Formation of TiN films on biomedical NiTi shape memory alloy by PIIID

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Abstract

TiN coatings with the characteristics of excellent corrosion and wear resistance, high hardness and good biocompatibility, have received much attention in biomedical applications. Plasma immersion ion implantation and deposition (PIIID) is a novel method that can not only ensure excellent bonding between the coating and underlying material, but also overcome the line-in-sight shortcoming. The aim of the present study is to deposit TiN coatings on the surface of Ti–50.6 at.% Ni alloy by the advanced PIIID method to improve the wear resistance and hardness of a NiTi alloy surface.

Two process parameters, i.e. voltage, and flows of Ar and N₂ were varied in the present experiments. The chemical composition, mechanical and corrosion resistance properties of the samples were investigated using XPS, nanoindentation and electrochemical method. The XPS results showed that the flows of Ar and N₂ had a great influence on the composition of the TiN films. The hardness and elastic modulus of the TiN films increased with an increase of pulse bias voltage and reached a maximum value for films deposited at −20 kV when the flow rate ratio of Ar to N₂ was 2/1. The experimental results revealed that the film preparation parameters directly affected the microstructure of the TiN, and thus influenced the mechanical and corrosion properties of the NiTi alloy, open circuit potential (OCP) values of the specimens increased with the negative pulse bias voltage and reached its maximum value when the flow rate of Ar/N₂ was 2/1. Combined with the results of Tafel and anodic polarization curves, an excellent corrosion resistant TiN coating by PIIID technique could be obtained by varying the process parameters.

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

1. Introduction

Since wear and ion release often take place at the surfaces of bio-metals, such as dental prosthesis, hip implants and heart valve replacements, TiN coatings with the properties of excellent corrosion and wear resistance, high hardness and good biocompatibility, are often used to modify their surface properties [1–6]. Also, it was worth noted that recently, Piscanec et al. [7] investigated the bioactivity of TiN-coated titanium implants and found that tri-calcium phosphate phases grew spontaneously and adhered strongly on TiN-coated hip prothesis heads, demonstrating a degree of bioactivity of the implant surface which was absent in standard, uncoated, titanium implants. To date, NiTi alloy has found numerous clinical applications, but its long-term biocompatibility has not been fully certified and has given rise to controversy due to its high content of nickel [8–10]. Currently, there are some reports on the surface modification by TiN coatings to improve its anti-corrosion property and depress the Ni⁺ ion release [11–13], yet the adhesive strength between the film and substrate uniformity of the coating are questionable. Plasma immersion ion implantation and deposition is a novel method combining the deposition and implantation processes that can not only ensure excellent bonding between the coatings and underlying materials, but also overcome the line-of-sight shortcoming. PIIID has been developed rapidly for complex-shaped three-dimensional biomedical devices [14–16]. However, there is still no report on the deposition of TiN coatings onto the surface of NiTi alloy by the PIIID method. Films grown by various techniques and with differing process parameters differ widely in morphology and microstructure, i.e. in phase, grain size, texture, defects, impurity content, and the state of residual stress, and thus their mechanical and tribological properties vary accordingly [17–20].

In the present experiments, TiN coatings were deposited onto the surface of Ti–50.6 at.% Ni alloy by the advanced PIIID method to improve the corrosion resistance and hardness of the NiTi alloy. Two process parameters, negative pulse bias voltage and nitrogen to argon gas ratio were varied. The chemical com-
position, mechanical and corrosion resistant properties of the samples were investigated using XRD, XPS, nanoindentation and electrochemical method.

2. Experimental procedure

2.1. Substrate preparation

The chemical composition of the experimental alloy was Ti–50.6 at.% Ni. Prior to deposition, the samples were firstly ground using 240, 400, 800, 1200, 2000 grit abrasive SiC papers and then mirror polished with diamond paste. Finally, the specimens were ultrasonically cleaned in acetone, alcohol and distilled water successively and dried.

2.2. Coatings deposition

The PIIID set-up is shown schematically in Fig. 1. To synthesize the TiN film, the work chamber was firstly evacuated to a pressure of $8 \times 10^{-4}$ Pa, then Ar gas was introduced into the chamber. After the specimens were biased to $-1000$ V for 10 min to sputter clean the surface, a thin titanium film was deposited on the surface of NiTi substrate. The nitrogen and argon gas was introduced as work gases to produce TiN coatings. The target current and voltage were kept constant at 2.4 A and 380 V, respectively. Nitrogen plasmas were generated in the implanter simultaneously by electron cyclotron resonance (ECR) microwave plasma source operated at a frequency of 2.54 GHz. The samples were mounted in the middle of the chamber. No external heating or cooling was employed. Square waves high pulse bias voltage with a pulse length of $5\mu s$ at a repetition rate of 300 Hz and $-70$ V dc bias voltage were applied to the samples. The ions are accelerated from the plasma through the sheath directly into the sample. Negative bias voltage and nitrogen to argon gas flow ratios were varied respectively, in order to study their effects on the coated samples. The implantation and deposition time was 40 min.

2.3. Characterization of the deposited films

XPS analysis was performed with an AXIS ultra spectrometer (Kratos, UK) equipped with a focused monochromatic X-ray source (Al $K_{\alpha}$, $h\nu = 1486.6$ eV) operated at 225 W with a corresponding voltage of 15 kV. To compensate for surface charges effects, binding energies were calibrated using C1s hydrocarbon peak at 284.4 eV. Energy resolution was 0.48 eV (Ag 3ds2), and the minimum analytical area was 15 μm.

2.4. Hardness and elastic modulus

Nanoindentation experiments were carried out using a NanoIndenter II (MTS Systems Corp.). The nanoindentor is maturing as an important tool for probing the mechanical properties of small volumes of material. Indentation load–displacement data contain a wealth of information. From the load–displacement data, many mechanical properties such as hardness and elastic modulus can be determined without imaging the indentations.

The hardness values and elastic moduli of the films were measured by nanoindentation using the continuous stiffness measurement (CSM). The instrument monitors and records the dynamic load and displacement of three-sided pyramidal diamond (Berkovich) indenter during indentation with a force resolution of approximately 75 nN and 0.1 nm. Ten indentations were performed on each sample, and the reported hardness and elastic modulus values were the average of 10 measurements.

2.5. Electrochemical tests

Open circuit potential, Tafel curves and anodic polarization plots were obtained using an EG&G Princeton Applied Research Model 283A potentiostat/galvanostat controlled from a computer. The electrochemical measurements were performed in a standard three-electrode cell with 1 cm² platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrolyte was Hank’s solution. All the corrosion experiments were conducted at $37 \pm 0.5$ °C. The anodic polarization curves were obtained with a scan rate of 20 mV/min from $-500$ to $1200$ mV.

3. Results and discussion

3.1. XPS results

In order to investigate the chemical composition of the deposited TiN coatings, XPS was used. Fig. 2 shows the XPS survey spectra of the as-deposited TiN film at $-20$ kV negative pulse bias voltage and 1:2 nitrogen to argon gas ratio. Signals originating from O 1s, Ti 2p, N 1s, and C 1s were clearly seen, and can be identified at binding energies around 529.7, 454.9, 396.3, and 285.2 eV. The features observed at about 1100, 1071, and 974 eV corresponded to the Auger peaks of N, Ti, and O. The carbon was related to surface contaminants in the atmosphere while the oxygen may be due to the surface oxidation during the process of deposition and afterwards exposure to the atmosphere.

Fig. 3 presents the results of the N/Ti atom ratio as derived from the XPS spectra analysis for TiN$_x$ deposited at various
negative pulse bias voltages. The films were sputtered by argon for 30 min. The N concentration in the film decreased slightly with the increase in bias voltage. All the films deposited at $-5$, $-15$, and $-20\, \text{kV}$ were near stoichiometric compositions indicating that the bias voltage had little influence on the chemical composition of the films.

The $\text{N/ Ti}$ atomic ratio of the coatings deposited at different nitrogen to argon gas ratios is shown in Fig. 4. A significant composition variation was observed for these films.

When the nitrogen gas concentration was lower, the $\text{N/ Ti}$ ratio of the coating ($r$) was also lower. In the case of $R = 1:2$, the coating was near stoichiometric. However, a further nitrogen concentration increase in the plasma resulted in a slight decrease of $r$. This result was in agreement with the literature [23], with the increase of nitrogen content, $\text{N/ Ti}$ ratios decrease slightly, which was suggested to the results of the nitrogen molecule incorporation in the films.

### 3.2. Hardness and elastic modulus

Fig. 5 shows the hardness ($H$) and elastic modulus ($E$) of the TiN coatings produced at various pulse bias voltages as a function of nanoindentation depth obtained by the CSM technique. Both the hardness and elastic modulus increased rapidly and reached their maximum values at the initial stage, and then
Table 1
Average values of hardness and modulus for each specimen

<table>
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<th>5 kV</th>
<th>15 kV</th>
<th>20 kV</th>
<th>Substrate</th>
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<tr>
<td>Hardness (GPa)</td>
<td>9.41</td>
<td>23.97</td>
<td>29.21</td>
<td>3.55</td>
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<tr>
<td>Modulus (GPa)</td>
<td>117.32</td>
<td>263.21</td>
<td>276.55</td>
<td>85.599</td>
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<tr>
<td>$H/E$</td>
<td>0.08</td>
<td>0.091</td>
<td>0.105</td>
<td>0.04</td>
</tr>
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</table>

Table 2
Average values of hardness and modulus for each specimen

<table>
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<th>1:3</th>
<th>1:2</th>
<th>2:3</th>
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<tr>
<td>Hardness (GPa)</td>
<td>20.69</td>
<td>29.21</td>
<td>18.70</td>
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<tr>
<td>Modulus (GPa)</td>
<td>197.30</td>
<td>276.55</td>
<td>180.67</td>
</tr>
<tr>
<td>$H/E$</td>
<td>0.104</td>
<td>0.105</td>
<td>0.103</td>
</tr>
</tbody>
</table>

decreased sharply and gradually reached constant values close to the substrate. The abrupt increase of the values at the initial stage was due to some factors including water adsorption, film surface roughness, elastic deformation from both the tip and the sample surface and the intrinsic error of the instrument.

The coating is constrained by the substrate and thus its properties depend on the penetration depth even in a depth smaller than the film thickness, the soft NiTi alloy substrate directly influences the values of hardness and modulus with the displacement into surface. Hardness values and elastic modulus determined as being equal to the relatively flat maximum of the hardness are summarized in Table 1. The hardness and modulus of the coating produced at $-5$ kV were the lowest and increased to 29.21 and 276.55 GPa at $-20$ kV. It has been reported that the hardness and modulus vary over a wide range with the deposition technique and process parameters that determine the microstructure and composition. Results were consistent with the values reported by Rawdanowicz et al. [25]. In addition, an estimation of the $H/E$ ratio was also made. For the lower pulse bias voltage, $H/E$ was equal to 0.08 at $-5$ kV, and for the $20$ kV high pulse bias voltage, the $H/E$ increases to 0.105, such an increase of the $H/E$ ratio indicated a better wear resistance behavior of the coatings. The variations of the hardness and elastic modulus of the coatings should be related to the changes in their microstructure, especially for their phase preferred orientation as a function of pulse bias voltage.

The effect of nitrogen to argon gas ratio on the hardness and elastic modulus is shown in Fig. 6, and the average values are summarized in Table 2. Both the hardness and elastic modulus of the coatings reached the maximum value when the N/Ti gas ratio was 1:2. This maybe attributed to its near stoichiometric composition. As has been reported that the TiN film with the near stoichiometric composition exhibits high hardness value [23].

3.3. Corrosion resistance

The corrosion potential ($E_{corr}$) recorded during immersion at open circuit potential can provide information regarding the possible corrosion reaction processes. Fig. 7 presents results obtained from specimens deposited at different negative pulse bias voltages with a 1:2 nitrogen to argon gas ratio. When the potential reached a relatively stable value, the corrosion potential of the samples coated at $-5$ kV was much lower than that of the samples coated at $-15$ and $-20$ kV, and for the specimens coated at $-20$ kV the corrosion potential was slightly higher than that of the $-15$ kV coated sample. Moreover, the corrosion potential of
the $-5\text{kV}$ coated samples exhibited decreasing tendency with immersion time, whereas the others were shifted to the noble direction. Often, the dissolution of the oxide layer, is indicated by a decrease in $E_{\text{corr}}$ as the sample is immersed in the solution, the increase of $E_{\text{corr}}$ represents the build-up of a passive layer of corrosion products. As a result can suggest that more severe corrosion occurs on TiN-coated sample at $-5\text{kV}$ compared to the other two samples.

Fig. 8 shows the results of $E_{\text{corr}}$ versus immersion time tests for samples coated at different nitrogen to argon gas ratios with $-20\text{kV}$ negative pulse bias voltages. From this figure it can be seen that the N$_2$/Ar ratio affected the corrosion potential significantly. The sample with 1:2 flow rate ratio shifted to the positive direction and reached constant rapidly, and the sample with 1:3 ratio shifted in the negative direction and reached stable value after a relatively long time. Also it was noted that the specimen with 2:3 flow ratio exhibited quite different characteristics compared to others, the corrosion potential exhibits great perturbation with time.

The Tafel plots for the coated samples deposited at different condition are shown in Figs. 9 and 10. The $E_{\text{corr}}$, cathodic ($\beta_c$) and anodic ($\beta_a$) Tafel slopes and the corrosion current densities ($I_{\text{corr}}$) were estimated from the Tafel plots and are summarized in Tables 3 and 4, respectively. The increase of negative pulse bias voltage, the $E_{\text{corr}}$ value increased, the $I_{\text{corr}}$ decreased, indicating an improved corrosion resistance property was obtained with the increase of bias voltage. When the N$_2$/Ar ratios varied, the
sample deposited at 1:2 ratio exhibited excellent corrosion resistance with respect to other samples, suggesting that the nitrogen to argon ratio had a great influence on the corrosion resistance of the coated samples.

Fig. 10 shows the representative anodic polarization curves of the coated (at 20 kV, 1:2 nitrogen to argon ratio) and uncoated NiTi alloys. As can be seen, the coated sample presented a typical passive state curve without pitting potentials in the range of −400 to 1200 mV, indicating that no pitting corrosion occurred. However, for the uncoated NiTi alloy, pitting corrosion occurred at a potential of about 600 mV. Another remarkable difference was a shift of the whole polarization curve towards the region of lower current density for the coated specimen, in particular, the passivation current density was around $10^{-8}$ A cm$^{-2}$, two orders of magnitude lower than that found for the uncoated samples. Clearly, the TiN-coated sample exhibited better corrosion resistance than the substrate.

4. Conclusions

1. The bias voltage had little influence on the N/Ti atomic ratio, whereas the $r$ varied with $R$ significantly.
2. The hardness and elastic modulus values of the coating deposited at −5 kV were lowest and strongly increased to 29.21 and 276.55 GPa at −20 kV with 1:2 nitrogen to argon gas ratio.
3. The negative pulse bias voltage and nitrogen to argon gas significantly affected the corrosion behavior estimated by the immersion test, Tafel extrapolation method and anodic polarization curves. The sample deposited at −20 kV and 1:2 nitrogen to argon gas ratio exhibited excellent corrosion resistant ability compared to other coated and uncoated samples.

References