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Review

The electrochemical and mechanical properties of Ti incorporated amorphous carbon films in Hanks' solution

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ABSTRACT

Ti incorporated amorphous carbon (a-C) films with variant Ti contents were prepared by the unbalanced magnetron sputtering process. Scanning electron microscopy, ultraviolet Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy were used to characterize the microstructure of a-C films. The hardness and lubricated tribological properties were assessed using nanoindentation and ball-on-disk tribometer. As the Ti content in a-C films increases from 0 to 15.2 at.%, the sp^3 volume fraction, the internal stress and the hardness of the films decreases gradually, while the disorder of sp^2 bond increases. The electrochemical tests reveal that the a-C films with lower than 1.5 at.% Ti possess good corrosion resistance in Hanks' solution, while the a-C film with 15.2 at.% Ti is susceptible to crevice corrosion. The reduced friction of the a-C films is due to the sp^2 bonded film surface and boundary lubrication of the Hanks' solution. The a-C film with 3.1 at.% Ti exhibits the best wear resistance in Hanks' solution among the studied films.

Contents

1. Introduction

Biomedical materials used for surgical purposes are required to possess high resistance to corrosion and wear. Ti alloys, such as Ti6Al4V have already been applied to clinical therapy due to their good bio-compatibility and excellent corrosion resistance [1–3]. However, when it comes to the application of artificial implants for joint replacement, Ti alloys exhibit high wear loss [4]. Therefore, the possible loosening of joint matching and accumulating of metal content in human body would limit the capability of long-term service of Ti alloys.

The amorphous carbon (a-C) film possessing high hardness, wear resistance, chemical inertness and bio-compatibility, has became one of the most promising candidates as protective coating of bio-materials [5–7]. In the past decades, numerous studies have been focused on the attractive hardness and wear properties with respect to the amorphous microstructure of a-C films [8–11]. The high inherent internal stress of the hard a-C films could confine the film thickness and the adhesion to the substrate [12–14]. Element incorporations are frequently used to reduce the internal stress of the a-C films [15–19]. Ti is one of the most important doping elements for a-C films in bio-medical applications. The sliding wear performance of Ti incorporated a-C films was studied recently [20,21], but little report is focused on the electrochemical corrosion behaviors of these films. Considering the electrolyte characteristic of body fluids, it is necessary to investigate the electrochemical and tribological behaviors of

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Table 1
Dependency of the Ti content of a-C films on process parameters.

Film composition (at.% Ti)	Current density of two Ti targets (mA cm^{-2})	Current density of two C targets (mA cm^{-2})
0	0, 0	15.4, 15.4
1.5	0, 0.92	15.4, 15.4
3.1	0.92, 0.92	15.4, 15.4
15.2	2.15, 2.15	15.4, 15.4

the a-C films under the simulated body fluids (Hanks' solution).

In the following, hard a-C films with variant Ti contents were deposited on Ti6Al4V alloy substrates by the unbalanced magnetron sputtering. The microstructure of the a-C films was characterized. The electrochemical and tribological behaviors of the a-C films were also studied in simulated body fluids.

2. Experimental

The a-C films with variant Ti contents were deposited on Ti6Al4V alloy and Si (1 0 0) wafer substrates by means of unbalanced magnetron sputtering. The details related to the machine configurations can refer a previous study [22]. The Ti6Al4V plate substrates with a thickness of 5 mm were cut into discs with a diameter of 20 mm and well polished. All substrates had been cleaned in acetone ultrasonically before putting into the sputtering chamber. Prior to deposition, the chamber was vacuumed to a base pressure of 4×10^{-3} Pa, and then argon stream was introduced to keep the process pressure at 0.17 Pa. The substrates were etched by sputter for removing the oxides and adsorptions, and followed by depositing a thin under-layer of pure Ti film. Subsequently, a transition layer with gradient content ratio of Ti/C was deposited by gradually decreasing the Ti content and increasing the C content until reaching the film composition, and then the required a-C films were deposited on the transition layer. The Ti content of films was modulated by controlling the current density of targets. During the deposition, the substrate bias of −60 V was applied for the ion bombardment towards the a-C films. The dependency of film composition on process parameters is shown in Table 1. The thickness of all a-C films was stabilized at about 1.5 μm.

The constitution of films was examined by an energy dispersive X-ray spectroscopy (HORIBA EMAX ENERGY EX-350). The surface morphology and the cross-section of the a-C films were observed using atomic force microscopy (AFM, Veeco Multimode, operating in tapping mode in air) and scanning electron microscope (SEM, Hitachi S-4700). The bonded structure of films was characterized by an X-ray photoelectron spectroscopy (XPS) using an ESCALab 220i-XL electron spectrometer, operating with a monochromated Al-K$_\alpha$ X-ray radiation source in a base pressure of 10^{-7} Pa. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon. The atomic bonding ordering of films was analyzed by a Raman spectroscopy (LABRAM HR-800), with the wave number shift among 4000 to 100 cm^{-1} in ultraviolet laser excitation line of 325 nm. Microstructure analysis was carried out by an analytical transmission electron microscope (TEM, JEM-200CX) at an acceleration voltage of 160 kV.

The electrochemical measurements of the a-C films were performed on a CHI-660B electrochemical workshop in Hanks' physiological solution at 37 °C by using a three-electrode cell with a saturated calomel electrode (SCE) as reference electrode and a Pt foil as counter-electrode. The composition of Hanks' solution is shown in Table 2. The isolated electrode potentials (open circuit potentials, OCP) as a function of time were used to assess the surface passivation of films in the simulated body fluid environment. A cyclic polarization experiments were performed by scanning the specimens from −300 mV with respect to corrosion potentials (E_{corr}) at a scan rate of 10 mV s^{-1} and reversing from 800 mV at the same scan rate. The potentiostatic experiments were carried out at pre-selected potential levels, in which the current density as a function of time was measured for the purpose of studying the electrochemical corrosion properties of a-C films.

Table 2
Chemical composition of the Hanks' solution.

Component	Concentration (g L^{-1})
NaCl	8.0
Glucose	1.0
KCl	0.4
$CaCl_2$	0.14
$NaHCO_3$	0.35
$MgCl_2 \cdot 6H_2O$	0.1
$Na_2HPO_4 \cdot 2H_2O$	0.06
KH_2PO_4	0.06
$MgSO_4 \cdot 7H_2O$	0.06

The internal stress of films was calculated according to the Stoney equation [23], by detecting the curvature of the substrate with the a-C film deposited on. Nanoindentation test was evaluated on a nanoindentation tester (CSM NHT) with a standard Berkovich diamond indenter, under a loading/unloading rate of 20 mN min^{-1}. The hardness and elastic modulus of the a-C films were measured based on the Oliver and Pharr method with hypothetic Poisson's ratio (ν) of 0.3. The adhesion of the a-C films was tested by 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 film at a constant linear velocity 10 mm min^{-1}, while increasing the load linearly from 10 to 60 N at a loading rate 50 N min^{-1}.

The tribological tests of the a-C films were performed on ball-on-disk tribometer, using silicon nitride (Si_3N_4) ball (3 mm in diameter, hardness HV = 1550) as the counter mate. The ball was fixed and contacted the rotating film specimens. The tests were carried out at normal load of 2.5 N, sliding velocity of 0.22 m s^{-1} for 10,000 laps with the contact surface submerged in the Hanks' solution. The friction coefficient was monitored continuously during the experiments by a linear variable displacement transducer and recorded on a data acquisition computer attached to the tribometer. After testing, the worn surface was observed by SEM. The specific wear rate of films was calculated by measuring the profile of wear tracks (mean of four traces per specimen) taken across the wear track using a Dektak 3 optical profiler.

3. Results and discussion

3.1. Microstructure

Typical morphologies of the surface and the cross-section of the a-C film with 3.1 at.% Ti deposited on silicon substrate are shown in Fig. 1a and b, respectively. The other a-C films prepared by the present magnetron sputtering process exhibit the similar surface morphologies as shown in Fig. 1. It can be seen that the surface of the a-C films are composed by fine sized particulates, which possess a low roughness. The a-C films can be grown by a self-smoothing process due to the influence of carbon ion impacts induced formation of downhill currents, which caused the species transports from the top layer of the growing film to the neighboring hollows [24]. From Fig. 1b, it is indicated that an excellent uniformity in thickness of the a-C films can be obtained by the present magnetron sputtering process and the thickness of the film is about 1.5 μm.

Fig. 2 gives the bond structure of the a-C films as a function of Ti contents, which was calculated by fitting the C 1s region of XPS spectra. The inset shows the C 1s deconvolution of a-C film