

# The Decomposition Mechanisms of a Perfluoropolyether at the Disk Interface of Hard Disk Drives

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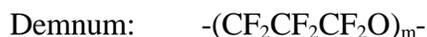
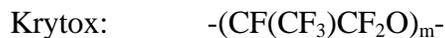
*The decomposition mechanisms of a perfluoropolyether (ZDOL) at the head/disk interface under sliding friction conditions were studied using an ultra high vacuum tribometer equipped with a mass spectrometer. Chemical bonding theory was applied to analyze the decomposition process. For a carbon coated slider/CNx disk interface, the primary decomposed fragments are CFO and CF<sub>2</sub>O, caused by the friction decomposition and electron bombardment in the mass spectrometer. For an uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider/CNx contact, CF<sub>3</sub> and C<sub>2</sub>F<sub>5</sub> fragments appear in addition to CFO and CF<sub>2</sub>O, resulting from the catalytic reactions and friction decomposition, indicating that the decomposition mechanism associated with friction leads to the breaking of the main chain of ZDOL and forms CF<sub>2</sub>=O, which reacts with Al<sub>2</sub>O<sub>3</sub> to produce AlF<sub>3</sub>, and the rapid catalytic decomposition of ZDOL on the AlF<sub>3</sub> surface follows. Moreover, the effects of frictional heat, tribocharge, mechanical scission and Lewis acid catalytic action, generated in friction process, on the decomposition of ZDOL are discussed.*

## KEY WORDS

Perfluoropolyether, ZDOL, Head/Disk Interface, Friction, Catalysis, Decomposition Mechanisms

## INTRODUCTION

The reliability and durability of magnetic storage systems depend on the tribological processes at the head/disk interface. In order to control the friction and wear, the magnetic media disks are usually coated with a thin carbon layer ( $< 20$  nm) as a wear-resistant overcoat and a very thin film of lubricant (0.7~10 nm). Hydrogenated carbon and nitrogenated carbon films have been recently developed as new disk overcoats [1, 2]. The head materials include  $\text{Al}_2\text{O}_3$ -TiC with or without amorphous carbon films and Mn-Zn ferrite. The lubricants are perfluoropolyethers (PFPEs) with molecular weight range of 2000 to 13000. These liquids have superior properties such as low vapor pressure, good viscosity characteristics, high thermal stability and chemical inertness. Typical commercial PFPEs can be classified into four groups: Fomblin Z, Fomblin Y, Krytox and Demnum. Their main molecular structures are listed below:



The Fomblin Z series is commercially available with different endgroups such as alcohol (ZDOL) and carboxylic acid (ZDIAC).

Because lubrication failure leads to direct contact and material removal of the two sliding bodies (slider and disk), it is necessary to study the decomposition mechanisms of PFPEs at the head/disk interface. These fundamental studies are conducive to development of new lubricants, selection of suitable tribomaterials and lubricants, and improvement of product lifetime. A literature review indicates that the decomposition mechanisms of PFPEs have been studied in simple systems, but the decomposition mechanisms caused by friction at the head/disk interface have not been revealed. The proposed mechanisms include three main modes in addition to the known thermal decomposition, (1) mechanical scission, (2) electron decomposition, (3) catalytic decomposition.

Karis et al. [3] investigated the degradation of two types of PFPEs (Y and Z) in a media mill with ZrO<sub>2</sub> particles and examined the scission products adsorbed on the ZrO<sub>2</sub> particles by <sup>19</sup>F-NMR. The results indicate that a primary functional group at the scissioned chain ends, -CO<sub>2</sub><sup>-</sup>, is formed after the milling. Through a hydrodynamic calculation of the shear rate (roughly 5×10<sup>6</sup> s<sup>-1</sup>), they proposed a mechanical scission mechanism. Although they excluded the possibility of the catalytic effect of ZrO<sub>2</sub> on the PFPEs, the ZrO<sub>2</sub> was found by Koka et al. [4, 5] to have significant catalytic degradation actions either in heating tests of mixtures containing ZrO<sub>2</sub> powder and PFPEs, or in friction tests with ZrO<sub>2</sub> slider.

Many experiments demonstrate that PFPEs, subjected to electron irradiation, are easily decomposed into smaller fragments [6]. Vurens et al. [7] 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). He proposed an electron decomposition mechanism, in which electrons attach to fluorocarbon compounds and form a negative ion resonant state, followed by the decomposition of the molecule into a negative ion and a radical. He also found that electron decomposed products of Krytox are different from the friction decomposed products. Strom et al [8] reported that the mass spectrum for Krytox degradation resembles that obtained under electron bombardment by Vurens et al., and suggested that the degradation may be related to triboelectrons produced in rubbing surfaces.

It is well known that, in the presence of metal and metal oxide, the rapid degradation of PFPEs takes place at temperatures below their decomposition temperatures [9, 10]. So far, two different mechanisms have been reported, one is the decomposition caused by Lewis acid sites [11, 12], another is the decomposition caused by non-Lewis acid sites [13, 14]. For the Lewis acid decomposition mechanism, a two step process is proposed, in which the conversion from metal and metal oxide to metal fluorides occurs slowly, and then the metal fluorides (AlF<sub>3</sub> [11], FeF<sub>3</sub> [12]) rather than the oxides themselves catalytically decompose PFPEs. The second step of catalytic reaction process on the AlF<sub>3</sub> surface is understood, but the initial first step of metal fluoride formation is not clear yet. For the non-Lewis acid decomposition mechanism, some surface active sites such as hydroxyl groups and oxide ion sites are proposed to be responsible for

the decomposition of perfluoroethers. Ng et al. [14] studied the interaction between  $(C_2F_5)_2O$  and  $Al_2O_3$ , and they suggested that the hydroxyl groups (-OH) adsorbed on the  $Al_2O_3$  surface are necessary for the thermal decomposition and oxidation of  $(C_2F_5)_2O$ .

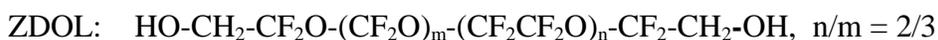
In this study, two decomposition processes of commercial ZDOL under sliding friction conditions are studied, one is with a carbon film coated slider/CNx coated disk system, another is with an uncoated  $Al_2O_3$ -TiC slider/CNx coated disk system. Chemical bonding theory is used to analyze the decomposition process of ZDOL. The decomposition mechanisms caused by friction, electron bombardment and catalysis are proposed, based on the experimental results, theoretical analyses and previous works. Moreover, the effects of frictional heat, tribocharge, mechanical action and Lewis acid catalysis on ZDOL decomposition are discussed for a better understanding of friction decomposition mechanism.

## **EXPERIMENTS**

The friction tests were conducted in an ultra high vacuum (UHV) chamber containing a disk spindle and a slider actuator. The chamber is equipped with a high resolution quadrupole mass spectrometer (MS), which was illustrated in a previous paper [1]. The hard disk is mounted onto the spindle that is coupled to a DC motor by a UHV compatible feedthrough. The maximum rotating speed of the spindle is 3000 rpm, but much lower speeds are used. The slider is mounted onto a suspension arm with strain gages for measuring both friction and normal load. The vacuum in the chamber is obtained by a mechanical pump and turbo molecular pump with a pumping speed of 380 l/s. A vacuum level below  $10^{-8}$  Torr can be achieved. A cold and a hot cathode ion gauge are used to monitor the pressure inside the chamber. The ionization chamber is located close to the head/disk interface to ensure the in situ detection of the gaseous products emitted from the interface. The mass spectrometer has 15 channels, which can monitor 15 different atom mass units (AMUs) simultaneously from 1 to 500. Friction data can also be recorded together with the mass intensities. Each channel is set up to monitor a specific AMU. The MS spectrum is obtained at an electron energy of 70 eV.

Before testing, the UHV chamber is baked at 150 °C for at least 24 hours until the base pressure of  $2 \times 10^{-8}$  Torr is achieved at room temperature. Before the friction tests, the slider and disk are mounted in the chamber, and the mass spectrometer is then run for a period of time (~160 s) to record the background mass intensities. When the friction tests start, a jump of mass intensities occurs for those monitored masses, accompanied by a sudden increase of friction. A load of 35 mN and a sliding speed of 0.2 m/s were used in all tests. To avoid possible deviations caused by different surface roughnesses of the disks, all tests were run on the same disk using different tracks. It is noted that all fragments (m/e) from 1 to 192 of ZDOL decomposition products generated at the Al<sub>2</sub>O<sub>3</sub>-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.

The sliders used in this study were 50% tape-flat Al<sub>2</sub>O<sub>3</sub>-TiC sliders with and without amorphous carbon films on their air bearing taper surfaces. The disks were commercial 95 mm smooth thin film disks with an amorphous nitrogenated carbon overcoat (75 Å). The surface roughness (Ra) of the disks was about 3 nm. The disks were lubricated with ZDOL by a dipping process. The thickness of ZDOL on the disks was about 8.5 Å, which was obtained by ellipsometrical measurement. ZDOL has an average molecular weight of 2000 and the following chemical structure:



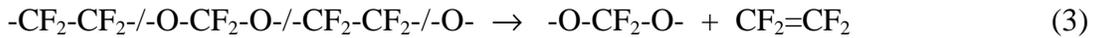
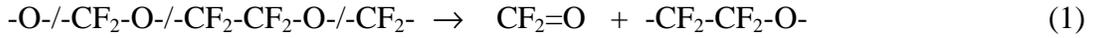
## RESULTS

### Thermodynamic Analyses

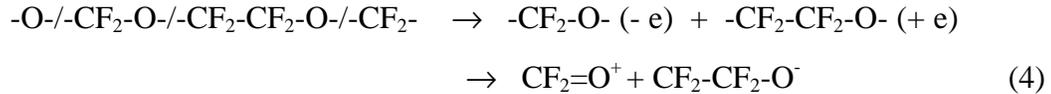
Because the decomposition process of ZDOL is directly related to the bond strength, it is crucial to ascertain the bond energy of each chemical bond in the ZDOL molecule. Table 1 gives typical values of the bond dissociation energies of the chemical bonds relating to the ZDOL molecule [15]. Some bond energies of ZDOL decomposition products are also listed here. The bond energy orders of various bonds are as follows:



The weakest bond in ZDOL is at the ether linkage (C-O-C). Bond cleavage occurs preferentially at the weakest sites, which is clearly the ether linkage (C-O-C) in ZDOL. From a chemical bonding viewpoint, the cleavage of ZDOL may take place in three main routes,

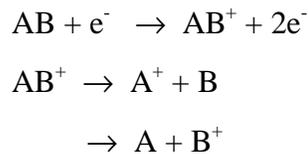


If electrons are involved in the above cleavage process, the charged products are formed, e.g.



Theoretically, the decomposition products of ZDOL under friction shear action include molecules (e.g.  $\text{CF}_2=\text{O}$ ), radicals (e.g.  $\text{CF}_2$ ) and ions (e.g.  $\text{CF}_2=\text{O}^+$ ), and the primary gaseous products should be among the following fragments:  $\text{CF}_2\text{O}$ ,  $\text{CF}_2\text{CF}_2\text{O}$ ,  $\text{CF}_2$ ,  $\text{OCF}_2\text{CF}_2\text{O}$ ,  $\text{C}_2\text{F}_4$  and  $\text{OCF}_2\text{O}$ .

It should be noted that the above products will be charged and further cleaved under electron bombardment in the head of the mass spectrometer. The charged particles are deflected and separated by an electromagnetic field and detected according to their mass/charge ratios (m/e). The basic cleavage process can be represented as follows (AB represents a simple molecule):



## Friction test results

Figure 1 shows the friction coefficients of CN<sub>x</sub> disks against a carbon film coated slider (a) and an uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider (b) under ZDOL lubricated conditions. A load of 35 mN and a speed of 0.2 m/s were used in these tests. In the carbon/CN<sub>x</sub> contact, the friction coefficient decreases slowly with increasing sliding time, and is below 0.1 after a running-in stage (about 5 seconds). No observable wear track is formed on the disk surface, but the decomposition of ZDOL takes place, which will be described later. This indicates that ZDOL, together with its decomposed products, can lubricate the head/disk interface in this condition. In the Al<sub>2</sub>O<sub>3</sub>-TiC/CN<sub>x</sub> contact, the friction coefficient is initially 0.2 and rapidly increases to 0.8 with sliding time up to 70 s, and suddenly drops to a very low value afterwards, which means that the CN<sub>x</sub> films are worn through. An obvious wear track is produced on the disk. The wear volume is  $9.9 \times 10^{-6} \text{ mm}^3$ . This indicates that ZDOL almost has no lubricating action for the Al<sub>2</sub>O<sub>3</sub>-TiC slider/CN<sub>x</sub> disk contact in the same condition.

### **ZDOL decomposition in the carbon/CN<sub>x</sub> contact**

Figure 2 shows the mass spectrum of ZDOL fragments produced from the carbon film coated slider/CN<sub>x</sub> disk interface. Two main peaks appear at  $m/e = 47$  and  $66$ , which correspond to CFO and CF<sub>2</sub>O. Moreover, strong F (19), HF (20) and CO<sub>2</sub> (44) peaks appear, but no N<sub>2</sub> or CO (28) peak is observed. These peaks are not shown in Figure 2 because they have very high background intensities. According to the theoretical analyses, CF<sub>2</sub>O is a friction decomposed product, CFO is an electron decomposition fragment. CF<sub>2</sub>O and CFO are very stable because their structures contain C=O bonds, which have higher dissociation energies than any single bonds in ZDOL. In addition, the F atom provides electrons to double bond and forms a stable resonance structure, which is called the p- $\pi$  resonance. No larger groups than CF<sub>2</sub>O appear in the mass spectrum, the reason is that the larger groups may contain weaker single bonds (e.g. C-O-C and C-C), which are easily cleaved by friction shear and electron bombardment.

Theoretically, ZDOL decomposes through the three different routes expressed by eq.(1) to (3). Route (1) produces CF<sub>2</sub>O and CF<sub>2</sub>CF<sub>2</sub>O. A large portion of CF<sub>2</sub>CF<sub>2</sub>O is in the ZDOL molecule (CF<sub>2</sub>CF<sub>2</sub>O/CF<sub>2</sub>O = 0.7). Whatever CF<sub>2</sub>CF<sub>2</sub>O that appears in radical or cycloether form is

chemically unstable and easily cleaved into  $\text{CF}_2\text{O}$  and  $\text{CF}_2$ , the  $\text{CF}_2$  may be further cleaved into the F atom. In this study, very weak  $\text{CF}_2\text{CF}_2\text{O}$  peak was found. A significant amount of CFO is formed mainly due to the partial cleavage of  $\text{CF}_2\text{O}$  under electron impact. Routes (2) and (3) seem not to occur since no obvious  $\text{CF}_2$ ,  $\text{CF}_2=\text{CF}_2$ ,  $\text{OCF}_2\text{O}$  and  $\text{OCF}_2\text{CF}_2\text{O}$  peaks are observed. Although fluorocarbon fragments ( $\text{C}_x\text{F}_y$ ) once formed may be further cleaved into F under electron bombardment, they can be detected if  $\text{C}_x\text{F}_y$  is largely produced during the friction process, e.g.  $\text{CF}_3$  and  $\text{C}_2\text{F}_5$  peaks appear when the carbon coated slider is replaced by the uncoated  $\text{Al}_2\text{O}_3\text{-TiC}$  slider. Based on the above results, we propose a model to describe the basic decomposition process of ZDOL, as shown in Figure 3. The decomposition process of ZDOL can be simply classified as two step cleavages. At the first step, friction causes the decomposition of ZDOL and forms the primary gaseous products,  $\text{CF}_2\text{O}$  and  $\text{CF}_2\text{CF}_2\text{O}$ . At the second step, electron bombardment causes partial cleavage of the primary products and forms secondary fragments such as CFO,  $\text{CF}_2\text{O}$  and F. It is noted that the real decomposition process of ZDOL should be more complicated, e.g.  $\text{CF}_2\text{CF}_2\text{O}$  may be cleaved into  $\text{CF}_2$  and  $\text{CF}_2\text{O}$  by friction shear as well as electron impact, and larger fragments than  $\text{CF}_2\text{O}$  may be formed and adsorbed on the frictional surface, which may still have lubricating actions.

### **ZDOL decomposition in the uncoated $\text{Al}_2\text{O}_3\text{-TiC/CN}_x$ contact**

Figure 4 is the mass spectrum of ZDOL fragments produced from the uncoated  $\text{Al}_2\text{O}_3\text{-TiC}$  slider/ $\text{CN}_x$  disk interface. It is clear that the MS pattern differs from that in Figure 2, and the mass intensities are one order of magnitude higher than in Figure 2. Besides the same peaks at 47 (CFO) and 66 ( $\text{CF}_2\text{O}$ ), new strong peaks appear at 69 ( $\text{CF}_3$ ) and 119 ( $\text{C}_2\text{F}_5$ ). It is noted that F (19), CO or  $\text{N}_2$  (28) and  $\text{CO}_2$  (44) with strong intensities are also formed during the friction tests (not shown in Figure 4). These gaseous products with strong background intensities have less significance because they are related to the UHV/MS system, the disk overcoat itself and surface contamination [16]. Similar peaks to those in Figure 2 may be due to the friction decomposition, while the new peaks are due to the catalytic effect caused by the  $\text{Al}_2\text{O}_3\text{-TiC}$  slider. Based on the experimental analyses, the catalytic decomposition mechanisms of ZDOL on the  $\text{Al}_2\text{O}_3\text{-TiC}$  surface are summarized as follows:

1. Friction shear breaks the main chain of ZDOL at weak bond sites and forms CF<sub>2</sub>O,



2. Partial CF<sub>2</sub>=O reacts with Al<sub>2</sub>O<sub>3</sub> and forms AlF<sub>3</sub>,



3. Rapid decomposition reactions along the main chain of ZDOL take place on the AlF<sub>3</sub> surface, and form methoxy (CF<sub>3</sub>-O-), ethoxy (CF<sub>3</sub>CF<sub>2</sub>-O-) compounds and acyl fluoride (R-CF=O),



It is noted that reaction (1) is demonstrated by friction test results; reaction (5) is supported by the occurrence of significant amount of CO<sub>2</sub> and the results of John et al. [10], where acyl fluoride (R-CF=O) reacts with alumina and forms AlF<sub>3</sub>; and reaction (6) was described in detail by Kasai et al.'s paper [11].

The mass spectrum in Figure 4 can be explained according to the above mechanisms and the electron bombardment effect. The decomposed products of ZDOL contain friction products and catalytic products. The adsorbed products on the slider and disk surfaces can not be examined, only gaseous products evaporated or desorbed from the head/disk interface can be detected.

The occurrence of CF<sub>2</sub>O and CFO peaks is a result of friction and electron decomposition as shown in Figure 3. Meanwhile, the catalytic process may also produce these fragments. One of the catalytic products, R-CF=O, may decompose into two fragments (CF<sub>2</sub>=O and CF=O) under electron impact,



The  $\text{CF}_3$  peak is due to the electron cleavage of the catalytic products with methoxy end groups ( $\text{CF}_3\text{-O-}$ ),



The  $\text{C}_2\text{F}_5$  peak is due to the electron cleavage of the catalytic products with ethoxy end groups ( $\text{CF}_3\text{CF}_2\text{-O-}$ ),



Moreover, the smaller peaks,  $\text{CF}$  and  $\text{CF}_2$ , are attributed to the partial cleavage of  $\text{CF}_3$  and  $\text{C}_2\text{F}_5$  under electron bombardment.

## DISCUSSIONS

### Friction Decomposition Mechanism

It is well known that PFPEs decompose and lose the lubricating actions under severe friction conditions. How does the friction cause the decomposition? This is a very complicated question, because the friction process is always accompanied by frictional heat, triboelectrons and mechanical action. In order to gain a better understanding of the friction decomposition mechanism, the effects of the individual factors occurring at the head/disk interface are briefly discussed as follows in terms of frictional heat, tribocharge and mechanical action.

Frictional heat generated at the rubbing surface results from the frictional power ( $w=Lvf$ , where  $f$  is the friction coefficient) that is dissipated into the contact asperities. The maximum temperature is called flash temperature, which is dependent on the materials, environment and test conditions. The flash temperature generated at the head/disk interface for an  $\text{Al}_2\text{O}_3\text{-TiC}$  slider on a rigid thin film magnetic disk has been measured and calculated according to Archard's equation. Suzuki et al. [17] found that the flash temperature is about  $150^\circ\text{C}$  under 1N impact load. Strom et al. [8] reported that the flash temperature does not exceed  $100^\circ\text{C}$  at a load of 50 mN and a speed of 0.1 m/s, which is similar to this test condition. These values are much lower than the decomposition temperature of ZDOL. It can be concluded that friction heat alone can not

stimulate the decomposition of ZDOL lubricant although it increases the kinetic energy of the lubricant molecule. It should be noted that the mass spectrum obtained in frictional sliding is very similar to that obtained in pure thermal decomposition of Fomblin Z at 300°C [11], but the friction decomposition mechanism is different from the thermal activation mechanism.

Tribocharge is produced by the emission of electrons, protons, and negative and positive particles on the sliding solid surface. Triboelectron is also called exo-electron. The energy of triboelectrons ranges from 0.5 to 80 eV, depending on the materials and test conditions. If the triboelectrons with high energies are largely generated at the head/disk interface, they may cause the decomposition of ZDOL either by high energy electron bombardment [6] or by low energy electron attachment [7]. Nagayama et al. [18] recently studied tribocharge emission during the wear of amorphous hydrogenated carbon films. Their results showed that electrons are emitted during the wear of carbon films, and their intensities depend strongly on the evolution of H<sub>2</sub> and the wear severity of the carbon films. In the case of mild wear, the intensity is very weak. Actually, our results and Novotny et al.'s [19] results have revealed that a significant amount of PFPEs has decomposed before the carbon films are removed. Since there is no test evidence on the number and energy of triboelectrons generated in the early stage of PFPE decomposition or before the wear of carbon films, the effect of triboelectron on the decomposition of ZDOL is uncertain. Some test results [6,7] showed that the electron decomposition products are different from the friction decomposition products although there are some products in common, indicating that the friction decomposition mechanism of ZDOL is different from the pure electron decomposition.

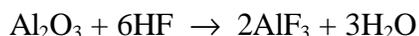
Lubricants are subject to the mechanical actions of stresses (shear, compressive, and tensile) under boundary lubrication conditions. It can be easily understood by the phenomena such as mechanical shear, surface deformation and exposure of a fresh surface [20]. The surface deformation causes many defects on the surface and sub-surface, which is beneficial to tribochemical reaction. Pure mechanical actions such as mechanical shear modify the interatom distance and thus may cause the bond breaking. When a lubricant molecule is stretched beyond a certain extent, the molecular bond will break. Some experiments show that mechanical scission

occurs under very high shear rates (e.g.  $10^6 \text{ s}^{-1}$ ) [3], indicating that the lubricant molecule may be scissioned at the weak bond sites by pure mechanical stretching.

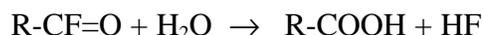
To sum up, the exact decomposition mechanisms of ZDOL during sliding friction are still uncertain. It can be controlled by many factors such as frictional heat, tribocharge and mechanical stimulation.

### Catalytic Decomposition Mechanism

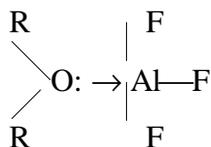
In the Lewis acid decomposition mechanism generated on the  $\text{Al}_2\text{O}_3$  surface, the conversion from  $\text{Al}_2\text{O}_3$  to  $\text{AlF}_3$  is a prerequisite for the occurrence of the catalytic process.  $\text{AlF}_3$  may be formed through two kinds of reactions. One is the reaction of  $\text{Al}_2\text{O}_3$  with  $\text{CF}_2=\text{O}$  or acyl fluorides ( $\text{R}-\text{CF}=\text{O}$ ), as shown in reaction (5). The  $\text{C}=\text{O}$  containing compounds are largely produced under static heating and friction conditions, which provide an environment for the conversion from  $\text{Al}_2\text{O}_3$  to  $\text{AlF}_3$ . Another is the reaction of  $\text{Al}_2\text{O}_3$  with HF,



Such a reaction is often used for the surface processing of alumina materials [21]. A HF peak was found for sliding of the  $\text{CH}_x$  disk against the  $\text{Al}_2\text{O}_3$ -TiC slider, which is responsible for the  $\text{AlF}_3$  formation [22]. In this study, only a weak peak of HF was found, indicating another possibility of  $\text{AlF}_3$  formation. The HF is also produced by the hydrolysis of acyl fluoride in a moist atmosphere,



Although  $\text{AlF}_3$  is very unstable at ambient conditions due to its strong hydrolysis, it has been identified on the alumina surfaces after static heating tests of PFPEs [4, 13]. Once  $\text{AlF}_3$  is produced, coordinated bonds ( $\text{O} \rightarrow \text{Al}$ ) between PFPEs and  $\text{AlF}_3$  are formed by electron transfer from O to Al atoms, because the O atoms in PFPEs have unshared electron pairs and the Al atoms have empty orbitals,



Strong coordinated bonds can be formed on the  $\text{AlF}_3$  surface for those PFPEs without branch groups, owing to no spatial hindrance. Subsequently rapid catalytic decomposition of PFPEs takes place on the  $\text{AlF}_3$  surface, which involves an intramolecular disproportionation reaction and results in the formation of  $\text{O}=\text{CF}-$ ,  $\text{CF}_3\text{-O}-$  and  $\text{CF}_3\text{CF}_2\text{-O}-$  groups [11].

Our results indicate that initially friction leads to the decomposition of ZDOL (as shown in the reaction (1)) and forms  $\text{CF}_2=\text{O}$ , which reacts with  $\text{Al}_2\text{O}_3$  to produce  $\text{AlF}_3$ , and then rapid catalytic decomposition occurs on the  $\text{AlF}_3$  surface. Unlike other model tests, the commercial slider ( $\text{Al}_2\text{O}_3\text{-TiC}$ ) used in this study has much less surface area than ceramic powders, and thus has very low reactivity. However, tribochemical reactions can be stimulated by friction. Under friction action, surface contamination on the alumina surface is easily removed, and a fresh surface is exposed. Meanwhile, surface deformation produces many defects. Since the deformed surfaces have very high reactivity, the formation rate of  $\text{AlF}_3$  and its catalytic activity become greatly increased. Nevertheless, the catalytic decomposition process of ZDOL does not proceed or proceeds very slowly without friction stimulation. It is therefore concluded that the decomposition process of ZDOL on the  $\text{Al}_2\text{O}_3\text{-TiC}$  surface is controlled by both catalytic and mechanical actions.

It should be noted that the experiments described here represent the simplified situation of friction in vacuum for the purpose of obtaining clear information, the actual situation at the head/disk interface is much more complex. For example, the commercial sliders consist of  $\text{Al}_2\text{O}_3$  and TiC, in which about 30% wt TiC is incorporated. Koka et al. [4] found that TiC,  $\text{TiO}_2$  and  $\text{ZrO}_2$ , together with  $\text{Al}_2\text{O}_3$ , can catalytically degrade the PFPEs to varying extents. Although the catalysis decomposition process of PFPEs is dominated by a high content of  $\text{Al}_2\text{O}_3$ , the possible catalytic effect caused by the TiC component still unknown. In addition, in ambient conditions, the presence of water and oxygen will increase the complexity of the catalytic mechanisms of PFPEs. Therefore, comprehensive decomposition mechanisms of PFPEs at the head/disk interface need to be further studied.

## CONCLUSIONS

The tribological properties and decomposition mechanisms of ZDOL at the head/disk interface were studied using an UHV tribometer equipped with a mass spectrometer under a load of 35 mN and a sliding speed of 0.2 m/s. The following conclusions can be drawn:

1. In the carbon film coated slider/CNx disk contact, the friction coefficient is below 0.1, no observable wear is formed on the CNx overcoat surface. However, in the uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider/CNx disk contact, the friction coefficient increases rapidly up to 0.8 at the beginning stage and then suddenly drops to a very low value, indicating that the CNx overcoat is worn through.

2. In the carbon film coated slider/CNx contact, the mass spectrum of the ZDOL decomposed products is composed of CFO and CF<sub>2</sub>O peaks, due to the friction decomposition and electron bombardment.

3. In the uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider/CNx contact, the mass spectrum of the ZDOL decomposed products includes CF<sub>3</sub> and C<sub>2</sub>F<sub>5</sub> peaks in addition to CFO and CF<sub>2</sub>O, due to the catalytic reactions and friction decomposition. The decomposition processes are proposed as follows: (1) friction causes the decomposition of ZDOL and forms CF<sub>2</sub>=O, (2) CF<sub>2</sub>=O reacts with Al<sub>2</sub>O<sub>3</sub> and forms AlF<sub>3</sub>, (3) Lewis acid catalytic reactions occur on the AlF<sub>3</sub> surface, leading to a rapid decomposition of ZDOL.

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## **CAPTIONS**

Figure 1. Friction coefficient curves for ZDOL lubricated CNx disks against a carbon coated slider (a) and an uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider (b).

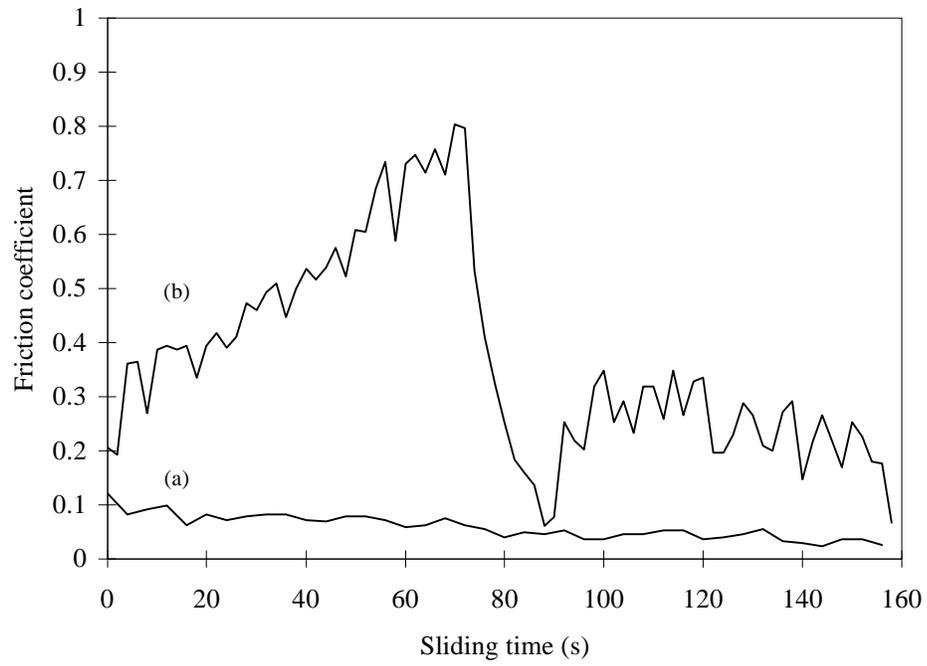
Figure 2. The spectrum of ZDOL generated at the carbon coated slider/CNx disk interface.

Figure 3. The decomposition mechanism of ZDOL induced by friction and electron bombardment.

Figure 4. The mass spectrum of ZDOL generated at the uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider/CNx disk interface.

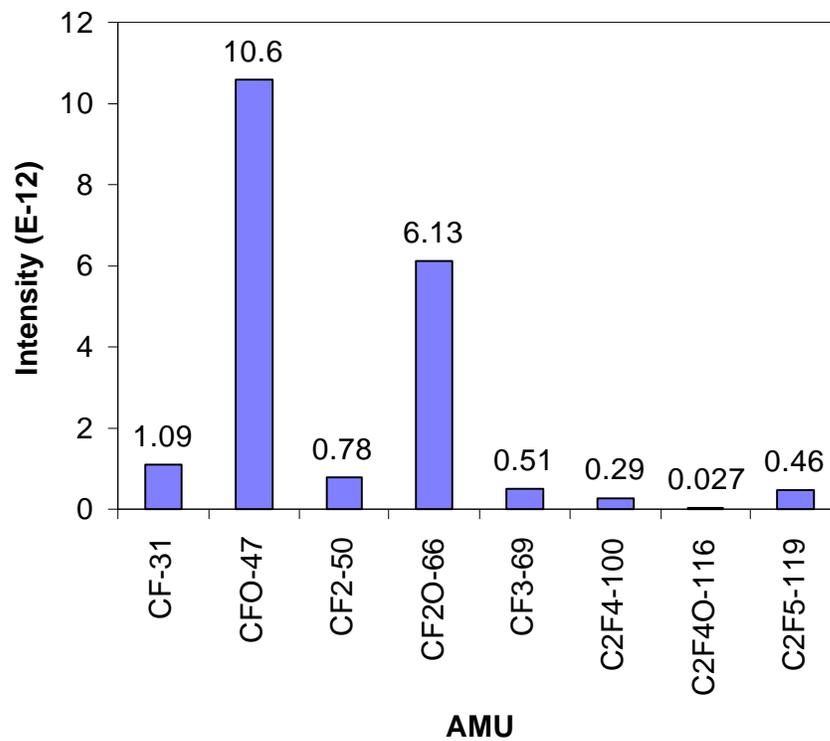
**Table 1 Bond dissociation energies**

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	145.8	6.3
C=O	179	7.8

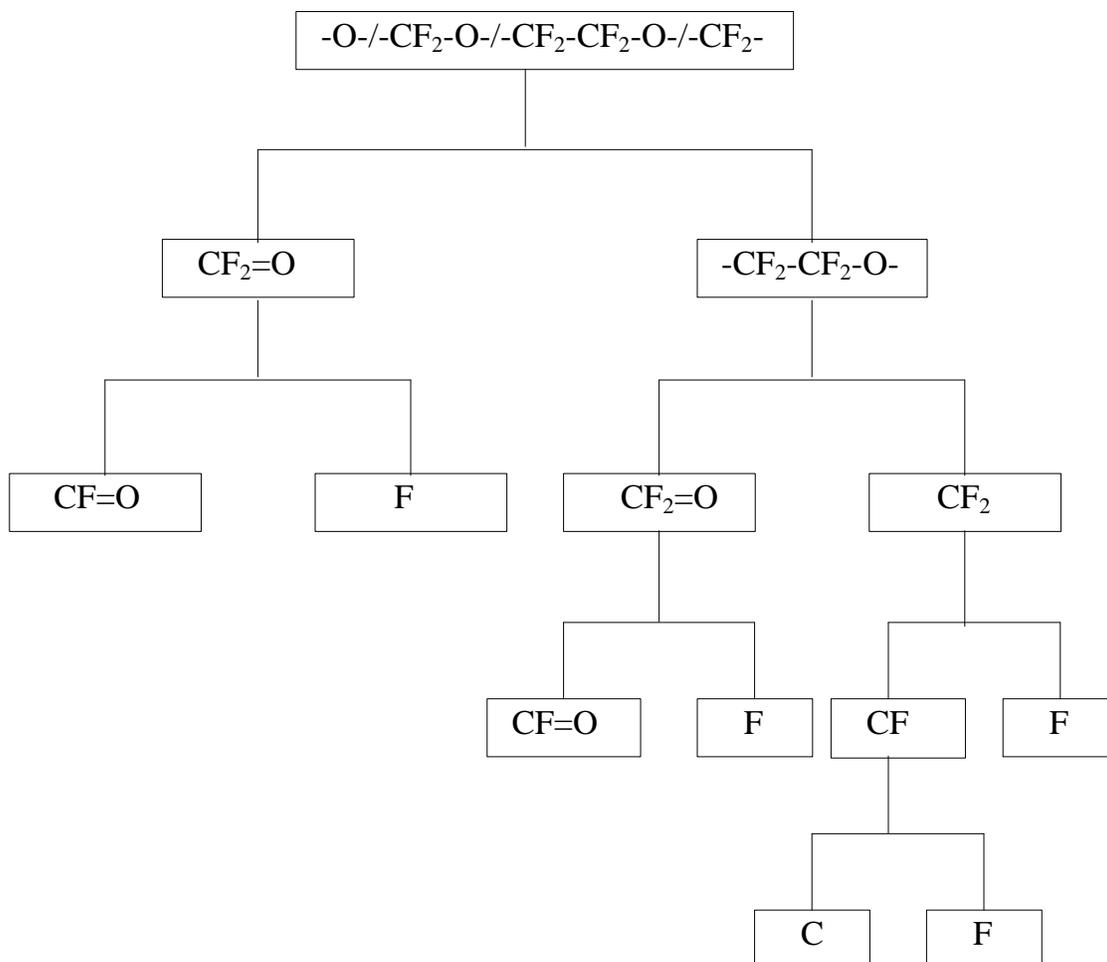


**slider (a) and an uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider (b).**

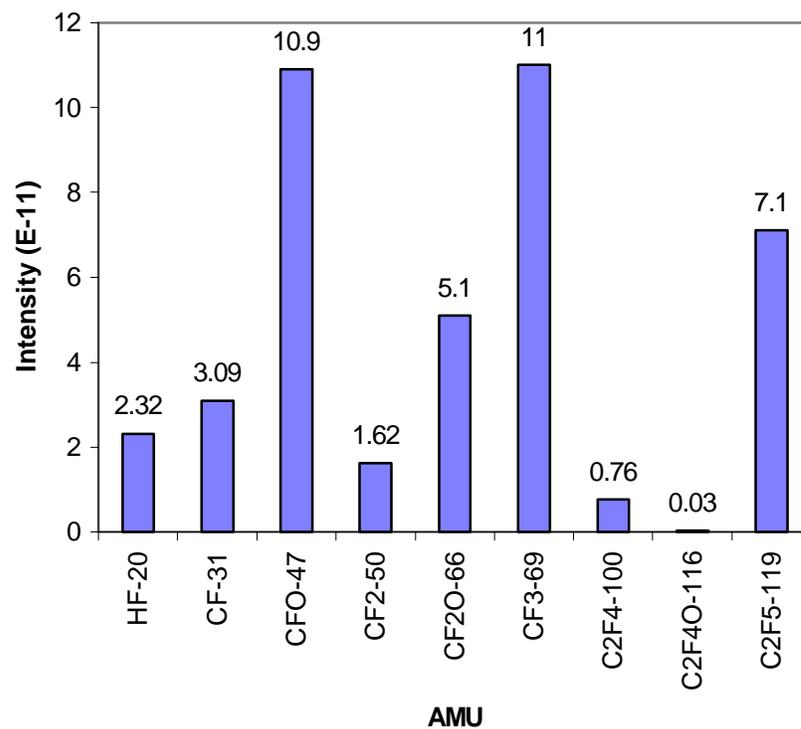
□



**Fig.2- The mass spectrum of ZDOL generated at the carbon coated slider/CNx disk interface**



**Fig.3 - The decomposition mechanism of ZDOL induced by friction and electron bombardment.**



**Fig. 4- The mass spectrum of ZDOL generated at the uncoated Al<sub>2</sub>O<sub>3</sub>-TiC slider/CNx disk interface**