The healing effect of stearic acid applied on amorphous carbon film with dispersed nanodiamonds

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Abstract. Diamond-like carbon (DLC) films have been shown to improve the friction and wear properties of applications with severe loads. Hydrogenated amorphous carbon films (a-C:H), a type of DLC film, were coated onto 440C stainless steel disk surfaces. The plasma enhanced chemical vapour deposition method was used as a coating process, and nanodiamond (ND) particles were dispersed into the film during the deposition process. Stearic acid was expected to affect the lubricating properties of the film because of its reported effectiveness on diamond surfaces. A lubricated reciprocal sliding friction test with 10,000 cycles confirmed that stearic acid improved the friction and wear properties of the ND dispersed a-C:H film. Furthermore, film wear caused by a sliding test without stearic acid could be healed by sliding with stearic acid as long as the level of critical damage was not reached. Raman spectra for the worn tracks revealed the healing effect of the stearic acid on the film because the spectra for the worn tracks after 10,000 cycles were identical to those of the control film, which was not worn. In contrast, the spectra for the worn tracks or debris showed a broad D band peak and no G peak, which was consistent with disordered amorphous carbon.

1. Introduction

Hard coatings, such as diamond-like carbon (DLC), applied on sliding surfaces, have been utilized in machines to suppress wear and friction [1]. However, the hard coating could become worn with use and unable to perform properly. The in situ healing of the film can sustain low friction and extended life. Thus, DLC films have been extensively utilized in the industry due to their ability to heal. For example, these films have been used in oil on valve lifters in gasoline engines, where the contact pressure can be as high as several GPa, as energy saving eco-materials. The term “diamond-like carbon” describes a diverse group of materials with different properties, and they can be used in a large number of applications. Donnet et al. investigated hydrogen containing-a-C:H films and DLC films containing transition metals with doped hydrogen [2], whereas Voevodin et al. investigated DLC films with embedded tungsten carbide (WC) and tungsten disulfide (WS₂) nanograins for aerospace use [3]. Nanocluster diamond (ND) powder is composed of particles with a diameter of 5 nm. Dispersed ND powders combined with a stearine lubricant can operate very quietly on sliding surfaces [4]. Hydrogenated amorphous carbon can produce smooth surfaces on a nanometer scale [5, 6]. Films with ND can operate under high contact pressure. Stearic acid acts as an adhesive for carbon films due
to its large number of end groups [7]; thus, it has been applied to films for its healing ability to improve the recovery of the surfaces and the friction coefficient in oil.

The difference between films with and without stearic acid after a reciprocal sliding test was investigated by Raman spectroscopic analysis. The Raman spectra of disordered and amorphous carbon are given in reference [8]. Performing X-ray photoelectron spectroscopy (XPS) for the film surface before and after the scratch test confirmed structural differences between using hydrocarbon, graphite and diamond. The XPS result was used to consider the differences between surfaces produced in a previous severe scratch test [9] and the current test near the conduction band.

2. Experimental procedures

2.1. Fabrication of ND/a-C:H Film

Substrate disks of 440C stainless steel were heat-treated for surface hardening and for precipitation of carbon to enable the adherence of the ND/a-C:H film. The disks were subsequently polished to produce a smooth surface. The average Vickers hardness of the disks was 640. The ND powder, which was washed in an H2SO4 and HNO3 acid solution at an elevated temperature and rinsed with distilled water, was obtained from Tokyo Diamond Tools Mfg. Co., Ltd [4, 10]. Approximately 0.5 mg of the ND powder was spread on a pure graphite lower electrode with a diameter of 80 mm, as shown in Figure 1. The films were deposited on the disks by radio frequency (RF) plasma-enhanced chemical vapour deposition in an atmosphere of methane, argon and hydrogen gas. The stainless steel disk was fixed on the water-cooled upper electrode. The disk was cleaned by argon ion sputtering for 10 minutes under a direct current (DC) high voltage of 2 kV after the chamber was evacuated to 10⁻³ Pa. A gas mixture of argon with 10% methane and hydrogen gas was injected into the chamber at the same flow rate of 0.83 × 10⁻⁶ m³/s (50 × 10⁻³ l/min) after the chamber was evacuated to 10⁻³ Pa again. The mixture gas pressure in the chamber was set to approximately 1 Pa. The distance between the electrodes was set to a maximum of 52 mm.

![Figure 1. RF plasma-enhanced chemical vapour deposition apparatus with parallel plates.](image)

Deposition was performed under the following conditions to produce an a-C:H film with 46 at% hydrogen [2]. An RF power of 220 W was applied to the lower electrode. Another RF power source was connected to the middle coil to maintain the plasma. A negative DC bias voltage (under –100 V) was applied to the disk. The highest amount of ND particles dropped out from the deposited film when
no voltage was applied. Therefore, the bias voltage was set to -100 V to secure the ND powder in the film. This plasma deposition process was maintained for one hour to deposit a 200 nm thick ND/a-C:H film on the disk. The deposited film was checked by measuring the electrical resistance over a length of about 10 mm at the surface. The threshold values were $10^4 \Omega$ for an a-C:H film, $10^6 \Omega$ for a ta-C film and $10^2 \Omega$ for a passive oxide film on stainless steel 440C.

Visual observations revealed transparent films with a lead-like surface lustre, which was in contrast to most DLC films, which are brown or black. The films adhered well to the 440C stainless steel disks. Figure 2 shows a photograph of a film deposited on a stainless steel sample. The upper corners were masked during deposition, so that the difference between the heights of the masked and unmasked areas can be used to determine the thickness of the film. An optical microscopy image of the film surface is shown in Figure 3. Several particles approximately 1 $\mu$m in diameter can be observed. These particles were observed when the ND particles were mounted on the graphite electrode in the deposition process.

The surface roughness $R_{\text{max}}$ of the film was about 10 nm according to the image shown in Figure 4, acquired by AFM in non-contact mode (NC-AFM). The grayscale in the figure indicates a range from 1 to 10 nm. The roughness probably resulted from the 5-nm-diameter ND particles that impinged on the film during the deposition. The small roughness value indicates that the ND powder particles were individually dispersed into the film during plasma deposition. Peng et al. investigated the relationship between the surface roughness and the ion impingement energy [5]. According to their results, a gas pressure of 1 Pa and a -100 V bias should produce a smooth DLC film with a surface roughness of $R_q < 0.1$ nm. The ND particles that precipitated electrostatically due to the low bias voltage remained on the film because of their mass, whereas the hydrocarbon ions accelerated by the voltage penetrated into the film. The experiment showed that the size of the ND powder particles influenced the surface roughness, which was consistent with reference [5].

2.2. Reciprocal sliding test

A reciprocal sliding test sensor was developed to apply a severe load to the deposited films at high contact pressure without the testing tip jumping on the substrate disk. Figure 5 shows the hemispherical shell structure of the sensor. A silicon nitride ball with a 1.7 mm diameter was mounted on the stainless steel tube plunger as a tip for the pin that contacted the film. The tip was fixed on the stainless steel hemispherical shell sensor. Thus, the tip produced a high contact pressure on the film. A friction test was performed following deposition of oil droplets on the film.

Reciprocal sliding motion was produced by a stepping motor and a linear guide gear fixed on the stage. The specimen disk was fixed on the X-axis stage, and the vertical load was applied by moving the Z-axis stage downward. The distortion of the hemispherical shell was detected by two strain gauges that were adhered to the shell.
The test conditions were as follows: the sliding length was 1 mm, the sliding velocity was 1 mm/s and the lubricant oil was paraffin-based oil VG32 with a dynamic viscosity of 28.8-35.2 mm²/s at 313 K (40°C). A stearine coat was applied to dissolve the stearic acid powder into the oil.

When the lubricant was tested, contact first occurred at a sliding velocity of zero, and was maintained to both ends of the reciprocal sliding test strip. The lubricant test was conducted with oil alone or oil with dissolved stearic acid.

![Figure 4](image1.png)
**Figure 4.** Topograph of the deposited film surface acquired by non-contact mode atomic force microscopy.

![Figure 5](image2.png)
**Figure 5.** High-stiffness reciprocal sliding test instrument.

![Figure 6](image3.png)
**Figure 6.** Output signal from strain gauges. Sliding velocity: 1.0 mm/s.

The output signals of the right and left strain gauges in the cases of sliding velocities of 1.0 mm/s are shown in Figure 6. The output signals reflected the sliding motion of the tip. The output signal from the left strain gauge was just the inverse of that from the right strain gauge during sliding motion. Therefore, the normal force was measured by reading the same value of the strain gauges at the intersection of the output signals, and the horizontal force with sliding was measured by reading the difference between the values from both strain gauges during sliding motion. In Figure 6, the normal load was calculated from the strain values. On the vertical axis, the value was 75, which corresponded to 7.5 με, and the load calculated from the linear equation was 0.98 N. On the other hand, the force...
related to friction was estimated from the strain difference between the output signals during sliding. The value was 20, which corresponded to 2.0 με; thus the friction force was estimated from the proportional relationship between the strain difference and lateral force to be 0.087 N. The friction coefficient was calculated to be 0.089. The change in the friction coefficient of the film revealed the effect of adding stearic acid to the oil within the first 10 sliding cycles. The friction coefficient decreased from 0.12 to 0.08 with friction. The structure on the scratched surface in the high contact region withstood the compressive stress and provided wear resistance, similar to the thin diamond film in reference [12], which also exhibited a buckling pattern produced by compressive stress. The small deformation represented by the arcs of the surface structure fixed on the ND in reference [9] indicated a low friction coefficient because a large surface deformation increases the surface roughness and prevents the pin from sliding smoothly.

In the case that the sliding velocity was 0.5 mm/s, the output signal showed a spike in response to the sticking motion of the pin at the initiation of reciprocal sliding. When the pin was stuck, the tip of the pin jumped up from the film. Thus, it was impossible to evaluate the damage to the film and its healing. The sliding velocity was set to 1.0 mm/s to prevent sticking.

When the load reached 3.93 N, the developed pin-on-disk sensor indicated severe abrasive wear conditions of the deposited film on stainless steel disk. The maximum Hertzian contact pressure, $P_{\text{max}}$ was estimated to be 3.8 GPa from equations (1, 2) [13].

$$P_{\text{max}} = \frac{3W}{2\pi a^2}$$  \hfill (1)

$$\frac{1}{a} = \left( \frac{RW}{K} \right)^{1/3} + \frac{1}{R_1} + \frac{1}{R_2}, \quad \frac{1}{K} = \frac{3}{4} \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)$$  \hfill (2)

In equation (1), $W$ is the load, and $a$ is the radius of the contact area in the Hertz contact model. In equation (2), two elastic spherical bodies are denoted by the subscripts 1 and 2. Number 1 represents the Si₃N₄ ball and Number 2 represents the ND/a-C:H film. $R$ is the radius of the body, $E$ is Young’s modulus, and $\nu$ is the Poisson ratio. For the Si₃N₄ ball, $E_1$ is 280 GPa and $\nu_1$ is 0.25. For amorphous carbon, $R_2$ is infinity, $E_2$ is 1076 GPa, which is almost identical with the value acquired by a nano-indentation test for ND/a-C:H, and $\nu_2$ is 0.2 [14].

3. Results and discussion

3.1. Number of critical sliding cycles and value of critical contact pressure

Figure 7 shows the traces of the friction coefficients with sliding cycles. The test conditions were as follows: a contact pressure of 2.49 GPa without stearic acid or 2.37 GPa with stearic acid. Figure 8 shows optical microscopy images of the wear tracks after 10,000 cycles of sliding; these correspond to the plots shown in Figure 7.

When the contact pressure was 2.0 GPa, the widths of the wear tracks after 10,000 cycles of sliding with or without stearic acid were both approximately 20 μm. The estimated value from equation (2) was 22.7 μm. These were related to the elastic deformation of the silicon nitride balls, stainless steel substrates and ND/a-C:H films and indicated a small amount of damage to the film. For the case without stearic acid shown in Figure 8(a), wear tracks were seen as a 50 μm wide ribbon, although the contact width was estimated to be a 28 μm wide band with the maximum contact pressure in the center of the mated silicon nitride ball. This was related to deep wear of the film. The friction coefficient of 0.13 at 4,000 cycles of sliding gradually decreased with sliding. This was related to a decrease of the maximum contact pressure as the contact area enlarged by wear. The sample with stearic acid shown in Figure 8(b) showed few wear tracks and had a friction efficient of 0.08 from Figure 7(b), and the wear tracks became wider than 28 μm. These images show deformation and wear of the films as dark particles. In the case that the contact pressure was approximately 3 GPa, the widths of wear tracks became wider, due to large deformation of the films and deep wear. Based on these wear tracks, the
critical number of reciprocal sliding cycles was set to 10,000 for the remaining sliding tests on the films at a contact pressure of 2.5 GPa.

Figure 7. Plots of average friction coefficient every 400 cycles at contact pressure of about 2.5 GPa with or without stearic acid.

Figure 8. Wear tracks after 10,000 cycles of sliding.

3.2. Raman spectra for wear tracks on the films
Raman spectra (laser input wavelength of 514.5 nm) from the ND/a-C:H film are shown in Figure 9. These spectra were acquired from the specimens after washing in an ultrasonic bath filled with acetone. The spectra differed from the reported spectra for amorphous carbon films. A sharp G peak was observed, but no D peak was seen. This was likely due to the higher optical band gap of ta-C:H [8]. The Raman peak indicated a Stokes shift related to the conduction band. The formation of a diamond structure with a tetrahedral arrangement of carbon atoms decreased the amount of conductive carbon.

As shown in Figure 10, this phenomenon was also observed in XPS results for the valence electron energy of the ND/a-C:H film before and after a scratch test in a previous study [9]. The scratch test was performed using the silicon cantilever of an atomic force microscope. Peaks from the benzene ring were observed for the scratched sample, but no peak was detected for the as-deposited sample. The results indicate the scratched surface was composed of benzene rings, similar to the reconstructed diamond surface [12, 15, 16]. Furthermore, the deposited surface was composed of disordered carbon containing hydrogenated carbon atoms. The author considers this crystallization mechanism to be similar to crystallization due to high internal stresses in amorphous material, because bombardment by high energy ions of the ND/a-C:H film increases the number of sp³ bonds [17-20].

The Raman spectra for the tracks after 10,000 cycles of the reciprocal sliding test without stearic acid exhibited a broad D peak and a diminished sharp G peak, as shown in the middle panel of Figure 9. In contrast, the Raman spectra for the tracks with stearic acid resembled the spectra of the ND/a-C:H control film, and a sharp G peak was observed. The wear track became wider than the elastically
deformed silicon nitride ball, as mentioned in section 3.1, and the friction coefficient and Raman spectrum indicated an undamaged film. The friction coefficient of 0.08 is similar to that for a hydrogenated amorphous carbon film [20] and it indicated that the stearic acid protected against the release of hydrogen atoms from the friction surface, with the stearic acid molecules adhered to the wear track or the silicon nitride ball.

Figure 9. Raman spectra from wear tracks with an input laser wavelength of 514.50 nm.

Figure 10. XPS analysis of valence electrons in ND/a-C:H film.
3.3. Healing effect of stearic acid on ND/a-C:H film

Figure 11 shows the change in friction coefficient due to the healing effect of applying stearic acid to a ND/a-C:H film after the film was damaged by sliding at a contact pressure of 2.5 GPa without stearic acid. Upon the application of stearic acid after 4,000 cycles, the friction coefficient decreased below 0.08, similar to the friction coefficient of the film with stearic acid applied at the beginning of the test. As shown in Figure 12, the friction coefficient reached 0.15 following 4,000 sliding cycles before stearic acid application. The healing effect was confirmed when the track, damaged after 4,000 cycles without stearic acid, recovered as stearic acid was applied. As a result, the friction coefficient decreased from 0.13 to 0.08. When the stearic acid was applied to the worn track after 10,000 cycles, the friction coefficient decreased to 0.10.

![Figure 11](image1.png)

**Figure 11.** Change in friction coefficient of worn film after stearic acid application.

![Figure 12](image2.png)

**Figure 12.** Healing effect of stearic acid on friction coefficient of film with contact pressure of about 2.5 GPa.
In the Raman spectrum in the top panel of Figure 13, a broad D peak is observed for the wear track for which the friction coefficient increased up to 0.15 with 400 cycles of sliding without stearic acid application. It resembles the Raman spectra for the specimen after the 10,000 cycles sliding test without stearic acid in Figure 9. The Raman spectrum for the healed specimen in the middle panel is the same as that in the bottom panel with stearic acid in Figure 9. It is clear that the stearic acid healed the worn ND/a-C:H film, and that the friction coefficient recovered to 0.08. Upon the application of stearic acid after 10,000 cycles, the decrease in the friction coefficient was smaller, becoming 0.10. The Raman spectrum in the bottom panel of Figure 13 shows a broad D peak, indicating that the severe damage to the film did not recover as stearic acid was applied. In this case, the healing effect from the stearic acid decreased the friction coefficient only minimally because the pin traveled across the worn tracks where the dark particles were produced by the pin under the high load.

4. Conclusions
Amorphous carbon films containing hydrogen and dispersed ND powders were produced using RF plasma-enhanced chemical vapour deposition. The deposited surface was very smooth, with a surface roughness within 10 nm. The films were approximately 200 nm thick and transparent with a visible surface lustre.
Friction properties between a silicon nitride tip and the film were investigated in oil using an instrument with high stiffness to withstand severe loads. Stearic acid has been reported to lubricate diamond surfaces, and it was shown that with 10,000 cycles of the reciprocal sliding friction test, the friction and wear properties of ND dispersed a-C:H film improved with the application of stearic acid. Furthermore, wear of the film caused by sliding tests without stearic acid could be healed by sliding with stearic acid, as long as critical damage has not been sustained. Noncritical damage occurred in the film after 4,000 cycles of reciprocal sliding at a contact pressure of 2.5 GPa, and the friction coefficient became 0.13. When stearic acid was applied to the film in oil, the friction coefficient was reduced to 0.08 after 10,000 cycles of reciprocal sliding.

Raman spectra for the worn track revealed the healing effect of the stearic acid on the film because the spectra for the wear tracks after 10,000 cycles were the same as the control ND/a-C:H film with no wear. In contrast, the spectra for the wear tracks or the debris spectra showed a broad D band peak and no G peak, consistent with the spectra for disordered amorphous carbon.

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