

Friction and Wear of Nitrogen Incorporated Diamond-like Carbon Films Under a Vacuum

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Abstract—Tribological behaviors of nitrogen incorporated amorphous diamond-like carbon films were experimentally measured under a vacuum (3×10^{-5} Torr) using a ball (AISI 52100 steel)-on-disk wear-rig. Nitrogen incorporated DLC films were deposited by r.f. plasma assisted chemical vapor deposition method. Mixtures of benzene and ammonia or nitrogen gases were used as the reaction gases for the r.f. PACVD, and Si (100) wafer was used as the substrate. In the tribo-test, effects of DLC film thickness and normal load in friction were measured and discussed. Results showed that friction of nitrogen incorporated DLC films from a mixture gas of benzene and ammonia was lower than that of 100% benzene, specially in the measurement of minimum coefficient of friction. Differences in frictional characteristics of nitrogen incorporated DLC films were explained with the changes in chemical structures of the films. Result also showed that friction of DLC films increased with the sliding contact cycle, which remarkably accompanied with roll-shaped wear debris. Mechanisms and roles of the polymer-like wear debris were presented and discussed.

Key Words : Friction, Wear, Vacuum, DLC Film

1. Introduction

During the past decade, surface coating by amorphous diamond-like carbon (DLC) films has been one of the exciting research topics in engineering over a world wide. As the coating technology has been finely developed to grow films of good quality on a variety of substrate (metals, polymers, ceramics), DLC films have been developed as an economical alternative to diamond in a variety of engineering application [1]. They have attractive tribological properties such as low friction, high hardness, chemical inertness, and superior surface finish. They can be surface-coated as a very thin film in sub-micron thickness, which is good enough for protecting surface damages with maintaining a very low friction. Such excellent tribological properties of the DLC films have, therefore, aroused a great concern to machine designers related with micro electro mechanical systems (MEMS) and magnetic storage devices [2-4]. Low friction characteristics under high vacuum or cryogenic temperature conditions

also suggest that they could be used for an effective dry lubricant for space applications [5]. Nevertheless, the improvement of tribological properties has been still required. Friction and wear behavior of the films and the dependence of those on the deposition parameters and on the operating environment should be better understood to expand the use of DLC films for tribological protection in new applications.

It was shown that surface properties and tribological behavior of the DLC films differed from each other with the film deposition method (r.f. or d. c. plasma assisted chemical vapor deposition, sputtering, iron beam deposition, etc.) and the deposition parameters or reaction gases [6-7]. Friction coefficients typically range from 0.1 to 0.3, but very low values (<0.01) or high values (>0.6) have been often reported under the special environmental conditions [2, 8, 9]. Works on tribochemistry of the films has been thus given special attention, though DLC films generally have a good chemical inertness. The friction and wear mechanisms how DLC films react with various ranges of environment were discussed

by several workers [8-13]. It is commonly argued that the properties of DLC films are strongly affected by the deposition conditions, and hydrogen contained in the DLC films has an important role in determining tribological properties of the films; since it passivates the dangling bond in the hydrogenated DLC films and permits only weak interaction between the contact surfaces. Huu *et al.* [12] showed that in vacuum, atomic hydrogen desorbs during friction and lubricates the surface in contact. Kim *et al.* [13] investigated the tribochemical reaction of DLC films with oxygen in air and humid environment, which resulted in different modes of friction and wear behavior of the films. Recently, it was reported that nitrogen doping or implantation modifies the chemical and electronic structure of DLC films [7, 14, 15]. One of the motivations of the investigation was that hypothetical carbon nitride (C_3N_4) of β - Si_3N_4 structure can have properties superior to those of diamond [16]. One of authors of the present work also showed, in the recent work [17], that nitrogen incorporation onto DLC films changes both atomic structure and mechanical properties of the films.

The purpose of the present work was to understand the tribological behavior of the nitrogen incorporated DLC films. Mixtures of benzene and ammonia or nitrogen were used as the reaction gases for the r.f. PACVD. Si (100) wafer was used as the substrate. Using a ball-on-disk wear-rig, friction and wear properties of the films were tested under a vacuum. Frictional characteristics with the change in the film deposition and with the film thickness were mainly discussed through the work. Experimental analyses of worn surfaces and the wear debris were also performed using scanning electron microscopy, Auger spectroscopy and surface profilometer.

2. Experimental Details

2-1. DLC deposition

Nitrogen incorporated DLC films were prepared by r.f. PACVD method using mixtures of benzene (C_6H_6) and ammonia (NH_3) or nitrogen (N_2) as the reaction gases. Details of the experimental set-up were described elsewhere [17]. Substrates were mounted on the water cooled cathode where 13.56 MHz r.f. power was delivered through the im-

pedance matching network. Prior to the deposition process, the substrates were sputter cleaned by an Ar discharge at the negative bias voltage -400V and the pressure 3.7 mTorr for 15 min. The films were then deposited with various NH_3 or N_2 fractions from 0 to 0.79 in reaction gases at a negative bias voltage of the cathode of -500 V. Deposition pressure measured by a capacitance manometer was fixed at 10 m Torr by adjusting the conductance of the main valve. The film thickness, the height of the step formed by the mask, was measured by an Alpha-step profilometer.

FTIR absorption spectra were obtained using a Bruker IFS 120 HR FTIR spectrometer. The spectra were received in diffuse reflectance Fourier transformation (DRIFT) mode at a resolution of 4 cm^{-1} and average over 64 scans for high signal to noise ratio. In order to remove the absorption bands originated from the environment, the analysis chamber was purged by dry nitrogen before the analysis.

2-2. Tribo-tester and the test conditions

Friction and wear were measured with a ball-on-disk wear-rig. The apparatus for the wear-rig under vacuum was described in detail elsewhere [18]. The overall layout is shown in Fig. 1. Tests were performed under a high vacuum condition (3.0×10^{-5} Torr). Ambient temperature in the chamber was controlled constantly at 30°C by a halogen lamp. The specimens of the wear-rig are 125 mm diameter thin Si (100) wafer disks on which thin films of DLC were deposited, and they were bonded on a steel disk using a double-side adhesive tape. Steel ball (AISI 52100, 12.7 mm diameter) slides over the surface. In order to measure the effect of DLC film thickness in friction and wear, film thickness was varied with the deposition time (from 5 to 40 minute), which resulted in about 0.1-1.0 μm in film thickness.

All of the tests were performed at unlubricated sliding surfaces at speed of 0.05 m/s for a fixed sliding contact cycle of 1600 (sliding distance: 360 m). Normal load was varied from 4.9 N to 39.2 N (average initial Hertzian contact pressure, 0.33-0.67 GPa; assuming that ball directly contacts with Si wafer); at a high load above 40 N, Si wafer was abruptly broken off. After tests, wear tracks of the film surfaces were measured with an Alpha-step profilometer.

3. Results and Discussion

3-1. Chemical analyses

Fig. 2 shows the atomic bond structures of the DLC films which were investigated by the FTIR absorption spectra. In order to compare the content of each bond between the films, FTIR absorbance spectra were normalized by the film thickness. Successive curves were translated upward for comparison. Numbers on the spectra are the nitrogen source fractions in reaction gases. Fig. 2(a) shows the FTIR spectra of the films when using NH_3 as the nitrogen source. Without NH_3 , the spectrum is the typical one for DLC films that is characterized by a smeared C-H stretching absorption band near 3000 cm^{-1} . The C-H stretching band consists of $\text{sp}^3\text{ CH}_3$ stretch-

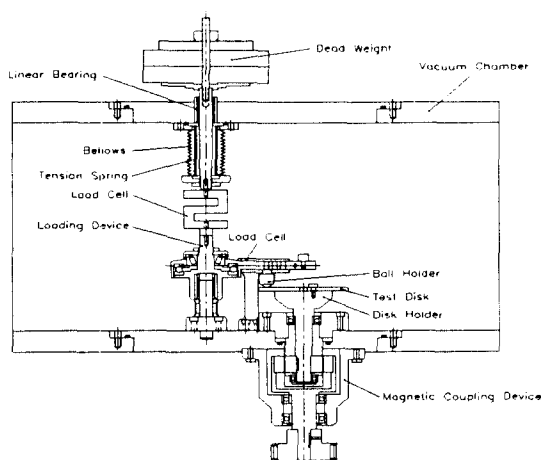


Fig. 1. An overall view of the wear-rig.

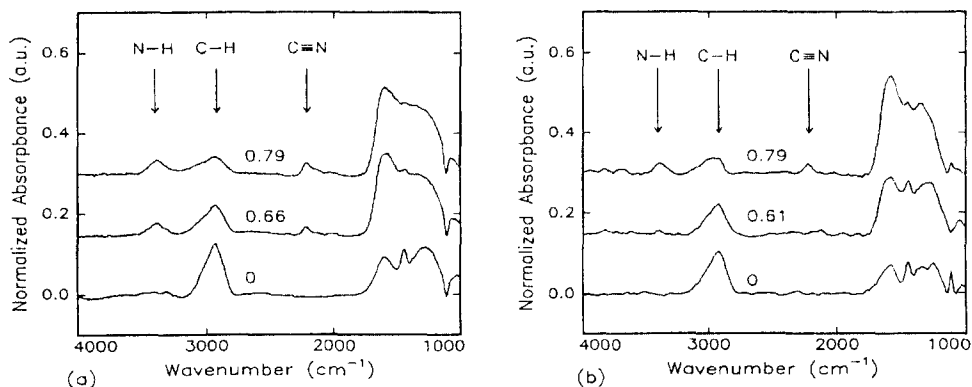


Fig. 2. FTIR absorption spectra of the DLC films when using (a) ammonia or (b) nitrogen as the nitrogen source.

ing (2875 and 2960 cm^{-1}), $\text{sp}^3\text{ CH}_2$ stretching (2920 cm^{-1}) and $\text{sp}^2\text{ CH}$ stretching (3045 cm^{-1}) bands. The C-H bending bands are observed in the region of $1000\text{--}2000\text{ cm}^{-1}$.

Nitrogen incorporation to the film resulted in three changes in the spectrum. With increasing NH_3 fraction, absorption bands centered at 3400 cm^{-1} increase in density, owing to NH_2 symmetric and asymmetric bending modes. This result showed that the hydrogen in the film is distributed between C-H and N-H bonds. A $\text{C}\equiv\text{N}$ nitrile stretching absorption band also appeared near 2200 cm^{-1} of which intensity increases with increasing NH_3 fraction. Since the chemical valence of nitrogen is normally three, triply nitrogens are the terminated sites of a three dimensional atomic bond network. $\text{C}\equiv\text{N}$ bonds hence reduce the inter-links of sp^2 clusters in DLC films. Finally, $\text{sp}^2\text{ C}=\text{C}$ stretching absorption band at 1600 cm^{-1} is enhanced by nitrogen incorporation.

When using NH_3 , the content of hydrogen that also terminates the atomic bond network was observed to be constant regardless of the NH_3 fraction [17]. Hence the reduction of inter-links due to hydrogen is assumed to be the same in these films. Dangling bonds in amorphous film also terminate the atomic bond network. The density of the dangling bonds measured by electron spin resonance (ESR) was in the order of $10^{18}/\text{cm}^3$. Its effect on the content of the inter-links was thus negligible in the present work. However, as shown in Fig. 2(a), $\text{C}\equiv\text{N}$ bonding increases with increasing NH_3 fraction. In the measurement of the residual stresses of the nitrogen incorporated DLC films, residual compressive stress

of the film decreased from 1.7 to 1.0 GPa with increasing NH_3 fraction [17]. The knoop hardness of the films showed the same behavior as the residual stress; the hardness monotonically decreased from 27.5 to 17.0 GPa with increasing NH_3 fraction [17]. It can be thus concluded that the films deposited under higher NH_3 fraction have a lower content of three dimensional inter-links of sp^2 clusters, resulting in lower hardness. Since the distortion of atomic bond angles and / or lengths is smaller in the films of lower content of the inter-links, the residual stress also decreases as the nitrogen is incorporated.

FTIR absorption spectra of the N_2 addition case are shown in Fig. 2(b). The C-H stretching absorption band also decreased with increasing N_2 fraction. Although N-H bending and $\text{C}\equiv\text{N}$ stretching bands were also observed, they were less prominent than in NH_3 addition case. This FTIR spectra is consistent with the composition change that the hydrogen concentration decreases with increasing N_2 fraction. As in the NH_3 addition case, the sp^2 C=C stretching absorption band at 1600 cm^{-1} also becomes significant as the N_2 fraction increases. Decreasing hydrogen concentration and increasing CN bonds reciprocally affect the content of inter-links of sp^2 clusters. These two effects seem to be balanced in the N_2 addition case, resulting in mechanical properties similar to those of pure DLC films. Residual compressive stress ($\approx 1.6\text{ GPa}$) and knoop hardness of the film ($27.0\pm 3.0\text{ GPa}$) when using N_2 also show that they are independent of the N_2 fraction with the error of the stress measurement.

3-2. Tribo-test results

Fig. 3 shows the effect of film thickness in the friction. Friction tests were performed under the nor-

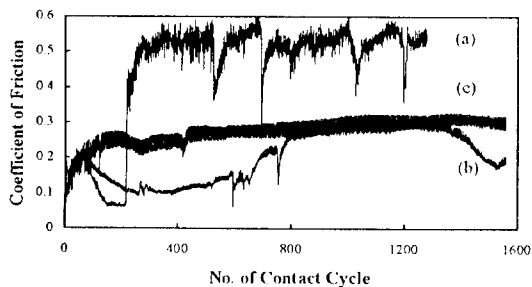


Fig. 3. Coefficient of friction of DLC films: (a) of $0.12\text{ }\mu\text{m}$, (b) of $0.22\text{ }\mu\text{m}$, (c) of $0.98\text{ }\mu\text{m}$ in the film thickness.

mal load of 4.9 N and vacuum condition (3.0×10^{-5} Torr). Tested DLC films in Fig. 3 were prepared using 100 % benzene. Film thickness was controlled by the deposition time, which was varied from 5 to 40 minute. In the figure, $0.12\text{ }\mu\text{m}$ (5 min.), $0.22\text{ }\mu\text{m}$ (10 min.) and $0.98\text{ }\mu\text{m}$ (40 min.) in the film thickness were typically shown. It shows that coefficients of friction of the DLC films ranged from 0.1 to 0.3, depending on both the film thickness and the sliding contact cycle. When film thickness was $0.12\text{ }\mu\text{m}$, the film was fast broken even after 220 sliding contact cycle, which resulted in a sharp rise in friction. Micrographs of the wear track in the disk surface, shown in Fig. 4(a), also showed that coated films were fully worn off, so that steel ball slid over the Si surface. When DLC films were good enough for the surface protection, they showed little evidences of the film damages and showed rather positive spikes in the surface profile due to wear debris as shown in Fig. 4(b). On the other hand, a circular

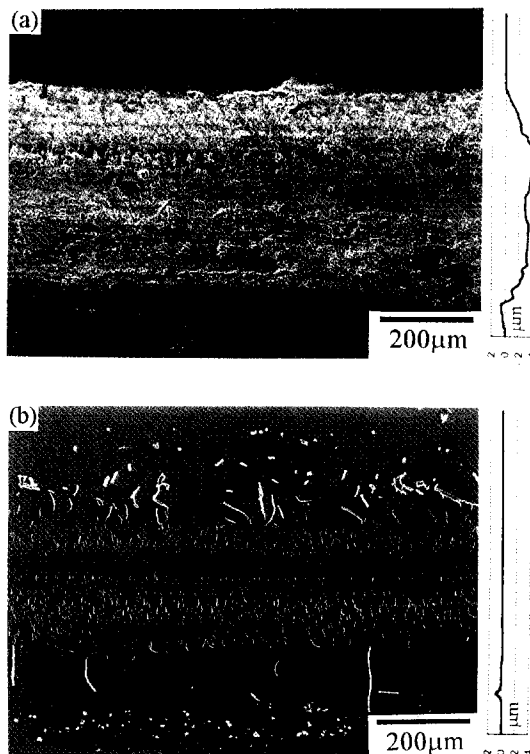


Fig. 4. Micrographs of the wear track in the disk surface, (a) of $0.12\text{ }\mu\text{m}$, (b) of $0.22\text{ }\mu\text{m}$ in the film thickness.

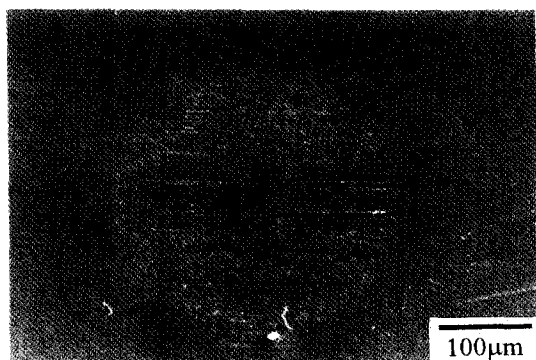


Fig. 5. Micrograph of a ball surface when the film thickness is $0.22 \mu\text{m}$.

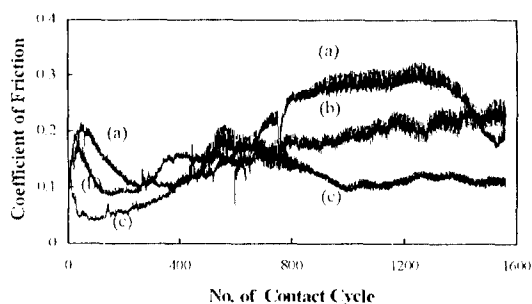


Fig. 6. Coefficient of friction of DLC films: (a) of 100% C_6H_6 , (b) of C_6H_6 and 0.79N_2 , (c) of C_6H_6 and 0.79NH_3 .

shaped wear scar was found, in Fig. 5, on the surface of steel ball with severe abrasive marks along the sliding direction.

Effects of nitrogen incorporation into the DLC films in the friction are shown in Fig. 6. Two films from the gas mixtures of both C_6H_6 and 0.79NH_3 fraction and C_6H_6 and 0.79N_2 fraction were compared with that of 100% C_6H_6 . Each film was about $0.2 \mu\text{m}$ in the film thickness. Frictional characteristic was almost the same in each film; friction generally drops to a minimum after some sliding contact and maintains before showing some fluctuations possibly due to the surface film wear. Decrease in friction in the first stage of sliding contact could be attributed to the fact that hydrogen desorbs from the DLC films under vacuum, suggested by Huu *et al.* It is, however, that they showed some differences in a minimum coefficient of friction; a minimum coefficient of friction was the lowest in the nitrogen incorporated DLC film which was from

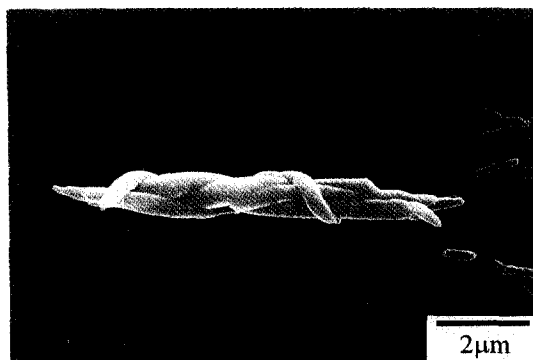


Fig. 7. An enlarged view of roll-shaped wear debris.

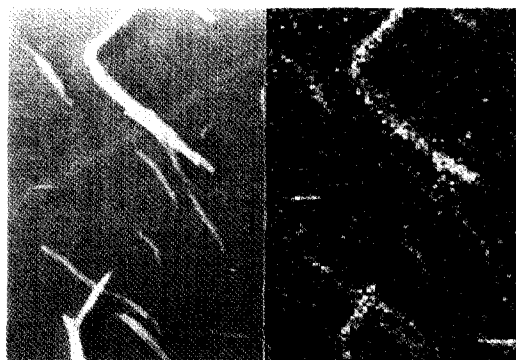


Fig. 8. An Auger oxygen map of a polymer-like wear debris.

the gas mixture of C_6H_6 and 0.79NH_3 fraction. It suggests that friction of DLC films is also affected by the film surface chemistry which was described in the chemical analyses, since hydrogen absorption is closely related with the chemical structure of the DLC films. Formation of $\text{C}\equiv\text{N}$ bondings and the reduction in inter-links of sp^2 clusters of the nitrogen incorporated DLC films may relate with the reduction in friction.

Increase in the friction of DLC films with the sliding contact cycle is also an interesting feature. Micrographs of wear track of DLC films showed that the surfaces were covered with roll-shaped wear debris, as shown in Fig. 4(b). Fig. 7 shows the enlarged view of a wear debris; they are long and twisted roll-shaped, with placed on the surface in perpendicular to the sliding direction. Form of the wear debris may suggest that very thin worn layer of DLC films was plastically deformed by rolling-up action at the contact surface. High plastic de-

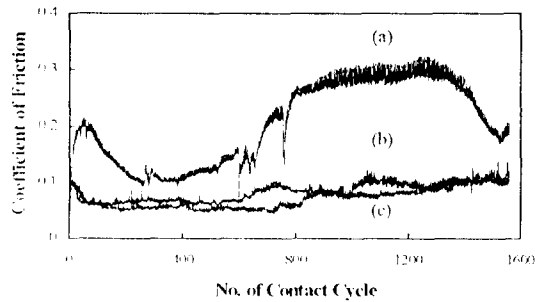


Fig. 9. Coefficient of friction of DLC films under various normal load: (a) of 4.9 N, (b) of 19.8 N, (c) of 39.2 N.

formation energy necessary for the wear debris formation and the rolling action in the sliding surfaces (as-like in a three-body abrasive wear process) may be thought to attribute to the increase in friction. Such formation of wear debris also reported by Kim *et al.* They also argued that wear debris protected the sliding surface, though it made the frictional force increased. Fig. 8 shows an Auger oxygen map of the worn surface. It shows highly distributed oxygen over the wear debris. Auger spectroscopy analysis (after ion sputtering the surface) also showed a high oxygen peak on the wear debris. Surfaces of worn DLC films also showed a little trace of oxygen. But it was relatively smaller than those in wear debris. Contamination of oxygen onto the DLC films was supposed to occur due to physically absorbed water vapor in storage of test specimens in air. Another possibility would be that oxidation occurred under a vacuum in our tribo-test conditions, though it was not confirmed in this study yet. Chemisorption of atomic oxygen onto the amorphous hydrogenated DLC films may attribute to the polymerization of the DLC films as suggested by Kim *et al.*, resulting in the formation of polymer-like wear debris. However, it has been still unknown that formation of polymer-like wear debris is directly affected either by water vapors or by atomic (or molecular) oxygen in the test environment. We plan another tests of pre-treated DLC films under vacuum at which films will be thermally baked to remove absorbed water vapors on the surface. It will be separately reported later.

Fig. 9 shows effects of the normal load in friction. Tested DLC films were those from gas mixture of C_6H_6 and 0.79 NH_3 fraction. Under the high

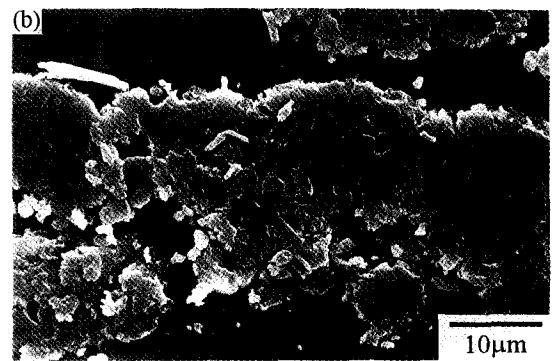
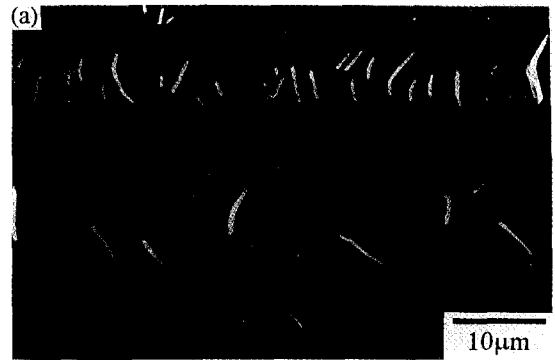


Fig. 10. Micrographs (a) of wear track under the high load (39.2 N), and (b) of compacted fine wear debris.

normal loads of 19.8 and 39.2 N, friction coefficients were lower (<0.1) and more stable than those under 4.9 N. Micrographs of wear track under the high load of 39.2 N showed that surface was rather clean without any sites of the film failures or abrasive marks. Compared with that of 4.9 N, polymer-like wear debris was much less detected on the surface, sometimes cut in short length as shown in Fig. 10(a). Fig. 10(b) shows that fine wear debris produced from the contact surfaces are compacted in patches around the boundary of wear track. It seems that humidity contaminated top layers of DLC films were easily worn off under the high normal loads and then contact directly took place between ball and pure DLC film, consequently resulting in low friction of the DLC films under the high load.

4. Conclusions

- (1) Friction of nitrogen incorporated DLC films

from a mixture gas of benzene and ammonia is lower than that from 100 % benzene, specially in the measurement of minimum coefficient of friction.

(2) Differences in frictional characteristics of nitrogen incorporated DLC films are made by the changes in chemical structures of the films, which mainly relates with the formation of C≡N bondings and the reduction in inter-links of sp² clusters of the films.

(3) Friction of DLC films increases with the sliding contact cycle, which remarkably accompanied with roll shaped wear debris. Formation of polymer-like wear debris relates with oxidation of the top layers of DLC films.

(4) Under the sliding conditions of high loads, friction of DLC films decreases due to the direct contact between ball and the DLC film.

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