Lubricant thickness effects on friction between Pd(100) surfaces

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Friction measurements have been made between pairs of Pd(100) surfaces prepared in vacuum with adsorbed *n*-octane films ranging in thickness from 0 to 20 monolayers on each surface. These measurements have been made at lattice misorientation angles of 0° and 45°. Both sets of measurements reveal friction anisotropy at all except the highest *n*-octane coverages. The friction coefficient drops with increasing *n*-octane coverage until it reaches a limiting value of $\mu_s \approx 0.4$. The static friction coefficient reveals a different dependence on *n*-octane coverage than has been observed for alcohols. The friction coefficient decreases more slowly with increasing *n*-octane coverage than for increasing alcohol coverage.

KEY WORDS: lubricant, *n*-octane films, UHV chamber

1. Introduction

Friction and lubrication at interfaces are very complex phenomena and as a result are sensitive to many characteristics of the interface. These include the morphology of the surfaces, the chemical composition of the surfaces, the surface contaminants and lubricant contamination, to name a few. Investigation of lubricant interactions with surfaces under controlled conditions requires the level of environmental control that is provided by ultra-high vacuum (UHV). Several studies of friction have been performed under UHV conditions using various surfaces modified by a variety of lubricants or adsorbates. In one such study, McFadden *et al.* probed the effect of molecular adsorbates on the friction between single crystalline Cu(111) surfaces [1,2]. They found that the adsorption of alcohols at the sliding interface had no observable effect on friction at coverages of less than one monolayer (ML). A dramatic decrease in friction was observed when the alcohol coverage exceeded 1 ML. Furthermore, the friction coefficient dropped discontinuously as the coverage was increased past 1 ML. They attributed the high friction at submonolayer coverages to the high propensity of metal surfaces to "wet" one another. Junctions are formed between asperities of the mating metal surfaces through holes in the lubricant film. Metallic junction formation provides an extremely strong driving force for squeezing the adsorbate out of the contact region, leading to high friction. They suggested that complete adsorbate films (>1 ML) may inhibit wetting of the metallic surfaces to one another. In a similar study

performed under UHV conditions, Ko *et al.* used Ni(100) surfaces modified by ethanol and observed a significant decrease in friction as the coverage was increased past 1 ML [3]. Interestingly, they also noticed that the drop in friction was a discontinuous function of the ethanol coverage even at coverages in excess of 1 ML. The two aforementioned studies used highly controlled and reproducible measurements of friction between single crystalline surfaces to show that submonolayer coverages of alcohols had no effect on the friction coefficient while coverages of 1 ML or more resulted in a significant reduction in friction.

We have performed friction measurements under UHV conditions between two identical single crystal Pd(100) surfaces modified by the presence of adsorbed *n*-octane. *n*-Octane was chosen because it is a short chain hydrocarbon which can adsorb and desorb reversibly from the Pd(100) surfaces in UHV without decomposing. This work follows a previous study in which we studied friction anisotropy at the interfaces between these Pd(100) surfaces modified by adsorbed *n*-octane [4]. In that study it was shown the friction was high between the surfaces when their crystallographic lattices are misaligned by all angles other than ~45°. When misaligned by 45° there is a minimum in the friction coefficient. That result corroborates a similar observation made when studying the friction anisotropy between Ni(100) surfaces [5].

The effect of adsorbed *n*-octane as a lubricant at the interface between two Pd(100) surfaces is quite different from that observed using alcohols on the Cu(111) and Ni(100) surfaces [1–3]. Contrary to the results of previous studies, we observed that *n*-octane reduces the friction between Pd(100) surfaces over a much wider

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coverage range. The discontinuous decrease in friction observed using ethanol as a lubricant, was not observed with *n*-octane. The comparison of these studies reveals a distinct difference in the coverage dependence of the friction between single crystal metal surfaces modified by alkanes or by alcohols. Since all these experiments were conducted in a highly controlled UHV environment, it appears that the difference in friction is due to differences in the properties of monolayer films of *n*-octane and ethanol on metal surfaces.

2. Experimental

All experiments were conducted in a stainless steel UHV chamber with a base pressure below 10^{-10} Torr. The UHV chamber is equipped with a variety of instruments to allow *in situ* surface preparation and analysis. In addition, it is equipped with a UHV tribometer that allows measurement of the normal and shear forces between the surfaces of two identical single crystalline samples prepared and then brought into sliding contact within the UHV chamber. The sample manipulator and tribometer each hold a Pd(100) surface that can be heated and cooled in the temperature range 100–1000 K and exposed to gases. The details of the apparatus and the Pd(100) surface preparation procedures have been described elsewhere [4,6].

The coverages of *n*-octane on the Pd(100) surfaces were determined using temperature programmed desorption measurements. The *n*-octane was adsorbed onto one of the Pd(100) surfaces by introducing its vapor into the chamber with the sample surface held at 100 K. The exposures are reported in units of Langmuir (1 L = 10^{-6} Torr s). The sample was then positioned in front of a quadrupole mass spectrometer and heated at a rate of 2 K/s while the mass spectrometer monitored the signal at $m/q = 43$. The areas under the TPD peaks were used as the basis for the determination of coverage.

The procedures used to make the friction measurements have been described in detail elsewhere [4]. Prior to making the friction measurements the surfaces were both cleaned using the same procedure and then modified by the adsorption of identical coverages of *n*-octane. The friction measurements were made with a normal load of $F_N = 25$ mN and a sliding speed of 20 μm/s. All measurements were repeated 12 times at different points of contact between the Pd(100) crystal surfaces in order to measure both the magnitude and the variance in the coefficients of friction.

3. Results and discussion

3.1. n-Octane adsorption on Pd(100)

In this study friction has been measured between Pd(100) surfaces modified by the presence of adsorbed *n*-octane. One purpose was to make a comparison with previous studies in which we have used atomic adsorbates or small alcohols as lubricants [1–3,7]. *n*-Octane was chosen for use as the lubricant in this study for several reasons. First, it is a small chain hydrocarbon which can adsorb and desorb reversibly from the Pd(100) surfaces without decomposing on the surface. Palladium surfaces would cause the decomposition of adsorbed alcohols such as ethanol [8–11]. The second reason for choosing *n*-octane is that it is the shortest alkane which can adsorb to form multilayers on the Pd(100) surfaces at 120 K, the minimum temperature achievable with the Pd(100) sample on the tribometer.

The coverage of *n*-octane on the Pd(100) surfaces was calibrated using TPD. The clean Pd(100) surfaces at 120 K were exposed to *n*-octane vapor while positioned in the UHV chamber as they would be prior to friction measurements. After the exposure to *n*-octane vapor, the manipulator sample was moved into a position approximately 2 mm from the aperture to the mass spectrometer. The Pd(100) sample was then heated at a constant rate of 2 K/s while the mass spectrometer monitored the signal from the primary ionization fragment of *n*-octane ($m/q = 43$). Figure 1 illustrates the TPD spectra of *n*-octane desorption from the Pd(100) surfaces obtained following different initial *n*-octane exposures. After low exposures the TPD spectra exhibit a single desorption peak at 273 K which saturates in intensity at an exposure of ∼3 L.
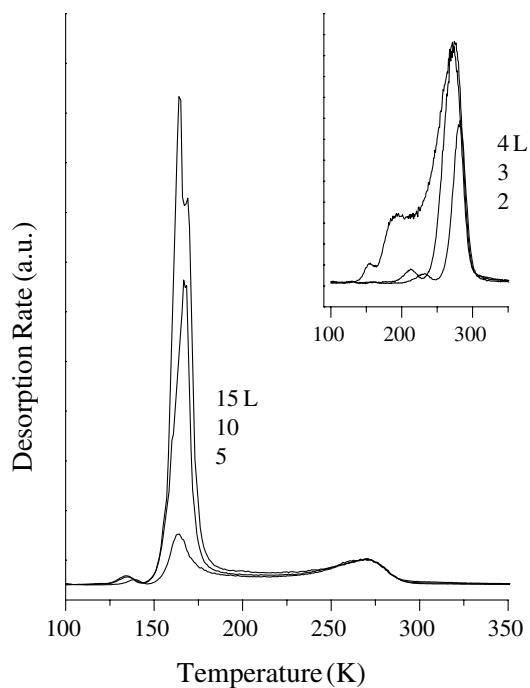

Figure 1. Temperature programmed desorption spectra of *n*-octane on the Pd(100) surface as a function of exposure. The inset shows the TPD spectra obtained for coverages up to 1 ML. $m/q = 43$, heating rate = 2 K/s.

This peak is associated with those *n*-octane molecules that are adsorbed directly onto the Pd(100) surface and form the first monolayer. The area under the saturated desorption peak at 273 K was defined as that of the monolayer and was used to determine *n*-octane coverages at other exposures. At high exposures a second desorption peak appeared in the TPD spectra at 170 K arising from desorption of molecules forming the multilayer. There was no sign of any decomposition of *n*-octane during adsorption and heating.

3.2. Friction between clean Pd(100) surfaces

Initially, friction measurements were made between the clean Pd(100) surfaces. In general, the measurement of friction between perfectly clean metal surfaces in UHV is difficult because strong metallic bonds are formed between the two surfaces. This phenomenon is known as cold-welding and can cause the two surfaces to stick together irreversibly. Even when cold-welding does not occur, friction and adhesion are high [2,3,6,7,12–14]. Friction between the clean Pd(100) surfaces was immeasurably high. The surfaces stuck to one another during shearing until the shear forces reached the maximum value for which the tribometer had been calibrated. Sliding never occurred during shearing of the clean surfaces and as a result, the maximum shear force reached during shearing could only be used to estimate a lower limit on the value of the static coefficient of friction, μ_s.

3.3. Friction between lubricated Pd(100) surfaces

Following the preliminary friction studies using the clean Pd(100) surfaces, all experiments were conducted with surfaces modified by the presence of adsorbed *n*-octane. Friction measurements were made at interfaces between the two surfaces modified by total coverages of *n*-octane ranging from 4 to 40 ML at the interface. Figure 2 shows the friction versus time traces obtained using a Pd(100)/Pd(100) interface with the two surface lattices aligned ($\theta = 0°$) and modified by the presence of 4 ML of adsorbed *n*-octane. The surfaces were first exposed to *n*-octane to give coverages of 2 ML on each and thus 4 ML at the interface between the two. Twelve friction measurements were made between the samples under this set of conditions and with the samples held at 120 K. Three typical single-pass forces versus time traces are shown in figure 2. Referring to the first trace shown in figure 2, friction measurements were obtained using the following sequence of steps. At point A, the surfaces were out of contact. The manipulator sample was brought into contact with the tribometer sample at point B, resulting in an increase in the normal force. Between points B and C, the surfaces were held in contact for a short
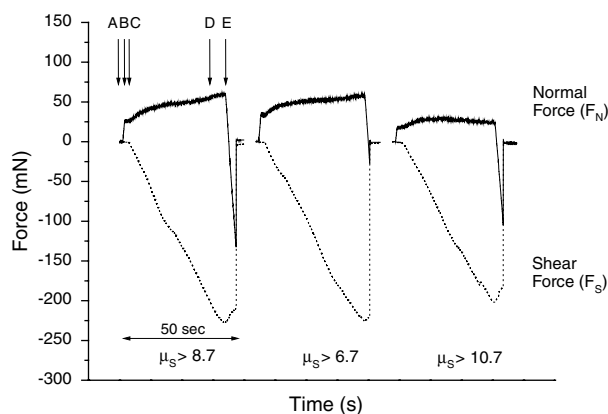

Figure 2. Three representative friction traces obtained between pairs of Pd(100) surfaces each modified by 2 ML of adsorbed *n*-octane. The two surface lattices were aligned, $\theta = 0°$. The normal forces, F_N, at the interface are depicted as solid lines with positive displacement and the shear forces, F_S, by dashed lines with negative displacement. $v_s = 20$ μm/s, T = 120 K.

period of time. At point C, the manipulator sample was sheared at a constant velocity relative to the stationary tribometer sample. This resulted in an increase in the shear force at the interface. The shear force continued to increase until movement of the manipulator sample was stopped at point D. At point E, the manipulator sample was separated from the tribometer sample and the shear and normal forces returned to zero. During separation of the two samples a large, negative normal force was generated indicating a tensile stress at the interface. This negative pull-off force is due to adhesion between the two samples. Adhesive forces were commonly observed following shearing with thin lubricant layers at the Pd(100)/Pd(100) interface.

With the two Pd(100) surfaces separated by 4 ML of adsorbed *n*-octane and the surface lattices aligned no sliding was observed during shearing of the interface. Instead, the shear forces increased until the measurement was stopped and the surfaces were separated. Shearing was terminated at this point to ensure that forces did not exceed those for which the tribometer had been calibrated and to prevent permanent deformation of the tribometer during a friction measurement. These measurements, therefore, yield only a lower limit for the static friction coefficient. Under these conditions of high friction and adhesion, friction coefficients were calculated by dividing the shear force reached when shearing was stopped by the applied load. The results of 12 such measurements yielded a lower limit on the static friction coefficient of $\mu_s > 8.0 \pm 2.0$. The friction traces of figure 2 are representative of all friction measurements made between Pd(100) surfaces lubricated with 4 ML of *n*-octane. They are also representative of the friction traces obtained between the clean Pd(100) surfaces and pairs of surfaces with less than 4 ML of

n-octane at the interface. At *n*-octane coverages of > 4ML at the interfaces there is some interfacial motion during shearing, however, at all but the highest coverage (40 ML) the motion would be described as stick-slip rather than sliding motion [4]. Thus the friction measurements have been used to determine the static coefficient of friction as a function of *n*-octane coverage.

Measurements of μ_s as a function of *n*-octane coverage at the Pd(100)/Pd(100) interface have been made at lattice misorientation angles of $\theta = 0°$ and 45°. The orientations measured using low energy electron diffraction patterns from the surfaces are accurate to $\Delta\theta = \pm 2°$. As mentioned earlier, studies of the lattice orientation dependence of friction at Ni(100)/Ni(100) and at Pd(100)/Pd(100) have shown that μ_s has a minimum at a misorientation angle of 45° between the two square lattices. At other angles μ_s appears to be insensitive to the lattice misorientation angle. Figure 3 shows the dependence of μ_s on the coverage of *n*-octane at misorientation angles of $\theta = 0°$ and 45°. At both angles μ_s is observed to decrease with increasing *n*-octane coverage and to have roughly the same dependence on *n*-octane coverage. At all coverages other than the highest of 40 ML, the average μ_s at a misorientation angle of 45° is roughly half that at 0° misorientation. At the highest *n*-octane coverage μ_s is

independent of the misorientation angle and has fallen to $\mu_s \approx 0.4$.

The origin of friction anisotropy at metallic interfaces is not yet clear. At interfaces between surfaces in elastic contact, friction anisotropy is often ascribed to the commensurability of the two lattices [15–18]. In the case of metal surfaces such as Pd or Ni, however, the contact between the two is plastic and results in deformation of the surfaces and the near surface region. The suggestion has been made that the friction anisotropy arises from anisotropy in the plastic work done in the bulk of the Pd(100) crystals as they slide past one another [5]. The anisotropy is observed so long as the friction is high and plastic deformation of the bulk is a significant contributor to the friction force. Once the *n*-octane layer (or any other adsorbed layer) reaches a sufficient thickness, the dominant contributor to the friction force arises from energy dissipation in the *n*-octane film and thus the anisotropy disappears.

The coefficient of friction between the Pd(100) surfaces decreases monotonically with increasing *n*-octane film thickness. The interesting feature of the data presented here is that the dependence on the film thickness is quite different from that observed in other such studies that have made use of either atomic adsorbate or small alcohols [1–3,7]. In the case of *n*-octane on the Pd(100) surfaces μ_s is still immeasurably high at coverages of 2 ML on each surface and is continuing to drop at coverages of 10 ML (or 20 ML at the interface). In the case of atomic adsorbates on Cu(111) surfaces μ_s was independent of coverage, however, it should be noted that in the case of atomic adsorbates the coverages never exceeded 1 ML [7]. For alcohols such as ethanol, trifluoroethanol and butanol adsorbed on the Cu(111) and Ni(100) surfaces, the sensitivity of μ_s to coverage is much more dramatic than in the case of *n*-octane on the Pd(100) surface [1–3]. In the cases of the alcohols μ_s does not change in the coverage range 0 – 1 ML but then drops quite rapidly once the coverage exceeds 1 ML. Furthermore, with alcohols the friction coefficient reaches its limiting value of $\mu_s \approx 0.3 – 0.4$ at coverages of ∼5 ML, whereas, in the case of *n*-octane the limit occurs at a coverage of ∼20 ML (40 ML at the interface).

The origin of the differences in the dependence of μ_s on the coverage of *n*-octane versus the coverages of the alcohols may arise from the different types of intermolecular interactions between the molecules in the adsorbed films. In the case of *n*-octane these are quite weak van der Waals forces, whereas, in the case of the alcohols the interactions arise from stronger hydrogen bonding. The consequence may be that the alcohol multilayers form more cohesive films on the surfaces that are less easily penetrated by asperities during contact and sliding. As a result metal–metal contact is prevented by single monolayers of the alcohols on the
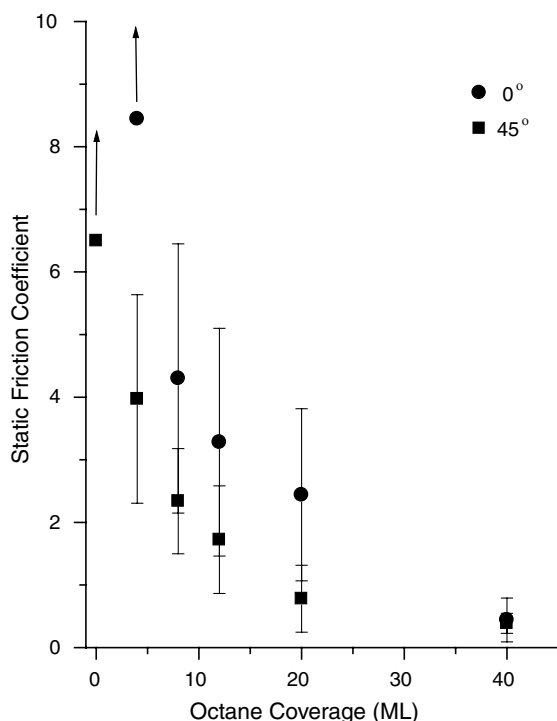

Figure 3. Static friction coefficient at the Pd(100)/Pd(100) interface as a function of the total amount of *n*-octane adsorbed at the interface. At the lowest coverages the data points marked with arrows are lower limits on the value of μ_s. The measurements were made with the surface lattices aligned, $\theta = 0°$, and misaligned by $\theta = 45°$. $F_N \approx 25$ mN, $v_s = 20$ μm/s, T = 120 K.

metal surfaces and thus the alcohols are better able to serve as lubricants and reduce friction.

4. Conclusions

The presence of thin films of *n*-octane at the interface between Pd(100) single crystal surfaces reduces friction. The interfacial friction exhibits anisotropy in the sense that friction depends on the relative orientations of the two crystalline surfaces for *n*-octane coverages up to 20 ML at the interface. The decay in the friction with *n*-octane coverage is weaker than that observed in previous studies using alcohols adsorbed at interfaces between single crystal metal surfaces. The differences are attributed to weaker interactions in the *n*-octane films than in the films of adsorbed alcohols.

Acknowledgments

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