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Structure and tribological performance by nitrogen and oxygen plasma based ion implantation on Ti6Al4V alloy

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ABSTRACT

Ti6Al4V alloy was implanted with nitrogen–oxygen mixture by using plasma based ion implantation (PBII) at pulsed voltage −10, −30 and −50 kV. The implantation was up to 6×10^{17} ions/cm^2 fluence. The changes in chemical composition, structure and hardness of the modified surfaces were studied by XPS and nanoindentation measurements. According to XPS, it was found that the modified layer was predominantly TiO_2, but contained small amounts of TiO, Ti_2O_3, TiN and Al_2O_3 between the outmost layer and metallic substrate. Surface hardness and wear resistance of the samples increased significantly after PBII treatment, the wear rate of the sample implanted N_2–O_2 mixture at −50 kV decreased eight times than the untreated one. The sample implanted N_2–O_2 mixture showed better wear resistance than that of the sample only implanted oxygen at − 50 kV. The wear mechanism of untreated sample was abrasive-dominated and adhesive, and the wear scar of the sample implanted at −50 kV was characterized by abrasive wear-type ploughing.

1. Introduction

Ti6Al4V alloy is widely used in medicine for dental and non-cemented orthopedic implants due to its good mechanical, chemical properties, high corrosion resistance and biocompatibility [1–3]. However, Ti6Al4V releases harmful ions aluminum and vanadium and have a reputation for poor tribocharacteristics [4–8]. Thus, the surface treatments are necessary in order to prevent or reduce harmful ions and to improve wear resistance.

Plasma based ion implantation (PBII) is an advanced surface modification technique that allows three-dimensional ion implantation in complex shape industrial components [9,10]. There are many studies to show the effect of PBII with nitrogen or oxygen on hardness, wear, composition and structure of Ti6Al4V [11–15]. However, there are seldom studies on N_2–O_2 mixture PBII treatment of Ti6Al4V. Since oxygen ion implantation of Ti6Al4V cannot only oxidize harmful ions aluminum and vanadium but also can form TiO_2 layers that further enhance the bone bonding on the surface of Ti6Al4V implants [15], and nitrogen ion implantation can effectively improve the wear resistance for Ti6Al4V alloy. This paper focuses on the structure and tribological performance of the N_2–O_2 mixture implanted layer on Ti6Al4V alloy.

2. Experimental details

As the substrate materials, commercial Ti6Al4V alloy with a microstructure of-phase plus strip β-phase, was used. The sample of 15 mm × 15 mm × 5 mm size was mechanically grounded and polished to a mirror-finish, and the roughness of Ra was about 1.539 nm measured from atomic force microscopy (AFM). The PBII treatment was carried out in a type DLHZ-01 installation of Harbin Institute of Technology at a base pressure of 3×10^{-3} Pa and a working pressure of 0.09 Pa with oxygen and nitrogen mixture, both of them were 99.999% in purity, the volume ratio of nitrogen and oxygen was 4:1. The samples were sputter-cleaned with 1 kV Ar^+ ions for 20 min before implantation. The oxygen and nitrogen plasma was generated by radio frequency (RF) excitation at 400 W. During the PBII treatment, the sample holder was oil-cooled to achieve a low implantation temperature. The selected implantation conditions are listed in Table 1.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a PHI 5700 ESCA spectrometer employing an Al Kα (1486.6 eV) X-ray source operated at 12.5 kV and 250 W. Depth profiles were obtained by sputtering with a 3 kV Ar^+ ion beam, and analysis and sputtering were performed in an alternating mode. Nanohardness tests were performed by continuous stiffness measurement (CSM) method in a type Nano Indenter XP of American MTS Corporation. The hardness is defined by the ratio of the load to the projected contact area, $H = P/A$. The tribological experiments were conducted on a ball-on -disk tester of a type WTM-2E. Conditions of the tribo-experiments are listed in Table 2. The worn

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Table 1
Process parameters of PBII.

Sample no.	Implanted gas (volume ratio)	Pulse voltage (kV)	Pulse width (μs)	Repeat frequency (Hz)	Implanted dose (10^{17} cm^2)	Implantation time (min)
1	Untreated					
2	N_2:O_2 = 4:1	−10	50	100	6	120
3	N_2:O_2 = 4:1	−30	50	100	6	120
4	N_2:O_2 = 4:1	−50	50	100	6	120
5	O_2	−50	50	100	6	120

Table 2
Conditions of tribo-experiments.

Disk	Ti6Al4V implanted and unimplanted samples
Ball (Ø5 mm)	GCr15 steel
Load (N)	0.196
Diameter of wear circle (mm)	7
Sliding speed (mm/s)	73.3
Environment	Dry air
Temperature	Room temperature

surface morphology was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Composition and structure

Apart from C1s and O1s peaks, the Ti, N and Al peaks are detected by XPS in the wide scan spectra. No V signal is detected. The presence of C may be due to ambient contamination. Fig. 1 shows the results of Ar-ion depth profile of sample No. 4. We can see large quantities of O at the surface. The appreciable decrease in the O concentration and the simultaneous increase in that of Ti after 110 min of ion etch, which indicate the attainment of a kind of an interface between the closely stoichiometric oxide phase and the "diffusion zone" characterized by a gradually decreasing O content. The aluminum is enrichment in the outmost layer, the nominal bulk Al/Ti value is 0.116, while the Al/Ti value of sample No. 4 decrease gradually from 0.24 to 0.115 with the sputter time up to 24 min. Nitrogen content is litter in the outmost but with the increasing of sputter time it has some degree increase.

The XPS spectra presented in Fig. 2 depict the evolution of the chemical state of Ti at various stages of different sputtering time of sample No. 4. On the topmost surface (0 min etch), the position (BE = 458.5 eV) and the shape of the Ti 2p doublet represent the fully oxidized TiO_2 state of Ti [16]. With the increasing of sputtering time, the Ti 2p peaks broaden and shift to lower binding energies, which represent the presence of different titanium oxide. Further, to clearly see the different oxidation states, Gaussian peak-fit is done. Fig. 3 shows the peak-fit of the Ti 2p doublet into different chemical states of Ti. The peaks at 455.0, 456.6 and 458.4 eV are assigned to oxidation states 2+, 3+ and 4+, corresponding to TiO, Ti_2O_3 and TiO_2, respectively [17,18]. Fig. 4 show O1s and N1s spectra, the O 1s peak is located at a binding energy of 530.4 eV and the N1s at 396.8 eV, which denote the presence of Ti-oxide and Ti-nitride [19]. Fig. 5 shows Al2p spectra, the centre of the Al2p peak is located at 74.3 eV, denoting the formation of Al_2O_3 [20].

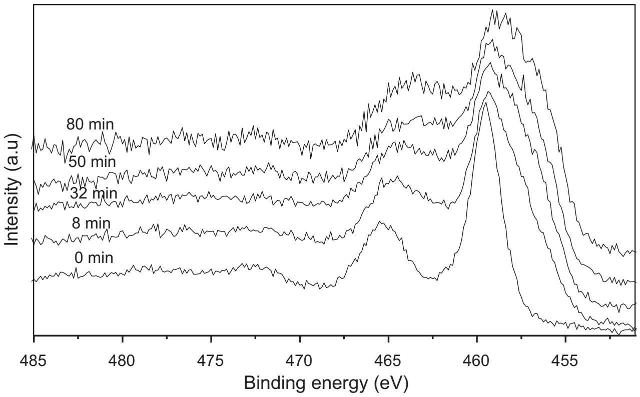

Fig. 2. Ti 2p doublet at various stages of depth profiling of sample No. 4.

The thickness of the modified layers are calculated by the TRIM code [21], the depths of oxygen implanted into Ti6Al4V are 59, 122.4 and 177.5 nm for the pulsed voltage at −10, −30 and −50 kV, respectively. It may be consider when ion implantation is carried under the same implantation voltage, the depths of N_2–O_2 mixture are more close to the depths of oxygen. This can be explaining oxygen diffusion is higher in many materials by either chemical or radiation enhanced segregation effects than nitrogen [22].

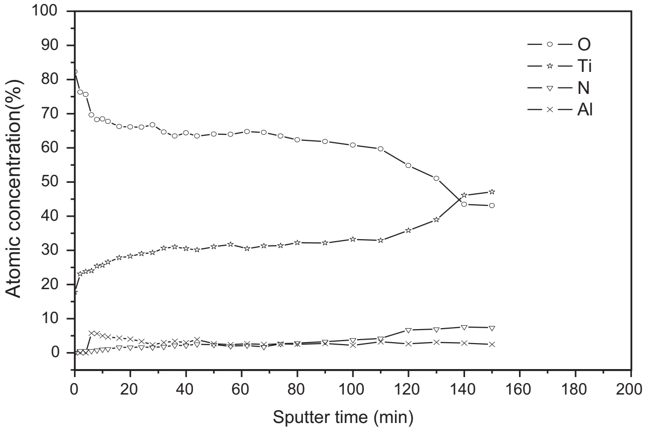

Fig. 1. XPS element depth profile of sample No. 4.

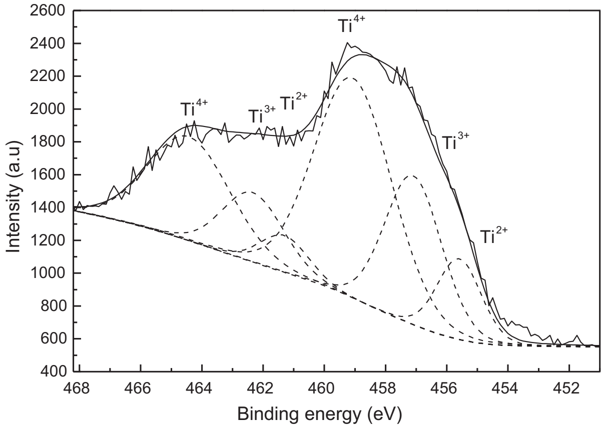

Fig. 3. Ti 2p doublet for sample No. 4 after 40 min of Ar-ion etch.