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Influence of duty cycle on microstructure, tribological and corrosion behaviors of a-C/a-C:Ti multilayer films

W.Q. Bai, X.L. Wang, C.D. Gu, J.P. Tu *

State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

a-C/a-C:Ti multilayer films were deposited on medical Ti6Al4V alloy using a closed field unbalanced magnetron sputtering system with various substrate bias duty cycle. The tribological and corrosion behaviors of the multilayer films in Hank's solution were evaluated by a ball-on-disk tribometer and an electrochemical workshop. The duty cycle has a significant effect on the bonding structure, and mechanical and tribological properties of the films. The polarization resistance of the films on Ti alloy is approximately ten times more than that of Ti6Al4V which indicates that higher corrosion resistance can be achieved in Hank's solution at 37 °C. However, the polarization resistance and corrosion current do not change so much with the variation of duty cycle, implying that its influence on corrosion behavior of these a-C/a-C:Ti multilayer films is not so obvious.

1. Introduction

Medical implants, such as hip and knee joints, allow for the rebuilding of biological and mechanical functions and hence attract lots of attention. Ti and its alloys are among the most biocompatible metals but they also have some drawbacks, for example low wear resistance [1]. It is well known that amorphous carbon (a-C) has attracted enormous interest in the last two decades, due to its high hardness, low friction coefficient and wear rate [2–11]. Besides, its excellent biocompatibility and good chemical inertness makes it promising in biomedical application [1,12]. However, in hard a-C films, residual stress could be very high which severely limits the film thickness and adhesion strength [13,14]. Recently, a-C/hard carbide composite and multilayer films had been studied as a substitute of pure a-C films due to their good toughness, high adhesion strength and the ability to minimize the adverse effects of residual stress [15–20]. For biomedical application, Ti is an appropriate element for doping due to its good biocompatibility. A number of methods such as filtered cathodic vacuum arc [21], plasma-assisted chemical vapor deposition [22], pulsed laser deposition [23], and magnetron sputtering [24,25] were employed to deposit a-C/hard carbide composite and multilayer films. The closed field unbalanced magnetron sputtering, which can maintain high levels of ion bombardment during deposition, becomes a well-established technique for the preparation of a-C/carbide composite and multilayer films. Some designed properties could be obtained by adjusting the deposition processing parameters [18,26–28].

Duty cycle, which is the fraction of time that a system is in an "active" state during one period and can be defined as $[t_{on} / (t_{on} + t_{off}) \times 100\%]$ where t_{on} and t_{off} are active time and nonactive time of the system respectively, is an important parameter of the deposition process. Wang et al. studied the effect of duty cycle and claimed that the microstructure and properties of graphite-like a-C films had a significant relationship with duty cycle [29]. Moreover, Wei et al. also did detailed research on the influence of pulse bias duty cycle and their work was focused on TiN/TiAlN multilayer films [30]. There are some reports on a-C/a-C:Ti multilayer films. However, few of them are about the influence of duty cycle on the microstructure and tribological properties. It is suggested that by carefully adjusting duty cycle, the properties of films could be controlled. In addition, the corrosion behavior of a-C/a-C:Ti multilayer films on Ti alloy, which is fairly significant for biomedical application, has hardly been reported. In the present work, the a-C/a-C:Ti multilayer films were deposited by closed field unbalanced magnetron sputtering on medical Ti6Al4V alloy with different duty cycles. The effects of duty cycle on the microstructure, mechanical and tribological properties as well as corrosion behavior of the multilayer films were investigated. Hank's solution, as one kind of simulated body fluid, is frequently used for corrosive or tribological environment in studies of biomedical materials [31,32], and is also used in this work.

2. Experimental details

2.1. Deposition of multilayer films

The a-C/a-C:Ti multilayer films were deposited on Ti6Al4V alloy and Si (100) wafer substrates by a closed field unbalanced magnetron sputtering system (TAJS-700, TENGAO). The details about the coating system were documented elsewhere [33]. The films deposited on the silicon wafers were used to characterize their microstructure and

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* Corresponding author. Tel.: +86 571 87952856; fax: +86 571 87952573.
E-mail addresses: tujp@zju.edu.cn, 21226074@zju.edu.cn (J.P. Tu).

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chemical composition, and the films on Ti6Al4V alloy were used to evaluate corrosion behavior, mechanical and tribological properties. The Ti6Al4V alloy was polished to Ra ≤ 0.2 μm with emery paper and diamond spray. All the substrates were ultrasonically cleaned in acetone for 20 min, in ethanol for 10 min, and then blow-dried by nitrogen, to clear impurities on the surface. Prior to deposition, the base pressure of the sputtering system was evacuated to 3×10^{-3} Pa, and then argon gas was introduced to keep the process pressure at 0.2 Pa. The frequency of bias voltage is 60 kHz. The substrates were etched by Ar^+ bombardment at a negative bias of 500 V for 30 min, in order to remove the oxides (titanium oxides, etc.) and adsorptions (due to exposure of substrate to air). Then a thin Ti buffer layer was deposited onto the substrates for 10 min, with a negative bias of 200 V. The rotation speed of the substrate holder was kept at 5 rpm and then an a-C/Ti transition layer with gradient content ratio of Ti/C was deposited by gradually increasing the graphite target current from 0 to 2.5 A and then decreasing the titanium target current from 2.5 A to 1 A for 60 min with a negative bias of 100 V. Subsequently, the a-C layers were deposited onto the substrates by facing graphite target (no rotation) and the a-C:Ti layers were deposited by co-deposition of graphite and titanium target with a two-fold rotation to form a multilayer structure with a negative bias of 100 V. The top layers of all the films are a-C layers. During the deposition, the current of the graphite targets was kept at 2.5 A and the current of titanium targets was kept at 1 A. Through the above deposition process, the a-C/a-C:Ti multilayer films designated as D1, D2, D3, D4 and D5 deposited with different duty cycle, 15%, 25%, 35%, 45% and 55% respectively. In this present work, the total thicknesses of multilayer films were controlled to be about 2.1 μm.

2.2. Characterization of films

The surface and cross-section morphologies of the multilayer film were characterized by scanning electron microscope (SEM, Hitachi S-4800 equipped with Genesis 4000 energy dispersive X-ray analysis detector). The microstructure observation was carried out with a transmission electron microscopy (TEM, Tecnai G2F30 S-Twin). The cross-section samples were prepared by mechanical polishing and Ar^+ ion-milling (Gatan 691). The atomic bonding ordering of films was analyzed by Raman spectroscopy (LABRAM HR-800), with the wave number shift from 4000 to 100 cm^{-1} in the excitation line of 514.5 nm. The bonded structures of films were characterized by X-ray photoelectron spectroscopy (XPS) using an ESCA Lab 220i-XL electron spectrometer, operating with a monochromated Al-K_α X-ray radiation source in a base pressure of 10^{-7} Pa. The binding energies were referenced to the C 1 s line at 284.6 eV from adventitious carbon.

The hardness and elastic modulus of the films were obtained 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 effects. 6 indentations in each sample configured on different areas were performed to have reliable statistics. The shown hardness and elastic modulus are the average value calculating from the results of the 6 indentations and the standard error is also calculated. Adhesion tests were performed on the films through the scratch and Rockwell tests. Standard scratch tests were used to assess the transverse adhesion with a conventional scratch tester (WS-2002 equipped with an acoustic emission detector). For these scratch tests, a diamond pin (0.2 mm in radius) was drawn across the surface of the film at a constant linear velocity of 4 mm min^{-1}, while increasing the load linearly from 0 to 80 N. The critical load L_c is the applied load for the first detected acoustic signal. The scratch craters were observed by an optical microscope (Nikon Eclipse ME600D).

The tribological properties of the multilayer films were performed on a WTM-1E ball-on-disk tribometer at room temperature. Si_3N_4 ceramic ball (4 mm in diameter, hardness HV = 1550) was used as the counter body. The tests were carried out at a normal load of 5 N at a sliding velocity of 0.2 m s^{-1} in ambient air (50% RH) and in Hank's solution. The composition of Hank's solution is 8.0 g L^{-1} NaCl, 1.0 g L^{-1} glucose, 0.4 g L^{-1} KCl, 0.14 g L^{-1} $CaCl_2$, 0.35 g L^{-1} $NaHCO_3$, 0.1 g L^{-1} $MgCl_2 \cdot 6H_2O$, 0.06 g L^{-1} $Na_2HPO_4 \cdot 2H_2O$, 0.06 g L^{-1} KH_2PO_4 and 0.06 g L^{-1} $MgSO_4 \cdot 7H_2O$. The pH of the solution is 7.4. The coefficient of friction was monitored continuously during the tests by a linear variable displacement transducer and recorded on a data acquisition computer attached to the tribometer. The wear traces of the films were observed by an optical microscope (Nikon Eclipse ME600D).

The electrochemical measurements of the films on Ti alloy were performed on a CHI-660B electrochemical workshop in Hank's solution at 37 °C by using a three-electrode. A platinum foil was selected as counter-electrode and a saturated calomel electrode (SCE) was chosen as reference electrode. The polarization experiments were performed at a scan rate of 10 mV min^{-1}.

3. Results and discussion

3.1. Microstructure of multilayer films

The film deposited with a duty cycle of 35% was selected as a representative to introduce the microstructure. The layer morphology and crystal phase were analyzed by cross-sectional TEM with corresponding selected area electron diffraction (SAED) pattern. Fig. 1a shows the TEM image of D3 deposited with duty cycle of 35%, from which the presence of a multilayer structure can be confirmed. Fig. 1b, c and d show the high resolution transmission electron microscopy images of the films with various duty cycles (15%, 35% and 55%). The a-C:Ti layer is darker than the a-C layer due to denser structure [34]. It can be seen that the bilayer period of all these films is about 10 nm. The thickness of a-C:Ti layer and a-C layer does not change with duty cycle basically. There is no obvious TiC nanocrystallite in all these films. As reported by Feng et al. [35], TiC-like short-range order surrounding Ti atoms dissolved within a-C matrix may persist when the Ti content is low, which is similar to the result in this work. The diffraction rings in the inset SAED pattern are not evident which may result from the existence of a great deal of amorphous phase.

The atomic bonding structure of the as-deposited films is studied by Raman spectroscopy because it is a nondestructive and powerful tool to characterize carbon-based films due to its sensitivity to the various forms of carbon [36]. The Raman spectra of a-C based film are usually fitted into two Gaussian bands: the D and G peaks. The D peak at about 1350 cm^{-1} is due to the breathing mode of sp^2 atoms in sixfold carbon rings, and the G peak at about 1560 cm^{-1} is owing to stretching vibration of all pairs of sp^2 atoms in both rings and chains [37–39]. The G peak position, D peak position, the full width half maximum (FWHM) ratio of the D and G peaks and I_d/I_g are depicted in Table 1. I_d/I_g, which is considered to be inversely proportional to the sp^3 fraction, decreases from 1.72 to 1.57 when the duty cycle is decreased from 15% to 55%, indicating an increase of sp^3/sp^2 hybrid ratio [40,41]. This variation trend is totally different from the report of Wang et al. [29], and can be explained as follows. Higher duty cycle leads to longer acceleration time of ion which could result in higher ion energy. It is well known that the growth process of a-C based film contains chemical absorption of species at the growing surface and the physical process of implantation at the subsurface, which mainly depend on the ion energy. Under the latter growth mode, the ion peen effect is associated with a compressive stress which in turn leads to an increase of sp^3 bond fraction [42,43]. In a previous work, the higher $FWHM_D/FWHM_G$ ratio suggests lower bond–angle disorder in the film [44]. The $FWHM_D/FWHM_G$ ratio firstly increases from 2.50 to 3.03 for the films deposited with duty cycle varying from 15% to 35%, then decreases from 3.03 to 2.84 with duty cycle reducing from 35% to 55%, indicating that D3 deposited with a duty cycle of 35% possesses the lowest bond–angle disorder.

The effect of Ti element on the bonding structure of the as-deposited films are further analyzed by XPS. As seen in Fig. 2a, the deconvoluted C 1s spectrum of the film deposited with a duty cycle of 35% exhibits three