Initiation of Lubricant Catalytic Decomposition by Hydrogen Evolution from Contact Sliding on CHx Overcoats

Chao-Yuan Chen, Walton Fong, and David B. Bogy

Computer Mechanics Laboratory Department of Mechanical Engineering University of California at Berkeley, CA 94720

C. Singh Bhatia SSD/IBM, 5600 Cottle Road, San Jose, CA 95193

Abstract

Tribo-chemical studies of the head/disk interface (HDI) were conducted using hydrogenated (CH_x) and nitrogenated (CNx) carbon disk samples coated with perfluoropolyether ZDOL lubricant. The studies involved drag tests with uncoated and carbon-coated Al_2O_3 -TiC sliders and thermal desorption experiments in an ultra-high vacuum (UHV) tribochamber. We observed that the hydrogen evolution from CHx overcoats initiates lubricant catalytic decomposition with uncoated Al_2O_3 /TiC sliders, forming CF₃ (69) and C₂F₅ (119). The generation of Hydroflouric acid (HF) during thermal desorption experiments provides the formation mechanism of Lewis acid, which is the necessary component for catalytic reaction causing Z-DOL lube degradation. On the other hand, for CNx films, lubricant catalytic decomposition was prevented due to less hydrogen evolution from the CNx overcoat.

Keywords: Tribochemistry; Hydrogenated carbon overcoat; Nitrogenated carbon overcoat, ZDOL decomposition; Friction and wear; Thermal desorption, Hydrogen Evolution, Lewis Acid, and Catalytic reaction

I. INTRODUCTION

To reduce friction and wear magnetic recording thin-film disks have a hard overcoat lubricated with a thin layer of a liquid lubricant. Because of the superior properties, such as low vapor pressure, good viscosity, high thermal stability and chemical inertness, perflouropolyethers (PFPEs) have been extensively used as the lubricants of magnetic media in hard disk drives. The molecular structure, containing only carbon, fluorine and oxygen atoms, gives PFPEs this set of properties. Their thermal stability and decomposition mechanisms have been extensively studied. Many experiments demonstrate that PFPEs, subjected to electron irradiation, are easily decomposed into smaller fragments [1]. Vurens et al. [2] used low energy electrons to bombard PFPEs and observed that the electron decomposition of PFPEs occurs at an energy below their ionization potential (about 14 eV). It is reported that the decomposition rates of PFPEs are much higher in the presence of Lewis acid forming materials, such as Fe₂O₃ [3], Al₂O₃ and AlCl₃ [4-6], than their intrinsic decomposition rate. Our earlier studies of the decomposition of ZDOL lubricant on nitrogenated carbon overcoats (CHx) [7, 8] indicate that the decomposition rate is significantly affected by the slider materials. The use of uncoated Al₂O₃-TiC sliders leads to the rapid decomposition of ZDOL due to catalytic reactions, while carbon coated sliders produce less intense decomposition due primarily to frictional actions [9].

The thermal stability of PFPE molecules has also been studied extensively. PFPE is intrinsically stable below ~570K, even in an oxygen atmosphere [10, 11]. However, Fomblin-Z dissociates in the presence of Lewis acid sites on Fe_2O_3 at 450K [12], and on Al_2O_3 at 470K [13]. Lin et al. [14] used temperature-programmed reaction/desorption (TRP/D) and electron

stimulated desorption (ESD) to study the roles of temperature and triboelectric charges in the decomposition of Fomblin-ZDOL lubricant molecules. They showed that the threshold temperature for dissociation of the Fomblin-ZDOL molecule is 500-550K in accordance with the known thermal stability of the free ZDOL molecule. Vurens [15] also showed that molecules having a CF_2 - CF_3 endgroup (Demnum S65) display enhanced thermal stability compared to molecules with the CF_2 - CF_2 - CH_2 - CH_2 O-phenyl endgroup (Demnum SP). Gellman [16] showed that the heat of adsorption of the hydrocarbon ether was greater than that of the corresponding fluorocarbon ether, suggesting that the ethers are bonded to the films through the donation of the electron pairs on the oxygen atom. Gellman also proposed a model in which the electropositive nature of the hydrogen in the a-CH films weakens the extent of electron donation from the ether lone pairs and, hence, weakens the bonding of the ethers to the a-CH films.

Furthermore, Perry [17] used temperature-programmed desorption and scanning force microscopy to probe the interaction of ZDOL with both hydrogenated carbon overcoats and nitrogenated carbon overcoats. The data showed that the nitride surfaces are more reactive toward the ZDOL lubricant and, as a result, the thin lubricant film is more tightly bound to the overcoats. As the flying height of sliders approaches zero and near contact, the chances of contact between the head and the disk are greater. Ettles [18] used a numerical solution in two dimensions to predict the thermal effects of the asperity contact between sliders and magnetic recording disks. He showed that temperatures exceeding several hundred degrees centigrade are quite possible. Suzuki et al. [19] estimated that the contact temperature for the MnZn ferrite slider/thin film disk may be up to 550K. The temperature rise and signal loss were especially significant when crash of the slider occurred, resulting in large-scale wear of the disk surface.

Therefore, understanding the thermal response of the materials used in hard drives becomes imperative.

Recently, a number of manufacturers of magnetic recording media have replaced the CHx overcoat with an amorphous nitrogenated carbon (a-CNx) overcoat. Most reports have attributed the tribological benefits of CNx overcoats relative CHx overcoats to the increased hardness of the CNx film [20-22]. However, altering the nature of the carbon surface could also strongly influence the PFPE lubricant by modifying the adhesive strength, bonding kinetics, lubricant orientation, and lubricant mobility [23]. A change in any of these properties could easily manifest itself in substantially different tribological properties of the computer hard disk.

In this paper, we study the ZDOL decomposition mechanisms on hydrogenated carbon films (CHx) and nitrogenated carbon films (CNx) using an ultra-high vacuum (UHV) tribochamber equipped with a mass spectrometer. The studies consist of drag tests and thermal desorption experiments in the UHV tribochamber. Two decomposition processes of ZDOL under sliding friction conditions are studied, one is with a carbon film coated slider, and another is with an uncoated Al₂O₃-TiC slider. Chemical bonding theory is used to analyze the decomposition process of ZDOL. The decomposition mechanisms caused by friction, electron bombardment and catalysis are proposed. Moreover, the effects of thermal stability, tribocharge, mechanical action and Lewis acid catalysis on ZDOL decomposition are discussed. The results show that for CNx films the catalytic reactions were much than for CHx, presumably due to less hydrogen evolution from the CNx overcoat.

II. Experimental procedure and set-up

The UHV tribochamber consists of a disk spindle, a slider actuator, a substrate heater, and a high-resolution quadrupole mass spectrometer (QMS) equipped in a vacuum chamber with base pressure $< 2 \times 10^{-8}$ Torr, which was illustrated in a previous paper [24]. The QMS provides in-situ detection of the gaseous products generated during drag tests and thermal desorption studies. The QMS can monitor simultaneously 15 different atomic mass units (AMUs) ranging from 1 to 500 along with friction or temperature data from strain gauge transducers or a thermocouple, respectively. It is noted that all AMUs from 1 to 192 of ZDOL decomposition products generated at the Al₂O₃/TiC slider/CHx disk interface were previously investigated in the same test conditions in our laboratory, thus only the most important AMUs were monitored in this study.

Drag tests in the tribochamber were conducted as follows. Initially, the tribochamber was baked out at 350K in high vacuum for 24 hours. The chamber was then backfilled with Argon gas as the disk and slider samples were mounted inside. Next, the chamber was pumped down to a base pressure of 2 x 10^{-8} Torr and the channels of the QMS were assigned to selected AMUs. Background intensities were recorded before the drag tests were initiated with the following parameters: 0.2 m/s drag speed, a load of 30 mN, and a sliding time of 20 minutes. The sliders were 30% (1.2mm x 1mm) negative pressure Al₂O₃/TiC sliders with and without amorphous carbon films on the air bear surfaces. The disks were commercial 95mm thin film disks with 105Å amorphous hydrogenated carbon overcoat (CHx) or 105Å amorphous nitrogenated carbon

overcoat (CNx). The hydrogen content in the CHx film was 30 atomic %, and it was 5 atomic % in the CNx film. The disks were lubricated with ZDOL by a dipping process. The resulting thickness of ZDOL on the disks was 12Å, measured by FTIR.

In preparation for the thermal desorption tests in the tribochamber, in addition to baking the chamber, the heater was also baked at 600K in high vacuum for 4 hours to bake out the residual lubricants left on the heater after each thermal desorption tests. A CHx/ZDOL disk was cut into square pieces of roughly 4 cm². The lubricated samples were mounted onto a heater and the temperatures of the samples were measured by a thermocouple in contact with the heater near the testing samples. As with the drag tests, the chamber was pumped down to 10⁻⁸ Torr and the channels of the QMS were assigned to selected AMUs. A typical experiment consisted of heating a sample at a rate of 0.2K/s starting at room temperature and stopping before 550K. A mass spectrum was collected on a computer every two seconds (i.e., every 0.4K) during the heating of the samples. Afterwards, the spectra were analyzed in order to obtain the thermal desorption profile for each mass as a function of sample temperature.

III. Results and discussion

A. Study of the decomposition mechanisms of ZDOL lubricant/hydrogenated carbon (CH_x) overcoats

In this section, we present and discuss the results from the UHV drag tests. Figure 1 shows the friction coefficient curves for the ZDOL lubricated CHx disks against an uncoated

Al₂O₃/TiC slider and a carbon coated Al₂O₃/TiC slider. Before the friction tests started, the background intensities were recorded for 40 cycles by the mass spectrometer. For the uncoated Al₂O₃/TiC slider, the friction coefficient increased to a peak value of 1.7 within 10 cycles and dropped to 1 after reaching its peak value. One wear track was observed on the disk just after the friction coefficient had dropped. This is due to three body contact resulting from the small wear particles that were generated at the head-disk interface, which yielded in an unstable friction curve as exhibited in Fig. 1. For the carbon coated slider, the friction coefficient started at 1.3 and increased steadily to 1.8 within 220 cycles before wear occurred. The above results indicate that ZDOL has little lubricating action against the uncoated slider but it has good lubricating action against the carbon coated slider.

Figure 2 shows the integrated mass spectra of ZDOL fragments produced from the ZDOL/CHx disk. The mass spectra signals were integrated over the first 10 cycles (before wear occurred) of the sliding time during the UHV drag tests. The three primary peaks for the coated slider in Fig. 2, in decreasing intensity order, belong to mass fragments F (19), CO₂ (44), CFO (47), CO (28), and CF₂O (66). This mass spec is similar to that of ZDOL vapor as reported by Kasai et al. [4]. Because no contact with Lewis acid is possible in this case, the ZDOL decomposition is expected to be caused by friction/thermal actions only, and therefore it should be directly related to the molecular bond energies. The relevant bond dissociation energies (shown in Table I) are used to judge the bond strength and possible decomposition trends [25]. Because the weakest bonds in ZDOL are C-O-C (3.5 eV), and C-C (3.8 eV), the molecule is expected to cleave preferentially at these locations. A mechanism proposed by Sianesi et al. [26]

postulates that PFPEs dissociate by breaking the weaker C-C bonds followed by β scission to form perfluorinated aldehyde and alkene.

The following decomposition mechanism is proposed for this case: (1) the ZDOL molecule decomposes under frictional action and then (2) the gaseous by-products are further cleaved by electron bombardment in the QMS. In other words, the following processes occur:

$$-O-/CF_2-O/-CF_2-CF_2-O-/-CF_2- \to CF_2=O(66) + -CF_2-CF_2-O-(116)$$
(1)

$$-CF_2-CF_2-O- \rightarrow -CF_2(50) + CF_2=O(66)$$
 (2)

$$-CF_2 \rightarrow -CF(31) + F(19) \tag{3}$$

$$CF_2 = O \rightarrow CFO (47) + F (19) \tag{4}$$

$$CFO \rightarrow CO(28) + F(19) \tag{5}$$

Therefore, F (19), CO₂ (44), CFO (47), CO (28), and CF₂O (66) are the primary decomposition fragments according to reactions (1) through (5). In reactions (4) and (5), Oxygen is not a decomposition product because the C=O bond is stronger than the C-F bond within the CF₂=O and CFO molecules. The occurrence of HF may result from the formation of F and subsequent attack of F on surface adsorbates [14] such as hydroxyl groups (-OH) or surface CH groups. In the same way, CO₂ results from the formation of CO and the hydroxyl

group (-OH). Moreover, the intensity of CO_2 is stronger than that of CO since the CO_2 molecule (two C=O bonds) is more stable than the CO molecule (one C=O bond). The maximum degradation intensity is from the F (19) component because F is the final decomposition product of ZDOL. No larger groups than C_2F_5 (119) appear in the mass spectrum; the reason is that the groups may contain weaker single bonds (e.g., C-O-C and C-C), that are easily cleaved by frictional shear and electron bombardment.

For the uncoated slider case, the integrated mass spectra (the first 30 seconds before wear) of ZDOL fragments are also shown in Fig. 2. Besides the peaks associated with the frictional decomposition of the ZDOL molecule, new peaks appear at CF_3 (69), and C_2F_5 (119), which are due to the catalytic effect of the Al₂O₃-TiC slider material. Moreover, the major five peaks in descending order are F (19), CO₂ (44), CO (28), CF₃ (69), and C₂F₅ (119) which is slightly different from those of the coated slider case.

The following catalytic decomposition mechanism of ZDOL on an AL₂O₃-TiC surface is proposed, based on our results and those in literature:

1. ZDOL decomposes and forms $CF_2=O$ from friction stimulation, while the CH_x film degrades and produces H_2 .

$$-O_{-/-CF_2}-O_{-/CF_2}-CF_2-O_{-/-CF_2-} \rightarrow CF_2=O(66) + -CF_2-CF_2-O_{-}(116)$$
(1)

2. Complex chemical reactions of the ZDOL decomposition products occur with H₂ and produce HF [14].

3. CF₂=O and HF react with Al₂O₃ to produce a strong Lewis acid, AlF₃.

$$Al_2O_3 + 6HF \rightarrow AlF_3 + 3H_2O \tag{6}$$

$$Al_2O_3 + 3CF_2O \rightarrow 2AlF_3 + 3CO_2(44) \tag{7}$$

4. Finally, rapid decomposition reactions along the main ZDOL chain take place on the AlF_3 surface to form methoxy (CF₃-O-), ethoxy (CF₃CF₂-O-) compounds, and acyl fluoride (R-CF=O).

$$\begin{array}{c} F \\ \text{R-CF}_2\text{-O-CF}_2\text{-R} \rightarrow \text{R-C=O+CF}_3\text{-R} \\ \text{(where R is -O- or -CF}_2\text{-O-)} \end{array}$$
(8)

Subsequent electron impact fragmentation of the products from (8) then leads to the CF₃ (69) and CF₃CF₂ (119) fragments observed in the mass spectrum. It is noted that reaction (1) is demonstrated by our test results. Reaction (6) is often used to etch alumina surfaces (Al₂O₃ films are etchable in HF) [27], and reaction (7) is supported by the occurrence of significant amounts of CO₂ (44) and the results of John et al. [28], where acyl fluoride (R-CF=O) reacts with alumina and forms AlF₃. Catalytic reaction (8) was obtained by Kasai et al. [4-6]. He proposed an intramolecular disproportionation reaction when a Lewis acid site such as AlF₃ interacts simultaneously with a lone pair of electrons on each of the two ether oxygen atoms of PFPE,

forming a bridged adduct. The adduct subsequently facilitates the transfer of an F atom to replace an oxygen atom, forming CF_3 and C_2F_5 .

Berry et al. [29] also investigated the unimolecular decomposition of perfluorodimethyl ether, PFDME, to CF₂O and CF₄. They observed that, in the absence of a Lewis acid catalyst, disproportionation via a transition state proceeds (TS1) with a reaction barrier of 374 kJ/mole, while the AlF₃ Lewis acid assisted disproportionation via another transition state (TS2) and reduced the reaction barrier to 165 kJ/mole, reflecting a more than 50% lowering of the barrier due to the Lewis acid catalyst. Pacansky and Waltman [30, 31] also proposed a model for the Lewis acid interaction and the origin for the catalytic degradation. From the optimized geometries, they identified a strong electrostatic interaction between the aluminum surface and the lubricant ether oxygen atom, which stabilizes the transition structure during the catalytic reaction. At the transition geometry, the Al-O interaction develops some covalent character. The effect of the Lewis acid catalyst is to reduce the activation energy for decomposition from 431 to 197 kJ/mole. These results provide a fundamental understanding of why catalytic surfaces must be avoided to ensure the integrity of polyperfluorinated ether lubricants.

The mass spectrum in Fig. 2 can be explained according to the above mechanisms. The decomposed products of ZDOL contain both frictional products and catalytic products. The occurrence of the CF_2O (66) and CFO (47) peaks is a result of friction and electron decomposition as shown in Fig. 2. The CF_3 peak is due to the cleavage of the catalytic products with methoxy end groups (CF_3 -O-) as shown in reaction (9). The C_2F_5 peak is due to the

cleavage of the catalytic products with ethoxy end groups (CF_3CF_2 -O-) as shown in reaction (10).

$$CF_3-O-R \rightarrow CF_3(69) \tag{9}$$

$$CF_3CF_2-O-R \rightarrow CF_3CF_2(119) \tag{10}$$

Strom and Bogy [32] also observed that CF_3 , CF, CF_2 , and CF_2H are the primary ZDOL decomposition fragments against an uncoated Al_2O_3/TiC slider. They suggested that the degradation reaction is activated by low energy electrons produced at the tribological interface. Vurens et al. [2] used the electron stimulation method and mass spec to observe the ZDOL desorption behavior. They observed that HF, CO_2 , CO, CF_2O are the primary fragments, but no CF_3 peak was observed. From our data and Vurens's data, the fragment CF_3 is mostly from the catalytic reaction at the $Al_2O_3/ZDOL$ interface. The occurrence of the HF is due to the H_2 evolution of the worn CHx surface and subsequent complicated reactions of H_2 with ZDOL decomposition products (CFx). The formation of HF involves a basic radical reaction of the H and F radicals as shown in reaction (11). The formation of CF_2H may involve more complicated radical reactions.

$$H^{\cdot} + F^{\cdot} \to HF \tag{11}$$

One very important issue in mass spectrometer measurement is the lubricant decomposition due to fragmentation of the parent compound in the mass spectrometer analyzer. To investigate the artifact effect of the measurement, we used a doser to fill the chamber with

ZDOL at $3x10^{-7}$ Torr (the same pressure condition used during the drag tests) [8]. Masses 66 (CF₂O) and 116 (CF₂CF₂O) are the strongest peaks in contrast to our results shown in Fig. 2. These two fragments (CF₂O and CF₂CF₂O) are the backbone groups in the main body of ZDOL. Most big molecules (e.g., CF₂CF₂O) did not break into small particles (e.g., CFO) in the mass spectrometer analyzer. These results indicate that the generation of fragments CFO (47) and CF₃ (69) during the drag tests are primarily due to sliding in the contact region instead of the fragmentation in the mass spectrometer analyzer. More details on this issue are given in another paper [8].

Based on the above mass spectroscopy results, it is found that the decomposition mechanisms of ZDOL in the case of the uncoated Al₂O₃/TiC slider are much more complicated than those with the carbon coated slider. For the carbon-coated slider, ZDOL decomposition is caused by frictional actions, which include frictional heat , triboelectrons, and mechanical shearing actions. For the uncoated slider, ZDOL decomposition is controlled by tribochemical and catalytic reactions. Tribochemistry involves three aspects: the first part is the tribochemical decomposition of ZDOL and the tribochemical degradation of the CHx overcoats, producing significant amounts of gaseous products such as CFO, CF₂O and H₂. The second part is the tribochemical reactions of the Al₂O₃ surface with HF and ZDOL decomposition products, forming a strong Lewis acid AlF₃. Once the AlF₃ is formed, the catalytic decomposition reactions dominate the decomposition process of ZDOL, forming CF₃ and C₂F₅, which are responsible for the high decomposition rate of ZDOL.

B. Study of thermal desorption data – Hydrogen evolution

In this section, we show and discuss the results from UHV thermal desorption experiments. Before starting the thermal desorption tests, the background intensities were recorded for 80 seconds. The data presented in this study results after the background intensity from the mass spec signals has been subtracted. Figure 3 shows the thermal desorption profiles of the hydrogen (H₂) evolution from a CHx film and a CNx film, respectively. Figure 4 shows the thermal desorption profile of HF. More hydrogen evolution was observed from the CHx (30% hydrogen content) film than from the CNx (5% hydrogen content) film due to their intrinsic hydrogen content. At the same time, HF was formed as the hydrogen evolution occurred. These data provide the evidence of reaction (11), where the occurrence of HF is due to a basic radical reaction of the H and F radicals. Lin et al. [14] observed that HF is evolved starting at 500-550K, which is probably due to reactions with surface OH groups and surface CH groups present at the ZDOL/hard carbon interface. HF is responsible for the AlF₃ formation, which is the necessary component for the occurrence of the catalytic process as shown in reactions (6) and (7).

Figure 5 shows the thermal desorption profile of the ZDOL fragment CFO (47). The peak desorption temperature of ZDOL from the a-CNx surface is 32K lower than the peak temperature from the a-CHx surface. Perry et al. [17] also observed that the peak temperature of ZDOL from the a-CNx surface is 60K lower than the peak temperature from the a-CHx surface. Vurens and Mate [15] attributed the lower peak temperatures to a more reactive amorphous

carbon surface to Fomblin ZDOL decomposition. These results indicate that the carbon films become more reactive with the incorporation of nitrogen.

One important issue in thermal desorption measurements in UHV is the possibility of interfering artifacts. Thermal desorption measurements are notoriously prone to interfering desorption from species adsorbed on heaters, etc. This could be the source of H_2 (2), CO₂ (44) and CO (28). In order to reduce the hydrogen evolution from the heater, the heater was baked at 600K for four hours before the samples were set up in UHV. The thermal desorption intensities from the background (no sample on the heater) were monitored at the heating rate of 0.2K/sec. In another paper [8], we observed that the interfering effect on the major ZDOL decomposition fragments (CFO and CF₃) are very little (below 10%). Therefore, our previous analysis on thermal desorption data are considered reliable.

C. UHV Drag Test - Comparison of the CHx and CNx films

In this section, we present and discuss the results from the UHV drag tests to compare the tribological performance of the ZDOL/CHx film with the ZDOL/CNx film. Figure 6 shows the friction coefficient curves for the ZDOL lubricated CNx disks against an uncoated Al_2O_3/TiC slider and a carbon coated Al_2O_3/TiC slider. For the uncoated Al_2O_3/TiC slider, the friction coefficient increased to a peak value of 1.7 within 20 cycles and dropped to 1 after reaching its peak value. One wear track was observed on the disk just after the friction coefficient had dropped. For the carbon coated slider, the friction coefficient started at 1.3 and increased steadily to 1.5 within 290 cycles before wear occurred. The above results further support the

claim that ZDOL has little lubricating action against the uncoated slider but it has good lubricating action against the carbon coated slider. In addition, the wear durability of ZDOL/CNx film is better than ZDOL/CHx film.

Figure 7 shows the normalized mass spectra of four ZDOL major fragments produced from the ZDOL/CHx and ZDOL/CNx disks. The first two fragments CFO (47) and CF₂O (66) are related with the mechanical shear/friction action, while the last two CF₃ (69) and C₂F₅ (119) are due to catalytic decomposition. The mass spectra signals were integrated over the first 10 cycles (before wear occurred) of the sliding time during the UHV drag tests. For the CHx film, the intensities of catalytic fragments (CF₃ and C₂F₅) increased when using an uncoated slider as compared to a coated slider, although the increase was not very large. These results together with the thermal desorption data in Figs. 3 & 4 indicate that less hydrogen evolution from CNx film prevents the forming of HF, which is the necessary component for the lubricant catalytic reaction, resulting in the better tirbological performance of the CNx film as compared to the CHx film.

IV. CONCLUSIONS

The experiments presented here illustrate the complex tribochemical relations that occur at the head/disk interface during drag tests. The UHV tribochamber was used to monitor the gaseous wear products generated at the HDI during dragging. In the studies of CH_x carbon overcoats paired with carbon-coated sliders, the primary decomposition mechanism of ZDOL was due to frictional effects, and it was characterized by the generation of F (19), HF (20), CO₂ (44), CFO

(47), and CF₂O (66) fragments. The absence of a carbon-coating on the slider led to a more complex catalytic decomposition mechanism of ZDOL during the drag tests: (1) initial friction decomposition of ZDOL and degradation of CH_x to form gaseous products such as CF_2O and H_2 ; (2) reaction of these products with H_2 to produce HF and CF_2H ; (3) production of AlF₃ when CF_2O and HF react with Al₂O₃; and then Lewis acid catalytic reactions on the AlF₃ surface that rapidly decompose ZDOL.

We observed that the hydrogen evolution from the CHx overcoat initiates lubricant catalytic decomposition with an uncoated Al_2O_3/TiC slider, forming CF₃ (69) and C₂F₅ (119). The generation of Hydroflouric acid (HF) during the thermal desorption experiments provides the formation mechanism of Lewis acid, which is the necessary component for catalytic reaction causing Z-dol lube degradation. On the other hand, for CNx films, catalytic reactions were prevented with an uncoated slider due to less hydrogen evolution from the CNx overcoat, resulting in the better tirbological performance for the CNx film as compared to the CHx film.

ACKNOWLEDGMENTS

This work was supported by the Computer Mechanics Laboratory at the University of California, Berkeley. The authors would like to thank Dr. R.J. Waltmann of IBM and Dr. M. Donovan of Quantum for preparation of the disks and sliders, and Dr. Tai Cheng of HMT, Dr. Bruno Machon, and Dr. Waltmann for their helpful discussions on lubricant decomposition mechanisms.

REFERENCES

[1] Pacansky J. and Waltmann R. J., "Electron Beam Irradiation of Polyperfluoroethers: Experimental Analysis of Main-chain Degradation", Chem.Mater. 5, pp486-494, (1993).

[2] Vurens G., Zehringer R. and Saperstein D., "The Decomposition Mechanisms of Perfluoropolyether Lubricants during Wear", Surface Science Investigations in Tribology, Chung Y.W., Homola A. M. and street B., Eds, Washington, D. C.: American Chemical Society, pp169-180, (1992)

[3] M.J. Zehe and O. O. Faut, "Acid Attack of Perfluorinated Alkyl Ether Lubricant Molecules by Metal Oxide Surfaces", Tribology Trans., 33, pp634-640, (1990)

[4] P.H. Kasai, "Degradation of Perfluoropolythers Catalyzed by Lewis Acids", Adv. Info.Storage Syst. 4., pp291-314, (1992)

[5] P.H. Kasai, "Perfluoropolyethers: intramolecular Disproportionation", Macromolecules, Vol.25, pp6791-6799, (1992)

[6] P.H. Kasai, and P. Wheeler, "Degradation of Perfluoropolyethers Catalyzed by Aluminum Chloride", Applied Surface Science, Vol. 52, pp91-106, (1991)

[7] Jianjun Wei, Walton Fong, D. B. Bogy and C. S. Bhatia, "The Decomposition Mechanisms of a Perfluoropolyether at the Head/Disk Interface of Hard Disk Drives", Tribology Letters, Vol. 5, pp203-209, (1998)

[8] Chao-Yuan Chen, Jianjun Wei, Walton Fong, D.B. Bogy, and C. Singh Bhatia, "The Decomposition Mechanisms and Thermal Stability of ZDOL Lubricant on Hydrogenated Carbon Overcoats", CML Technical Report No. 98-016, Journal of Tribology, in press

- [9] D. B. Bogy, X. H. Yun, and B. J. Knapp, "Enhancement of Head-Disk Interface Durability by Use of DLC Overcoats on the Slider's Rails", IEEE Trans on Magnetics, Vol. 30, No.5, pp369-373, (1994)
- [10] W.R. Jones, Jr., K. J. L. Paciorek, T.I. Ito, and R. H. Kratzer, Industrial and Engineering Chemistry Production Research, pp166, (1983)
- [11] L.S. Helmick and W.R. Jones, Jr., "NASA Tech. Mem. 102", p493, (1990)
- [12] M.J. Zehe and O. D. Faut, "NASA Tech. Mem. 101", p962 (1989)
- [13] P.H. Kasai, W.T. Tang and P. Wheeler, "Degradation of Perfluopolyethers Catalyzed by Alumina Oxide", Appl. Surf. Sci. 51, pp201-211, (1991)
- [14] Jong-Liang Lin, C. Singh Bhatia, and John T. Yates, Jr., "Thermal and Electron-simulated Chemistry of Fomblin-ZDOL Lubricant on a Magnetic Disk", J. Vac. Sci. Technol. A 13(2), pp163-168, (1995)
- [15] G. H. Vurens and C. M. Mate, "The Thermal Stability of Perfluoropolythers on Carbon Surfaces", Applied Surface Science, 59, pp281-287, (1992)
- [16] Laura Cornaglia and Andrew J. Gellman, "Fluoroether Bonding to Carbon Overcoats", J.Vac. Sci. Technol. A 15(5), pp2755-2765, (1997)
- [17] Scott S. Perry, Philip B. Merrill and Hyun I. Kim, "Comparative Studies of Perfluorinated Lubricants Adsorbed on Hydrogenated Amorphous Carbon and Amorphous Carbon Nitride", Tribology Letters 2, pp393-404, (1996)
- [18] C.M. McC. Ettles, "Possible Flash Temperatures in Slider and Recording Disk Transient Contact", ASLE Transactions, Vol. 29, pp321-328, (1986)

[19] Shouji Suzuki, and Francis E. Kennedy, Jr., "Friction and Temperature at Head-Disk Interface in Contact Start/Stop Tests", Tribology and Mechanics of Magnetic Storage Systems, Vol. V, pp30-36

[20] E. Cutiongco, D. Li, Y.W. Chung, and C. S. Bhatia, "Tribological Behavior of Amorphous Carbon Nitride Overcoats for Magnetic Thin-Film Rigid Disks", ASME J. Tribology, Vol. 118, pp543-552, (1996)

[21] D. Li, Y-W Chung, M-S Wong, and W.D. Sproul, "Mechanical Properties of Amorphous Carbon Nitride Thin Films Prepared by Reactive Magnetron Sputter-Deposition", Tribology Letters, Vol.1, pp87-93, (1995)

[22] X. Yun, R. C. Hsiao, and D. B. Bogy, "Hardness and Tribochemical Evaluation of Ultra-Thin CHx and CNx Overcoats", IEEE Trans. Magn., Vol.33, pp938-943, (1997)

[23]G.W. Tyndall, R.J. Waltman, and D.J. Pocker, "Concerning the Interactions between ZDOL Perfluoropolyether Lubricant and an Amorphous-Nitrogenated Carbon Surface", Langmuir, Vol.14, pp7527-7536, (1998)

[24] X. H. Yun, D. B. Bogy, and C. S. Bhatia, "Tribochemical Study of Hydrogenated Carbon Coatings with Different Hydrogen Content Levels in Ultra High Vacuum", J. Tribology, 119, pp437-443, (1997)

[25] A. Steritwieser, and C. H. Heathcock, "Introduction to Organic Chemistry", Macmillan Publishing Co., Inc., New York, (1976)

[26] D. Sianesi, V. Zamboni, R. Fontanelli, and M. Binaghi, "Perfluoropolythers: Their Physical Properties and Behavior at High and Low Temperatures", Wear, 18, pp85-100, (1971)

[27] J.L. Vossen and W. Kern, "Thin Film Process", Academic Press, pp416-417, (1978)

[28] P.J. John and J. Liang, "Initial Metal Fluoride Formation at Metal/Fluorocarbon Interfaces",J. Vac. Sci. Technol. A, Vol. 12, pp199-203, (1994)

[29] R.J. Berry, J.N. Cutler, B.E. Ream, J.W. Bozzelli, and R.J. Waltman, "An AB Initio Investment of the Unimolecular and AlF₃ Catalyzed Decomposition of Perfluorodimethyl Ether", submitted to J. Phys. Chem., 1998

[30] J. Pacansky and R.J. Waltman, "The Effect of Lewis Acid Catalysis on the Decomposition of CF₃OCF₃ to COF₂ and CF₄", J. Fluorine Chemistry, Vol.83, pp41-45, (1997)

[31] R.J. Waltman, "A Computer Modeling Study on the Interaction of –(CF2CF2O)-Polyperfluorinated Ethers with Lewis Acid Sites: Perfluorodiethyl Ether", J. Fluorine Chemistry,Vol. 90, pp9-16, (1998)

[32] B. D. Strom and D. B. Bogy, "Gaseous wear products from perfluoropolyether lubricant films", Wear, 168, pp31-36, (1993)

CAPTIONS

Table I: Bond Dissociation Energies

Figure 1. The friction coefficient curves of ZDOL lubricated CHx disks on uncoated Al_2O_3/TiC slider and carbon coated slider.

Figure 2. The integrated mass spectrum of ZDOL decomposition products generated at the ZDOL/CHx disk interface during UHV drag tests.

Figure 3. The thermal desorption profile of H_2 (2) evolution from both CHx and CNx coated disks in UHV.

Figure 4. The thermal desorption profile of HF (20) formation from both CHx and CNx coated disks in UHV.

Figure 5. The thermal desorption profile of ZDOL fragment CFO (47) from both CHx and CNx coated disks in UHV.

Figure 6. The friction coefficient curves of ZDOL lubricated CNx disks on uncoated Al_2O_3/TiC slider and carbon coated slider.

Figure 7. The normalized mass spectrum of four major ZDOL decomposition products generated at the ZDOL/CHx and ZDOL/CNx disk interface during UHV drag tests.

TABLE I BOND DISSOCIATION ENERGIES

Bond	[kcal/mol]	[eV]
C-F	116	5.0
C-O-C	81	3.5
C-C	88	3.8
C-H	98	4.2
C-OH	91	3.9
O-H	103	4.5
C=C	146	6.3
C=O	179	7.8



Figure 1. The friction coefficient curves of ZDOL lubricated CHx disks on uncoated Al_2O_3/TiC slider and carbon coated slider.



Figure 2. The integrated mass spectrum of ZDOL decomposition products generated at the ZDOL/CHx disk interface during UHV drag tests.



Figure 3. The thermal desorption profile of H_2 (2) evolution from both CHx and CNx coated disks in UHV.



Figure 4. The thermal desorption profile of HF (20) formation from both CHx and CNx coated disks in UHV.



Figure 5. The thermal desorption profile of ZDOL fragment CFO (47) from both CHx and CNx coated disks in UHV.



Figure 6. The friction coefficient curves of ZDOL lubricated CNx disks on uncoated Al_2O_3/TiC slider and carbon coated slider.



Figure 7. The normalized mass spectrum of four major ZDOL decomposition products generated at the ZDOL/CHx and ZDOL/CNx disk interface during UHV drag tests.