Surface characterization and electrochemical studies of biomedical NiTi alloy coated with TiN by PIIID

Y. Cheng, Y.F. Zheng *

State Key Laboratory for Turbulence and Complex System, Department of Mechanics and Engineering Science, Peking University, Beijing 100871, China

Received 15 April 2005; received in revised form 27 October 2005; accepted 19 December 2005

Abstract

TiN coatings were deposited on the surface of Ti–50.6 at.% Ni alloy by the advanced plasma immersion ion implantation and deposition (PIIID) technique to improve the wear and corrosion resistances. The surface characteristics and corrosion property of the samples were investigated by atomic-force microscopy (AFM) and electrochemical measurement. The AFM results showed that negative pulse bias voltage and N2/Ar flow rate greatly influence the surface roughness of the TiN films. Combined with the results of Tafel curves, anodic polarization curves and electrochemical impedance spectroscopy, we found that an excellent corrosion resistant TiN coating by PIIID technique could be obtained by varying the process parameters. The sample deposited at −20 kV, with 1:2 nitrogen to argon flow ratio, exhibited excellent anti-corrosion property, which had a more positive value of corrosion potential $E_{\text{corr}}$, a higher value of polarization resistance $R_p$ and a low corrosion current density $I_{\text{corr}}$. An appropriate equivalent circuit model was proposed to describe the corrosion process of the TiN coated samples in the present study.

© 2006 Elsevier B.V. All rights reserved.

Keywords: NiTi alloy; TiN; EIS

1. Introduction

TiN coatings have found wide application in the field of orthopedic, cardiac valves and dental prostheses based on well toleration by the human body and excellent wear resistance [1–4]. Moreover, Piscanec et al. [5] recently found that calcium phosphate phases grow spontaneously and stick strongly on TiN-coated hip prophesies heads, demonstrating a degree of bioactivity of the implant surface which is absent in standard uncoated titanium implants. Up to date, NiTi shape memory 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 [6–8]. Currently, many works have been done to modify the surface property of NiTi alloy [9–13], yet to our knowledge, there is still no report on the deposition of the TiN coatings on the surface of NiTi alloy by the plasma immersion ion implantation and deposition (PIIID) method which is a novel method combining the deposition process with the implantation process that cannot only insure excellent bonding strength between the coatings and underlying materials, but also overcome the line-in-sight shortcoming. PIIID has been developed rapidly for complex-shaped three-dimensional biomedical devices [14–16].

In the present paper, we investigate the influence of the pulse negative bias voltage and the N2/Ar flow ratio on the surface morphology, roughness and the corrosion resistance of the TiN-coated NiTi alloy.

2. Experimental

The chemical composition of the experimental substrate alloy is Ti–50.6 at.% Ni. Prior to deposition, the 1 cm × 1 cm samples were ground and polished, ultrasonically cleaned in acetone, alcohol and distilled water successively and dried. To synthesize the TiN film, the working chamber was firstly vacuumed to a pressure of $8 \times 10^{-4}$ Pa, and then Ar gases were introduced into the chamber. After the specimens were biased to $-1000$ V for 10 min to sputter clean their surface, a thin pure titanium film was deposited on the surface of all NiTi substrates. The nitrogen and argon gases were introduced as working gases to deposit TiN coatings. The target current and voltage were kept at 2.4 A and 380 V, respectively. Nitrogen and titanium plasmas were
generated in the implanter simultaneously by electron cyclotron resonance (ECR) microwave plasma source at 2.54 GHz. Square high pulse negative bias voltage was varied with a length of 5 μs at a repetition rate of 300 Hz and -70 V dc bias voltage were applied to the samples. Keeping the nitrogen to argon gas flow ratio 1/2, the negative bias voltage is set to be 5, 15, 20 and 30 kV, respectively, in batch. And when the negative bias is kept at 20 kV, the nitrogen to argon ratio is varied to be 1/3, 1/2 and 2/3. The total implantation and deposition time was 40 min.

A Nano-ScopeIII (Digital Instruments Inc.) instrument was used for atomic-force microscopy (AFM) of the surfaces. Tafel curves and anodic polarization plots were obtained through 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 electrode as a counter and a saturated calomel electrode (SCE) as reference electrode. The Hank’s solution is used as the electrolyte. All the corrosion experiments were conducted at 37 °C. The anodic polarization curves were obtained with a scan rate of 20 mV/min from −500 to 1200 mV. The measurement of EIS spectra was performed at the open circuit potential. The spectra were recorded in the 0.01 Hz–100 kHz frequency range, with a data density of eight frequency points per decade.

3. Results and discussion

Fig. 1 shows the AFM images of the TiN coatings deposited at different bias voltages, with the uncoated NiTi alloy as a control. It can be seen that the surface morphology of the substrate before coating is smooth. At lower negative bias voltage (5 kV), very large clusters present on the surface with some defects coexisting after coating. At higher voltage (15, 20 and 30 kV), abundant small clusters appear on the surface. In the case of 15 and 20 kV, the surfaces are relatively smooth. In comparison, many deep hole-like defects appear on the surface of the sample treated at 30 kV. The different surface morphologies at different bias voltage may be due to the difference in the energy deposited into the substrate by the incident ions. At lower bias voltage, more energy is dissipated in the near surface region enhancing atomic mobility to form larger cluster. When the bias voltage is increased, the incident ions lose their energies over a larger depth that is unfavourable for the cluster growth, resulting in abundant small clusters formed on the surface. It is worth noted that when the bias voltage is quite high, some defects such as deep holes appear on the surface of TiN coatings. In our opinion, this phenomenon may be due to the strong ion irradiation arising from high bias voltage.

The bias voltage can also affect the surface roughness, as shown in Table 1. The 15 kV samples possesses the smallest roughness corresponding to a root-mean-square (RMS) of 4.591 nm. In contrast, the surface roughness of the 5 kV sample is larger by a factor of 2.45. With the bias voltage increases, the RMS roughness value increases. Based on the above-mentioned results, we can conclude that the pulse negative bias voltage has great influence on the surface morphology and the roughness of TiN coating. Through adjusting the processing parameters, we
Table 1
Surface roughness of TiN coatings as a function of pulse negative bias voltage

<table>
<thead>
<tr>
<th>Samples</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated substrate</td>
<td>4.591</td>
</tr>
<tr>
<td>5 kV</td>
<td>11.223</td>
</tr>
<tr>
<td>15 kV</td>
<td>5.52</td>
</tr>
<tr>
<td>20 kV</td>
<td>8.72</td>
</tr>
<tr>
<td>30 kV</td>
<td>18.894</td>
</tr>
</tbody>
</table>

Table 2
Tafel analysis results of the coated samples at different pulse bias voltage

<table>
<thead>
<tr>
<th>Bias voltage (kV)</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$R_p$ ($\Omega \text{ cm}^{-2}$)</th>
<th>Cathodic Tafel (mV)</th>
<th>Anodic Tafel (mV)</th>
<th>$I_{\text{corr}}$ (A cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-0.310</td>
<td>5.861 $\times 10^4$</td>
<td>4.460</td>
<td>3.99</td>
<td>8.803 $\times 10^{-8}$</td>
</tr>
<tr>
<td>15</td>
<td>-0.294</td>
<td>2.822 $\times 10^6$</td>
<td>6.305</td>
<td>3.23</td>
<td>2.885 $\times 10^{-9}$</td>
</tr>
<tr>
<td>20</td>
<td>-0.194</td>
<td>1.936 $\times 10^6$</td>
<td>5.094</td>
<td>2.691</td>
<td>1.616 $\times 10^{-9}$</td>
</tr>
<tr>
<td>30</td>
<td>-0.337</td>
<td>6.222 $\times 10^6$</td>
<td>6.991</td>
<td>3.222</td>
<td>6.842 $\times 10^{-9}$</td>
</tr>
</tbody>
</table>

can readily optimize the surface topography of the TiN coatings. Quite low (5 kV) and high (30 kV) bias voltage are not favourable for the formation of smooth and uniform TiN coatings.

The atomic-force microscope was used to analyse the influence of the nitrogen to argon gas ratio on the morphology of the coatings, as illustrated in Fig. 2. All the coating surfaces exhibit island morphology. The island size for the coating deposited at $N_2/Ar = 1/3$ is larger than that of other two specimens. The surface of the samples at $N_2/Ar = 1/2$ and $N_2/Ar = 2/3$ show more compact macroscopic structure. The average root mean square (RMS) roughness of the samples are 2.912 ($N_2/Ar = 1/3$), 4.152 ($N_2/Ar = 1/2$) and 4.227 nm ($N_2/Ar = 2/3$), respectively.

The $E_{\text{corr}}$, cathodic ($\beta_c$) and anodic ($\beta_a$) Tafel slopes and the corrosion current densities ($I_{\text{corr}}$) can be estimated from the Tafel plots and are summarized in Tables 2 and 3, respectively. Clearly, we can see that with the increase of negative pulse bias voltage, the $E_{\text{corr}}$ value increases, the $I_{\text{corr}}$ decreases, indicating an improved corrosion resistant property is obtained with the increase of bias voltage. But when the $N_2/Ar$ ratio varies, the sample deposited at 1/2 ratio exhibits the best corrosion resistant property with respect to other samples, suggesting that the nitrogen to argon gas ratio has a great influence on the anti-corrosion property of the coated samples.

Fig. 3 shows the representative anodic polarization curves of the coated (at 20 kV, $N_2/Ar = 1/2$) and uncoated NiTi alloys. As can be seen, the coated sample presents the 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 occurs at the potential about 600 mV. Another remarkable difference is a shift of the whole polarization curve towards the region of the lower current density for the coated specimen, in particular, the passivation current density is around $10^{-8}$ A/cm$^2$, two order of magnitude lower than that found for the uncoated one. Clearly, the TiN
coated samples present better anti-corrosion behaviour than the substrate.

Fig. 4 shows the Bode plots of the coated sample (20 kV) obtained at open-circuit potential after immersion for 30 min in Hank’s solution. The experimental data are shown as individual points, while the theoretical spectra resulting from the fits to the equivalent circuit shown in Fig. 5 are illustrated as lines. The equivalent circuit consists of a solution resistance $R_e$, a capacitance CPE1 and a charge transfer resistance $R_{po}$ for the non-defective coating, and a capacitance CPE2 and a charge transfer resistance $R_s$ for defects in the coatings. It can be seen from Fig. 4 that the lines representing the simulation data coincides well with the experimental data, indicating that a good fitting to the proposed circuit. Although the active pits created via pores are described using the parallel subcircuit (CPE2, $R_s$), the corresponding peak on the phase angle plot cannot be distinguished from the peak at higher frequency clearly, indicating a relatively stable film formed at the pores alleviating the localized corrosion.

4. Conclusions

(i) At lower negative bias voltage (5 kV), very large clusters present on the surface with some defects coexisting after coating. At higher voltage (15, 20 and 30 kV), abundant small clusters appear on the surface. The 15 kV samples possesses the smallest roughness corresponding to a root-mean-square (RMS) roughness of 4.591 nm.

(ii) All the coatings deposited at different nitrogen to argon gas ratio exhibit island morphology. The surface of the sample at $N_2/Ar = 1/2$ and $N_2/Ar = 2/3$ show more compact macroscopic structure. The average root mean square (RMS) roughness of the samples are 2.912 ($N_2/Ar = 1/3$), 4.152 ($N_2/Ar = 1/2$) and 4.227 nm ($N_2/Ar = 2/3$), respectively.

(iii) The sample deposited at $-20$ kV, with 1:2 nitrogen to argon flow ratio, exhibits excellent anti-corrosion property, which has a more positive value of corrosion potential $E_{corr}$, a higher value of polarization resistance $R_p$ and a low corrosion current density $I_{corr}$.

References