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The frictional properties of thin inorganic halide films on iron measured in ultrahigh vacuum

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Friction coefficients are measured in ultrahigh vacuum using a tungsten carbide tribopin against thin films of sodium chloride and potassium iodide deposited onto clean iron. It is found, in accordance with previous measurements for potassium chloride on iron, that the friction coefficient falls from an initial value of ~ 2 for the clean iron surface to a minimum value after a few tens of Ångstroms of the halide have been deposited onto the surface, and remains constant for thicker films. The minimum friction coefficient is independent of applied load and therefore obeys Amontons' law. Simple theories for the effect of a low-shear-strength film suggest that the friction coefficient should depend on the shear strength of the film. This idea is tested by plotting the minimum friction coefficient versus the hardness of the film material, which is proportional to its shear strength, where a linear correlation was found. The lack of dependence of friction coefficient with film thickness for thicker films implies that ploughing forces do not contribute significantly to the friction coefficient.

KEY WORDS: halide films, ultrahigh vacuum tribometer, friction coefficient

1. Introduction

It has been shown previously that chlorinated hydrocarbons thermally decompose on the iron surface during extreme-pressure lubrication to form a film that consists of $FeCl_2$, which incorporates small carbonaceous particles [1–14]. In addition, particularly when carbon tetrachloride is used as an additive, carbon diffuses into the bulk of the iron sample to form a carbide [15]. It has further been shown that this chemistry can be reproduced in ultrahigh vacuum using molecular beams of chlorinated hydrocarbons incident onto a heated iron sample [15–18]. In this case, the nature of the gas-phase reaction products can be determined using a mass spectrometer. It was found that the variation in the rate of product formation as a function of sample temperature yielded an activation energy that was in good agreement with similar values from the temperature dependence of the film growth rate measured at higher pressures in a microbalance. It thus appears that the tribological chemistry can be reproduced in ultrahigh vacuum. Since the reactively formed tribological interfaces are relatively complicated, we have embarked on a study of thin inorganic films on iron measured using an ultrahigh vacuum tribometer. These studies were initiated using potassium chloride since this has a relatively low shear strength [19]. They showed that the high friction coefficient of the initially clean surface (~ 2) was reduced to 0.27 ± 0.03 by the addition of ~ 40 Å of KCl. Addition of more KCl resulted in no further reduction in the friction coefficient. It was also found that the completion of the first KCl monolayer was responsible for the reduction in friction [20]. Since the formation of a thicker film did not substantially affect the friction coefficient, this implies that the ploughing contribution to the friction coefficient was negligible and that the lateral force arises primarily due to shear of the film. Since friction is reduced by the presence of a monolayer of KCl, the lateral force is presumably due to shear occurring close to the metal substrate/film interface. Conventional theories for the manner in which low-shear-strength films lower the friction suggest that the real contact area at the asperities is given by the hardness of the substrate, while the lateral force is given by the shear strength of the material so that:

$$\mu = \frac{S_F}{H_S} \tag{1}$$

where S_F is the shear strength of the film and H_S is the hardness of the substrate, in this case, iron [21,22]. Since the substrate is constant during the tribological experiments, this theory can be simply tested by comparing the friction coefficient of the film with its shear strength. However, the shear strength is often difficult to obtain. Since the hardness is proportional to the shear strength [21], and the hardness is a much easier quantity to measure, a similar correlation between the measured friction coefficient and the material hardness will similarly provide an experimental test for this theory. In the following, therefore, the friction coefficient is measured for various materials deposited onto clean iron in ultrahigh vacuum and the resulting limiting

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friction coefficient compared with the hardness of the film material.

2. Experimental

Experiments were carried out in a stainless-steel, ultrahigh vacuum chamber operating at base pressures of 5×10^{-10} Torr following bakeout, which has been described in detail elsewhere [19]. The chamber is equipped with an ultrahigh vacuum compatible tribometer which simultaneously measures normal forces, lateral forces and the contact resistance between the tip and substrate. All tribological measurements were made using a single pass on a freshly prepared surface and the tribopin was heated by electron bombardment *in vacuo* prior to each experiment. The chamber also contained a single-pass, cylindrical-mirror analyzer for Auger analysis of the surface, a quartz crystal microbalance (Sigma Instruments Model SQM-160) for measurement of the thickness of the deposited film, an argon ion bombardment source for sample cleaning and an evaporation source for deposition of inorganic materials. This source has been described in detail elsewhere [23]. The potassium iodide and sodium chloride (Alfa Aesar, 99.99% purity) were loaded into the small alumina tube furnace and outgassed in ultrahigh vacuum prior to use. The X-ray diffraction (XRD) patterns of the thin halide films on iron were collected using a Scintag Model XDS 2000 diffractometer using the copper Kα line. The clean iron foil sample (0.5 mm thick, Aldrich, 99.999% pure) was attached to a sample manipulator where it was mounted onto a steel plate (1.0 mm thick) to provide a rigid base for the tribological measurements. Prior to mounting onto the steel plate, the sample was polished with 1 μ diamond pasted to a mirror finish. The sample can be resistively heated and was cleaned using ion bombardment to remove any impurities (primarily carbon, chlorine and sulfur) and annealed to 1000 K prior to carrying out any tribological measurements. The iron sample following this treatment was almost atomically smooth and no significant surface features could be discerned using atomic force microscopy (AFM). The tribopin (12.7 mm diameter) was made from tungsten carbide containing some cobalt binder. This was cleaned by electron beam heating via a retractable filament that can be placed in front of the pin. An Auger analysis of the pin following this treatment was in accord with the bulk structure. Measurement of the pin topology using AFM showed that it was substantially rougher than the iron substrate with an approximately Gaussian height distribution with a width at half height of ~ 2000 Å [19].

3. Results

Frictional measurements were made for a number of inorganic halides including sodium chloride and potassium iodide since these represent, along with the potassium chloride that has been measured previously [19], a relatively large range of hardness. In addition, they are all of the same cubic sodium chloride crystal structure [24]. The hardness for each of the materials is displayed in table 1 [25,26]. Previous X-ray photoelectron spectroscopic (XPS) analyses of KCl films [19] confirmed that KCl was deposited onto the surface. Since the hardnesses of the halides were measured for single crystals, the crystallinity of the deposited films was measured using XRD for 2000-Å-thick halide films deposited onto iron in ultrahigh vacuum. The results are displayed in figure 1 for KI, NaCl and KCl films. The presence of diffraction features due to the halides confirms that these have been deposited onto the surface and that these are crystalline. The most intense diffraction features are assigned to (2n, 0, 0) planes of the halide film implying that the (100) planes of the halide films are oriented parallel to the substrate. A doublet is also detected for iron and the features are assigned to diffraction from the iron foil and the steel support below.

The coefficient of friction is displayed in figure 2 as a function of film thickness. The data shown in figure 2(a) for the deposition of NaCl on iron were collected in four separate experiments with different iron samples, which are represented by four different symbols. Clearly the agreement between the values measured in each experiment is excellent, thereby emphasizing the reproducibility of the data. The friction coefficient decreases rapidly from the clean surface value of ~ 2 to a limiting value of 0.55 ± 0.05, and remains constant with the addition of further NaCl. A similar behavior is observed for a potassium iodide film (figure 2(b)) where a similar rapid decrease is noted, in this case, reaching a limiting value of 0.23 ± 0.02. A similar shape of the plot of friction coefficient versus film thickness has been found previously for KCl deposited on iron [19], where, in that case, the limiting friction coefficient was found to be 0.27 ± 0.03.

A plot of contact resistance versus film thickness, measured while the frictional data presented in figure 2(b) were collected, is displayed in figure 3. The point on this curve for zero KI film thickness is due to the tribopin rubbing against clean iron and represents the resistance of the external circuit and the pin–metal

Table 1
The hardnesses in MPa of various halides used as model lubricant films.

Material	Hardness/MPa
KI	49
KCl	71 (100)
NaCl	179

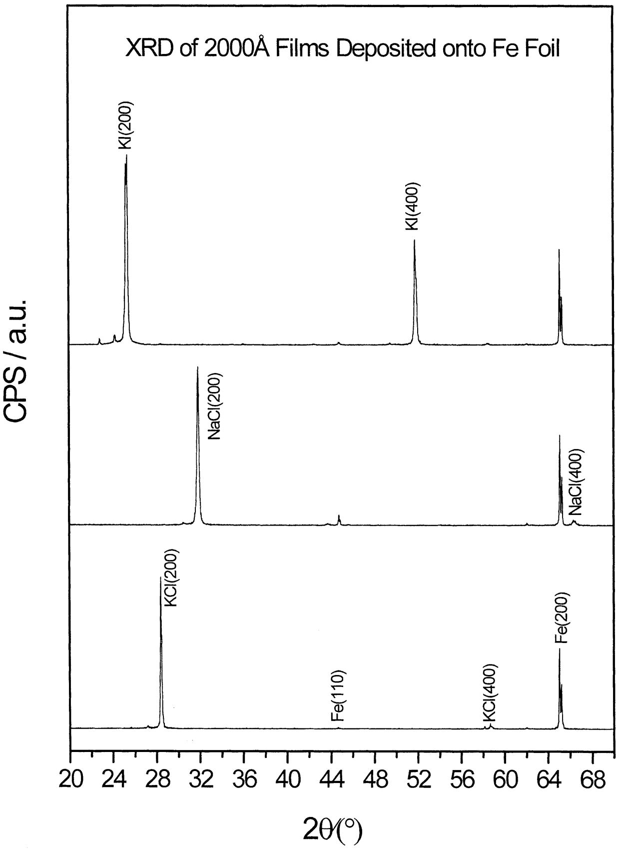

Figure 1. X-ray diffraction patterns of 2000-Å-thick films of KI, NaCl, and KCl deposited onto clean iron in ultrahigh vacuum.

contact. This value remains constant up to a KI film thickness of ~40 Å and then increases. Similar behavior has been noted previously for KCl films deposited onto iron [19] and the rapid increase in resistance was suggested to correspond to the completion of the first KCl monolayer. This notion was subsequently confirmed by measuring the proportion of bare iron surface in the presence of a KCl film by titrating the bare iron with deuterium [20]. This implies that the completion of the first monolayer of the halide film is responsible for the rapid decrease in friction coefficient when a film is deposited, again suggesting that this is a general phenomenon for these inorganic films.

The friction coefficient is plotted versus applied load in figure 4. In the case of the KI films (figure 4(a)), this experiment was carried out for various film thicknesses larger than 40 Å (where the limiting frictional behavior is observed). This shows that the friction coefficient is independent of load for all the film thicknesses tested indicating that these systems obey Amontons' law. A similar behavior is noted for NaCl films (figure 4(b)), which display a similar independence of applied load, in this case, for a 2000-Å-thick film. A similar behavior was observed previously for potassium chloride films [19] indicating that this "classical" behavior is a feature of all films so far investigated.

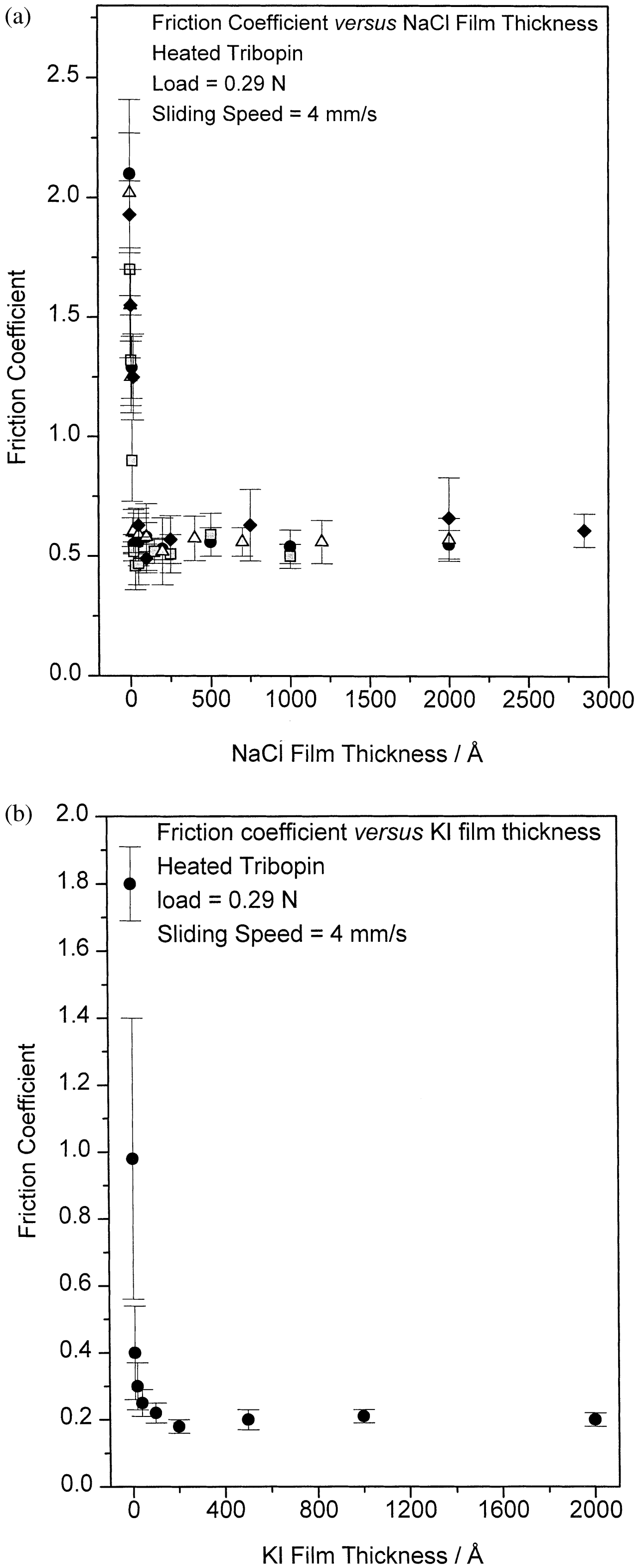

Figure 2. Plot of friction coefficient versus film thickness for (a) sodium chloride and (b) potassium iodide deposited onto clean iron in ultrahigh vacuum.

4. Discussion

The general tribological behavior of the KI and NaCl films measured here, as well as that of the KCl films

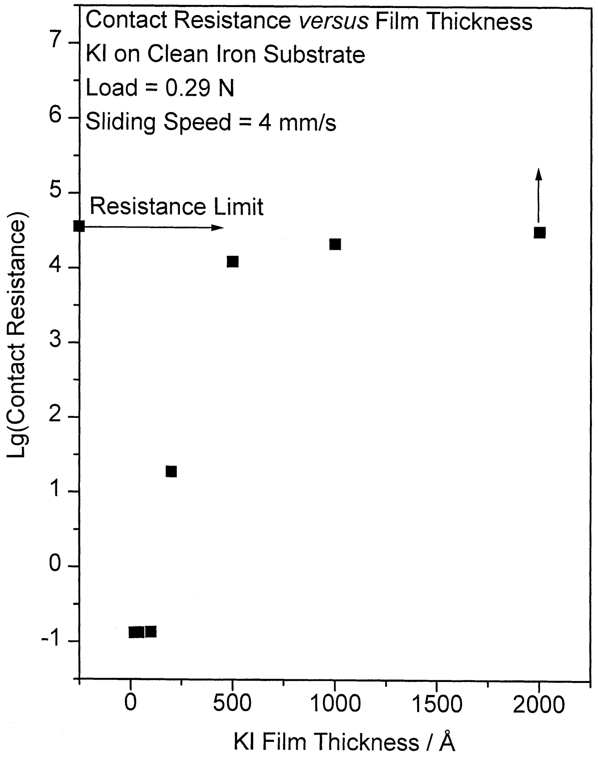

Figure 3. Plot of $\log_{10}$ (contact resistance) versus film thickness for potassium iodide deposited onto clean iron in ultrahigh vacuum.

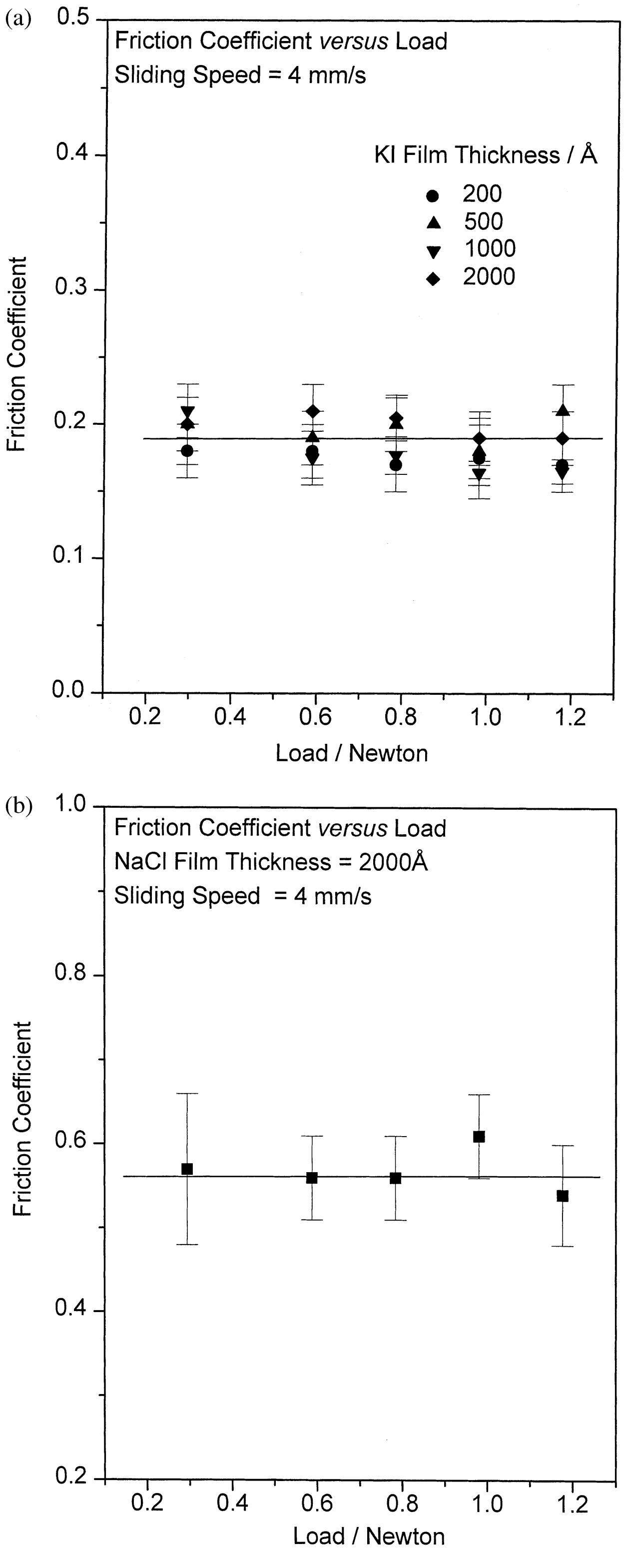

Figure 4. Plot of friction coefficient versus applied load for (a) various thicknesses of potassium iodide and (b) 2000 Å of sodium chloride deposited onto iron in ultrahigh vacuum.

measured previously [19], is essentially identical since the friction coefficient falls rapidly from the clean-surface value to a minimum after the deposition of a small amount of halide, and remains constant thereafter. The contact resistance behavior for a KI film (figure 2) is also very similar to that found for KCl, where the rapid increase was ascribed to the completion of the first monolayer of KCl. In addition, all of these systems obey Amontons' law (figure 4, [21]). AFM images of the halide film collected following a tribological experiment show that the majority of the film is removed, leaving a thin layer between the tip and the iron substrate. The presence of this remaining layer is responsible for the increase in contact resistance (figure 3). The lack of variation of friction coefficient with increasing film thickness in all cases further suggests that ploughing of the film does not a contribute to the frictional force. This observation is in accord with previous suggestions [21] that shear of the thin surface film is the major contributor to the lateral force. In this case, friction is envisaged to arise from the shear at small asperities formed at the contacting interface yielding the theoretical friction coefficient given in equation (1), which depends only on the shear strength of the film and the hardness of the substrate. Since the substrate is identical in all of the experiments carried out, this implies that the friction coefficient of different films should depend only on the shear strength of the film. Note that this model also predicts that the friction coefficient should be independent of applied load as found experimentally (figure 4). Shear strengths are difficult to measure but are proportional to the hardness of the material, a quantity that is far easier to measure [21]. Thus, the friction coefficient of thin films of various materials should similarly scale with hardness. The experimental values of limiting friction coefficient are plotted versus hardness in figure 5, where the data for iron are included for completeness. Clearly, the correlation between hardness and friction coefficient is very good, thereby confirming the general simple theory [21]. This linear relationship applies even to clean iron. Note that this theory, while appearing to be obeyed empirically, assumes that the thin film has the same shear strength as the bulk material, while the results presented above suggest that the friction is reduced by the saturation of the first layer by the inorganic film, which is unlikely to have bulk-like properties. None of the halides studied have lattice spacings that are epitaxial with iron surfaces [24]. Note that even reactively grown halide and sulfide films exhibit diffraction patterns indicating that they crystallize in their bulk lattice structures and the data of figure 1 confirm that the evaporated films are crystalline. Thus, the lattice mismatch between the halide film and the surface must be accommodated at or close to the interface. If the first-layer halide film bonds more strongly to the iron surface than to the rest of the halide film above it, its structure is likely to relax so that it is more in registry with the iron substrate and therefore out of registry with the remainder of the film. Conversely, if the first halide monolayer bonds more strongly to the rest of the halide film above it than to the iron surface, it will be out of registry with the iron and more closely in registry with the halide film. Shear can thus be expected to occur at the interface that is out of registry so that, in the first case, shear will occur between the first monolayer and the film, while in the second case shear will occur between the film and the iron surface. Temperature-programmed desorption data collected for KCl adsorbed onto clean iron [20] show that the first monolayer desorbs at a higher temperature than the bulk, suggesting, following the above arguments, that shear will occur between the first monolayer and the rest of the film above it. This view is in accord with the suggestion that the friction coefficient is lowered once the first halide monolayer is complete. This shear process, since it involves shear between halide planes, may be related to the shear strength in the bulk material and may account for the correlation between friction coefficient and hardness found in the data of figure 4.

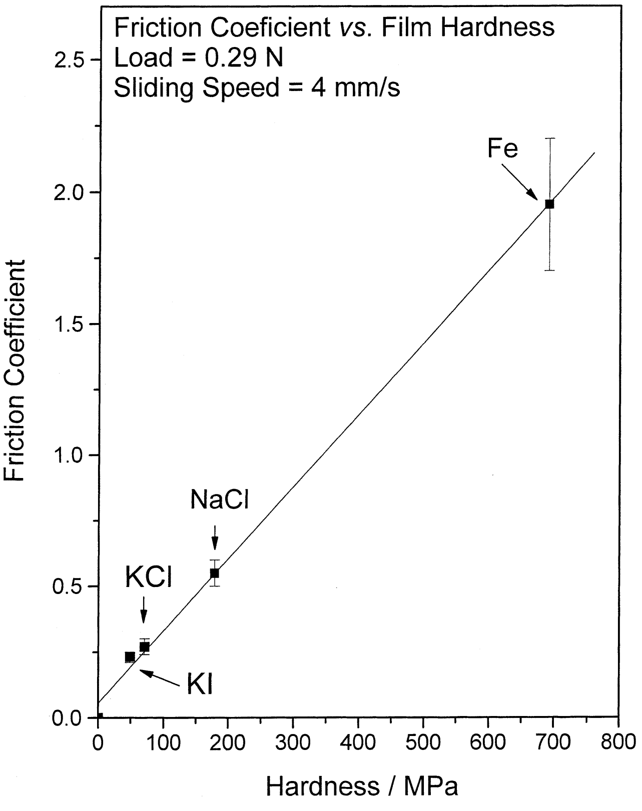

Figure 5. Plot of minimum friction coefficient versus hardness for various inorganic films deposited onto iron in ultrahigh vacuum. The data for potassium chloride are taken from Ref. [19]. The value for clean iron is included for completeness.

5. Conclusions

The friction coefficient of thin, crystalline halide films comprising NaCl and KI deposited onto iron show the same behavior, where a thin layer causes the friction coefficient to fall from the initial high value of ~ 2 for the tribopin rubbing against clean iron to a constant value. This behavior is identical to that found previously for thin KCl films. Amontons' law is obeyed by all of the films where the friction coefficient is independent of the applied load. Finally, the limiting friction coefficient is linearly proportional to the hardness of the film, consistent with a simple model that suggests that the lateral force is due to shear of the deposited film. The friction coefficient does not increase with increasing film thickness, suggesting that ploughing of the film does not make a large contribution to the lateral frictional force.

Acknowledgments

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