-carrying contacts and eventual malfunction of the system.

CONCLUSIONS

It is found that the friction coefficient of a sliding copper—copper interface measured under UHV conditions decreases when the copper sample is exposed to DMDS. It is shown that friction is reduced due to the transport of sulfur into the subsurface region to form a tribofilm. Because the interfacial temperature rise under the experimental conditions used to measure friction is very small, tribofilm formation is not thermally induced. This conclusion is further confirmed by the fact that sulfur is thermodynamically more stable on the copper surface than in the bulk.[11] The novel, low-temperature tribofilm formation observed here is ascribed to a shear-induced intermixing of the surface layer(s) with the subsurface region as suggested using molecular dynamics simulations.[8−10] Although the tribofilm contains predominantly sulfur, a small amount of carbon is also found.

The results presented here suggest a mechanism for forming lubricious boundary-layer films for systems operating under mild conditions, such as for brushes in electric motors. Shear-induced tribofilm formation is likely to dominate when the surface temperatures are low, whereas at very high temperatures such as those present during EP lubrication, the film formation kinetics are dominated by thermal processes. However, at intermediate temperatures, it may well be that the overall tribofilm formation pathway results from a complex combination of thermally and shear-induced mechanisms.

AUTHOR INFORMATION

Corresponding Author

*Phone: (414) 229-5222. Fax: (414) 229-5036. E-mail: wtt@uwm.edu.

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