Tantalum coated NiTi alloy by PIIID for biomedical application

Y. Zhou a,b, M. Li a, Y. Cheng a,*, Y.F. Zheng a,c,*, T.F. Xi a, S.C. Wei a,d

a Center for Biomedical Materials and Tissue Engineering, Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, China
b Suzhou Institute of Biomedical Engineering and Technology (SIBET), Chinese Academy of Sciences (CAS), Su Zhou 215163, China
c Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing 100871, China
d Department of Oral and Maxillofacial Surgery, School and Hospital of Stomatology, Peking University, Beijing 100871, China

A R T I C L E   I N F O

Available online 9 November 2012

Keywords:
PIIID
Ta coating
Corrosion resistance
NITI

A B S T R A C T

Plasma immersion ion implantation deposition (PIIID) technique was employed to fabricate tantalum coatings on NiTi alloys with the aim to obtain a more adherent, corrosion resistant and radiopaque coatings in our present study. The surface characteristics and corrosion behavior were investigated by SEM, AFM, XRD, AES, XPS and electrochemical measurement. The results show that a relatively rough, dense and adhesive tantalum coating has been successfully fabricated on NiTi alloy by the PIIID method with the thickness of about 3.3 μm. The surface topography of the tantalum coatings is characterized by regularly spaced grain facets. The coating is combined with a mixture of predominantly α-phase tantalum with a small concentration of β-phase tantalum. The outmost surface of the coating is oxidized, consisting of majority of stoichiometric Ta₂O₅ and a small quantity of Ta₂O₅−x. It can be concluded that the dense and adhesive tantalum coatings on NiTi alloy improve its corrosion resistance, implying the decrease of Ni ions released into human body fluids.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

NiTi shape memory alloys have been widely used as functional materials for industrial and medical applications due to their remarkable shape memory effect (SME), pseudoelasticity (PE), and biocompatibility [1–3]. A potential problem of using NiTi alloys is the release of Ni, which is known to be an allergenic and toxic element though essential to the human body [4,5]. When NiTi alloys are used as stents, guide wires, heart occluders/closure devices, etc., poor radiopacity is another problem, which hinders NiTi devices from being used for minimal access surgery, interventional radiology and flexible endoscopy [6]. Surface modification may be the most promising techniques to solve the above mentioned problems and keep their excellent properties [7–9].

Tantalum is gaining more attention as a new metallic biomaterial due to its excellent corrosion resistance, MRI compatibility, high radiopacity and histocompatibility, as well as bioactive and biologically bonds to bone [10,11]. It has been found in clinical applications in intraluminal stents and orthopedics, including the flexible tantalum cordis stent and porous tantalum [12,13]. Some former studies suggest that Ta films prepared by electrodeposition [14], magnetron sputtering [15], plasma immersion ion implantation (PIII) [16,17] and multi-arc ion plating [18], have greatly improved corrosion resistance of NiTi substrates.

As the PIII technique combines the advantages of plasma immersion ion implantation (PIII) and magnetron deposition methods, which cannot only insure a high bonding strength between the coatings and the substrate, but also enable the deposit of relatively thick coatings [19]. However, to our knowledge, there is no report about the deposition of tantalum coatings on NiTi alloy by this method. In our present work, the PIIID technique was employed to fabricate tantalum coatings on NiTi alloys with the aim of obtaining a more adherent, corrosion resistant and radiopaque coatings. Surface morphology, microstructure, chemical state and corrosion resistance have been investigated.

2. Experimental

2.1. Substrate preparation

The experimental alloy with a nominal composition of Ti–50.6 at% Ni were cut into sizes of 10 mm × 10 mm × 1 mm sheets, polished progressively with 400–2000 grits SiC emery papers and then cleaned ultrasonically in acetone, alcohol and de-ionized water for 10 min, separately, and finally dried in the air before being put into the vacuum chamber.

2.2. Tantalum plasma immersion ion implantation and deposition

The preparation of tantalum films was conducted by using an equipment of plasma immersion ion implantation and deposition
Plasma was generated in the implanter simultaneously by electron cyclotron resonance microwave plasma source at 2.54 GHz. The purity of the tantalum target was 99.97%. The distance between the target and the substrate holder was 120 mm. The base pressure of the vacuum chamber was about $4 \times 10^{-3}$ Pa.

Tantalum and argon ion plasma were excited by impulsing DC power at an input voltage of 380 V with a target current of 1.5 A. Prior to the deposition of the Ta film, the samples were cleaned by Ar ion bombardment at $-2$ kV to remove residual surface contaminants. In order to obtain a more adherent coating, the samples were first treated by plasma immersion and ion implantation processes with a high pulse-biased negative voltage of 17 kV for 10 min. Subsequently, the deposition of relatively thick Ta coatings began at a much lower substrate negative bias voltage of 200 V for 50 min. The working pressure was kept at $8 \times 10^{-2}$ Pa during the preparation process.

2.3. Surface characterization

The coating surface observation was carried out by a scanning electron microscope (SEM; model Nova NanoSEM 430, FEI, The Netherlands); an atomic force microscope (AFM, model Triboindenter, Hysitron, USA) was used to investigate the surface roughness and nanoindentation characters; and X-ray diffraction (XRD) was performed by using a model DMAX-2400 diffractometer (Rigaku, Japan). Surface chemical composition and states were determined by X-ray photoelectron spectroscopy (XPS; model AXIS Ultra, Kratos, UK); and elemental depth profiling analysis was performed with PHI-610 (Perkin-Elmer, US) Auger electron spectroscopy (AES).

2.4. Electrochemical measurement

The electrochemical corrosion behavior was studied with potentiodynamic polarization in a Hank’s solution at $37 \pm 1 \, ^\circ C$ by using an electrochemical analyzer (CHI 650C, CHI, Austin, TX). The sample was set as a working electrode; a platinum electrode acted as an auxiliary electrode; and a saturated calomel electrode (SCE) was used as the reference electrode. The polarization curves were measured from $-600$ mV to 2500 mV with a scan rate of 1 mV/s after the specimen was immersed in the electrolyte for 7200 s ($\text{pH}=7.4$).

3. Results and discussions

3.1. Surface characteristics

The SEM image of the coatings shows a relatively uniform coverage of the NiTi substrate without cracks or droplets. Nevertheless, defects such as pinholes were observed (Fig. 1a). Fig. 1b presents a high resolution of the image of the coating surface, with dense regularly spaced grain facets, which are very similar to the $\alpha$-Ta coating on the rough steel substrate being observed [20]. The cross-sectional morphology in Fig. 1(c) indicates that the tantalum coating is about 3.3 $\mu$m thick and has a good bonding with the NiTi substrate; this is in agreement with the result of AES, as illustrated in Fig. 2. In addition, a transitional interface combined with Ta, Ni and Ti elements produced by PIII can also be observed, which can enhance the bonding strength between the Ta coating and the NiTi substrate, and finally be of benefit to the corrosion resistant property.

Phase microstructure is the most important factor in controlling coating performance. As we have known, there are two distinct crystalline phases or structures of Ta, including $\alpha$-Ta and $\beta$-Ta. A stable, tough and ductile $\alpha$-phase Ta is the common and most desired phase in most applications. The metastable $\beta$-Ta is hard and brittle, the presence of $\beta$-phase Ta may compromise thin film performance. It can be identified from Fig. 3 that the coating consists of predominantly $\alpha$-Ta, with a small concentration of $\beta$-phase tantalum. In

![Fig. 1. SEM images of the tantalum coating surface (a, b) and cross-sectional (c) morphology.](image-url)
order to verify this phase microstructure, nanoindentation hardness curves of the coatings were measured as illustrated in Fig. 3b, and the value was calculated at about 11.9 GPa, which is lower than that of α + β phase as earlier reported [21]. Undoubtedly, this result further proves the correct analysis of XRD, as α-phase tantalum is much softer than the brittle β-phase tantalum. It has been suggested that the crystallographic structure of tantalum is greatly influenced by deposition parameters, purity of sputtering gas, substrate nature, substrate temperature, and substrate bias [22]. In our present study, NiTi substrates were firstly treated by plasma ion implantation with a high pulse-biased negative voltage of 17 kV, which could provide a high energy of ions bombarding during the film deposition, and as a consequence, promote the growth of α-Ta. However, as NiTi alloys have a surface oxide, it is more likely to bring about the formation of β-phase as reported by Feinstein and Hutteman [23].

Fig. 4(a) is the XPS survey spectrum of the surface of the coated sample after 3 min of argon sputtering. Dominant Ta and O elements with residual carbon can be seen, indicating the oxidation of tantalum. The carbon was related to surface contaminants in the atmosphere. The analysis of Ta 4f and O 1s high resolution spectra (Fig. 5(b, c)) can further prove this conclusion. The Ta 4f7/2 line position at 26.1 eV and Ta 4f5/2 at 20.8 eV are typical of the Ta chemical states in Ta2O5 and Ta, respectively. Ta 4f7/2 line position at 24.1 eV proves the presence of the non-stoichiometric tantalum oxide (Ta2O5−x). This is also confirmed by the spectra of O 1s. The XPS results indicate that the outmost surface of the coating is oxidized, consisting of majority of stoichiometric Ta2O5 and a small quantity of Ta2O5−x.

AFM analysis was performed to evaluate the detailed topographical characterizations of surfaces on the micro and nanometer scales. Fig. 5 shows the AFM images for the surface of the Ta coating and the NiTi substrate. In comparison with the Ta coating, the surface of the NiTi substrate is relatively smooth despite some grindings and scratches. Obviously, the deposition of the tantalum coating results in the surface of NiTi roughening with compact and large facet grains, and this topography is much alike with that of α-Ta 50 μm on polished steel substrates as previously reported [20]. The RMS and Ra for the Ta coating are about three times higher than those of the NiTi substrate (21.99 nm compared to 5.36 nm and 17.9 nm to 4.22 nm).

3.2. Electrochemical behavior

Fig. 6 presents the potentiodynamic polarization curves for the Ta coated and uncoated NiTi alloys in a Hank’s solution. Apparently, there is no distinct rapid increase in the anodic current over a wide passive region from the tantalum coated curve, indicating that the Ta coating and its passive film effectively protect the substrate from pitting corrosion. On the contrary, the uncoated NiTi alloy is
characterized by a small passive region extending from $-0.309$ V to 0.416 V. The corrosion potential ($E_{corr}$), the pitting potential ($E_{pit}$) and the corrosion current density ($i_{corr}$) that are calculated from the polarization curves are summarized in Table 1. It can be concluded that the dense and adhesive tantalum coatings on the NiTi alloy improve its corrosion resistance, implying the decrease of Ni ion released into human body fluids. The improvement of the corrosion resistance can be attributed to the dense, adhesive tantalum coatings, which act as a corrosion barrier on the NiTi alloys. The inertness of Ta in contact with body fluids and tissues, and excellent histocompatibility make it useful in biomedical implants and orthopedics. However, as we can see the anti-corrosive improvement is limited, and the thin thickness and the presence of pinholes and metastable $\beta$-Ta of the coatings may account for this phenomenon. We deduce that a 3.3 $\mu$m thick coating is not enough to protect the NiTi substrate from corrosion, especially when there are defects in the form of pinholes, which may provide channels for electrolyte penetration to the NiTi substrate, thereby initiating a localized corrosion that would significantly influence the corrosion resistance of the coatings. In addition, the presence of metastable $\beta$-Ta, although with a low concentration, could also deteriorate the coatings’ corrosion performance.

4. Conclusions

It can be concluded that the dense and adhesive tantalum coatings on the NiTi alloy improve its corrosion resistance, implying the decrease of Ni ions released into human body fluids.

Acknowledgments

This work is supported by the National High Technology Research and Development Program of China (2011AA030103), the National Basic Research Program (973) of China (nos. 2009CB930004 and 2012CB619102) and the National Natural Science Foundation of China (nos. 30870623, 31070846).

References