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# Enhancement of adhesion by a transition layer: Deposition of a-C film on ultrahigh molecular weight polyethylene (UHMWPE) by magnetron sputtering

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ABSTRACT

An amorphous carbon (a-C) film is deposited on the plasma-treated UHMWPE substrate using a closed field unbalanced magnetron sputtering to improve its tribological properties. During the plasma treatment period, a transition layer is prepared by high energy ion bombardment at a bias voltage of −500 V to enhance the adhesion between the a-C film and the substrate. The mechanical and tribological properties of the a-C film were evaluated by nano-indentation and ball-on-disk tribometer. After deposition of a-C film with a thickness 900 nm, the nano-hardness of UHMWPE significantly increases from 47 MPa to 720 MPa and the wear rate decreases from $9.82 \times 10^{-15}$ $m^3 N^{-1} m^{-1}$ to $4.78 \times 10^{-15}$ $m^3 N^{-1} m^{-1}$ in bovine calf serum solution. The formation of the transition layer is believed to be the reason why the vertical adhesion between the a-C film and the UHMWPE substrate is enhanced.
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## 1. Introduction

A normal artificial joint is a friction pair containing an acetabular cup and a metallic/ceramic femoral head that lies against each other. UHMWPE is considered as a promising material for acetabular replacement due to its excellent mechanical properties, low friction coefficient, good biocompatibility and chemical stability [1–8]. Nonetheless, the worn debris of UHMWPE in the artificial joint can induce adverse biological reactions in the body, such as tissue reactions and bone resorptions. Additionally, the loosening problem caused by worn debris may result in the failure of the artificial joint. Compared to the metallic/ceramic femoral head, the mechanical and wear performance of UHMWPE acetabular cup is vulnerable. From this aspect, the key to prolong the life cycle of the artificial joint is to achieve high wear resistance for the relatively soft acetabular cup.

It is well known that a-C films display superior mechanical and tribological properties, chemical inertness, biocompatibility as well as hemocompatibility [9–15], which can pioneer the potential application for the surface modification of UHMWPE. Unfortunately, the adhesion between the substrate and a-C films is restricted by some drawbacks of UHMWPE, such as molecule's inertness, low surface energy and non-polar nature. Frequently-used methods for surface treatment of UHMWPE are plasma treatment, corona discharge, gamma radiation, ion implantation, etc. [16]. Among them, the plasma treatment is considered an efficient strategy because it can cause polymer chain scission and enlarge the crosslink between diverse polymer chains [17,18]. Meanwhile, plasma treatment is attractive because of its environmental compatibility and high treatment efficiency without changing the textural characteristics of the bulk material [8,19–21]. The plasma-treated UHMWPE can offer polar functional groups for the formation of covalent bonds between the UHMWPE matrix and the carbon particles coming from the graphite target [22,23]. Simultaneously, magnetron sputtering is defined as one of the cheapest industrial equipment involving plasma treatment [14,24]. Besides, its continuity of plasma treatment and subsequent coating process can prevent the formation of oxides. By the bombardment of high energy ions, the interactions between the polar functional groups and the carbon particles may not only take place on the surface but also in the sublayer of the substrate. This may lead to the formation of a thin transition layer which can realize a graded composition variation from the UHMWPE to the a-C film.

Due to the high level of residual stress and the diversity in physical and chemical character, the adhesion of a-C film to some substrates decreases with the film thickness increasing [25,26]. The formation of transition layer is an effective strategy to release the residual stress and to improve the adhesion of a-C films with

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**Table 1**
Depositing parameters for the transition layer and a-C films.

| Process | Target cleaning | Substrate cleaning | Transition layer | a-C film |
|---|---|---|---|---|
| Time (min) | 5 | 5 | 20 | 100 |
| Substrate bias (V) | −500 | −500 | −500 | −300 |
| C target current (A) | 0.2 | 0 | 0.25/0 | 2.5 |
| Degree of vacuum (Pa) | 0.2 | 0.2 | 0.2 | 0.3 |

the substrates [25,27–33]. In this present work, an a-C film with thickness of 900 nm including a transition layer was deposited on UHMWPE substrate. The transition layer was prepared via a small graphite target current and a bias voltage of −500 V during the high energy argon plasma treatment process. Owing to the formation of the transition layer, the a-C film on UHMWPE substrate exhibited good tribological performance and preferable adhesion with the substrate.

## 2. Experimental details

### 2.1. Deposition of films

The a-C films on UHMWPE substrates were deposited by a closed field unbalance magnetron sputtering system (TAJS-700, TENGAO) whose details were documented elsewhere [34]. All the substrates were firstly ultrasonically cleaned in ethanol for 20 min, and blow-dried by nitrogen. The self-rotation speed of the substrate holder was kept at 15 rpm, and the distance between the substrate holder and the graphite target was set at 10 cm. The vacuum chamber pressure was evacuated to $4 \times 10^{-3}$ Pa before a high purity argon gas was introduced to keep the working pressure at 0.2 Pa. A 5-min ion etching at a bias voltage of −500 V was applied to remove the oxides and adsorptions of the substrate. Subsequently, 20-min plasma treatment under the bias voltage of −500 V and with the target current density of 0.25 mA cm$^{-2}$ was carried out to form the transition layer.

UHMWPE is so sensitive to temperature that only small target current can be applied during the coating process of 100 min. Therefore, the graphite target current density of coating was set at 2.5 mA cm$^{-2}$ and the argon gas flow was 45 sccm. The pressure value was 0.3 Pa under the steady gas flow of 45 sccm and the temperature during the coating process was kept between 27 °C and 34 °C. An a-C film without the transition layer was deposited on UHMWPE for the comparison of adhesion. The detailed depositing parameters of the two a-C films are listed in Table 1. As shown in Table 1, the only difference between the depositing parameters of the two a-C films was the current density of graphite target during the plasma treatment process, namely 0.25 mA cm$^{-2}$ and 0 mA cm$^{-2}$.

### 2.2. Characterization of films

The surface morphology of the film was examined by scanning electron microscope (SEM, Hitachi S-4800 equipped with GENENIS 4000 EDAX detector). AFM (Nanosurf Naio, Switzerland) was applied to assess the surface roughness before and after plasma treatment. The thickness of a-C film was measured by a stylus profilometer with a substrate that is half-covered during the coating process. The contact angle (CA) with deionized water was conducted by a contact angel meter (SL200B, Solon Tech., Shanghai) based on a sessile drop measuring method with a water droplet volume of 4 μL. The C—C bonding structure analysis was performed by Raman spectroscopy (LABRAMHR-800) with the wave number shift from 4000 to 100 cm$^{-1}$ in the visible excitation line of 514.5 nm, and X-ray photoelectron spectroscopy (XPS, ESCALab 220i-XL electron spectrometer) operating with a monochromated Al Kα X-ray radiation source in a base pressure of $10^{-7}$ Pa. The hardness ($H$) of the film was evaluated using a nanoindentor (Agilent technologies, G-200) with a Berkovich diamond indenter. The maximum indentation depth was kept around 10% of the film thickness to minimize substrate effect and 10 s was kept at the peak load. Six indentations in each sample configured on different areas were performed to ensure reliable statistics.

The tribological properties of the a-C films were conducted on a WTM-1E ball-on-disk tribometer with a $Si_3N_4$ ceramic ball (4 mm in diameter, hardness HV = 1550) as the counter body. The tests were carried out at a normal load of 1 N with a sliding velocity of 0.1 m s$^{-1}$. The friction coefficient was monitored continuously during the tests by a linear variable displacement transducer and recorded on a data acquisition computer attached to the tribometer. The profile across the wear track was taken using a stylus profilometer and the wear rates of the films were calculated by integrating the profile of the wear track. Scratch and Rockwell tests were performed on the a-C films to evaluate the transverse and vertical adhesion, respectively. For the scratch tests, a diamond pin with a radius of 0.2 mm was drawn across the surface of the film at a constant linear velocity of 5 mm min$^{-1}$ and a linearly increasing load from 0 to 1 N. Rockwell tests were performed using a Rockwell indenter of 0.2 mm in diameter at a constant load of 10 N to assess the vertical adhesion of the film to the substrate. Both the scratch traces and Rockwell craters were observed by an optical microscope (Nikon Eclipse ME600D).

## 3. Results and discussion

Fig. 1a shows the surface morphology of the a-C film on UHMWPE. There are many dense clusters on the surface of the a-C film and only some small gaps exist among the clusters. The formation of this structure is related to the strong bombardment effect of the highly energetic particles. To confirm the thickness of a-C film on the UHMWPE substrate, during the deposition process, the UHMWPE substrate is half covered with a silicon slice to create a step which can be seen from Fig. 1b. By measuring the height of the step with a stylus profilometer, the thickness of the film is approximately 900 nm. It is reported polar functional groups and dangling bonds produced by plasma bombardment make it easier to deposit on the UHMWPE substrate than other substrates such as silicon slice [21]. As shown in Fig. 2, in order to analyze the bonding structure of C—C and verify the formation of the transition layer, a XPS depth etching test was carried out. According to the C 1s scan results of XPS depth etching tests conducted with a sample after plasma treatment and ion implantation, the binding energies of the peak position after etching time of 100 s, 200 s, 300 s, 500 s and 900 s were 283.88 eV, 283.78 eV, 283.78 eV, 284.08 eV and 284.08 eV, respectively. It can be seen that after etching time of 500 s, the binding energy of the peak position stopped changing even with another 400 s of etching. The results confirmed the formation of the covalent bonds between the substrate and the particles from the graphite target as well as the formation of the transition layer. Besides, Fischer et al. [35] discussed three different possibilities of interaction between carbon from the plasma source and the soft plastic material which were, (a) direct deposition of carbon material, (b) mechanism for a successive interlayer

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