

Properties of titanium oxide biomaterials synthesized by titanium plasma immersion ion implantation and reactive ion oxidation

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Abstract

As an artificial heart valve material, titanium oxide is superior to low temperature isotropic pyrolytic carbon in terms of mechanical properties and biocompatibility. The irregular shape of a heart valve makes conventional fabrication techniques like beam-line ion implantation and ion beam enhanced deposition (IBED) difficult. Plasma immersion ion implantation (PIII) does not suffer from the line-of-sight limitation and is an excellent technique for this purpose. In this work, titanium oxide thin films are synthesized on Ti6Al4V by titanium metal PIII and oxygen PIII. By controlling the deposition/implantation rate of titanium and oxygen plasma density, TiO_x films with different compositions and properties can be fabricated. The film properties are evaluated by techniques including atom force microscopy (AFM), X-ray diffraction (XRD), and various mechanical testing methods. AFM results reveal that the TiO_x film surface is quite dense without gross voids. The microhardness is enhanced with increasing oxygen partial pressure between the range of 0–3 × 10⁻² Pa and reaches a maximum value of 17 GPa at an oxygen partial pressure of 3 × 10⁻² Pa. The wear resistance is also much better than that of Ti6Al4V. In spite of our encouraging results, the TiO_x films synthesized in our experiments are still too thin. In order to exploit its full potential as an artificial heart valve material, the films must be thicker. It can be achieved by using a more efficient metal arc source or by increasing the PIII duty cycle. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Titanium oxide; Plasma immersion ion implantation; Microhardness; Wear resistance; Microstructure; Surface morphology

1. Introduction

In China, valvular heart failure accounts for 30% of heart diseases and approximately 100 000 patients must have their heart valves replaced every year. Presently, low temperature isotropic pyrolytic carbon (LTIC) is generally regarded to be the best material for fabricating artificial heart valves. However, the material is brittle and its blood compatibility is still not sufficient for prolonged clinical use. As a result, thrombus often

occurs in the patients who must continuously take anti-coagulation medication. Hence, the development of a material with better surface properties and blood compatibility is a real necessity for the biomedical community.

Titanium oxide films are widely used in the optical and electronics industry because of their high refractive index and dielectric constant [1–3]. The blood compatibility of titanium oxide has also been studied in recent years. Rutile type titanium oxide ceramics and thermally oxidized TiO₂ and TiO_x prepared by ion beam assisted deposition generally have good blood compatibility, and it has been found that when the oxide thickness exceeds 40 nm, its blood compatibility is better than that of LTIC [4–8]. Hence, titanium oxide

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is a hopeful substitute for LTIC in artificial heart valves.

Techniques such as thermal oxidization [5], physical vapor deposition (PVD) [1,2,9], and ion beam enhanced deposition (IBED) [6,7] have been proposed to prepare titanium oxide films, but they all have limitations. Thermally oxidized TiO₂ films are typically thin and rough as the formation requires O₂ diffusion through the titanium oxide film. The adhesion of titanium oxide films synthesized by PVD such as sputter deposition is weaker than that of thermally oxidized or IBED TiO₂ films. In addition, conventional plasma processes such as IBED are ‘line of sight’ techniques suitable only to planar substrates. For non-planar samples possessing a complex shape such as artificial heart valves, complicated substrate manipulation is required adding to the process costs and complexity. On the other hand, plasma immersion ion implantation (PIII) circumvents the line-of-sight restriction inherent to conventional beam-line ion implantation, eliminates complex focusing elements in the instrument, is capable of processing large and complex-shaped components, and is potentially more economical [10,11].

Ti6Al4V alloys have attracted much attention as a biomaterial because they possess excellent mechanical properties, corrosion resistance, and plasticity. Thus, TiO_x films on Ti6Al4V alloys should possess the mechanical properties and blood compatibility required for artificial heart valves. In this work, we demonstrate the superiority of titanium oxide films fabricated by PIII utilizing titanium metal plasma and reactive plasma oxidation. By controlling the deposition and implantation rates of titanium and the density of the oxygen plasma, TiO_x films with various compositions and properties can be fabricated. Ti6Al4V was chosen as the substrate in lieu of LTIC for this work because the surface of Ti6Al4V has a natural titanium oxide surface thin film, and so good adhesion between the fabricated TiO_x film and the substrate can be accomplished. The combination of TiO_x and Ti6Al4V yields good blood compatibility as well as mechanical strength.

2. Experimental

Synthesis of the titanium oxide films was conducted in a multi-purpose plasma immersion ion implanter equipped with several plasma generating tools, including radio frequency (RF) discharge, hot-filament discharge, and a vacuum arc metal plasma source [12]. Hence, Ti metal plasma and oxygen gas plasma could be generated at the same time in this instrument. Table 1 lists the instrumental parameters. For samples 1–5, the Ti metal plasma and oxygen gas plasma were generated at the same time. The high voltage pulse on the sample was synchronized with the metal arc pulse. The metal arc pulse duration was 220 μs and the repetition rate was 66 Hz. It enveloped the entire sample high voltage having a pulse duration of 30 μs and pulse repetition rate of 66 Hz. Hence, both Ti implantation (during the 30-μs when the sample high voltage was on) and deposition (during the remaining 220 μs–30-μs = 190 μs of the metal arc pulse) took place on the samples.

When the sample high voltage (–25 kV) was on, oxygen (mostly O₂⁺) was also implanted from the surrounding oxygen plasma into the substrates. During the remaining time, plasma oxidation of the implanted Ti took place as the samples were exposed to the oxygen plasma all the time. For sample 6, Ti metal plasma was generated by the vacuum arc source and oxygen gas was bled into the chamber without igniting the oxygen plasma. Hence, even though Ti was implanted, no oxygen implantation took place on these two samples. During our experiments, the Ti ion flux from the vacuum arc source was constant, but the partial pressure of oxygen in the vacuum chamber was varied to obtain different Ti/O ratios.

Since the surface of the Ti-6Al-4V substrate was too rough to assess the degree of surface roughening by oxygen implantation, two films were deposited on mirror-surface silicon wafers using conditions similar to samples 3 and 6 (Table 1). The surface morphology was studied using atomic force microscopy (AFM) in the

Table 1
Instrumental parameters for samples 1–6

	1	2	3	4	5	6
Cathode Materials	Ti	Ti	Ti	Ti	Ti	Ti
Arc Pulse Duration (μs)	220	220	220	220	220	220
Arc Current (A)	3.5	3.5	3.5	3.5	3.5	3.5
Oxygen Partial Pressure (×10 ⁻² Pa)	0	1.8	3	4.5	15	1.8
RF Power (W)	0	450	450	450	450	0
Sample Voltage (kV)	25	25	25	25	25	25
Pulse Width (μs)	30	30	30	30	30	30
Pulse repetition Rate (Hz)	66	66	66	66	66	66
Base Pressure (×10 ⁻⁴ Pa)	6	6	6	6	6	6
Treatment Time (min)	90	90	90	90	90	90

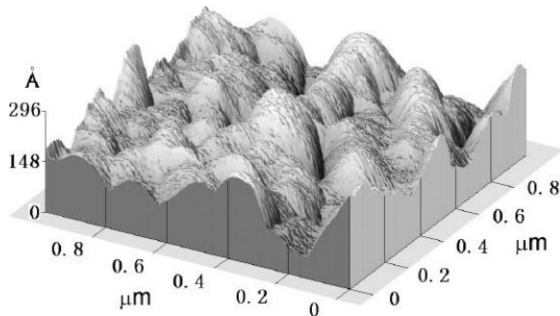


Fig. 1. Contact mode AFM image of Sample 3 (TiO_x on Si).

contact mode. The scans were performed in an area of $1000 \times 1000 \text{ nm}^2$. X-Ray diffraction was employed to determine the phases and structure of the films synthesized on Ti6Al4V substrates. The wear resistance of the films was measured using a pin-on-disc wear tester equipped with a SiN ball 6 mm in diameter. An HXD-1000B digital microhardness tester was operated using loads of 5, 10 and 25 g to assess the microhardness of the samples.

3. Results and discussion

Fig. 1 shows the three-dimensional AFM image of sample 3 (on silicon) and Fig. 2 depicts that of sample 6 (on silicon). Both films were quite dense and do not show gross voids. However, the surface of sample 3 was rougher than that of sample 6. The mean height variation of sample 3 was 18.3 nm compared to 8.9 nm for sample 6. The root-mean-square (RMS) roughness of sample 3 and 6 was 2.98 nm and 2.32 nm, respectively. To confirm the results, two more samples (TiO_x on silicon) were fabricated using the conditions similar to samples 2 and 4. The mean height variations measured on these two samples were 17 and 17.3 nm. This shows that surface roughening was indeed caused by oxygen ion bombardment. However, it is premature to say if this has any impact on the mechanical behavior and biocompatibility of the materials in a patient. More clinical work must be conducted to assess this effect.

Fig. 3 displays the microhardness data acquired from samples 1–6 as well as the untreated substrate Ti6Al4V

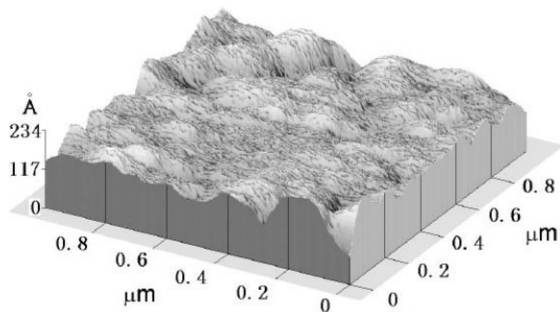


Fig. 2. Contact mode AFM image of Sample 6 (TiO_x on Si).

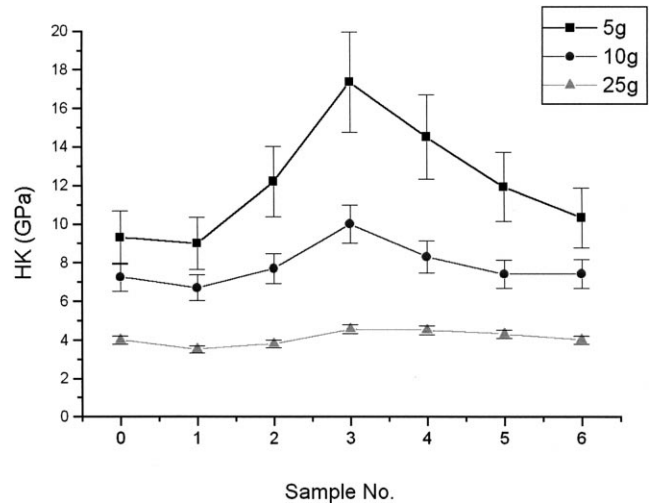


Fig. 3. Microhardness of sample 0 (control)–6 under three different loads.

(sample 0). Because the TiO_x film was quite thin ($< 1 \mu\text{m}$), the measured hardness is affected by the substrate. For example, there was not much difference among the samples when the load was 25 g, because the values basically reflect that of the substrate. In order to truly measure the microhardness of these thin films, a smaller load was used. The microhardness of the TiO_x films was observed to increase with the oxygen partial pressure between the range of $0\text{--}3 \times 10^{-2}$ Pa. When the oxygen partial pressure reaches 3×10^{-2} Pa, the microhardness attains a maximum value of 17 GPa. However, further increase in the oxygen pressure degrades the microhardness. We believe that the increase in the film hardness was due to the development of Ti_3O_5 and TiO_2 phases. As shown in the XRD spectra (Fig. 4), the TiO_2 phase increases with higher oxygen partial pressure. The maximum hardness measured on sample 3 was probably due to the co-existence of Ti_3O_5 and TiO_2 double phases. Our data show that the incorporation of too much oxygen renders the films not as hard, and we speculate that it could be due to the existence of other titanium oxide phases. We are investigating this behavior in more detail and will report our results later.

As some artificial heart valves are currently made of Ti6Al4V, we compare the wear resistance between sample 3 and the control (untreated Ti6Al4V substrate). Table 2 shows the wear track widths after pin-on-disk wear test using 25 g load/1500 rotating cycles, 50 g load/1500 rotating cycles, as well as 25 g load/5000 rotating cycles. Sample 3 shows smaller track widths than Ti6Al4V, especially for 25 g load/1500 rotating cycles. However, the difference between the two samples was smaller for the other two pin-on-disk conditions, further illustrating that the film was too thin to withstand a large load.

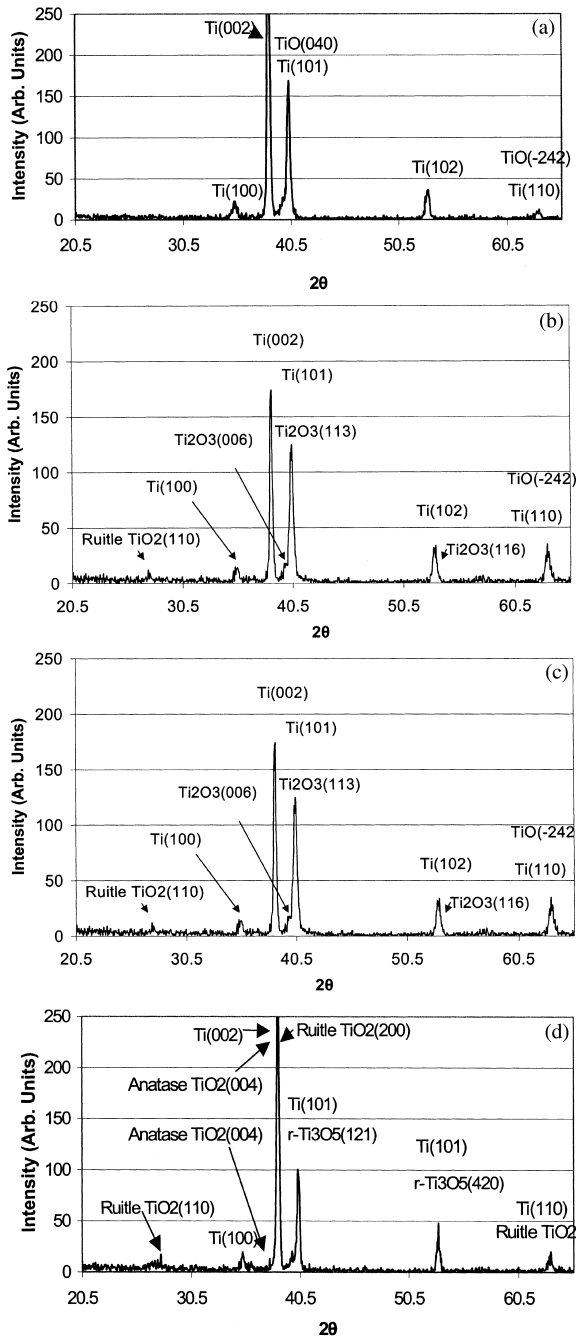


Fig. 4. X-Ray diffraction patterns of: (a) Ti6Al4V; (b) Sample 1; (c) Sample 2; and (d) Sample 3.

Fig. 5 is a qualitative illustration of the experimental microhardness profiles of sample 3 and the untreated

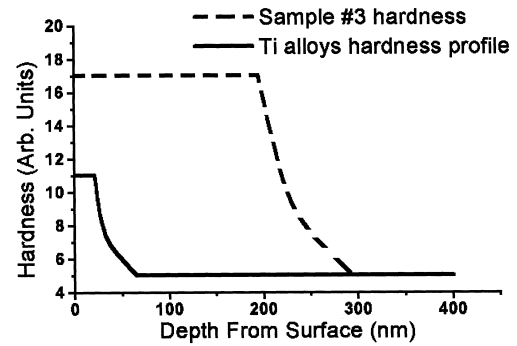


Fig. 5. Schematic of the microhardness profiles of sample 3 and control.

sample (control sample). On the surface, the microhardness was high due to the surface TiO_x film and the shear strength was directly proportional to the hardness. When we apply a load on the sample while it was rotating, the sample experiences a shear stress, and the measured results are exhibited in Fig. 6. The untreated sample exhibits substantial wear in spite of the thin native oxide on the surface. Severe plastic deformation of the subsurface was apparently the main reason for the rapid wear.

When the load is small, such as 25 g, the local shear strength is greater than the local maximum shear stress, and so, shear plastic deformation was not possible and shearing was limited to the near surface zone. Hence, wear occurs quite slowly throughout the 25 g/1500 rotating cycles test. After 1500 rotations, some TiO_x was worn, and the shear stress exceeds the local shear strength in the TiO_x-substrate interface (between points A and B in Fig. 6). Consequently, plastic deformation results leading to the rapid wear degradation, and there is little difference on the wear width compared to the Ti alloy in the 25 g load/5000 rotating cycles test. When a 50-g load is applied, the shear stress exceeds the local shear strength of the TiO_x-substrate transition zone (between A and B for Sample 3 or A and C for Ti

Table 2
Wear track widths of sample 3 and the control sample

	25 g load, 1500 rev.	50 g load 1500 rev.	25 g load 5000 rev.
Sample 3	22 μm	410 μm	530 μm
Ti6Al4V	470 μm	620 μm	700 μm

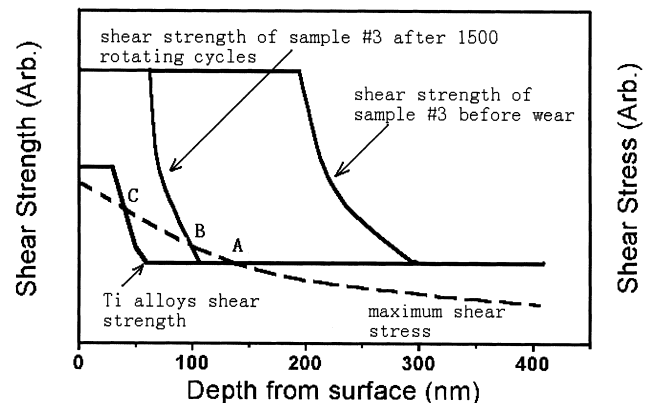


Fig. 6. Schematic of the shear yield strength and shear stress profiles under an applied load of 25 g for sample 3 and control.

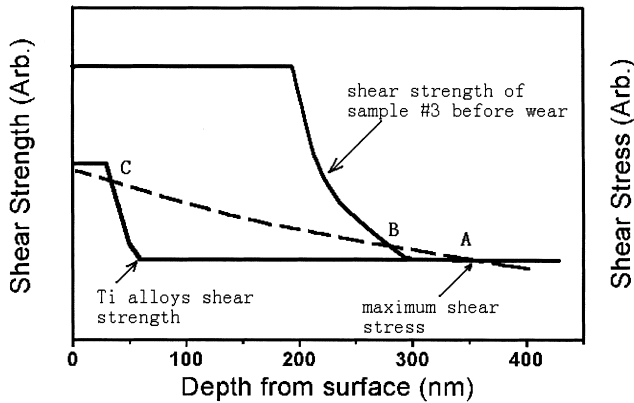


Fig. 7. Schematic of the shear yield strength and shear stress profiles under an applied load of 50 g for sample 3 and control.

alloy), as shown in Fig. 7. Plastic deformation of the subsurface was again the main wear mechanism. The solution to this was to increase the film thickness [13]. It can be achieved by increasing the duty cycle of the PIII experiments and the Ti ion flux (more efficient vacuum arc source).

4. Conclusion

Titanium oxide thin films were synthesized by titanium and oxygen plasma immersion ion implantation. The films were dense and do not exhibit gross voids illustrating that the Ti metal and oxygen PIII method produces good results. The microhardness of the TiO_x films increases with higher oxygen partial pressure in the range of $0\text{--}3 \times 10^{-2}$ Pa. A maximum microhardness of 17 GPa is achieved at an oxygen partial pressure of 3×10^{-2} Pa. The TiO_x films have better wear resistance than Ti6Al4V under a small load. In order to

fully exploit the full potential of titanium oxide as an artificial heart material, the films must be thicker, thereby requiring a higher PIII duty cycle and more efficient metal arc sources.

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