

Shear-Induced Surface-to-Bulk Transport at Room Temperature in a Sliding Metal–Metal Interface

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Abstract Predictions from molecular dynamics (MD) simulations, that sliding at a metal–metal interface causes vortices in the near-surface region that transport atoms from the surface into the subsurface region, is tested experimentally. This is accomplished by rubbing a methyl thiolate overlayer grown on a clean copper foil by exposure to dimethyl disulfide at room temperature. Repeatedly rubbing a 1.27×10^{-2} m diameter pin over a thiolate-covered copper surface at an applied load of 0.44 N and sliding speed of 4×10^{-3} m/s in an ultrahigh vacuum tribometer, results in the removal of sulfur from the wear track as measured using spatially resolved Auger spectroscopy. Any remaining surface species, in particular, outside the wear track, are removed by argon ion bombardment. Since sulfur is more thermodynamically stable at the surface, heating the sample causes the sulfur to segregate to the surface only inside the wear track, thereby directly confirming the predictions from MD simulations.

Keywords Ultrahigh vacuum tribometer · Surface-to-bulk transport · Auger spectroscopy · Surface analysis · Copper · Dimethyl disulfide

1 Introduction

Understanding the structural changes that occur at a sliding metal–metal interface is important for a number of phenomena, such as sliding friction [1, 2], formation of

nanograined materials [3, 4] and tribo-film formation [5, 6]. At high interfacial temperatures, such processes occur by chemical reaction or by thermal diffusion. Recent analytical models [7] and molecular dynamics (MD) simulations [8–10] of the sliding interface between two contacting metals have proposed that sliding induces vortices near the interface that cause the atoms in the near-surface region to become intermixed. In particular, atoms originally present on the surface become distributed into the bulk. This phenomenon is therefore not thermally driven but induced by the shear occurring at the interface. While experiments have been carried out to examine the morphology of the surfaces after rubbing [8, 11], there has been no direct experimental verification of such shear-induced, surface-to-bulk transport for room temperature sliding. In addition to leading to structural changes at the surface, such shear-induced mixing provides a possible non-thermal mechanism for tribofilm formation.

While the sliding solid–solid interface is extremely difficult to interrogate in situ, the following reports on experimental tests of the effects that are predicted by MD simulations, by following the fate of a sulfur-containing overlayer on a copper surface prepared under ultrahigh vacuum (UHV) conditions. In particular, the conditions are selected such that the interfacial flash temperature rise during rubbing is sufficiently low ($\ll 1$ K [12]) that thermal effects are negligible.

2 Experimental

Experiments were carried out in a stainless-steel, UHV chamber operating at a base pressure of 5×10^{-10} Torr following bakeout, which has been described in detail elsewhere [13]. Briefly, the chamber was equipped with a

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UHV compatible tribometer, which allows normal forces, lateral forces, and the contact resistance between the tip and substrate to be simultaneously measured. All tribological measurements were made using a sliding speed of 4×10^{-3} m/s, and the tribopin could be heated by electron bombardment in vacuo to clean it. The chamber was also equipped with a single-pass, cylindrical-mirror analyzer (CMA) for Auger analysis and an argon ion bombardment source for sample cleaning. The copper foil samples (Alfa Aesar, 99.99% pure, 1 mm thick) were polished to a mirror finish using 1 μ m diamond paste in a random orbit polisher. Once in UHV, copper foils were cleaned using a standard procedure which consisted of argon ion bombardment with a uniform ion flux (~ 1 kV, ~ 2 μ A/cm²) and annealing cycles up to ~ 850 K in vacuo, to remove any surface damage induced by polishing or argon ion bombardment. This process results in a surface that produces a square (1×1) low-energy electron diffraction pattern and is therefore well ordered [14]. The cleanliness of the samples was monitored using Auger spectroscopy. The tribopin (1.27×10^{-2} m diameter) was made from tungsten carbide containing some cobalt binder.

The vacuum chamber also incorporated a high-resolution electron gun with a Channeltron, secondary-electron detector, where the beam could be rastered over the surface to allow scanning electron microscope (SEM) images of the wear scar to be collected with a resolution of ~ 1 μ m. The electron gun could be configured to emit a higher current beam (~ 1 μ A), which is sufficient to collect high-quality Auger spectra with the CMA using a peak-to-peak modulation amplitude of 4 eV. In order to calibrate the spatial resolution with which Auger spectra could be collected, a 100 μ m diameter silver wire was attached to the copper surface. Note that the silver Auger features have energies completely different from those of the copper substrate. Figure 1 shows a line scan at 354 eV kinetic energy through the silver wire, in this case, carried out by translating the sample manipulator, which was equipped with calibrated, high-precision micrometers to precisely measure the translation. This clearly reveals that the electron beam diameter is less than 100 μ m since no signal from the copper substrate is detected when the electron beam is located directly over the wire (Fig. 1, inset). In addition, assuming that the edge of the silver wire produced an abrupt interface allows the width of the electron beam to be estimated to be ~ 70 μ m. Subsequent profiles across the wear scar were obtained using a LabView script that outputs a voltage to the deflection plates on the electron gun while monitoring the output from the lock-in amplifier used to collect Auger data. Finally, the chamber also included a quadrupole mass spectrometer for leak checking and gauging sample purity.

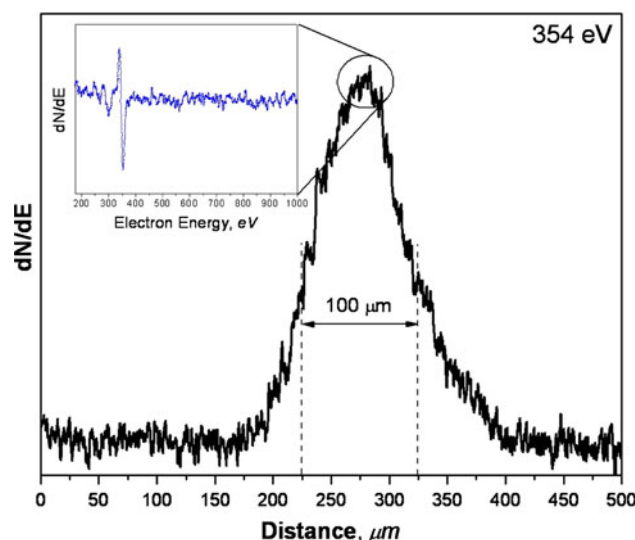


Fig. 1 Auger profile (at 354 eV kinetic energy) across a 100 μ m diameter silver wire attached to the copper substrate. The width of the silver wire is also indicated

The DMDS (Aldrich, 99.0% purity) was transferred to a glass bottle and attached to the gas-handling system of the vacuum chamber. The purity was monitored using mass spectroscopy and it was dosed onto the surface by means of a 6 mm diameter tube directed towards the copper sample.

3 Results and Discussion

The experimental strategy for testing whether shear at the metal–metal interface can cause surface layer atoms to be transported into the sub-surface region, is as follows. First, the copper surface is covered with a monolayer of an adsorbate that can be distinguished from the substrate atoms by saturating the surface with dimethyl disulfide (DMDS, $(\text{CH}_3\text{S})_2$) using an exposure of 10 L (1 L (Langmuir) = 1×10^{-6} Torr s) at 300 K. Next, the surface is rubbed to explore whether sliding has caused the surface atoms to disappear by transport into the bulk. However, since wear could also occur at the interface, the disappearance of the surface layer could simply be due to wear of the adsorbed layer. In principle, a depth profile of the elemental composition could have been obtained to establish that the surface atoms have been transported into the bulk. However, the distribution of a single monolayer of an adsorbate throughout the surface region will result in low bulk concentrations that are difficult to measure precisely using Auger spectroscopy. An alternative strategy was taken in this work by choosing an adsorbate that is more thermodynamically stable on the surface than in the bulk, so that heating will cause any subsurface species to diffuse back to the surface and be easily detected.

DMDS is selected for these experiments for a number of reasons. It reacts rapidly with copper at ~ 100 K via facile cleavage of the S–S bond to deposit thiolate species ($\text{CH}_3\text{--S}$) on the surface, which are stable to ~ 450 K and decompose to desorb methane and deposit sulfur atoms on the surface [14]. The thiolate monolayer is bonded to the surface via the sulfur atom, with the methyl group oriented away from the surface. Adsorbed sulfur is thermodynamically stable on the copper surface; heating to high temperatures (~ 850 K) results in no loss of adsorbed sulfur by desorption, or diffusion into the bulk. This also ensures that subsurface sulfur is not produced by thermal diffusion. Additionally, sulfur has a relatively intense LMM Auger feature at ~ 152 eV kinetic energy (KE).

The experiments were carried out as follows: first, the clean copper foil was rubbed in the UHV tribometer (normal load = 0.44 N, sliding speed = 4×10^{-3} m/s). This running in process resulted in a constant friction coefficient of ~ 0.45 . This ensures that there is no change in the nature of the contact region for tribological experiments performed after dosing the surface and produces a ~ 150 μm wide wear track. The copper surface was then exposed to DMDS at 300 K to form a saturated overlayer of methyl thiolate species [14]. Figure 2a, profile I shows the resulting profile across the wear track of the S LMM Auger (with a kinetic energy of 152 eV) peak-to-peak intensity ratioed to that of the copper LMM Auger peak (with a kinetic energy of 920 eV), where the center of the wear track is located at ~ 300 μm . The arrows on the figure indicate the value of the S/Cu Auger ratio, which varies from 0.42 ± 0.05 outside the wear track to 0.58 ± 0.05 inside it. This indicates that more sulfur adsorbs inside the wear track than outside, possibly due to shear-induced surface roughening.

The wear track was then rubbed using the same load (0.44 N) and sliding speed (4×10^{-3} m/s). No significant change in the friction coefficient was observed for the methyl thiolate-covered surface compared to clean copper. The composition inside the wear track was measured after each sliding pass by Auger spectroscopy, and the ratio of the peak-to-peak intensity of the sulfur Auger signal to the peak-to-peak intensity of the copper feature is shown as a function of the number of passes in Fig. 3. The first point (at $t = 0$) shows the amount of sulfur in the wear track after initial DMDS exposure. The data reveal that the sulfur coverage in the wear track decreases as a function of the number of rubbing cycles, falling below the detection limit after about 50 passes. The resulting profile of the sulfur coverage across the wear track is shown in Fig. 2a, profile II confirming the complete removal of sulfur. Note that the carbon in the methyl thiolate species is not detected since it undergoes rapid electron-stimulated desorption of the methyl moiety via S–C bond cleavage [15]. However, the

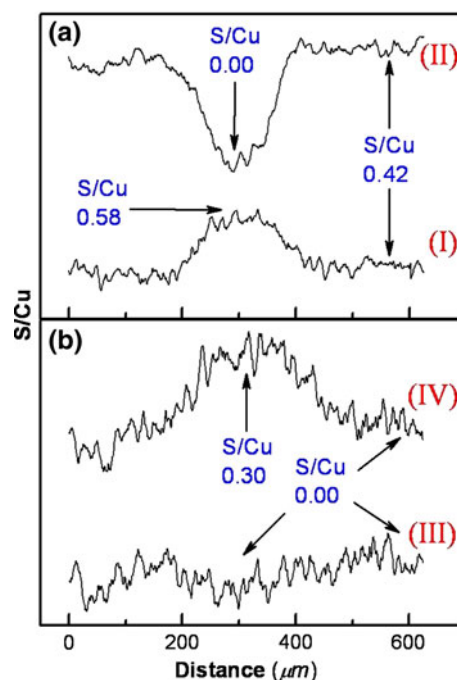


Fig. 2 Plots of sulfur peak-to-peak LMM Auger (152 eV kinetic energy) intensity ratioed to the peak-to-peak intensity of the Cu LMM Auger transition (920 eV kinetic energy) as a function of position through the wear track, which is centered at ~ 300 μm . **a** Shows the effect of rubbing, where profile I plots the sulfur coverage after the sample was dosed with DMDS after rubbing the clean surface, and profile II shows the result of subsequently rubbing the surface 50 times under a normal load of 0.44 N at a sliding speed of 4×10^{-3} m/s. **b** Shows that all of the sulfur is removed from the surface by argon ion bombardment (profile III), but that subsequently heating the sample to ~ 780 K causes sulfur to segregate to the surface only in the region of the wear track (profile IV)

presence of thiolate species on a copper surface was confirmed by surface infrared spectroscopy in a different UHV chamber, where subsequent Auger spectra of the same surface revealed only the sulfur Auger feature. Reinserting the sample into the infrared spectrometer confirmed that the methyl thiolate species were still present on the surface.

The traditional explanation for the results shown in Fig. 3 would be that the sulfur was worn from the surface. However, MD simulations predict an alternative possibility that the loss is due to shear-induced transport into the subsurface region. This presence of subsurface sulfur is measured by heating the sample to resegment it to the surface. However, since the surface around the wear scar is also covered by thiolate species, the wear scar region could be replenished by diffusion from the surroundings. In order to preclude this possibility, the surface was argon ion bombarded using a uniform ion flux (1 kV, $1 \mu\text{A}/\text{cm}^2$, 20 min) until no sulfur was detected (neither inside nor outside the wear scar) prior to being heated. Figure 2b, profile III, collected following this procedure, shows a uniform S/Cu Auger ratio of 0.00 ± 0.05 ; therefore, ion

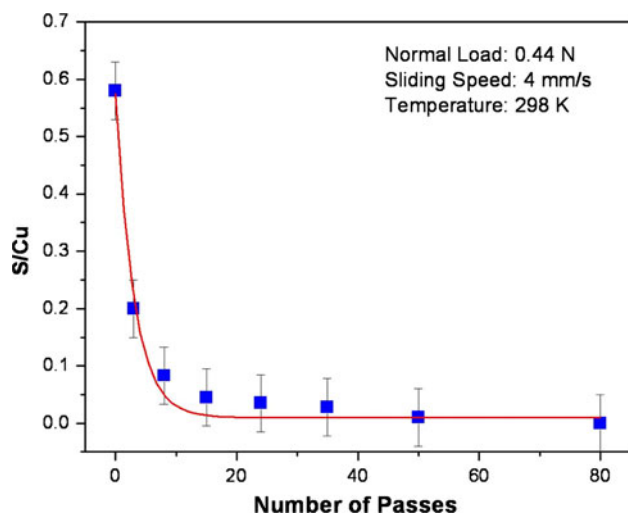


Fig. 3 Plot of the peak-to-peak intensity of the sulfur LMM Auger feature within the wear track, ratioed to the peak-to-peak intensity of the Cu LMM feature as a function of the number of passes over the wear track

bombardment has removed all sulfur from the surface. The sample was then heated to ~ 780 K for 10 s and then allowed to cool to room temperature once again. Figure 2b, profile IV shows the resulting variation in the S LMM to Cu LMM Auger ratio across the wear track. This reveals that there is no sulfur outside the wear scar, but sulfur is now present inside it, and the resulting S/Cu Auger ratio is 0.30 ± 0.05 . This demonstrates that the loss of sulfur caused by rubbing (Figs. 2a, 3) is due to tribologically induced transport of sulfur from the surface to the bulk, and that heating has caused it to diffuse once again to the surface, where it is more thermodynamically stable. The absence of sulfur outside the wear scar after heating confirms that all of the sulfur on the surface was removed by ion bombardment and that none was implanted into the bulk of the sample. In addition, control experiments by heating the clean sample after the run-in period, without dosing DMDS, for prolonged periods show neither sulfur nor carbon segregation inside or outside the wear track. This indicates that the sulfur detected in Fig. 2b, profile IV is not due to sulfur contamination. A complete Auger spectrum collected within the wear scar reveals the presence of a small amount of carbon. As noted above, this is not due to the presence of thiolate species on the surface, and must be due to the carbon in the bulk of the sample, also caused by rubbing, since no carbon is detected outside the wear scar. The experiments above provide no information on the depth to which the sulfur has penetrated. However, it has penetrated sufficiently far that no residual sulfur is detected in the wear scar by Auger spectroscopy after rubbing (see Figs. 2a, 3).

The amount of sulfur present in the wear scar after heating the sample to ~ 780 K (Fig. 2b, profile IV; S/Cu

Auger ratio ~ 0.30) is less than originally present in the wear scar (Fig. 2b, profile I; S/Cu Auger ratio ~ 0.58). This may be due to some of the sulfur initially present in the subsurface region of the wear track having been removed by argon ion bombardment or by some of the sulfur having been transferred to the tribopin, or some may have been worn from the surface.

Thus, while it is impossible to interrogate the structure of solid–solid sliding interface in situ, the results presented here are consistent with the predictions of MD simulations, that rubbing at a metal–metal interface causes vortices in the near-surface region, which result in intermixing of the surface layer atoms with those in the sub-surface. This is demonstrated by adsorbing thiolate species on the surface from DMDS and showing that the removal of sulfur from the surface is due to transport into the bulk to form a metastable film. It should be emphasized that the maximum temperature increase at the surface under the sliding condition used in these experiments is substantially lower than 1 K [12]. The experimental conditions yielded a Peclet number of $\sim 1.5 \times 10^{-3}$, resulting in a value of the maximum flash temperature for a circular contact of $\sim 10^{-2}$ K. This occurs because of the relatively low load and sliding speed, and the high thermal conductivity of copper.

The experimental observations are not only in accord with the results of the MD simulations, but also reveal possible routes to low-temperature formation of metastable films. The experiments in this work were carried out using DMDS, and sulfur-containing molecules are used as lubricant additives [16, 17]. Since rubbing results in the formation of a metastable film and the regeneration of a clean surface, this is available to adsorb more DMDS, which will then be tribologically transported into the subsurface region; repetition of this process will result in the formation of a sulfur-containing film.

Finally, it should be pointed out that, while the results presented here are consistent with the predictions from MD simulations, they do not preclude the possibility of there being other mechanisms by which shear can induce surface-to-bulk transport, by the formation of defects such as dislocations that facilitate thermal diffusion into the bulk.

4 Conclusions

Tribological experiments on a sulfur-containing overlayer on an initially clean (i.e., sulfur free), polished copper foil reveal that shear at the interface, under conditions in which the temperature increase is negligible, causes atoms at the surface to be transported to the subsurface region. The negligible surface temperature rise allows thermal effects to be excluded in this process. This observation is consistent with the predictions from MD simulations that shear at

the interface produces vortices that cause intermixing of the surface and sub-surface atoms. However, since it is not possible to examine the nature of the surface directly, the participation of this process to the observed shear-induced, surface-to-bulk transport cannot be unequivocally proven. However, these results reveal a non-thermal pathway for the formation of boundary-layer films.

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