Deposition of TiN coatings on shape memory NiTi alloy by plasma immersion ion implantation and deposition

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Received 4 April 2005; received in revised form 20 March 2006; accepted 20 March 2006
Available online 15 May 2006

Abstract

An investigation has been carried out to study the effect of pulse negative bias voltage on the morphology, microstructure, mechanical, adhesive and tribological properties of TiN coatings deposited on NiTi substrate by plasma immersion ion implantation and deposition. The surface morphologies were relatively smooth and uniform with lower root mean square values for the samples deposited at 15 kV and 20 kV negative bias voltages. X-ray diffraction results demonstrated that the pulse negative bias voltage can significantly change the microstructure of TiN coatings. The intensity of TiN(220) peak increased with the increase of negative bias voltage in the range of 5–20 kV. When the negative bias voltage increased to 30 kV, the preferred orientation was TiN(200). Nanoindentation test indicates that hardness and elastic modulus increased with the increase of the negative bias voltage (5 kV, 15 kV and 20 kV), and then dropped sharply at 30 kV. The adhesion between the TiN and NiTi alloy and tribological properties of TiN coated NiTi alloy depend strongly on the bias voltage parameter; the sample deposited at 20 kV possesses good adhesion strength and excellent tribological property.
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Keywords: Titanium nitride; Nickel titanium alloy; Plasma immersion ion implantation and deposition; Hardness

1. Introduction

TiN coatings have found wide applications in the field of orthopedic and dental prostheses based on excellent biocompatibility and wear resistance [1–4]. Moreover, Piscanec et al. 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 [5]. Up to date, the 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]. So far, many studies have been done to modify surface properties of the 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. Plasma immersion ion implantation and deposition is a novel method that combine the deposition process with the implantation process and insure excellent bonding strength between the coatings and underlying materials. PIIID has been developed rapidly for the complex-shaped three-dimensional biomedical devices [14–16]. In order to design coatings with optimal wear and corrosion resistance performance, knowledge of the structure and properties of the coatings and dependence on the process parameters is required. Thus, in the present experiments, TiN coatings were deposited on the surface of a Ti–50.6 at.% Ni alloy by varying the pulse negative bias voltage. Surface morphology, microstructure, hardness, elastic modulus, adhesive strength and wear resistance were evaluated.

2. Experimental details

The chemical composition of the experimental alloy is Ti–50.6 at.% Ni. Prior to deposition, the samples were ground by 240, 400, 800, 1200 and 2000 grit abrasive papers and then polished with diamond paste. Finally, the specimens were ultrasonically cleaned in acetone, alcohol and distilled water, successively, and then dried. The PIIID setup is shown...
schematically in Fig. 1. To synthesize the TiN film, the work chamber was firstly vacuumed to a pressure of \(8 \times 10^{-4}\) Pa, and then Ar gas was introduced into the chamber. Then, the specimens were biased to \(-1000\) V for 10 min to sputter clean their surfaces. A thin pure titanium film was deposited on the surface of NiTi substrate. Nitrogen and argon gases were introduced as work gases to deposit TiN coatings. Nitrogen to argon gas flow ratio was 1:2. 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 an electron cyclotron resonance microwave plasma source at 2.54 GHz. The samples were mounted in the middle of the chamber. No external heating or cooling was employed. Square high pulse negative bias voltage was varied with a length of 5 \(\mu\)s at a repetition rate of 300 Hz and \(-70\) V dc bias voltage were applied to the samples. The negative bias voltages were set to 5 kV, 15 kV, 20 kV, and 30 kV, respectively, in batch. The ions were accelerated from the plasma through the sheath directly into the sample. The implantation and deposition time was 40 min.

A Digital Instruments Nano-Scope III atomic force microscope (AFM) was used for surface observations of samples. The AFM analyses were performed in contact mode using an optical deflection system in combination with silicon cantilevers and tips. Topographic images were recorded over scanned areas of \(5 \times 5\) \(\mu\)m\(^2\), and the scan rate was 1.969 Hz, each with a resolution of 256 \times 256 data points.

The crystalline structure was analyzed by X-ray diffraction (XRD) using Cu \(K_\alpha\) radiation with energy of 40 keV, the patterns were obtained using Bragg-Brentano geometry. Nanoindentation experiments were carried out using a NanoIndenter II (MTS Systems Corp.). The hardness values and elastic modulus of the films were measured by nanoindentation using the continuous stiffness measurement (CSM). The instrument monitored and recorded 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 the ten measurements.

Scratch tests were used to determine the adhesion strength between film and substrate, the scratching speed was 2 mm/min with 50 N/min loading rate. During scratching acoustic emission signal intensity was continuously monitored to determine the critical load (\(L_c\)) to evaluate the adhesive strength, and the results were then verified by optical microscope to determine the value of the critical load. The tribological properties were determined by a ball-on-disk sliding test without lubrication. The counterpart was a GCr15 ball bearing of 1.5 mm diameter. The sliding speed was 0.942 m/min and the normal load was 30 g.

3. Results and discussion

3.1. Surface characterization and microstructure of the coatings

AFM was used to provide independent and direct evidence of the change in the microstructure of the coatings with the negative bias voltage. Fig. 2 shows the AFM images of the TiN coatings deposited at different bias voltages. Obviously, significant morphology differences can be observed. At lower bias voltages (5 kV), some large dish-like defects can be observed on the surface of coating. At higher voltages (15 kV, 20 kV, and 30 kV), the TiN crystallites become abundant but smaller, distributed densely and homogeneously with hemispherical units. In comparison, the surface morphology of the sample treated at 30 kV shows an entirely different pattern, some holes near the boundaries appear between the columnar grains. The different surface morphologies at different bias voltages may be due to the differences in the energy transferred into the substrate by the incident ions. At lower bias voltages, 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. This process is unfavorable for the cluster growth, resulting in a large number of small clusters forming on the surface. It is worth noting 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.

Bias voltage affects surface roughness, as shown in Fig. 3. 15 kV samples possess the smallest roughness corresponding to root mean square values (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 increase of the bias voltage, 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 roughness of TiN coating. Through adjusting the processing parameters, we can readily optimize the surface topography of the titanium nitride coatings. Quite low (5 kV) and high (30 kV) bias voltages are not favorable for the formation of smooth and uniform TiN coatings.

The SEM cross-sectional morphology and the concentration profiles of Ti, N and Ni of the coated sample deposited at 20 kV is presented in Fig. 4. It can be seen from Fig. 4(a) that the nitride titanium coating is relatively uniform without micro-cracks or pores and fairly well adhesive to the NiTi substrate. The pure titanium play a joining role, because reacting with metal substrate and TiN coating as shown in Fig. 4(b), interface 1 between the substrate and Ti coating and interface 2 between Ti and TiN are observed. The existence of interfaces improves the adhesion strength of the TiN coating, and gives a good compactness of the whole coating. In addition, the Ti/TiN bilayer film exhibits excellent corrosion resistance [17]. The thickness of the coatings deposited at different negative pulse bias voltages is listed in Table 1. It can be seen from this table that bias voltage has little effect on the thickness of the coatings. We found that the thickness of the coatings was determined mainly by the deposition time during our experiments.

Fig. 5 shows the diffraction patterns of TiN coatings on NiTi at different bias voltages. The uncoated NiTi substrate is given for comparison. It can be seen from this figure that with the increase of bias voltage, the preferred orientation of TiN changes greatly. The intensity of TiN(220) peak increases with the increase of the negative bias voltage in the range of 5–20 kV, and TiN(111) and TiN(220) peaks are relatively weak. But when the negative bias voltage increases to 30 kV, the preferred orientation is TiN(200), TiN(220) peak almost disappears. Our present experiments demonstrate that the pulse negative bias voltage can significantly change the microstructure of TiN coatings deposited by PIIID technique.

3.2. Nanoindentation hardness and elastic modulus

Fig. 6 shows hardness and elastic modulus as a function of nanoindentation depth obtained by the CSM technique for the coatings deposited at different bias voltages. It can be seen from this figure that when the indenter goes deeper into the coating, the effect of the NiTi substrate becomes evident. Beyond 900 nm, the values of hardness and elastic modulus stabilize at about 3.55 GPa and 85.599 GPa, respectively. It is noteworthy that the maximum values of hardness and elastic modulus of the coatings vary with bias voltage, as summarized in Table 2.
Obviously, hardness and elastic modulus increase with the increase of bias voltage (5 kV, 15 kV and 20 kV), reaching the maximum values at 20 kV. In our opinion, this result may directly relate to the microstructures of the coatings, especially to the TiN phase preferred orientation. The strong increase of TiN(220) preferred orientation with the increase of bias voltage (from 5 kV to 20 kV) may contribute to the increase of hardness and modulus. Whereas, for the 30 kV sample, the preferred orientation transfer to TiN(200) leads to lower hardness and elastic modulus. It is worth noted that the hardness and elastic

Table 1
Thickness of the coatings deposited at different negative pulse bias voltages

<table>
<thead>
<tr>
<th>Negative pulse bias voltage (kV)</th>
<th>5</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>3.04±0.30</td>
<td>2.95±0.29</td>
<td>2.92±0.29</td>
<td>2.87±0.29</td>
</tr>
</tbody>
</table>

TiN(220) preferred orientation with the increase of bias voltage (from 5 kV to 20 kV) may contribute to the increase of hardness and modulus. Whereas, for the 30 kV sample, the preferred orientation transfer to TiN(200) leads to lower hardness and elastic modulus. It is worth noted that the hardness and elastic

Fig. 4. SEM cross-sectional morphology (b) and EDS spectra scanning along a line in (a).

Fig. 5. XRD results of TiN coatings on NiTi substrate at different negative bias voltages.

Fig. 6. (a) Hardness and (b) Elastic modulus of TiN coated NiTi alloy vs. the indentation depth at different pulse bias voltages.
The modulus of TiN coating we obtained is comparable with that reported by other authors [18–20].

An estimation of the H/E ratio has also been made. For the lower pulse bias voltage, H/E is equal to 0.08 at 5 kV, and for the 20 kV high pulse bias voltage, H/E increased to 0.105, such an increase of the H/E ratio could indicate a better wear resistance behavior of the coatings, whereas the H/E drops to 0.061 at 30 kV, indicating poor wear resistance in this case.

3.3. Adhesion strength and tribological property

A popular method for evaluating the strength of the interface between TiN coatings and substrate is the scratch test. The purpose of the scratch test is to determine the critical load Lc needed to strip the coating off the substrate. Fig. 7 demonstrates the critical load of TiN coatings measured from the scratch test at different bias voltages. It can be found that the critical load increases with the increase of bias voltage. It has been reported that the increase of implanting bias voltage will lead to a larger mean projecting range of the incident ions, and therefore, the implanting depth will be larger. Thus, the interfacial mixing effect will be enhanced and will result to a strong adhesion between the coatings and the substrate [21].

Fig. 8 shows the typical morphology of the scratch tracks for samples deposited at 5 kV and 20 kV. For the lower bias voltage sample, large-scale and continuous flaking or spalling on both sides of the scratch channel are observed when the cracks propagate along the interface between the coating and the substrate. Moreover, some coating debris can be seen in the scratch track accompanying severe ploughing trace. Clearly, this damage pattern belong to a kind of flaking (or spalling), suggesting poor adhesion between the coating and the substrate. Yet on the side of scratch channel of 20 kV sample, no flaking is observed, only some minute cracks can be seen. The scratch track is relatively smooth and clean, free of coating debris. This cracking form

Table 2

<table>
<thead>
<tr>
<th>Negative bias voltage (kV)</th>
<th>5</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum hardness (GPa)</td>
<td>9.41</td>
<td>23.97</td>
<td>29.21</td>
<td>8.99</td>
<td>3.55</td>
</tr>
<tr>
<td>Maximum modulus (GPa)</td>
<td>117.32</td>
<td>263.21</td>
<td>276.55</td>
<td>145.5</td>
<td>85.599</td>
</tr>
<tr>
<td>H/E</td>
<td>0.08</td>
<td>0.091</td>
<td>0.105</td>
<td>0.061</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Fig. 7. Critical load of TiN coatings deposited at different pulse negative bias voltages measured from the scratch test.

Fig. 8. Typical scratch channel of TiN coatings deposited at different negative bias voltages (a) 5 kV, (b) 20 kV.

Fig. 9. Friction coefficient curves of the TiN coatings deposited at different pulse negative bias voltages.
failure indicates that the TiN coating adhere to the substrate strongly under this condition.

To investigate the friction and wear characteristic of the coated NiTi alloys, the changes in friction coefficient signal is measured in sliding motion against the GCr15 ball in air environment. Fig. 9 shows the variation of coefficient of friction of different samples, the uncoated NiTi substrate as a comparison. For the coated (deposited at 5 kV, 15 kV and 20 kV), the friction coefficient as a function of contact number of cycles exhibits the same tendency, first increases sharply and then reaches stable value quickly. In contrast, the friction coefficient of 30 kV sample presents quite different behaviour, increases slowly at the initial stage and reaches stable value after 1500 contact number of cycles. In addition, the uncoated NiTi sample demonstrates quite different friction behaviour. A sharp increase followed by an obvious decrease of the friction coefficient is observed during the early stage of friction and then the friction coefficient increases slowly with the increase of the cycles, reaching constant value when the contact number is over 2500 cycles.

We find that the friction coefficient of NiTi substrate is higher than that of the coated samples (deposited at 15 kV and 20 kV), and lower than that of the coated specimens (deposited at 5 kV and 30 kV). The highest and lowest friction coefficients are observed for the films at 30 kV and 20 kV, respectively.

From the above results, we find that the friction and wear resistance of TiN coated NiTi alloy depends strongly on the bias voltage parameter, especially, in some cases, TiN coatings will not benefit for the improvement of wear resistance of NiTi alloys. As it has been reported that the NiTi alloy exhibits good wear resistance [22–25], thus, we should optimize the process parameter to gain ideal TiN coatings. We suggest that the reason for the excellent tribological property of TiN coated at 20 kV may be attributed to the following reason: firstly, the TiN coatings possess very high hardness insuring no significant plastic deformation happened under the contact stress, as hard TiN coating can serve as a protective layer for improving load bearing capacity, therefore avoid producing severe ploughing groove and adhesive abrasion. The second reason is that the smooth surface compared to the other coated samples (5 kV, 30 kV). And the third is that the ion implanting effect improves the adhesion strength between the coating and substrate refraining from the coating delamination during the process of abrasion. In addition, the chemical bond of TiN coating is quite different from that of the GCr15, which makes the coating not liable to adhesion. This also results to a small friction coefficient.

4. Conclusions

Plasma immersion ion implantation and deposition (PIIID) was successfully used to deposit TiN coating on the NiTi shape memory alloy by varying the bias voltage. In the case of 15 kV and 20 kV, the surface morphologies are relatively smooth and uniform with lower RMS roughness values; X-ray diffraction results demonstrated that the pulse negative bias voltage could significantly change the microstructure of TiN coatings. The intensity of TiN(220) peak increases with the increase of negative bias voltage in the range of 5–20 kV. When the negative bias voltage increases to 30 kV, the preferred orientation is TiN(200). Nanoindentation test indicates that hardness and elastic modulus increase with the increase of bias voltage (5 kV, 15 kV and 20 kV), reaching maximum values at 20 kV and then dropping sharply at 30 kV. The adhesion and tribological properties of TiN coated NiTi alloy depend strongly on the bias voltage parameter; the samples deposited at 20 kV possesses good adhesion strength and excellent tribological property.

Acknowledgments

This investigation has been conducted with the financial support of “the Instrumental Analysis Fund of Peking University”. The author acknowledges the collaboration of Dr Chen and other workers for SEM and EDS analyses.

References