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Formation of diamond-like carbon (DLC) film on the NiTi alloys via plasma immersion ion implantation and deposition (PIIID) for improving corrosion resistance

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Abstract

NiTi alloys are potentially useful in biomedical application due to their unique superelasticity and shape memory effect. However, the materials are vulnerable to surface corrosion and the most serious issue is out-diffusion of toxic Ni ions from the substrate into body tissues and fluids. In this paper, Diamond-like carbon (DLC) film is fabricated on the NiTi alloys using plasma immersion ion implantation and deposition (PIIID) at room temperature to improve their corrosion resistance and block the out-diffusion of the Ni ions. The results show that the DLC films cannot only improve the corrosion resistance of the NiTi substrate, but also effectively suppress the Ni ions release from the substrate. The reason that the corrosion resistance of the coated samples is markedly improved due to the DLC films formation is systematically investigated.

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

1. Introduction

The extraordinary properties of the NiTi shape memory alloys have attracted considerable interests in medical applications due to their unique shape memory effects, superelasticity, radiopacity and biocompatibility. The alloy has been used for making self-locking, self-expanding and self-compressing implants, which offers great opportunities for a vast number of applications, from vascular stents to orthodontic and surgical implants [1]. However, several studies reported that NiTi exhibits poor resistance to localized corrosion in chloride-containing environments, with arguably low pitting potential values [2–4]. In addition, the healing of the passive film on NiTi has been reported to be a slow and difficult process. Especially, the toxicity and carcinogenesis of Ni ions released from NiTi alloy are a very concerned problem [5,6]. Therefore, it is necessary to modify the surface of NiTi alloys to improve their corrosion resistance and impede the Ni ions release.

To achieve the goal, different surface treatments were proposed to modify the surface of the alloys to improve the corrosion and biocompatibility. These methods include chemical and electrochemical passivation [7,8], thermal oxidation [9], nitriding [10], laser surface melting [11,12], ion-beam treatment [13], and sol–gel [14]. It is clear that most of the treatment methods listed above have their disadvantages. For example, thermal oxidation and nitriding involves a temperature which is well above 400 °C. Laser surface treatment, though versatile and efficient, is a high-temperature and Ni incorporated in the surface as well as a line-of-sight process. The ion-beam implantation has inherent disadvantages because of its line-of-sight nature. In the present study, the plasma immersion ion implantation and deposition (PIIID) technique is especially suited for the surface modification of NiTi alloy because of its low process temperature and non-line-of-sight, which should not significantly alter the microstructure and bulk properties of the alloy and can treat irregular-shaped samples without complex manipulation. Additionally, because the modified surface layer is compositionally graded, there is no distinct interface between the surface modified layer and the bulk material. This is a critical point because the surface layer must be able to conform to large reversible strains when the

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bulk material transforms. In fact, there have been reports on the surface modification of NiTi alloys using plasma immersion ion implantation [15–20].

Diamond-like carbon (DLC) films have attracted considerable attention due to its high hardness, low friction coefficient, chemical inertness and good biocompatibility. It is coincident that the PIIID technique is one of the methods to synthesize the DLC films, and can directly solve the poor adhesion strength of DLC films unlike other techniques using interlayer [21,22]. Poon et al. have reported the electrochemical corrosion behavior of NiTi alloys using carbon plasma immersion ion implantation and deposition. However, the mechanism of the corrosion resistance for the coated samples has not been clarified. In the present paper, the improvement in the corrosion resistance and suppression of Ni ion release of the coated samples due to DLC films formation is systematically investigated in terms of the cross-sectional microstructure, depth profiles analysis, surface morphology after potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Fabrication of DLC film

All samples were cut to 13 mm × 13 mm × 1 mm from a sheet of cold rolled $Ni_{50.8}Ti_{49.2}$ (at%) alloys. For all samples, 13 mm × 13 mm surface was polished down to 2000 grit specification and mirror polished with 1 μm diamond paste. Fabrication of DLC film was carried out by plasma immersion ion implantation and deposition. Prior to PIIID, the NiTi samples were subsequently cleaned ultrasonically with acetone and alcohol for 10 min and dried in ambient air. 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 layer. C_2H_2 gas was supplied via gas lines controlled by mass flow meters and a RF was applied to the antenna inside the vacuum chamber to ignite the plasma. The detailed experimental conditions are listed in Table 1.

2.2. Characterization

Raman measurement was performed at room temperature using a spectrometer of the type Jobin Yvon T 6400, France. 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). The elemental depth profiles of the DLC coated NiTi alloys were determined by X-ray photoelectron spectroscopy (XPS) with an ion sputter etching method using argon ion-beam.

The corrosion resistance of the coated and uncoated samples in Hank's solution (the composition given in Table 2) at 37 °C was evaluated by electrochemical impedance spectroscopy and potentiodynamic polarization with Potentiostat PARC 273, EG&G Instruments. A saturated calomel electrode (SCE) was used as reference and a Pt foil served as the auxiliary electrode. Prior to the beginning of the potentiodynamic polarization test and EIS, the specimens were kept in the solution for 6 h to obtain a steady value. For EIS study, AC impedance measurements were made with an amplitude of 10 mV about the open-circuit potential for frequency from 100 kHz to 10 mHz. The polarization scan started at 200 mV below E_{OC} and continued in the anodic direction with a potential sweep rate of 0.6 V/h. Samples corroded were rinsed in distilled water and dried in a cold air stream. In order to interpret the corrosion behavior, surface morphology were analyzed with scanning electron microscopy (SEM).

To study the effect of DLC coating on the metal ion release, the coated and uncoated NiTi samples were immersed in Hank's solution at 37 ± 0.5 °C for different days (3, 7, 10 and 20 days). The graphite-furnace atomic absorption spectrometry (AAS) was used to measure the Ni release content of the coated and uncoated samples.

3. Results and discussion

3.1. Structure and depth profile analysis

Fig. 1 shows a Raman spectroscopy of the carbon film. The spectrum of the film shows a broad peak at approximately 1560 cm^{-1} and an obvious shoulder at a lower wavenumer. The broad peak of Fig. 1 can be decomposed into the Gaussian centered at 1555.6 cm^{-1} (*G* peak ascribed to the graphite carbon) and at 1339.8 cm^{-1} (*D* peak ascribed to the disordered graphitic carbon), and the I_D/I_G (denoted as the integral area) ratio for the DLC coatings is 1.38. The spectrum possesses the most dominant characterizations of the typical DLC [23]. This result indicates the film fabricated on the NiTi alloys by PIIID is diamond-like carbon.

Table 1
Working parameters of plasma immersion ion implantation and deposition

Parameters	Value
Working pressure (Pa)	1.5×10^{-2}
Pulse frequency (Hz)	100
Substrate temperature (°C)	<100
RF power (W)	600
Pulse duration time (μs)	60
Time (h)	2
Bias voltage (kV)	25

Table 2
Chemical component of Hank's solution

Components	Concentration (g/l)
NaCl	8
KCl	0.4
$MgSO_4 \cdot 7H_2O$	0.06
$NaH_2PO_4 \cdot 2H_2O$	0.06
$NaHCO_3$	0.35
Glucose	1.0
KH_2PO_4	0.6
$MgCl_2 \cdot 6H_2O$	0.1
$CaCl_2$	0.14