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Influence of negative voltage on the structure and properties of DLC films deposited on NiTi alloys by PBII

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Diamond-like carbon (DLC) films have been successfully deposited on Ti-50.8 at.%Ni using plasma based ion implantation (PBII) technique. The influences of the pulsed negative bias voltage applied to the substrate from 12 kV to 40 kV on the structure, nano-indentation hardness and Young's modulus are investigated by the X-ray photoelectron spectroscopy (XPS) and nano-indentation technique. The results show that C 1s peak depends heavily on the bias voltage. With the increase of bias voltage, the ratio of sp^2/sp^3 first decreases, reaching a minimum value at 20 kV, and then increases. The DLC coating deposited at 20 kV shows the highest hardness and elastic modulus values as a result of lower sp^2/sp^3 ratio. The corrosion resistance of specimen deposited under 20 kV is superior to uncoated NiTi alloy and slightly better than those of the other samples deposited at 12 kV, 30 kV and 40 kV.

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1. Introduction

NiTi alloys are well known for their remarkable mechanical and chemical properties such as shape memory effect (SME), superelasticity and biocompatibility. They have great potential use in surgical devices in the human body, such as orthodontic wires, cardiovascular stents, artificial bone joint, etc. [1–4]. However, the high Ni content has been a crucial problem for the long-term implantation of NiTi alloy device, as it has been reported that Ni is toxic and can cause allergic reaction as a biomaterial [5, 6]. To further improve its biocompatibility and to suppress the Ni^+ ion release, various studies have been reported on the surface modification of NiTi alloys, including ion implantation, multi arc ion-plating as well as TiN and polymer chemical vapor deposits [7–9].

It is well known that DLC is a candidate coatings for metal biomaterials, with the feature of better biocompatibility, high wear resistance and chemical inertness [10, 11]. Coating implants with DLC can extend the lifetime of implants in the body of the patient [12–14]. However, good quality DLC films depend critically on the deposition technique and parameters. Plasma based ion implantation (PBII) which is characterized by high dose rates, wide ion energy range, large implant areas, and the ability to treat workpieces of complex shapes, appears to be an ideal technique for surface modification [15, 16].

Up to now, no report has been given on the deposition of DLC coatings on the NiTi alloys by PBII with the aim to improve its surface properties. In this study, Ti-50.6 at% Ni alloy samples are coated with DLC by PBII method in order to improve their biocompatibility. The aim of the present study is to investigate the surface characteristics and mechanical properties of NiTi shape memory alloy coated with DLC.

2. Experimental techniques

2.1. Substrate preparation

The experimental alloy has a composition of Ti-50.8 at.%Ni, and all samples were cut into sizes of 13 mm × 10 mm × 1 mm from the as-received hot rolled NiTi alloy sheet. The A_f phase transformation temperature was settled to 17° through a series of heat treatment. For all samples, one side of 10 mm × 10 mm surface was ground and mirror polished, then cleaned ultrasonically in acetone, methanol and distilled water, progressively, and then dried in clean cold air immediately prior to transferring to the deposition unit.

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2.2. Coatings preparation

PBII technique was employed to deposit DLC on the surface of the NiTi alloy. The deposition chamber was evacuated to a base pressure of approximately 1×10^{-4} Pa. Prior to deposition, argon gas was used to sputter clean the substrate surface for 30 min. Subsequently, a negative pulsed bias voltages was applied to the substrate, with a repetition frequency of 60–100 Hz and a pulse duration of 20–30 μs. A mixture of C_2H_2 and H_2 were used to realize DLC coatings growth. The gas pressure was 0.3–0.6 Pa during the deposition process. The negative pulsed bias voltage was controlled to be 12 kV, 20 kV, 30 kV and 40 kV, with deposition time of 120 min.

2.3. Characterization of the deposited films

ESCA PHI500 X-ray photoelectron spectroscopy was used to study the composition and the valence condition at the surface. Cu K_α X-ray source was employed with 12.5 KV voltage and 250 W powers. The ion sputter profiling was performed with Ar^+ ion beam over a 4 mm × 4 mm area. Since argon sputtering would make the binding energy of DLC films shift to higher positions and destroy the metastable carbon structure, the investigated surface is not sputtered by argon.

2.4. Nanoindentation tests

Nanoindentation experiments were carried out using a Nanoindenter II (MTS Systems Corp.). The hardness values and elastic modulus of the films were measured by nanoindentation using the continuous stiffness measurement (CSM). The instrument monitors and records the dynamic load and displacement of three-sided pyramidal diamond (Berkovich) indenter during indentation with a force resolution of approximately 75 nN and 0.1 nm. Ten indentations were performed on each sample, and the reported hardness and elastic modulus values are the average of the ten measurements.

2.5. Electrochemical tests

Open circuit potential, Tafel curves was obtained through an EG&G Princeton Applied Research model 283 A potentiostat/galvanostat controlled from a computer. The electrochemical measurements were performed in a standard three-electrode cell with 1 cm^2 platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was 0.9%NaCl solution. All the corrosion experiments were conducted at 37°C.

3. Results and discussion

3.1. XPS analysis of the DLC coatings

Fig. 1 shows a typical XPS survey spectra of the DLC films without and with sputtering for 3 min. The peaks observed at 285.2 eV and 532.5 eV are due to the photoelectrons excited from the C 1s and O 1s levels, respectively. The spectra indicate that there are two elements including O and C presented on the outmost surface of DLC film. After 3 min sputtering with argon ions, the O signal disappears, indicating that O element presents only on the top surface of DLC coatings. The trace of O elements is probably due to the contamination of the film after exposure to air.

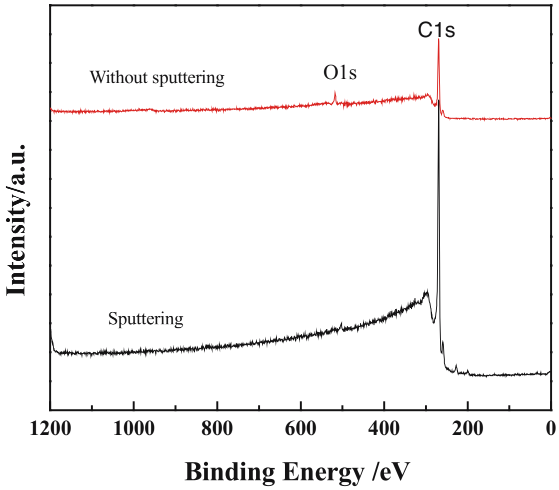

Figure 1 Survey XPS spectra of the DLC films without sputtering and *t* sputtering for 3 min.

Fig. 2 depicts the C 1s spectra for the DLC formed at different pulsed negative bias voltages. The C 1s peak position is between the diamonds peak 286.6 eV and the graphite peak 284.2 eV. All films could not be identified to be 100% percent of diamond or graphite, since the value of the binding energy C 1s is substantially higher than that of graphite and lower than that of the diamond. As the bias voltage increase from 12 kV to 20 kV, the XPS peak position shifts to higher binding values from 285.1 eV to 285.3 eV, and then decreases when the bias increases from 20 kV to 40 kV.

To identify the state of carbon more precisely, the C 1s spectrum of the films analyzed precisely as illustrated in

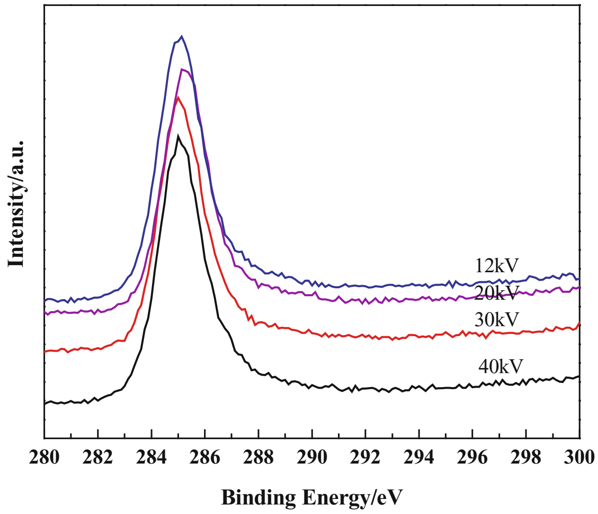

Figure 2 C 1s XPS spectra of DLC coatings deposited at different pulsed negative bias voltages.

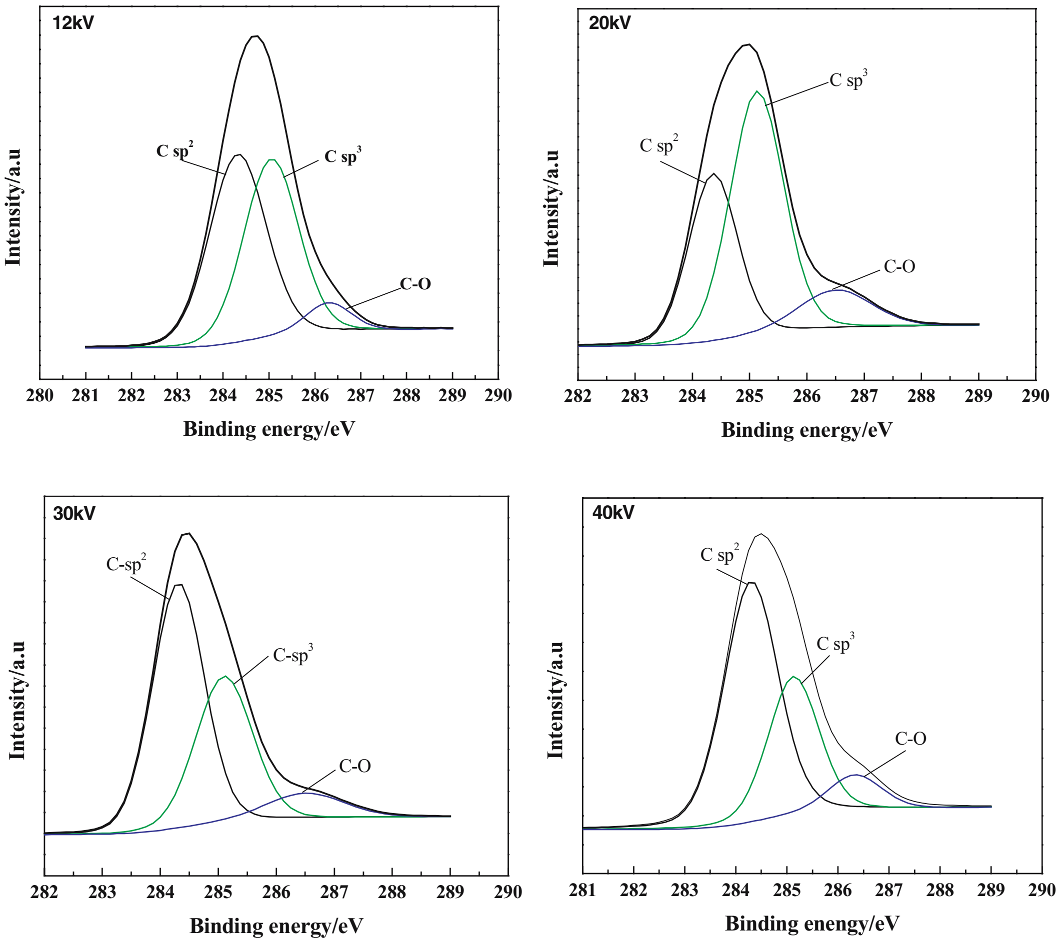

Figure 3 C 1s XPS spectra of DLC coatings deposited at different pulsed negative bias voltages.

Fig. 3. It can be seen that the C 1s photoelectron peak could be resolved into three components, as detonated C sp^2, C sp^3 and C=O bonds. The first component peak is about 284.2 eV, which corresponds to the trigonal sp^2 bonding. While the second component peak appears at 285.3 eV, corresponding to the tetrahedral sp^3 bonding. And the third peak appears at 296.5 eV, corresponding to C=O bonding.

The most important factors governing the film quality of DLC is the hybridized sp^2/sp^3 atomic carbon ratio. The sp^2 sites form clusters consisting of several atoms and are embedded within a σ bonded matrix [17]. By controlling the deposition parameter we can control the ratio of sp^2/sp^3 in the deposited films and consequently tailor the film properties in accordance with the application. For hard coatings, we prefer sp^3 rich bonding, whereas for good tribology performance, rich sp^2 bonds are preferred. As we know, the number of carbon atoms in a certain state in a hybridized mixture is proportional to the area under the corresponding peak divided by its sensitivity factor. The sensitivity factor depends only on the atomic factors and is independent of the chemical state of the atoms, thus the sensitivity factors for the sp^2 and sp^3 peaks are considered the same under this condition [18]. Therefore, the area fraction under the peaks associated with these two components can be used to estimate the sp^2/sp^3 ratio of the DLC coatings. The calculated results are illustrated in Table I. A minimum value of the sp^2/sp^3 ratio of 0.63 is obtained at 20 kV.

TABLE I. sp^2/sp^3 ratio of DLC films deposited on NiTi alloys at different bias voltages

Specimen	12 kV	20 kV	30 kV	40 kV
sp^2/sp^3 ratio	1.11	0.63	1.54	1.85

This result is in good agreement with the literature [19]. It can be explained as follows: as the mobility of atoms on the growing surface is increased with pulse bias voltage, the extent of C structure disordering increases, resulting in an increase in the population of sp^3 bonds. However, when the bias voltage increase further, the ion energy is too high, which may damage the sp^3 bonds and cause sp^3 bonds to transform into sp^2 bonds. As a consequence, there is an optimum bias voltage favoring sp^3 bond formation.

3.2. Nano-indentation tests

The hardness and elastic modulus of DLC coatings on NiTi alloys are important parameters for the characterization of the surface modification. Hardness is a measure of

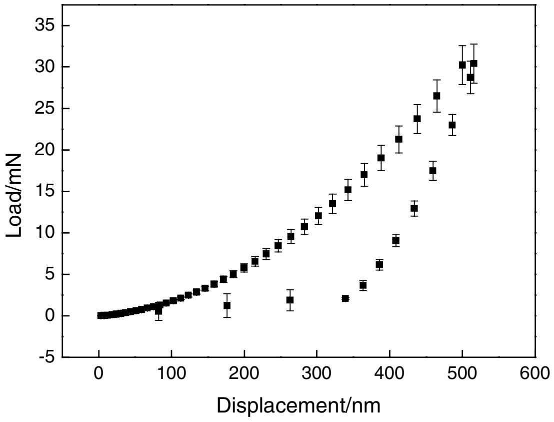

Figure 4 Typical load-unload curves of DLC coatings on NiTi alloy deposited at 20 kV bias voltage.

the resistance to plastic deformation while the elastic modulus is important in determining the maximum allowable elastic strain in the material. It is well know that the hardness and modulus of DLC film are functions of the deposition technique as well as the deposition conditions [19].

Typical loading-unloading curves in DLC are shown in Fig. 4. In the present work, hardness and Young's modulus were obtained by CSM technique. Hardness and Young's modulus of DLC film deposited on NiTi alloys at 20 kV bias voltages as a function of indenter displacement is shown in Figs 5 and 6. With the increase of penetration depth, the hardness and modulus of the films decrease and tend to approach the value measured for the substrate. This result may be attributed to the evident effect of the substrate with the increase of indent depth [20].

Table II summarizes the hardness and elastic modulus of the film deposited on the NiTi alloy at different bias voltages. The hardness and modulus of each samples are determined as being equal to the relatively flat maximum of the hardness and elastic modulus obtained at depths ranging between 15 and 150 nm. It is clearly that both hardness and modulus are significantly higher than that of the uncoated NiTi alloys. The highest values of hardness and Young's modulus about 16.2 GPa and 148 GPa are found for the film deposited at a bias of 20 kV. It is obvious that the pulsed negative bias voltage highly affects the mechanical properties of the films. Hardness and elastic modulus increases with increasing bias voltage to a maximum and then decreases at further higher bias voltage. The improved mechanical properties of the films deposited at 20 kV may be attributed to the maximum amount of carbon transformation from sp^2 form to sp^3 form, which is verified by the XPS analysis. The lowest sp^2/sp^3 ratio result in that the packing density of the samples and the fraction of sp^3 sites be the maximum, and makes the local bonding environment more favorable for the diamond-like formation. Therefore, the DLC coating deposited at 20 kV shows the highest hardness and Young's modulus values.

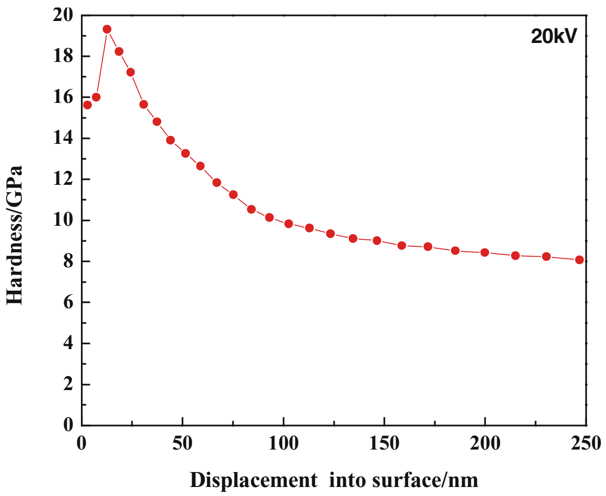

Figure 5 Hardness of DLC film on NiTi alloys as a function of penetration depth.

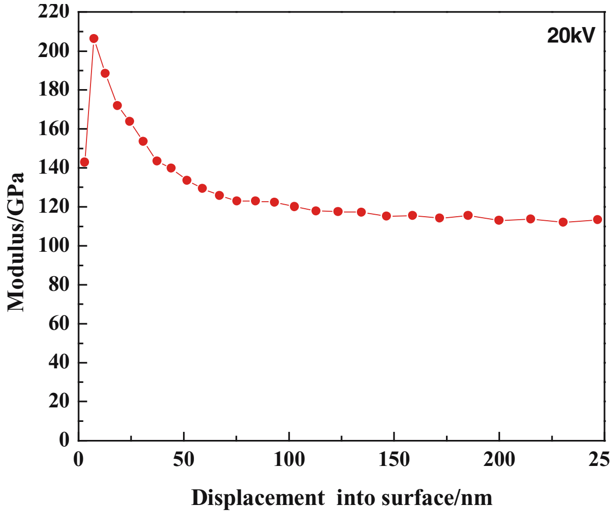

Figure 6 Young's modulus of DLC film on NiTi alloys as a function of penetration depth.

TABLE II. Hardness and Young's modulus of DLC films on deposited on NiTi alloys at different negative bias voltages

Specimen	12 kV	20 kV	30 kV	40 kV
Hardness (Gpa)	12.6	18.2	11.1	11.8
Young' smodulus (GPa)	100	186	117	120

3.3. Electrochemical behavior

Figs 7 and 8 show the Tafel curves for uncoated specimen and the specimens coated at different negative bias voltages, respectively. Table III summarizes the corrosion current density and potential obtained by the Tafel measurements. The corrosion current density of NiTi substrate is 7.068×10^{-7} A/cm^2, one order higher than that of the specimen deposited at 20 kV negative bias voltage for 120 min. This indicates that the corrosion resistance of

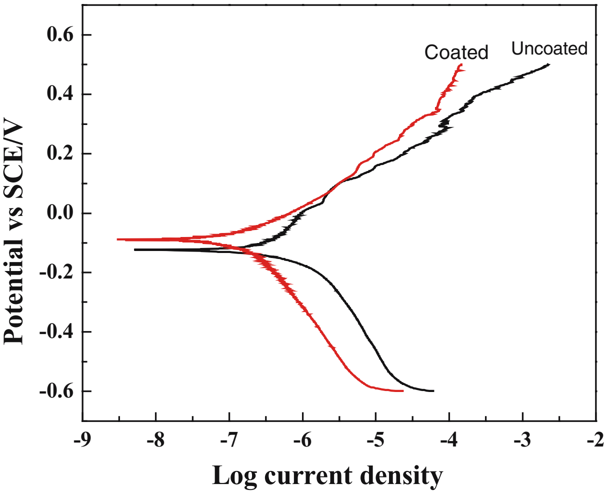

Figure 7 Tafel curves for uncoated and coated specimen.

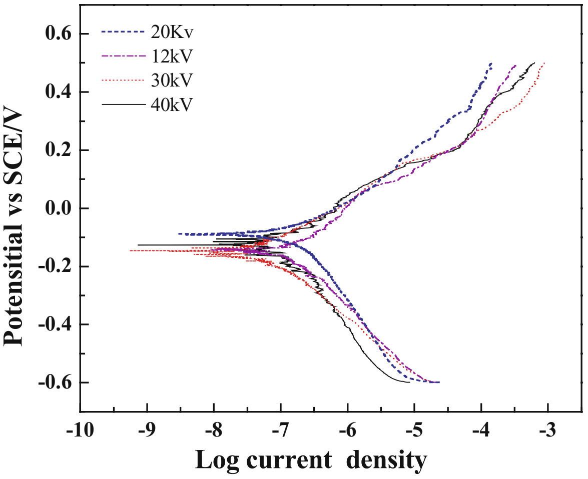

Figure 8 Tafel curves for coated specimens at different bias voltages.

specimen deposited under 20 kV is superior to the uncoated NiTi alloy. For the coated samples, the specimen deposited at 20 kV exhibits excellent corrosion resistant compared to others.

TABLE III. Corrosion parameters deposited at different negative pulse bias voltages

Samples	Bias voltage (kV)	I_{corr} (A/cm^2)	E_{corr} (V)
Coated	12	7.461×10^{-8}	–0.1259
	20	3.846×10^{-8}	–0.1197
	30	3.234×10^{-7}	–0.1450
	40	1.985×10^{-7}	–0.0878
Uncoated NiTi substrate		7.068×10^{-7}	–0.1259

4. Conclusions

1. Diamond-like carbon (DLC) films have been deposited on Ti-50.8 at.%Ni using plasma based ion implantation technique. The XPS results show that C 1s peak depends on the bias voltage. With the increase of bias voltage, the ratio of sp^2/sp^3 first decreases, reaching a minimum value at 20 kV, and then increases.

2. Nano-indentation tests indicate that DLC coating deposited at 20 kV have the highest hardness and elastic modulus values.

3. The corrosion current density of NiTi substrate is 7.068×10^{-7} A/cm^2, one order higher than that of the specimen deposited at 20 kV negative bias voltage for 120 min. This indicates that the corrosion resistance of specimen deposited under 20 kV is superior to the uncoated NiTi alloy.

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