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A novel diamond-like carbon film

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ABSTRACT

In this work, we fabricate a novel DLC film through shortening the deposition periods. The novel DLC film included F and Si doped multi-layer structure, and a silicon interlayer that is able to reduce internal stress, improve the bonding and adhesion, and bridge the film and substrate. This work mainly focused on discussing the cause of the corrosion behavior of the novel DLC film. Corrosion resistance is assessed by potentiodynamic polarization tests in 3.5 wt.% NaCl solution. The corrosion test results show that the novel DLC film exhibits good adhesion to Ti alloy substrate and good resistance to corrosion.

1. Introduction

Diamond-like carbon films are well known for low friction and wear, high hardness, good corrosion resistance and their many applications in high technology areas [1–3]. As we known, dopant of elements such as fluorine, silicon and boron into the DLC films is a useful method to tailor the sp^3 and sp^2 bonding and thus reach special electrical, physical and mechanical properties [4–8]. It is reported that F or Si doped DLC films could well enhance corrosion resistance [9–11]. Moreover, F and Si codoped DLC films also exhibited good corrosion resistance properties as reported in our previous work [12,13]. We pointed out that the corrosion resistance of the multilayer F and Si codoped DLC film is better than that of the single layer one. It revealed that the microstructure of the DLC film had a significant effect on the corrosion behaviour of the DLC film. Especially, the DLC film with multilayer structure exhibited variable corrosion behaviour. Moreover, the corrosion resistance tended to be poor with increasing the immersion time. Zeng et al reported that the nanopores had a significant effect on the corrosion resistance of the DLC films. And they pointed out that the porosity density in film could increase with immersion time, which could be directly related to the corrosion resistance of the DLC film [14,15]. Based on our previous work [12,13], we focus on fabricating the DLC film with multilayers through shortening the film deposition period, which is expected to possibly enhance the corrosion resistance of DLC film.

Herein, in this work, we fabricate a novel DLC film containing layers with different F and Si composition using a plane hollow cathode plasma-enhanced chemical vapour deposition technique, which aims at improving the corrosion resistance. The potentiodynamic polarization results show that the novel DLC film exhibits good corrosion resistance in 3.5 wt.% NaCl solution compared to the bare Ti alloy substrate.

2. Experimental procedure

The DLC film is deposited on TC4 Ti alloy substrates using a plane hollow cathode plasma-enhanced chemical vapor deposition (PHC-PECVD) method. The chemical composition of TC4 Ti alloy is listed in Table 1. The schematic of the deposition system and the process of deposition could be proposed by Wang et al. [16,17] First, the stainless steel substrates are ultrasonically cleaned in acetone and alcohol. The base pressure of depositing chamber is pumped down to the value of 1.0×10^{-3} Pa. Substrates are pre-sputtered at a pressure of 1.5 Pa for 15 min with a constant flow of argon (Ar) gas fed into the chamber. Second, before the film deposition, a silicon interlayer of about 200 nm is deposited with SiH_4 gas of 50 sccm (–10.0 kV bias voltage, 10 Pa and 30% duty ratio), in order to improve the adhesion of the films and the substrate. Subsequently, the F and Si codoped DLC film is fabricated on the Ti alloy substrate as follows, the preparation processes are shown in Fig. 1. The layer “A” is deposited at a pressure of 1.8 Pa for 4 min with SiH_4 and CF_4 (22.5 and 25 sccm), Ar (80sccm), and acetylene (150 sccm). The layer “B” is deposited at a pressure of 1.8 Pa for 2 min with SiH_4 and CF_4 (22.5 and 25 sccm), Ar (80sccm), and acetylene (50 sccm). The substrate bias voltage, duty cycle and a repetition frequency is set as -0.8 kV, 30%, and 1.5 kHz. No external heating of the substrate is employed, and the maximum temperature during deposition is about 180 °C.

The cross-sectional microstructure of the DLC film is obtained by a thermal field electron emission scanning electron microscope (FEI

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Table 1
The chemical composition (at. %) of TC4 Ti alloy.

Ti	Fe	C	N	H	O	Al	V
Balance	0.21	0.03	0.02	0.01	0.15	5.8	3.2

Quanta FEG 250). The composition of DLC film is examined using time-of-flight elastic recoil detection analysis (TOF-ERDA). The top layers (total thickness about 1.5 µm) of the cyclical film are examined due to the TOF-ERDA only getting a signal from the first 1–2 µm beneath the surface. Raman spectra of the DLC film are obtained by a Horiba Jobin Yvon LABRAM-HR800 spectrometer using an excitation wavelength of 532 nm. The typical spectrum is recorded in the range of 800–2000 cm^{-1}, data acquisition time is 60 s and diameter of beam spot is 0.2 µm. The adhesion of the samples is tested by a scratch tester (CSEM Revetest) equipped with a diamond tip of radius 200 µm. The curvature radii of the substrate before and after coating deposition are measured by the observation of Newton's rings using an optical interferometer system, and then the residual stress is calculated by the Stoney equation. The corrosive properties are evaluated by using a computer controlled potentiostat/frequency response analyzer (Autolab PGSTA T302N). A typical three electrode cell, consisting of the working electrode (1.0 cm^2 exposed area), a saturated Ag/AgCl electrode (saturated with KCl) as a reference electrode, and platinum as the counter electrode, is used in the corrosion tests. The corrosive medium is 3.5 wt.% NaCl solution. All the solutions are prepared from deionized water with pH value of around 6.8 ± 0.2. Potentiodynamic polarization tests are carried out at the scan rate of 0.5 mV s^{-1} from −160 mV with reference to the open circuit potential (OCP) to a final anodic current density of 0.1 mA cm^{-2} after an initial 30 min exposure to the test electrolyte for achieving a stabilized OCP [18].

3. Results

3.1. Microstructure and composition

Fig. 2a shows the cross-sectional morphology of the novel DLC film. The thickness of the film is about 3 µm. Inset image in Fig. 2 shows the periodic F and Si codoped “A” and “B” layers in the novel DLC film. EDS analyses suggest that the DLC film mainly consists of C, O, Si and F (Fig. 6b-e).

In order to probe the detailed element composition of the DLC film, the elemental depth profiling of the film examined by TOF-ERDA is plotted in Fig. 3. The composition of the DLC film is determined as follows: carbon 87.8 at.%, hydrogen 7.3 at.%, oxygen 0.63 at.%, fluorine 1.6 at.%, and silicon 2.67 at.%.

Furthermore, the amorphous carbon feature of the novel DLC film can be defined by the Raman spectrum. Fig. 4 shows the Raman spectrum of the novel DLC film. It can be seen from Fig. 4 that the G D^{-1} band centers at 1531.8 cm^{-1} and 1332 cm^{-1} respectively, which is a typical characteristic of DLC films [19].

3.2. Mechanical properties of the novel DLC film

Fig. 5 shows the optical scratch morphology of the novel DLC film. It reveals that the DLC film exhibits good adhesion to Ti alloy substrate due to the large critical adhesion load of 35 N, which is attributed to the

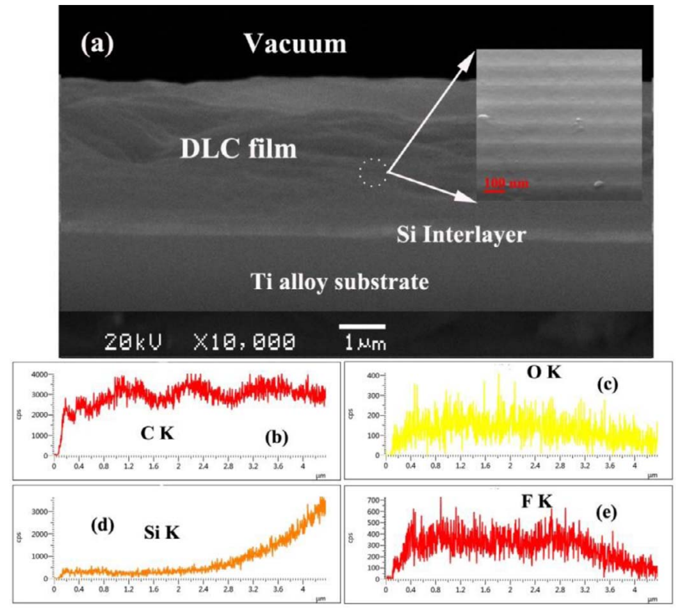

Fig. 2. (a) SEM cross-sectional image of the novel DLC film, (b)-(e) Line profiles across the cross-sectional of the novel DLC film. Inset in Fig. 2a is the enlarged SEM image of the red marked region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

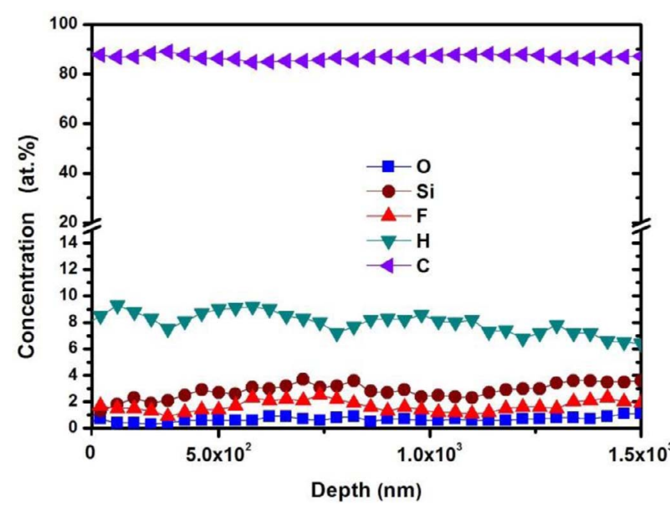

Fig. 3. Elemental depth profiling of the DLC film examined by TOF-ERDA.

low internal stress of the film (about −0.46 GPa). In addition, no debris is observed at the border of inside the scratch of the film until achieving the maximum load, which suggests exceptional adhesion between the film and Ti alloy substrate.

3.3. Corrosion behavior

Potentiodynamic polarization curves of Ti alloy and DLC film after exposure in 3.5 wt% NaCl are plotted in Fig. 6. The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) of Ti alloy and DLC film derived from polarization curves are listed in Table 2. It can be seen

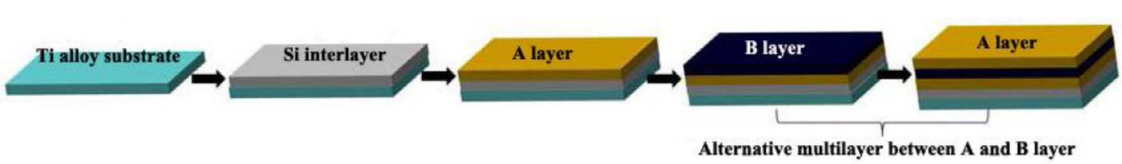

Fig. 1. Preparation processes of the DLC film.