Characterization of diamond-like carbon films deposited on commercially pure Ti and Ti–6Al–4V

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Abstract

The diamond-like carbon (DLC) films deposited on the articulating surface of medical-grade Ti and Ti–6Al–4V were characterized. The DLC films were synthesized by r.f. plasma assisted chemical vapor deposition (PACVD) using C₆H₆ at 10 mTorr. For wear tests, the ball-on-disk type wear tester was employed by wearing a 5-mm diameter ruby ball against a rotating metal disk. The DLC coating dramatically improved the wear performance of Ti and Ti–6Al–4V, and protected the substrates from corrosion. The wear behavior of DLC films on the Ti-alloy was that of normal abrasive wear. However, the softer Ti substrate deformed plastically and the films were prefractured. The lifetime of the DLC coating in saline solution was reduced due to the delamination of the coating.

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1. Introduction

Wear was not a major issue in orthopedics until about 1980 when the widespread use of Ti–6Al–4V alloy instead of the, then standard, cast Co–Cr–Mo alloys was considered. The principal advantages of the alloy were thought to be its very high biocompatibility and low modulus of elasticity. In articulating Ti–6Al–4V against ultra-high molecular weight polyethylene (UHMWPE) wear, although quite significant, is not as severe as for the alloy. This is apparently so because oxide wear debris became embedded in the polymer and continued to wear the alloy during subsequent rotations. The wear process is thought to be autocatalytic because the passivating oxide is only weakly adherent to the metal surface. Once an oxide particle is removed and becomes embedded in the UHMWPE, an associated wear band is formed, for which the sample is deeply grooved. Consequently, a large amount of new wear debris is generated. This process can be suppressed by hardening of the passive film on the surface; one method of which is ion implantation [1–4]. Implantation of nitrogen

or carbon into the Ti-alloy has been commercialized. However, due to its nature of shallow penetration by implantation process, the hardened titanium oxide surface layer is thin and not durable.

DLC films have distinct tribological properties, such as low friction and high wear resistance with a very smooth surface [5–11]. Such excellent tribological properties make them good candidates as wear-resistant layers, and many studies have reported DLC as a protective coating for the articulating surface of implants [12–17]. Firkins et al. [16] showed that the wear rate of UHMWPE was much lower on DLC-coated 316L stainless steel than on the bare metal itself. DLC films have also been reported to have good biocompatibility, such as the absence of inflammatory responses in vitro when assessed by mouse peritoneal macrophages [18], and the absence of histopathological changes in vivo when implanted in animal bone [17]. However, the tribological behavior of DLC films is strongly dependent on the substrate and the test conditions. For example, the very low friction coefficient, often below 0.05, when a steel slider slides over a DLC surface in dry air gradually increases with increasing humidity and reaches values in the range of 0.15–0.3 at 100% relative humidity [19,20].

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In this study, diamond-like carbon films formed by r.f. plasma assisted chemical vapor deposition (r.f. PACVD) were applied to commercially pure (CP) Ti and ELI Ti–6Al–4V, and the tribological performance was evaluated in both the atmosphere and a saline solution environment. In addition, electrochemical measurements and cytotoxicity tests using the agarose overlay method were performed.

2. Experimental procedures

2.1. Sample preparation

Samples of 2.5 cm diameter ELI Ti–6Al–4V and commercially pure Ti, with thickness of 2 mm, were cut from an annealed rod. The sample surfaces were ground and polished to 1 μ with a diamond paste. After cleaning with methanol, the polished samples were stored under vacuum.

The DLC films were deposited on the polished samples using a r.f. PACVD method with benzene (C_6H_6) as the reaction gas. The substrates were mounted on a water-cooled cathode where 13.56 MHz r.f. power was delivered through the impedance matching network. Prior to the deposition process, the substrates were sputter cleaned by an Ar discharge at the negative bias voltage of -750 V and the pressure of 3.8 mTorr for 15 min. The films were then deposited to the thickness of 1 μ m at a bias voltage of -500 V. The deposition pressure measured by a capacitance manometer was kept at 10 mTorr by adjusting the conductance of the main valve.

2.2. Wear tests

The wear tests were conducted with a ball-on-disk type wear test machine (TE67-8554, Plint, UK) as schematically shown in Fig. 1. The apparatus operates by wearing a 5-mm diameter ruby ball against a rotating metal disk. The ruby ball and metal specimen were secured to the holder, and exchanged after each wear test. A normal load of 32 N was applied on the ball. Tests were performed at room temperature either in ambient air or in a saline solution with a sliding velocity of 0.13 m/s. The wear tracks were examined with a surface profilometer (P-10, Tencor, USA). Four measurements were taken on each wear track, and the averaged area measurements were multiplied by the track circumference to compute wear volume. The wear tracks were also examined with an optical or scanning electron microscope (SEM).

2.3. Electrochemical measurements

The anodic polarization curves were determined with an EG&G Princeton Applied Research Model 273 potentiostat. The test solution, 1 N H_2SO_4 , was deoxygenated with nitrogen 30 min prior to immersion of the specimen and continuously purged during the test. The potential was

Fig. 1. Experimental set-up for wear test.

changed linearly in the noble direction at a scan rate of 1.2 V/h from the open-circuit corrosion potential 30 min after immersion. After determination of the polarization curve in 1 N H_2SO_4 , the samples were then rinsed thoroughly with distilled water and transferred to a saline solution. The anodic polarization curves were then determined using the same method as above, but in the absence of purging gas.

2.4. Cytotoxicity test

The cytotoxicity test of the DLC coating on Ti and Ti–6Al–4V was performed using the agarose overlay method as specified in ASTM F895. After incubation of the culture assay at 37 °C for 24 h, the number of cells affected within the zone of toxicity were measured with an inverted phase contrast microscope, and compared to the positive control material (nitroso guanadine: response rate is over 2/2), negative control (PBS: response rate is 0/0), polished Ti and Ti–6Al–4V. The samples prepared had an area of 1 cm².

3. Results and discussion

DLC films are generally extremely hard, chemically stable, and tribologically excellent having low static and dynamic friction and high wear resistance. The combination of such excellent properties make DLC films good candidates for various medical applications, especially for the articulating surface of an implant. Fig. 2 shows the average wear volumes of the samples tested at 3000 cycles in both ambient air and saline solution. For DLC-coated Ti and Ti–6Al–4V, the wear volume is much smaller than for uncoated samples in both environments, indicating protection of the

Fig. 2. Wear volumes at 3000 cycles (a) in atmosphere and (b) in saline solution.

substrate from abrasive wear by the hard layer coating of DLC. The wear of untreated Ti and Ti-6Al-4V were very severe even at the beginning of the test, which progressed with time. Ti-6Al-4V is harder than Ti, resulting in slightly less wear.

For DLC-coated Ti, the wear volumes seem to be larger than for DLC-coated Ti-6Al-4V in both environments. Fig. 3 shows representative wear track profiles for (a) DLC-coated Ti-6Al-4V at 3000 cycles, (b) DLC-coated Ti at 150 cycles, and (c) DLC-coated Ti at 3000 cycles. For DLC-coated Ti-6Al-4V, the size of wear track is even smaller than that of DLC-coated Ti at 150 cycles (equivalent to the beginning of the test). In the preliminary study, any measurable size of wear tracks for both DLC-coated Ti and Ti-6Al-4V could not be detected with the normal load of 5 N up to 180,000 cycles. The normal load of 32 N was therefore chosen for the present study. This load was high enough to produce wear tracks within a reasonable test period, and also to cause cold flow in Ti, but not in Ti-6Al-4V. As can be seen in Fig. 3, the size of the wear track for the DLC-coated Ti at 150 cycles is already large due to cold flow. The

Fig. 3. Wear track profiles of (a) DLC on Ti-6Al-4V at 3000 cycles, (b) DLC on Ti at 150 cycles, and (c) DLC on Ti at 3000 cycles.

wear volume caused by abrasive wear for DLC-coated Ti and Ti-6Al-4V might be similar at 3000 cycles if a correction for Ti cold flow was properly made. Increases in the size of the wear track due to cold flow had a minor effect for the wear volume of untreated Ti. The wear volumes of DLC-coated samples are similar in both environments, but they were more than four times lower than that for untreated samples owing to the lubricant effects of the saline solution.

The protective DLC coating layer certainly improved the wear resistance of both Ti and Ti-6Al-4V. The wear tests were extended until failure of the DLC coatings occurred, and the results are shown in Fig. 4. The DLC film deposited

Fig. 4. Number of cycles to rupture in DLC films.

on Ti–6Al–4V lasted for 92,000 cycles in the atmosphere, whereas on Ti, it prefractured after only 10,200 cycles.

Fig. 5 shows the wear track profiles from the DLC coating on Ti–6Al–4V at wear cycles of (1) 3000, (2) 6000, and (3) 9000, respectively in an atmospheric environment. The wear track grew in size as the test duration increased, indicating progressive and fairly steady wear. Microscopic examination of the wear track revealed that the surface was not deformed and was clean without any signs of film failure. In addition, the surface smoothness increased as the number of test cycles increased. Under the high normal load of 32 N, direct contact between the ruby ball and the films took place, and the layer of DLC was steadily worn off. The function of the coating is to separate the Ti–6Al–4V from the counterface and prevent ploughing by hardening the top layer of the surface. The prevention of ploughing reduces both friction and wear of Ti–6Al–4V dramatically. The DLC films on Ti–6Al–4V behaved typically as normal abrasive wear, and the substrates were protected against wear until DLC films had worn-out completely.

For the wear behavior of the DLC film on Ti, the softer Ti substrate deformed plastically when the normal load of 32 N was applied. Deformation was considerable thus adding a ploughing or hysteresis effect to friction, but DLC films were not as flexible as Ti. Therefore, repeated deflection of the coating caused fracture or fatigue cracks that eventually destroyed the DLC film. A scanning electron micrograph of the wear track at 6000 cycles is shown in Fig. 6. The white horizontal line in the top of figure corresponds to cracks located at the center of wear track, and fine cracks were also observed near the center of the wear track. The frictional situation is more favorable for Ti–6Al–4V when compared with Ti because the ploughing or hysteresis effects due to substrate deformation are relatively minor. The lifetime of the DLC coating on both the Ti and Ti-alloy in a saline solution was dramatically reduced as shown in

Fig. 5. Surface profiles of wear track in DLC-coated Ti–6Al–4V at 3000, 6000, and 9000 cycles.

Fig. 6. Scanning electron micrograph of wear track in DLC-coated Ti at 6000 cycles.

Fig. 4. Fig. 7a shows the optical micrograph of the wear track, in which the coating is partially detached over a wide track width. The surface profile of Fig. 7b presents two

Fig. 7. DLC coating on Ti–6Al–4V tested in saline solution (a) optical micrograph of wear track and (b) corresponding surface profile.

distinct regions of gradual decreases in depth around the edges of the wear track and sharp decreases in the center of the wear track. In the saline solution, the DLC films were initially worn-out by normal abrasive wear, and then suddenly delaminated after some time.

It has been reported that humidity has an adverse effect on the tribological performance of DLC films. In inert controlled environments, the tribological behavior of DLC is very similar to that of bulk diamond, but in humid air the coating behaves very much like bulk graphite [21]. Several mechanisms have been proposed for the deterioration of wear and friction resistance of DLC films in wet environments [9,21,22]. Drees et al. [9] proposed that the catastrophic failure of the coatings in an aqueous environment is due to the loss of adhesion between the coating and the substrate by the combined influences of both the load and the electrochemical environment, and would be improved by decreases in the coating porosity.

Fig. 8 shows the anodic polarization curves of polished and DLC-coated Ti–6Al–4V (a) in deaerated 1 N H₂SO₄

Fig. 8. Anodic polarization curves (a) in deaerated 1 N H₂SO₄, and (b) in saline solution.

Table 1
Cytotoxicity test results

	Decolorization index	Lysis
Positive reference	2	5
Negative reference	0	0
Ti	0	0
Ti-alloy	0	0
DLC on Ti	0	0
DLC on Ti-alloy	0	0

and (b) in aerated saline solution. Each anodic polarization curve was determined by increasing the potential from the open-circuit corrosion potential measured after 30 min of immersion. In both solutions, the DLC-coated Ti–6Al–4V produced a more noble open-circuit corrosion potential and much lower anodic current densities relative to the polished Ti–6Al–4V. The measured current densities of 10^{-9} – 10^{-8} A/cm² are probably the lowest current range detected by this kind of electrochemical measurement indicating the inertness of the DLC film and complete protection of the substrate from corrosion.

The tribological performance of the DLC films coated on the Ti and Ti-alloy are well above that of the other hard coatings even in wet environments. However, the relatively poor behavior of DLC films in wear and friction resistance when exposed to humidity remains an interesting question which requires further investigation. We deposited DLC films on a thin Si wafer and measured the curvature of the DLC-coated Si wafer before and after immersing in saline solution. Curvature of the DLC-coated Si wafer increased in the saline solution due to the external force caused by the hydrophobic characteristic of the DLC film. Delamination of DLC films could be reduced if the DLC films become less hydrophobic. Currently, attempts to improve the wear and friction resistance of DLC films are being made by controlling the surface energy of the film.

Table 1 shows the cytotoxicity test results done by a tissue culture assay using the agarose overlay method. The DLC films formed in this study were judged as nontoxic since there was no cell mortality in the proximity of the test sample as the FDA approved Ti and Ti–6Al–4V.

4. Conclusions

The wear properties of Ti and Ti–6Al–4V were much improved by coating with DLC. In atmospheric environments, the features of the wear track were different depending on the substrate. The DLC films on the Ti-alloy behaved typically as normal abrasive wear, and the substrates were protected against wear and friction until DLC films had worn-out completely. However, the wear behavior of DLC films on the softer Ti showed that the substrate deformed plastically when a normal load of 32 N was applied. The deformation was considerable and repeated deflection of the coating

caused fractures or fatigue cracks that eventually destroyed the DLC film.

The lifetime of the DLC coatings on both Ti and Ti–6Al–4V was dramatically reduced in the saline solution. DLC films were initially worn-out by normal abrasive wear, and then suddenly delaminated after an incubated time. The DLC film was as nontoxic as the FDA approved Ti and Ti–6Al–4V because no cell mortality was observed in the proximity of the test sample.

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