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ARTICLE

Characterization of Ti6Al4V Alloy with N+C, Ti+N and Ti+C Ion Implantation

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Abstract: TiN and TiC films were prepared on Ti6Al4V substrates by plasma based ion implantation. The effect of N+C and Ti+N hybrid ion implantation at 50 kV, and Ti+C ion implantation at 20, 35 and 50 kV on mechanical properties was studied. The implantation fluence was up to 2×10^{17} ions/cm^2. XPS and XRD were used to characterize the modified surface of the implanted samples. It was found that the modified layer of Ti+C implanted at 50 kV was TiC and Ti-O bond and the layer of Ti+N implanted at 50 kV was TiN and Ti-O bond. The nano-hardness and the friction coefficient were measured by nano-indentation measurements and pin-on-disc-test. Hardness tests have shown that the hardness increased with N+C, Ti+N and Ti+C ion implantation. For Ti+C implanted samples, the hardness was increased with increasing negative voltage. The sample implanted with Ti+C at 50 kV exhibited the highest hardness of 11.2 GPa. The results of wear tests showed that both Ti+C and Ti+N ion implanted samples had much better wear resistance compared with the un-implanted sample. The wear rate of the Ti+C implanted at 50 kV sample was 6.7×10^{-5}mm^3/N·m, which was decreased over one order compared with that of un-implanted sample.

Key words: ion implantation; XPS; hardness; wear

Titanium alloy is widely used in the aerospace, marine, military, automotive, chemical and other fields due to its superior corrosion resistance, high strength, low density, good ductility and so on[1-4]. In biomedical engineering, titanium alloy has enormous potential for prostheses and implants due to its good biocompatibility[5-7]. However, a significant disadvantage of titanium alloy is its poor wear property that restricts the widespread application in the biomedical field[8]. In the head prostheses, knee-joint and some bearing capacity joint, especially, its surface has to be treated or enhanced in order for better wear resistance, which can delay cracks initiation and reduce wear particles release [5].

Therefore, it is very important to improve the wear resistance of titanium alloys for their future use. Plasma based ion implantation is an effective surface modification technique that has several advantages: (1) good adhesion between the film and substrate; (2) implantation dose, implantation energy and so on individually adjustable; (3) especially, high cleanness[9]. There are some reports concerning the effects of ion implantation on the tribological properties of Ti6Al4V alloy with diversified implantation ions, such as nonmetal element N, O, C, He and metal element Ag, V, Ca[10-13]. Among the various ions implantation, nitrogen ion is the most common for biomedical applications. But it is found that the inflammatory cell may be formed and the better biocompatibility of Ti6Al4V could be changed after nitrogen ion implantation[14]. For the carbon implantation conditions, it has reported that more than 80% of C-C chemical bonds can be formed at high does into Ti6Al4V. It can influence surface properties, significantly reducing wear and friction[15]. Although helium-implanted layer can improve the hardness and wear resistance, helium is the inert gas that is not combined with the element of Ti6Al4V. J. L. Li et al[16] plasma implanted O into Ti6Al4V and the wear resistance only improved twice than

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un-implanted samples. Metal elements such as Ca and Ag are bio-friendly material, but they are not ideal in the aspect of improving surface hardness and it is not useful to restrain the Al and V ions releasing from Ti6Al4V[13]. Because the Al and V ions release from Ti6Al4V surface can impair normal bone healing process[17]. In our previous research[18], N+O ions implantation could effectively improve the wear behavior of Ti6Al4V alloy as a result of the formation of Ti-nitride and Ti-oxide in the implanted zone. However, the hardness in our previous work increased a little. In order to further improve the hardness and wear resistance based on the following factors: On the one hand, it shows that the research interests have been expanded to both metal and nonmetal ion simultaneous on Ti6Al4V alloy. The main driving force of co-implantation is to address the clinical and tribological issues concurrently. Moreover, co-implantation using metal and nonmetal ions has a possibility of forming some compounds (such as oxide, nitride and carbide) in their implanted layer, which may further improve their properties for clinical needs. On the other hand, Ti is non-toxic and safe element for excellent biomedical material and it is in the loose connection vascularized group as tissue reaction[19]. As we all know, TiN and TiC have better biocompatibility, high hardness and wear resistance[5, 20] while the effects of hybrid gas-metal Ti+N and Ti+C co-implantation on the mechanical and tribological properties of Ti6Al4V alloy received less attention in the literatures. So in this research, the TiN and TiC films are prepared on Ti6Al4V alloy substrate by hybrid plasma based ion implantation.

In this work, the microstructure, hardness and tribological properties of the TiN and TiC films prepared by PBII at different implanted voltages are investigated using X-ray photoelectron spectroscopy, X-ray diffractomer, hardness test and wear test.

1 Experiment

The PBII treatment was carried out in a type PSII-MF-800 installation of Lanzhou Institute of Physics. The inner dimension of diameter and height of the vacuum chamber were 800 and 1000 mm, respectively. Ti ions were generated from Ti cathodic arc source and diffused into the vacuum chamber by a magnetic filtration to reduce macroparticles. The nitrogen and acetylene plasma were generated by radio frequency glow discharge in the main chamber.

Commercial Ti6Al4V alloy samples were cut into 15 mm × 15 mm × 3 mm and used as substrate in the experiment. They were polished and cleaned with acetone and ethanol, respectively, before implantation. The chamber was evacuated to a base pressure of 1×10^{-3} Pa. Before ion implantation, the surface was cleaned for 15 min by Ar^+ to remove surface contamination. During the ion implantation, the sample holder was oil-cooled to achieve a low implantation temperature. The Ti metal source parameters were: trigger voltage 10 kV, trigger frequency 20 Hz, arc current 1.1 A, arc voltage 70 V. Hybrid gas-gas N+C, metal-gas Ti+N and Ti+C were implanted to the samples. Different conditions and instrument parameters are listed in Table 1.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a PHI 5700 ESCA spectrometer employing an Al Kα radiation source. The phase composition of the ion implantation films was characterized using an X-ray diffractometer (XRD, X-Pert PROX) with Cu Kα radiation and a glancing incident angle of 2°. Film hardness and modulus were measured with CSM nano-hardness with loads from 8 mN to 15 mN. Nine indentations were made for each specimen and the average value was reported. The tribological experiments were conducted on a ball-on-disk tester of a CSM wear tester using the GCr15 ball. The tests were performed using a normal load (P) of 2 N, and constant sliding speed of 6.0 cm/s. The diameter of the circle wear track (D) and the sliding distance (d) were set as 12 mm and 15 m, respectively. Each sample was tested three times. Following the wear test, a surface profiler (TALYSURF CCI) recorded the cross-sectional profile of the wear track. The cross-sectional area of the wear track (S) was averaged from eight points on the wear track, and then calculated the wear rate (W_R) using the following equation:

$$W_R = \frac{\pi D S}{P d} \tag{1}$$

2 Results and Discussion

2.1 Analysis of surface structure

Glancing angle X-ray diffraction patterns from 2θ varying from 30° to 80°of the samples with N+C, Ti+N and Ti+C at 50 kV are shown in Fig.1. For all the implanted samples, the dominant peaks are the Ti of the substrates, and a small TiN and TiC peaks can also be seen in the spectrum of the implanted sample.

The chemical states of the samples with Ti+C and Ti+N implanted at 50 kV have been studied by XPS. In order to remove the surface contaminant, depth profiles are obtained by sputtering with a 3 kV Ar^+ ion beam for 6 min. The high-resolution spectra of Ti 2p and C 1s are recorded for the sample with Ti+C implanted at 50 kV, as shown in Fig.2.

Table 1 Process parameters of hybrid ions implanted Ti6Al4V substrate

Hybrid ion	Working gas	Pulse voltage/kV	Implantation dose/$\times10^{17}$ cm^{-2}
N+C	N_2 and C_2H_2	50	2
Ti+N	Ar and N_2	50	2
Ti+C	Ar and C_2H_2	50	2
Ti+C	Ar and C_2H_2	35	2
Ti+C	Ar and C_2H_2	20	2

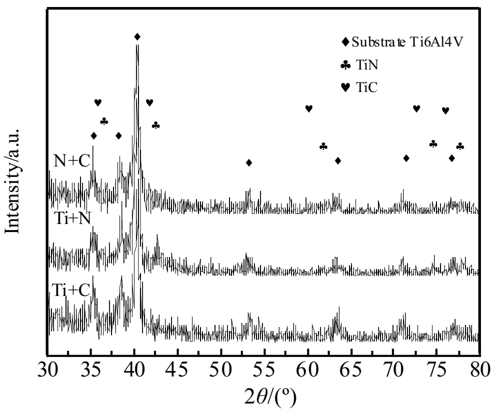

Fig.1 XRD patterns of samples with different ions implantation at 50 kV

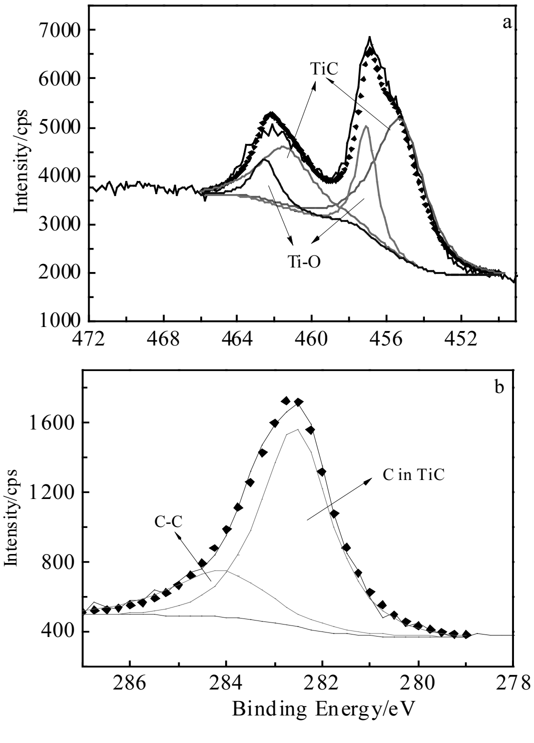

Fig.2 High-resolution XPS spectra of Ti+C ions implantation at 50 kV: (a) Ti 2p and (b) C 1s

From Fig.2a, the Ti 2p peak is composed of spin doublets, each separated by 5.9 eV. The Ti 2p signal is fitted with two sets of peaks, which are assigned to TiC and Ti-O bond. For the case of the TiC bond, bonding energies could be identified: Ti $2p_{3/2}$ at 455.0 eV and Ti $2p_{1/2}$ at 460.9 eV[21, 22], as for Ti-O bond: Ti $2p_{3/2}$ at 457.5 eV and Ti $2p_{1/2}$ at 462.9 eV[23]. The C 1s spectrum is shown in Fig.2b. The dominant C 1s is located at a binding energy of 282.0 eV, which is attributed to TiC[22, 24]. The secondary of the C 1s peak belongs to C-C at 283.4 eV [25]. Spectra of Ti 2p and N 1s for the sample with Ti+N implanted at 50 kV are presented in Fig.3a and 3b. The sample exhibits two distinct doublet peaks for Ti $2p_{3/2}$ and Ti $2p_{1/2}$ spectra: one at 456.2 eV and 462.3 eV, and the other at 457.6 eV and 462.8 eV. The low-energy side of Ti 2p double peaks (Ti $2p_{3/2}$ 456.2 eV and Ti $2p_{1/2}$ 462.3 eV) is considered to be associated with the TiN [21, 26]. The high binding energy peaks (Ti $2p_{3/2}$ 457.2 eV and Ti $2p_{1/2}$ 462.8 eV) should be attributed to Ti-O[19]. Fig.3b shows binding energy of N 1s with peak at 397.1 eV corresponding to TiN[27].

2.2 Analysis of mechanical properties

The thickness of the implanted layers was calculated by the TRIM code[28], The depths of N+C and Ti+C implanted at -50 kV and Ti+C implanted at -20, -35 and -50 kV were ~210, ~198, ~105, ~170 and ~210 nm, respectively. The hardness and modulus of the samples implanted and un-implanted at different indentation loads are shown in Fig.4. The un-implanted sample presents values of hardness and modulus varying from 4.6 GPa to 4.4 GPa and 116.8 GPa to 113.2 GPa, respectively, and the load has little effect for its hardness and modulus. It is clearly seen that the hardness of implanted samples decreases with increasing the indentation load. The smaller the indentation load is, the less influence on substrate will be. All of the implanted samples have a highest hardness and modulus at the load of 8 mN,

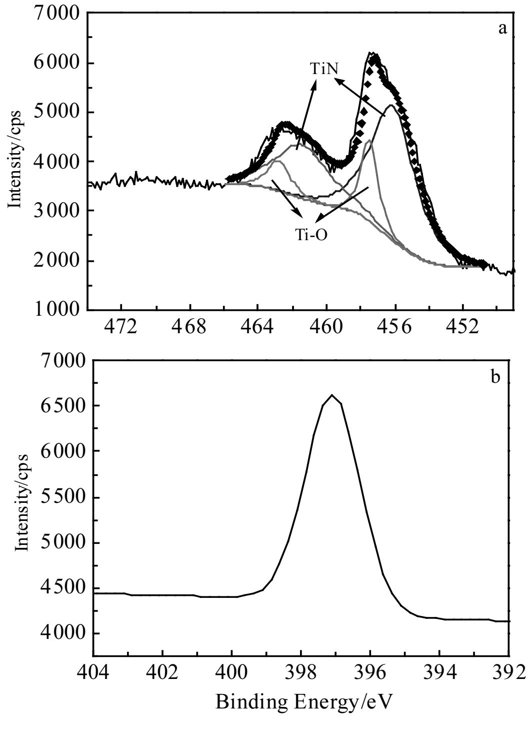

Fig.3 High-resolution XPS spectra of Ti+N ions implantation at 50 kV: (a) Ti 2p and (b) N 1s

which approach to that of the substrate at the load of 15 mN. It is remarkable that the PBII treatment of the Ti6Al4V alloy samples with N+C, Ti+N and Ti+C increased their hardness significantly. This can be attributed to two enhancing factors: First, the formation of mixed layer of TiN, TiC; Second, the implanted films may be strengthened by the effect of lattice deformation and solution hardening in the implantation layers, which can make the movement of the dislocations more different[29]. For the negative voltage at 50 kV, it can be seen that the hardness of the sample with Ti+C has the highest hardness 11.2 GPa, followed by the ones of implanted Ti+N and N+C samples which are 7.6 and 6.3 GPa, respectively. This fact can be explained by two reasons. One is that TiC can enhance the hardness more effectively than TiN. The other is incorporation of carbide bonded carbon within the implanted zone after carbon implantation[30]. It also can be observed that the hardness of the samples with Ti+C implanted increases with increasing negative voltage. This can be attributed to the fact that high implant voltage leads to a high implantation depth, which promotes the increase of hardness. The best result of hardness was obtained for Ti6Al4V alloy implanted with Ti+C at 50 kV negative voltages.

The friction coefficients of the samples implanted at 50 kV with Ti+C, Ti+N, N+C and the substrate are 0.14, 0.28, 0.38 and 0.52, respectively, as shown in Fig.5. The friction coefficients of the samples implanted are found to become lower than that of the substrate Ti6Al4V alloy. This means that the films implanted have good tribological properties. Fig.6 shows the friction coefficient of the samples with Ti+C implanted at different implanted voltages. It can be seen that the friction coefficient of the samples implanted at 20, 35 and 50 kV is decreased in different levels compared with about 0.52 of untreated sample, and decreased with increasing the implanted voltages. The friction coefficient of the samples implanted at 20, 35 and 50 kV is 0.42, 0.25 and 0.14, respectively. This may be attributed to the decrease in surface roughness caused by the increasing implanted voltage.

The wear track morphologies of implanted and substrate are shown in Fig.7. The wear track areas are found to be significantly decreased for the samples with Ti+C implanted at 50 kV, Ti+N implanted at 50 kV and Ti+C implanted at 35 kV. For the samples with N+C implanted at 50 kV and Ti+C implanted at 20 kV, the maximal depth of the wear track is close to that of the un-implanted sample but the width of the wear track is much smaller than that of the un-implanted sample. It is also found that the depth of the

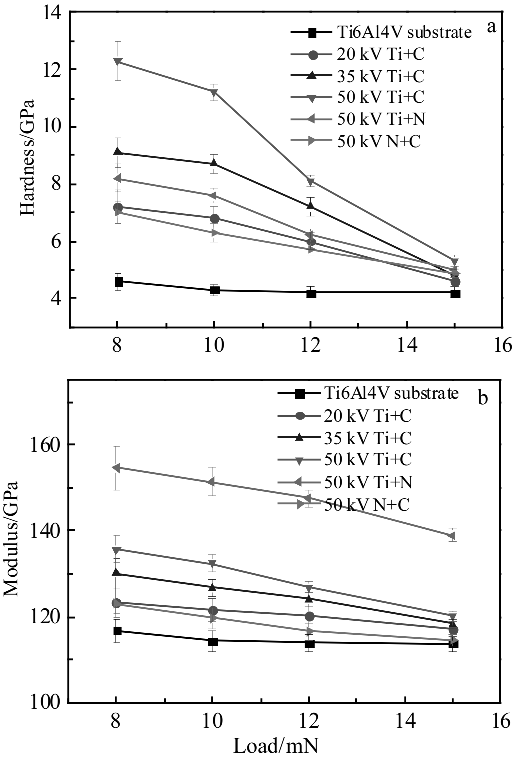

Fig.4 Hardness (a) and modulus (b) of samples at different loads

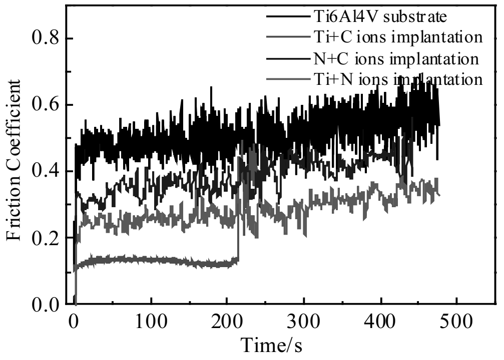

Fig.5 Friction coefficient of Ti6Al4V substrate and implanted samples at 50 kV

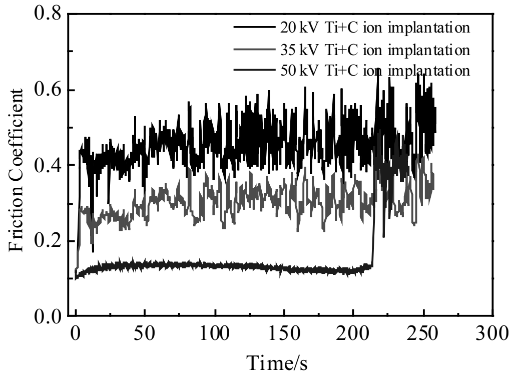

Fig.6 Friction coefficient of the samples with Ti+C implanted at different implanted voltages

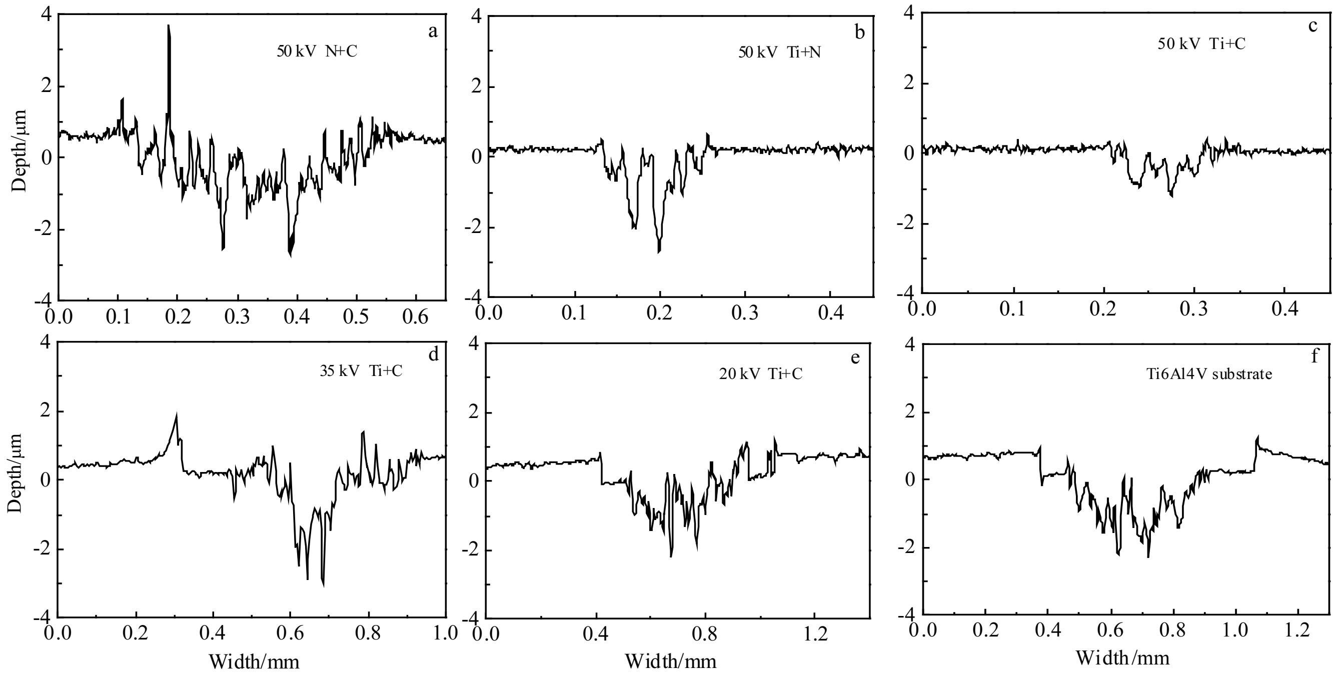

Fig.7 Wear track morphologies of implanted samples and substrate: (a) N+C implanted at 50 kV, (b) Ti+N implanted at 50 kV, (c) Ti+C implanted at 50 kV, (d) Ti+C implanted at 35 kV, (e) Ti+C implanted at 20 kV, and (f) substrate sample

wear track for the samples implanted with Ti+C becomes shallower and the width becomes narrower with the increasing of implanted voltage. Based on the calculated worn volume of the samples following the wear test, the estimated wear rate is shown in Fig.8. It can be seen that the wear rate is decreased compared with un-implanted sample. The wear rate of the sample implanted with Ti+C at 50 kV, Ti+N at 50 kV and Ti+C at 35 kV is 6.7×10^{-5} $mm^3/N\cdot m$, 1.28×10^{-4} $mm^3/N\cdot m$ and 1.92×10^{-4} $mm^3/N\cdot m$, respectively, which is decreased over one order, six times and four times than that of the un-implanted sample (8.17×10^{-4} $mm^3/N\cdot m$), respectively. This indicates that the implanted samples have a good wear resistance. The reason for this can be attributed to the following two facts: First, according to the composition analyses and the XRD peak shown in Fig.1, Fig.2 and Fig.3, it is found that the hard TiC and TiN are formed, which contribute to wear reduction. Second, it is found that the sample has a lower friction coefficient with a lower wear rate. This phenomenon suggests that there is a relationship between friction coefficient and wear resistance. R. S. Mason[31] had found that the value of H/E could reflect the tribological behavior of the films; the higher the values of the H/E, the better the tribological properties. According to Fig.4, it can be calculated that the sample with Ti+C implanted at 50 kV has the highest H/E value. This means that the sample with Ti+C implanted at 50 kV has superior wear resistance than other samples. From the H/E calculation and the wear resistance experimentation, it is identical. The wear rate of the samples with Ti+C is decreased with increasing of the implanted voltage. This can be attributed to the fact that a thinner film can be formed with increasing the implanted voltage. Optical images of wear track for the samples with Ti+C implanted at 50 kV and un-implanted sample are shown in Fig.9. It is obvious that the wear width and depth of un-implanted sample is much larger than those of the samples with Ti+C implanted at 50 kV. The wear width of the samples with Ti+C implanted at 50 kV and un-implanted sample is about 0.10 and 0.65 mm, respectively, which is consistent with the wear trace profile (seen in Fig.9). Comparing the adhesive wear characteristics on the worn surface of un-implanted, it is demonstrated that the wear mechanism of implanted sample is ploughing wear.

2.3 Discussion

Nitrogen, oxygen and carbon ions have been implanted into Ti6Al4V alloy to improve the mechanical properties, corrosion and biocompatibility. In this study, N+C, Ti+N and Ti+C ions are implanted in Ti6Al4V alloy, separately. Compared to our previous research[18], it can be seen that co-implantation Ti+C ions at 50 kV have better mechanical properties than N+O ions implantation at 50 kV, which can produce more than a two-fold hardening effect on Ti6Al4V

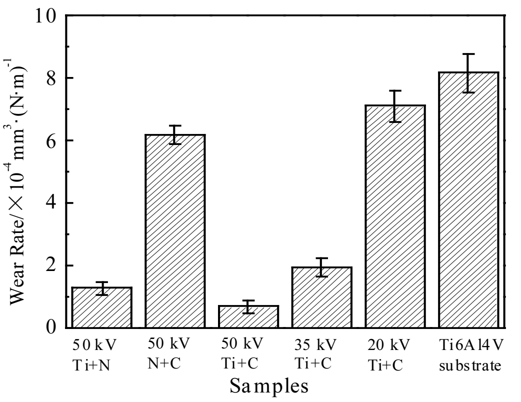

Fig.8 Wear rate of different samples

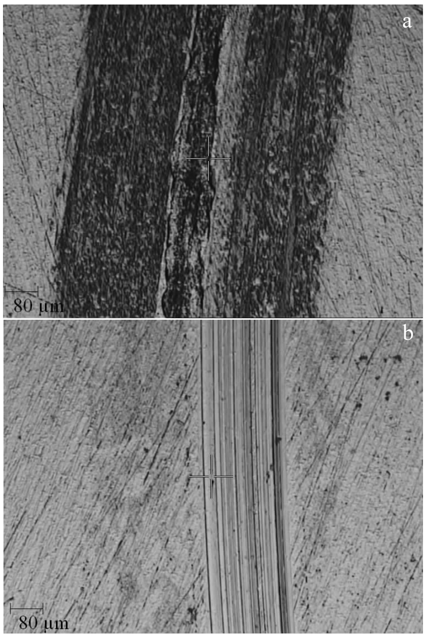

Fig.9 Optical images of wear track of samples: (a) substrate and (b) implanted with Ti+C at 50 kV

alloy. The friction coefficient and wear rate of Ti+C ions implantation decrease one time and exceed 20% compared N+O ions implantation, respectively. The improved hardness and wear behavior of Ti+C ions implantation is considered to be due to some major factors. Firstly, from XPS analyses, it is found that the Ti+C ions are bound both to titanium to form titanium carbides and to carbon atoms to form C-C bonds near the surface. This may result in improvement of the mechanical properties as well as biocompatibility of titanium alloys. Secondly, after ion implantation, the Ti and C have very different atomic radii, Considerably larger lattice strain may be another reason for enhanced hardness. From this research and our previous research[18], it is also found that the N+C ions implantation at 50 kV has higher hardness, but lower wear resistance than N+O ions implantation at 50 kV. This phenomenon can be explained by the following reasons. The friction coefficient of N+C ions implantation is much higher than that of the N+O ions implantation. The friction coefficient is related to not only the surface roughness but also its mechanical properties. Low surface roughness can increase the wear resistance and thus, it is possible that the sample with N+O ions implantation has a lower roughness than that with N+C ions implantation. On the other hand, the rutile titanium ceramic TiO_2 is formed after N+O ions implantation, which is very effective to improve the wear resistance.

3 Conclusion

1) XPS investigation indicate that the samples with implanted Ti+N and Ti+C form TiN and Ti-O bond, TiC and Ti-O bond, respectively.

2) The hardness of all the implanted samples is improved, and reaches maximum value of 11.2 GPa for Ti+C implanted at 50 kV sample.

3) The samples implanted with N+C, Ti+N and Ti+C at 50 kV have friction coefficients of 0.38, 0.28 and 0.14, respectively. After implantation, the wear rate of all the implantation samples is decreased. For Ti+C implanted samples, the friction coefficient and wear rate are decreased with increasing the implanted voltage, and the sample at 50 kV implantation has the lowest wear rate of 6.7×10^{-5}mm^3/N·m, which is decreased by over one order compared with that un-implanted sample.

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Ti6Al4V 合金表面离子注入 N+C, Ti+N 和 Ti+C 性能研究

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摘 要：采用等离子体基离子注入的方法在 Ti6Al4V 合金表面分别注入 N+C、Ti+N 和 Ti+C 元素，注入剂量均为 2×10^{17} ions/cm^2，N+C 和 Ti+N 元素的注入负脉冲偏压为-50 kV，Ti+C 元素的注入电压分别为-20，-35 和-50 kV。通过 X 射线光电子能谱仪（XPS）和 X 射线衍射仪（XRD）对注入层进行了微观结构分析。结果表明：Ti+C 注入层中存在 TiC 和 Ti-O，Ti+N 注入层中存在 TiN 和 Ti-O 键。采用纳米压痕仪和球盘磨损试验机对注入层的硬度和摩擦学性能进行了研究。结果表明：在相同注入电压下，Ti+C 注入层的硬度最高，其次是 Ti+N 注入层，N+C 注入层的硬度最低；Ti+C 注入层的硬度随着注入电压的增大而增大，最大硬度为 11.2 GPa。50 kV 注入层 Ti+C 具有最低的比磨损率，其值为 6.7×10^{-5} mm^3/N·m，比磨损率较未处理 Ti6Al4V 基体下降了 1 个数量级以上，表现出优异的耐磨损性能。

关键词：离子注入；XPS；硬度；摩擦学性能

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