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Tribological Characteristics of Diamond-like Carbon Deposited on Ferrite

Nam-Soo Kim, Dae-Soon Lim, Heng-Wook Kim* and Sang-Ro Lee**

Dept. of Materials Engineering, Korea Univ., Seoul 136-701, Korea
**Institute of Industrial Technology, Korea Univ., Seoul 136-701, Korea*
***Korea Institute of Machinery and Metals, Changwon 641-010, Korea*
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Tribological behavior of the diamond-like carbon (DLC) films sliding on floppy disk has been investigated. Hydrogenated DLC films have been prepared by plasma enhanced chemical vapor deposition (PECVD) using methane and hydrogen mixture in different volume ratios on ferrite substrates. DLC films show lower friction coefficients (0.2~0.4) than those of the uncoated ferrite (0.4~0.5). DLC films containing more hydrogen exhibit higher wear resistance. To investigate the roughness effect on wear, the substrates were polished with SiC papers prior to deposition. Too fine or too rough DLC surfaces result in poor wear resistance. Wear resistance of annealed DLC films at higher temperature slightly increases with respect to as-deposited film.

Key words : Diamond-like carbon, Ferrite, Friction coefficient, Wear, Roughness, Annealing

I. Introduction

Diamond-like carbon (DLC) possessing excellent hardness, chemical inertness, high thermal conductivity and optical transparency is considered to be applied in many industrial and technical fields.[1-6] DLC films have been prepared by various methods, including sputtering,[7] PECVD,[8-10] and ion beam deposition.[11] It has been reported that the electrical, optical, and mechanical properties of DLC films vary depending on the deposition methods and conditions.[12] Since DLC films exhibit low friction even in the unlubricated conditions,[5,13-15] they are very attractive in the tribological applications such as the head or head drum of a video cassette recorder (VCR).[16]

In order to better DLC films apply in the wear resistant parts, it is necessary to find the optimum deposition conditions and the corresponding phases and microstructures, the proper preparation of substrate, and the relation between the operating parameters and wear. The bonding strength of the interface[17] and the residual stresses[5,13,18] due to the difference of thermal coefficients between the coating and substrate, the ratios of sp^3 to sp^2 bonding[19] in the film, and other factors including the mechanical properties and the contact geometry also should be considered. However, our understanding of the tribological behavior of DLC films related with these parameters are limited.

In this study, the effects of the gas ratio in deposition, the roughness, and the heat treatment on the tribological behavior of DLC films sliding on floppy disk were investigated.

II. Experimental Procedure

1. Preparation of substrate

Hexahedrons (18 mm×32 mm×72 mm) of Fe-Mn-Zn ferrite were prepared for DLC deposition. As shown in Fig. 1, two different types of pin geometry were used for the purpose of the pin-on-disk type wear tests. One end of ferrite samples was polished to have 10 degrees between the polished surface and the original flat plane for the tapered pin geometry. The substrate surfaces were polished for 3 minutes with SiC paper (# 400). Some specimens were polished with # 80 and # 2000-SiC papers to have different surface roughnesses.

2. Deposition of DLC film

DLC films were deposited by means of plasma enhanced chemical vapor deposition (PECVD). A schematic diagram of the deposition equipment is shown in Fig. 2; it consists of a cylindrical reaction chamber, a gas controlling unit, a power supplying unit, a vacuum and venting system, and a substrate heating unit. Methane and hydrogen (more than 99.99% purities) were supplied as gaseous sources to produce a hydrogenated DLC and each gas was independently controlled by a mass flow controller (MFC). A 13.7 MHz radio frequency generator was used to create plasma state.

Prior to depositing, the substrate surfaces were cleaned by washing ultrasonically in ethyl alcohol for 3 minutes. After cleaning, they were dried and etched with hydrogen gas in the plasma assisted reaction chamber. The deposition of DLC film was carried out at 200°C for the annealing experiments and at 400°C for the rest of

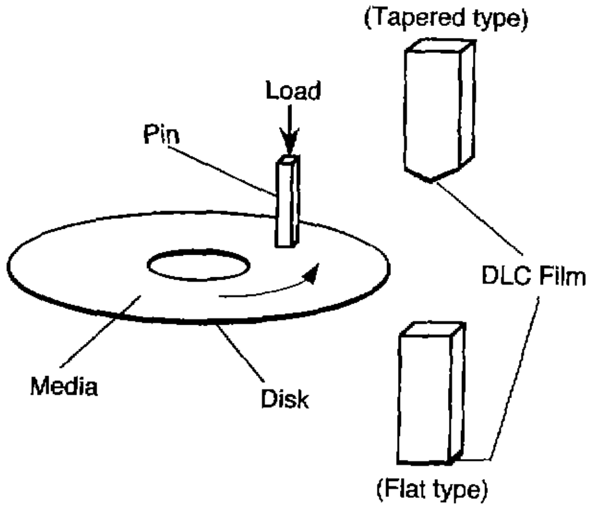

Fig. 1. Schematic diagram of ferrite pin geometry.

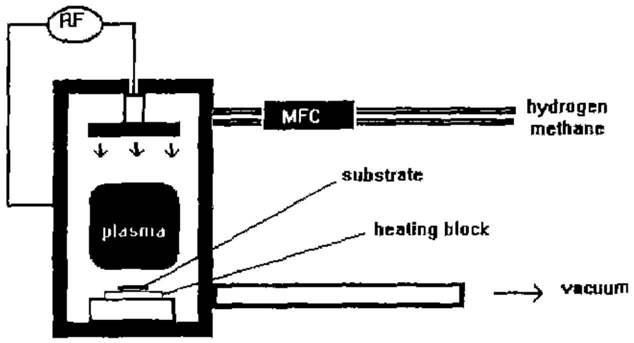

Fig. 2. Schematic diagram of plasma enhanced chemical vapor deposition (PECVD) process.

the tribological tests. A gas pressure of 300 mtorr was maintained during the deposition. The distance between the substrate and the powered electrode was kept as 35 mm. The volume ratios of methane to hydrogen were varied from 1 : 1 to 1 : 100. Various DLC films having the same thickness of 500 Å thick but various DLC films were deposited in the different gas ratios on the prepared ferrite for further friction and wear experiments. Different deposition time was selected for deposition in the different gas ratio to maintain same film thickness. Film thickness was measured by α-step.

3. *Tribological experiments*

The friction and wear tests were performed on a pin-on-disk tribometer. A schematic diagram of the test configuration is shown in Fig. 3. The stationary pin (DLC film deposited on ferrite) was loaded by a dead weight against a rotating disk (medium). Commercially available floppy disks were used as rotating media. The vertical bar which holds the pin was mounted on a stepping motor so that the wear track could be precisely set to a chosen diameter during the tests. The sliding speed was controlled by a variable power supply connected to a

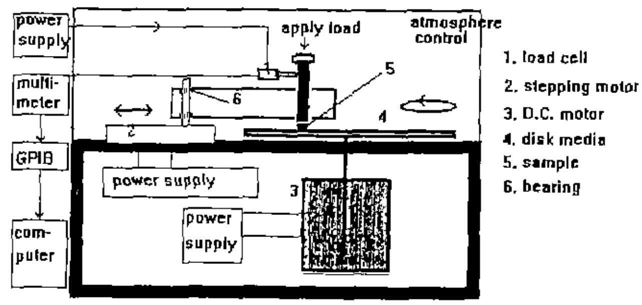

Fig. 3. Schematic diagram of pin-on-disk type tribometer.

Table 1. Annealing Conditions of Diamond-like Carbon

specimen	heating rate	annealing time	annealing temperature
#1	-	-	-
#2	5°C/min	3 h	250°C
#3	5°C/min	3 h	300°C
#4	5.5°C/min	3 h	400°C
#5	6°C/min	3 h	500°C

DC motor. The frictional force transferred to a load cell was recorded throughout the tests. The load cell produces an electric output depending on the elastic deformation of a diaphragm on which the force is transferred. The electric signal amplified by a multimeter is stored in a computer via GPIB (general purpose interface bus).

The friction and wear tests were performed at a normal load of 1.2 N and at a sliding speed of 500 RPM which is equivalent to a linear velocity of 0.52 m/sec. The experiments were performed at room temperature and in laboratory air. After every certain (100 or 500) rotations, failure of the DLC film due to sliding was checked by an optical microscope and then the sliding was continued on a new track of the floppy disk by advancing the pin, which is controlled by the stepping motor. Worn surfaces of the DLC film were also observed by an scanning electron microscope.

4. *FTIR (Fourier transform infrared) spectroscopy of DLC films*

In order to examine the bonding types between carbon atoms and carbon and hydrogen atoms, especially the ratio of sp^3 to sp^2, absorption of DLC films was investigated by means of FTIR spectroscopy. Absorption spectra were obtained from DLC films annealed at elevated temperatures (up to 500°C) for 3 hours and compared to that of as-deposited film. The heating rate was relatively fast to minimize the spectrum changes due to the hydrogen release during heating. The annealing conditions are summarized in Table 1. These analyses were performed with the powders obtained from the most wear resistant DLC film.

III. Results and Discussion

1. Effect of the gas ratio ($CH_4 : H_2$ ratio) on the tribology of DLC film

Sliding of DLC film (tapered type-pin geometry) against the commercial floppy disk at 1.2 N and 500 RPM (0.52 m/sec) was performed until the film failed. The lifetime or the wear resistance of DLC film was determined by the number of rotations when failure occurred.

The sliding tests were repeated three times and the averaged results are shown in Fig. 4; the number of rotations (cycles) are plotted for various DLC films deposited in different volume ratios of methane to hydrogen. It is found that as the relative flow rate of hydrogen with respect to methane increases from 1 : 1 to 1 : 100 (as more hydrogen is incorporated in DLC film), the wear resistance of the DLC film is improved. This observation is possibly explained by the increase in sp^3 carbon formation with increasing hydrogen content.

Friction between the DLC film 500 deposited on ferrite substrate and the floppy disk was also measured and the coefficients of friction during the first 500 rotations are shown in Fig. 5. All the DLC films deposited in different gas ratio of CH_4 to H_2 show less friction against the floppy disk (friction coefficient, μ=0.2~0.4) than that of uncoated ferrite (μ=0.4~0.5).

Generally, the friction coefficients of DLC sliding against ceramics or metals are reported as smaller than 0.2.[5,13-15] The values of friction coefficient in this work are higher than that of most reported one. This is because our counterpart is a floppy disk which is much softer than ceramics and metals, and our DLC film which is deposited on the ferrite finished by SiC paper (# 400) is rougher than other's. The direct relation between the wear resistance and the friction coefficient is not found.

Figure 6 shows the scanning electron micrograph of the worn surface of most wear resistant DLC film deposited in the $CH_4 : H_2$ ratio of 1 : 100 after sliding of 4000 rotations (cycles) on floppy disk. DLC film is partially delaminated [in lower bright part (B), the substrate material is revealed due to the delamination of the DLC film] and the worn surface of DLC film [upper dark part (A)] is rough. Many scratches due to hard wear particles are also observed on the DLC film. These are the evidences of abrasive wear.

2. Annealing effect on the tribology of DLC film

Since hydrogen incorporated in the DLC film during the deposition process is released as temperature increases, the proportion of sp^3 to sp^2 bonding types changes.[19] To find out such temperature effect on the bonding types of the DLC film, FTIR spectroscopy was employed for the most wear resistant DLC film deposited in the $CH_4 : H_2$ ratio of 1 : 100 at 200°C. The results are as shown in Fig. 7; FTIR absorption spectra

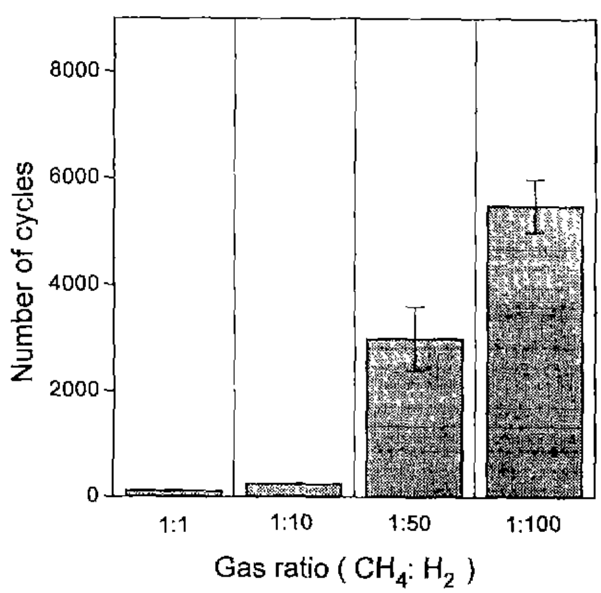

Fig. 4. The number of cycles for DLC failure as a function of gas ratio.

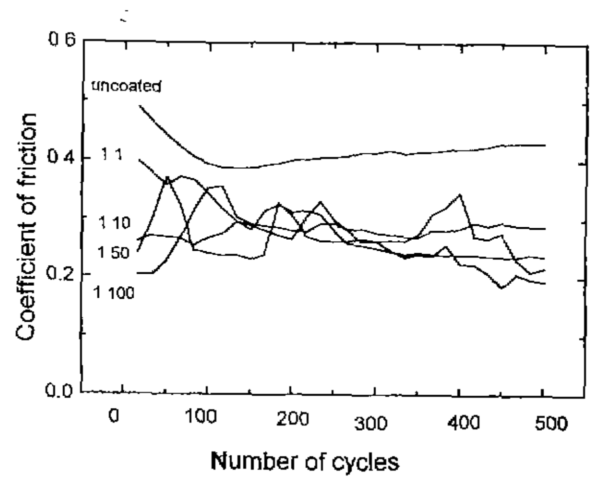

Fig. 5. Coefficient of friction between the pin coated with DLC and floppy disk as a function of number of cycles in the pin-on-disk test.

Fig. 6. SEM micrographs of the worn DLC films deposited with gas ratio 1 : 100 after 4000 cycles tested. Area B (brighter region) indicates ferrite surface after peeling of DLC film; Area A indicates remained DLC film.

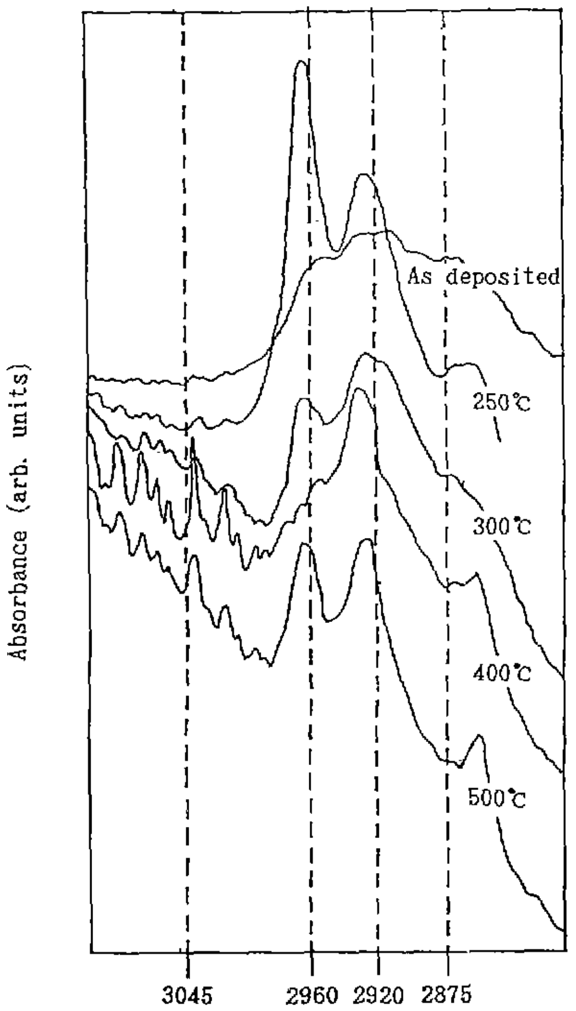

Fig. 7. Changes of IR absorbance spectra of DLC deposited at 200°C by varieties of annealing temperature.

were obtained from both deposited and annealed DLC films. As deposited DLC film shows a broad peak in the range from 2870 to 3100 cm^{-1}. This broad peak separates into distinct peaks at around 2875, 2920, 2960, and 3045 cm^{-1} when the DLC films were annealed.

Depending on the bonding types between carbon and hydrogen or carbon and carbon, and the vibrational modes, a particular molecule shows its characteristic absorption. The above four peaks are identified and summarized in Table 2[20]; the absorption at around 2875, 2920, and 2960 cm^{-1} are assigned to sp^3 tetrahedral bonding and that at about 3045 cm^{-1} to sp^2 trigonal bonding. The broad peak in the FTIR spectra obtained from as deposited DLC film is related to sp^3 bonding. At 300°C, the intensities at 2875, 2920, and 2960 cm^{-1}, which are related to sp^3 bonding, decrease with respect to those at 250°C. Notice, however, a small absorption peak is observed at 3045 cm^{-1}, which is originated from sp^2 bonding at this temperature. This peak at 3045 cm^{-1} is even pronounced at 400 and 500°C. Previous work proposed that the structure changes upon heating upto 600°C arised from the desorption of hydrogen and/or hydrocarbon.[21]

Table 2. IR Absorption Frequencies in Diamond-like Carbon

wave number (cm^{-1})	assignment (Bonding type)	type (Vibrational mode)
2875	sp^3 CH_3 symn.	stretching
2920	sp^3 CH_2	stretching
2960	sp^3 CH_3 asymm.	stretching
3045	sp^2 CH	stretching

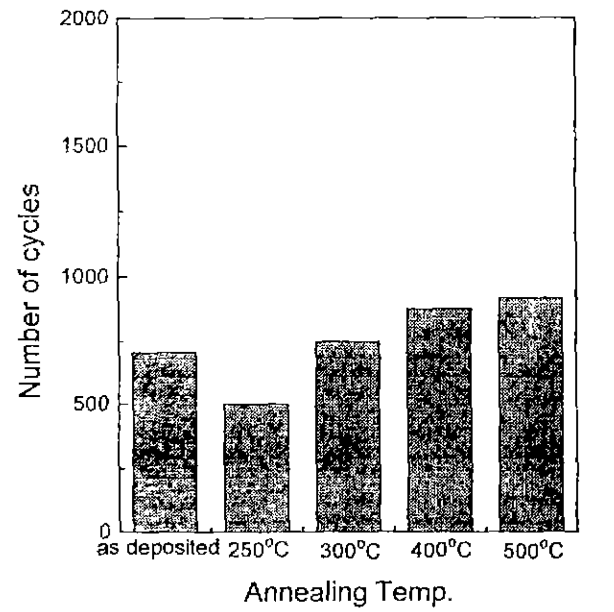

Fig. 8. The number of cycles for DLC failure as a function of annealing temperature.

The lifetime or the wear resistance of the DLC film annealed at various temperature is compared to as-deposited film as presented in Fig. 8. Since the flat type-pin geometry was adapted in these wear tests, failure of the as-deposited DLC film occurred earlier than that of tapered type geometry (Fig. 4). It is observed that the annealed DLC films last slightly longer than as-deposited film and that the wear resistance of DLC film is improved as the annealing temperature increases. This may be attributed to the rearrangement of crystalline phases as observed by FTIR spectroscopy even though the detailed mechanism has not yet been understood. Another possible explanation is the stress relief during annealing.

After annealing, changes in friction coefficient were not measured, however, Memming and coworkers[14] and Miyoshi[15] observed no change.

3. *Roughness effect on the tribology of DLC films*

Before depositing DLC film, the substrates (ferrite)

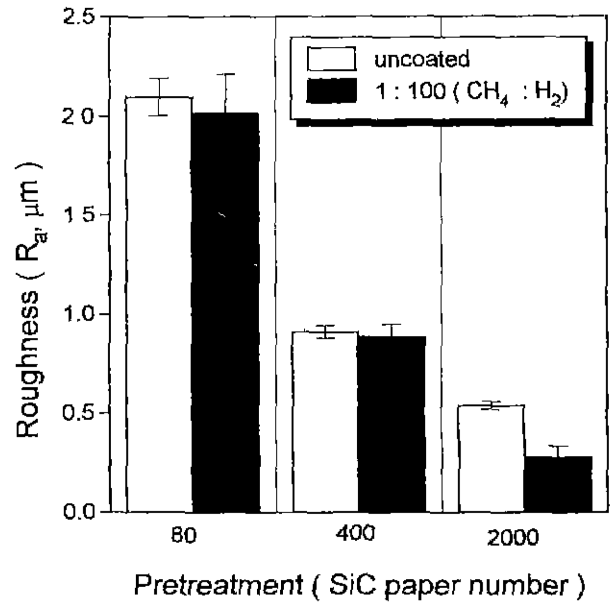

Fig. 9. Roughness (Ra) of DLC coated and uncoated surface versus different polishing pretreatments of ferrite pins.

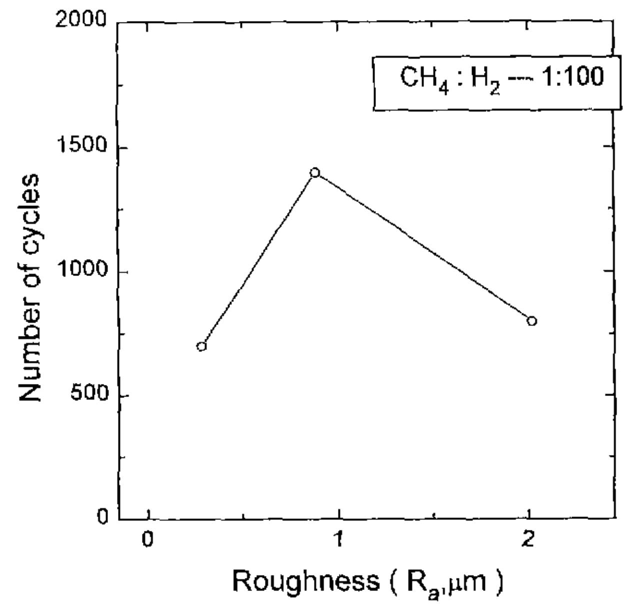

Fig. 11. The number of cycles for DLC failure as a function of different roughness (Ra).

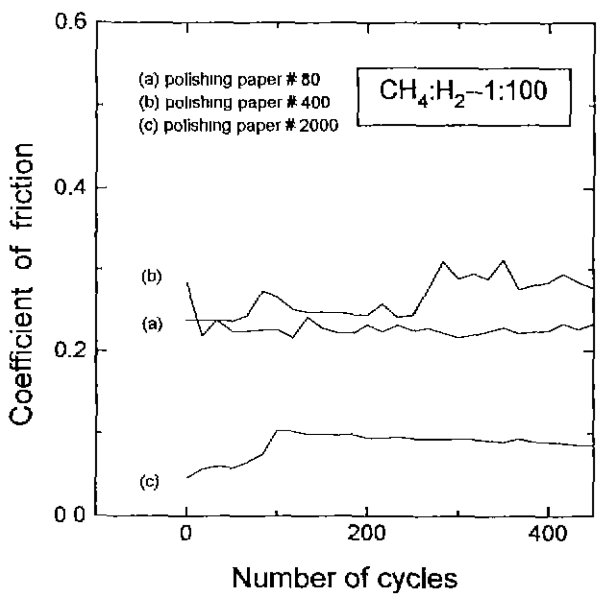

Fig. 10. Variation of coefficient of friction with number of cycles depending on roughness.

with flat type geometry were pretreated in different degrees by polishing with # 80, 400, and 2000-SiC papers respectively so that their surfaces could have various roughnesses. The surface roughnesses of the substrates and their changes after depositing DLC film are shown in Fig. 9. Roughness changes are examined after the deposition of the most wear resistant DLC film in the CH_4 : H_2 ratio of 1 : 100 at 400°C. Although the roughness is changed more (about 50% decrease) after the deposition when the substrate was polished by # 2000-SiC paper with respect to # 80-SiC paper and # 400-SiC papers, the final roughness of the DLC film is determined by the initial roughness condition of the substrate.

Fig. 10 represents the friction coefficients of the DLC films which have different roughnesses. The rougher the DLC film is, the higher the friction shows. The roughness effect on the wear resistance of the DLC films is investigated and the results are shown in Fig. 11. A maximum wear resistance is found at the intermediate roughness. As the surface becomes rougher, the surface energy increases, therefore, the nucleation sites for films and nucleation rate increase which in turn lead to a fine microstructure and a strong interfacial bonding between the deposited film and the substrate is obtained. The DLC film deposited in the CH_4 : H_2 ratio of 1 : 100, however, shows abrasive wear, where interfacial bonding strength and roughness of the rubbing material are major parameters to influence wear. The two parameters compete with each other and a maximum is exhibited at a intermediate roughness. A careful examination of Fig. 11 and Fig. 8 reveals that DLC film deposited at 400°C is more wear resistant than that deposited at 200°C.

IV. Conclusions

The tribological behavior of diamond-like films deposited in the different ratios of methane to hydrogen by PECVD on ferrite exhibiting various roughnesses was studied. The DLC films sliding on a floppy disk decrease friction (μ=0.2~0.4), compared to the uncoated ferrite (μ= 0.4~0.5). The wear resistance of DLC film increases as more hydrogen is incorporated during the deposition. It is observed that abrasive wear is dominant for most wear resistant DLC film deposited in the CH_4 : H_2 ratio of 1 : 100. The ratio of sp^2 to sp^3 bonding of DLC film increases and the wear resistance also improves slightly as the annealing temperature is raised. The roughness of DLC film strongly affects friction; the rougher, the higher. The wear resistance of the DLC film exhibits a maximum at the intermediate roughness due to two competing factors, i.e., the roughness effect on frictional sliding and the bonding strength of the interface between the deposited DLC film and substrate.

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