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

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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.

Keywords: Titanium nitride; Nickel titanium ally; 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 grounded 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

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schematically in Fig. 1. To synthesize the TiN film, the work chamber was firstly vacuumed to a pressure of 8×10^{-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 μs 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 5×5 μm^2, and the scan rate was 1.969 Hz, each with a resolution of 256×256 data points.

The crystalline structure was analyzed by X-ray diffraction (XRD) using Cu K_α radiation with energy of 40 keV, the patterns were obtained using Bragg-Brentano geometry.

Nanoindentation experiments were carried out using a Nano-Indenter 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 (Lc) 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 negative bias voltage (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

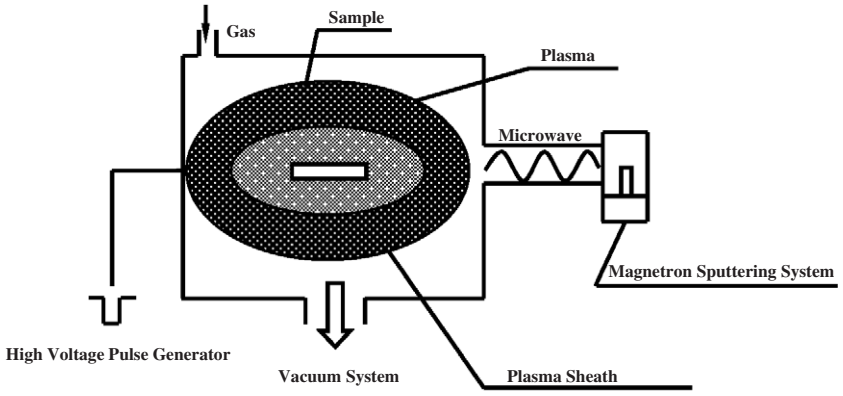

Fig. 1. Experimental set-up.