The Effect of Bias on Properties of DLC Coatings for Artificial Joints

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DOI: 10.5185/amlett.2020.101568

Diamond-like carbon (DLC) coatings, due to excellent tribological and biological properties, were used wildly to improve the wear resistance and corrosion resistance of the metal-based artificial joints. In this work, DLC coatings were deposited by a vacuum arc using the anode-cathode diameter ratio of d_a/d_c=3/1 with the negative bias applied to the P2000 steel substrate. The relation between the substrate bias and properties of DLC coatings was investigated. The study showed that DLC coating had lower ratio of sp^2/sp^3 and lower friction coefficient at higher bias of – 750 V. With increasing bias, the wear particle size of DCL coatings tended to move towards the distribution of smaller particles. Comparing with the uncoated P2000, P2000 coated with DLC deposited at – 750 V had better biocompatibility. It was revealed that DLC coating deposited by a vacuum arc technique in conjunction with high substrate DC biasing can improve the tribological property and biocompatibility of P2000.

Introduction

For conventional metal-based artificial joints, e.g. Metal-on-Polyethylene parings (MOP) and Metal-on-Metal parings (MOM), the wear particles produced during the motion of joint have been as the main factor limiting the lifetime of the implants [**1,2**]. Additionally, the increased blood levels of metal ion releasing from the metal joint may negatively influence the biocompatibility of the surface and cause a delayed-type metal hypersensitivity [**3,4**].

Diamond-like carbon (DLC), known as amorphous carbon, is a class of materials with excellent mechanical, tribological and biological properties, which makes them particularly attractive for biomedical applications. DLC coatings, deposited on the metal substrate, can be used as a barrier to prevent leaching of metallic ions into the body and improve the wear resistance and corrosion resistance of artificial joints [**5-9**]. Therefore, DLC surface modification for traditional artificial joints has attracted more researchers' interesting in the field of biomedical materials. There were three different hip joints coated DLC reported in Ref. [**4,9**]: DLC-coated femoral heads against Polyethylene implanted cups (DLC-P) [**6-9**], DLC-coated femoral heads against metal cups (DLC-M) [**5,10-11**] and DLC-coated femoral heads against metal DLC-coated cups (DLC-DLC). Actually, the material of femoral head was metal or ceramic [**7**].

For metal-based artificial joints, the Co-Cr-Mo and Ti-6Al-4V alloys were used as substrate materials of DLC coatings. It was found that Co-Cr-Mo is the superior of the two. However, it was too hard for the deposition of thick DLC coatings [**12**]. Sheeja *et al.,* [**13**] found that the tribological characteristics of UHMWPE/Co-Cr-Mo sliding pair were not improved significantly by coating only one of the sliding surfaces with DLC. In addition, the wear particles from the counter-face, i.e. Co-Cr-Mo, were observed. The research focus on DLC-coated joint pairs was mainly aimed at its wear resistance and corrosion resistance of only one of the sliding surfaces with DLC. In contrast, less research has been done on DLC-DLC friction pairs. According to Alakoski's report [**7**], the superior candidate material for articulating implants was adherent DLC on both sliding surfaces. Coating both the sliding surfaces with DLC coating reduced the wear rates of the sliding surface [**13,14**].

Moreover, most biocompatibility studies concerning DLC were conducted with hydrogenated DLC (a-C:H) coatings and in vitro [**15-18**]. The a-C:H films tended to promote the growth and adhesion of cells without inducing any toxicological effect in a review report by Roy [**18**]. In vivo studies on DLC coated implants are scarce, but those conducted thus far have shown no adverse reactions to DLC coatings [**19-20**]. When DLC coatings with a low ratio of sp^2/sp^3 were beneficial for cell adhesion and growth because of better protein adsorption without electrostatic repulsion [**20**].

Our earlier research work revealed that DLC coatings deposited with an anode–cathode diameter ratio of d_a/d_c = 1/1 exhibited good tribological properties with a low friction coefficient of 0.035 and low wear rate (1.04×10^{-5} g/h) [**14, 21**]. In this work, Cr-Mn-N steel (P2000) was used as the metal-based artificial joint. The aim is firstly to study the influence of DC bias on the DLC coated P2000/P2000 artificial joint, and secondly to improve tribological properties and bio-compatibility of P2000 by depositing DLC coatings.

Experimental

Material details

In this work, discs of 31 mm diameter and 4 mm thickness were used as substrates made of P2000. P2000 was a Cr-Mn-N-Steel as shown in **Table 1** developed by the company Energietechnik-Essen and passed the bio-compatibility test. Chemical composition of P2000: C<0.15%, Si<1.00%, Mn 12.00%-16.00%, N 0.75%-1.00%, Cr 16.00%-20.00%, Mo 2.50%-4.20%, P<0.05%, Al <0.10%, Ni <0.30%, V <0.20%, Nb <0.25%.

Table 1. Physical properties a of P2000.

Determination	Unit	Value
Tensile strength	MPa	>900
Impact toughness	J/cm^2	>350
Vickers hardness	Kgf/mm^2	380HV30

For optimum tribological performance, the surfaces of discs were polished (Ra<0.05μm). After polishing, the substrates were pre-cleaned in an ultrasonic bath with an Isopropanol solution for 10 min, and then blown dry with N_2.

Material synthesis

In order to improve the adhesion between DLC coatings and substrates, titanium as interface layer was deposited on the substrates by cathodic arc evaporation [**14**]. The DLC coatings were deposited on P2000 substrates with Ti as interface layer of 480 nm by vacuum arc method with an anode-cathode diameter ratio of d_a/d_c=3/1 at a DC bias of −250 V, −500 V and −750 V. The thickness of DLC coating was in the range of 360 ~ 635 nm depending on the substrate bias. Deposition process parameters and schematic diagram of deposition system were shown in Ref. [**22**].

Characterizations

The internal structure of the coating was investigated using a micro-Raman system of JOBIN YVON with the visible excitation of the 514.5 nm Ar+ laser line. The friction coefficient was measured by a Wazau TRM 1000 tribometer (Berlin, Germany) using the disc-on-disc test. Two discs were coated with DLC coatings. The test was carried out in deionized water with an applied load of 120 N and with a sliding speed of 0.01 m/s. The wear particles were collected in suspension in the deionized water during tribological tests, then measured using a laser scattering particle size analyzer Horiba LA-950 with 17 channels per decade. The biological behaviour was evaluated by fluorescent staining. Esophageal tumor cells (Eca 109) were directly seeded on the surfaces of DLC coatings at a density of 4.0 × 10^3 cells / mL and cultured in standard condition for 1 day [**23-24**]. Fluorescent images of cell morphology were evaluated by fluorescence microscopy.

Results and discussion

Fig. 1 shows the Raman spectra of samples deposited at various DC bias voltage. It was found that there was a broad Raman band in the range between 1000 and 1800 cm^{-1}, which indicated coatings deposited at different DC bias voltage were typical amorphous carbon. They were non-hydrogenated DLC (a-C) coatings because of no hydrogen used during depositing. Usually, it can be often fitted very well by two Gaussian curves on a linear background using D peak (~1350 cm^{-1}) and G band (~1580 cm^{-1}) [**25**]. However, for DLC coatings deposited by vacuum arc there were no match using two Gaussian curves at the lower frequency (<1200 cm^{-1}) and a weak peak at ~ 1400 cm^{-1} seen in **Fig. 1**.

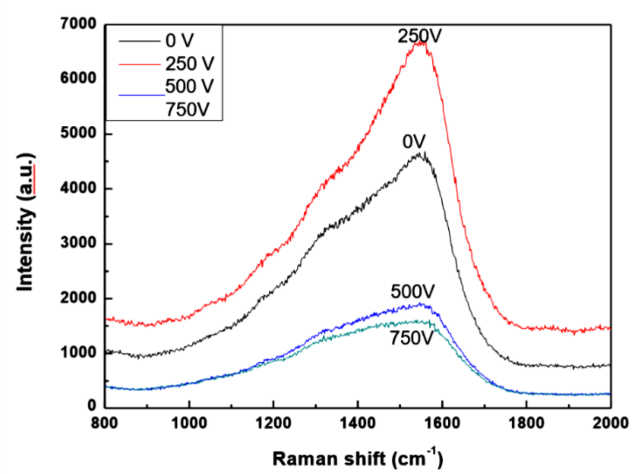

Fig. 1. Raman spectrum of DLC coatings deposited at various DC bias voltage.

Raman spectra were deconvoluted into four Gaussian peaks (~1100cm^{-1}, ~1350cm^{-1}, ~1400cm^{-1} and ~1580cm^{-1}). More details about these four peaks were shown in Ref. [**26**]. After a Gaussian fit, the corresponding information for example D and G positions and the I_D/I_G ratio was shown in **Table 2**. In this paper, I_D/I_G was the ratio of peak heights obtained by fitting. The I_D/I_G ratio was used to estimate indirectly sp^2/sp^3 ratio in DLC coatings [**25,27**].

Table 2. D positions, G positions and I_D/I_G ratios with DC bias.

Bias/V	0	−250	−500	−750
D peak	1354	1353	1369	1348
G peak	1551	1560	1557	1550
I_D/I_G	0.53	0.55	0.73	0.49

It was observed from **Table 2** that, the G position moved to lower wavenumber and the relative intensity ratio of D and G peaks reached to the minimum with increasing the bias, indicated a increase of sp^3 content in DLC coating deposited at −750 V. The result showed that the DLC coating deposited at – 750 V had the lowest sp^2/sp^3 ratio corresponding to the highest sp^3 content [**20**].

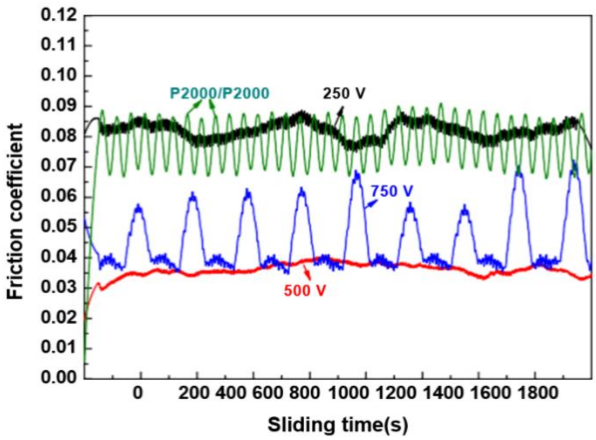

Fig. 2. Friction coefficients of DLC coatings deposited at various DC bias voltage as functions of sliding times.

The wear resistance of the coating was determined using a disc-on-disc method, simulating a metal/metal joint with both sides coated with DLC. The friction coefficient of DLC coatings deposited at various substrate bias voltage were given in **Fig. 2**. The coefficient of friction was varied between 0.03 and 0.08. P2000/P2000 joint had the higher friction coefficient of 0.08. When the metal/metal joint with both sides deposited with DLC coating by vacuum arc presented a lower friction coefficient. With increasing the bias to -500 V, the friction coefficient was decreased to 0.035. It was indicated that the tribological properties of P2000 was improved when both sides coated with DLC coatings. DLC coatings with outstanding tribological properties showed the lowest friction coefficient among all tested coatings.

The particles were generated by a disc-on-disc test and then measured using a particle size analyzer.

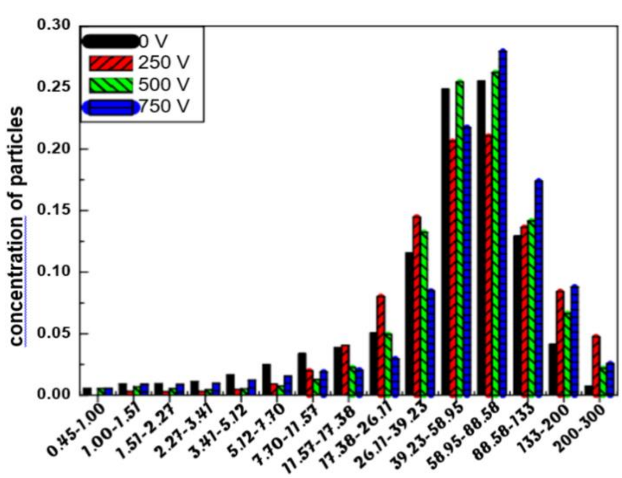

Fig. 3. Particles size distribution: comparison of substrate biases of 0 V to -750V.

Fig. 3 shows the concentration of particles in a certain particle size interval which can be calculated by the volume cumulative distribution $Q_3(x)$. $Q_3(x_i)$, the range from 0 to 1, represents the concentration of particles equal to or smaller than a given particle size x_i. It was found that all particles were distributed in the range of 0.45 ~ 300 µm, and the maximum concentration of particles was distributed in the larger range of 39.23 ~ 58.95 µm and 58.95~88.58 µm. Few amounts of larger particles maybe came from the peeling-off films, another from the wear debris or impurity and contamination which was difficult to avoid. As discussed above, the DLC coating deposited at –750 V with the minimum ratio of I_D/I_G has the highest sp^3 content, however almost 90% of all particles generated are larger than 11.57 µm.

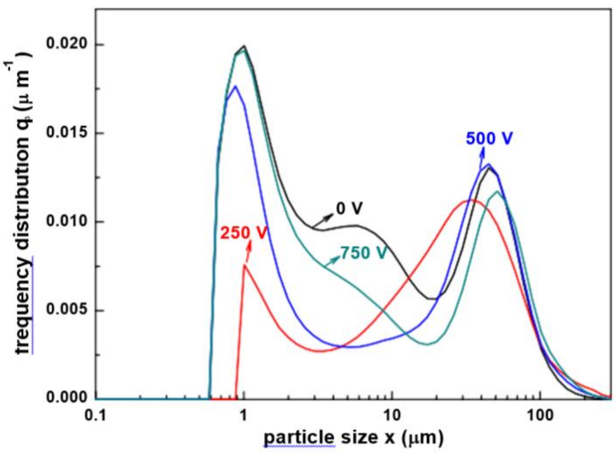

Fig. 4. Frequency distribution $q_3(x)$ of DLC coatings at substrate biases of 0 V to -750V.

Fig. 4 is the curve of the frequency distribution $q_3(x)$ as a function of particle size. The frequency distribution $q_3(x)$ which represented the amounts of particles of a given particle size x, relative to the entire particle size distribution, can be obtained from the following equation:

$$q_3(x_i) = \frac{dQ_3(x)}{dx}$$

The main peaks found in each of the curves were assigned to the modal values x_{mod}, which indicated these particle sizes ~ 1, ~ 5, and ~ 50 µm occurred most often when the DLC coatings were deposited at the bias of 0, –250, –500 and –750 V. With increasing the bias, the peak heights at~ 5 µm and ~ 50 µm were decreased, however, the peak height at ~ 1 µm was increased. It was concluded that the wear particle size could be adjusted by applying the substrate bias during the deposition of DLC coatings.

To evaluate the bio-compatibility of DLC coating, Esophageal tumor cells (Eca 109) were cultured for 24 h and stained by Rhodamin and 2-(4-amidinophenyl)-6-indolecarbamidine dihydrochloride (DAPI) for staining the cytoplasmic layer of cells and the nuclei, respectively. Fluorescence micrographs of Eca 109 morphology were shown in **Fig. 5**. Eca 109 on surfaces of P2000 and DLC coating presented a polygonal morphology, indicating good cytoplasm development. P2000 with good bio-compatibility can be used as implant materials. The morphology of Eca 109 on DLC coating deposited at -750 V was more uniform and complete compared with P2000 at

24h. What's more, higher cell numbers and better spreading were observed shown in **Fig. 5(c)** and **Fig. 5(d)** with comparing with **Fig. 5 (a)** and **Fig. 5 (b)** by cell counts using Image J. It was found that no nuclear debris appeared, indicating no early apoptosis and necrosis, which confirmed that the bio-compatibility of P2000 could be improved by depositing DLC coating at – 750V.

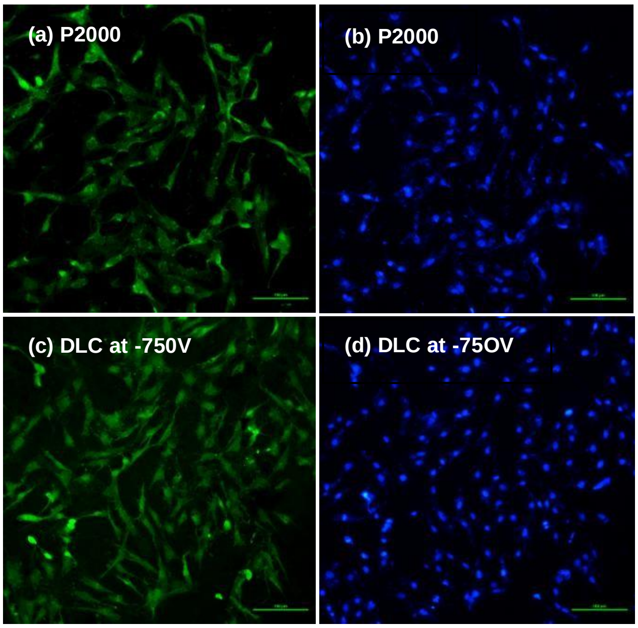

Fig. 5. Fluorescence microscopic images of Eca 109 stained by rhodamine (green) and DAPI (blue) on substrates.

Conclusion

DLC coatings, amorphous carbon (a-C), were deposited on P2000 substrates by vacuum arc technique using an anode-cathode diameter ration of $d_a/d_c = 3/1$ with the application of a DC bias to the substrate from 0 V to –750V. The effects of bias voltage on the tribological property, the wear particle size distribution and the bio- compatibility were investigated. The DLC coating deposited at –750V exhibited higher sp^3 content and lower friction coefficient of 0.05. The lowest friction coefficient of 0.035 was attained at a bias of –500 V. All particle size distributions were in a range of 0.45 ~ 300µm and most of the particles distributed around 39.23 ~ 88.58µm. With increasing the bias, the frequency distribution curve showed that the peak height of the small particle size distribution increased, and the peak height of the large particle size decreased gradually. Comparing with P2000, DLC coating deposited on P2000 at a bias of –750V exhibited the better bio-compatibility.

Acknowledgements

This work was financially supported by Project of Henan Science and Technology Research Program in 2019 (192102210036).

Conflicts of interest
There are no conflicts to declare.

Supporting information

Supporting informations are available online at journal website.

Keywords

Diamond-like carbon coatings, bias, wear particle size distribution, biocompatibility.

Received: 29 March 2020
Revised: 21 April 2020
Accepted: 27 April 2020

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Authors biography

Dr. Ying Ren has been actively involved in the research of the preparation and application of diamond-like carbon coatings, especially in the biomedical field since 2009. She has been committed to construct diamond-like coated artificial joint heterostructure to solve the problem of short life expectancy of traditional artificial joints under the combined action of high-load friction and corrosion in the complex physiological and mechanical environment of the human body.

Dr. Renjie Wang received his PhD degree in science from Université Toulouse III – Paul Sabatier in 2017. He is currently a lecturer in the faculty of Material Science and Engineering at Henan University of Technology (China). His current research interests focus on preparation of PI aerogel materials and the study of the chromosome conformation in living budding yeast cells.

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