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Friction and wear study of diamond-like carbon gradient coatings on Ti6Al4V substrate prepared by plasma source ion implant-ion beam enhanced deposition

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Abstract

DLC gradient coatings had been deposited on Ti6Al4V alloy substrate by plasma source ion implantation-ion beam enhanced deposition method and their friction and wear behavior sliding against ultra high molecular weight polyethylene counterpart were investigated. The results showed that DLC gradient coated Ti6Al4V had low friction coefficient, which reduced 24, 14 and 10% compared with non-coated Ti6Al4V alloy under dry sliding, lubrication of bovine serum and 0.9% NaCl solution, respectively. DLC gradient coated Ti6Al4V showed significantly improved wear resistance, the wear rate was about half of non-coated Ti6Al4V alloy. The wear of ultra high molecular weight polyethylene counterpart was also reduced. High adhesion to Ti6Al4V substrate of DLC gradient coatings and surface structure played important roles in improved tribological performance, serious oxidative wear was eliminated when DLC gradient coating was applied to the Ti6Al4V alloy.

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Keywords: Diamond-like carbon; Gradient coating; Friction and wear behavior; Plasma source ion implant-ion beam enhanced deposition

1. Introduction

The Ti6Al4V alloy has been widely used as artificial joint for its low modulus, high specific strength and superior corrosion resistance [1,2]. However, the Ti6Al4V alloy surfaces are susceptible to oxidative wear caused by repetitive disruption of passive oxide films and subsequent reoxidation of the exposed metal surface [3,4]. As a result, the hard oxide wear debris and metal ion released into the local joint environment causes biological reaction and failure of the joint.

The diamond-like carbon (DLC) coatings are not only chemically inert and biocompatible in these applications, but exhibit high chemical resistance to oxygen, the oxide wear debris and metal ions are

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prevented from releasing into the surrounding organic tissue, which make DLC coatings as a potential candidate artificial joint material [5–8]. Moreover, DLC demonstrates low friction coefficient and high wear resistance in various environments. Especially, the formation of wear particles needs to be prevented because they could enforce or release critical reactions of the organic tissue. Therefore, a surface modification of the implant by the deposition of optimized DLC coatings can be considered.

Though many deposition methods, including sputtering [9], plasma enhanced chemical vapor deposition (PECVD) [10] and ion-beam assisted deposition (IBAD) [11], can be used successfully to deposit DLC films, one of the greatest challenges of DLC coating technology is the poor adhesion between coating and metal substrate because of the mismatch of their thermal expansion coefficient and structure [12]. As a solution of this problem, the gradient coating technology is introduced to provide a route of enhancing adhesion. In the present study, plasma source ion implantation-ion beam enhanced deposition (PSII-IBED) is applied to prepare DLC gradient coatings on Ti6Al4V alloy substrate.

In this study, we investigated and analyzed the friction and wear behavior of DLC gradient coatings deposited on Ti6Al4V substrate by PSII-IBED method against ultra high molecular weight polyethylene (UHMWPE). For comparison, the non-coated Ti6Al4V alloy is also evaluated.

2. Experimental

2.1. Preparation of DLC gradient coatings

A plasma source ion implantation-ion beam enhanced deposition (PSII-IBED) reactor was applied in this study. In order to combine the ion implantation with deposition, the ion beam enhanced deposition was introduced into this reactor. In order to prepare the gradient DLC coatings in which the distribution of carbon concentration could gradually increase and reach a maximum on surface, the energy of the depositing carbon ions decreases gradually during processing. The carbon ion energy is controlled by a high frequency negative pulse bias applied to the sample in the presence of the plasma. By optimizing the carbon ion energy the DLC gradient coatings can be prepared [13,14].

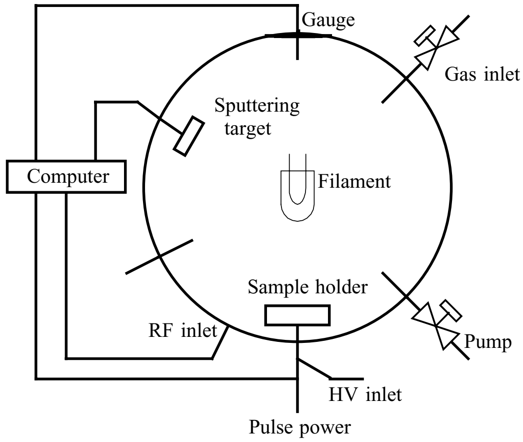


Fig. 1. The schematic diagram of PSII-IBED.

A schematic diagram of this reactor is shown in Fig. 1. The main technical specifications of this reactor are as follows: vacuum chamber dimension $\phi 500 \times$ 1000 mm, background pressure <2×10^{-4} Pa; working pressure $(2-50) \times 10^{-3}$ Pa; plasma density $10^8 \pm 10^{10}$ cm^{-3}; negative pulse amplitude 5–80 kV; pulse repetition frequency 50–1000 Hz.

The disk-shaped Ti6Al4V substrates with 24.0 mm in diameter and 7.8 mm in thickness were polished to a mirror finish with a roughness of 0.2 μm using alumina paste, and ultrasonically cleaned in acetone followed by alcohol, and fully dried. The polished substrates were then mounted in the PSII-IBED vacuum chamber on a water-cooled sample holder. Prior to film deposition the substrates were sputter-cleaned in an argon glow discharge. PSII-IBED process was carried out promptly after sputter cleaning, the substrates were immersed in the carbon plasma produced by a repetitively pulsed vacuum arc plasma gun with methane as carbon source. Carbon was implanted into substrates for 20 min under ion energy 65 keV and for 40 min under ion energy 45 keV, then for 30 min under ion energy 10–15 keV. Moreover, the deposition of carbon continued for another 40 min without pulse bias. For our operating parameters the final gradient coatings were about 2–3 μm in thickness with an improved surface roughness of 0.1 μm.

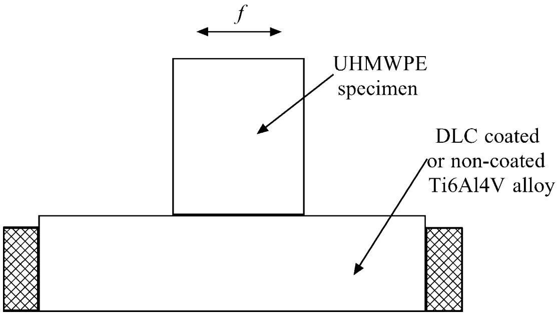


Fig. 2. Surface–surface configuration of friction pair.

The structure of gradient coatings was subsequently characterized by Raman spectroscopy and second ion mass spectrum (SIMS). The coatings adhesion to Ti6Al4V substrate was evaluated by acoustic emission scratch tests. In addition, the Vicker's microhardness of coatings was measured by a Knoop indenter.

2.2. Friction and wear tests

Friction and wear tests were performed on an Optimol-SRV friction and wear tester with a surface–surface configuration as shown in Fig. 2. DLC gradient coated or non-coated Ti6Al4V alloy sample was fixed on a platform while UHMWPE counterpart slides on sample surface at a constant frequency of 40 Hz and amplitude of 1 mm. UHMWPE counterpart was machined into disk-shape with 10.0 mm in diameter and 5.0 mm in thickness, the sliding surface was polished to a roughness of 0.1 μm. A load of 200 N was applied to the tribological system (thus, the nominal stress about 2.55 MPa). The tests were conducted at temperature 310 K under dry sliding, lubrication of bovine serum and 0.9% NaCl solution, respectively. Both long distance tests of 2000 m and short distance tests of 500 m were performed, long distance tests were interrupted intermittently every 200 m for weight loss examinations. The wear rate K of sample was calculated from weight loss as $K = \Delta m/\rho PL$, where Δm is the weight loss, ρ the density of sample, L the sliding distance, and P the applied pressure. The coefficient of friction was continuously recorded in situ during sliding tests. The wear surface evolution was examined progressively using scanning electron microscopy (SEM, OPTON CSM950).

3. Results and discussion

3.1. Structural characteristics and high adhesion

The C–C bond structure of as-deposited coatings was characterized by Raman spectroscopy. Fig. 3 shows the Raman spectra for the coatings prepared by PSII-IBED. The G peak centered around 1580 cm^{-1} could be assigned to the sp^2-bonded carbon and the D peak centered around 1320 cm^{-1} could be assigned to the sp^3-bonded carbon. These two peaks revealed a common feature of typical DLC structure [15].

The distribution of carbon between coating and Ti6Al4V substrate was analyzed by SIMS. Fig. 4 shows the carbon and titanium concentration depth profiles derived from SIMS. The carbon fraction gradually decreased while the titanium fraction increased from the surface region containing only C–C bonds to the inner region with both C–C and C–Ti bonds, and finally to the region containing only C–Ti bonds. Both carbon and titanium concentration profiles showed smooth transitions, which suggested that the DLC coatings on Ti6Al4V substrates prepared by PSII-IBED had gradient structure.

Acoustic emission scratch tests were conducted to evaluate the adhesion to substrates of DLC gradient coatings. A continuously increasing load at a rate of 1.67 N s^{-1} was applied to a diamond cone with radius of 0.1 mm. The diamond cone was moved with a constant speed of 10 mm min^{-1} over the surface of the sample. Due to the materials damage the emission

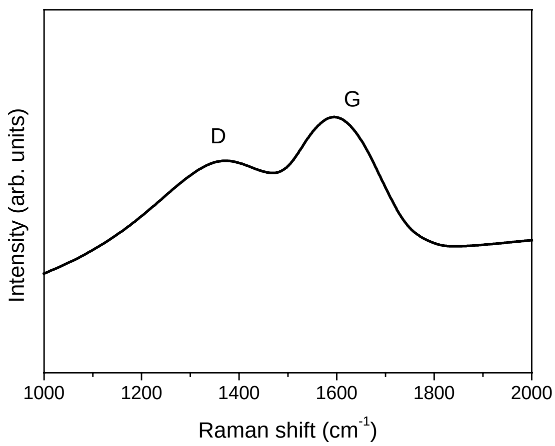


Fig. 3. Raman spectra of DLC coatings prepared by PSII-IBED.

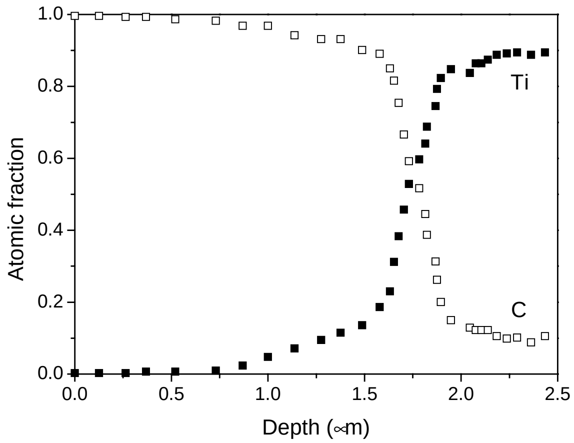


Fig. 4. Carbon and titanium concentration depth profile derived from SIMS.

of acoustic signals occurred. In our experiments, no emission of acoustic signals was observed until at load of 40 N for DLC coated Ti6Al4V. The results suggested that the adhesion was much better than the DLC coating made by micro-wave chemical vapor deposition, of which emission of acoustic signals had been recorded at load of 32 N.

The Vicker's microhardness of coatings was measured by a Knoop indenter. Fig. 5 shows the Vicker's microhardness measurements at different loads from 5 to 50 g. For the DLC coatings with a thickness of 2–3 μm, the results at low load of less than 15 g should be more reliable. Improved microhardness of almost 1400 kg/mm^2 for DLC gradient coatings, which was

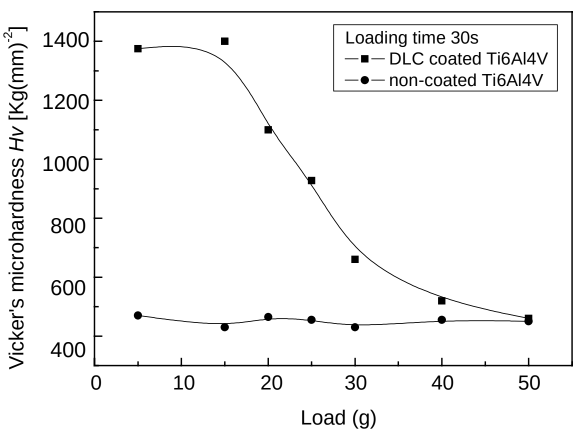


Fig. 5. Comparison of Vicker's microhardness between DLC coated and non-coated Ti6Al4V alloy.

about triple of non-coated Ti6Al4V alloy, had been measured.

3.2. Low friction coefficient of DLC gradient coatings

An evident reduction of friction coefficient was observed when DLC gradient coating was deposited on Ti6Al4V alloy. After 500 m sliding distance, friction coefficient reached a steady value, Table 1 lists the friction coefficient of DLC gradient coated and non-coated Ti6Al4V alloy under dry sliding and different lubricated conditions. Compared to non-coated Ti6Al4V alloy, the friction coefficient of DLC coated Ti6Al4V alloy reduced 24, 14 and 10% under dry sliding, lubrication of bovine serum and 0.9% NaCl solution, respectively. The low friction coefficient of DLC coatings can be attributed to the partial graphite sp^2-bonded structure, it has been proposed that the graphitized layer has low interlayer strength and can be easily sheared [16].

3.3. Improved wear resistance performance of DLC gradient coatings

A significant improvement of wear resistance was also demonstrated with DLC gradient coating applied to Ti6Al4V alloy. Fig. 6 compares the wear rates of DLC gradient coated and non-coated Ti6Al4V alloy after 2000 m sliding distance under different lubricants. The DLC gradient coatings shown good wear resistance performance, for the wear rates of DLC gradient coatings were about half of non-coated Ti6Al4V under the same conditions.

The surface structure plays an important role in the wear behavior of tribo-system. Because of the content of sp^3-bonded carbon, DLC coatings demonstrate extremely high surface hardness. Moreover, by PSII-IBED method, the involved components can be controlled to distribute gradually along the depth from the DLC coating to metallic substrate and the interface between DLC coating and substrate has disappeared, so that the stress can be greatly relaxed and the adhesion has been highly improved. The improved wear resistance of DLC gradient coated Ti6Al4V alloy is believed to be attributed to its sp^3-bonded structure and gradient structure.

Meanwhile, wear resistance performance was affected by lubricants. Under lubrication of bovine

Table 1
Steady coefficients of friction after 500 m sliding distance under different conditions

Counterparts	Roughness, R_a (μm)	Lubricants	Steady friction coefficient, μ
Non-coated Ti6Al4V/UHMWPE	0.2/0.1	Dry sliding	0.181 ± 0.004
	0.2/0.1	Bovine serum	0.149 ± 0.002
	0.2/0.1	0.9% NaCl solution	0.122 ± 0.002
DLC coated Ti6Al4V/UHMWPE	0.1/0.1	Dry sliding	0.137 ± 0.002
	0.1/0.1	Bovine serum	0.128 ± 0.002
	0.1/0.1	0.9% NaCl solution	0.110 ± 0.002

serum, whether DLC coated Ti6Al4V alloy or non-coated Ti6Al4V alloy demonstrated the lowest wear rate. Meanwhile, the wear rates under dry conditions, though higher than those in bovine serum, were observed to be even lower than those in NaCl solutions. Under dry conditions, debris was liable to be absorbed by the counterface and its release was prevented.

3.4. Wear behavior of UHMWPE counterpart

The wear of UHMWPE was obviously affected by tribological counterpart and lubricants. Fig. 7 shows the accumulated wear rates of UHMWPE sliding against DLC gradient coated and non-coated Ti6Al4V alloy under lubrication of bovine serum and 0.9% NaCl solution. Though the initial wear rate of UHMWPE coupled with DLC gradient coatings was greater than that of UHMWPE coupled with non-coated Ti6Al4V alloy, it reduced rapidly and finally became less than the latter after 500 m sliding distance. Therefore it can be concluded reasonably that the total weight loss of UHMWPE coupled with DLC gradient coatings would be less than that of UHMWPE coupled with non-coated Ti6Al4V alloy after more long time. That is, the application of DLC gradient coatings deposited on Ti6Al4V alloy had

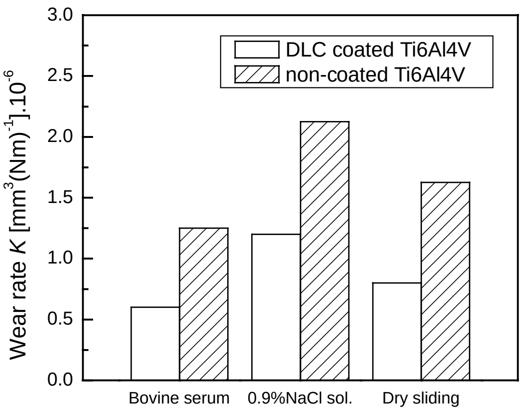


Fig. 6. Wear rates of DLC coated and non-coated Ti6Al4V alloy under different condition after 2000 m sliding distance.

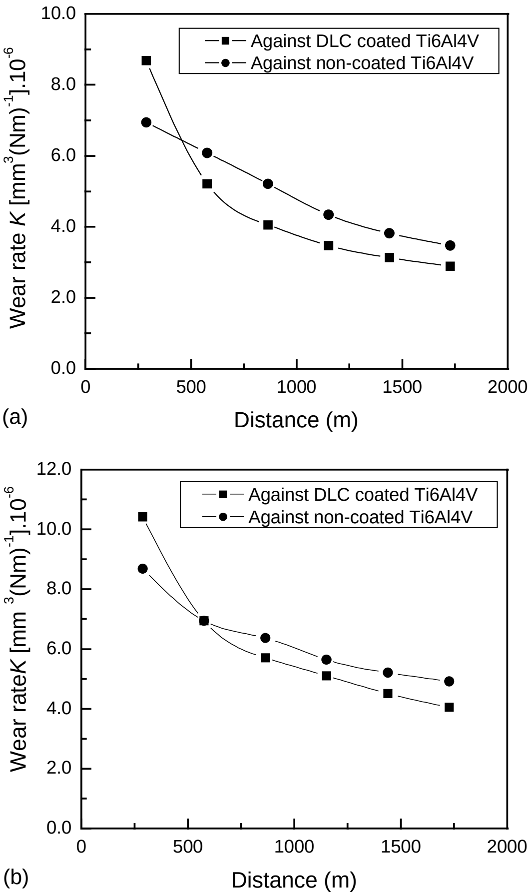


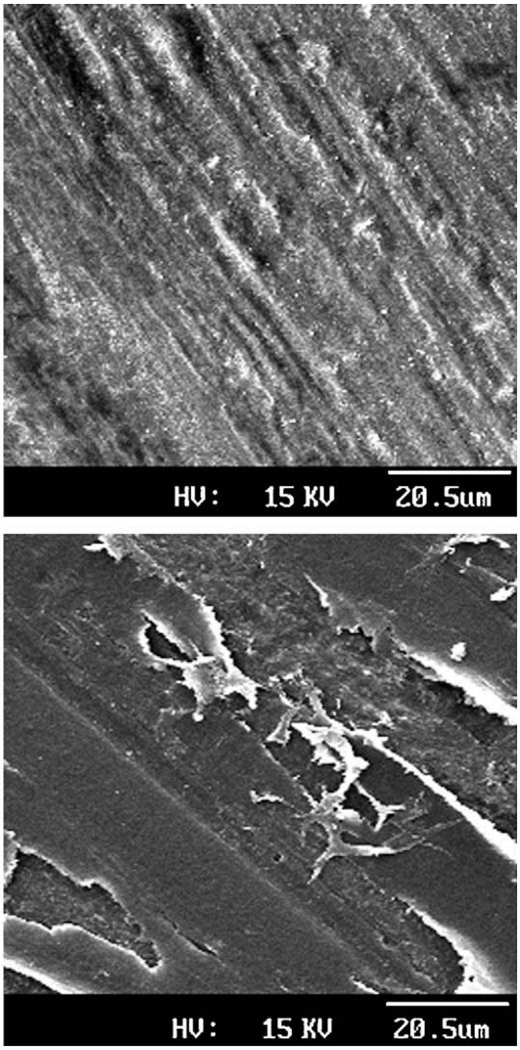
Fig. 7. Wear rates of UHMWPE sliding against DLC coated and non-coated Ti6Al4V alloy under (a) bovine serum and (b) 0.9% NaCl solution.

effectively reduced the wear of UHMWPE counterpart. Since the fine wear debris of UHMWPE in body tissue could cause adverse cell response and bone resorption [17], therefore, reduction of the wear of UHMWPE was also of vital importance.

3.5. SEM analysis of worn surfaces

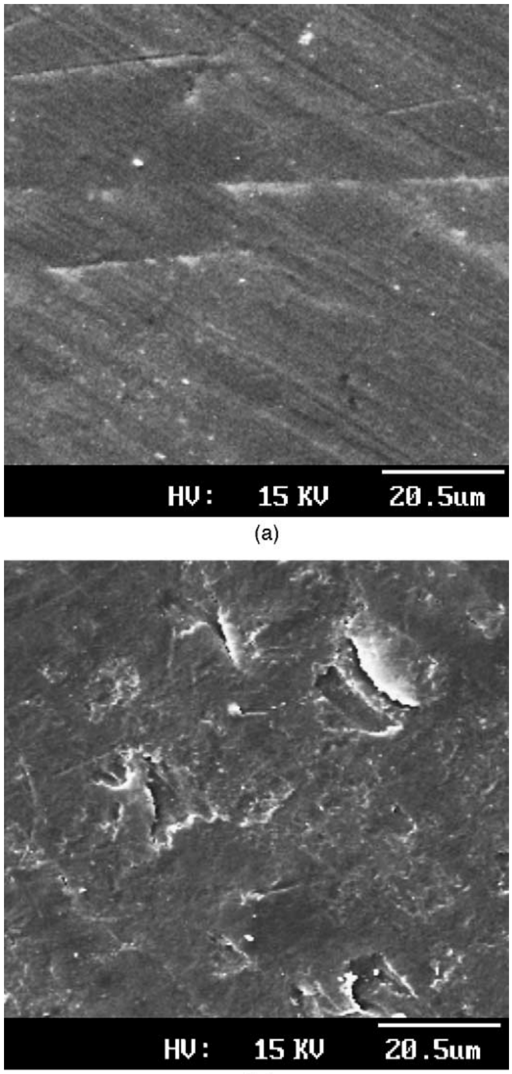
It was commonly considered that the wear of Ti6Al4V alloy was due to surface oxidation mechanism [4,18]. Fig. 8 shows the surfaces of (a) non-coated Ti6Al4V alloy and (b) UHMWPE counterpart after 2000 m sliding distance under the lubrication of bovine serum. The surface of Ti6Al4V alloy was scored by metal oxide debris; simultaneously, the surface of UHMWPE counterpart was plastically torn with deep abrasion grooves.

Fig. 9 shows the surfaces of (a) DLC gradient coating and (b) UHMWPE counterpart. The surface of DLC gradient coated Ti6Al4V alloy had only slight



(a) (b)

Fig. 8. SEM micrographs of the worn surfaces of (a) non-coated Ti6Al4V alloy and (b) UHMWPE counterpart after 2000 m sliding under lubrication of bovine serum.



(b)

Fig. 9. SEM micrographs of the worn surfaces of (a) DLC coated Ti6Al4V alloy and (b) UHMWPE counterpart after 2000 m sliding under lubrication of bovine serum.

scratches rather than serious scoring. This observation indicated that the use of DLC gradient coatings significantly changed the chemical and mechanical properties of Ti6Al4V alloy, the severe oxidative wear of the Ti6Al4V was eliminated thus the wear resistance performance was significantly improved.

On the other hand, coupled with DLC gradient coating, the worn surface of UHMWPE counterpart was progressively burnished with very slight strikes, in contrast, there were no plastic tearing and deep grooves. This behavior was consistent to the low wear rate of UHMWPE as shown in Fig. 7.

4. Conclusions

The DLC gradient coatings had been deposited on Ti6Al4V alloy by plasma source ion implant-ion beam enhanced deposition method and the tribological performance had been evaluated. The low friction coefficient and considerable improvement of wear resistance can be attributed to the structural characteristics of the DLC coatings. The SEM observations revealed that the severe oxidative wear of the Ti6Al4V was eliminated when DLC coatings were applied to surfaces of Ti6Al4V alloy, and the wear of UHMWPE counterpart could also be reduced.

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