Microstructure, mechanical properties, and blood compatibility of zirconium nitride deposited on nickel–titanium shape memory alloy

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Abstract

ZrN is deposited on electropolished NiTi shape memory alloy to enhance the surface properties. The microstructure, mechanical properties, and blood compatibility are evaluated by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), nanoindentation, and blood platelet adhesion test. The ZrN film has a fine fibrous structure composed of the desirable stable ZrN phase together with a small amount of a second ZrO2 phase. The hardness and modulus values increase initially with larger nanoindentation depths and after reaching maximum values, gradually decrease finally attaining stable values of about 3.4 GPa and 68 GPa, respectively which reflect the composite hardness and modulus values of the system. Our study reveals that the ZrN film may degrade the surface wettablity, but the hemolysis resistance and thromboresistance can be improved thereby making the surface treated materials more suitable in biomedical implants.

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1. Introduction

Recently, zirconium nitride (ZrN) has attracted much attention due to its favorable mechanical properties, corrosion resistance, and warm golden color compared to TiN [1–3]. It has many applications such as hard coatings, coatings for improved corrosion resistance and decoration, and diffusion barriers in microelectronic devices. Zr and N are suitable elements from the perspective of optimization of surface chemistry. Furthermore, ZrN is the most stable nitride and promotes fast osteointegration. Hence, the materials have large potential as multifunctional and biocompatible films on biomedical implants [4,5]. A surface ZrN film can improve the biological safety of biomedical NiTi shape memory alloys (SMA) [6–8] because the ZrN film as a barrier layer can effectively block the leaching of toxic nickel ions from the NiTi substrate into surrounding tissues and fluids thereby improving the biocompatibility of NiTi SMA. For instance, Kiss et al. have reported that ZrN coatings obtained by vacuum arc deposition can improve the corrosion and wear resistance of TiNiNb shape memory alloys [9].

In spite of the large potential, there have been few systematic studies on the microstructural, mechanical, and biomedical characteristics of ZrN coated NiTi SMA. In this work, ZrN films are deposited on electropolished NiTi SMA by magnetron sputtering and the microstructure is studied by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The mechanical properties and blood compatibility are determined by nanoindentation, hemolysis analysis, and blood platelet adhesion test.

2. Experimental details

2.1. Preparation of samples

NiTi (50.8 at% Ni) SMA plates for medical applications were cut into small rectangular blocks with dimensions of 10 mm × 10 mm × 1 mm. The samples were chemically polished for several minutes using a H2O2, HF, and HNO3 solution (5:1:4 ratio in volumes) and then electropolished at a constant voltage of 10 V for 6 min at room temperature in an electrolytic cell with a magnetic stirrer and graphite cathode. The electrolyte consisted of 21 vol.% perchloric acid (HClO4, 70–72 wt.%) and 79 vol.% acetic acid (CH3COOH, 99.5 wt.%). The samples were ultrasonically washed in acetone for 10 min and deionized water for 10 min and then divided into two groups with the first group being the substrate to deposit ZrN films using a reactive DC (direct current) magnetron sputtering system (JGP450A2). A pressure of 1 × 10⁻³ Pa was established prior to film deposition. The carrier gas (Ar) and reactive gas (N2) had purity of 99.95%. The working pressure was set at 0.5 Pa [the ratio of the flux of N2 to the total flux of Ar and N2 was about 6.25:100 and the total gas flow was 30 cm³/min]. The substrates were first cleaned by argon sputtering for 6 min and during deposition. The substrate was heated to 250 °C. It is well known that significant aging occurs above 300 °C in NiTi SMA and may impact the shape memory effect [6,10]. Hence,
the deposition parameters were chosen very carefully in our experiment in order to minimize the influence on the shape memory properties. The DC power was about 150 W which was equivalent to a target DC offset voltage of 280 V. The substrate current was 0.54 A at a substrate biases of −50 V. The distance between the 99.9% pure Zr target and substrate holder was 60 mm. The target was 80 mm in diameter and 3 mm thick and the deposition time was about 60 min.

2.2. Microstructural characterization

The surface and cross section morphologies were evaluated by field-emission scanning electron microscopy (SEM, Sirion 2000, FEI Co.) at 20 kV after the surface was coated with gold to improve electrical conductivity. X-ray diffraction (RAD IIA, Rigaku, Japan) employing the Cu Kα line at 40 kV and 25 mA radiation was used to determine the phase constituents. The samples were analyzed by XPS using a VG Scientific ESCALAB 5 spectrometer with monochromatic Al Kα (1486.6 eV) X-ray radiation. The base pressure in the analysis chamber was better than 10⁻⁸ mbar. Survey spectra in the range of 0–1400 eV were obtained at a 50 eV constant pass energy. High-resolution spectra were also acquired for Zr3d, N1s and O1s using a 20 eV pass energy. The high-resolution XPS spectra were used to determine the chemical states as well as for quantification.

2.3. Nanoindentation

The mechanical properties were evaluated by nanoindentation using a nanoindenter (MTS Nano Instruments XP) with the continuous stiffness measurement (CSM) capability. The experiments were carried out on a Berkovich (three-sided pyramid) indenter. A small-harmonic, high-frequency amplitude was superimposed on the indentation loading and the contact stiffness of the sample was measured from the displacement response at the excitation frequency.

The indentation experiments were conducted in displacement control to a depth of 2000 nm on each sample. The modulus and hardness values were derived instantaneously as a function of depth from the contact stiffness. Load and hardness calibration was performed employing a fused silica reference. At least three indentations were conducted for each group of samples.

2.4. Evaluation of biomedical properties

2.4.1. Hemolysis and water contact angle

The surface contact angles were measured by the liquid drop method using a contact angle goniometer (JC2000B, China). A 10 μl droplet of deionized water was put onto the sample surface to measure the contact angle. Each contact angle was the average of 10 measurements. In the hemolysis test, 8 ml of fresh blood was collected from a rabbit and then diluted with 10 ml of 0.9 wt.% saline. Each sample was put into a test tube containing 10 ml saline and incubated at 37 °C for 30 min. Afterwards, 0.2 ml of diluted blood was added into each test tube and incubation continued for another 60 min. Afterwards, the suspension was centrifuged at 2500 rpm for 5 min. The absorbance of the supernatant fluid was measured by a spectrophotometer (UV240, China). The positive control was a mixture of blood and deionized water and the negative control was a mixture of...
blood and saline. Each hemolysis result was the average of 3 measurements. The hemolysis ratio (HR) was calculated according to the following formula:

$$HR(\%) = \frac{D_t - D_{nc}}{D_{pc} - D_{nc}} \times 100\%,$$

where $D_t$, $D_{nc}$ and $D_{pc}$ are the absorbances of the treatment group, negative control group, and positive control group, respectively.

### 2.4.2. Blood platelet adhesion test

The thromboresistant property was evaluated by the platelet adhesion test utilizing fresh rabbit blood. The samples were put into a 24-well tissue culture plate. A 3.8 wt.% citrate acid solution was added to a blood to citrate acid ratio of 9:1. The solution was centrifuged to form a platelet-rich plasma (PRP) and erythrocyte. 0.1 ml of the PRP was added to each well. After incubation at 37 °C for 3 h, the PRP was taken out from the wells. A phosphate buffer solution (PBS) was added to the wells and gently rinsed 2 to 3 times to get rid of the platelets adsorbing loosely onto the sample surface. The samples were then soaked in 2.5 wt.% glutaraldehyde at room temperature for 12 h to fix the adhered platelets. The samples were then dehydrated in 50 wt.%, 75 wt.%, 90 wt.% and 100 wt.% ethanol for 10 min sequentially. After dehydration, the residual alcohol on the samples was cleaned off in 50 wt.%, 75 wt.%, 90 wt.% and 100 wt.% isooamyl acetate water solutions for 10 min. After critical point drying, the samples were coated with thin gold films and the distribution and morphology of the platelets were observed by SEM.

### 3. Results and discussion

#### 3.1. Microstructure of the ZrN films

The ZrN film deposited on the NiTi surface in this work exhibits a golden color. As shown in Fig. 1(a), the ZrN film has a microscopically porous surface structure in which there are some pores and particles mainly composing of Zr and N as confirmed by energy-dispersive X-ray analysis (EDS) conducted in conjunction with SEM. The cross sectional morphology in Fig. 1(b) indicates that the ZrN film has a fine fibrous structure, is about 2.5 μm thick, and makes good contact with the NiTi substrate.

Fig. 2 depicts the representative XPS survey spectrum acquired from the surface of the ZrN film. The dominant surface elements are Zr, N and O and their concentrations are about 45 at.%, 20 at.% and 50 wt.%, 75 wt.%, 90 wt.% and 100 wt.% ethanol for 10 min sequentially. After dehydration, the residual alcohol on the samples was cleaned off in 50 wt.%, 75 wt.%, 90 wt.% and 100 wt.% isooamyl acetate water solutions for 10 min. After critical point drying, the samples were coated with thin gold films and the distribution and morphology of the platelets were observed by SEM.

Fig. 4. (a) Zr3d and (b) N1s XPS spectra acquired from the surface of the ZrN film.
35 at.% respectively. There is a high surface oxygen content arising from the strong oxygen chemisorption onto Zr and surface contamination when the sample is exposed to air.

Fig. 3 displays the XRD pattern of the ZrN/NiTi structure and the desired ZrN compound is the predominant phase in the film. In the Zr–N system, ZrN is the only stable phase [2]. Here, other metastable phases such as Zr3N6 or Zr2N5 cannot be found. With the exception of the (110) peak corresponding to the intermetallic NiTi substrate phase, the weak peak associated with the (111) and (120) planes of ZrO2 phase is present. The emergence of the second ZrO2 phase can be attributed to strong oxygen chemisorption. Brown et al. have also found that the formation of ZrO2 phase in the ZrN film is due to substitution of N in ZrN by O from the environment [11].

The Zr3d and N1s XPS spectra acquired from the surface of the ZrN film are shown in Fig. 4. The Zr3d spectra can be deconvoluted into four peaks as illustrated by Fig. 4(a). The four different peaks correspond to two different Zr compounds from a doublet consisting of Zr3d5/2 and Zr3d3/2, two peaks for ZrN, i.e., 3d5/2 (179.5 eV) and 3d3/2 (181.9 eV), and two peaks for ZrO2, i.e., 3d5/2 (182.2 eV) and 3d3/2 (184.6 eV). Fig. 4(b) shows one dominant peak at 397.1 eV which can be assigned to N1s of the nitride (ZrN) [12].

3.2. Mechanical properties of the ZrN films

Fig. 5a shows the representative load vs. displacement curves acquired from the different samples by nanoindentation which is a suitable method to determine the mechanical characteristics of thin films [13]. The peak value of the load at a depth of 2000 nm of each sample is different, for example, 200 mN for the electropolished NiTi SMA and 240 mN for the ZrN film. At the same nanoindentation depth, the loads for ZrN are higher than those for electropolished NiTi SMA, indicating that the ZrN film can enhance the load bearing ability of NiTi substrate.

Fig. 5b and c shows the corresponding hardness and Young’s modulus values, respectively obtained from the CSM system. The hardness and modulus values determined from each sample display a similar trend with increasing depths. The hardness and modulus not only depend on the surface films, but also are influenced by the NiTi substrate because the total nanoindentation depth of 2000 nm is larger than or comparable to the thickness of the surface films (a native titania film about 10 nm thick on electropolished NiTi SMA as the control and 2500 nm thick ZrN film).

At the initial stage of nanoindentation, the hardness and modulus values of the electropolished NiTi SMA reach their maximum values of 4.2 GPa and 85 GPa, respectively. This is because the thickness of the native titania film on the electropolished NiTi sample is generally less than 10 nm. The NiTi substrate decreases the hardness and modulus and so with increasing depths, the hardness and modulus finally decrease reaching stable values near 2.7 GPa and 66 GPa, respectively, which reflect the composite hardness and modulus taking into account both the titania film and NiTi substrate.

In comparison, the hardness and modulus values obtained from the ZrN/NiTi system increases initially with nanoindentation depths due to increased densification of the ZrN film. They reach their maximum values of 7.2 GPa and 120 GPa, respectively. Afterwards, they decrease gradually finally attaining stable values of about 3.4 GPa and 68 GPa, respectively, where the indentation depth is comparable to the thickness of the ZrN film, that is, the indenter gradually approaching the substrate surface. Hence, the variation in the hardness and modulus values in this region is the result of the increasing contributions from the substrate that can decrease the numbers. It is reasonable because the ZrN film possesses a porous structure on the nanometer scale (Fig. 1a).

It is obvious that the composite modulus and hardness values derived from the ZrN film and NiTi substrate are higher than those of the electropolished NiTi SMA. This is a big advantage of the ZrN coating. It is a common practice to determine the average properties of the thin film at indentation depths of less than 10% of the film thickness in order to minimize contributions from the substrate [14]. Here, the average hardness and modulus values measured from the ZrN film are about 5.5 GPa and 106 GPa respectively.

3.3. Blood compatibility of the ZrN films

Table 1 lists the hemolysis ratios and water contact angles measured from the EP-NiTi and ZrN/NiTi structure. The hemolysis ratios determined from the two samples are less than 5% suggesting that both samples can meet the requirements for biomedical implants. However, a smaller hemolysis ratio (1.05%) means that less hemolysis occurs on the surface of the ZrN film. The EP-NiTi SMA has relatively better wettability with a small contact angle about 45.3°. It can be attributed to the native titania surface film rich in Ti–OH groups. The contact angle on the ZrN film can reach 70.8°.

The morphology of the adhered blood platelets on the two samples after 3 h of incubation is shown in Fig. 6. The number of adherent platelets on the ZrN film is much less that on the electropolished NiTi SMA. The platelets on the ZrN film form a single layer and are isolated (Fig. 6b). There is no sign of accumulation and only slight pseudopodium can be observed. Hence, platelet adhesion is reduced remarkably on the ZrN film and the thromboresistance of biomedical NiTi implants can be improved by the ZrN film. Ikada et al. [15,16] have reported that the number of adherent cells or platelets on various polymers increases with increasing contact angle up to 70° but decreases above 70°. It is well known now that there is a complex dependence between platelet...

![Fig. 6. SEM morphology of adherent platelets on the sample surfaces after 3 hours of incubation in PRP — (a) EP-NiTi SMA and (b) ZrN film.](image-url)
adhesion and surface wettability. In this study, it is found that although the ZrN film degrades the wettability, but the hemolysis resistance and thromboresistance are improved.

4. Conclusion

The ZrN film deposited on the electropolished NiTi SMA by magnetron sputtering has a fine fibrous structure consisting of mainly the stable ZrN phase as well as a small amount of the ZrO₂ phase which stems from the strong affinity of Zr to oxygen. The hardness and modulus values determined from the ZrN/NiTi system increase initially with larger nanoindentation depths and then reach maximum values. Afterwards, they diminish gradually finally attaining stable values of about 3.4 GPa and 68 GPa, respectively resulting from the synergistic effects of the ZrN film and NiTi substrate. Although the ZrN film appears to degrade the surface wettability, the hemolysis resistance and thromboresistance are enhanced thereby making ZrN coated NiTi more suitable in biomedical implants.

Acknowledgements

The work was jointly supported by Program for New Century Excellent Talents in University (NCET-06-0464) of the Ministry of Education of China, the Natural Science Foundation of Jiangsu Province (Project No.: BK2007515), and the City University of Hong Kong Strategic Research Grant (SRG) No. 7008009.

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