

Structure and tribological properties of modified layer on 2024 aluminum alloy by plasma-based ion implantation with nitrogen/ titanium/ carbon^①

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Abstract: 2024 aluminum alloy was implanted with nitrogen then titanium finally carbon by plasma-based ion implantation to form a gradient layer. The structure and tribological properties of the layer were investigated. Its composition profiles and chemical states were analyzed with X-ray photoelectron spectroscopy (XPS). The surface carbon layer was analyzed by Raman spectrum. The appearances were observed by atomic force microscope (AFM). The surface hardness was measured with the mechanical property microprobe. The dry wear tests against GCr15 steel ball at various sliding loads were performed with a ball-on-disk wear tester in ambient environment. The results show that the thickness of the modified layer is 1 200 nm, the carbon layer is a smooth and compact diamond-like carbon (DLC) films, and the carbon/titanium interface is broadened due to carbon ions implantation, resulting in a good composition and structure transition between DLC films and titanium layer. Surface hardness is improved markedly, with a slow and uniform change. Tribological properties are improved greatly although they reduce with the increase of sliding loads because the modified layer becomes thin rapidly.

Key words: aluminum alloy; plasma-based ion implantation (PBII); structure; tribological properties

CLC number: O 613; O 484

Document code: A

1 INTRODUCTION

Good machinability, low density and high specific strength make aluminum and its alloys extensively be used in many industries, especially in aviation and space flight industry. However low surface hardness and low wear resistance often limit their engineering applications. Nitrogen ion implantation into aluminum and its alloys offers the possibility of applications where both high wear resistance and low density are required^[1-5]. Moreover, our previous investigation^[6, 7] presented that when aluminum alloy was implanted with nitrogen then titanium by PBII, not only the dual modified layer was much thicker than the single nitrogen-implanted layer, but also the corresponding appearances, surface hardness, tribological properties and the degree of adhesive wear were obviously improved. Implanted with nitrogen then carbon by PBII^[6, 8], aluminum alloy was markedly improved in surface hardness and the corresponding tribological properties due to the formation of a smooth and compact diamond-like carbon (DLC) films with an excellent combination of low friction coefficient, high surface hardness and excellent wear resistance.

However, PBII with nitrogen then titanium could form a titanium-deposited layer rich in α -Ti on aluminum alloy, while PBII with nitrogen then carbon could not form a good carbon/aluminum interface.

The functionally gradient metal/ceramic/DLC design was applied to improve the coating adhesion to steels^[9, 10]. If the functionally gradient design is applied to improve aluminum alloy, there should be a great improvement in its surface hardness and tribological properties. The aim of this paper is to study the structure and the corresponding tribological properties of the functionally gradient modified layer.

2 EXPERIMENTAL

PBII experiments were performed on the DLZ-01 facility^[6]. 2024 aluminum alloy treated by solution strengthening was used as substrate. The samples were made into a size of $d40\text{ mm} \times 5\text{ mm}$ for wear test and $d10\text{ mm} \times 5\text{ mm}$ for the others. The samples were mechanically polished to a surface roughness about $0.025\text{ }\mu\text{m}$, ultrasonically cleaned with absolute alcohol and acetone for 5-10 min, and

① **Foundation item:** Project(59771059) supported by the National Natural Science Foundation of China

Received date: 2002-12-16; **Accepted date:** 2003-03-28

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then dried in air. Sputtered with Ar^+ at a bias voltage of 2 kV for 30 min to remove the residual surface contaminations, the samples were implanted with nitrogen under the conditions of 75 kV, 40 μs , 80 Hz and 3 h, then with titanium under the conditions of 75 kV, 30 μs , 80 Hz and 3 h (Ar as working gas), and at last with carbon under the conditions of 10 kV, 45 μs , 80 Hz and 3 h (C_2H_2 as working gas).

XPS measurements were performed using a Perkin-Elmer PHI-5700 system equipped with a hemispherical analyzer, and the base pressure maintained at 10^{-9} Pa. The $\text{AlK}\alpha$ radiation (photon energy of 1476.6 eV) was used as the excitation source^[7, 8].

The nanohardness at different depth was measured using Nano-IndenterTM II tester with a mechanical property microprobe, indenting depth of 50, 150, 300–1200 nm.

The appearances were measured using Nanoscope IIIa-D3000 atomic force microscope (AFM), with long-wide pin, NP-S pin tip. The highness of the tip was 180 μm , and the elastic constant of the tip is 0.12 N/m.

The ball-on-disk dry sliding wear property measurements were carried out against GCr15 steel ball with diameter of $d = 5$ mm, hardness of RHC 61 and $R_a = 25$ nm in ambient environment with temperature 25 °C, humidity approximately 50%, sliding loads 1 N, 2 N and 5 N and speed 0.06 m/s.

Wear data were automatically recorded by a computer. Wear life is defined as the number of sliding cycles (n) when the modified layer was just worn out, i. e. a steady sliding friction coefficient was sharply increased to a maximum, then was fluctuated to a steady value. The depth and the width of wear track were measured with a profilometer, and by which wear volume was obtained. The wear volume divided with the product of the number of sliding cycle and sliding load is defined as the wear ratio whose reciprocal is called wear-resistance or wear resistant property.

3 RESULTS AND DISCUSSION

3.1 Composition depth profiles

Fig. 1 shows composition depth profiles of the modified sample. The thickness of the modified layer can reach 1200 nm, and the modified layer can be artificially divided into three layers corresponding to the three modified processes: a 400 nm-thick carbon layer containing almost 100% carbon element except some oxygen in the first 50 nm depth due to the sample exposure to the atmosphere, a Ti interlayer containing a large amount of titanium and a N-implanted layer where nitrogen depth profile presents a Gaussian-like distribution.

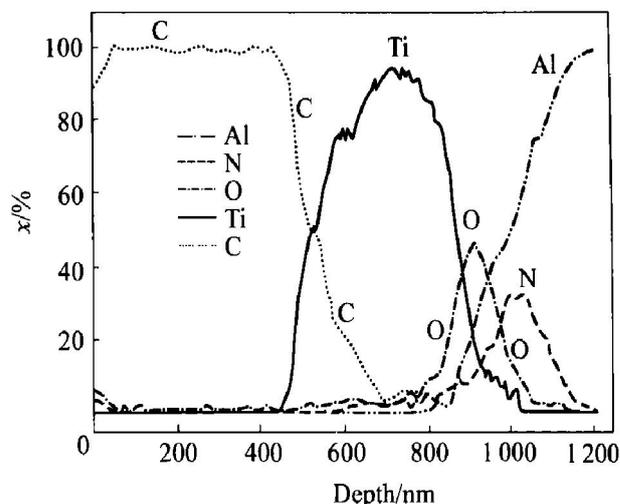


Fig. 1 XPS depth profiles of gradient layer implanted with N/Ti/C

In fact, the three layers are connected without obvious interface. Furthermore the C/Ti interface was broadened due to implantation of carbon ions into Ti interlayer, resulting in a good composition transition between the carbon layer and the Ti interlayer; whereas the Ti/Al interface was widened owing to implantation of titanium ions into the N-implanted layer to result in a composition and phase transition, which was reported in previous studies^[7].

3.2 Raman spectra

Fig. 2 shows the Raman spectra of the carbon layer. The Raman spectrum is a distinctive broad band ranging from 1100 cm^{-1} to 1800 cm^{-1} . It is different from that of diamond carbon at 1332 cm^{-1} , that of single crystalline graphitic carbon at 1580 cm^{-1} , and those of other disordered polycrystalline and noncrystalline graphitic carbons. It presents the typical Raman spectra of DLC films^[11, 12]. The spectrum can be fitted with two broad bands at 1552 cm^{-1} (G band) and 1391 cm^{-1} (D band). The G band corresponds to the symmetric E_{2g} vibrational mode in graphite-like carbons, while the D band is attributed to bond angle disorder in the graphite-like microdomains affected by sp^3 bonds. Thus it is assumed that the broad feature at 1391 cm^{-1} be attributed to both sp^3 bonds (diamond) at 1332 cm^{-1} and sp^2 at 1357 cm^{-1} (graphitic carbon D band) in the films. While the broad feature at 1552 cm^{-1} may be indicated that some amorphous sp^2 bonds at 1580 cm^{-1} (graphitic carbon G band) in the films.

3.3 Chemical states

The chemical states of carbon element at various depths in the modified layer are shown in Fig. 3 (the vertical lines across the XPS peaks refer to the standard binding energy (BE)^[13]. At 300 nm depth

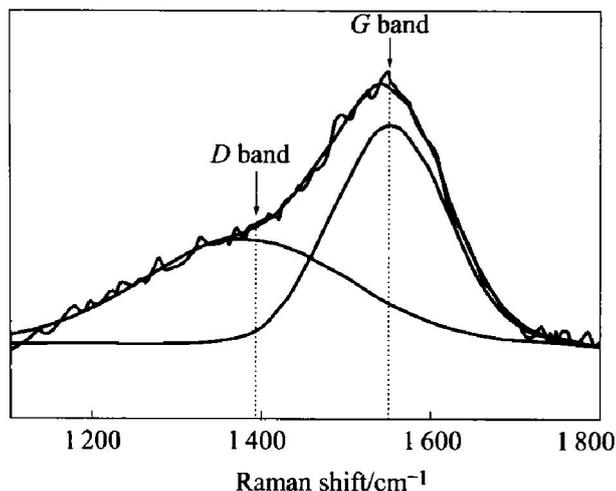


Fig. 2 Raman spectra of carbon layer

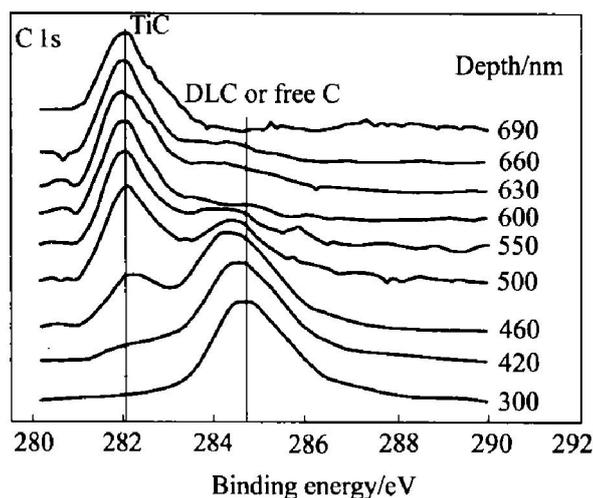


Fig. 3 XPS spectra of C 1s at various depths

of carbon layer, the peak of C 1s at 284.8 eV is symmetric corresponding to DLC or free carbon, which is in good agreement with that in Fig. 1. While at 420 nm depth where titanium appears, one new peak at 282.1 eV appears corresponding to TiC, but the free carbon peak is dominant. As the sputtering depth is increased, the TiC peak becomes dominant, while the free carbon peak gradually disappears. This indicates that carbon ions can be implanted into titanium to form TiC in C/Ti interface, resulting in a broadening C/Ti interface not only with a good composition transition but also with a good phase transition. This can be seen clearly from the fittings of peaks of C 1s and Ti 2p at 460 nm depth, as shown in Fig. 4. The results in Fig. 4 (a) are consistent with those in Fig. 3. As shown in Fig. 4(b), the core peak of Ti 2p can be fitted into five pairs of Ti 2p_{3/2} and Ti 2p_{1/2} peaks with the peaks of 454.4 eV, 455.0 eV, 455.6 eV, 456.5 eV and 458.5 eV corresponding to α -Ti, TiC, TiN, Ti₂O₃ and TiO₂^[14], respectively. In these phases, α -Ti holds most, which is corresponding to that of Fig. 1. Correspondingly, N 1s exists as TiN and solid solution N, and O 1s exists as TiO₂, Ti₂O₃ and solid solution O, but these

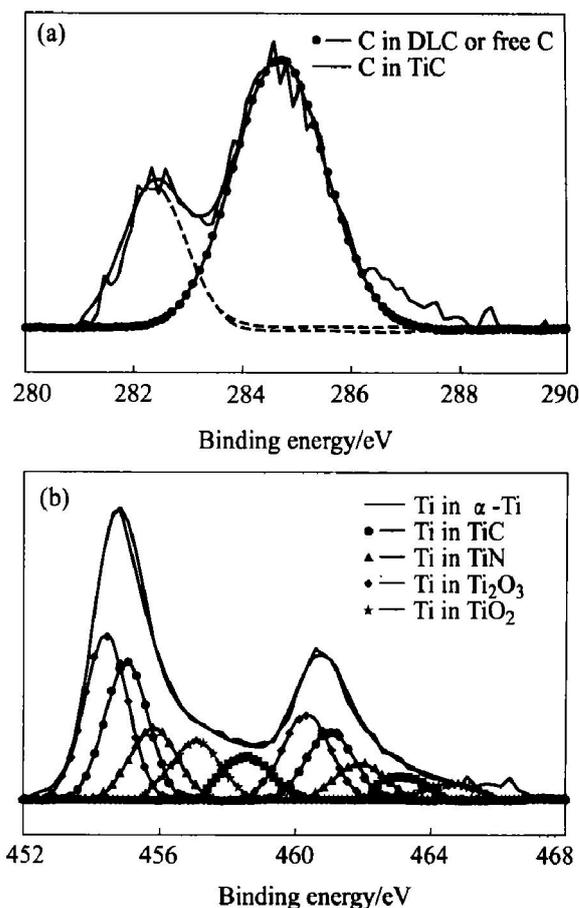


Fig. 4 XPS fit-spectra of C 1s and Ti 2p at 460 nm depth in gradient layer
(a) -C 1s; (b) -Ti 2p

phases hold little because the contents of nitrogen and oxygen are little.

3.4 Surface hardness

Fig. 5 presents the nano-hardness at various penetrating depth of the modified layer with mechanical property microprobe. The hardness is improved greatly from 16.3 GPa at 50 nm to peak value of 17.7 GPa at 300 nm. It is then slowly and evenly decreased to 8.6 GPa at 1000 nm, finally to 3 GPa at 1200 nm. This is consistent with the composition depth profiles. The hardness in the first 400 nm depth is contributed by DLC films, that in 400–700 nm depth is due to the good composition and phase transition between DLC films and Ti interlayer, and that in 700–1200 nm depth is attributed to N-implanted layer^[6,9].

3.5 Surface appearance

Fig. 6 shows the appearance and roughness of the modified sample by AFM. The appearance is obviously smooth and compact although it is composed of a large number of little heaves and concaves, with maximum height of heaves of 292 nm, and the average roughness of about 20 nm. This inherits those of the sample implanted with nitrogen then titanium. The appearance is also im-

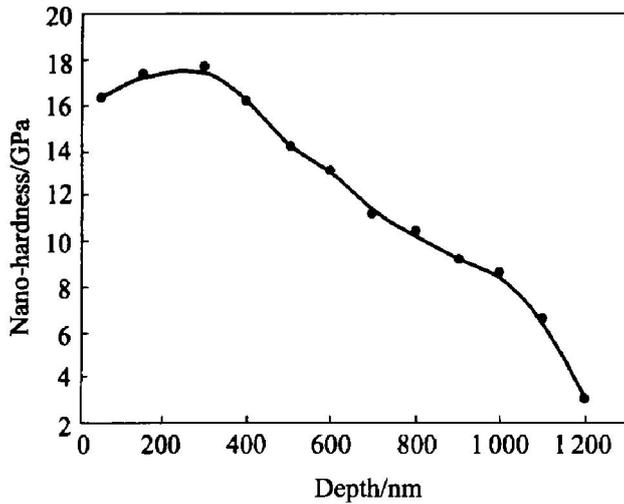


Fig. 5 Nano-hardness as a function of penetrating depth for modified layer

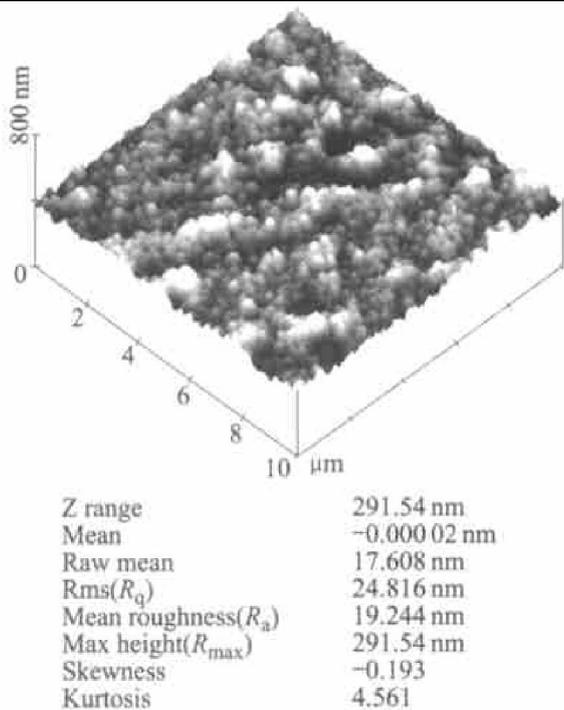


Fig. 6 AFM image of gradient layer

proved more obviously than that of the sample implanted with nitrogen then carbon^[8]. This is closely related to the fact that the continuously deposited carbon atoms or their clusters cover and polish the heaves and concaves, which is much similar to that of the continuously deposited titanium atoms or their clusters^[6].

3.6 Tribological properties

Table 1 lists the tribological properties as a function of sliding load. It is evident that the tribological properties are improved greatly, particularly, the friction coefficient is less than 0.12, the wear life can reach approximately 7000 cycles, and the average volume wear ratio is about $1 \times 10^{-8} \text{ mm}^3/\text{N}^{-1}$ at low load (e. g. 1N). These tribological properties are improved in orders of magnitude in comparison with those of the sample implanted with nitrogen or the sample implanted with nitro-

Table 1 Tribological properties of modified layer as a function of sliding load

Sliding load/ N	Friction coefficient	Wear life/ Cycle	Wear rate/ ($10^{-8} \text{ mm}^3 \cdot \text{N}^{-1}$)
1	0.117	6 623	1.2
2	0.093	3 800	2.1
5	0.082	1 926	3.9
10	0.093	1 344	8.3
20	0.103	815	13.6

gen then titanium^[6] mainly owing to the unique wear-resistant DLC films. And they are also improved in times of magnitude in comparison with those of the sample implanted with nitrogen then carbon^[15] mainly due to the gradient modified layer with the slow and even change of hardness. However, as the load is increased, the friction coefficient presents a parabolic-like change, the wear life is reduced and the average volume wear ratio is increased, which is associated with the transformation of DLC films to graphite-like carbons and the modified layer becoming thin rapidly at high contacting stress^[15].

As seen from the above, after three continuous modification by PBII, 2024 aluminum alloy was greatly improved in surface appearances, surface hardness and tribological properties owing to the following factors. First of all, DLC films made main contributions because of their low friction coefficient, high hardness, and unique self-lubricated property. Secondly, the broadening carbon/titanium interface with a good composition and phase transition between DLC films and titanium-interlayer also made great contributions because this gradient modified layer eliminated the poor adhesive force between DLC films and the substrate, and decreased the composition and phase difference between DLC films and the substrate^[6, 9]. Thirdly, this is closely associated with titanium-interlayer. This layer effectively increased the thickness of the modified layer, made the hardness change slowly and evenly, dispersed or released the contacting stress, prevented the cracks from extending, and improved the surface appearances^[6, 9, 16, 17]. In addition, the nitrogen-implanted layer was helpful to strengthening of the substrate and support the DLC films.

However, there should be appropriate thickness of titanium-interlayer. If it is too thick, there is almost no difference between the DLC films on titanium-interlayer and the DLC films on aluminum substrate, thus there will appear the same problem as that of the DLC films on aluminum substrate. If it is too thin, the DLC films on titanium-interlayer are comparative for the DLC films on nitrogen-implanted layer, therefore the thickness of the modified layer is

difficult to increase effectively, moreover there is not a good phase transition between the DLC films and the titanium-interlayer. At the same time, titanium-interlayer may be replaced by a layer implanted with nitrogen and titanium or that implanted with titanium, and then nitrogen and titanium, or other layers. Fortunately, these considerations may be controlled by optimizing PBII parameters and processes.

4 CONCLUSIONS

1) The thickness of the gradient AlN/Ti/DLC layer can increase to 1200 nm.

2) The surface carbon layer is a smooth and compact DLC film; the C/Ti interface is broadened due to carbon ions implantation; and there is a good composition and phase transition between DLC films and Ti-interlayer.

3) Surface hardness is improved markedly and it shows a slow and uniform change.

4) Tribological properties are improved greatly, but they reduce with the increase of sliding load because the modified layer becomes thin rapidly.

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(Edited by YANG Bing)