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Surface modification of NiTi alloys using diamond-like carbon (DLC) fabricated by plasma immersion ion implantation and deposition (PIIID)

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Abstract

DLC films with various bias voltages were deposited on polished NiTi alloys by plasma immersion ion implantation and deposition (PIIID) using graphite as plasma precursor. Microstructure and nano-hardness of the DLC films were characterized by Raman spectroscopy and nano-indentation system, respectively. The electrochemical corrosion behavior of DLC coated and uncoated NiTi alloys is investigated in Hank's solution by means of potentiodynamic polarization tests. The results show that on the one hand the corrosion resistance and surface hardness and elastic modulus of the NiTi alloys are remarkably improved due to the deposition of the DLC films, and on the other hand the sp^3/sp^2 ratio inferred from Raman spectra, hardness, elastic modulus and the corrosion resistance of the DLC films on the NiTi alloys first increase and then decrease with the increase of the bias voltage. It can be concluded that the corrosion resistance of the DLC films is influenced by their microstructure.

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Keywords: NiTi alloys; Diamond-like carbon (DLC); Plasma immersion ion implantation and deposition (PIIID); Raman spectroscopy; Corrosion resistance

1. Introduction

NiTi alloys have gained much attention in biomedical application such as orthodontics and orthopaedics due to their shape memory effect and superelasticity. In particular, NiTi alloy is characterized by a specific stress–strain diagram that is different from the deformation behavior of conventional materials but similar to that of living tissues [1]. The Ni content in the alloy is more than 50 at.%, and the release of Ni ions in all metallic implants takes place during the corrosion process in the physiological environment [2–4]. Even though Ni is an essential element in the human body, excess of Ni ions may cause allergic reactions and promote carcinogenesis and toxic reactions [5,6]. As is known, Ni ions release of the NiTi alloys is closely related with their surface corrosion resistance. However, NiTi exhibits poor resistance to localized corrosion in chloride containing environments, with arguably low pitting potential values [7–9]. Therefore, surface modification of NiTi alloys is necessary to improve their corrosion resistance.

Diamond-like carbon (DLC) coatings have attracted considerable attention in biomedical applications due to their high hardness, low friction coefficient, chemical inertness and good biocompatibility. Meanwhile, many investigations have been carried out to examine the feasibility of DLC coatings on stainless steel [10], Ti6Al4V [11], Ti [12], CoCrMo alloys [13,14] and NiTi alloys [15] for improving their corrosion resistance. Reports on the DLC coatings,

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fabricated by plasma immersion ion implantation and deposition (PIIID) using acetylene as plasma precursor, used to improve the corrosion resistance of the NiTi alloys have been reported [15]. However, to our knowledge, No literatures about the DLC coatings fabricated by PIIID using graphite as plasma precursor to improve the corrosion resistance of the NiTi alloys were reported. In this study, DLC coating fabricated by PIIID using graphite acting as plasma sources is used to modify the surface properties of the NiTi alloys.

2. Experimental procedure

All substrates of $10 \times 10\,\text{mm}^2$ were spark cut from $Ni_{50.8}Ti_{49.2}$ (at.%) plates of thickness 1 mm. The substrates were mechanically polished. The substrates were successively cleaned with acetone, ethanol and deionized water and finally dried with air prior to coating preparation. Fabrication of DLC films was carried out by plasma immersion ion implantation and deposition. The vacuum chamber was evaluated to a base pressure of 5×10^{-3} Pa, then Ar^+ sputtering was introduced into the chamber to remove undesirable oxide and contamination layers for 30 min prior to coatings deposition. Graphite plasma was generated by pulsed cathodic arc plasma source with a curved magnetic duct. The detailed experimental conditions were listed in Table 1. Note that the bias voltage was varied from 10 kV to 30 kV. (DLC-1, DLC-2 and DLC-3 denote the DLC films fabricated at the bias voltage of 10, 20 and 30 kV, respectively.)

Raman measurements were performed at room temperature using a spectrometer of the type Jobin Yvon T64000, France. In the quasi-back scattering geometry of an Ar laser operating with a power of 200 mW, the 514 nm radiation was focused on a 2 μm spot on the films. Hardness and elastic modulus of the DLC films were evaluated using nano-indenter indentation system (MTS Systems Corporation). Six points was measured for each sample to reduce errors.

Electrochemical experiments were carried out with a standard three-electrode system. A saturated calomel electrode (SCE) was used as the reference electrode with a platinum counter electrode. The corrosion resistance was examined in Hank's solution at $37 \pm 0.5\,°C$ (pH = 7.4). The composition of Hank's solution is given as follows: NaCl 8 g/l, Na_2HPO_4 0.0475 g/l, $NaHCO_3$ 0.35 g/l, KCl 0.4 g/l, KH_2PO_4 0.06 g/l, $MgCl_2$–$6H_2O$ 0.10 g/l, $MgSO_4$–$7H_2O$ 0.10 g/l, $CaCl_2$ 0.18 g/l, Glucose 1 g/l. Potentiodynamic polarization experiments started after the specimen immersed in the experimental solution for an hour under open-circuit conditions and performed at a rate of 20 mV/min.

3. Results and discussion

3.1. Microstructure of the DLC films

Fig. 1 shows a typical Raman spectrum of the DLC films at the bias voltage of 10 kV, which are fitted by Gaussian distribution. All the spectra of the DLC films show similar broad peak at around 1560 cm^{-1} and an obvious lower frequency shoulder at approximately 1350 cm^{-1}, commonly referred to as the G band and D band, respectively. It should be noted that an obvious D peak observed in Fig. 1 is attributed to the carbon particles, which are not completely filtered by the curved magnetic duct. Based on the fitting parameters, the peak position and I_D/I_G (the ratio of the integrated areas under the D and G peaks) are summarized in Table 1. It has been reported that the position of G band is related to the bond-angle disorder or sp^3 bonding content, while the I_D/I_G ratio is correlated with the ratio of sp^3/sp^2 bonds [16–18]. These two factors play the most important role in determining the Raman spectra. The sp^3/sp^2 ratio in the DLC films cannot be derived from the Raman spectra, but some qualitative information can be extracted. The results from Table 2 show that as bias voltage increases from 10 to 30 kV, G

Table 1
PIIID processing parameters for DLC films fabrication

PIIP processing steps	Parameters
Sputter cleaning (Ar)	$P = 6.0 \times 10^{-1}$ Pa $V = 6$ kV $\tau = 60$ μs $f = 100$ Hz $T = 30$ min
DLC deposition (Graphite)	$P = 4.0 \times 10^{-2}$ Pa $V = 10, 20, 30$ kV $\tau = 60$ μs $f = 100$ Hz $T = 2$ h $t = 0.4$ μm

The parameters listed are working pressure (P), pulsed bias magnitude (V), pulse width (τ), pulse frequency (f), duration of the step (T) and film thickness (t).

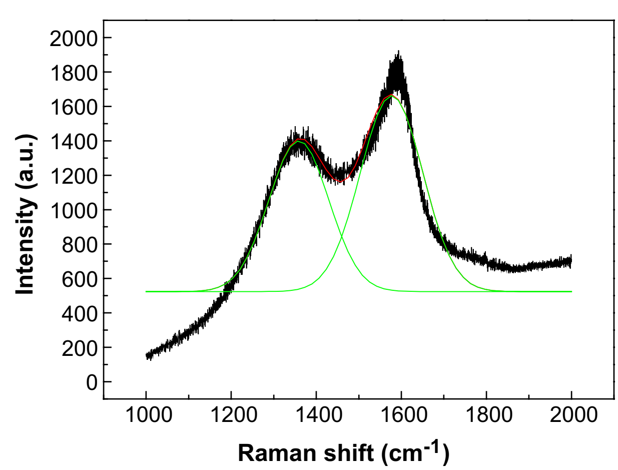

Fig. 1. Raman spectrum of the carbon films fabricated at the bias voltage of 10 kV on the NiTi alloys.