Surface & Coatings Technology 231 (2013) 418–422

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Characterization and haemocompatibility of fluorinated DLC and Si interlayer on Ti6Al4V

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ARTICLE INFO

Available online 18 January 2012

Keywords:
Fluorinated diamond-like carbon
Titanium alloy
PECVD
Blood compatibility

ABSTRACT

Fluorinated diamond-like carbon (F-DLC) films were deposited on Ti6Al4V substrates by radio frequency plasma enhanced chemical vapor deposition (rf PECVD) technique using a mixture of methane (CH_4) and tetrafluoromethane (CF_4) gasses. A 100 nm Si interlayer was coated in advance by physical vapor deposition (PVD) to improve the adhesion between F-DLC and Ti alloy. A 200 nm TiN-coated specimen with the same Ti6Al4V substrate was also built by PVD as a benchmark. The structure and surface properties of F-DLC coatings, prepared with various fluorine flow ratios, were investigated by using X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy, liquid drop goniometry, and electrochemical corrosion tests. The blood compatibility was evaluated by measuring haemolysis ratio and platelet-covered area in vitro. The films' spectroscopic results show that the CF_x group and fluorine atomic concentration increase as CF_4 flow ratio is promoted in the mixture. The surface energy is reduced due to the increased fluorine content. The modified surfaces are characterized by higher hydrophobicity, lower thrombogenicity, and better corrosive protection than the virgin and TiN ones.

1. Introduction

Thrombosis and haemolysis are two major concerns in the blood compatibility of prosthetic heart valves, blood pump, stent, and other blood contacting cardiovascular devices. For mechanical heart valves (MHVs), pyrolytic-carbon (PyC) is widely used, but it does not have adequate thromboresistant properties, and its failure due to crack propagation originated from the material's brittleness also results in problems with durability [1,2]. Biomedical Ti alloys with modified coatings [3–6] are a promising solution. TiN, TiC, Ta, TaN, diamond-like-carbon (DLC) and the multilayers of these films are common coatings for the enhancement of blood compatibility [7]. Among these coatings, the bio- and haemo-compatibility of diamond-like-carbon (DLC) films have been widely investigated and reported [1,8–18]. Besides, the outstanding wear-resistance of various DLC films [1,16,17,19,20] makes them the most effective candidates for dynamic blood contact. Fluorinated DLC (F-DLC) film, compared with other DLC derivatives, has attracted extensive interest due to its superiorly low friction coefficient, smooth surface, good chemical inertness, low dielectric constant, and wide optical band [21–23]. Freire et al. [24] discussed the transformation of the DLC's microstructure with increasing fluorine content. Yu et al. [25] found that the F content leads to a reduction in surface energy of the samples as compared with that of diamond-like carbon (DLC) film. Sui et al. [26] demonstrated the relationship between the corrosion resistance and the F-DLC structure as well as the surface hydrophilicity of the films. Hasebe et al. [27] concluded from their human platelet incubation study that the localized fluorine in the topmost thin layer is one of the key factors in the promotion of the non-thrombogenicity of F-DLC film. Marciano et al. [10] also verified that the reduced compressive stress and increased I_D/I_G ratio, hydrogen content, and water contact angle of F-DLC enhance the DLC antibacterial activity. The aim of this work is to study the effect of a process parameter, i.e. mixtures with various CF_4/CH_4 ratios, on the surface characteristics of F-DLC films with an amorphous Si (a-Si) interlayer on Ti6Al4V substrates. The anticorrosion capability and blood compatibility were investigated and compared with the original Ti alloy and a sample with a 200 nm TiN coating as benchmarks.

2. Experimental procedure

Ti6Al4V substrates with dimensions of 20×20×6 mm were ground and polished down to 0.09 nm (Ra). The substrates were washed in distilled water, ultrasonically degreased in acetone

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doi:10.1016/j.surfcoat.2012.01.020

for 20 min, and rinsed in alcohol. A 100 nm amorphous Si (a-Si) interlayer was coated by using a pulsed DC reactive magnetron sputtering system with Si target in an Ar atmosphere. A 200 nm TiN film was also produced on the substrate as a benchmark by the same PVD system with a Ti target in a 25% N_2/Ar atmosphere. The F-DLC films were prepared by a radio frequency plasma enhanced chemical vapor deposition (rf PECVD) system following the parameters listed in Table 1. During the process, the deposition time and the temperature were kept at 15 min and room temperature (24 °C), respectively. The separation between the parallel plates of the rf reactor was 4.5 cm. The thickness of the coatings in Table 1 was determined by an α-stepper across the boundaries between the films and the bare substrates, which were shielded by tape during the deposition process. Optical emission spectrometry (OES) was used to detect the emitting species of the plasma. The chemical compositions and bonding states of the surfaces of F-DLC film samples were measured by XPS (ESCA PHI 1600) with an Al anode. A contact-mode AFM (Dimension 3100, DI VEECO) with a silicon cantilever (OTR8) was utilized to measure samples' surface centerline average roughness, Ra. The surfaces were scanned in areas of 10 μm × 10 μm at a frequency of 0.5 Hz. At least three locations were randomly measured for each sample. The wettability of each F-DLC film layer was evaluated by measuring the static contact angles of droplets of distilled water (2 μl each) on sample surfaces. All measurements are reported as the mean of 3 replicates and the corresponding standard deviation. An electrochemical system (Jeihan 5000 Electrochemical Workstation, Taiwan) was used to determine the corrosion behavior of the samples. All electrochemical tests were carried out in a 0.9 wt.% NaCl solution (normal saline) with a platinum net as counter-electrode and a saturated calomel electrode (SCE; Ag/AgCl) as the reference electrode at room temperature.

Human whole blood (WB) was collected from healthy volunteers who had not taken any medication for at least 14 days. The blood was mixed with sodium citrate (SC) and ethylene diaminete traacetic acid (EDTA), respectively. The SC blood and EDTA blood were centrifuged at 100 *g* under 37 °C for 10 min to obtain platelet-rich plasma (PRP). Both WBs were also diluted by phosphate-buffered saline (PBS) (WB: PBS = 8 ml: 10 ml) to prepare the diluent WB. Haemolysis ratio and platelet adhesion of the films were evaluated in this study, and more than 3 runs were implemented for both tests. The specimen was submerged in 2.4 ml diluted WB and incubated at 37 °C for 60 min. After the incubation, the blood was collected into a vial, which was centrifuged at 100 *g* for 5 min. The upper clean solution in the vial was measured by spectrophotometer at 542 nm. The absorbency of the solution was recorded as A_s. Distilled water and PBS were used respectively as positive and negative controls for this work, and the corresponding absorbencies were respectively recorded as A_{pc} (Distilled water: diluted WB = 10 ml:0.2 ml) and A_{nc} (PBS: diluted WB = 10 ml : 0.2 ml). The haemolysis ratio (HR) of the samples was calculated by the following formula:

$$HR = \frac{A_s - A_{nc}}{A_{pc} - A_{nc}}.$$

Table 1
rf PECVD deposition conditions and thicknesses of F-DLC films. Base pressure (=0.029 Pa), rf power (=20 W), deposition time (=15 min), and CH_4 flow rate (=5 sccm) were kept constant in this work.

Sample name	CF_4 flow rate (sccm)	CF_4:CH_4 ratio	Working pressure (Pa)	Film thickness (nm)
F-1	5	1:1	0.53	179 ± 13
F-2	10	2:1	1.6	149 ± 14
F-3	15	3:1	2.5	244 ± 28
F-4	20	4:1	3.2	273 ± 5
F-5	25	5:1	3.9	229 ± 23

The specimen was soaked in 2.4 ml PRP for 24 h at 37 °C. Adhered platelets on the plate were fixed by using 2.5% glutaraldehyde for 30 min and followed by a dehydration procedure including rinsing in PBS three times and drying in a vacuum dryer. After the procedure, the specimen was coated with gold and examined by scanning electron microscopy (SEM). The adhesion area was evaluated by the image processing method from the SEM images.

3. Results and discussion

3.1. Thicknesses and compositions of F-DLC films on Ti6Al4V substrates with an a-Si interlayer

Thicknesses of F-DLC films deposited by various CF_4 flow rates are listed in Table 1. As the coating duration was kept constant, they can also represent the variation of deposition rate. For an F-DLC deposition process, the competition of the growing and etching mechanisms will determine the final status. It is believed that, at a lower CF_4 flow rate ($CF_4/CH_4 = 1$), the growing mechanism should dominate the deposition process. On the other hand, a significant etching mechanism was observed under a CF_4 flow rate higher than 20 sccm ($CF_4/CH_4 = 4$). However, it is notified that the deposition rate for F-2 samples of 10 sccm CF_4 becomes lower than that of F-1 samples with 5 sccm CF_4. Fig. 1(a) shows the XPS F1s spectra of carbon films with

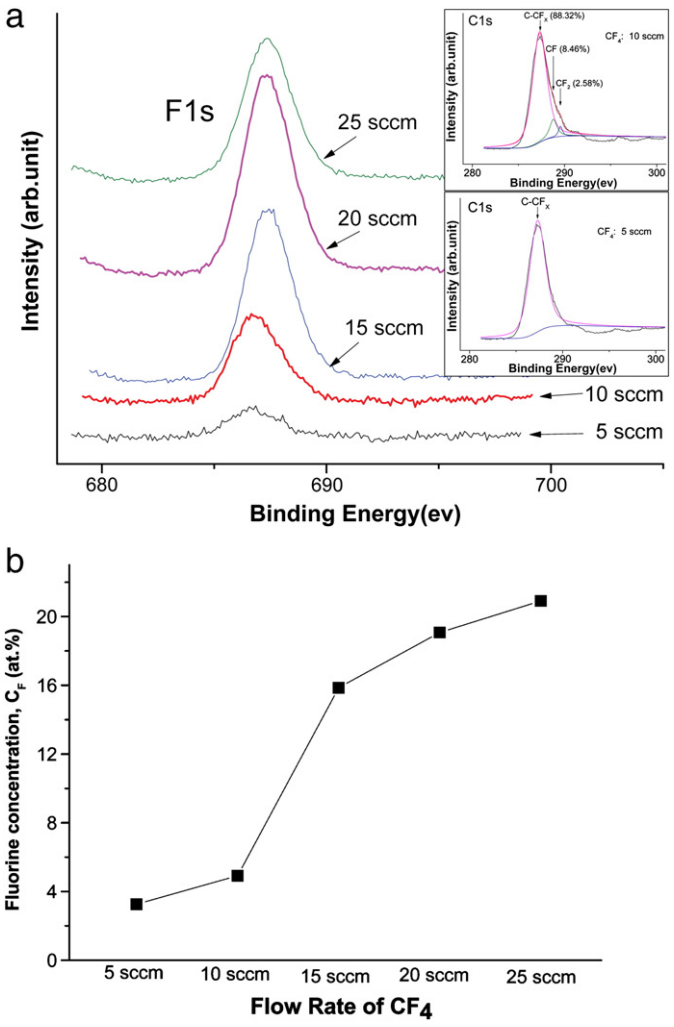

Fig. 1. (a) XPS F1s spectra of the samples with different CF_4 flow rates and, in the insets, the corresponding C1s spectra with the fitted Gaussian curves at the CF_4 flow rate of 5 sccm and 10 sccm. (b) The fluorine concentrations (C_F) in the films with different CF_4 flow rates.