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Effect of substrate bias on biocompatibility of amorphous carbon coatings deposited on Ti6Al4V by PECVD

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ABSTRACT

Long service life of implants is of high importance to patients. This study deposited amorphous carbon (a-C) coatings on biomedical grade Ti6Al4V substrate using plasma-enhanced chemical vapor deposition (PECVD). The effect of substrate bias power on microstructure and corrosion of the coatings is investigated and compared with the bare Ti6Al4V substrate. The experimental results show that the substrate bias power of 30 W leads to amorphous carbon in microstructure. With increased bias nanocrystalline graphite appears. All coated samples have significant improvements in corrosion resistivity as compared to Ti6Al4V alone. The sample deposited at bias power of 30 W with a thickness of 150 nm demonstrated the lowest corrosion current of 6.47 nA/cm^2 and the lowest corrosion rate of 8.05 nm/year, which can postpone the corrosion of the Ti6Al4V substrate for at least 18 years. From the in-vitro cell culture studies, the best sample also registered the higher cell viability and biocompatibility as compared to bare Ti6Al4V, thus could be helpful in promoting healing.

1. Introduction

Currently, the most widely used materials for orthopedic implants is titanium alloy or Ti6Al4V due to its good biocompatibility [1,2]. Once implanted, the surface of the implants is exposed to cells and body fluid of the surrounding organism [3], thus is subject to body fluid corrosion that would eventually render premature failure of the implant. Coating protection of the alloy is a way out. Amorphous carbon (a-C) has emerged as a promising coating material owing to its high Young's modulus, high hydrophobicity, high dielectric strength, wear resistance, low friction, biocompatibility and chemical inertness [4,5], suitable for coating of stents, heart valves, hip joint and prostheses [6]. The a-C can be deposited through sputtering, ion beam systems, laser ablation and chemical vapor deposition system [7,8]. In particular, plasma enhanced chemical vapor deposition (PECVD) system achieves the deposition at significantly lower temperatures thus renders the implant materials much less thermal stress thus is especially useful for samples of irregular shape [9]. In structure, a-C consists of varying amount of sp^2 (graphite-like structure) and sp^3 carbon bonds (diamond-like structure), depending on the process conditions [10–14]. At high ratio of sp^2/sp^3, it is said to be graphite-like carbon (GLC), and when the sp^2 is low or sp^3 is high, it is referred to as diamond-like carbon (DLC). As the microstructure of a material dictates how the materials respond to the attacks from the environment, the mechanical [10,15], chemical and biological properties of the coating therefore depend on the sp^2/sp^3 ratio.

Although various structures of the a-C coatings have been extensively studied, there is little literature focusing on the comparison of biocompatibility and anticorrosion (which are the most important properties for biomedical implants) between these structures. In this study, we prepared a-C coatings on medical grade Ti6Al4V substrates using PECVD at a low temperature. The substrate bias power is varied to study the effect on the coating structure, morphology and subsequent chemical and biological response. The corrosion resistivity and

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biocompatibility of the a-C coatings are discussed and compared with that of the Ti6Al4V alone.

2. Experimental details

The Ti6Al4V and silicon wafer substrates were ultrasonic-cleaned with deionized water, acetone and ethanol for 10 min in each solution. The substrates were then blow dried in nitrogen and placed in an oven at temperature of 80 °C for 30 min. The a-C coatings were deposited in 27.13 MHz PECVD (CC-200, ULVAC, Japan) system at substrate temperature of 150 °C and plasma power of 50 W with flowing methane (CH_4) gas at 80 sccm to remain a pressure of 50 Pa. The radio-frequency 13.56 MHz substrate bias power was varied from 10 to 60 W at a step size of 10 W. As the electrode had an area of 20 × 20 cm^2, the bias power density varied from 0.025 to 0.15 W/cm^2. The deposition parameters are summarized in Table 1. The thickness of the coatings was measured using an α-step profiler (Alpha-step IQ, KLA-Tencor, USA). The morphologies of the samples were observed using scanning electron microscope (SEM, JSM-7000F, JEOL Ltd., Japan). The microstructure of the a-C coatings was studied by Raman spectroscopy (Nanofinder 30, Tokyo Instruments Inc., Japan). The root mean square (rms) of the surface roughness was determined by an atomic force microscopy (AFM, Bruker Dimension Icon, Bruker, USA). The biocompatibility of the a-C coated samples was assessed by in-vitro cell culture method [16–18], wherein the samples were washed using phosphate buffered saline (PBS, Sigma-Aldrich, USA) solution and placed into a 24-well plate. The main elements of the PBS solution included 8.01 g/L NaCl, 0.2 g/L KCl, 1.78 g/L $KH_2PO_4{\cdot}H_2O$ and 0.27 g/L KH_2PO_4. In-vitro cell tests were conducted on the samples by using osteoblast-like MG-63 cells in Dulbecco's Modified Eagle Medium with 10% fetal bovine serum (Gibco, USA) and 100 U/mL of penicillin-–streptomycin–amphotericin (Invitrogen, USA). The cells with a density of 1×10^4 cell/mL were seeded directly onto a-C-coated and uncoated Ti6Al4V specimens. The cell culture was carried out in an incubator at a temperature of 37 °C ± 0.5 °C in a humidified atmosphere of 5% CO_2. The cells incubated in the culture medium with no specimen were considered as the controls. After 1, 3, 5 and 7 days of cell culturing, 20 μL of Alamarblue solution (Invitrogen, USA) was added to each well and the plate was incubated for 4 h. The viable cells would be stained with Alamarblue, and the optical density (OD) of each well was measured by using an enzymelinked immunoadsorbent assay reader (U2000, Hitachi, Japan) at a wavelength of 570 nm. The data were then compared with the results of the controls, which were considered as 100% cell viability. The corrosion behavior of the coatings was evaluated using potentiodynamic polarization test in PBS solution at 37 °C. The Tafel curves were recorded in a range of −1 to 0.25 V with a scanning rate of 1 V/s.

3. Results and discussion

Fig. 1 shows the deposition rate of the a-C coatings as a function of substrate bias power. The deposition rate increases from 0.04 to 0.24 nm/s when the substrate bias power increases from 10 to 30 W. The increased substrate bias power activates more gas dissociation in the substrate vicinity and substrate adsorption sites, leading to an enhancement of the deposition rate. However, the a-C coatings deposited at the substrate bias powers of less than 30 W are no longer discussed in the following because of their low deposition rates. The deposition rate slightly decreases from 0.24 to 0.22 nm/s as the substrate bias power increases from 30 to 60 W, and this is attributed to the ion bombardment effect that facilitates the etching of the deposited coatings [19].

Table 1
Deposition parameters of a-C coatings on Ti6Al4V substrates.

Parameter	Value
Power (W)	50
Substrate bias power (W)	30, 40, 50, 60
Pressure (Pa)	50
Substrate temperature (°C)	150
CH_4 flow rate (sccm)	80
Thickness (nm)	150

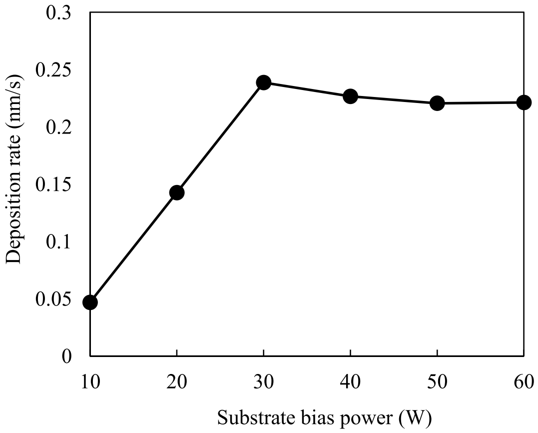

Fig. 1. Deposition rate of the a-C coatings as a function of substrate bias power.

Fig. 2(a) shows Raman spectra of the a-C coatings deposited at different substrate bias powers. There are two broad bands in the region of 1100–1700 cm^{-1}. The deconvoluted spectra shows two peaks centered at approximately 1580 cm^{-1} (G band) and 1350 cm^{-1} (D band). The G band is a result of in-plane vibrations of sp^2 bonded carbon atoms whereas the D band is due to out of plane vibrations attributed to the presence of structural defects. [20,21]. Fig. 2(b) shows the peak area ratio of the D band to G band (I_D/I_G) as a function of the substrate bias power. The I_D/I_G ratio increases from 0.77 to 1.45 as the substrate bias power increases from 30 to 60 W. According to Ferrari et al. [22] the Raman spectra of a-C coatings can be divided into three groups based on the G band position and I_D/I_G ratio. These three groups are (i) perfect graphite to nano-crystalline graphite (nc-graphite) with G band positions of 1581–1600 cm^{-1} and I_D/I_G of 0–2, (ii) nc-graphite to a-C with G band positions of 1510–1600 cm^{-1} and I_D/I_G of 0.3–2, and (iii) a-C to tetrahedral a-C with G band positions of 1510–1570 cm^{-1} and I_D/I_G of 0–0.3. In this work the Raman spectra show G band positions of 1587–1599 cm^{-1} and I_D/I_G ratios of 0.77–1.45. All of the deposited a-C coatings are therefore in the group (i) or (ii), inferring that the coatings contain nc-graphite and a-C in the network. A higher I_D/I_G ratio of the coating as in the case of the substrate bias power of 60 W indicates the disordered of nc-graphite with lots of defect due to the presence of grain boundaries. The formation of the nc-graphite can be enhanced by ion bombardment effect, which etches away the weak C—C bonds and leaves the relatively strong bonds that could possibly form nanocrystals. Fig. 2(c) shows the peak position and full width at half maximum (FWHM) of the G band for the a-C coatings deposited at different substrate bias powers. The G band position and FWHM decrease with increasing the substrate bias power from 30 to 60 W, which indicates an increase of graphitic carbon structure and cluster size in the coatings [21–23].

Fig. 3 has the SEM images of the a-C coatings deposit on Ti6Al4V at different substrate bias power. It can be seen that the surface of medical grade Ti6Al4V substrates is still rough and rigid although the substrates have been polished. After the a-C deposition at the substrate bias power of 30 W, there seems to have clusters aggregated together and adhered well to the substrate. As the coating is thin and the cluster size is small, therefore the morphology is similar to the substrate. The surface becomes smoother when the bias power increases. In order to observe the morphology of the a-C coatings without the interference caused by the