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Methane and nitrogen plasma immersion ion implantation of titanium metal

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Abstract

Plasma immersion ion implantation (PIII) is employed to enhance the tribological properties of titanium. The effectiveness of methane PIII and glow discharge nitrogen PIII, as well as radio-frequency (RF) nitrogen PIII, is compared by measuring the microhardness, mass loss due to wear and the coefficient of friction of samples treated by the three methods. Nitrogen PIII is a hybrid surface treatment technique combining nitrogen-ion implantation, which occurs during the high-voltage pulses, and plasma nitriding, which takes place in between pulses. Our experimental data show that the surface properties of titanium are enhanced by all three treatment processes, but nitrogen PIII yields better results than methane PIII, and RF nitrogen PIII is the best treatment process of the three. On the basis of our Auger depth profiling results, the discrepancy appears to be related to the larger penetration depth (implantation plus radiation-enhanced diffusion) of nitrogen by the RF PIII process. The slight difference between methane PIII and glow discharge nitrogen PIII samples appears to arise from the absolute implanted dose. © 1998 Elsevier Science S.A.

Keywords: Plasma immersion ion implantation; Plasma nitriding; Titanium

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1. Introduction

Titanium has many excellent features such as high strength-to-weight ratio, good high-temperature properties, and excellent corrosion resistance and biocompatibility. Hence, it is widely used in prosthetic devices and aerospace components. Unfortunately, it is prone to wear because of its poor tribological properties and premature wear–corrosion failure can occur in the field. Conventional nitrogen-ion implantation has been shown to substantially improve the hardness and wear resistance of titanium and its alloys. However, being a line-of-sight process, it is very difficult to process components of an irregular or odd shape by conventional beamline ion implantation and the associated cost can be quite high [1–5].

Plasma immersion ion implantation (PIII) circumvents the line-of-sight drawback and is a viable technique to enhance the tribological properties of titanium and its alloys for biomedical applications [6–10]. Nitrogen PIII is a hybrid surface treatment technique combining nitrogen-ion implantation, which occurs during the high-voltage pulses, and plasma nitriding, which takes place in between pulses. It has been shown that after nitrogen PIII treatment at 550 °C, the tribological properties of titanium and its alloys are greatly improved because of the nitriding action and formation of a TiN superhard layer on the surface [11]. In a similar fashion, methane PIII treatment can also improve the tribological properties of titanium and its alloys by forming a TiC superhard layer on the surface. In this work, we investigate the efficacy of three treatment methods: methane PIII, glow discharge nitrogen PIII and radio-frequency (RF) nitrogen PIII, by measuring the microhardness, mass loss due to wear, and coefficient of friction of the modified samples.

2. Experimental

The experiments were performed in a custom-designed plasma immersion ion implanter. Its main vacuum chamber is a stainless steel cylinder 100 cm in diameter and 120 cm in height. A 13.56 MHz, 2 kW RF plasma source is placed on top of the chamber and the plasma

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produced in the discharge chamber diffuses into the main vacuum chamber from the top discharge chamber. The characteristics of the plasma immersion ion implanter have been described elsewhere [12,13]. The RF instrumental conditions were: nitrogen pressure 8.0×10^{-1} Pa, RF input power 300 W, implantation voltage 35 kV, pulse repetition rate 200 Hz, and pulse duration 10 μs. For the glow discharge experiment, four sets of multifilament electron guns in the vacuum chamber were used to emit electrons to ignite the uniform gas discharge plasma in the entire vacuum chamber. The gas discharge plasma parameters were: nitrogen pressure 2×10^{-2} Pa, filament heating current 50 A, discharge voltage 110 V, implantation voltage 35 kV, pulse repetition rate 200 Hz, and pulse duration 10 μs.

Test specimens, 15 mm in diameter and 3 mm in thickness, were sectioned from a 20 mm diameter pure titanium bar and underwent a series of grinding and polishing processes. The final surface roughness was approximately 0.06 μm "peak-to-valley" and was achieved by a polishing step with a Mastermet Colloidal Silica suspension. These specimens were chemically and ultrasonically cleaned prior to the implantation experiments. They were divided into four groups. The first group consisted of the untreated titanium samples and constituted the control. The other samples were treated by methane PIII, glow discharge nitrogen PIII or RF nitrogen PIII; the treatment parameters are listed in Table 1. No additional heating was applied to the samples on top of in situ heating by the plasma, and the processing temperature was below 400 °C throughout our experiments. The average implantation current density was about 200 μA cm^{-2}.

The microhardness measurement was conducted with a fully automated mechanical properties microprobe (MHT-4 Microhardness Tester) to make ultralow load microindentation hardness measurements. Indentations were made normal to the sample surface. The applied loads were 2 gf, 4 gf, 6 gf, 8 gf and 10 gf. Each indentation was for 5 s. Impression sizes were measured with a Zeiss optical microscope and the calculated microhardness is the average value from five indentations for each sample. An unlubricated pin-on-disc tribological test was performed to measure the coefficient of friction for the treated and untreated titanium samples. The wear track was 7 mm in diameter, the applied load was 30 gf, the rotation speed was 42 cycle min^{-1} and the pin was made of ruby. Elemental depth profiles were acquired by Auger electron spectroscopy (AES). An argon-ion beam was accelerated to 4 kV to sputter the samples incrementally, to disclose the elemental depth distributions.

3. Results and discussion

In order to examine the change in tribological properties, the microhardness, mass loss due to wear and coefficient of friction were measured on treated and untreated titanium samples. Fig. 1 shows the microhardness data of the untreated and treated titanium samples at various applied loads. It can be observed that the microhardness decreases with increasing load, indicating that a harder region has formed in the near-surface layer. All three treatment techniques are shown to improve the microhardness of titanium, and separate X-ray photoelectron spectroscopy (XPS) results confirm the formation of partial TiN or TiC layers on the surface of the treated titanium samples. The titanium sample treated by RF nitrogen PIII possesses the highest micro-

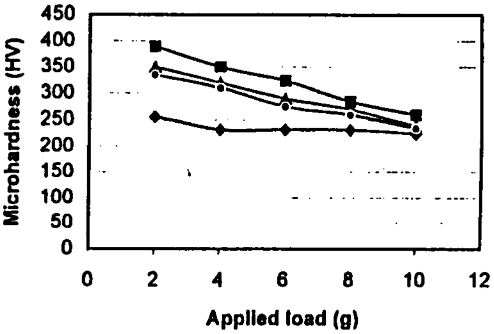

Fig. 1. Microhardness of the untreated and treated titanium samples at various applied loads (◆, untreated sample; ●, methane PIII; ▲, glow discharge nitrogen PIII; ■, RF nitrogen PIII).

Table 1
Treatment parameters

Group	1	2	3	4
Treatment technique	Control (untreated)	Methane PIII	Glow discharge nitrogen PIII	RF nitrogen PIII
RF input power (W)				300
Working gas		CH_4	N_2	N_2
Implantation voltage (kV)		35	35	35
Pulse duration (μs)		10	10	10
Repetition rate (Hz)		200	200	200
Treatment time (h)		3	3	3
Implantation dose (10^{17}/cm^2)		5.8	6.3	5.7

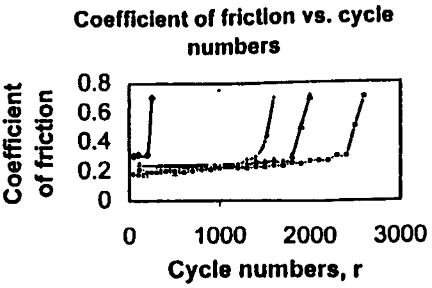

Fig. 2. Variation in the coefficients of friction with number of sliding cycles for the treated and untreated titanium samples (◆, untreated sample; ●, methane PIII; ▲, glow discharge nitrogen PIII; ■, RF nitrogen PIII).

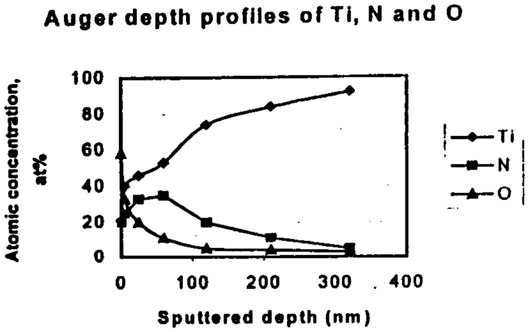

Fig. 3. Auger depth profile of the titanium sample treated by RF nitrogen PIII.

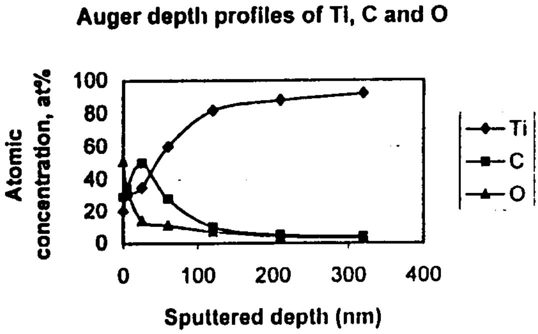

Fig. 4. Auger depth profile of the titanium sample treated by methane PIII.

hardness. Compared with the other two techniques, glow discharge nitrogen PIII yields slightly higher microhardness than methane PIII probably because the experimental nitrogen dose is higher than that of carbon (Table 1).

The mass loss due to wear was measured with a pin-on-disc wear tester and a precision balance. The measured mass losses after a 125.66 m wear track for both the treated and untreated samples are listed in Table 2. It can be seen that all three treatments can effectively decrease the mass loss due to wear, and there is a correlation between the mass loss due to wear and the surface microhardness.

The variation in the coefficients of friction with the number of sliding cycles for the treated and untreated titanium samples is displayed in Fig. 2. The measured coefficient of friction for the untreated titanium sample is 0.7, and the coefficients of friction for the other three treated samples are lower. The coefficient of friction at the beginning is about 0.16 for the methane-PIII-treated titanium sample, and layer breakthrough occurs at 1600 cycles. The coefficient of friction is 0.18 for the other two treated titanium samples, but the breakthrough behaviour of the glow discharge nitrogen PIII sample and RF nitrogen PIII sample is different. It occurs at 2000 cycles for the former sample but at 2600 cycles for the latter specimen, and the results are in line with the microhardness improvement.

For further investigation, elemental depth profiles were acquired by means of AES. The results are depicted in Figs. 3 and 4. Fig. 3 reveals that the maximum implanted nitrogen concentration is about 35% at a depth of approximately 60 nm for the sample treated by RF nitrogen PIII. The total implantation depth (modified layer thickness) is about 220 nm and the presence of a partial TiN layer is indicated. The maximum implanted carbon concentration of the methane PIII sample exhibited in Fig. 4 is approximately 50% at a depth of 25 nm, but the total implantation depth is only about 120 nm — i.e., about half of the thickness of the modified layer in the RF nitrogen PIII sample. The fact that we have obtained better tribological data from the RF nitrogen PIII sample suggests that the total implantation/radiation-enhanced diffusion depth, rather than the absolute concentration, is more critical. It is believed that the RF plasma has a higher ion density and better chemical activation can be achieved, resulting in a thicker modified layer. The current findings are

Table 2
Mass loss due to wear and microhardness of the treated and untreated titanium samples

Group	1	2	3	4
Treatment technique	Control (untreated)	Methane PIII	Glow discharge nitrogen PIII	RF nitrogen PIII
Mass loss due to wear (mg)	3.6	1.6	1.4	1.0
Microhardness (2 gf load) HV	256	335	350	390

consistent with our previous results for Ti–6Al–4V alloy and 45# carbon steel [14,15].

4. Conclusion

Methane PIII, glow discharge nitrogen PIII and radio frequency nitrogen PIII improve the tribological properties of titanium metal, such as microhardness, mass loss due to wear and coefficient of friction. RF nitrogen PIII yields the best results, and the superiority appears to be due to the thicker modified layer, i.e., larger combined implantation/radiation-enhanced diffusion depth. It is believed that the RF nitrogen plasma has a higher ion density and better chemical activation, to allow a deeper penetration of nitrogen into the sample. When comparing glow discharge nitrogen PIII and methane PIII, the former treatment yields slightly better results that can probably be attributed to the higher implanted dose.

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References

[1] B.L. Garside, Mater. Sci. Eng. A 13 (11) (1991) 179.
[2] D.M. Ruck, H. Schmidt, N. Angert, O. Yoda, Y. Aoki, H. Naramoto, in: Proceedings of the Ninth International Conference on Ion Beam Modification of Materials, Canberra, Australia, 5–10 February 1995, p. 1016.
[3] P. Sioshansi, R.W. Oliver, F.D. Matthews, J. Vac. Sci. Technol. A 3 (6) (1985) 2670.
[4] G. Dearnaley, N.E.W. Hartley, Thin Solid Films 54 (1978) 215.
[5] W.C. Oliver, R. Hutchings, J.B. Pethica, Metall. Trans. A 15 (1984) 2221.
[6] J.A. Chen, J.T. Scheure, C. Ritter, R.B. Alexander, J.R. Conrad, J. Appl. Phys. 70 (11) (1991) 6757.
[7] B.Y. Tang, Phys. 23 (1994) 41.
[8] J.R. Conrad, Mater. Sci. Eng. A 116 (1989) 201.
[9] J.R. Conrad, R.A. Dodd, S. Han, M. Madapura, J.T. Scheure, K. Saidaram, F.J. Worzala, J. Vac. Sci. Technol. A 8 (1992) 3146.
[10] J.R. Conrad, J.L. Radtke, R.A. Dodd, F.J. Worzala, N.E. Tran, J. Appl. Phys. 62 (1987) 4591.
[11] S.M. Johns, T. Bell, S. Samandi, G.A. Collins, Surf. Coat. Technol. 85 (1996) 7.
[12] P.K. Chu, B.Y. Tang, Y.C. Cheng, P.K. Ko, Rev. Sci. Instrum. 68 (4) (1997) 1866.
[13] S.Y. Wang, P.K. Chu, B.Y. Tang, X.C. Zeng, X.F. Wang, Nucl. Instrum. Meth. Phys. Res. B 127128 (1997) 1000.
[14] S.Y. Wang, P.K. Chu, B.Y. Tang, X.B. Tian, X.F. Wang, Q.Z. Lin, Thin Solid Films 311 (1997) 190.
[15] S.Y. Wang, P.K. Chu, B.Y. Tang, X.C. Zeng, Y.B. Chen, X.F. Wang, Surf. Coat. Technol. 93 (1997) 309.