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ScienceDirect
Surface & Coatings Technology 201 (2007) 5194–5197
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Effect of working pressure on the structure and the electrochemical corrosion behavior of diamond-like carbon (DLC) coatings on the NiTi alloys

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Available online 28 August 2006

Abstract

DLC coatings with different working pressure (2×0^{-2}, 6×10^{-2} and 8×10^{-2} Pa) were deposited on polished NiTi alloys by plasma immersion ion implantation and deposition (PIIID) using graphite as plasma source. The results of Raman spectra and X-ray photoelectron spectroscopy (XPS) indicate the sp^3/sp^2 ratio is decreased with the increase of the working pressure. The cross-section microstructure of the DLC coated NiTi alloys indicates that the DLC coating is dense and compact. The corrosion results show that the corrosion resistance of the NiTi alloys is improved by the DLC coating, and the corrosion resistance of the DLC coatings on the NiTi alloys is decreased with the increase of the working pressure. It can be concluded that the sp^3/sp^2 ratio has obvious effect on the corrosion resistance of the DLC coatings.

PACS: 52.77.Dq; 81.05.Uw; 81.65.Rv; 87.64.Je
Keywords: NiTi alloys; Diamond-like carbon; Plasma immersion ion implantation and deposition; Corrosion resistance

1. Introduction

NiTi shape memory alloys have been found widespread applications due to their unique shape memory effect, superelasticity, good corrosion resistance and biocompatibility. The good corrosion resistance and biocompatibility of NiTi alloys is ascribed to the formation of a thin passive film. However, this passive film formed on the NiTi surface is not stable and can be locally destroyed in some specific environments, leading to the occurrence of corrosion. For application in the human body, the corrosion resistance of NiTi alloys becomes extremely important, as the amount and toxicity of corrosion products control the alloy biocompatibility. The Ni content in the alloy is about 50 at.%, and the release of Ni ions in all metallic implants takes place during the corrosion process in the physiological environment [1,2]. 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 [3,4]. There have been reports on the studies of the corrosion resistance of NiTi in simulated human body fluids [5–7]. It has been found that NiTi alloys exhibit poor resistance to localized corrosion in chloride-containing environments, with arguably low pitting potential values. Moreover, the healing of the passive film on NiTi has been reported to be a slow and difficult process. Therefore, the improvement of the corrosion resistance of NiTi alloys is required.

Surface modification of biomaterials is becoming an increasingly popular method to improve the corrosion resistance, which is closely related to the biocompatibility of the materials. Recently, diamond-like carbon has attracted much attention because of its hardness, wear resistance, chemical inertness, low coefficient of friction and good biocompatibility. There have been reports on the corrosion behavior of DLC coated stainless steel [8], Ti [9] and CoCrMo alloys [10,11]. In fact, the corrosion resistance of these alloys is improved by the DLC coatings. However, the reports on the corrosion behavior of DLC coated NiTi alloys are very scarce. In order to take advantage of the bulk properties of NiTi alloys and the surface properties of the DLC, DLC coating is deposited on NiTi alloys by PIIID technique.

In this paper, the effect of working pressure on the structure and the electrochemical corrosion behavior of diamond-like carbon

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doi:10.1016/j.surfcoat.2006.07.164

(DLC) coatings on NiTi alloys is investigated by means of XPS, Raman scattering spectroscopy and potentiodynamic polarization tests. Meanwhile, the corrosion resistance of NiTi alloys is also measured to compare with that of DLC coating. The relationship between corrosion behavior of DLC coatings and its structure was discussed briefly.

2. Experimental

2.1. Fabrication of DLC film

All substrates were cut to $10\times10\times1$ mm^3 from a sheet of cold rolled $Ni_{50.8}Ti_{49.2}$ (at.%) alloys. For all substrates, 10×10 mm^2 surface was polished down to 2000 grit specification and mirror polished with 1 μm diamond paste. 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. Graphite plasma was generated by pulsed cathodic arc plasma source with a curved magnetic duct. The experimental conditions were as follows: temperature, RF power, the cathodic arc pulse duration, the implantation pulse duration and the pulse bias voltage is below 100 °C, 500 W, 1 ms, 60 μs and −25 kV, respectively. The working pressure was varied from 2×10^{-2} to 8×10^{-2} (DLC1, DLC2 and DLC3 are fabricated at 2×10^{-2}, 6×10^{-2} and 8×10^{-2} Pa, respectively).

2.2. Characterization

Raman measurements were performed at room temperature using a spectrometer of the type Jobin Yvon T64000, France. Chemical compositions and carbon–carbon bonding configurations were determined by X-ray photoelectron spectroscopy (PHI-5700 ESCA System) with a monochromatic Al Kα source. A cross-section sample of the coated sample was also prepared for microstructure characterization by mounting the sample by resin and mechanical polishing and then gold coating. Microstructure observation was carried out using scanning electronic microscopy (SEM).

Electrochemical experiments were carried out with a standard three-electrodes 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±0.5 °C (pH 7.4), the composition of which is given in Table 1. Potentiodynamic polarization experiments started after the specimen were immersed in the experimental solution for 1 h under open-circuit conditions and performed at a rate of 20 mV/min.

Table 1
Chemical component of Hank's solution

Component	Concentration (g/l)
NaCl	8
KCl	0.4
$MgSO_4\cdot7H_2O$	0.06
$NaH_2PO_4\cdot2H_2O$	0.06
$NaHCO_3$	0.35
Glucose	1.0
KH_2PO_4	0.6
$MgCl_2\cdot6H_2O$	0.1
$CaCl_2$	0.14

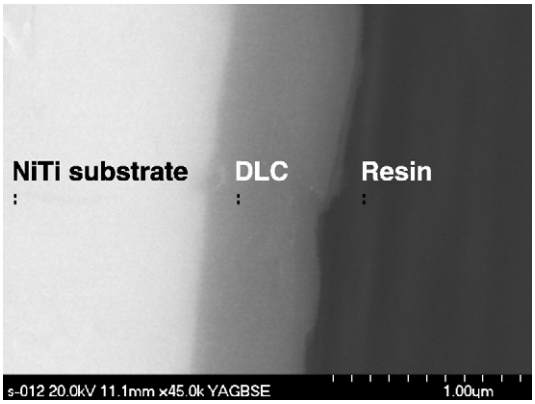

Fig. 1. Raman spectroscopy of DLC coating.

3. Results and discussion

3.1. Structure and composition

Fig. 1 shows a representative cross-section microstructure of the DLC coated NiTi alloys. An even DLC layer about 600 nm thick is clearly observed. Also no pore is found through the whole section of the DLC coating and no interval can be observed at the interface between the DLC coating and the NiTi substrate, which shows that there is a highly dense coating and good interface bonding.

Fig. 2 shows the Raman spectroscopy and the fitting curves for peaks G and D of DLC coatings fabricated by PIIID. The Raman spectra of the coatings show a broad peak at approximately 1560 cm^{-1} and an obvious shoulder at a lower frequency. The broad peak of Fig. 2 can be decomposed into the Gaussians centered at 1530 cm^{-1} (G peak contributed to the graphite carbon)

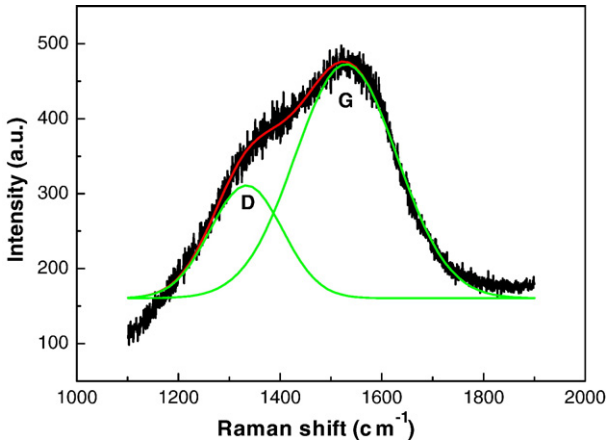

Fig. 2. The position of G peaks and I_D/I_G ratio of the DLC coatings with different working pressure.