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Tribological properties of films formed by the reaction of carbon tetrachloride with iron

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The tribological properties of halide films grown on iron by reaction with carbon tetrachloride vapor at a temperature of 617 K and a pressure of 1.7 Torr are compared, in ultrahigh vacuum, with $FeCl_2$ films evaporated onto the surface. It is found that the reactively formed film has a slightly lower limiting friction coefficient than the evaporated layer (~0.06 compared to ~0.08), which may be due either to the diffusion of some carbon into the substrate or the formation of a more oriented layer when this is formed reactively. The major difference between the reactively grown and evaporated film is that the evaporated layer attains the minimum friction when ~40 Å of $FeCl_2$ has been evaporated, while the reactively formed layer has a minimum friction coefficient when a film of 6 ± 2 Å has been deposited. In the case of the evaporated $FeCl_2$ film, the growth of second and subsequent layers proceeds before the first layer is complete. It has been shown that the friction coefficient reaches its minimum value after completion of the first monolayer, a process that is complete after the evaporation of ~40 Å of $FeCl_2$. In the case of the film formed by reaction with CCl_4, the halide film grows directly on the surface implying that the $FeCl_2$ monolayer thickness is ~6 Å. This value is in good agreement with the layer thickness in bulk ferrous chloride.

KEY WORDS: halide films, $FeCl_2$, carbon tetrachloride, ultrahigh vacuum tribometer, friction coefficient, extreme-pressure lubrication

1. Introduction

It has been demonstrated that reactively formed extreme-pressure films consisting primarily of $FeCl_2$ are produced when using model extreme-pressure lubricants consisting of methylene chloride, chloroform or carbon tetrachloride dissolved in a poly α-olefin [1,2] where friction coefficients of $11 \pm 1 \times 10^{-2}$ were found for a film formed from methylene chloride [3] and $7.1 \pm 0.6 \times 10^{-2}$ for films grown from chloroform or carbon tetrachloride [4,5]. The mean contact pressure during these experiments was between 500 and 1000 MPa with a linear sliding speed of 9.6×10^{-2} m/s. In order to gain a fundamental understanding of the frictional behavior of thin inorganic films on iron, we have studied a number of alkali halides evaporated onto clean iron in ultrahigh vacuum [6-10] and found, in general, that the deposition of a few tens of Ångstroms of these halides substantially reduces the interfacial friction coefficient from ~2 for clean iron to values less than ~0.6 [7]. The formation of thicker films causes a slight increase in the friction coefficient [9].

It has also been shown that a ferrous chloride film *evaporated* onto iron in ultrahigh vacuum reduces the friction coefficient to ~0.08, in good agreement with the values found above for model lubricants comprising small chlorinated hydrocarbons dissolved in a poly α-olefin [10]. Transfer of the $FeCl_2$ from the iron to the tungsten carbide tribopin was also observed. In the following, the tribological properties of films formed by the reaction of carbon tetrachloride vapor with iron surfaces is investigated [5,11]. The growth kinetics of these films has been studied previously, where film growth rates were measured on an iron foil using a microbalance, from the change in sample mass as a function of time [12]. This resulted in the deposition of an $FeCl_2$ film, along with the rapid diffusion of carbon into the bulk of the iron sample [13]. It has been demonstrated that carbon diffusion into the bulk is more pronounced for carbon tetrachloride than for either methylene chloride or chloroform, an effect that was attributed to a lowering of the activation barrier for diffusion due to the presence of co-adsorbed chlorine on the surface [13]. Such an enhanced surface-to-bulk transport of carbon is anticipated to have several effects. First, it is expected to result in an increase in substrate hardness causing a decrease in contact area and thus a lower friction coefficient. Second, once conditions have been reached at which the halide film is removed (at a surface temperature of ~940 K [14,15]), seizure is prevented by the presence of the underlying carbide layer resulting in CCl_4 being an extremely effective extreme-pressure additive [13].

2. Experimental

Experiments were carried out in a stainless-steel, ultrahigh vacuum chamber operating at base pressures

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of $\sim 2 \times 10^{-10}$ Torr following bakeout, which has been described in detail elsewhere [6]. 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. It also contains a single-pass, cylindrical-mirror analyzer for Auger analysis of the surface, a quartz crystal microbalance (Sigma Instruments Model SQM-160) for measuring the thickness of evaporated films, an argon ion bombardment source for sample cleaning and an evaporation source for deposition of inorganic materials [16]. Prior to mounting onto the steel plate, the iron sample is polished with 1 μm diamond paste to a mirror finish. The sample can be resistively heated and it is 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 is almost atomically smooth and no significant surface features can be discerned using atomic force microscopy (AFM). The tribopin (6.35×10^{-3} m radius) is made from tungsten carbide containing some cobalt binder. This is 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 is in accord with the bulk structure. Experiments were generally carried out using an applied load of 0.29 N, yielding a maximum Hertzian stress of 420 MPa.

Films were reactively grown on the clean iron using a reactor cell attached to the ultrahigh vacuum chamber depicted schematically in figure 1. The cell is attached to the main chamber by means of a gate valve and a clean iron foil sample (0.1 mm thick, Aldrich, 99.999% purity) is attached to a hollow, polished stainless steel tube using electrical feedthroughs, enabling the sample to be resistively heated. The sample temperature is measured by means of a chromel–alumel thermocouple spot-welded to the sample. The sample mounting tube can be moved into the main chamber where the vacuum seal is provided by a viton O-ring. The outer portion is enclosed in an evacuated, stainless-steel bellows to minimize the pressure differential on either side of the O-ring and to avoid contaminating the retracted transfer rod.

3. Results

The growth rates of films formed by the reaction of carbon tetrachloride with clean iron have been measured previously using a microbalance [12]. The film growth kinetics depend on pressure, varying from parabolic growth ($X^2 \propto t$) at high pressures (above $\sim$4 Torr) to linear at low pressures (below $\sim$2 Torr). A CCl_4 pressure of 1.4 Torr was selected for these experiments first to facilitate cell evacuation following completion of the experiment and second, to provide a constant film growth rate. At this CCl_4 pressure and a reaction temperature of 617 K, the film growth rate is 20 ± 5 Å/min.

Figure 2 shows the variation in friction coefficient of films grown by reaction with CCl_4 vapor as a function of film thickness with an applied load of 0.29 N at a sliding speed of 4×10^{-3} m/s. Figure 2(a) shows the data for thin films grown by reaction with carbon tetrachloride vapor, where the friction coefficient decreases from the clean surface value of $\sim$2 to $\sim$0.06 following the deposition of a 6 ± 2 Å thick film. Figure 2(b), for thicker films, shows that this value remains constant as the film thickness increases to $\sim$5000 Å and increases for films thicker than this value. Shown for comparison as an inset to figure 2(a) is the variation in friction coefficient for pure $FeCl_2$ evaporated onto iron in ultrahigh vacuum. The friction coefficient, in this case, decreases more slowly with film thickness since second and subsequent layers are deposited prior to completion of the first monolayer [8]. Assuming that the friction coefficient for the evaporated layer reaches its minimum value when the first layer is complete leads to an esti-

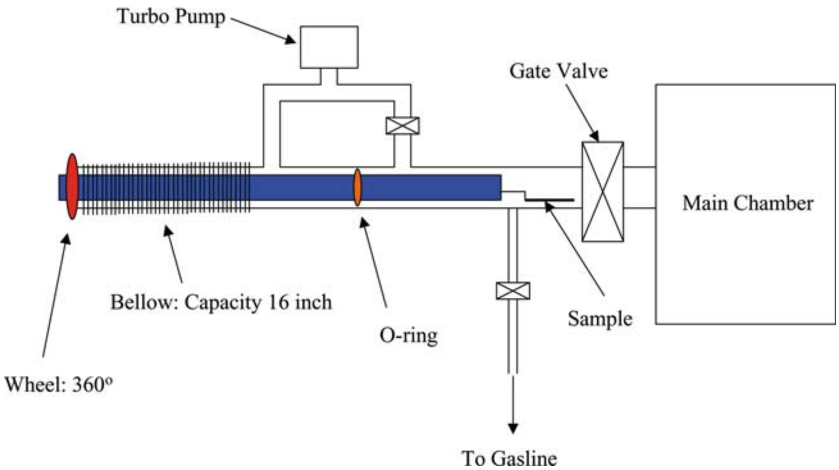

Figure 1. Schematic diagram of the reaction cell attached to the ultrahigh vacuum chamber used to grow films by reaction with carbon tetrachloride.

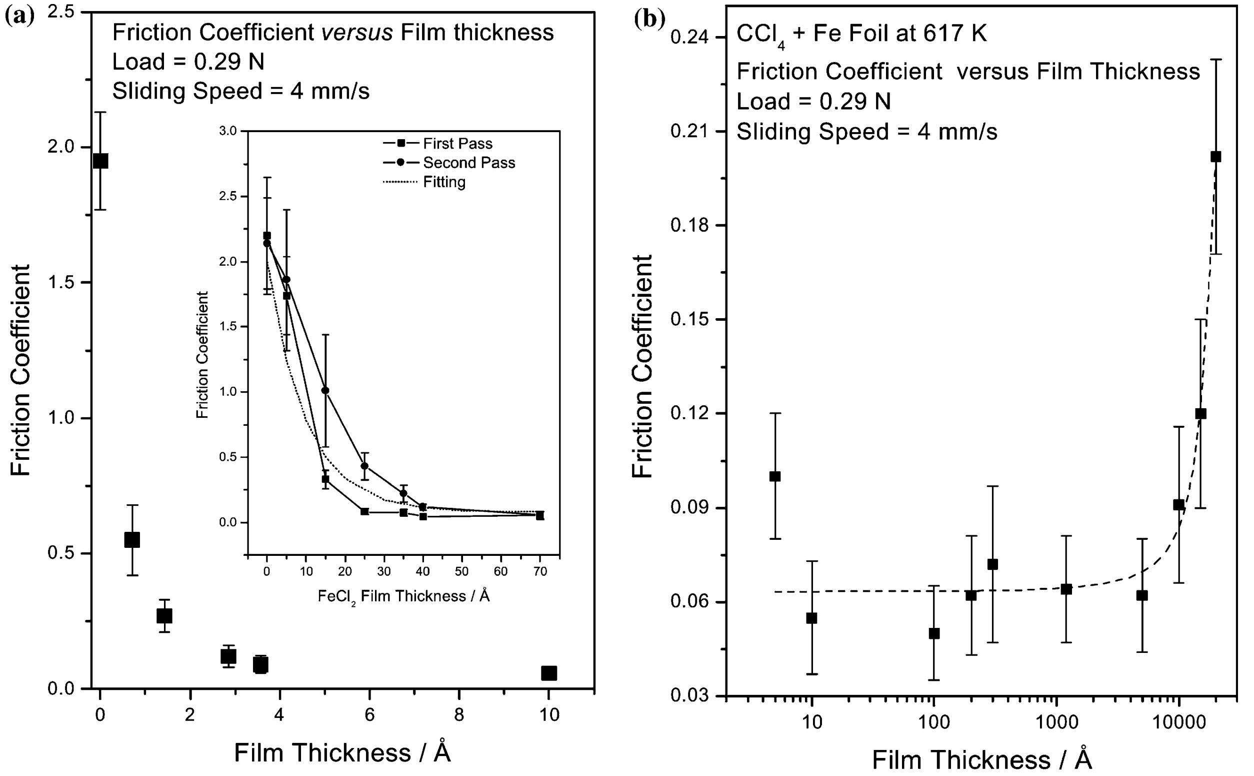

Figure 2. Plot of friction coefficient vs. film thickness for films grown from carbon tetrachloride vapor on clean iron at 617 K at a pressure of 1.4 Torr, (a) for films between 0 and 10 Å thick and (b) for films between 4 and 20,000 Å thick. Shown as an inset to (a) is the variation in friction coefficient with films thickness for FeCl$_2$ evaporated onto iron.

mate of the monolayer film thickness of 10 ± 2 Å [10]. The limiting friction coefficient for the reactively formed FeCl$_2$ film (0.06 ± 0.02) is slightly lower than that for the evaporated film (0.08 ± 0.02).

The variation of friction coefficient with applied load for reactively formed FeCl$_2$ films is displayed in figure 3 showing that the 10 and 200 Å thick films obey Amontons' law [17], while the 1200 Å thick film shows a variation of friction coefficient with load. A very thin (5 Å thick) film obeys Amontons' law for loads below ~1 N, but the friction coefficient increases at higher loads, presumably due to penetration of the film.

The friction coefficients of thick evaporated (■) and reactively formed (●) FeCl$_2$ films are compared in figure 4. This reveals that the friction coefficients of reactively formed films are substantially lower at a given film thickness than those that are evaporated onto the surface.

4. Discussion

It has been shown previously that carbon tetrachloride reacts with clean iron to form a film of FeCl$_2$ where at least a portion of the carbon diffuses into the bulk of the iron to form a carbide [13]. The film growth rate has been measured by monitoring the change in sample mass as a function of time and reaction conditions, where the film thickness was calculated by assuming that the film had the same density as bulk FeCl$_2$ [12]. These growth kinetics are used in the following to determine the thickness of the reactively formed films. The data of figure 2 reveal that the friction coefficient of a reactively formed FeCl$_2$ film on iron decreases rapidly with thickness, reaching a minimum value of 0.06 ± 0.02 when the film thickness reaches ~6 Å. Shown as an inset to figure 2(a) is a plot of the variation in friction coefficient for FeCl$_2$ evaporated directly onto the surface. This shows a similar decrease in friction coefficient with film thickness. However, there are some notable difference in the behavior of each system. First, the friction coefficient for the evaporated film reaches its minimum value when ~40 Å of FeCl$_2$ has been evaporated, while the reactively formed film attains its minimum value for a film 6 ± 2 Å thick. Second, the minimum friction coefficient for the reactively formed film is slightly lower than that for the evaporated film. It has been shown previously that the total average thickness of a KCl film required to minimize the friction coefficient corresponded to the saturation of the iron surface by KCl [8]. The first-layer film thickness was measured to be ~2.6 Å, while the total film thickness at this point was substantially larger. This effect was ascribed to the deposition of second and subsequent KCl layers prior to

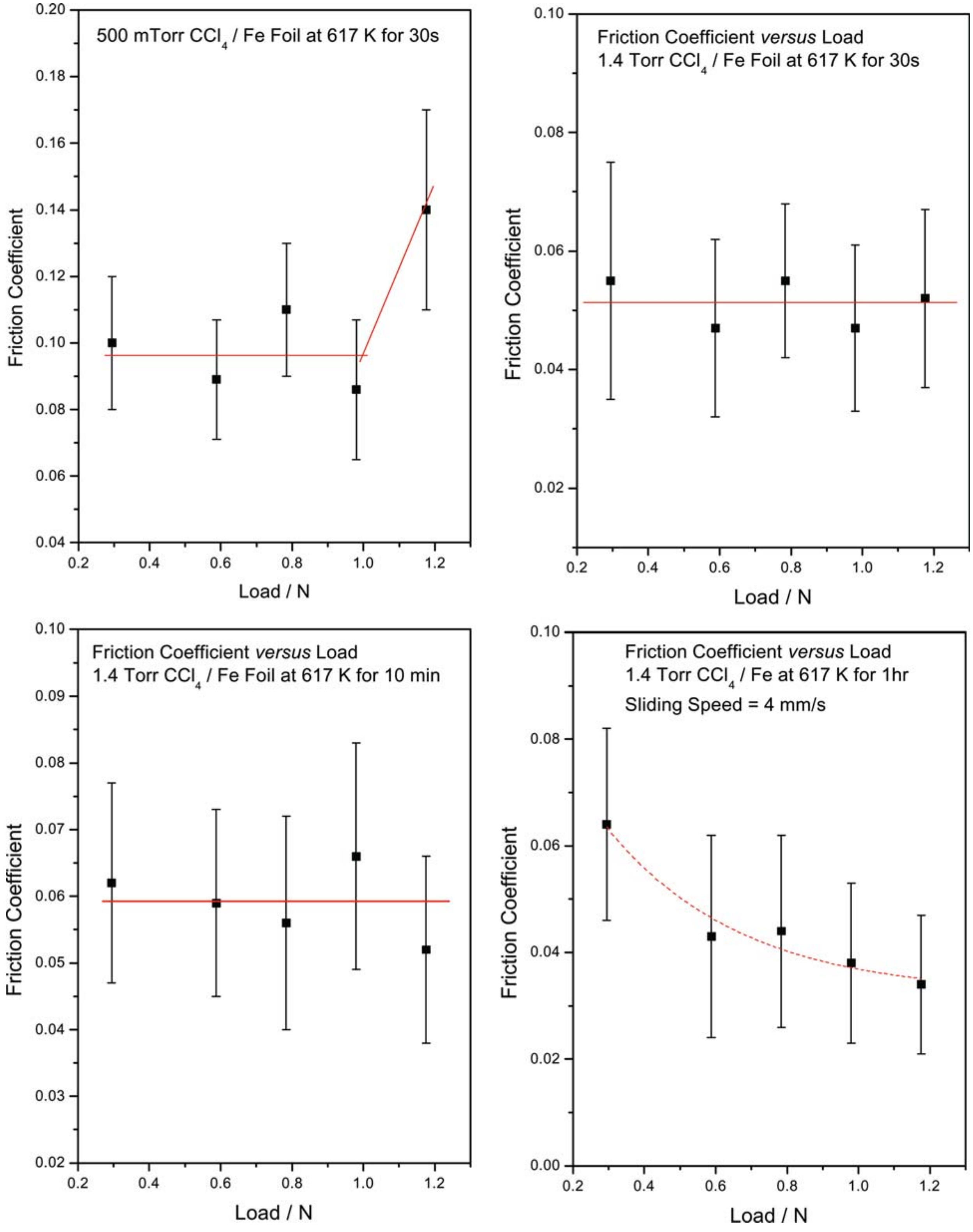

Figure 3. Plots of friction coefficient vs. applied loads for films grown from carbon tetrachloride vapor on clean iron at 617 K at a pressure of 1.4 Torr to give film thicknesses of 5, 10, 200 and 1200 Å.

the completion of the first. A similar situation applies in the case of evaporated $FeCl_2$ layers and a similar analysis in this case reveals that the first-layer $FeCl_2$ film thickness is 10 ± 2 Å [10]. Ferrous chloride forms a layer structure with the thickness of each layer being about ~8.5 Å [18], in good agreement with the estimate of the first-layer thickness of the evaporated film. This value is close to the thickness of the reactively formed $FeCl_2$

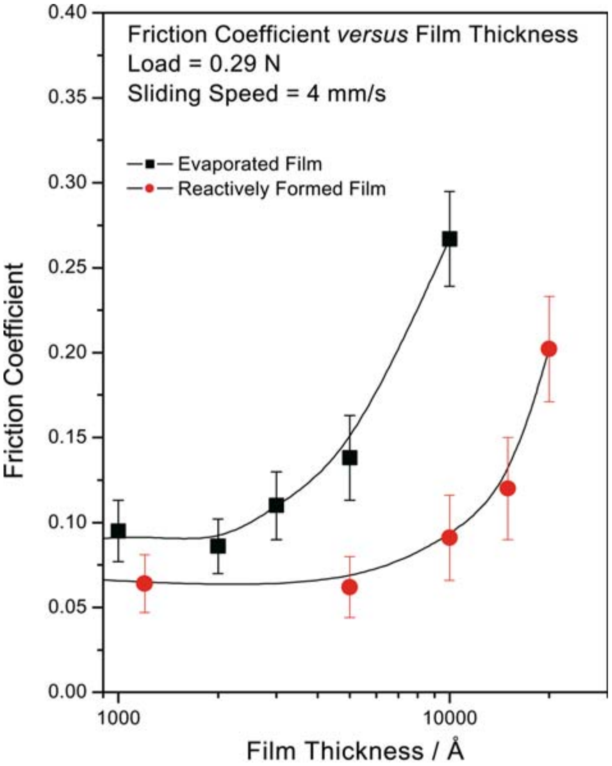

Figure 4. Comparison of the friction coefficient vs. film thickness for films between 10 and 20,000 Å thick grown either from carbon tetrachloride vapor on clean iron at 617 K at a pressure of 1.4 Torr (●) or by evaporation of $FeCl_2$ (■).

layer at which the minimum value of friction coefficient is initially attained (figure 2). The interpretation of this effect is that carbon tetrachloride reacts directly with the clean iron surface to form a $FeCl_2$ layer, causing the minimum in friction coefficient to be reached at a film thickness corresponding to this layer thickness. Following completion of this first monolayer, the friction coefficient obeys Amontons' law for films up to at least 200 Å thick (figure 3). Thinner films (~5 Å) show an increase in friction coefficient for higher loads, presumably due to the film being displaced from the contact region. The friction coefficient of thicker (~1200 Å) films formed after reaction for 1 h varies with applied load (figure 3). One possible explanation for this effect is that the film thickness is now larger than the roughness of the tribopin surface. This would form a conformal, elastic contact between the soft film and the tribopin such that the contact area no longer varies linearly with applied load leading to a decrease in friction coefficient with load as observed in figure 3. However, other effects such as a change in film morphology cannot be ruled out at this stage.

The slightly lower friction coefficient for the reactively formed film compared to the evaporated film may be ascribed to two possible effects. First, it may be due to the presence of some carbon in the substrate for the reactively formed film resulting in an increase in substrate hardness and a decrease in contact area [19]. Second it may be due to low-shear-strength crystal planes of the reactively formed film being oriented more parallel to the surface than in the evaporated films. This friction coefficient difference is illustrated more clearly for thicker $FeCl_2$ films in figure 4 where the reactively formed film now has a substantially lower friction coefficient than the evaporated film. This larger difference for thicker films may either be due to the larger amount of carbon in the bulk for the thicker films or indicate that the evaporated film is more randomly oriented than the reactively formed one.

5. Conclusions

The tribological properties of ferrous chloride films grown on pure iron at high pressures is investigated in ultrahigh vacuum. The friction decreases from the clean surface value of ~2 to a limiting value of 0.06 ± 0.02 after a film 6 ± 2 Å has been grown on the surface. In contrast, when $FeCl_2$ is evaporated onto iron, a minimum friction coefficient of 0.08 ± 0.02 is attained after a film ~40 Å thick has been deposited. It has been suggested previously that, during ferrous chloride evaporation onto the surface second and subsequent layers grow prior to the completion of the first layer and that the total film thickness of 40 Å corresponds to saturation of the first layer. In the case of a reactively formed film, carbon tetrachloride reacts directly with the surface to immediately form the monolayer. In this case, the friction coefficient reaches its minimum value at a thickness of ~6 Å, close to the $FeCl_2$ layer thickness in the bulk halide.

Acknowledgments

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