Tribochemical Study of ZDOL Lubricated CNx-CHy Overcoats on Magnetic Disks

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Abstract

The tribological properties and tribochemical mechanisms of nitrogenated-hydrogenated carbon overcoats (CNx-CHy) with and without ZDOL lubrication were studied using an ultra-high vacuum (UHV) tribo-chamber equipped with a mass spectrometer. The dual layer overcoats consist of a top CNx layer and a bottom CHy layer. The results indicate that a thicker overcoat (CNx-CHy, 50Å/50Å) exhibits better wear resistance than a thinner overcoat (50Å/25Å) in different head/disk contact conditions. During the wear of CNx-CHy overcoats, a significant amount of H_2 is released but no obvious N_2 appears, showing that the tribochemical degradation behaviors of CNx and CHy are different, which is evidently associated with their chemical structures.

Keywords: Nitrogenated-hydrogenated carbon overcoat; Tribochemistry; ZDOL decomposition; Friction and wear

1. Introduction

In order to improve the reliability and durability of magnetic storage systems, much effort has been spent on the development and evaluation of new tribomaterials for head and disk overcoats, as well as lubricants. Previous experimental investigations indicate that, compared to uncoated Al_2O_3-TiC sliders, carbon coated sliders have better wear durability and lower friction coefficient in oxygen rich [1] as well as in high vacuum environments [2]. The hydrogenated carbon overcoats (CHx) with higher hydrogen content (>25%) have substantially improved tribological performance, which is believed to be associated with enhanced formation of a diamond-like structure (sp^3 bonding) [2]. Nitrigenated carbon overcoats (CNx) have also been shown to exhibit improved tribological performance [3]. The commonly used lubricants on hard disks are perfluoropolyethers (PFPEs). While the tribological properties of various materials used in the head/disk systems have been extensively studied, few studies have been concerned with the fundamental understanding of the tribochemistry. There are many unanswered questions regarding the tribochemistry of lubricants, sliders and disk overcoats, e.g. the lubrication and decomposition mechanisms of the lubricants, the tribochemical interactions of the lubricants with the head and disk interfaces and the tribochemical degradation mechanisms of diamond-like carbon overcoats during wear.

In this study, we investigate the friction and wear properties of dual layer nitrogenated and hydrogenated carbon films (CNx-CHy) as potentially new hard disk overcoats, in both dry and lubricated sliding using an UHV tribo-chamber equipped with a mass spectrometer. In addition, we explore the tribochemical degradation and wear mechanisms of CNx-CHy overcoats and the decomposition mechanism of ZDOL lubricant in the case of carbon coated and uncoated Al_2O_3-TiC sliders.

2. Experimental details

The friction tests were conducted in an UHV tribo-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 [2]. The hard disk is mounted on 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 were used here, just 56 rpm. The slider is mounted on 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 is 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 atomic 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 2×10^{-8} Torr is achieved at room temperature. Then the slider and disk are mounted in the chamber, and it is again pumped down. The mass spectrometer is then run for a period of time (80 s) to record the background mass intensities. When the disk begin to rotate, a jump of mass intensities usually occurs for those monitored masses, accompanied by a sudden increase of friction force. A sliding speed of 0.2 m/s and a sliding time of 220 seconds were used in all tests. After testing, the profiles of the wear tracks on the hard disks were measured by an optical interference microscope. It is noted that all fragments (m/e) from 1 to 192 of ZDOL decomposition products generated at the Al_2O_3-TiC slider/CHx disk interface were investigated in the same test conditions in previous studies, thus only the most important AMUs were monitored in this study. During these tests it was discovered that the normal load strain gauge was malfunctioning, so the load was not accurately known. However, this does not detract significantly from the usefulness of the results.

The sliders used in this study were 50% tape-flat Al_2O_3-TiC sliders with and without amorphous carbon films on their air bearing surfaces. The disks were commercially available 95 mm thin film disks with dual layer amorphous carbon overcoats (CNx-CHy), which consisted of a top nitrogenated carbon layer (CNx) and a bottom hydrogenated carbon layer (CHy). One overcoat (#2) is composed of 50 Å CNx and 50Å CHy layers, The other overcoat (#4) is composed of 50Å CNx and 25Å CHy layers. The nitrogen and hydrogen content of the dual layer overcoats has not been measured. 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:

ZDOL: $HO\text{-}CH_2\text{-}CF_2O\text{-}(CF_2O)_m\text{-}(CF_2CF_2O)_n\text{-}CF_2\text{-}CH_2\text{-}OH$, $n/m = 2/3$

3. Results and discussion

3.1. Friction and wear

Figure 1 shows the friction force curves of CNx-CHy overcoats (#2) tested under three interface conditions (uncoated Al_2O_3-TiC slider/unlubricated disk, Al_2O_3-TiC slider/ZDOL lubricated disk and carbon coated slider/ZDOL lubricated disk). In all three cases, similar friction behaviors are observed in the running-in stage, i.e. the friction is quite high at the beginning and decreases gradually to a relatively stable value after 20 seconds. After running-in stage, the friction on the ZDOL lubrication is lower than that in unlubricated sliding for a period of time, but in general, there is not much difference in the three friction curves.

Figure 2 presents the friction force curves of CNx-CHy overcoats (#4) tested under the same three contact conditions. Unlike Figure 1, high friction values do not occur in the running-in stage for these test series. Among the three contacts, the friction with the carbon coated slider is lower than the uncoated Al_2O_3-TiC sliders. Otherwise, there is no significant difference among the three contact conditions. Moreover, the friction behaviors of the #4 overcoat are similar to those for the #2 overcoat after the running-in stage.

After friction tests, the worn surfaces and wear track profiles of the CNx-CHy overcoats were measured using an optical interference microscope. It was found that relatively deep grooves were formed for the uncoated Al_2O_3-TiC sliders against the unlubricated and ZDOL lubricated disks (#4). Some wear particles were produced and distributed on the outer edges of the wear tracks. The wear depths for the above two cases were about 800 nm, much beyond the overcoat thickness. This indicates that the dual layer overcoats were worn through and severe wear of the substrate and magnetic layers occurred. The deep and sharp wear tracks are attributed to the penetration of hard wear particles. However, the wear depth was much smaller in the carbon coated slider/ZDOL lubricated disk case. The maximum wear depth was about 28 nm in small spots around the wear track while the average wear depth was about 5 nm, indicating that the wear process takes place mainly in the first CNx layer. It is reported [4] that CNx films are harder than CHx films, and the CNx-CHy overcoats are much harder than the substrate and magnetic layers. The destruction of the CNx and CHy layers produces hard particles, that cause abrasive wear of the overcoat and substrate.

Table 1 lists the wear volumes of the two CNx-CHy overcoats tested in this study. It also includes the wear volumes from two single layer overcoats (CNx and CHx) tested under the same conditions as a comparison. It is noted that the depth profile along the wear track is not uniform, it is difficult to obtain the accurate data from these wear tracks. Table 1 lists the average of five measurements for each wear track. Wear data indicates that the #2 overcoat has better wear resistance than the #4 overcoat, probably due to the thicker overcoat on sample #2 (100Å vs. 75Å). The single layer overcoats have higher wear resistance than the dual layer overcoats under the same test conditions, this may be related to their preparation processes. Better wear resistance was observed on ZDOL lubricated disks paired with carbon coated sliders versus uncoated Al_2O_3-TiC slider. The reason is that carbon coated slider prevents rapid catalytic decomposition that is caused by the Al_2O_3-TiC material of uncoated slider.

3.2. Chemical analyses of wear gas products

The mass spectrometer can be used to monitor in-situ the formation of wear gaseous products generated from the head/disk interface. Before the sliding tests start, the background intensity for each mass fragment of interest is recorded for 80 seconds. Since the CNx-CHy dual overcoats consist of a top CNx layer and a bottom CHx layer, significant amounts of N_2 and H_2 should be released when wear occurs in these two layers. Thus, N_2 (m/e=28) and H_2 (m/e=2) peaks were monitored in this study. Note that the mass/charge ratio of N_2 is the same as CO (28), the peaks at 28 may be attributed to either N_2 or CO. Figure 3 presents N_2 and H_2 intensities versus time for the CNx-CHy overcoats (#2) under three test conditions. The recording time corresponds to the 80 s before disk rotates. No obvious N_2 peak at 28 was observed during testing of the unlubricated disk. A strong peak at 28 appears for the uncoated slider/ZDOL lubricated disk combination, but none appear for the carbon coated slider case. Relative to the background, there is no significant increase in H_2 for the three contact conditions. A small H_2 peak appears during the friction process for the unlubricated disk. These results imply that wear of CNx-CHy overcoat (#2) occurs primarily in the top layer (CNx).

Figure 4 presents the N_2 and H_2 intensities as functions of time for CNx-CHy overcoat (#4). Similar to the unlubricated #2 case, no N_2 peak appears during the test even though the dual overcoats were worn through. Moreover, only a weak CO_2 (44) peak was found in this case (not shown in Figures). However, a strong 28 peak appears for the uncoated slider/ZDOL lubricated disk case and a weaker peak appears for the carbon coated slider/ZDOL lubricated disk contact. Since no significant N_2 peak was found during the testing of the unlubricated CNx-CHy overcoat, the peaks at 28 in the ZDOL lubricated disks should be attributed to the CO rather than N_2, which is associated with the decomposition of ZDOL. On the other hand, for the unlubricated #4 disk, a large amount of H_2 emits from the head/disk interface at the beginning of the sliding test and remains at high intensity for the test duration. This indicates that severe wear occurs in the initial sliding stage, the first layer (CNx) is worn through and the second layer (CHx) is being removed. In the uncoated slider/ZDOL lubricated disk case, no H_2 is released before 200 seconds, but a significant amount of H2 is found at just past 200 seconds. At this point, wear of lower CHy layer initiates. In the coated slider/ZDOL lubricated disk case, there is no increase in H_2, indicating that wear occurs primarily in the first layer. Though the above analysis of the H_2 intensity, we can conclude the order of the wear resistance for the three cases as follows: uncoated slider/unlubricated disk < uncoated slider/ZDOL lubricated disk < coated slider/ZDOL lubricated disk. This analysis is consistent with the wear data listed in Table 1. This demonstrates that the mass spectrum of H_2 can be used as a relative measure of the wear severity in those dual layer overcoats and an indication when wear transition from top layer to bottom layer in some cases. It is noted that significant amounts of H_2 was observed during the wear of CNx-CHy overcoats but no N_2. This is probably related to their different chemical structures.

The decomposition process of ZDOL lubricant is closely related to the extent of wear in the carbon overcoats. Figure 5 gives the intensity variation of fragments (H_2, HF, N_2, CO, CO_2 and CF_3) with recording time for the uncoated slider/ZDOL lubricated CNx-CHy (#4) case. During the wear of the CNx layer, strong peaks appear at 28 (CO) and 44 (CO_2), which are associated with the decomposition of ZDOL. Figure 5 (b) presents the details of HF and CF_3 intensities. When the sliding time approaches 200 seconds (the wear transition point), the generation of CF_3 halts while HF production increases, indicating that the decomposition of ZDOL is not complete until the first layer is worn away. Before the wear transition point, ZDOL and its decomposition products still provide some lubricating action, thus, lower friction values were observed within this period (see Figure 2). Moreover, the increase in HF intensity is associated with the evolution of H_2 during the wear of the CHx layer.

3.3. ZDOL decomposition mechanisms

Figures 6 and 7 present the mass spectra of ZDOL decomposition products generated from the CNx-CHy (#2) and CNx-CHy (#4) overcoats. It is found that the mass spectra of Figures 6 and 7 have similar characteristics. For the carbon coated slider, only two main peaks appear at 47 (CFO) and 66 (CF_2O); for the uncoated Al_2O_3-TiC slider, CF_3 (69) and C_2F_5 (119) peaks appear in addition to CFO and CF_2O. We have previously studied the decomposition mechanisms of ZDOL in the presence of the carbon coated slider and the uncoated Al_2O_3-TiC slider. As was reported [5], the decomposition mechanism of ZDOL is controlled by friction decomposition and electron cleavage in the mass spectrometer for the carbon coated slider/ZDOL lubricated disk case; the decomposition mechanism is dominated by friction and Lewis acid catalytic decomposition for the uncoated Al_2O_3-TiC slider/ZDOL lubricated disk case,. Therefore, the occurrence of CFO and CF_2O results from friction decomposition and electron cleavage, whereas the occurrence of CF_3 and C_2F_5 is due to the catalytic decomposition of ZDOL.

3.4. Discussions

Friction and wear at the head/disk interface depends strongly on ZDOL decomposition. For the carbon coated slider case, the ZDOL decomposition mechanism is dominated by the friction effects such as frictional heat, triboelectrons and mechanical stretching. For the uncoated Al_2O_3-TiC slider case, the ZDOL decomposition results from frictional and catalytic effects. The initial decomposition step is due to friction, where reactive gaseous products (CF_2O and HF) are produced and then strong Lewis acid (AlF_3) is formed by the following reactions,

$$CF_2O + Al_2O_3 \longrightarrow AlF_3 + CO_2 + CO$$

$$6HF + Al_2O_3 \longrightarrow 2AlF_3 + 3H_2O$$

The second step is a rapid catalytic decomposition of ZDOL on the AlF_3 surface. This decomposition process can be expressed as follows,

$$R\text{-}CF_2\text{-}O\text{-}CF_2\text{-}R \longrightarrow R\text{-}CF{=}O + CF_3\text{-}R$$

The above catalytic reaction has been well studied by Kasai et al [6]. It is noted that the catalytic reaction has a low activation energy and may proceed at a very high reaction rate under friction stimulation. Carbon coating on the air bearing surface prevents the direct contact of Al_2O_3-TiC with ZDOL and its decomposition products, eliminating the rapid catalytic decomposition of ZDOL. Therefore, the wear durability of ZDOL lubricated disks with the carbon coated slider is better than that with the uncoated Al_2O_3-TiC slider.

The MS analyses show that a significant amount of H_2 is produced but no obvious N_2 is released during the severe wear of CNx-CHy overcoats, indicating that the degradation behaviors of CNx and CHy are different. This difference may be due to their different chemical structures. Ideally, diamond like carbon has the same structure as diamond (tetrahedron configuration), i.e. the carbon atom is incorporated with four other carbon atoms in a sp^3 hybrid form. Actually, the amorphous hydrogenated carbon overcoat consists of three dimensional networks of threefold (sp^2) and fourfold (sp^3) bonds. Hydrogen incorporated into the carbon films may stabilize tetrahedral coordination of carbon atoms (sp^3 bonding). It was reported [7] that the amount of chemically bonded hydrogen in the CHx film is less than the total hydrogen content. The non-bonded hydrogen may be chemisorbed to the carbon atoms. During the wear of CHx films, the chemisorbed hydrogen is initially released as H_2. The chemical bond (C-H) may be cleaved by friction, releasing the bonded hydrogen. The release of the bonded hydrogen atom damages the original diamond-like structure of CHx films, causing a decrease in the wear resistance of the CHx films. On the other hand, some studies [8, 9] indicated that nitrogen atoms are chemically bonded to carbon atoms with large numbers of double bonds (C=N) and triple bonds (C≡N), no physisorbed or chemisorbed N atoms were found in the amorphous CNx films. Since those C-N bonds have higher bond dissociation energies and chemical stabilities than C-C single bonds, they are unlikely to be cleaved by friction. Therefore, no significant amount of N_2 is found during the wear of CNxCHy overcoats. Based on the above analysis, the different tribochemical degradation behaviors of CHx and CNx films are related to their chemical bonding and structures, but their exact degradation mechanisms are not clear yet.

4. Conclusions

1. The wear of CNx-CHy overcoats with ZDOL lubrication is less than that without lubrication. Compared to uncoated Al_2O_3-TiC sliders, the use of carbon coated sliders significantly reduce the wear of ZDOL lubricated disks. A thicker CNx-CHy overcoat (#2) has better wear resistance than a thinner overcoat (#4); single layer overcoats have

better wear resistance than dual layer overcoats under the same test conditions. However, the friction does not vary much with various head/disk combinations.

2. The mass spectrum analysis indicates that a significant amount of H_2 is released during the wear of CNx-CHy overcoats but no obvious N_2 appears, indicating that the degradation behavior of CNx is different from CHy, which is due to the different chemical bonding of carbon atoms with nitrogen and hydrogen atoms. The mass spectrum intensity of H_2 may be used to monitor the wear severity of dual layer CNx-CHy overcoats.

3. Optical interference microscope images show that damage of the CNx-CHy overcoats produces hard wear particles that cause the severe abrasive wear of the disk (#4).

4. The decomposition mechanism of ZDOL at the head/disk interface is controlled by friction effects for the carbon coated slider/hard disk case, and is dominated by friction and Lewis acid catalytic effects for the uncoated Al_2O_3-TiC slider case. Carbon coating of the Al_2O_3-TiC surface prevents the catalytic decomposition of ZDOL by producing a barrier between the Al_2O_3-TiC material and the ZDOL.

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Captions

Figure 1 The friction curves of CNx-CHy overcoats (#2) under three contact conditions.

Figure 2 The friction curves of CNx-CHy overcoats (#4) under three contact conditions.

Figure 3 The intensities of N_2, CO (a) and H_2 (b) as function of recording time for CNx-CHy (#2) overcoat.

Figure 4 The intensities of N_2, CO (a) and H_2 (b) as function of recording time for CNx-CHy (#4) overcoat.

Figure 5 The intensities of H_2, HF, N_2, CO, CO_2 and CF_3 as function of recording time for uncoated Al_2O_3-TiC slider/CNx-CHy (#4) disk with ZDOL lubrication (a) and the details of the intensities of HF and CF_3 (b).

Figure 6 The mass spectra of ZDOL decomposition products generated from ZDOL lubricated CNx-CHy (#2) disks rubbed against carbon coated slider (a) and uncoated Al_2O_3-TiC slider (b).

Figure 7 The mass spectra of ZDOL decomposition products generated from ZDOL lubricated CNx-CHy (#4) disks rubbed against carbon coated slider (a) and uncoated Al_2O_3-TiC slider (b).

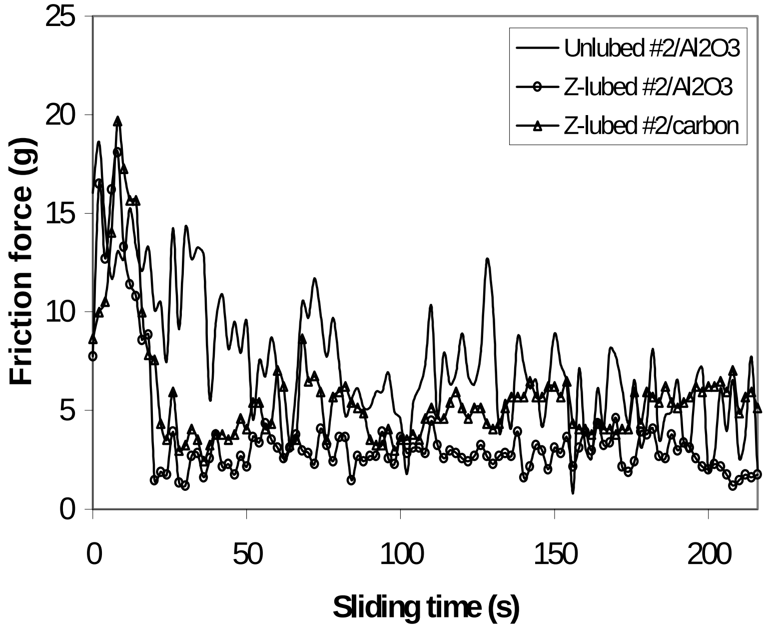

Figure 1 The friction force curves of CNx-CHy overcoats (#2) under three contact Conditions.

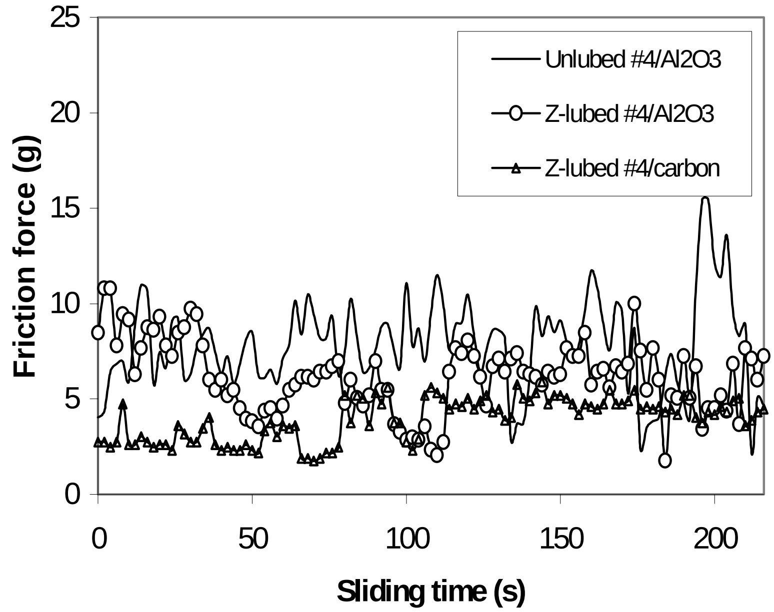

Figure 2 The friction force curves of CNx-CHy overcoats (#4) under three contact conditions.

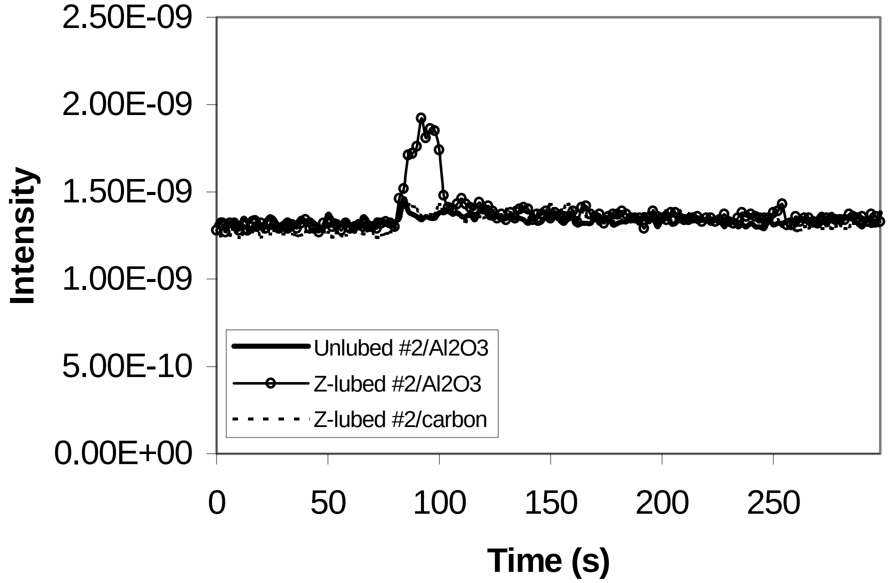

Fig. 3 (a)

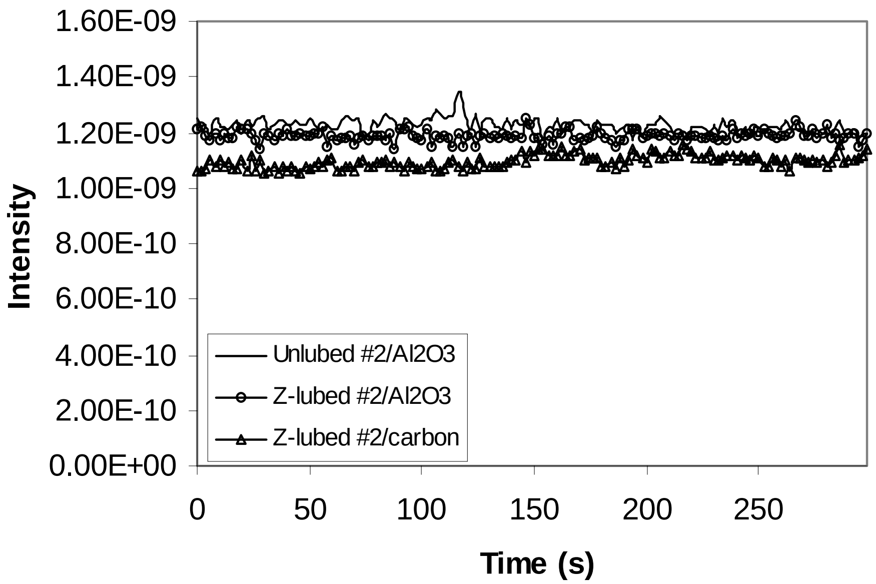

Fig. 3 (b)

Figure 3 The intensities of N_2, CO (a) and H_2 (b) as function of recording time for the CNx-CHy (#2) overcoat.

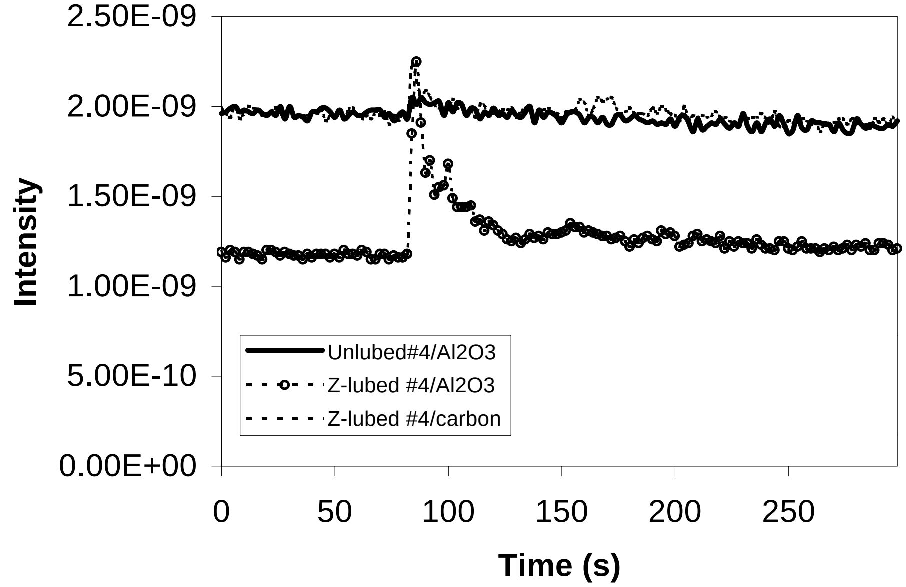

Fig. 4(a)

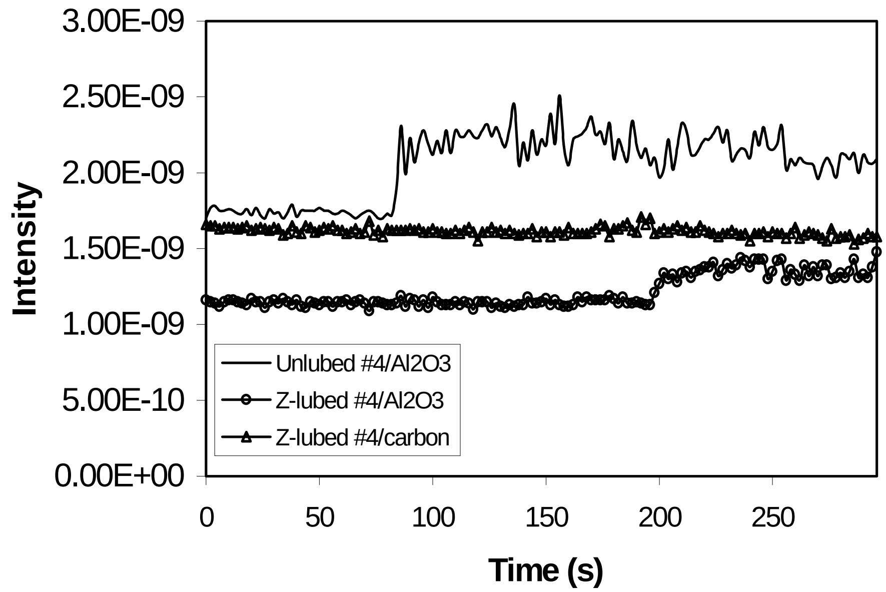

Fig. 4(b)

Figure 4 The intensities of N_2, CO (a) and H_2 (b) as function of recording time for CNx-CHy (#4) overcoat.

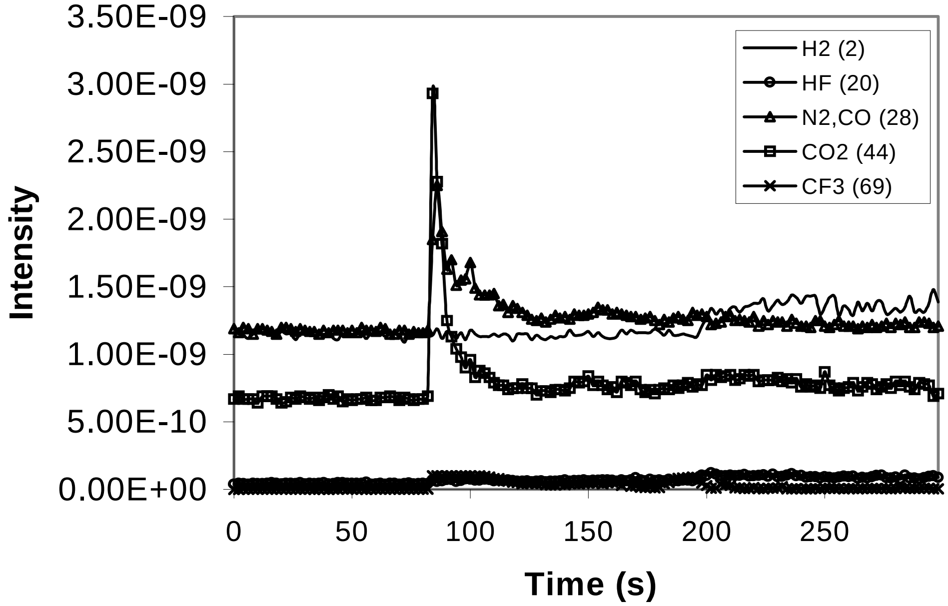

Fig. 5(a)

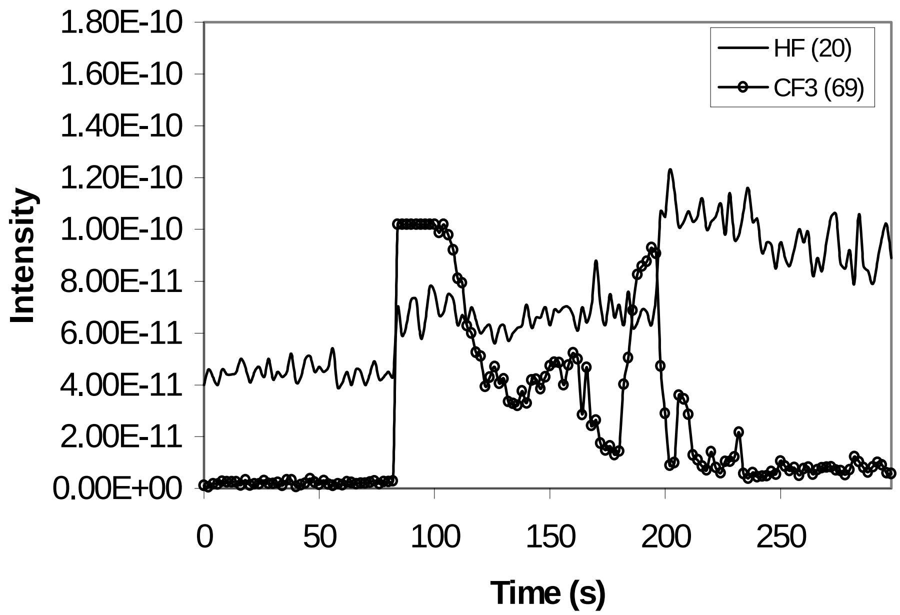

Fig. 5(b)

Figure 5 The intensities of H_2, HF, N_2, CO, CO_2 and CF_3 as function of recording time for uncoated Al_2O_3-TiC slider/CNx-CHy (#4) disk with ZDOL lubrication (a) and the details of the intensities of HF and CF_3 (b).

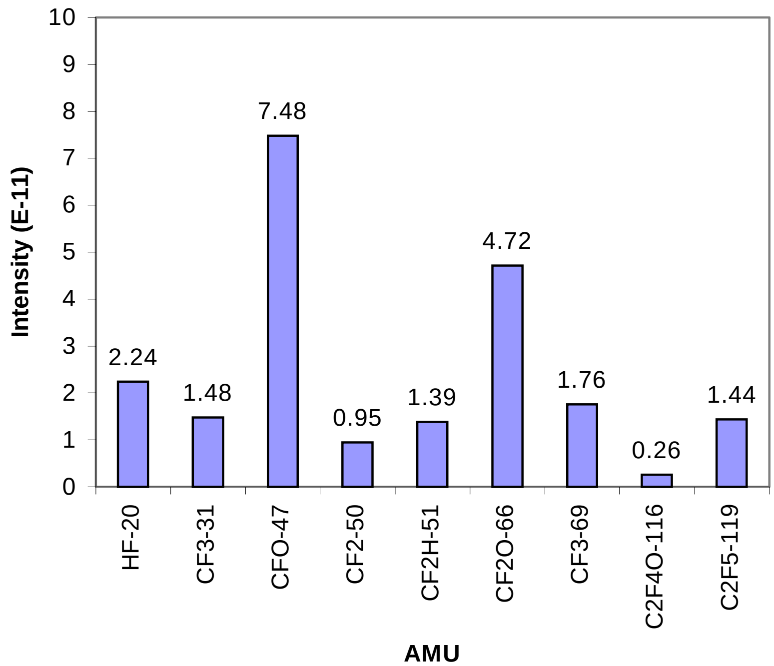

Fig 6(a)

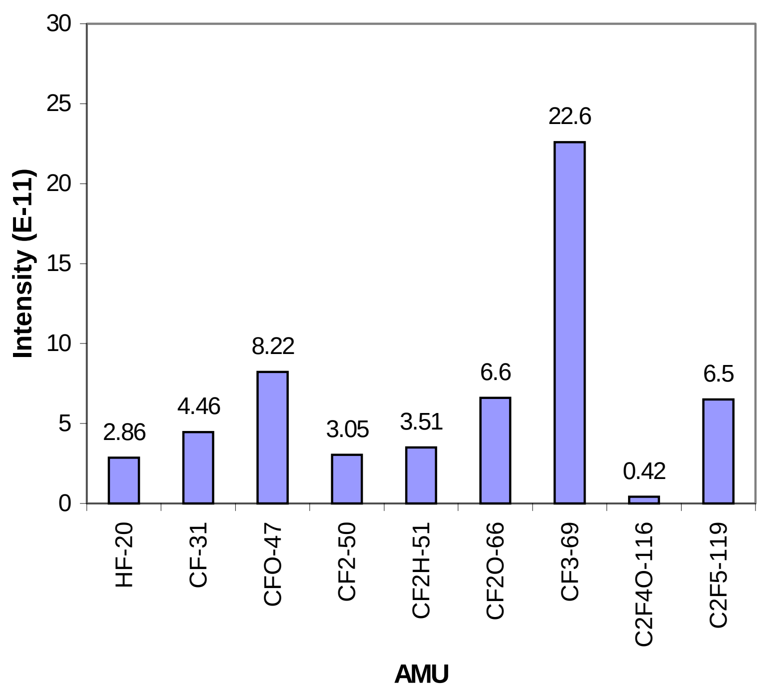

Fig. 6 (b)

Figure 6 The mass spectra of ZDOL decomposition products generated from ZDOL lubricated CNx-CHy (#2) disks against carbon coated slider (a) and uncoated Al_2O_3-TiC slider (b).

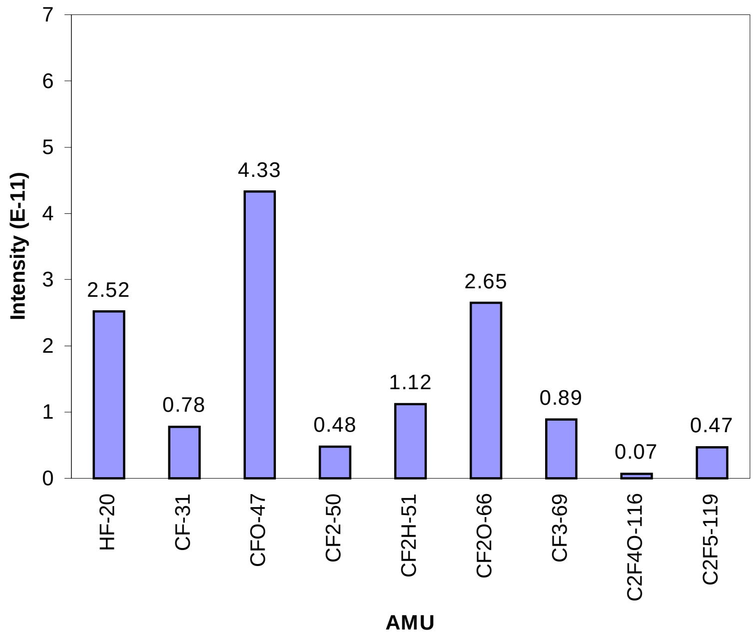

Fig. 7(a)

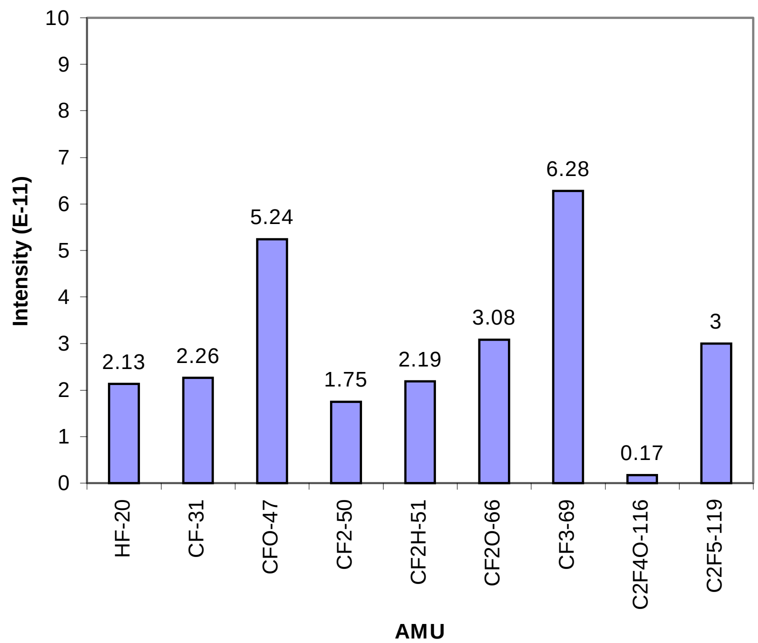

Fig. 7(b)

Figure 7 The mass spectra of ZDOL decomposition products generated from the CNx-CHy (#4) disks against carbon coated slider (a) and uncoated Al_2O_3-TiC slider (b).

Table 1 The wear volume of hard disk overcoats under various head/disk contacts, mm^3

	CNxCHy (No. 2, 50Å-50Å)	CNxCHy (No. 4, 50Å-25Å)	CNx (MNM 87, 75Å)	CHx (G664, 75Å)
Unlubed disk/Al_2O_3 slider	2.8×10^{-5}	5.8×10^{-3}	------	------
Z-lubed disk/Al_2O_3 slider	1.7×10^{-5}	2.2×10^{-3}	9.9×10^{-6}	Unmeasurable
Z-lubed disk/carbon slider	1.4×10^{-5}	3.3×10^{-5}	Unmeasurable	Unmeasurable