Hardness and Tribochemical Evaluation of Ultra-Thin CH_x and CN_x Overcoats

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Abstract—In this paper we present the results of nano-indentation hardness measurements, nano-wear measurements as well as tribochemical wear tests on a series of hydrogenated and nitrogenated carbon films. It is shown that the mechanical properties, such as hardness and abrasive wear resistance, while important, are not the primary determining factors in the wear durability of the head disk interface in magnetic hard disk drives.

I. Introduction

Hydrogenated (CH_x) carbon overcoats have been found to produce better wear durability than the pure sputtered carbon. Usually hydrogen gas is introduced into the deposition environment to obtain a CH_x film on the disk. Studies have shown that variations of hydrogen percentage in the overcoat can result in different atomic bonding in the carbon film [1,2]. Besides amorphous carbon (a:C) and hydrogenated carbon (CH_x) films, nitrogenated carbon (CN_x) films are also being used as the protective overcoat on disks. Since nitrogen atoms can network better with carbon atoms in the film, usually CN_x coatings are harder than CH_x coatings [3,4]. Recently, contact-start-stop and pin-on-disk type tests have been conducted to demonstrate the superior wear durability of nitrogenated carbon coatings compared to the amorphous carbon (a:C) [5]. It is known that the wear at the head-disk interface is not only affected by the hardness of the coating but also by the other mechanical and chemical properties of the contacting surfaces. Usually a good combination of slider materials, disk coating and lubricant can improve the wear durability at the head-disk interface significantly.

The objective of this paper is to understand the controlling factor of wear at the head disk interface by studying the mechanical and tribochemical properties of CH_x and CN_x films sliding in contact with Al_2O_3/TiC sliders. The mechanical properties of the contacting surfaces have been traditionally studied as the controlling parameters in wear tests. Results presented in this paper show that the chemical properties are of equal importance in understanding the friction and wear at the HDI.

II. Experiment And Results

A. Nano-Indentation Test

1). CHx Coatings With Different Hydrogen Levels

Nano-indentation experiments on CH_x were performed using a Hysitron tester, a schematic illustration of which is shown in Fig. 1. The system serves as a portable add-on equipment to commercially available AFM's and performs precise nano-indentation with load-displacement curves, plus high resolution surface imaging, allowing the test region to be aligned over the exact region of interest. The instrument uses a capacitive force/displacement transducer made by Hysitron. It generates the loading force and measures both force and displacement. A three-sided triangular diamond tip with a nominal radius of 50 nm was used in these experiments.

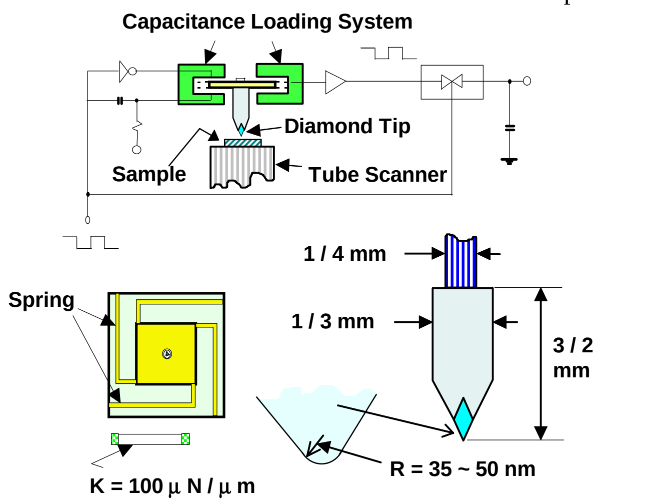

Fig. 1 Schematic Diagram of the Hysitron Tester.

The CHx samples used in the study were chosen to span a wide range of hydrogen concentration. These amorphous carbon films of 25 nm thickness were deposited on silicon <100> substrates by magnetron sputtering with a graphite target. During the sputtering process, the flow rates of argon and hydrogen gases were adjusted to control the hydrogen content of the films. Silicon was also chosen to provide some insight into the comparison of relative nano-indentation hardness.

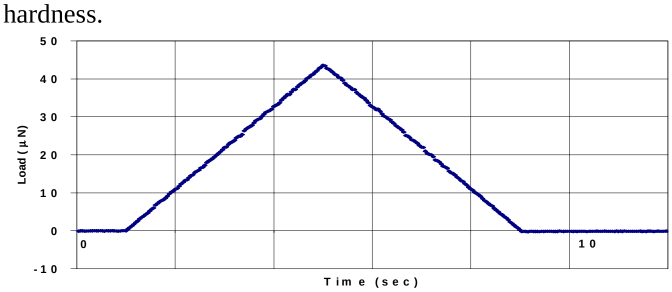

Figure 2 Load-Time Profile of nano-indentation using Hysitron Tester.

Experiments were performed using a triangular load-time profile like that shown in Fig. 2. The indenter was first loaded to the peak load set up by the user and then unloaded with a certain total time duration of about 10 seconds in these tests. After the test, the load-displacement and resulting surface image of the indentation mark were carefully examined to establish a method for determining relative nano-indentation hardness on all of the samples. A nano-indentation mark on a 28 % hydrogen film of 25 nm thickness made with a 45 μN peak load using the Hysitron tester is shown in Fig. 3. The circular indentation mark provides an excellent picture of this residual contact impression and clearly indicates a spherical indenter geometry. The load versus indenter displacement data for this test is shown in Fig. 4. The relatively large elastic recovery during unloading exhibits a predominantly elastic behavior of these films during the deformation. For each material, two independent tests with the same peak load at 45 μN were performed and investigated to produce repeatability of the results.

It is well known that the effect of the substrate is not significant if the indentation depth is smaller than one fifth of the film thickness. Hence, it is acceptable to compare the hardnesses of the different films without significant influence of the substrates using the results obtained with indentation depths less than 5 nm, which is one fifth of the film thickness. It is useful to begin by assuming that overcoat films must be highly resistant to plastic deformation during contact events. This follows from the observation that many of the mechanisms of disk failure begin with or directly involve plastic deformation. In this regard, a comparison of residual depths from the nano-indentation results at the same peak load is carefully considered and plotted in Fig. 5. A notable feature in Fig. 5 is the influence of hydrogen on the mechanical properties of the sputter-deposited films. The films containing low hydrogen have relatively high hardness as indicated by shallow residual depth, in the range of 1.4-1.5nm, but the hardness for the 40 % film is considerably lower with residual depth as large as 6 nm. The indentations for the 40 % film are in fact so deep that they are more than one fifth of the film thickness.

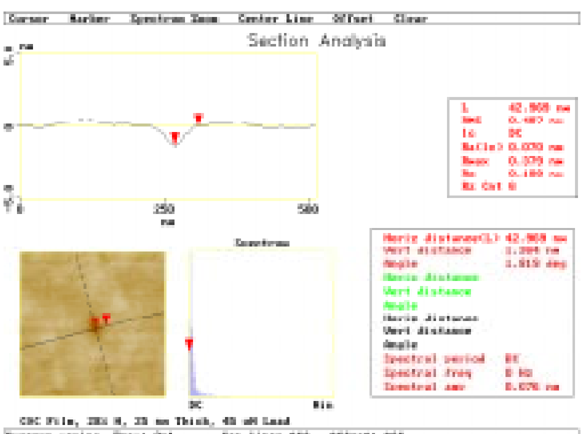

Fig. 3 Section Analysis of Nano-Indentation Test on CHx Films using Hysitron Tester.

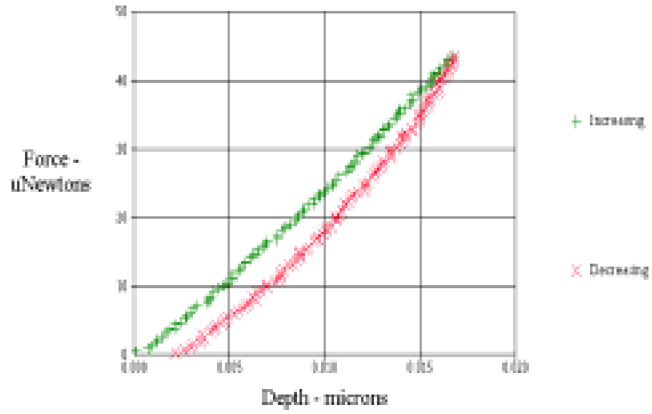

Fig. 4 Load-Displacement Curve of Nano-Indentation Test using Hysitron Tester

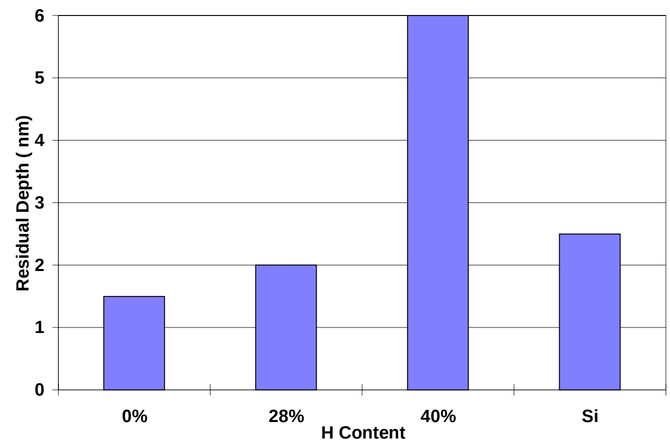

Fig. 5 Residual Depth vs. Hydrogen Content in Nano-Indentation Tests using Hysitron Tester at 45 μN load with a Diamond Tip of 50 nm in Radius.

2).Comparison of CN_x Coatings and CH_x Coating

Three samples were used in the study of nano-indentation tests : CNx films of 15 nm thickness with no lube, CNx films of 15 nm thickness with 1.2 nm Z-dol and CHx films with 1.2 nm Z-dol. All films were deposited on magnetic layers over aluminum disks. The nano-indentation hardness for comparison of CNx and CH_x films were performed by the Point Contact Microscope (PCM). In these investigations, a diamond tip with nominal radius of 100 nm was attached to a single parallel-leaf cantilever beam for the PCM, as described by Kaneko and his colleagues [6]. At 52 μN load, the residual depths on these carbon films together with Si were plotted in Fig. 6. Each value in Fig. 6 represents the average of two independent tests. Nano-indentation tests on Si were performed at the beginning and end to ensure repeatability of the results. With a mere 3% difference of residual depth between these two tests on Si, we concluded that the effective tip radius was not affected significantly by the Z-dol throughout the measurements. It was observed that all of these film were relatively softer than Si. The 30% N_2 CNx films were relatively harder than the 35% H_2 carbon film by about 30-40%.

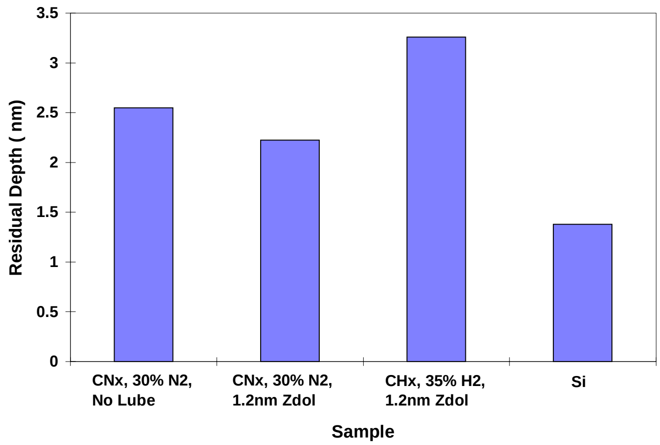

Fig. 6 Residual Depth of Nano-indentation Test on CHx and CNx Films using the PCM at 52 μN Load with a Diamond Tip of 100 nm in Radius.

B. Nano-wear test

1). CHx Coatings With Different Hydrogen Levels

Nano-wear tests were performed by the Point Contact Microscope (PCM) where diamond tips were used to plow or cut the sample surface by raster scan. In these investigations, a diamond tip with nominal radius of 60 nm was attached to a single parallel-leaf spring with spring constant of 17.0 N/m for the PCM. By using a very light load, the PCM can measure surface topography without causing any damage to the surface, just as the standard AFM can do. However, using the PCM, heavier loads with a wide range of values can be applied to the tip, so that nano-wear tests under various loading conditions with certain wear cycles can be achieved. Many investigations show that this technique is very effective for evaluating microscale tribological properties, especially wear durability of ultra-thin films for magnetic recording applications [7,8,9,10].

The tip usually starts to plow and cut the tested surfaces when the normal load is greater than a critical load for wear initiation. The degree of damage actually reflects the wear durability of the tested film from the nanotribological point of view. In nano-wear tests using the PCM, the surface of an area 5 μm by 5 μm is scanned with a light load to obtain the surface topography image. Then the scan size is reduced to 2 μm by 2 μm with the same center location, and the loading force is increased to a value large enough to cause wear. After every certain number of cycles, the loading force and scan size are reset to the imaging values and the surface topography is obtained. The wear depth can be acquired from the cross section of the wear mark. The wear depth versus wear cycles is plotted from the results to compare the wear resistance of different films.

For the same group of carbon films used in the part 1) nano-indentation tests, Fig. 7 shows the wear depth versus wear cycles obtained from the nano-wear tests with a loading force of 28 μN acting on the diamond tip. For the 0 % hydrogen film, the wear rate is very low, with a wear depth of only 6 nm at the 24th wear cycle. The 28 % hydrogen film has a higher wear rate with a wear depth at the 24th wear cycle of 15.5 nm. Both curves are nearly linear with wear cycles because the film thickness is 25 nm. The wear depth of the 40 % hydrogen film increases relatively faster with wear cycles, with the wear depth reaching 29.5 nm at the 16th wear cycle. After 16 wear cycles, the wear rate drops dramatically. The reason for this is that the film is worn off, and the tip scans the silicon substrate with a load too low to wear it much. The drop in the wear rate indicates that the silicon substrate is harder and more wear resistant than the film. A typical wear mark for the 28 % hydrogen film after 16 wear cycles is shown in Fig. 8. For better observation, the wear mark is displayed by its inverse image, showing depth as height. The wear depth for this 28 % hydrogen film is 11nm.

To illustrate the effect of hydrogen content on the wear depth, a comparison of wear depths versus hydrogen concentration after 16 wear cycles for these films is made. It is observed that the wear depth increases with hydrogen concentration. In other words, the film with lower hydrogen content has higher microscopic wear resistance. This result is quite consistent with the previous nano-indentation hardness measurements, which show that the hardness decreases with the hydrogen content.

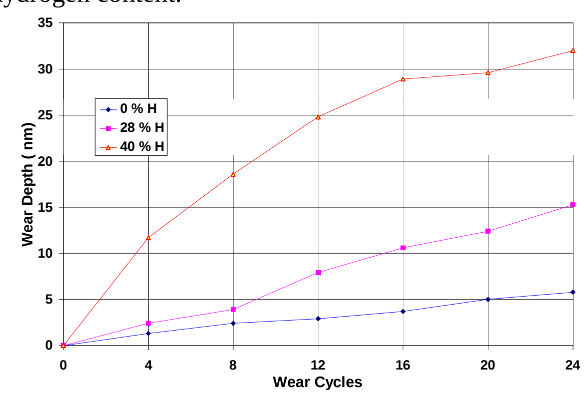

Fig.7 Wear Depth vs. Wear Cycle in Nano-Wear tests with 28 μN Load using the PCM.

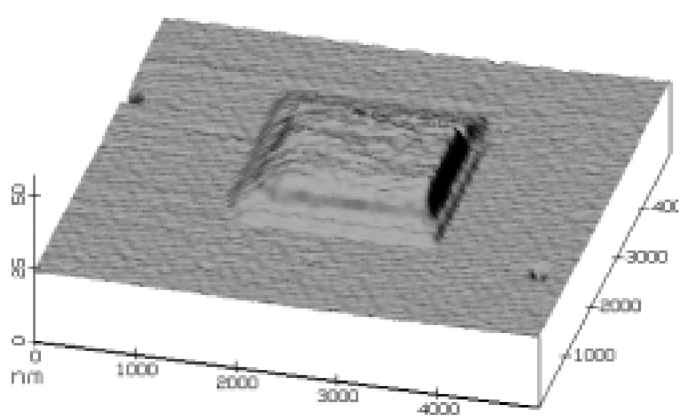

Fig. 8 Wear Mark of the 28% CHx after 16 Wear Cycles using the PCM.

2).Comparison of CN_x and CH_x Coatings

The same samples used in the part 2) nano-indentation tests were used in nano-wear test. They were CNx films of 15 nm thickness without lube, CNx films of 15 nm thickness with 1.2 nm Z-dol and CHx film with 1.2 nm Z-dol. With 80 μN applied to the diamond tip with nominal radius of 100 nm, the wear resistance of these films can be compared by determining the changes in surface profile resulting from the nano-wear tests using the PCM. A comparison of wear depths after 3 wear cycles on these films is plotted in Fig. 9. Each value in Fig. 9 represents the average of three independent tests. Perhaps the most notable feature in Fig. 9 is the extreme value of wear depth of the 35% H_2 carbon film; the 21 nm value that is larger than the film thickness 15 nm in the figure clearly indicates that the film was broken during the test. As shown in the results, there is little difference between lubed and unlubed CNx films suggesting that the nano-wear tests were basically "lubricant-indifferent" as the load applied to the diamond tip is too large to "observe" the lubricant. The fact that only the CHx film was broken implies that CNx films have a higher protective property than the CHx film and may have a great potential for application as excellent hard disk overcoat materials. In the nano-wear tests, the wear depth exhibited the behavior of toughness which is a combined performance of hardness and film adhesion. This can be better appreciated by comparing the 930-1100% difference of wear depth and the 30-40% difference of residual depth on CHx and CNx films in the nano-wear and nano-indentation test, respectively.

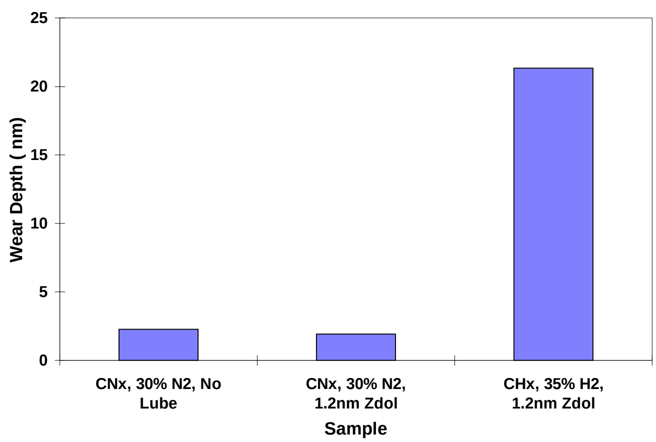

Fig. 9 Nano-wear Tests on CHx and CNx Films using the PCM.

C. Tribochemical Tests

A photograph of the tribochamber is shown in Fig. 10. It is equipped with a mass spectrometer which can simultaneously monitor intensities of 15 different atomic mass units versus time. Friction can also be recorded. The vacuum is obtained by a turbo pump and a mechanical pump. The base pressure during a drag test is 2.0E-8 Torr. Resistance heating tapes are used to bake the chamber. Detailed description of this system is given in a previous paper [11]. The experimental procedures were as follows: The chamber was baked at vacuum at 150 °C for 48 hours. The filaments of the mass spectrometer were fully degassed during the bake-out. Argon was back filled into the chamber when it was opened to set up the disk and slider. The drag test usually started with a certain period of delay after the mass spectrometer had been turned on. This period enabled the mass spectrometer to register the background mass intensities. When wear occurred at the interface, the spindle was stopped and the mass spectrometer continued to record for a certain period of time before the experiment was completed.

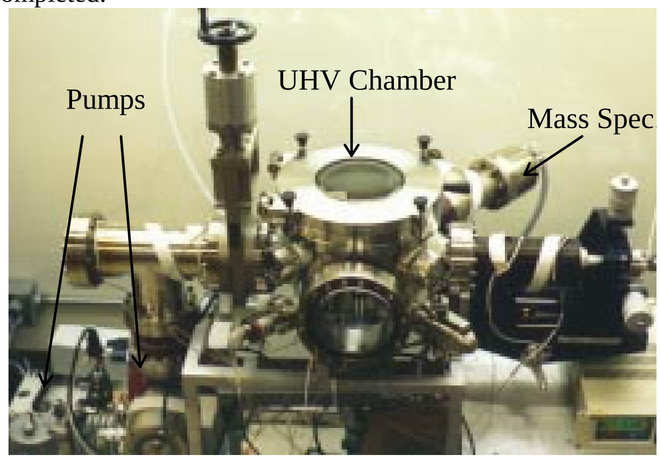

Fig. 10. Photograph of the tribochemical chamber.

1). CHx Coatings With Different Hydrogen Levels

CH_x carbon coated disks with 10%, 16%, 25%, 35% and 41% hydrogen content were tested inside the vacuum chamber. Masses 2 (H_2), 15 (CH_3), 28 ($CO+N_2$), 31 (CF), 44 (CO_2), 47 (CFO), 50 (CF_2), 51 (CF_2H), 66 (CF_2O), 69 (CF_3), 100 (C_2F_4), 119 (C_2F_5), and 169 (C_2F_7) were recorded in these tests. These disks were supersmooth disks lubricated with Z-dol. Fig. 11 shows the averaged intensities of the strongest peaks in the Z-dol spectra produced by uncoated and CH_x coated 50 % Al_2O_3/TiC sliders dragging on five different CH_x disks. The general trend in Fig. 11 is that mass intensities released from the head-disk interfaces decreased as the hydrogen content increased. Fig. 12 shows the durabilities of uncoated and coated sliders on the five CH_x disks. Durability of these interfaces is defined as the drag revolutions they can endure before a wear track can be obserbed optically at 1x. Erratic friction changes and the appearance of wear tracks on disks are also indications of wear. The number of drag revolutions before wear is plotted versus the hydrogen percentage in the coatings. For both types of sliders, the wear durability of the disks increased with the increasing hydrogen content. Disks generally had longer life with use of carbon coated sliders than with uncoated ones. The improvement of the durability using carbon coated sliders on 35% and 41% hydrogen content coatings were better than on the other three CH_x coatings. A more detailed discussion of these results was published in a previous paper [11].

2).Comparison of CN_x Coatings and CH_x Coatings

CN_x coated disks were drag tested inside the same vacuum chamber shown in Fig. 10. The sliders used in this study were 30% pico Al_2O_3/TiC sliders with and without nitrogenated carbon coating on their air bearing surfaces. The suspension load of these sliders was 1.8 grams. The disks used were 95 mm smooth thin film disks with CN_x and CH_x coatings. The lubricant on the disks was Z-dol.

First the nitrogenated carbon coated disk was tested by dragging a bare Al_2O_3/TiC slider on the disk surface. The nitrogen content in the disk coating was 30%. The results are presented in Figs. 13 and 14 which show the friction coefficient vs. the number of revolutions and the mass spectrum of the lubricant fragments, respectively. In Fig. 13, the initial friction started at 0.62 then stabilized at around 0.41 for 277 revolutions before it dropped. The initial friction decrease suggests burnishing of the disk surface and generation of small particles at the interface. These small particles resulted in rolling contact and the friction reduction. The friction drop at 277 revolutions indicates wear at the head-disk interface. Damage to the disk coating can result in a change in real contact area at the head-disk interface which can cause the friction drop. The average intensities of the recorded masses are plotted in Fig. 14. High peaks are located at mass 47 (CFO) and 66 (CF_2O), while all other masses are relatively weak. This pattern suggests that the degradation of the lubricant was mainly due to the mechanical energy introduced by the sliding as discussed in a different paper [12]. In the same paper, it is concluded that high peak at masses 69 (CF_3) and 119 (C_2F_5) could suggest catalytic reaction between the slider and the lubricant.

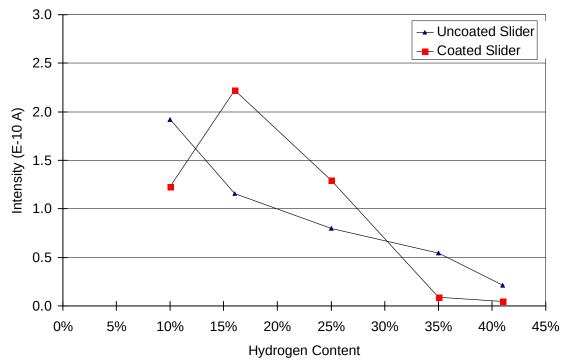

Fig. 11. Strongest peak intensities in each Z-dol spectrum on five CH_x disks for both uncoated and carbon coated sliders.

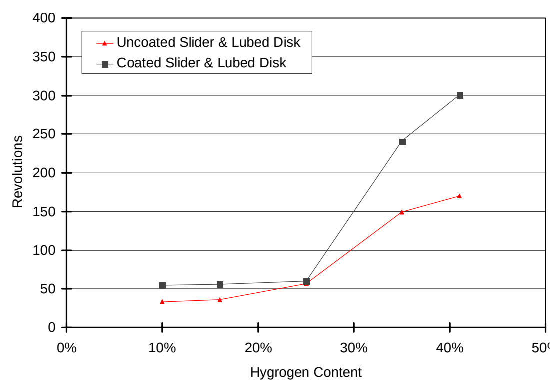

Fig. 12. Number of revolutions before wear on five CHx disks with by uncoated and coated sliders. Loading force was 3g. Drag speed was 0.2m/s.

To compare the tribological performance of the nitrogenated carbon coating in the first test with a hydrogenated carbon coating under similar testing conditions, the same type of Al_2O_3/TiC slider was tested on a hydrogenated carbon disk. The hydrogen percentage in the disk coating was 35%. Figs. 15 and 16 show the results of the test. The friction value stayed at about 0.19 at the beginning of the test then dropped after 23 revolutions. Comparing these results to those shown in Fig. 13, we can see that the CN_x overcoat on the disk had better wear durability than the CH_x overcoat, but the friction of the Al_2O_3/TiC slider on the hydrogenated carbon coating was much lower than on the nitrogenated carbon coating. The spectrum of the mass fragments released during the test is given in Fig. 16. The peaks at mass 69 (CF_3) and 119 (C_2F_5) indicate a chemical reaction occurred at the head-disk interface [11, 12]. Due to their relatively weak intensities comparing to those of masses 47 (CFO) and 66 (CF_2O), the chemical reaction might not be the first order mechanism that resulted in the poorer performance of the hydrogenated carbon coating in wear durability.

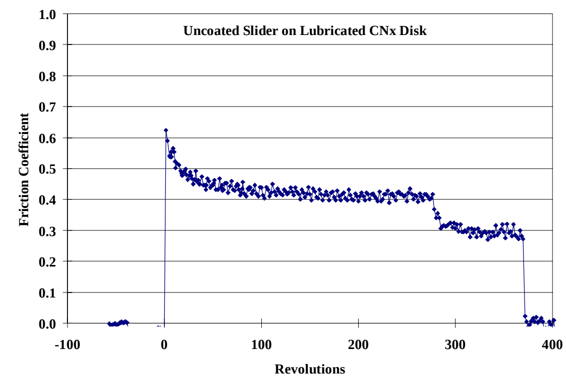

Fig. 13. Friction coefficient of an Al_2O_3/TiC slider on a Z-dol lubricated nitrogenated carbon coated disk.

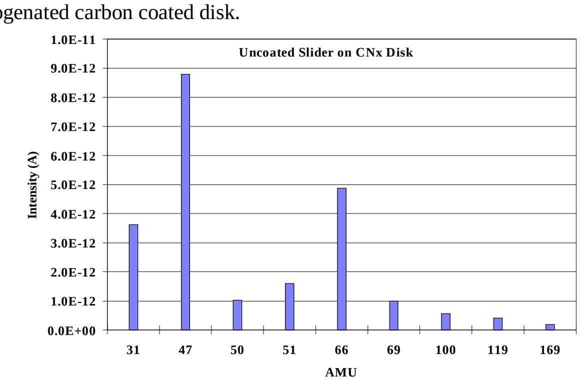

Fig. 14. Mass spectrum of the lubricant fragments released by an Al_2O_3/TiC slider on a Z-dol lubricated nitrogenated carbon coated disk.

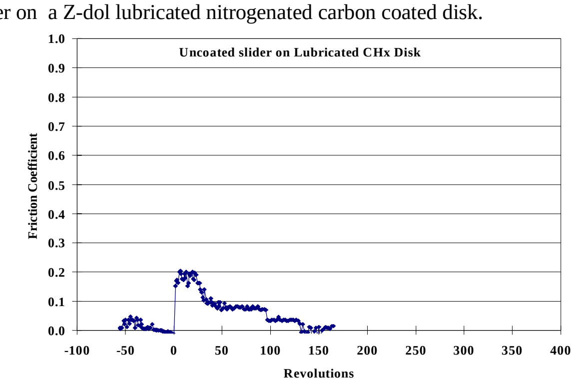

Fig. 15. Friction coefficient of an Al_2O_3/TiC slider on a Z-dol lubricated hydrogenated carbon coated disk.

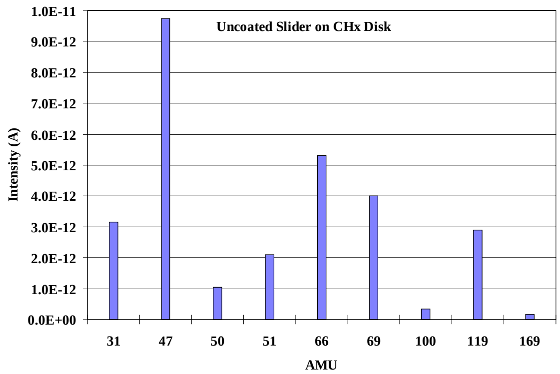

Fig. 16. Mass spectrum of the lubricant fragments released by an Al_2O_3/TiC slider on a Z-dol lubricated hydrogenated carbon disk.

III. CONCLUSIONS

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1). Hydrogenated carbon coatings with different hydrogen content percentages were tested. Two newly developed nanotribological characterization techniques based on scanning probe microscopy were employed to evaluate the mechanical and tribological properties of the carbon films. These two techniques include nano-indentation hardness tests using the Hysitron tester and nano-wear tests using the point contact microscope. Drag tests inside a UHVchamber were also conducted to study the tribochemistry of these coatings. It can be concluded that the mechanical properties, such as hardness and abrasive wear resistance, while important, are not always the primary determining factors in the wear durability at the head disk interface.

Nano-indentation and nano-wear tests show that a higher hydrogen content in the carbon overcoat results in lower film hardness and wear resistance. But the increase of hydrogen content helped to improve the wear durability of drag tests in the UHV chamber.

Controlling lubricant degradation is important for improving wear durability at the head-disk interface. Generally, better protection of the lubricant can help improve the durability of the HDI. The degradation of the lubricant by uncoated and coated sliders is controlled by different mechanism. Carbon coating on the ABS of Al_2O_3/TiC sliders can protect the lubricant from catalytic reaction. The hydrogen content in the CH_x coating can affect the chemical reaction between the lubricant and slider materials. Higher hydrogen content in the coatings can help the lubricant resist the catalytic effect of Al_2O_3 [11, 12].

2). The results obtained from the nano-indentation and nano-wear tests suggest that CN_x films may provide significant advantages over CH_x as a protective overcoat material in hard disk applications. CN_x overcoats on disks also have better wear durability than CH_x overcoats when tested with Al_2O_3/TiC sliders. Chemical reactions between slider and Z-dol can not be observed on the CN_x coated disk.

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