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Tribological Properties of 1-Alkenes on Copper Foils: Effect of Low-Coordination Surface Sites

Brendan P. Miller · Octavio J. Furlong · Wilfred T. Tysoe

Abstract It has been suggested from molecular dynamics simulations that low-coordination-number sites are produced at a sliding metal–metal interface, but, because of their instability, they may rapidly relax to increase their coordination number. The possible presence of such low-coordination sites on the surface is tested by exploiting the observation that the desorption temperatures of 1-alkenes on copper increase with both the number of carbons atoms in the 1-alkenes and the surface roughness. Thus, 1-alkenes desorb from a Cu(111) single crystal, with relatively few low-coordination sites, at temperatures between 60 and 100 K lower than from a polycrystalline copper foil. The decrease in friction after impinging a flux of various 1-alkenes on a copper foil, while rubbing in an ultrahigh vacuum tribometer, correlates very well with the corresponding 1-alkene coverages on a copper foil, estimated using the desorption kinetics. This suggests either that rubbing does not result in the formation of lower-coordination sites or that they relax sufficiently rapidly that they do not influence the surface chemistry of 1-alkenes. Surface analyses indicate that shear at the interface causes carbon to diffuse into the subsurface region to form a tribofilm.

Keywords Copper foils · 1-Alkenes · Friction · Auger analysis

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1 Introduction

It has been shown that shear of thiolate species on a copper surface causes the sulfur from the thiolate species to penetrate into the bulk of the copper sample [1–3]. These results are consistent with molecular dynamics simulation studies of a sliding metal interface, which show intermixing of surface and subsurface layers proposed to be due to Kelvin-Helmholtz instabilities produced at the shearing interface [4–6]. The simulations also suggest that the surface is roughened by the shear process, which will have the effect of producing low-coordination number atoms at the surface [7]. It has been shown that such low-coordination surface sites bind adsorbates more strongly and are more reactive than high-coordination sites [8]. The adsorption of ethylene on low-Miller-index and stepped copper surfaces provides an example of the effect of low-coordination sites on bonding and reactivity. Ethylene adsorbs rather weakly and reversibly on relatively defect-free, low-Miller-index surfaces of copper [9–13]. However, the presence of low-coordination sites on a stepped Cu(410) surface induces the complete thermal decomposition of ethylene to carbon on the steps [14–16]. Similar effects are found for 1-alkenes on copper foils compared to Cu(111) single crystals, where selective dehydrogenation of 1-alkenes to 1-alkynes is found [17]. This is ascribed to the presence of low-coordination copper atoms on the copper foil, which are rare on the well-ordered Cu(111) surface. In addition, the heat of adsorption of 1-alkenes was found to increase with increasing alkyl chain length due to the van der Waals interaction between the alkyl chain and the surface [17–22]. This effect is illustrated by the data shown in Fig. 1, where the desorption peak temperatures for 1-alkenes on polycrystalline copper (square) and a Cu(111) single crystal (circle) increase linearly with the number of

carbons in the 1-alkene. It is evident that the 1-alkene desorption temperatures are consistently higher on copper foils than those on the Cu(111) single crystal, which is due to the presence of low-coordination sites on the foil [17]. The 1-alkenes also selectively dehydrogenate on the copper foil to form 1-alkynes, which are much more stable on the surface than the corresponding 1-alkenes due to the stronger bonding of the C≡C group compared to the C=C group with the surface (Fig. 1). Adsorbed 1-alkynes distort on the copper surface so that the carbon atoms become ∼sp^2 hybridized [23–26]. The plane of the resulting vinyl-like group in the adsorbed 1-alkyne is oriented perpendicularly to the surface, causing the alkyl group to point away from the surface so that it can no longer easily interact with it. An exception to this is 1-decyne where the alkyl chain becomes sufficiently long that some interaction with the end of the alkyl chains can still occur (Fig. 1) causing the desorption temperature to increase to ∼400 K. As indicated in Fig. 1, two desorption states appear for 1-nonyne, suggesting that the end of the alkyl chain of a portion of the adsorbed 1-nonyne can interact with the surface, while the remainder cannot [17].

These results clearly indicate the effect of both the presence of low-coordination sites and the number of carbon atoms in the alkyl chain on the chemistry of 1-alkenes on copper; the desorption temperatures of 1-alkenes increase with the presence of low-coordination sites and increasing length of the alkyl chain. Once the 1-alkene adsorbs on the surface, it dehydrogenates to form the corresponding 1-alkyne, which is then rather stable [17]. Thus, the chemistry of 1-alkenes is sensitive to the presence and nature of the low-coordination sites
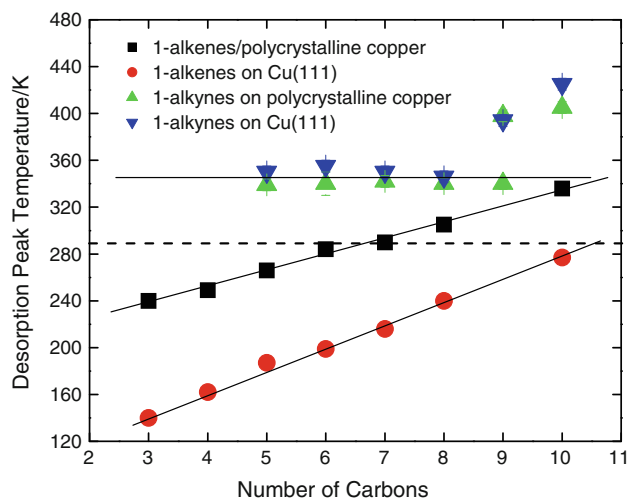

Fig. 1 Plot of the peak desorption temperatures in temperature-programmed desorption at low coverages for 1-alkenes on a Cu(111) single crystal (*circle*) and on a copper foil (*square*), and for 1-alkynes on a Cu(111) single crystal (*inverted triangle*) and on a copper foil (*triangle*) as a function of the number of carbon atoms

on the surface, and since such low-coordination sites may be created during rubbing, a more reactive surface might be expected to be produced at the sliding interface. However, these low-coordination sites are inherently less stable than higher-coordination copper atoms and can rapidly relax to increase their coordination numbers [7]. The results illustrated in Fig. 1 can be used to probe this effect, by exploring which alkenes react with the surface while rubbing to form a tribofilm. This experiment is carried out by measuring which 1-alkene causes a change in friction when the surface is dosed during rubbing; no change in friction will indicate that the 1-alkene does not adsorb on the rubbed surface, while a variation in friction will indicate that it does. The resulting friction coefficients are then compared to the coverages expected on the copper foils while exposing the surface at the same dosing pressure. A correlation between the 1-alkene coverage on the copper foil and the change in friction will indicate that the number and nature of the low-coordination sites on the surface do not strongly influence the surface chemistry, because either rubbing the surface does not change the nature and concentration of the low-coordination sites or that, if it does, they can relax sufficiently rapidly at room temperature to reform a surface that resembles the copper foil. A more stringent test would be to carry out a similar experiment using the Cu(111) single crystal to compare the results with those for a copper foil. However, the tribological experiment produces wear tracks that would destroy the sample, making such experiments prohibitively expensive.

The tribology experiments were carried out on a clean copper foil in an ultrahigh vacuum (UHV) tribometer, and the foils were prepared in an identical manner to those used to collect the surface chemical results shown in Fig. 1 [17]. The temperature at which the friction measurements were made (∼290 K) is indicated by a horizontal dotted line in Fig. 1. Thus, exploring which 1-alkenes react with the surface to form tribofilms provides an in situ gauge of the state of roughness of the surface. If the average coordination number of the surface is not affected, or if the atoms relax rapidly, those 1-alkenes that adsorb and react at ∼290 K (1-hexene and higher 1-alkenes) should form tribofilms and exhibit a change in friction when the copper foil is dosed while rubbing. Correspondingly, 1-pentene and lower molecular weight hydrocarbons (propene and 1-butene) should not cause a change in friction.

In order to explore the nature of the resulting tribofilms formed by reaction with the 1-decene, the wear tracks were analyzed using in situ Auger spectroscopy. In addition, the evolution of the friction coefficient of the surface after gas dosing had ceased was followed to provide a depth profile of the sample [27].

2 Experimental

Tribological measurements were carried out in a stainless-steel, UHV chamber operating at a base pressure of $\sim 2 \times 10^{-10}$ Torr following bakeout, which has been described in detail elsewhere [1]. The chamber was equipped with a UHV-compatible tribometer, which simultaneously measured the normal load, lateral force, and contact resistance between the tip and substrate. Previous work has demonstrated that the maximum interfacial temperature rise for a copper sample under the same experimental conditions (4×10^{-3} m/s sliding velocity, ~ 0.44 N normal load) is much less than 1 K [1]. All experiments were carried out by initially rubbing the spherical tribopin (of 1.27×10^{-2} m in diameter, made from tungsten carbide containing some cobalt binder) against the clean copper sample until a constant friction coefficient was obtained, a process that usually required ~ 50 scans, referred to as a run-in period. This formed a wear track on the surface, likely resulting in the transfer of copper to the tribopin so that the friction results are for a sliding copper–copper interface. The reactants were dosed through a variable leak valve connected to a dosing tube (with an internal diameter of 4×10^{-3} m) directed toward the sample, so that the pressure at the sample was enhanced by a factor of ~ 20, estimated by comparing with the coverages obtained by background dosing. The chamber also contained a single-pass cylindrical-mirror analyzer (CMA) for Auger analysis and an argon ion bombardment source for sample cleaning and depth profiling. A high-resolution electron gun with a beam energy of 5 kV and a channeltron secondary electron detector were also incorporated into the system. This allowed scanning electron microscopy (SEM) images and Auger profiles of the wear scars to be collected. Finally, the chamber also included a quadrupole mass spectrometer for leak checking and for gauging reactant purity.

The copper samples (Alfa Aesar, 99.99 % pure, 1 mm thick) were polished to a mirror finish using 1 μm diamond paste, then rinsed with deionized water and ultrasonically degreased in acetone. Once in UHV, the copper foils were cleaned using a standard procedure which consisted of Argon ion bombardment (~ 1 kV, ~ 2 μA/cm^2) followed by annealing cycles up to ~ 850 K. The cleanliness of the samples was monitored using Auger spectroscopy.

The 1-alkenes and 1-alkynes (Aldrich, 99.0 % purity) were transferred to glass bottles and attached to the gas-handling system of the UHV chamber, where they were subjected to several freeze–pump–thaw cycles. The purity of the 1-alkenes and 1-alkynes was monitored using mass spectroscopy.

3 Results

Experiments were carried out to explore the variation in friction coefficient as a function of the number of sliding passes of the tip against the copper surface, after completion of a run-in period, while dosing a polycrystalline sample with a background pressure of $\sim 1 \times 10^{-8}$ Torr of 1-alkenes from a dosing tube incident on the sample, using a sliding speed of 4×10^{-3} m/s with an applied load of 0.44 N. The sample was initially rubbed using the same conditions for ~ 50 passes prior to 1-alkene dosing until the friction coefficient had attained a constant value in order to ensure that any subsequent changes in friction were caused by reaction with the 1-alkene.

1-pentene was the smallest 1-alkene for which a change in friction was detected when dosing at 290 K (Fig. 2), where the friction coefficient dropped to a steady-state value of ~ 0.46 while 1-pentene was incident on the sample. No change in friction was found for lower molecular weight 1-alkenes (propene and 1-butene).

A substantially larger decrease in friction coefficient was observed for 1-hexene (Fig. 3), where the friction coefficient dropped to a value of ~ 0.34 after 5 sliding passes and then rose slightly. The friction coefficient measured after dosing had ceased (after ~ 100 passes), increased to ~ 0.5, and then remained reasonably constant.

In the case of dosing with 1-heptene (Fig. 4), an initial rapid drop in friction was found, reaching a value of ~ 0.31 after three passes, which then slowly rose as the surface was being dosed and rubbed, to a value of ~ 0.35 after ~ 105 passes. At this point, 1-heptene dosing was stopped while measurement of the friction coefficient continued.
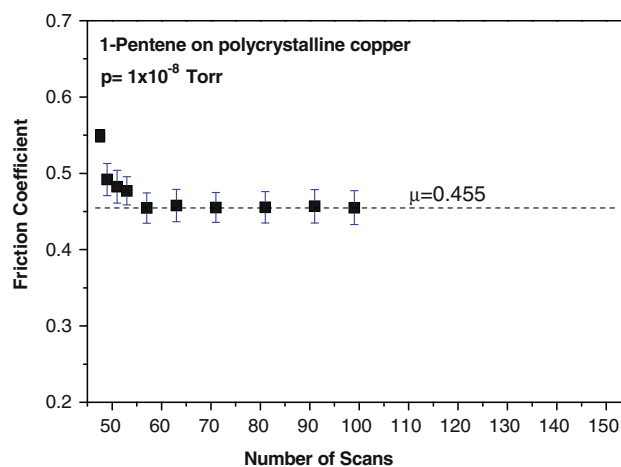
Fig. 2 Plot of friction coefficient as a function of the number of passes when dosing a polycrystalline copper sample with a background pressure of 1×10^{-8} Torr of 1-pentene from an incident dosing tube, measured using a sliding speed of 4×10^{-3} m/s at a normal load of 0.44 N. Only the results after the completion of the run-in period are displayed
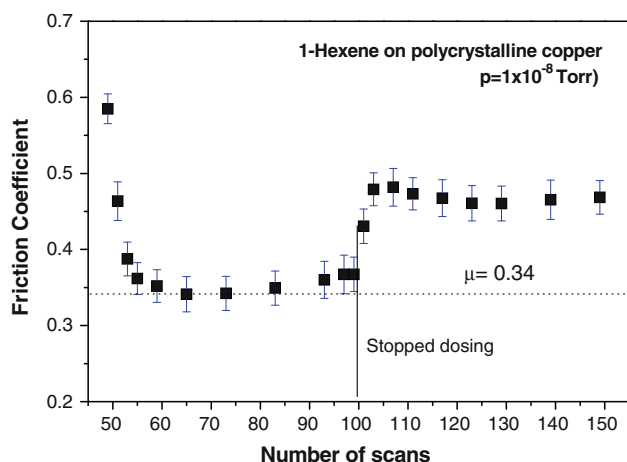
Fig. 3 Plot of friction coefficient as a function of the number of passes when dosing a polycrystalline copper sample with 1-hexene. Also shown is the evolution in friction coefficient as a function of the number of passes after 1-hexene dosing was stopped
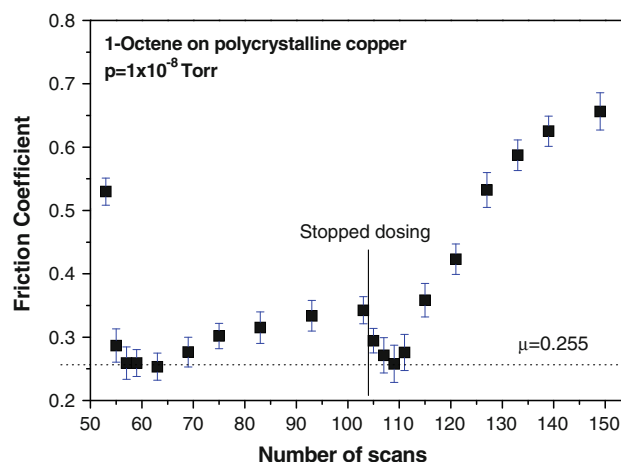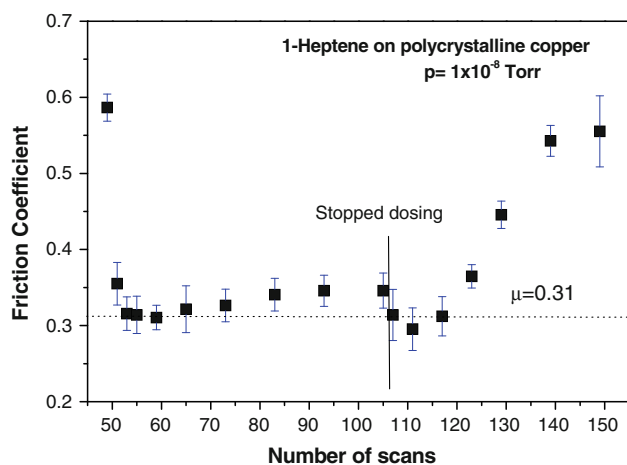

Fig. 5 Plot of friction coefficient as a function of the number of passes when dosing a polycrystalline copper sample with 1-octene. Also shown is the evolution in friction coefficient as a function of the number of passes after 1-octene dosing was stopped

Fig. 4 Plot of friction coefficient as a function of the number of passes when dosing a polycrystalline copper sample with 1-heptene. Also shown is the evolution in friction coefficient as a function of the number of passes after 1-heptene dosing was stopped
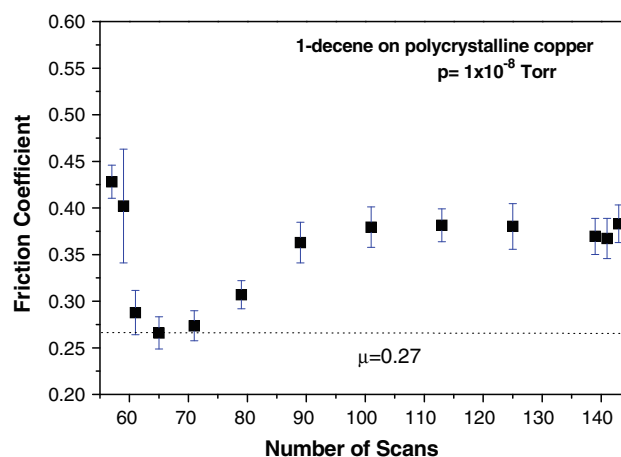

Fig. 6 Plot of friction coefficient as a function of the number of passes when dosing a polycrystalline copper sample with 1-decene. Only the results after the completion of the run-in period are displayed

The friction coefficient decreased to ~ 0.3 and then continued to rise to the original, clean surface value of ~ 0.6.

This general trend continued for a surface dosed with 1-octene (Fig. 5), where the friction coefficient decreased while dosing to ~ 0.26 after two passes and then slowly rose to ~ 0.35. When 1-octene dosing is stopped, the friction coefficient dropped once again to ~ 0.26 and then slowly rose to ~ 0.68.

Similar behavior was found when dosing with 1-decene (Fig. 6), where the friction coefficient decreased to ~ 0.27 and then slowly increased once again to ~ 0.35 with rubbing after ~ 80 scans. Note that, in this case, rubbing was stopped when 1-decene dosing had ceased, to allow the wear track to be analyzed (see below). The results for the

initial lowest friction coefficients attained after dosing the 1-alkenes are summarized in Fig. 7 (square).

The nature of the wear track was analyzed in situ by Auger spectroscopy after rubbing a polycrystalline copper sample while dosing with 1-decene for ~ 80 scans. A depth profile of the wear scar by argon ion bombardment (~ 1 kV, ~ 2 μA/cm^2) was performed, and the results are displayed in Fig. 8 as a function of bombardment time. An initial C(KLL)/Cu(LMM) peak-to-peak Auger ratio of ~ 0.56 was found inside the wear track. Also shown is the C(KLL)/Cu(LMM) peak-to-peak Auger ratio measured outside the wear track due to a thermal reaction between 1-decene and the copper foil. This shows that 1-decene does react with the copper foil as expected from the data in
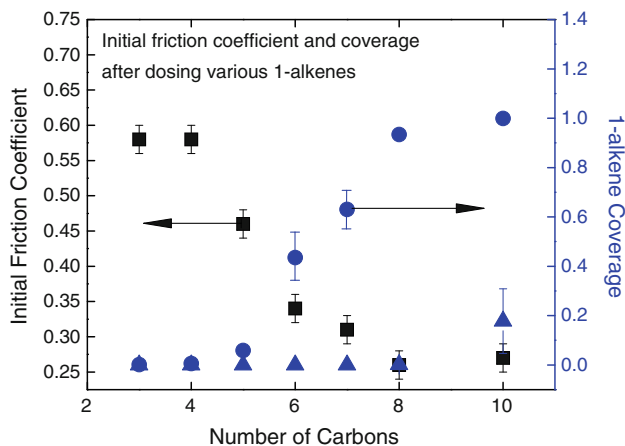
Fig. 7 Plot of the value of the minimum friction coefficient after 1-alkene dosing during rubbing as a function of the number of carbon atoms in the 1-alkene (*square*). Also shown is the estimated 1-alkene coverage based on the dosing pressure and 1-alkene desorption temperatures on the copper foil (*circle*) and a Cu(111) single crystal (*triangle*)

Fig. 1, but that shear at the interface causes an enhancement in the surface carbon concentration and transport of carbon into the subsurface region. Using the Auger sensitivities for a 5 kV beam energy for the carbon KLL (0.73) and the copper LMM features (0.26) indicates that the surface region contains ∼17 at.% carbon [28]. The carbon concentration decreases as the surface is ion bombarded to a peak-to-peak Auger ratio of ∼0.22 after 30 min of bombardment, corresponding to ∼7.3 at.% of carbon in the subsurface region [28]. The inset to these data shows the C KLL Auger profiles in the wear scar, before and after ion bombarding.

4 Discussion

While the main goal of the work was to use 1-alkenes as an in situ probe of the presence of low-coordination sites on copper induced by sliding, it is also clear that the higher molecular weight hydrocarbons can reduce the interfacial friction. In particular, the data shown in Fig. 7, summarizing the initial friction coefficients found after dosing the samples with various 1-alkenes while rubbing (Figs. 2, 3, 4, 5, 6), reveal that some friction reduction is found when dosing the surface with 1-pentene (Fig. 2), while no effect is seen for 1-butene and propene. Dosing with higher hydrocarbons causes even larger drops in friction coefficient. The desorption temperatures for 1-alkenes in Fig. 1 can be used to estimate their desorption activation energies [29] using a pre-exponential factor of 1×10^{16} s^{-1} [30, 31]. The resulting activation energies and pre-exponential factor can then be used to calculate the 1-alkene desorption rate during dosing: $A_{des}\Theta$, where Θ is the coverage, at the
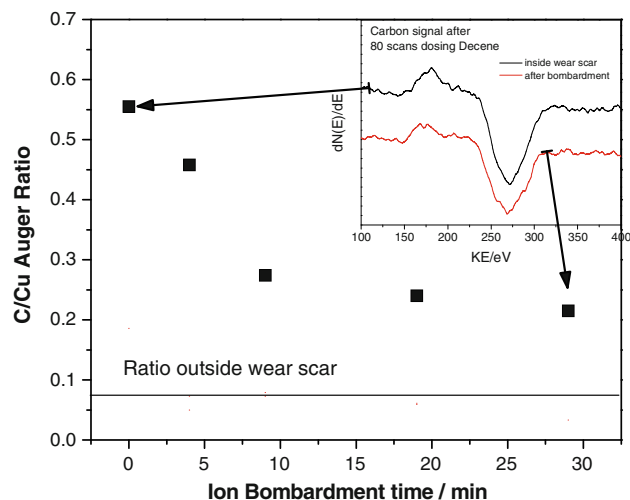

Fig. 8 Auger depth profile plotting the C(KLL)/Cu(LMM) Auger ratio as a function of ion bombardment time (~ 1 kV, ~ 2 μA/cm^2) after initially rubbing for 80 passes while dosing a polycrystalline copper sample with a background pressure of 1×10^{-8} Torr of 1-decene from an incident dosing tube, measured using a sliding speed of 4×10^{-3} m/s at a normal load of 0.44 N. The inset shows the C KLL Auger spectra inside the wear track before and after ion bombardment

experimental sample temperature of 290 K. The rate of adsorption is calculated by assuming Langmuir adsorption kinetics [32] at a temperature T as $A_{ads}(1 - \Theta)$ where $A_{ads} = \frac{SP}{\sqrt{2\pi mkT}}$, where m is the mass of the molecule, k is the Boltzmann constant, S is the sticking probability, and P the pressure. Since the alkenes saturate at an exposure of ~ 1 L (Langmiur, $1L = 1 \times 10^{-6}$ Torr s), it is assumed that the sticking probability of the 1-alkenes on copper is unity [17]. The resulting equilibrium coverage is given by $\Theta = \frac{A_{ads}}{A_{ads} + A_{des}}$ and the estimated coverages (circle) are plotted along with the friction data (square) in Fig. 7. Similar calculations were carried out for Cu(111) (triangle), where the resulting equilibrium coverages are much lower than those found on the foil, due to the lower desorption temperatures of the 1-alkenes from Cu(111) (Fig. 1). The initial friction coefficients measured immediately following 1-alkene dosing correlate very well with their coverages on the copper foil, estimated from the temperature-programmed desorption (TPD) data (Fig. 1). In particular, neither propene nor 1-butene is expected to adsorb significantly on polycrystalline copper at 290 K in accord with the observation that no friction reduction is found when using these 1-alkenes as gas-phase lubricants. Correspondingly, both 1-octene and 1-decene essentially saturate the surface ($\Theta \sim 1$) at 290 K, resulting, in both cases, in the lowest friction coefficients (of ~ 0.26). For intermediate 1-alkenes, the increase in estimated coverage with increasing number of carbon atoms in the 1-alkenes follows the variation in initial friction coefficient quite well.

The only possible exception is 1-pentene, which is predicted to have an equilibrium coverage of ~ 0.06 monolayers during the experiment, while it still shows a measurable decrease in friction from the clean surface. Nevertheless, the inverse correlation between the coverage calculated on the foil and the initial friction coefficient indicates that the reactivity of the copper foil prior to rubbing is essentially identical to that in the tribological interface. Thus, any metastable, low-coordination sites that might have formed during rubbing relax sufficiently rapidly that they do not substantially increase the reactivity of the copper foil.

The resulting carbonaceous species on the surface can penetrate the subsurface region due to interfacial shear in a similar manner to that found previously for sulfur- [2, 3, 33] and boron-containing compounds [27]. The solubility of carbon in copper is extremely low, but significant bulk carbon concentrations (up to 28.5 at.%) have been found by mechanical alloying [34, 35]. The carbon concentrations on the surface of the copper foil (~ 17 at.%) and in the bulk (~ 6.3 at.%) measured using Auger spectroscopy are well within this limit.

The surfaces show generally similar variations in friction coefficient as a function of the number of passes when dosed with the different 1-alkenes while rubbing (Figs. 3, 4, 5, 6). The initial response is a rapid friction decrease to the values displayed in Fig. 7, followed by a relatively slow increase as rubbing continues. When dosing ceases, the friction coefficient decreases to the minimum value found after initial dosing and subsequently rises once again. In the case of 1-octene, it increases to a value greater than the initial friction coefficient of the pin sliding against clean copper of ~ 0.6 (Fig. 5). The Auger analyses suggest that shear of the hydrocarbon-covered surfaces results in the formation of a carbon-containing tribofilm. The mechanically formed copper–carbon alloy has been reported to be much harder than pure copper [36]. The presence of a hard film on a softer (copper) substrate would be expected to lead to a relatively high friction coefficient and likely accounts for the eventual rise in friction coefficient to values higher than that for the clean surface (~ 0.6) when dosing has stopped (Fig. 5). However, the evolution in friction coefficient as a function of the number of rubbing cycles, both while dosing with 1-alkene and while rubbing after the 1-alkene dosing has stopped (Figs. 3, 4, 5, 6), suggests that the situation is more complex. For example, in all cases, when the friction coefficient has increased during 1-alkene dosing and rubbing, it then decreases rapidly after dosing has ceased to the initial value measured after the surface is dosed (Figs. 4, 5) and then increases once again. This observation is consistent with the formation of a relatively thin outer-surface film during 1-alkene dosing that is quickly removed as 1-alkene dosing stops. The Auger analyses indicate that the surface region has a higher carbon content than further below the sample. It may be that the harder, high-carbon-content surface region on a slightly softer film with less carbon causes the friction coefficient to increase slightly. As the surface is then rubbed without 1-alkene dosing, the surface layer is either worn away or shear causes the more concentrated surface layer to be more uniformly distributed through the surface region.

5 Conclusions

Surface-science experiments show that 1-alkenes react on polycrystalline copper surfaces to form 1-alkynes and that the heat of adsorption of the 1-alkenes increases linearly with the length of the alkyl chain. It was also found that the heat of adsorption of 1-alkenes on copper surfaces increases when low-coordination sites are present, so that the heat of adsorption on copper foils is larger than that on a Cu(111) single crystal surface. Molecular dynamics simulations have shown that the surface is roughened during rubbing, but that the surface atoms subsequently relax to a more stable state. The reactivity of 1-alkenes on copper was therefore used to probe the possible presence of shear-induced, low-coordination surface sites by comparing the estimated 1-alkene coverage during dosing with the friction coefficient of polycrystalline copper, shortly after dosing the sample with the corresponding 1-alkene. A good correlation between the increase in 1-alkene coverage with chain length and the decrease in friction coefficient suggests that surface roughening during rubbing does not drastically alter the surface chemical properties. This implies that low-coordination sites that might have formed on the surface during rubbing relax sufficiently rapidly at ~ 290 K that they do not strongly influence the surface chemistry. In addition, shear at the interface causes the surface carbon to be transported into the subsurface regions due to shear, as has been found previously for sulfur- and boron-containing compounds.

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