Surface characterization and mechanical property of TiN/Ti-coated NiTi alloy by PIIID

Y. Cheng, Y.F. Zheng *

Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University,
No. 5 Yi-He-Yuan Road, Hai-Dian District, Beijing, 100871, P. R. China

Available online 27 October 2006

Abstract

A hard and adherent TiN/Ti thin film of approximately 3 μm in thickness was deposited on the surface of Ti–50.6 at.% Ni alloy by the PIIID technique. The surface composition and chemical state of the coated samples were evaluated by XPS. The XPS results indicate that titanium oxide and titanium oxynitride were present on the TiN surface. The spectra of Ti 2p, N 1s, O 1s and C 1s electrons before and after the film being sputter etched were also discussed. Scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS) analyses demonstrate that an interfacial layer, containing Ti, N and Ni, was formed at the interface between the TiN and Ti coatings. Sliding wear tests show that the TiN coating significantly reduces the friction coefficient and improves wear resistance of the NiTi alloy.

© 2006 Elsevier B.V. All rights reserved.

Keywords: TiN film; NiTi alloy; Plasma immersion ion implantation and deposition

1. Introduction

NiTi alloys have been used as construction materials for some surgical implants and instruments because of their novel properties of shape memory effect and superelasticity [1]. However, in these applications, their corrosion and wear resistances are not quite satisfactory. Much effort has been made in the literature to modify the surface of NiTi alloys [2–5]. Among these methods, TiN surface coating is the most frequently used technique, due to its good chemical stability, high hardness, high wear resistance and excellent biocompatibility. TiN coating has been used in a wide range of applications, such as dental prosthesis, heart valve replacement and biosensors [6,7]. TiN surface coating has also been found to encourage bioactivity in biological systems. Piscanec et al. recently reported that calcium phosphate phases grow spontaneously and adhere strongly to the TiN-coated hip prosthesis heads. Such bioactivity is absent in standard uncoated titanium implants [8].

Plasma immersion ion implantation and deposition (PIIID) is a novel method for surface modification, which not only can insure excellent bonding strength between the coating and underlying material but also overcome the line of slight shortcoming. The PIIID technique has experienced rapid development in the recent years to be able to process complex-shaped three-dimensional biomedical devices [9,10]. Yet to our knowledge, there is still no report on the deposition of the TiN coatings on the surface of NiTi alloys by PIIID method.

2. Experimental procedures

2.1. Deposition of TiN coating

The chemical composition of the alloy used is Ti–50.6 at. % Ni. Prior to deposition, plates samples with the size of 1 × 1 × 1 cm³ were first polished to metallographic quality and then ultrasonically cleaned and dried. The coating was conducted using PIIID apparatus. The work chamber was evacuated to 8 × 10⁻⁴ Pa and then purged with Ar gas. The samples were sputter cleaned prior to coating. A thin layer of pure titanium was first deposited on the surface of NiTi sample.
 THEN nitrogen was introduced as the working gas for the formation of TiN. Nitrogen to argon gas flow volume ratio was 1:2, the total pressure was $8 \times 10^{-2}$ Pa. The target current and voltage were kept at 2.4 A and 380 V, respectively. Nitrogen plasmas were generated in the implanter simultaneously by an electron cyclotron resonance (ECR) microwave plasma source at 2.54 GHz. The samples were mounted in the middle of the chamber. The implanting bias charge applied was a square-form high-pulse negative voltage of 20 kV with a duration of $5 \mu$s at a repetition rate of 300 Hz. The deposition bias applied was a dc voltage of $-70$ V. The two bias voltages were applied to the samples for 40 min simultaneously. During this process the temperature was kept at $\sim 250$ °C.

X-ray photoelectron spectrum (XPS) analysis was performed to obtain the in-depth nitrogen, titanium, oxygen and carbon profiles of the TiN coating. Fig. 2 shows the XPS survey of a TiN coating at different depths achieved by sputtering the sample with argon for different times. Signals originating from O 1s, Ti 2p1/2, Ti 2p2/3 and N 1s electrons are easily identified at binding energies of 531, 464, 458 and 397 eV, respectively. The features observed at 1075 and 979 eV correspond to the Auger peaks of Ti LMM and O KLL. It is obvious that the surface of the sample is oxidized. The main component of the C 1s peak at 284.93 eV corresponds to the C–C bonding. This indicates that the carbon detected is related to surface contamination from the atmosphere. With the increase of sputtering time, the C 1s signal also disappears.

Fig. 3 shows the variations of atomic concentration in terms of elemental ratio of the coating. It is seen that the oxygen concentration increases slowly with sputtering time. The carbon concentration decreases sharply from the surface and becomes constant when the sputtering time reaches 500 s. The titanium concentration increases quickly at first and then remains constant at sputtering times greater than 300 s. The nitrogen concentration also increases rapidly with sputtering time initially and then decreases slowly at above 300 s of sputtering time. The nitrogen concentration is higher than that

3. Results and discussion

The SEM image of the cross-sectional morphology of a coated sample and the concentration profiles of Ti, N and Ni are presented in Fig. 1. It is seen from Fig. 1(a) that the TiN coating is relatively uniform without micro-cracks or pores and is fairly adhered to the NiTi substrate. Between the TiN coating and the NiTi substrate, there is a thin layer of pure Ti. The titanium layer appears to serve as a binder between the NiTi substrate and the TiN coating, as shown in Fig. 1(b). In the figure, interface 1 is between the substrate and the Ti layer and interface 2 is between the Ti layer and the TiN coating. The existence of interfaces can improve the adhesion strength of the TiN coating, and can give good compactness of the coating. In addition, the Ti/TiN bilayer film is reported to exhibit excellent corrosion resistance [11].

XPS analyses were performed to obtain the in-depth nitrogen, titanium, oxygen and carbon profiles of the TiN coating. Fig. 2 shows the XPS survey of a TiN coating at different depths achieved by sputtering the sample with argon for different times. Signals originating from O 1s, Ti 2p1/2, Ti 2p2/3 and N 1s electrons are easily identified at binding energies of 531, 464, 458 and 397 eV, respectively. The features observed at 1075 and 979 eV correspond to the Auger peaks of Ti LMM and O KLL. It is obvious that the surface of the sample is oxidized. The main component of the C 1s peak at 284.93 eV corresponds to the C–C bonding. This indicates that the carbon detected is related to surface contamination from the atmosphere. With the increase of sputtering time, the C 1s signal also disappears.

Fig. 3 shows the variations of atomic concentration in terms of elemental ratio of the coating. It is seen that the oxygen concentration increases slowly with sputtering time. The carbon concentration decreases sharply from the surface and becomes constant when the sputtering time reaches 500 s. The titanium concentration increases quickly at first and then remains constant at sputtering times greater than 300 s. The nitrogen concentration also increases rapidly with sputtering time initially and then decreases slowly at above 300 s of sputtering time. The nitrogen concentration is higher than that

Fig. 1. (a) SEM cross-sectional morphology; (b) and EDS spectra scanning along a line in panel a.

Fig. 2. XPS survey spectra of the TiN coating sputtered for different times.
of titanium at the initial stage of sputtering, and it then decreases with the increase of sputtering time. The lower value of the nitrogen concentration at the surface is believed to be due to oxidation, by which nitrogen is replaced by oxygen. The presence of oxygen in these films is attributed to contamination from the residual atmosphere in the vacuum chamber and the oxidation of Ti. This observation is in agreement with that reported by Guillot et al. [12]. It has been reported that the presence of oxygen in TiN coatings can promote the in vivo formation of bone-like materials [8]. This is attributed to the fact that the oxynitride on the surface is favorable for the first step of calcium phosphate nucleation due to the presence of mixed-valence states of the surface Ti atoms which leads to the localization of the negative charge on the oxidized surface.

High-resolution narrow-scan spectra of N 1s, Ti 2p, O 1s and C 1s were recorded at various depths after sputtering for different times; measurements are shown in Fig. 4. The N 1s peak remains at the TiN position with increasing sputtering time (Fig. 4(a)). The Ti 2p spectrum shows a complex structure. In the initial sputtering stage, the curves present broad features without predominant peaks. After 135 s of ion bombardment, a relatively steady state is reached, with two obvious peaks of Ti 2p as shown in Fig. 4(b). The O 1s spectra are shown in Fig. 4(c). The O 1s peak is asymmetric and broad in the early stages of sputtering and gradually evolves to becoming symmetric and sharp with increasing sputtering time. The evolution of the C 1s peak as a function of sputtering time is presented in Fig. 4(d). A strong peak is observed prior to ion sputtering. The peak then gradually diminishes in intensity and finally disappears totally after 330 s of sputtering. This implies that C is present only on the surface.

It is known that the properties of TiN coating are dependent not only on their crystalline structure but also on the short-range chemical environment of Ti and N. Furthermore, due to
the variability of its valence state of and the tendency to form vacancies in its compounds, Ti has a high degree of freedom to form various stoichiometric and non-stoichiometric compounds in Ti–N and Ti–N–O systems. A detailed analysis of TiN coating after 2770 s of sputtering is performed, as shown in Fig. 5. The Ti 2p peak in Fig. 5(a) can be deconvoluted into three groups of doublets, which can be assigned to Ti–N bonds, Ti–N–O bonds and Ti–O bonds, implying the coexistence of three phases of titanium nitride, titanium oxynitride and titanium oxide. The titanium nitride phase can be identified by the 2p 3/2 peak at 455.05 eV and the 2p 1/2 peak at 460.61 eV. The peaks appearing at the binding energies of 456.76 eV and 462.48 eV correspond to Ti 2p 3/2 and Ti 1/2 of titanium oxynitride. Titanium oxide can be assigned by the doublet peaks at 458.25 eV and 463.98 eV. The N 1s line in Fig. 5(b) is asymmetric, having shoulders on the high binding energy side. This peak can be deconvoluted into two peaks. The high-intensity peak at 396.83 eV is representative of N in stoichiometric TiN and the low-intensity peak at a higher binding energy may be attributed to titanium oxynitride (TiN$_x$O$_y$). O 1s spectrum contains three peaks as shown in Fig. 5(c). The main peak centered at 529.69 eV is related to O chemically bonded to Ti. The other two peaks appearing at 531.37 eV and 532.68 eV are assigned to TiN$_x$O$_y$ and hydroxyl groups (O–H).

Fig. 6 shows the friction coefficients of the coated and uncoated specimens. For the coated specimens, the friction coefficient increases rapidly with the number of testing cycles initially and then stabilizes at 0.4. In comparison, the uncoated NiTi sample demonstrates quite different friction behaviour. Its friction coefficient increases rapidly in the initial stage, then decreases with increasing number of cycles, and then increases again at a much slower rate with further testing and finally gets a relatively stable value of 0.6. The friction coefficient of the uncoated NiTi sample is higher than that of the coated sample, indicating that the wear resistance of the TiN coating is better than that of uncoated NiTi.

4. Conclusions

A uniform and adhesive TiN coating was obtained by PIII on NiTi. XPS analysis demonstrates that the coating consists of titanium nitride, oxynitride and oxide. The friction coefficient of uncoated NiTi is higher than that of the coated NiTi, indicating that the wear resistance of the NiTi alloy is improved by the TiN coating.
References