Growth Kinetics and Structure of Films Formed by the Thermal Decomposition of Methylene Chloride on Iron

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The kinetics of the formation of films by the thermal decomposition of methylene chloride on an iron surface is investigated using a microbalance where the film thickness X is shown to vary with time t as $X = X_m(1 - \exp(-Bt))$ where X_m is the maximum film thickness. X-ray photoelectron, Auger, and Raman spectroscopic analyses show that the film consists of an iron chloride and carbon, where Raman spectroscopy indicates that the carbon is present as small (~50 Å) particles. The observed kinetics are rationalized by assuming that growth is limited by thermal decomposition of methylene chloride at the gas-phase/film interface rather than transportation through the film and that the sites for thermal decomposition become poisoned as the reaction proceeds. Surface spectral analysis indicates that both the amount of surface carbon and the proportion of covalently bonded chlorine increase during film growth so that either the formation of a carbonaceous layer or the accumulation of an organochlorine species could be responsible for the cessation of growth.

Introduction

Lubricants that operate under conditions of extreme pressure are generally synthesized by dissolving chlorinated hydrocarbons in a base hydrocarbon fluid, and in this case, the chlorinated hydrocarbon provides the active component in the lubricant.[1–13] We have previously demonstrated that these extreme pressure (EP) additives thermally decompose at the hot interface between the lubricated surfaces to deposit a film that consists of an iron halide and carbon.[14–18] This film plays the role of a solid lubricant which prevents seizure under the influence of the large applied loads. Insights into the growth kinetics and structure of the films formed by the thermal decomposition of chlorinated hydrocarbons at iron surfaces are, therefore, crucial to a full understanding of the process of extreme pressure lubrication using chlorinated hydrocarbons. A more detailed understanding of this chemistry should also prove useful in the design of alternative, more environmentally benign, lubricant additives.[19–24]

It has been shown previously that interfacial temperatures as high as ~900 K can be attained at the contacting surfaces under the conditions encountered in the extreme pressure regime. Methylene chloride thermally decomposes at these temperatures to form a film of thickness X which empirically has been shown to vary as a function of time t as

$$X = X_m \left(1 - e^{-Bt}\right) \qquad (1)$$

where X_m is the maximum film thickness and B a constant.[14,18]

Such film growth kinetics are completely different from those encountered for oxidative growth of films where parabolic ($X^2 \propto t$) or logarithmic growth curves are generally encountered.[25] Limitation of growth by thermal decomposition of methylene chloride at the growing interface should yield a linear growth law ($X \propto t$), the growth rate merely reflecting the decomposition kinetics. The following addresses questions concerning processes that control film growth and scrutinizes the nature of the film formed by methylene chloride decomposition both as a function of reaction time and distance through the film.

Experimental Section

Film growth kinetics were measured using a microbalance to monitor the change in sample mass as described previously.[15,18] Films were deposited on an iron foil (Johnson Matthey, 99.99%) which was 0.025 mm thick, and the sample was removed from the microbalance following film deposition and stored in an evacuated desiccator for subsequent analysis. The film was analyzed using Auger, X-ray photoelectron, and Raman spectroscopies.

Auger spectra were collected using a Physical Electronics chamber equipped with a single-pass, cylindrical-mirror analyzer, and normal-incidence electron gun using an incident current of ~8 μA at ~3 kV beam energy. A diminution in the chlorine Auger peak was noted following repeated spectral scans, and experiments that were performed by continuously monitoring the Cl KLL Auger transition as a function of time indicated a half-life of ~60 min for the decay in intensity of this peak. Care

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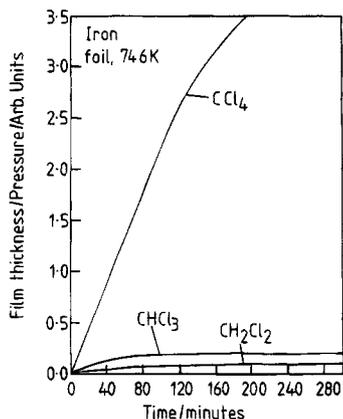(25) Cabrera, N.; Mott, N. F. *Rep. Prog. Phys.* **1949**, *12*, 163.

Figure 1. Film thickness normalized to the pressure of the chlorinated hydrocarbon plotted *versus* time for a number of volatile chlorinated hydrocarbons obtained with a microbalance using 15.0 Torr of methylene chloride, 7.5 Torr of chlorform, and 4.0 Torr of carbon tetrachloride.

was therefore taken to minimize electron exposure by extinguishing the electron beam when spectra were not being accumulated. This chamber was also equipped with an ion-bombardment source operating at a beam energy of ~2 kV. Typical ion currents of 10^{-2} A/m^2 were used, which resulted in a removal rate of approximately 5–20 Å/min.[18]

X-ray photoelectron spectra were obtained using a VG Escalab spectrometer equipped with a fast-entry interlock, which allowed up to six samples to be loaded onto a carousel and introduced simultaneously into the UHV portion of the chamber. Spectra were collected using unmonochromatized Mg Kα radiation, and the 100-mm radius hemispherical analyzer operated at a pass energy of 50 eV. This yields an overall spectral resolution of 0.8 eV.

Raman spectra were collected in backscattering mode, and the incident exciting radiation was furnished using an argon ion laser operating at 466 nm. Typically, laser powers of 1 W were used. Scattered radiation was analyzed using a Spex double monochromator and detected using a Peltier-effect-cooled photomultiplier tube operating in pulse-counting mode. The monochromator was under computer control, which was also used to store the resulting Raman signals.

Results

Figure 1 shows film growth kinetics measured using a microbalance at a temperature of 746 K for CCl_4, $CHCl_3$, and CH_2Cl_2. The ordinate indicates the film thickness normalized to the reactant pressure. Clearly, films grow significantly more vigorously when CCl_4 is used, and indeed, growth ceased in this case after ~240 min due to the complete consumption of the iron substrate. Films are formed significantly less rapidly when both CH_2Cl_2 and $CHCl_3$ vapors are used, and although $CHCl_3$ is slightly more reactive than CH_2Cl_2, both of these chlorinated hydrocarbons exhibit very similar growth kinetics. The relative film growth activities correlate well with the effectiveness of each of these chlorinated hydrocarbons as extreme pressure lubricant additives.[18]

Film growth kinetics for the thermal decompositions of methylene chloride on an iron foil were measured as a function of both temperature and pressure, and these results are presented in ref 18. In all cases, growth curves are well fit by a function of the form shown in eq 1, and the saturation film thickness X_m and the initial growth rate $r_0 = dX/dt|_{t=0}$ increase as a function of both sample temperature and pressure.

The nature of the film deposited by the thermal decomposition of methylene chloride is analyzed using Raman, X-ray photoelectron, and Auger spectroscopies. The first technique (Raman spectroscopy) probes the bulk nature of the sample since signals emanating from the
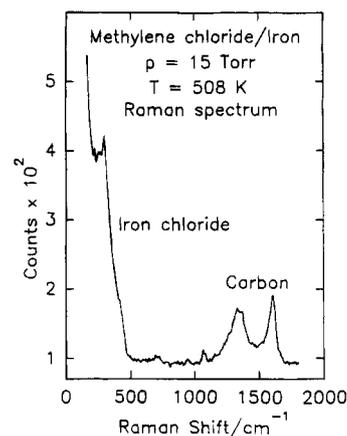

Figure 2. Raman spectrum obtained for a film grown by the thermal decomposition of methylene chloride on an iron foil at 508 K using a methylene chloride pressure of 15 Torr.

whole film are detected.[26] The last two techniques (Auger and X-ray photoelectron spectroscopies) are surface sensitive and probe the outermost layers of the film.[27] Depth profile information can be obtained in these cases by removing material using argon ion bombardment. Both Auger and X-ray photoelectron spectroscopies reveal the presence of iron, chlorine, and carbon, consistent with previous analyses of the films and V-blocks indicating that the film consists of an iron halide and incorporates carbon. These analyses are also consistent with previous results which show that the tribological behavior of methylene chloride as an extreme pressure lubricant additive can be effectively described by a model that assumes that an $FeCl_2$ layer grows on the iron substrate and that this acts as a solid lubricant,[14–18] which ultimately fails when the interface reaches the melting point of $FeCl_2$ (943 K[28]).

Figure 2 displays a typical Raman spectrum, in this case, of a film grown at 508 K by methylene chloride decomposition. Spectra of films formed using other temperatures and pressures are essentially identical. The spectrum shows a broad feature between 200 and 400 cm^{-1} due to lattice vibrations of an iron halide, consistent with the above interpretation of the tribological behavior in terms of melting of an iron halide film. Also evident is a broad doublet with peaks at 1600 ± 10 and 1350 ± 10 cm^{-1}. Such peaks have previously been assigned to the presence of small carbonaceous particles, and this will be discussed in greater detail below.[29–31]

Figure 3 displays the results of an Auger analysis of the outer layer of films deposited from methylene chloride as a function of growth time at a reaction temperature of 508 K using a pressure of 15 Torr. The ratio of the intensity of the chlorine peak to the sum of the carbon and chlorine signals (designated Cl/(C+Cl)) is plotted *versus* growth time where the chlorine signal is measured from the peak-to-peak amplitude of the Cl LMM signal (180 eV kinetic energy (KE)) and the carbon concentration from the C KLL Auger peak (at 275 eV KE). The Cl/(C+Cl) Auger ratio decreases as the reaction proceed, indicating a relatively larger amount of carbon at the surface of the

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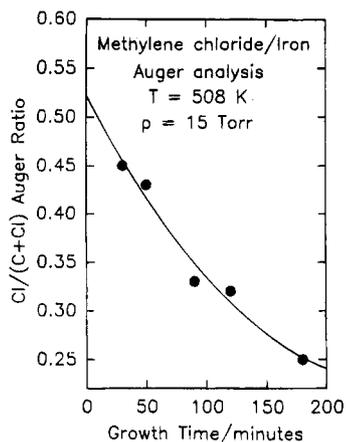(31) Plano, L. S.; Adar, F. *Proc SPIE* **1987**, 822.

Figure 3. Plot of the Cl/(C+Cl) Auger ratio for a film deposited from 15 Torr of methylene chloride at 508 K as a function of growth time.
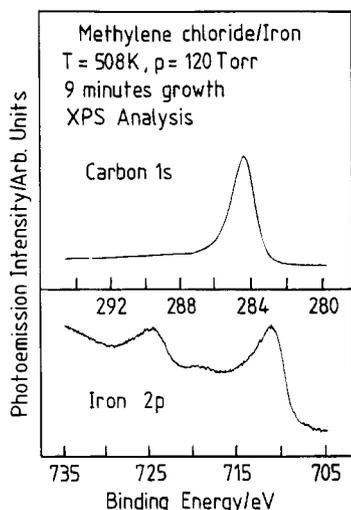

Figure 4. Typical C 1s and Fe 2p photoelectron spectra for films deposited on iron by the thermal decomposition of 120 Torr of methylene chloride at 540 K.

as it film grows. As noted above, the chlorine Auger signal decreases with increasing electron exposure, and care was taken to minimize exposure to the exciting electron beam. In addition, the consistency of the data was checked by periodically moving the sample slightly so that the focused electron beam intercepts a different, previously unaffected, portion of the sample. The detection of substantial electron stimulated desorption confirms the presence of a halide, since previous experiments have shown that these exhibit relatively large esd cross sections.[32,33]

X-ray photoelectron spectra for films grown from methylene chloride (120 Torr) at 508 K are displayed in Figures 4 and 5. Figure 4 shows typical Fe 2p and C 1s features which do not change in binding energy as the film grows. The C 1s binding energy of the prominent peak at 284.4 eV corresponds to graphitic carbon.[27,34] The iron 2p spectrum has a $2p_{3/2}$ peak at 711.3 ± 0.2 eV and the $\Delta(2p_{1/2} - 2p_{2/3})$ spacing is 13.6 ± 0.2 eV. Peaks at these binding energies indicate the presence of either Fe^{2+} or Fe^{3+} (both yielding essentially identical binding energies)[27,34] so that the spectrum is consistent with the

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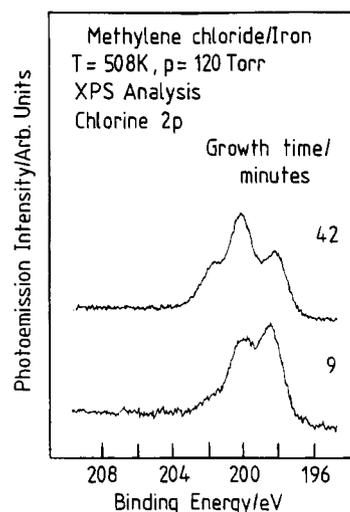(35) Yang, R. T.; Yang, K. L. *J. Catal.* **1984**, *90*, 194.

Figure 5. Cl 2p X-ray photoelectron spectra of films deposited by the thermal decomposition of methylene chloride (120 Torr, 508 K) after 9 and 42 min deposition.
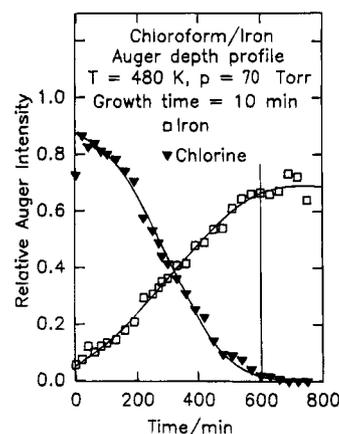

Figure 6. Results of a depth profile of a film grown by methylene chloride decomposition on iron at 480 K using a pressure of 70 Torr for 600 s. The peak-to-peak intensities of the Cl LMM and Fe LMM peaks are displayed as a function of ion bombardment time when a beam energy of 2 kV with a flux of 10^{-4} A/m^2 is used.

presence of an iron halide at the surface. An additional small peak is observed at ~719 eV and is due to a shake-up satellite. Figure 5 displays Cl 2p spectra of the surface of films grown from methylene chloride for 9 and 42 min. The spectrum after 9 min of deposition shows two peaks centered at 198.7 ± 0.2 and 200.3 ± 0.2 eV binding energies. The peak at 198.7 ± 0.2 eV binding energy is assigned to the $2p_{3/2}$ level of a halide and the peak at 200.3 ± 0.2 eV to the corresponding $2p_{1/2}$ state. Additional peaks are evident in the spectrum after 42 min of deposition (Figure 5) so that it now exhibits peaks at 198.7 ± 0.2, 200.3 ± 0.2, and 202.0 ± 0.2 eV binding energies. The extra peaks are assigned to the presence of another surface chlorine species with a $2p_{3/2}$ binding energy of 200.3 ± 0.2 eV with a corresponding $2p_{1/2}$ peak at 220.0 ± 0.2 eV.

Finally, shown in Figure 6 is the result of an Auger analysis depth profile of a film grown by $CHCl_3$ decomposition at 480 K with a pressure of 70 Torr for 600 s. Note that the growth kinetics for methylene chloride and chloroform are essentially identical. Extrapolation of kinetic data obtained in the microbalance indicates that this leads to a film of ~1000 Å thick. The chlorine and iron Auger signals are plotted as a function of bombardment time using argon ions (1 kV, 10^{-2} A/m^2), and the results indicate that the chlorine concentration decreases

essentially linearly with distance into the film and the iron Auger signal *increases* linearly. The chlorine Auger signal diminishes to zero after 600 min of ion bombardment, and the iron signal reaches a constant value after the same time; the film is removed by 600 min of ion bombardment. Taking an approximate sputtering rate of 5–20 Å/min[16] suggests a film thickness of 3000–12 000 Å. As mentioned above, microbalance results show that a ~1000 Å thick film should be deposited under these conditions, and although ion bombardment indicates a film thickness of the correct order of magnitude, this thickness appears to be somewhat larger than measured from the change in mass of the sample. This may be due to systematic errors referred to above that arise from assuming that the film consists entirely of $FeCl_2$ whereas it, in fact, incorporates carbon. It should also be noted that the quoted sputtering rates are approximate values.

Discussion

It has been demonstrated that films grow from the thermal decomposition of methylene chloride on iron so that the film thickness varies according to eq 1. Analysis of the composition of the film shows that it consists of an iron halide and carbon, and the X-ray photoelectron data of Figures 4 and 5 are consistent with this view. These conclusions are confirmed by the Raman spectrum in Figure 2 which displays a broad feature between 200 and 400 cm^{-1} due to lattice vibrations of an iron halide. In addition, the doublet evident at ~1350 and ~1600 cm^{-1}, the so-called d and g bands, respectively, indicates the presence of graphitic carbon particles in the film.[29-31] The peak at 1350 cm^{-1} is a disorder-induced feature due to the M-point phonon because of a breakdown of the $k = 0$ selection rule for graphitic carbons with small particle sizes.[30] The peak at 1600 cm^{-1} has been assigned to an E_{2g} carbon–carbon stretching mode. This mode has a vibrational frequency of 1580 cm^{-1} in the case of crystalline, graphitic carbon. However, the shift of the g band peak to higher frequency (to 1600 cm^{-1}) appears to be consistent with observed spectra for noncrystalline, mainly graphitic carbons. The zone boundary phonon at 1620 cm^{-1} has also been known to contribute to small shifts in the g band. In the data presented here, this contribution is likely to be small due to the sharpness of the 1600 cm^{-1} peak. It has been demonstrated that the relative intensities of the d and g bands provide an approximate indication of particle size where it has been shown that the particle size L_a and the intensity ratio of the d and g bands I_d/I_g are approximately related by $L_a = 44(I_d/I_g)^{-1}$ Å. Measurement of this intensity ratio for films formed by methylene chloride decomposition on iron indicates that the graphitic particles are ~50 Å in diameter. The shapes and, in particular, the g band width give an indication of the form of carbon present in the film. Analysis of the Raman spectra in Figure 2 yields an average g band width of 60 cm^{-1}. This is consistent with observed spectra for noncrystalline, mainly graphitic, carbons specifically in the region of glassy carbons.

The growth kinetics observed for films deposited by methylene chloride decomposition on metal surfaces are not typical for these processes where logarithmic laws are found for growth of thin films at relatively low temperatures, and parabolic growth laws are found at higher temperatures.[25] In addition, the saturation film thickness is significantly less than would be anticipated for direct oxidation of the metal. For example, for parabolic growth where $X^2 = 2At$, writing $A = A_0 \exp(-U/RT)$ and using typical values of $A_0 \sim 1$ cm^2/s and $U \sim 1.5$ eV[25] indicate that a film of ~5 μm should be deposited after 200 min growth at ~470 K, whereas a film of only 0.05

μm is deposited, about 2 orders of magnitude less. The idea that halide films *can* grow more rapidly than observed for methylene chloride is confirmed by the results of Figure 1, which demonstrate that films formed by CCl_4 decomposition grow much more rapidly than when either CH_2Cl_2 or $CHCl_3$ is used.

Rapid oxidative growth of thin films is facilitated by the electric field that develops across the film due to a contact potential difference between the film surface and substrate which varies as $1/X$, where X is the film thickness. A theoretical analysis of this model leads to the parabolic growth law referred to above. In addition, it predicts that the concentrations of both oxidant (in this case chlorine) and reductant (iron) should vary linearly through the film. The data shown in Figure 6 reveal such a linear variation in concentrations throughout the film, and these results are consistant with an electric-field-assisted model for transportation of ions through the film.

One possible explanation for the slow growth rate from methylene chloride is that ion diffusion is inhibited in this case, perhaps by the presence of carbon within the film. This should, nevertheless, lead to a similar parabolic growth law, the only difference being a smaller value of the constant A corresponding to a lower diffusion coefficient.

An alternative explanation is that film formation is limited by reaction of the chlorinated hydrocarbon at the growing iron chloride + carbon interface. This view is supported by the variation in growth kinetics as a function of reactant pressure[18] where both the initial rate and maximum film thickness increase as a function of increasing reactant pressure. In this case, however, a linear initial growth rate would be expected, just reflecting the decomposition kinetics at the interface, subsequently becoming a parabolic growth law for much thicker films as the reaction becomes limited by transport through the film. This suggests that growth ceases due to blocking of surface decomposition sites as the reaction proceeds. The model that will be adopted assumes that ion transport through the film is a fast (and electric-field-assisted) process and that film growth is limited by thermal decomposition of the reactant (here CH_2Cl_2) at the growing interface and that the surface becomes poisoned, eventually leading to a complete cessation of growth. It is assumed that, at some point during the growth reaction, the *coverage* of "active" sites for methylene chloride decomposition is Θ, so that at $t = 0$, $\Theta = 1$ and at $t = \infty$, $\Theta = 0$ (growth stops). The kinetic equation for the removal of active sites is written as follows:

$$-\frac{d\Theta}{dt} = k_s P_r{}^n \Theta \qquad (2)$$

where the active site removal rate is assumed to be first order in "active site" coverage and nth order in reactant pressure, P_r. k_s is the rate constant for site blockage, which is also assumed to be temperature dependent. This yields a time dependence of the "active" site coverage as

$$\Theta = \exp(-k_s P_r{}^n t) \qquad (3)$$

If the number of potential active sites for methylene chloride decomposition at the interface is N per unit area and the film growth rate dX/dt is limited by surface reaction rather than transport through the film, then

$$\frac{dX}{dt} = k_r P_r{}^m N \Theta \Omega \qquad (4)$$

which is independent of film thickness X. Here Ω is the

volume of the film formed by each reaction at an active site, k_r is the reaction rate constant for methylene chloride decomposition (also taken to be temperature dependent), and m is the decomposition-rate reaction order.

Combining eqs 3 and 4 yields

$$\frac{dX}{dt} = k_r P_r{}^m \Omega N \exp(-k_s P_r{}^n t) \qquad (5)$$

and putting $A = k_r P_r{}^m \Omega N$ and $B = k_s P_r{}^n$ gives

$$\frac{dX}{dt} = A \exp(-Bt) \qquad (6)$$

which is simply integrated to yield the experimentally observed growth kinetics. The initial rate r_0 of film growth $dX/dt|_{t=0} = A$ is given by

$$r_0 = k_r P_r{}^m \Omega N \qquad (7)$$

and the maximum film thickness X_m is

$$X_m = \frac{k_r \Omega N}{k_s} P_r{}^{(m-n)} \qquad (8)$$

The initial growth rate r_0 is measured as a function of reactant pressure from the parameters used to obtain the best fits to a curve of the form shown in eq 1 (X_m, B), as shown previously,[18] and yields and order of 1.02 ± 0.13, indicating that the initial film growth rate is first-order in reactant pressure. According to eq 7 therefore, $m = 1$, so that

$$r_0 = k_r P_r \Omega N \qquad (9)$$

The corresponding pressure dependence for the maximum film thickness X_m is shown in Figure 7, which plots $\ln X_m$ versus $\ln(\text{pressure})$, referring to methylene chloride pressure. The slope of this curve is 1.07 ± 0.14 so that according to eq 8, $m = n = 1.07 \pm 0.14$; since $m = 1$, then $n = 0$, so that eq 8 can be rewritten:

$$X_m = \frac{k_r \Omega N}{k_s} P_r \qquad (10)$$

The temperature dependence of the rate constants can be rewritten explicitly using the usual Arrhenius form so that $k_r = A_r \exp(-E_r/RT)$ and $k_s = A_s \exp(-E_s/RT)$, where T is the absolute temperature, A_s and A_r the reaction pre-exponential factors, respectively, and E_s and E_r the corresponding activation energies. Equations 9 and 10 can therefore be rewritten as

$$r_0 = A_r P_r \Omega N \exp(-E_r/RT) \qquad (11)$$

and

$$X_m = \frac{A_r \Omega M P_r}{A_s} \exp(-(E_r - E_s)/RT) \qquad (12)$$

The Arrhenius plot for r_0, the initial growth rate ($\ln(r_0)$ versus $1/T$), is shown in Figure 8. The slope yields an activation energy of 9.7 ± 0.9 kcal/mol for E_r. Note that this value differs from that quoted in ref 18, which is in error. The corresponding plot for the maximum film thickness ($\ln X_m$ versus $1/T$) is shown in Figure 9. In this case, the slope of this curve yields an energy of 7.5 ± 0.6 kcal/mol which, according to eq 12, is $E_r - E_s$. This yields straightforwardly a very low value of E_s, the activation energy due to site blocking, of $\sim 2.0 \pm 1.5$ kcal/mol.
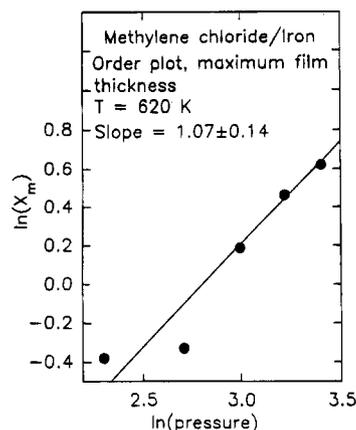

Figure 7. Plot of $\ln X_m$, where X_m is the maximum film thickness, *versus* $\ln(\text{pressure})$ for film growth on iron at 620 K.
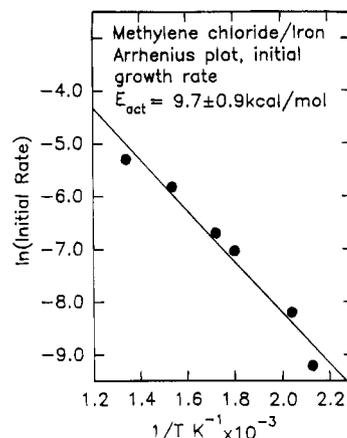

Figure 8. Arrhenius plot for the initial growth rate r_0 for methylene chloride on iron using a reactant pressure of 15.0 Torr.
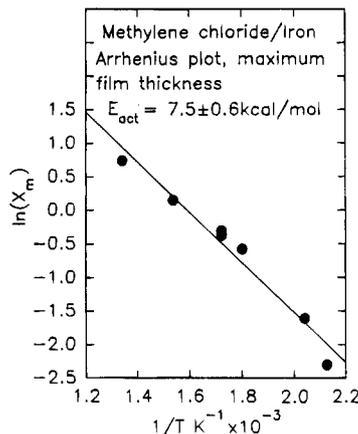

Figure 9. Arrhenius plot for the saturation film thickness X_m for methylene chloride on iron using a reactant pressure of 15.0 Torr.

A striking feature of the film growth curves as a function of temperature[18] is the relative constancy of the time required for film growth to saturate over a large temperature range between 470 and 650 K. This is a direct consequence of the low value of E_s. This can be illustrated by taking the time to 90% saturation, (i.e., $X/X_m = 0.9$) as a measure of the growth period. This value is designated $t_{0.9}$ and is given by $t_{0.9} = (2.3/A_s)\exp(E_s/RT)$ and depends only on E_s. Taking $t_{0.9} = 160$ min at 650 K and using the above value of E_s shows that $t_{0.9}$ is 198 min at 570 K, 260

min at 490 K, and 290 min at 470 K, in good agreement with experimental data.[18]

The buildup of a carbonaceous deposit at the surface of the growing film is a possible candidate for the poisoning of film growth by methylene chloride decomposition since the presence of small graphitic particles which are incorporated into the growing film is revealed using Raman spectroscopy (Figure 2). In addition, the presence of carbonaceous films on catalyst surfaces is a well-known source of poisoning.[35-37] The data of Figure 3 indicate that the relative amount of carbon at the surface of the growing film does increase as growth proceeds in support of this hypothesis. Note, also, that the presence of surface carbon has been shown to affect the rate of halide formation on iron using a single crystal surface in ultrahigh vacuum.[38]

On the other hand, the data of Figure 5 show that the Cl 2p peak also changes significantly in shape as growth proceeds, with the 200.3 eV peak growing relative to that at 198.7 eV as the deposition time increases from 9 to 42 min. The binding energy of this peak corresponds to chlorine covalently bonded to carbon[27] and may possibly be due to the accumulation of some chlorine-containing organic species on the surface. Accumulation of such an organochlorine species on the surface of the growing film would also inhibit subsequent thermal decomposition of the chlorinated hydrocarbon.

The presence of an outer, either carbon or organochlorine, poisoning layer is not generally likely to substantially affect the tribological properties of the layer since the outermost selvedge of the growing film is continually removed because of the relative motion of the contacting surfaces.

Conclusions

Films consisting of iron chloride and incorporating graphite particles of ~50 Å in diameter are grown on iron by the thermal decomposition of methylene chloride, where the film thickness X varies with time according to $X = X_m(1 - e^{-Bt})$, where X_m is the maximum film thickness and B a constant. These growth kinetics and the temperature and pressure dependencies of X_m and B are rationalized by a model that assumes that growth is limited by the surface decomposition of methylene chloride rather than transportation through the film and that the concentration of active sites for methylene chloride decomposition decreases *via* first-order kinetics as growth proceeds.

Analyses of the interface as the film grows suggest that the formation of either surface carbonaceous species or an organochlorine species (or both) may be responsible for the poisoning of the surface of the film.

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