Defect effect on tribological behavior of diamond-like carbon films deposited with hydrogen diluted benzene gas in aqueous environment

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ABSTRACT

This study examined the friction and wear behavior of diamond-like carbon (DLC) films deposited from a radio frequency glow discharge using a hydrogen diluted benzene gas mixture. The DLC films were deposited on Si (1 0 0) and polished stainless steel substrates by radio frequency plasma-assisted chemical vapor deposition (r.f.-PACVD) at hydrogen to benzene ratios, or the hydrogen dilution ratio, ranging from 0 to 2.0. The wear test was carried out in both ambient and aqueous environments using a homemade ball-on-disk type wear rig. The stability of the DLC coating in an aqueous environment was improved by diluting the benzene precursor gas with hydrogen, suggesting that hydrogen dilution during the deposition of DLC films suppressed the initiation of defects in the film and improved the adhesion of the coating to the interface.

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1. Introduction

Diamond-like carbon (DLC) films have excellent tribological properties, such as high hardness, high wear-resistance and low friction coefficients, which are favorable for a variety of applications in magnetic storage, textile industry, car and engine parts, etc. [1–3]. Many attempts have been made to exploit DLC films for surface protective coatings on biomedical implants, such as artificial hip joints, heart valves or vascular stents [4,5]. In particular, hydrogenated amorphous carbon (a-C:H) films show high corrosion resistance and biocompatibility, allowing the cells to grow without an inflammatory response and cell integrity [6,7]. However, the spallation or cracking of DLC films in an aqueous environment is considered one of the major obstacles to biomedical applications. Significant delamination wear with the spallation of a film is observed frequently during wear tests in aqueous environments, while abrasive wear occurs in dry or ambient air environments [8–12]. A clinical test of a DLC coated artificial hip joint also reported that the failure of the DLC coated hip joint is closely related to delamination of the coating, causing the formation of corrosion pits [8]. Chandra et al. [9] examined the effect of various fluids on the adhesion strength between the DLC coatings and substrates. It was reported that a phosphate buffered saline (PBS) solution could reach the interface of a-Si:H/a-C:H layer

through small perforations or defects pre-existing in the protective coating of the DLC layer, resulting in interfacial failure [10–12].

Recently, Park et al. reported that the delamination wear of the coating was suppressed significantly by removing the through-film defects formed with the solid particles nucleated at the interface of the reaction chamber [13]. They produced defect- or pinhole-free DLC films using a multi-step coating method. They also reported that the incorporation of Si in the DLC films could improve the corrosion resistance with low porosity [14] because Si in an amorphous carbon network can increase the three-dimensional interlinks and improve the stability in an aqueous environment. In order to suppress defect formation in the DLC films, it was also reported that hydrogen dilution would reduce the nucleation of solid particles in the plasma or the initial hydrocarbon, forming pinholes or defects in the film [15–19].

This study examined the tribological behavior of DLC films synthesized with a mixed precursor gases of benzene and hydrogen at different hydrogen dilution ratios. As less hydrogen was added to the mixture precursor, more and larger defects appeared in the film at lower amounts of hydrogen, while almost no defects were observed at higher hydrogen ratios, as shown in Fig. 1. The wear behavior of the DLC film was investigated by measuring the spallation area on the wear track under dry and aqueous environments. In particular, the stability of the DLC films during the tribo-test under aqueous environments was examined at different hydrogen dilution ratios. Scratch tests were used to estimate the relative adhesion strength between the DLC film and the steel substrate. Cross-sectional analysis of the defect sites

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formed during deposition was performed using a focused ion beam system, revealing open holes throughout the DLC film at lower hydrogen dilution ratios.

2. Experimental details

2.1. DLC film preparation

DLC films were prepared by radio frequency plasma-assisted chemical vapor deposition (r.f.-PACVD) using a mixture of benzene and hydrogen. Details of the deposition conditions are reported elsewhere [20]. The hydrogen dilution ratio or H_2/C_6H_6 volume flow ratio ranged from 0 to 2.0. The DLC films coated on Si (1 0 0) wafers were used for the wear test and scratch test, and films coated on stainless steel (or SUS 316L) were used to observe the defect regions on the DLC surface. To improve the interfacial strength between steel and DLC films, a 0.4 nm thick a-Si:H layer was sputtered on the 316L stainless steel substrate after 30 min Ar plasma cleaning at −750 V. The films were then deposited at a negative bias voltage of −400 V at a pressure of 1.33 Pa. The thickness of the DLC films was fixed to 1.0 ± 0.05 μm by controlling the deposition time and hydrogen dilution ratio from 12 to 21 min and 0 to 2.0, respectively.

2.2. Characterization

The defects or pinholes in the DLC films were observed from the high magnification and cross-sectional images of the surface defects taken using a focused ion beam system (FIB, NOVA 600, FEI Co.). The defect density on the film surface was estimated from the FE-SEM images and normalized to the scanning area. The film thickness was measured using an alpha-step profilometer (Alpha-step IQ surface profiler, KLA-Tencor Corp.). The hardness of the films was characterized using a nano indentation method (TriboIndenter®, Hysitron Inc.) and the residual stress of the film was determined using the curvature method with the help of the Stoney equation. Raman spectroscopy (LabRAM HR, HORIBA Jobin-Yvon Inc.) was used to analyze the atomic bond structure of the DLC films.

The scratch test of the DLC coating was performed at various hydrogen dilution ratios using a scratch tester (JLST022, J&LTech Corp.). A diamond tip, 200 μm in radius, was used as the scratching stylus with increasing normal load from 0 to 10 N at a fixed loading rate of 12 N/min and a scratching speed of 6 mm/min under ambient conditions. The acoustic emissions and friction forces were monitored continuously during the wear tests. The micro-structure of the scratch track was examined by optical microscope in differential interference contrast (DIC) mode.

2.3. Tribology test in aqueous condition

The friction and wear behaviors of the DLC films on the Si substrate were examined using a homemade ball-on-disk type wear rig. The tangential force was measured using a load cell of 9.8 N in full scale. The tribological tests were performed under completely soaked conditions in deionized (DI) water. The results were compared to those obtained under ambient air with a relative humidity of 20–30%. A sample was adhered to a plate and rotated against a stationary sapphire hemisphere ball, 6 mm in diameter, at a sliding speed of 12.6 cm/s and a normal load of 4 N for a total sliding distance of 440 m. Sapphire balls were chosen in this study in order to avoid the surface corrosion problems in water. The wear track of the DLC film and the wear scar of the ball were observed using an optical microscope (Axiotech, Carl ZEISS Inc.) and field emission scanning electron microscope (SEM, NOVA Nano-SEM 200, FEI Co.). The diameter of the wear scar on the mating ball was
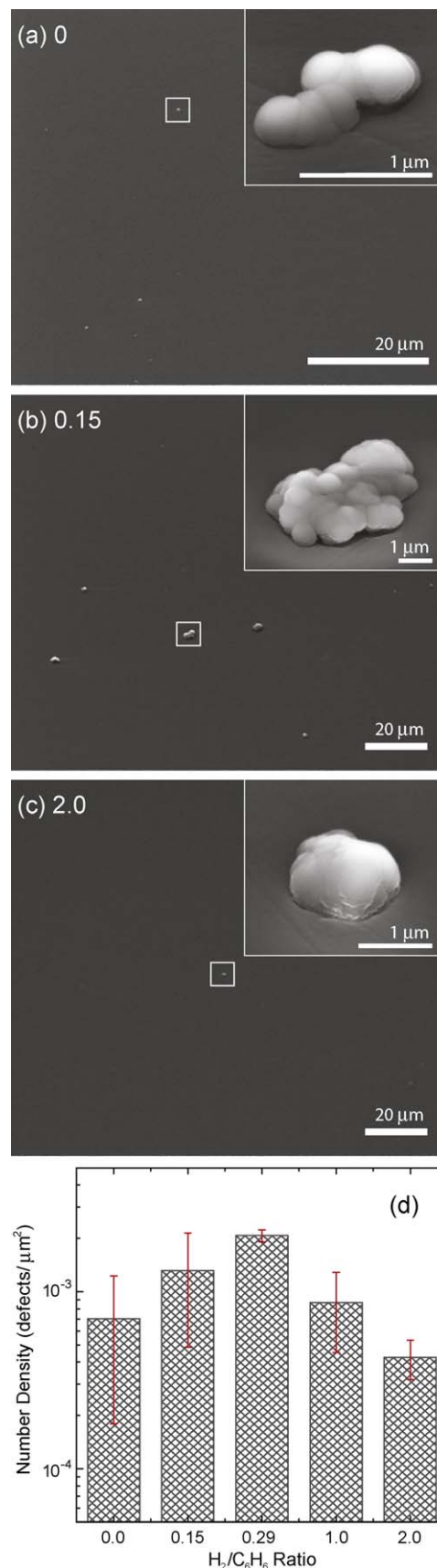

Fig. 1. FE-SEM images of the DLC film surfaces and the insets of the magnified regions with a thickness of 0.5 μm for different ratios of hydrogen in the mixed precursor gas; H_2/C_6H_6 are (a) 0, (b) 0.15 and (c) 2.0. The number density of defects on the film surface (d).

measured from the optical microscope images after the wear test. The wear volume of the ball was calculated from the diameter of the scar using the following equation [21]:

$$V_{ball} = \pi \left\{ hR^2 - \frac{R^3}{3} + \frac{(R-h)^3}{3} \right\},$$

where $h = R - \sqrt{R^2 - r^2}$ given by the Pythagorean theorem, R and r are the radii of the mating ball and the circular wear scar area on the mating ball, respectively. For simplicity, the wear scar is flat and circular in the above equation.

3. Results and discussion

Fig. 1 shows SEM images and magnified images of the defect sites on 0.5 μm thick DLC film surfaces. Compared to the DLC film deposited without adding hydrogen gas in Fig. 1(a), it appears that there is a critical hydrogen dilution ratio to form bump-like defects on the film surface. When the hydrogen dilution ratio was <1.0, many defects were observed on the film surface and the size of the defects was larger than approximately 5 μm, as shown in Fig. 1(b). On the other hand, with further increases in the hydrogen dilution ratio ≥1.0, there were few defects on the film surfaces and their sizes were smaller than approximately 1.5 μm, as shown in Fig. 1(c). Fig. 1(d) shows the number density of these defects on the film surface as a function of the hydrogen dilution ratio. The density of defects on the film surface increased at a relatively low hydrogen dilution ratio but decreased with further increases in the hydrogen dilution ratio. These imperfections or defects in the films

are believed to be a cause of the instability in the wear behavior of DLC films in aqueous environments.

Fig. 2(a) shows the change in hardness and residual stress of the DLC films as a function of the hydrogen dilution ratio. The hardness (open square) of the DLC films was varied from 13.09 to 15.43 GPa at different hydrogen dilution ratios. As the hydrogen dilution ratio was increased, the residual stress of the film increased gradually from 1.11 to 1.45 GPa but the increase was not significant. The Raman spectra of the films shown in Fig. 2(b) indicated no significant changes in the shape of the Raman spectrum with the hydrogen dilution ratio. All the spectra are typical of hydrogenated amorphous carbon (a-C:H), which is characterized by the G-peak near 1532 cm^{-1} with a broad D-peak shoulder near 1320 cm^{-1}. The G-peak is induced by the lattice vibration in the graphite-like hexagonal ring, and the D-peak is associated with the existence of graphitic clusters with short range crystallinity [22]. The results in Fig. 2 indicate that the mechanical properties and chemical structure of the films were relatively unaffected by the hydrogen dilution ratio in the precursor gas.

The frictional behavior in ambient air and water was characterized by measuring the friction coefficients of the DLC films at various hydrogen dilution ratios, as shown in Fig. 3. In ambient air with a relative humidity of 30–40%, a significant run-in stage was observed at the early sliding distance (Fig. 3(a)). The
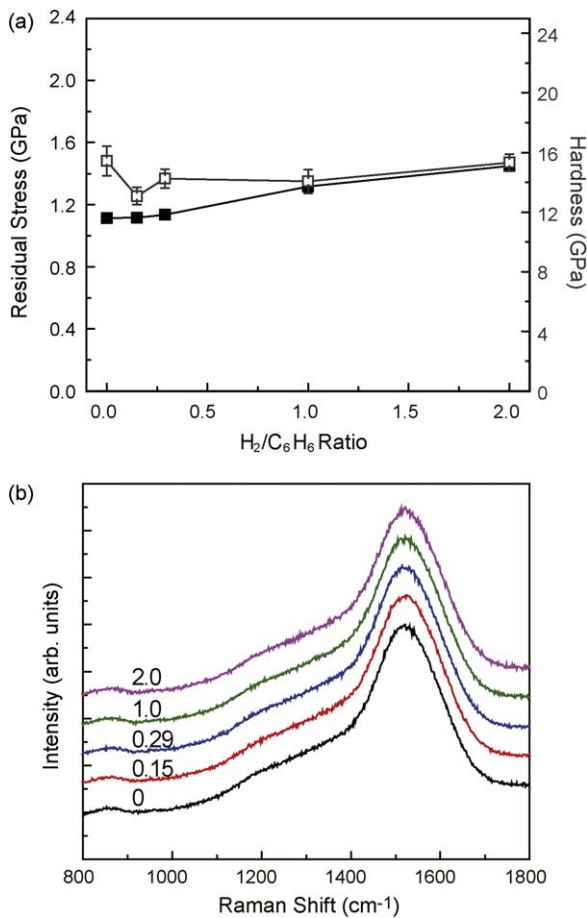

Fig. 2. (a) Hardness (open square) and residual stress (solid square) of the DLC films as a function of the hydrogen dilution ratio and (b) Raman spectra of DLC films at different H$_2$/C$_6$H$_6$ ratios of volume flow. The numbers are H$_2$/C$_6$H$_6$.
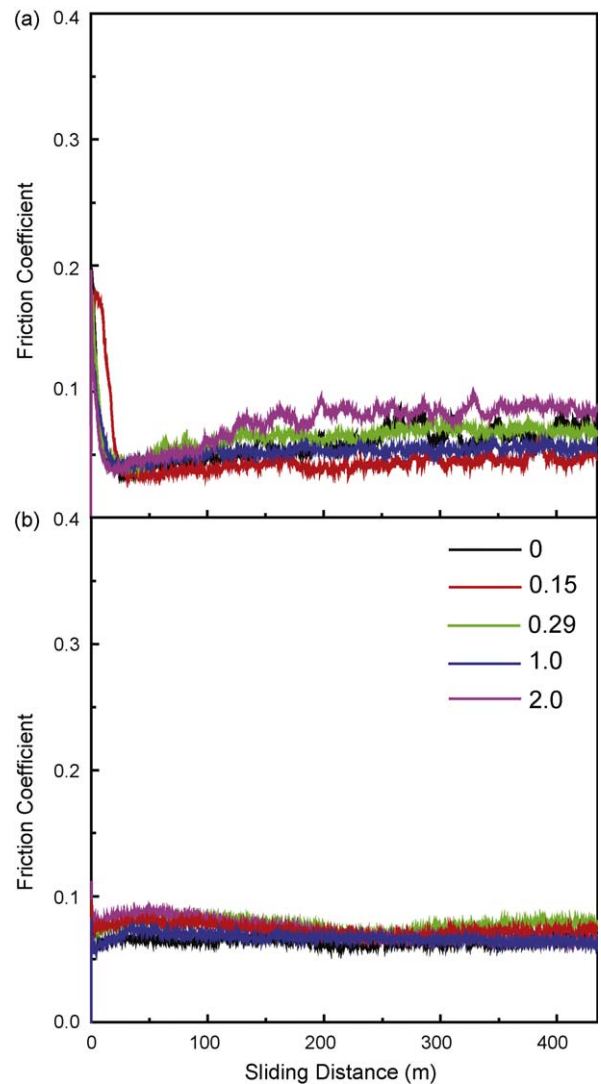

Fig. 3. Frictional behavior of the DLC films in (a) ambient air and (b) aqueous environment. The numbers are H$_2$/C$_6$H$_6$.

average friction coefficients in the steady state after the initial run-in ranged from 0.045 to 0.085. However, there was no obvious relationship with the hydrogen dilution ratio. In aqueous environments (Fig. 3(b)), stable friction without any run-in stage was observed regardless of the hydrogen dilution ratio. Stable friction in an aqueous environment is due to the lubricating effect of water at the interface between the DLC film and sapphire ball [13].
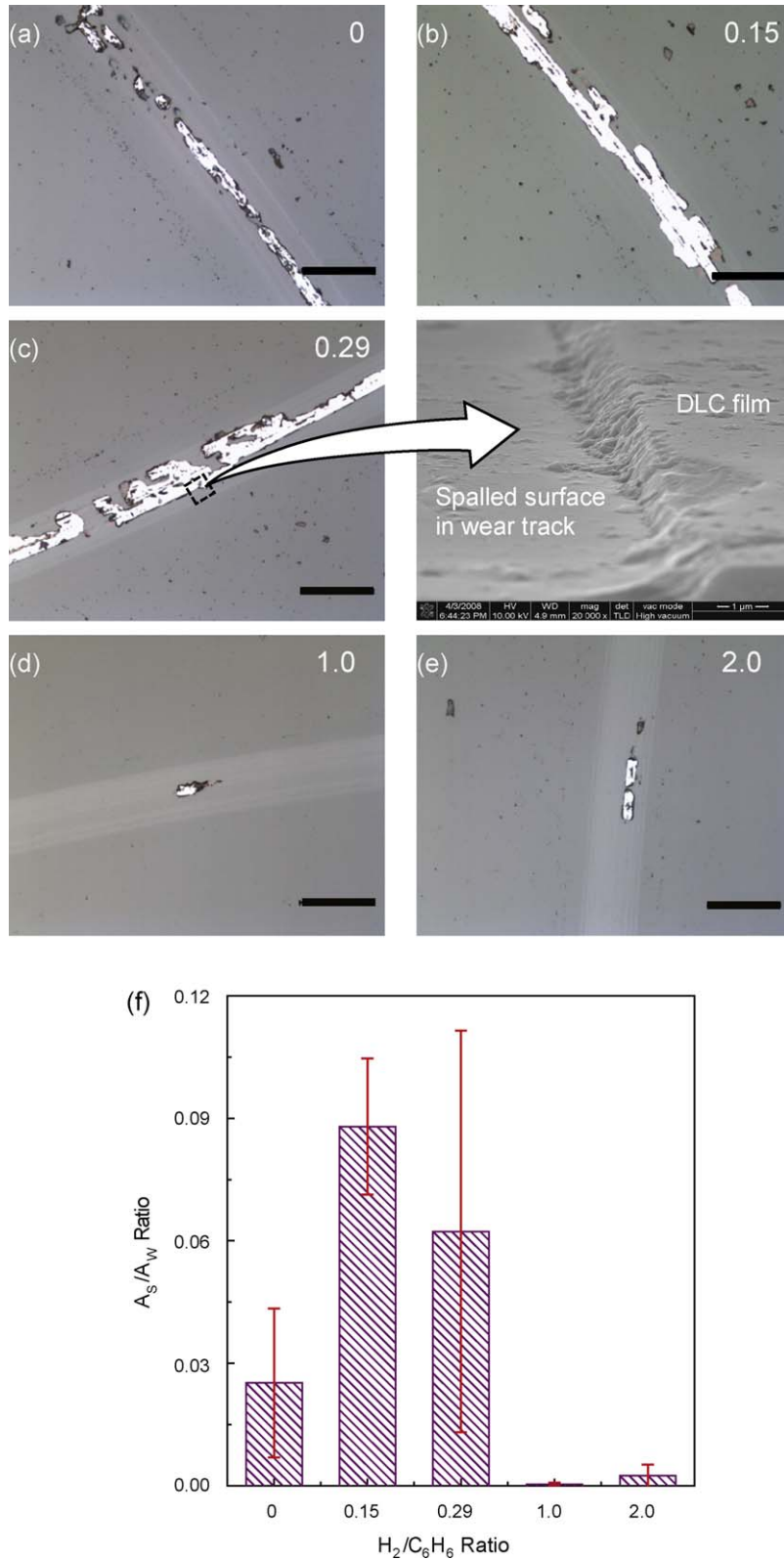

Fig. 4. Optical images of the worn surface of a DLC film after the wear test in an aqueous environment (a–e) (bar = 100 μm and numbers are hydrogen dilution ratio) and the magnified image from (c) was taken by FE-SEM (bar = 1.0 μm). The rate of the spalled area on the worn surface after the wear test in an aqueous environment (f) as a function of the ratio of H_2/C_6H_6. A_S and A_W are the spalled area and total area of the wear track, respectively.

Fig. 4(a–f) shows the wear tracks after sliding 440 m under aqueous conditions. While no delamination was observed in ambient air, significant delamination wear was observed in the aqueous environment, particularly when the hydrogen dilution ratio was <0.3. The square of broken line in Fig. 4(c) was further examined by SEM. The magnified SEM image from Fig. 4(c) showed not only wholly spalled areas at the interface between the DLC film and Si substrate but also brittle cracking throughout the DLC film thickness. The spallation of the DLC coating under aqueous conditions was suppressed when the hydrogen dilution ratio was higher than 1.0. Fig. 4(f) summarizes the quantitative ratio of the spalled area of the wear track under aqueous conditions. For a quantitative comparison, the spalled area, A_S, was scaled with the area of the wear track, A_W. The spalled area of the DLC film increased with increasing the hydrogen dilution ratio from 0 to 0.15. However, the spalled area decreased significantly at hydrogen dilution ratios ≥ 1.0, where the ratio of the spalled area/wear track area was <1%, which is consistent with the defect density discussed in Fig. 1(d). Under aqueous conditions, the spallation of DLC was increased for higher defect density at lower hydrogen dilution ratio, while suppressed significantly for lower defect density at higher dilution ratio

≥ 1.0. This shows that the wear-resistance of the DLC film in the aqueous environment was improved considerably by increasing the level of hydrogen dilution of the benzene precursor, while the bond structure and the mechanical properties of the DLC films were almost unchanged.

Under ambient air conditions, there was no significant difference in the wear scar of the sapphire ball, which was attributed to the almost identical mechanical properties of the DLC film regardless of the hydrogen dilution ratios, as shown in Fig. 2. In contrast, the size of the wear scar varied in aqueous environment at various hydrogen dilution ratios observed after the wear test, as shown in Fig. 5. Fig. 5(f) shows the relationship between the wear volume of the sapphire ball and the A_S/A_W. The wear volume of the sapphire ball decreased with increasing spallation wear in the wear track of DLC film. This is consistent with previous results in that the wear rate or wear volume of the ball is proportional to the strength of the film and interface [23,24].

In order to examine the main reason for the improvement in wear behavior under an aqueous environment, the surface defects and the interfacial adhesion strength were further investigated at different hydrogen dilution ratios. In previous work, it was reported that the size of the defect or pre-existing imperfection
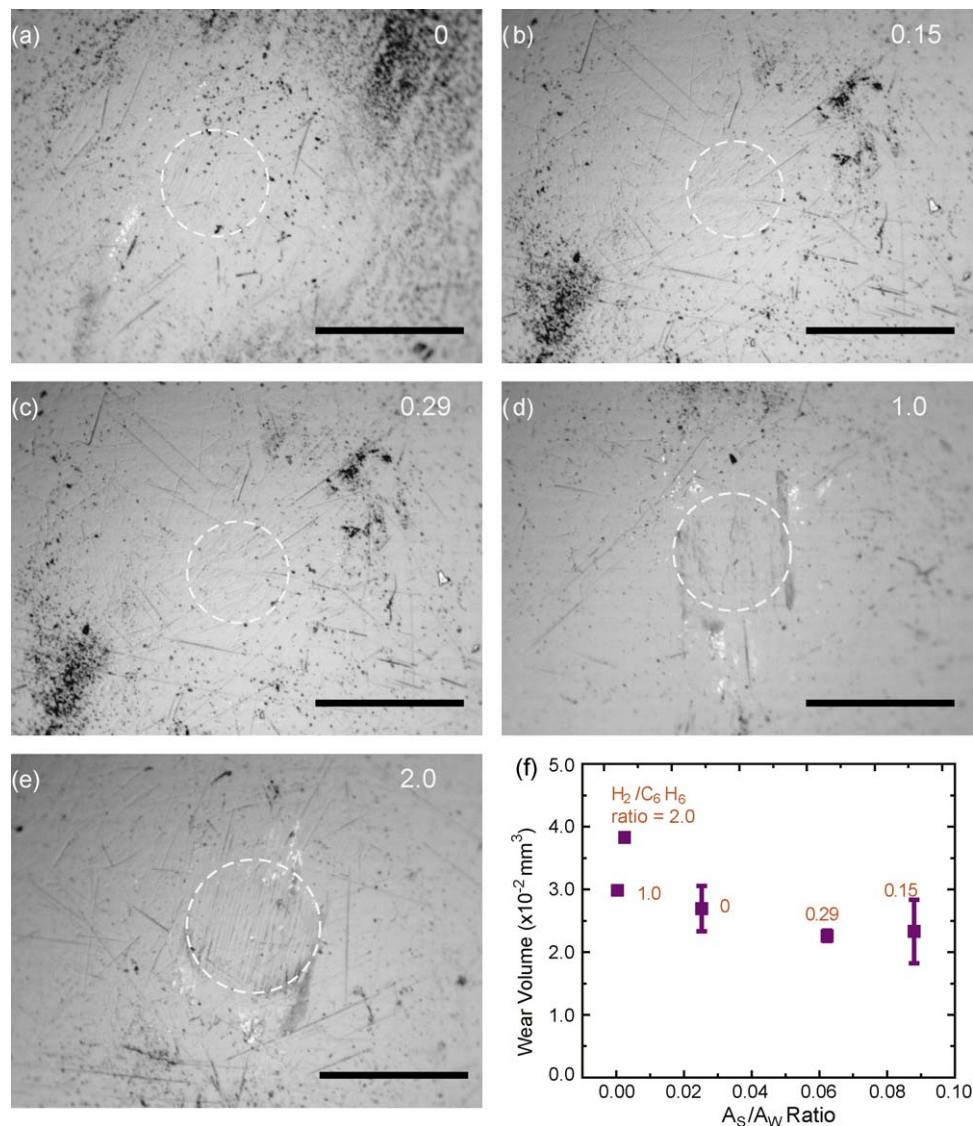

Fig. 5. Optical microscope images of the wear scars on sapphire balls after the wear test in an aqueous environment (a–e). The numbers are H_2/C_6H_6 and the white dotted circles indicate the wear scar in (a–e). Relationship between the wear volume of the mating ball and the A_S/A_W ratio (f). Bar = 100 μm.
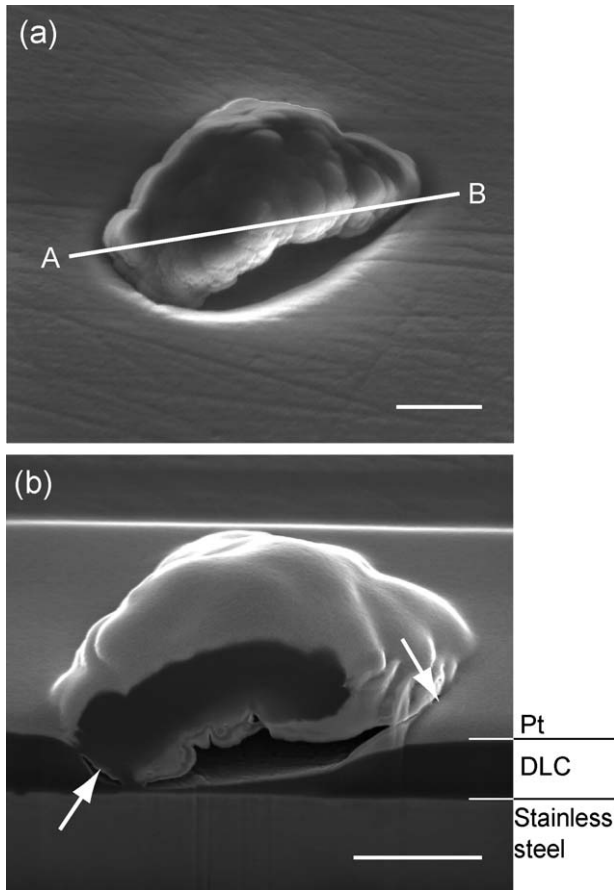
Fig. 6. The SEM images of the imperfections on a 0.5 μm thick DLC film with a hydrogen dilution ratio of 0.15 using a focused ion beam system, before (a) and after (b) sectioning. The white arrows show the cracks in the film, forming holes through the film. Bar = 1.0 μm.

at the interface plays an essential role in the instability of delamination in a compressive thin film [25]. Similarly, it is believed that the defects formed during the CVD process would trigger the instability, such as cracking or spalling of DLC film during the wear test. Fig. 6 shows a cross-sectional image of a defect on the DLC surface with a hydrogen dilution ratio of 0.15. A delaminated region was observed under the imperfect sites, in which there were also cracks or holes through the film at both sides, as indicated by the white arrows in Fig. 6(b). Without an external force like a normal or compressive load, the adhesion of

the films appears to be strong enough to prohibit delamination or spallation from spreading outside the defect site. However, the region surrounding the defects is still likely to be a weak point for the failure during the wear tests. In aqueous environments, the liquid molecules can penetrate the defect sites with holes and reach the interface between the film and substrate. Consequently, the liquid would reduce the adhesion strength through the mechanism proposed by Chandra et al. [9] and confirmed experimentally by Park et al. [13]. However, in the case of a relatively higher hydrogen dilution ratio, the formation of imperfect defects would be suppressed during deposition (see Fig. 1(c)), which would reduce the amount of spallation or delamination wear (Fig. 4(f)).

A scratch test was used to evaluate the adhesion strength between the DLC coating and stainless steel substrate. Fig. 7 shows the scratch tracks of the DLC coating with different hydrogen dilution ratios. There was a clear difference in the fracture behavior of the coating depending on the hydrogen dilution ratio. The DLC film without hydrogen dilution spalled almost entirely on and near the scratch track, as shown in Fig. 7(a). The spallation of the film even spread beyond the scratch track resulting in large area delamination. On the other hand, the DLC coatings with hydrogen dilution ≥1.0 showed better adhesion behavior. Only cracks were observed in the wear track without large area spallation of the coating. When the hydrogen dilution ratio was 2.0, spallation of the film was suppressed to a great extent, showing a similar result to that shown in Fig. 4. The improved stability of the DLC coating by diluting benzene with hydrogen in the precursor gas would be a natural consequence of the improved adhesion. Although the reason for the improved adhesion is unclear, it is possible that hydrogen rich deposition conditions may affect the initial transition phase of the substrate, that is chemically compatible with the DLC coating.

4. Conclusion

This study examined the tribological behavior of DLC films synthesized from a benzene precursor gas at different levels of hydrogen dilution. The mechanical properties and chemical bond structure of the DLC films showed no significant dependence on the hydrogen dilution ratio. However, spallation of the DLC coating in aqueous environment was suppressed significantly when the hydrogen dilution ratio was ≥1.0 due to suppression of the initiation of defects in the film. The scratch test of the samples showed that the adhesion strength increased with increasing hydrogen dilution ratio. This study showed that the adhesion strength at the interface was improved by increasing the hydrogen dilution ratio in the benzene precursor gas.
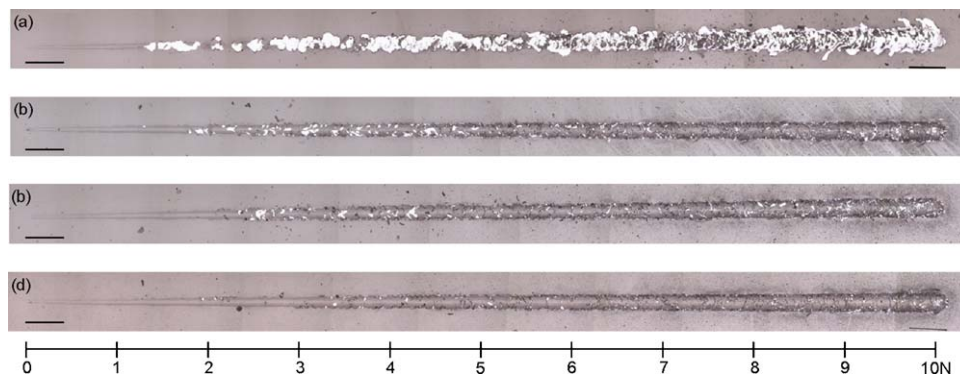

Fig. 7. Optical microscope images of microstructure of the scratch tracks on the DLC films deposited at different hydrogen dilution ratios, (a) 0, (b) 0.29, (c) 1.0 and (d) 2.0. Scale bar = 200 μm, corresponding to 0.4 N in normal load.

Acknowledgments

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