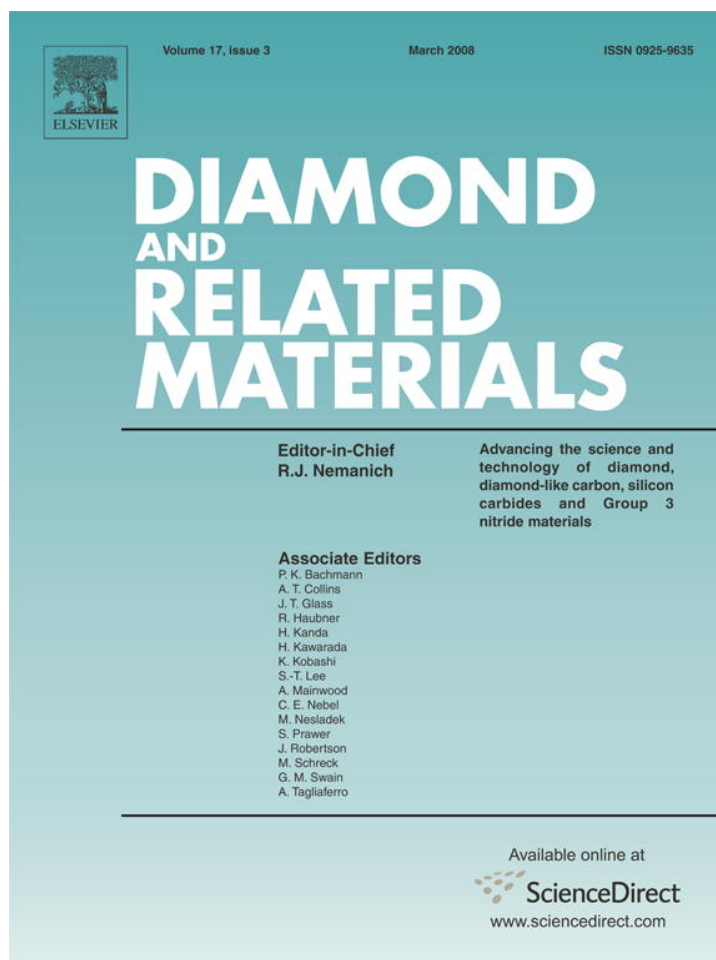


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Instability of diamond-like carbon (DLC) films during sliding in aqueous environment

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Abstract

The instability of diamond-like carbon (DLC) film deposited on Ti-6Al-4V alloy substrate using the r.f.-PACVD method was investigated under sliding conditions in an aqueous environment. Significant adhesive wear was observed when tested in this environment, while normal abrasive wear occurred in an ambient air of relative humidity about 25%. A critical test was performed to elucidate the reason for the instability which limits the biomedical applications of the DLC coating. By employing a multi-step coating process, it was shown that the instability is closely related to the penetration of water molecules to the interface via through-film defects or pinholes. These results suggest that the stability of DLC film in aqueous environment can be improved by controlling the through-film defects in the DLC coating layer.

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1. Introduction

Accelerated spallation of diamond-like carbon (DLC) coatings in aqueous environments has been well known for several decades [1–5]. This instability causes adhesive wear of the DLC film under sliding condition in aqueous environments, whereas gradual abrasive wear occurs in ambient air. The instability has been a particular concern for biomedical applications such as orthopedic implants. There is growing interest in the application of diamond-like carbon (DLC) film to orthopedic implants or various biomedical implants owing to its good biocompatibility combined with excellent mechanical and tribological properties [6–9]. When orthopedic implants are coated by the DLC film, the life time of the implant is expected to increase by suppressing the aseptic loosening [9]. However, recent follow-up test of 101 patients with DLC-coated femoral heads concluded that the clinical failure rate is as high as 45% after 8.5 years [10]. The authors found that numerous surface pits and

spallation of the DLC coating were formed on the surface of the retrieved femoral head and were caused by the instability. These defects of the femoral head accelerated the wear of the counterface polymer surface (ultrahigh molecular weight polyethylene). This case definitely shows that the stability of the DLC coating in body fluid environment is a critical issue for the applications to biomedical implants.

The instability has been widely used to test the adhesion of the coating in industry. However, the reason for the instability in aqueous environment has not yet been clarified. Drees et al. suggested that the absence of a transfer layer results in higher contact stress in aqueous environments [1]. Ronkainen et al. proposed that the failure of the coating is not caused by the delamination of the coatings but is more likely a rapid wear process [3]. On the other hand, Chandra et al. focused on the possibility of water penetrating through preexisting small perforations or defects in the coating. They suggested that this penetrating water degrades the interface between the DLC coating and the adhesive Si layer [4,5]. Ohana et al. also suggested that the cracks formed on the wear track during initial stage of wear test provide paths for the liquid to penetrate to the interface, which results in significant spallation of the coating [2].

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In the present work, we investigated the tribological behavior of DLC deposited on Ti-6Al-4V substrate in deionized water. It was observed that the instability is closely related to the penetration of water molecules via through-film pinholes or defects to the interface, which support the mechanism proposed by Chandra et al. [4,5]. Such pinholes can be formed by particles homogeneously nucleated in the plasma during film growth [11]. To highlight the effect of the through-film defects, we used a multi-step coating process that can reduce the probability of formation of through-film defects. The stability of DLC coatings in aqueous environment was much improved by the multi-step coating. The reduction of the through-film defects by the multi-step coating was confirmed by porosity measurements using the potentiodynamic polarization test.

2. Experimental

2.1. Film preparation

Using a 13.56 MHz radio frequency plasma-enhanced CVD method, 1 μm thick DLC film was deposited on Ti-6Al-4V substrates. Details of the deposition equipment have been published previously [12]. The substrates were mechanically polished using 1 μm diamond suspension and ultrasonically cleaned for 30 min in trichloroethylene (TCE), acetone, and methanol in sequence. Prior to the deposition of the DLC film, the substrates were sputter cleaned with Ar plasma at a bias voltage of -400 V for 15 min. A Si adhesive layer was then deposited using silane diluted by hydrogen ($\text{SiH}_4:\text{H}_2 = 1:9$) as the precursor gas in the glow discharge. The thickness of the Si adhesive layer was varied from 0.4 to 1.6 nm by adjusting the deposition time. The DLC film was then deposited from a benzene glow discharge at a bias voltage of -400 V or -800 V and the deposition pressure was 1.33 Pa. Residual stress and hardness of the film deposited at the bias voltage of -400 V were 0.9 ± 0.02 GPa and 10.5 ± 0.5 GPa, respectively. A denser and harder coating was obtained as the negative bias voltage increased [13]. The residual stress and hardness of the film deposited at -800 V were 1.8 ± 0.04 GPa and 17.0 ± 0.5 GPa, respectively.

2.2. Friction test

The stability of the coating was characterized by using a ball-on-disk type wear rig, either totally soaked in deionized water or in ambient air of relative humidity about 25%. Fig. 1 shows the schematics and photograph of the wear rig used in the present work. A sapphire ball of diameter 6 mm was used for the wear test. Normal load and sliding speed were 5.9 N and 10 cm/s, respectively. Total number of contact, i.e. total number of rotation was 15,500. Diameter of the wear track was 17 mm and the sliding distance was thus 827.8 m in total.

2.3. Porosity measurement by potentiodynamic polarization test

Potentiodynamic polarization test was performed in a 0.89% NaCl solution of pH 7.4 at 37 °C using an EG&G Princeton

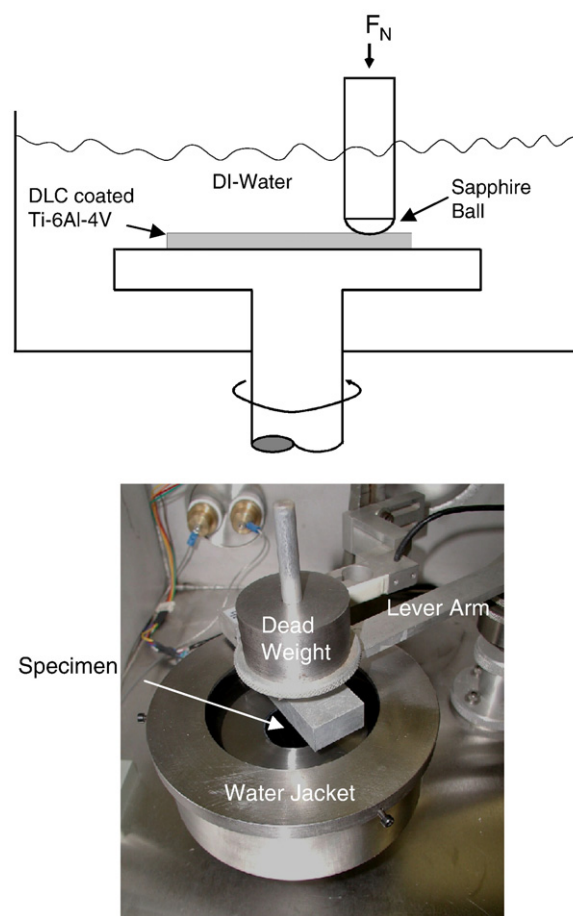


Fig. 1. Photograph of the wear rig used in the present work.

Applied Research Model 273A potentiostat for DC measurement. The solution was thoroughly deaerated by bubbling high purity nitrogen gas for 0.5 h prior to the immersion of the specimen and continuously purged during the test. The exposed coating area was 1 cm^2 . Reference and counter electrodes were used for a saturated calomel electrode (SCE) and a pure graphite, respectively. Prior to the potentiodynamic polarization test, the specimens were kept in the solution for 6 h in order to establish the open circuit potential (OCP). The potential of the electrode was swept at a rate of 0.166 mV/s from the initial potential of -250 mV versus E_{corr} to the final potential of 1500 mV.

Porosity is a characteristic of coatings manifested by the existence of pores. A coating with pores cannot inhibit the diffusion of aggressive agents through the coating that leads to the formation of local corrosion, galvanic corrosion, and blistering of the coating. The porosity can be determined from the measured polarization resistance. The polarization resistance can be experimentally determined from the DC polarization curve. The porosity corresponds to the ratio of the polarization resistance of the uncoated and the coated substrate [14],

$$P = \frac{R_{p,u}}{R_{p,r-u}}$$

where P is the total coating porosity, $R_{p,u}$ is the polarization resistance of the substrate and $R_{p,r-u}$ is the polarization resistance of the coating-substrate system.

3. Results and discussion

Fig. 2(a) shows the coefficient of friction of the DLC coating against sapphire ball in ambient air. After the initial run-in stage, the coefficient of friction fluctuates in the range between 0.05 and 0.1, which is the typical friction behavior of hydrogenated DLC film in a relatively dry environment (relative humidity about 25%). On the other hand, in the aqueous environment, the initial run-in stage becomes much shorter and the coefficient of friction exhibits a stable value of around 0.06 as shown in Fig. 2 (b). These friction behaviors are independent of the thickness of the Si adhesive layer or the substrate bias voltage during the DLC film deposition. It can be thus said that the friction behavior in aqueous environment is dominated by the lubricating effect of water.

However, wear of the film showed contrasting behavior depending on the test environment and the thickness of the Si adhesive layer. Fig. 3(a) and (b) shows the wear tracks of DLC coating after the wear test in ambient air and in the aqueous environment, respectively. The DLC film was deposited at the bias voltage -400 V with a Si adhesive layer of thickness 0.4 nm. The wear track in ambient air reveals only abrasive wear without delamination of the DLC coating. However, significant delamination was observed in the track created in the aqueous environment. Fig. 3(c) shows the wear track after testing in the aqueous environment when the Si buffer layer was 1.6 nm. The increased thickness of the Si adhesive layer

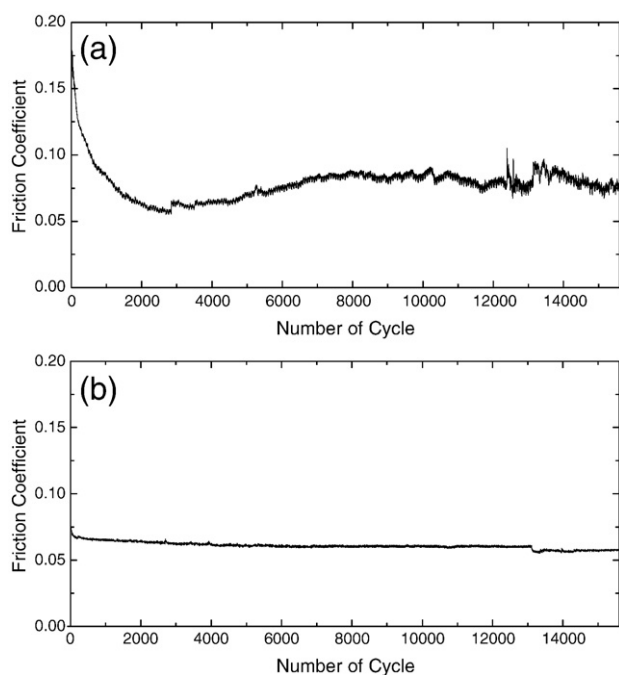


Fig. 2. Coefficient of friction between the DLC film and the sapphire ball in (a) ambient air and (b) deionized water. The DLC film was deposited on Ti-4Al-6V substrate from benzene glow discharge at a bias voltage -400 V with 0.4 nm thick Si adhesive layer.

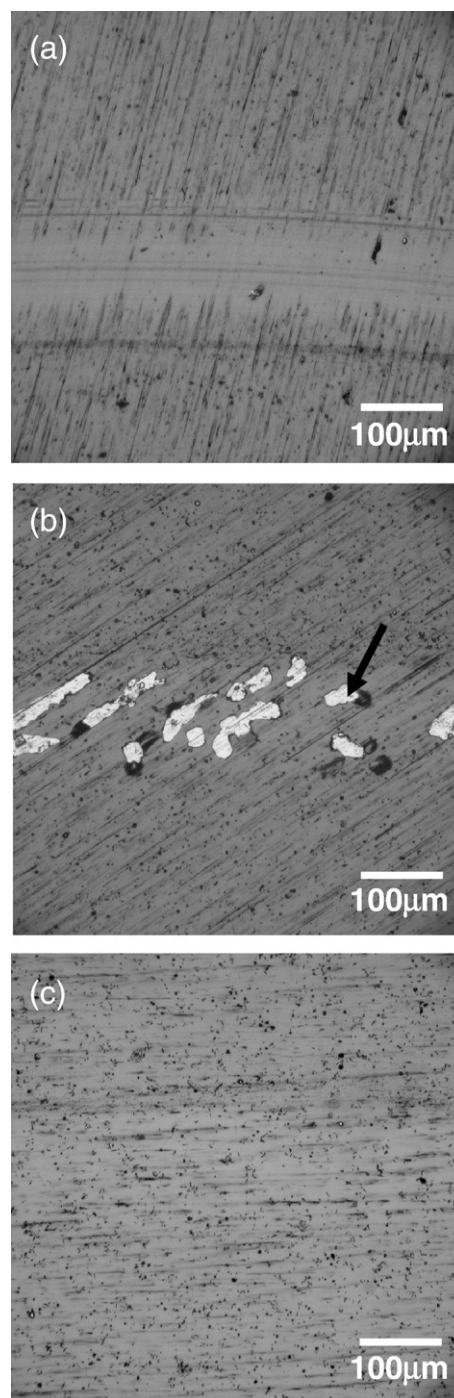


Fig. 3. (a) Optical microstructure of wear track after testing in ambient air of the DLC coating with 0.4 nm thick Si adhesive layer. (b) Optical microstructure of wear track after testing in an aqueous environment of the DLC coating with 0.4 nm thick Si adhesive layer. (c) Optical microstructure of wear track after testing in aqueous environment of the DLC coating with 1.6 nm thick Si adhesive layer.

improved the stability of the coating in the aqueous environment. The stability of the DLC coating seems to be related to the coverage of the Si adhesive layer. The same behavior was observed in the films deposited at the bias voltage -800 V.

Auger electron spectroscopy was employed to characterize the surface concentration of the delaminated area indicated by

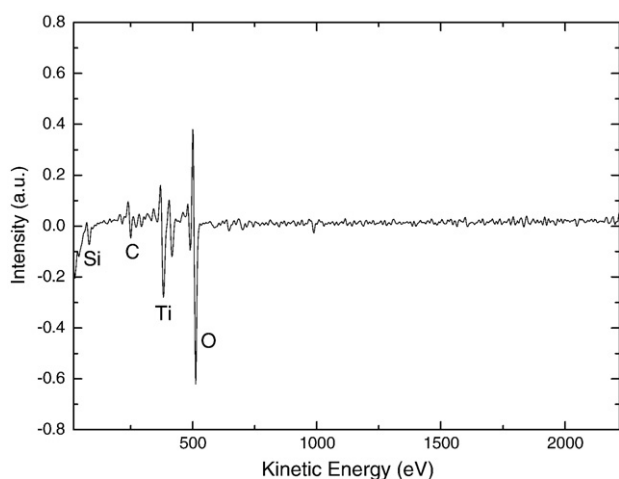


Fig. 4. Auger electron spectroscopy of delaminated area of wear track indicated by an arrow in Fig. 3(b).

an arrow in Fig. 3(b). Fig. 4 shows the Auger spectrum of the delaminated surface after cleaning by Ar ion beam in the analysis chamber. The spectrum revealed that the delaminated surface is composed of titanium and oxygen with small amounts of carbon and silicon, indicating that the delamination mainly occurs at the interface between the substrate and the Si adhesive layer. Al and V were not observed on the delaminated surface,

(a) Multistep Coated DLC Film

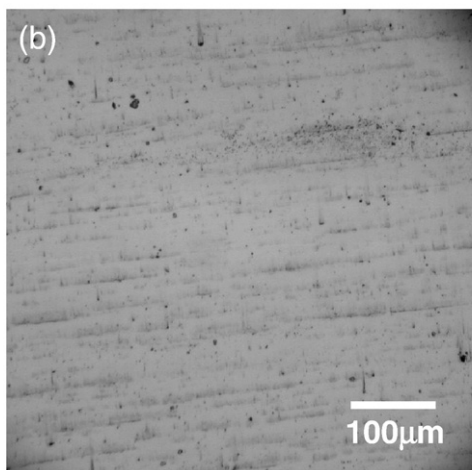
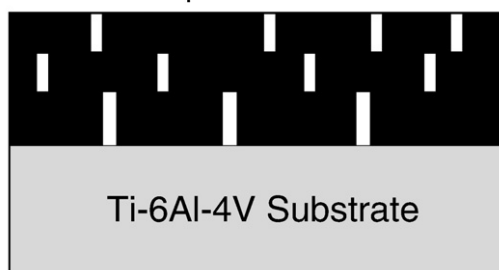


Fig. 5. (a) Schematic of multi-step coatings and (b) the wear track after testing in aqueous environment.

presumably because of the thick Ti oxide layer on the substrate surface.

These observations show that the instability of DLC coatings in aqueous environments is not associated with the atomic bond structure of the film but is closely related to the interface between the film and the substrate. One possible reason for the instability would be the increase in the residual stress of DLC film in water, which can increase the shear stress at the interface beyond the interfacial toughness. Lee et al. reported that the residual compressive stress of hydrogenated DLC film increased with relative humidity in the environment [15]. They showed that the residual compressive stress of DLC film abruptly increased by 27 MPa as the relative humidity increased from 20 to 90%. However, significant increases in the residual stress were observed only in polymeric films with high concentration of hydrogen. It must be further noted that adhesive wear occurs in both films deposited at the negative bias voltages of -400 and -800 V, where the difference in the residual stress is as high as 900 MPa.

Another possible reason is degradation of the interfacial chemical bond because water molecules penetrate to the interface via through-film defects. Chandra et al. suggested that the biological fluid, particularly phosphate buffered saline solution (PBS), could penetrate the coating through pinholes and slowly corrode the interface between DLC and a-Si:H/DLC films [4,5]. For a critical test of this possibility, we created a multi-step coating to reduce the through-film defects in the film. Through-film pinholes can be generated by landing particles homogeneously nucleated in the plasma of supersaturated composition [11]. After depositing a Si adhesive layer of thickness 0.4 nm, the coating process for the 1 μm thick DLC coating was divided into three consecutive processes of 0.33 μm thick DLC coating. After each process, the specimen was removed from the reaction chamber and ultrasonically cleaned in ethanol for 10 min. The multi-step coating process suppresses the formation of the through-film defects because of the very low probability of aligning the defects generated in each coating step. Fig. 5(a) shows the schematic of the coating obtained by this multi-step coating process. Table 1 summarizes the corrosion resistance and the estimated porosity of coating-substrate system characterized by the potentiodynamic polarization test. The porosity of the coating-substrate system by single-step coating was 0.126. However, the porosity was significantly reduced to 0.051 by the multi-step coating process. The residual compressive stress and the Raman spectra of this film are essentially the same as those of the film prepared by the single-step coating process. Fig. 5(b) shows the wear track of the film when tested in the aqueous environment. No adhesive wear was observed in the track, which is in dramatic contrast to

Table 1
Results of potentiodynamic polarization test

	R_p ($\text{k}\Omega/\text{cm}^2$)	Porosity	Protective efficiency (%)
Substrate	202.2		
DLC coated (single-step deposition)	1605.5	0.126	73.60
DLC coated (multi-step deposition)	3989.8	0.051	96.82

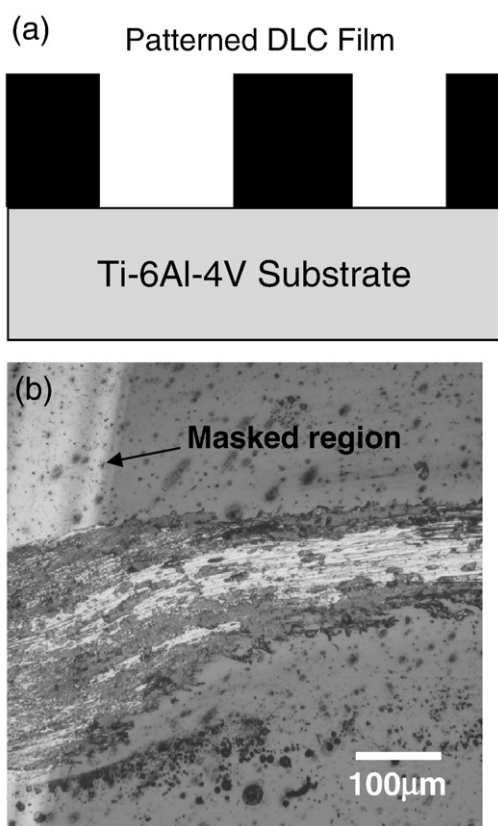


Fig. 6. (a) Schematic of grid patterned coating and (b) the wear track after testing in aqueous environment.

the severe delamination of the films prepared by single coating process (see Fig. 3(b)). It is evident from this result that the instability of DLC coatings in aqueous environments is closely related to the penetration of water via through-film defects, which degrades the interfacial strength between the film and the substrate.

To confirm the result, we introduced artificially exaggerated defects in the film using a mask with a grid pattern with line-width 100 μm and the spacing between lines 1 cm. Because of the grid pattern, the edge of the interface is exposed to the water. Fig. 6(a) shows the schematic of the coating of patterned film. For these samples, we employed a 1.6 nm thick Si adhesive layer where no delamination was observed during sliding in the aqueous environment, as shown in Fig. 3(c). However, Fig. 6(b) shows significant delamination along the wear track, which would be caused by the degradation of the interface by the water molecules. Because of the grid pattern, the edge of the interface would be

widely exposed to the water. It must be noted that the severe adhesive wear occurs once the film/substrate interface is exposed to the water. In an ambient environment, the adhesive wear in the wear track of the patterned coating was not observed.

4. Conclusions

The instability of DLC coatings in aqueous environment is caused by the degradation of the interfacial strength because water molecules penetrate via through-film defects. The stability of the film can thus be significantly improved by removing the through-film defects. Multi-step coating was effective in reducing the through-film defects caused by the particles nucleated in the plasma reaction chamber. The present results suggest that particle control in the deposition environment is very important to improve the stability of DLC coatings in aqueous or body fluidic environments.

Acknowledgement

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