[Article ID] 1003 - 6326(2000)04 - 0493 - 05

Tribological behavior of different films on Ti-6Al-4V alloy prepared by plasma-based ion implantation①

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[Abstract] The tribological behaviors of TiN coating and TiN + TiC + Ti(C, N)/diamond like carbon (DLC), TiN/DLC, TiC/DLC multilayers on Ti-6Al-4V alloy prepared by plasma-based ion implantation (PBII) were compared. Under the test conditions of counterbody AISI 52100, load 1 N and speed 0.05 m/s, the tribological properties of the alloy are improved by these films in the order of TiN, TiC/DLC, TiN/DLC and TiN + TiC + Ti(C, N)/DLC. Tribological behavior is affected by the conditions of surface modification and triboexperiments. The appearance of "peaks" in the wear dynamic resistance profiles may be due or correspond to the process of formation and breaking apart of transition films. The breakthrough of the DLC coated samples may start from partially wearing out, and end with joining piece dilamination. There are transition films on all counterbodies AISI 52100. When AISI 52100 counterbody is changed to Ti-6Al-4V, the wear of most modified samples is changed from only disc to both disc and ball abrasive dominated.

[Key words] diamond like carbon; Ti-6Al-4V alloy; plasma-based ion implantation; friction; wear
[CLC number] TG155 **[Document code]** A

1 INTRODUCTION

Ti-6Al-4V alloy is widely used in aviation, space and medical industries but restricted to tribological applications to a certain extent[1,2]. The use of a new cost-effective technique, plasma-based ion implantation (PBII), for improving surface properties by forming TiN, carbide, carbonitride, DLC hard films or their multilayers on this alloy has been demonstrated in Ref.[3 ~ 9]. Comparison of structure and microhardness of TiN coating, TiN + TiC + Ti(C, N)/DLC, TiN/DLC and TiC/DLC multilayers prepared by this technique has been made. In this paper, the tribological behavior of the films is compared. Obviously, these comparisons are of significance for not only surface modification of the alloy but also application and improvement of this technique.

2 EXPERIMENTAL

Ti-6Al-4V substrate with as-received (mill-annealed) microstructure of α-phase plus intergranular β-phase (average Vickers hardness of 380 HV) was mechanically surface ground to a roughness of 0.1 μm Ra, then ultrasonically degreased and sputter cleaned with 2000 eV Ar^+ ions before surface modification on self-designed multifunctional PBII device (vacuum chamber size: 700 mm × 700 mm × 1 000 mm, with a target stage oil cooled)[8]. Table 1 gives out the modification mode. Tribological tests were conducted on a ball-on-disc tribological tester, with test conditions listed in Table 2. Wear dynamic resistance (resistance across the counterface during the wear process) was determined as the triboexperiments proceeded. Wear topography was observed with scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

The PBII with N_2 (mode 1-2 in Table 1), PBII with N_2 then C_2H_2 plus H_2 (mode 3-4 in Table 1), PBII with N_2 then glow discharge deposition with C_2H_2 plus H_2 (mode 5-6 in Table 1), PBII with C_2H_2 then glow discharge deposition with C_2H_2 plus H_2 (mode 7-9 in Table 1) have led to TiN coating and TiN + TiC + Ti(C, N)/DLC, TiN/DLC, TiC/DLC multilayers formed on Ti-6Al-4V alloy, respectively[7~9].

Changes of friction coefficient with the number of wear cycles for the unmodified and as-modified samples are illustrated in Fig.1. Initial friction coefficient (at 1 wear cycle) increases for samples in the order of: those deposited with DLC (about 0.04 for mode 6 and 8), those implanted with DLC (about 0.1 for mode 4), those only implanted with nitrogen (about 0.14 for mode 1), and the unmodified (about 0.23). For the unmodified sample, there is no stage of low stable friction coefficient; for those only implanted with N_2, the low stable stage is not obvious; for those coated with DLC, such stable stages corresponding to different wear cycles are observed, and the wear cycles of samples increase by multilayers in the order of TiC/DLC (about 650 cycles, stable friction coefficient 0.19 for mode 8), TiN/DLC

① [Received date] 1999 - 06 - 21; [Accepted date] 1999 - 10 - 27

Table 1 Surface modification mode and corresponding films

Mode	Surface modification method	Corresponding films
1	PBII with N_2 (pulse voltage - 60 kV, time 120 min)	TiN
2	PBII with N_2 (pulse voltage - 60 kV, time 60 min)	TiN
3	PBII with N_2 (same as mode 1) then C_2H_2 plus H_2 (pulse voltage - 30 kV, time 120 min)	TiN + TiC + Ti(C, N)/ DLC
4	PBII with N_2 (same as mode 1) then C_2H_2 plus H_2 (pulse voltage - 20 kV, time 120 min)	TiN + TiC + Ti(C, N)/ DLC
5	PBII with N_2 (same as mode 1) then glow discharge deposition with C_2H_2 plus H_2 (bias voltage - 30 kV, time 120 min)	TiN/ DLC
6	PBII with N_2 (same as mode 1) then glow discharge deposition with C_2H_2 plus H_2 (bias voltage - 20 kV, time 120 min)	TiN/ DLC
7	PBII with C_2H_2 (pulse voltage - 50 kV, time 180 min) then glow discharge deposition with C_2H_2 plus H_2 (bias voltage - 20 kV, time 120 min)	TiC/ DLC
8	PBII with C_2H_2 (pulse voltage - 50 kV, time 120 min) then glow discharge deposition with C_2H_2 plus H_2 (same as mode 7)	TiC/ DLC
9	PBII with C_2H_2 (pulse voltage - 50 kV, time 60 min) then glow discharge deposition with C_2H_2 plus H_2 (same as mode 7)	TiC/ DLC

Table 2 Conditions of triboexperiments

Item	Condition
Disc	Ti-6Al-4V surface (un) modified
Ball (d 5 mm) (as counterbody)	AISI 52100 (Vicker's hardness of 830 HV) and Ti-6Al-4V surface modified as disc
Load/ N	1, 5
Sliding speed / ($m \cdot s^{-1}$)	0.03, 0.04, 0.05, 0.06
Environment	Dry air
Temperature	Room temperature

(about 2000 cycles, stable friction coefficient 0.19 for mode 6), TiN + TiC + Ti(C, N)/ DLC (about 53 200 cycles, stable friction coefficient 0.23 for mode 4). From the low stable stage to breakthrough, the friction coefficient for those coated with DLC undergoes large variations. We have defined wear life as the test duration at which friction starts to increase rapidly. It can be seen that friction coefficient usually increases rapidly and stabilizes over 0.4 after breakthrough. Thus, the wear life of samples increases by films in the order of TiN (about 400 cycles), TiC/ DLC (about 1 520 cycles), TiN/ DLC (about 7 600 cycles), TiN + TiC + Ti(C, N)/ DLC (about 62 019 cycles). For comparison, the friction coefficient for unmodified sample increases rapidly and stabilizes at about 0.435 after only 150 cycles. So the surface modification effect is considerable. And among all the modification methods used, the best effect belongs to the PBII with nitrogen then acetylene plus hydrogen with which the stage of low stable friction coefficient as well as wear life is the longest.

However, tribological behavior is affected by not only the conditions of surface modification but also the conditions of triboexperiments such as counterbody, load, etc. Table 3 shows that different modification methods used lead to different responses to the change of counterbody. As counterbody is changed from AISI 52100 to Ti-6Al-4V, friction (coefficient) may change in the opposite direction in response to the change of counterbody, so may wear. There seems to be no direct relations between friction and wear.

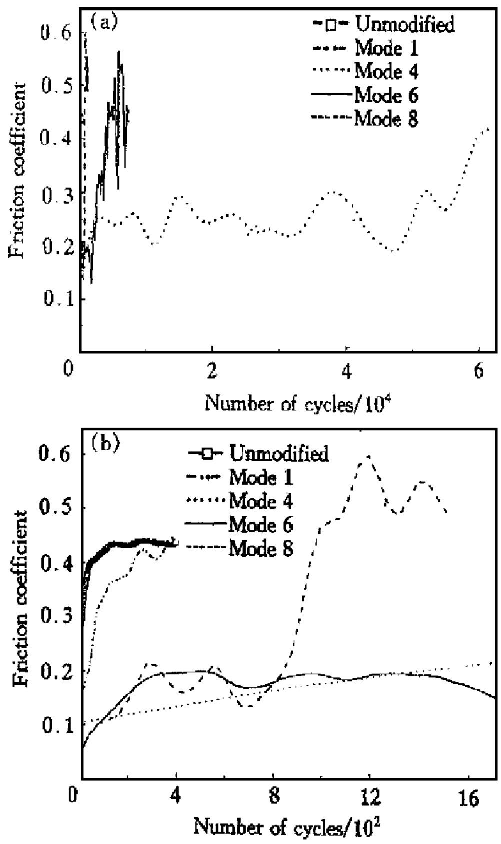

Fig.1 Changes of friction coefficient with number of wear cycles ((b) is partial magnification of (a))
(counterbody AISI 52100; load 1 N; speed 0.05 m/s)

The changes in wear have also been demonstrated in Fig.2 in which variations in width of wear scar

Table 3 Changes of tribological behavior as counterbody AISI 52100 changed to Ti-6Al-4V (load 5 N, speed changed from 0.04 to 0.03 m/s)

Surface modification method	Friction coefficient	Wear life
Unmodified	Decreased somewhat	Increased somewhat
PBII with N_2	Decreased greatly	Increased greatly
PBII with N_2 then C_2H_2 plus H_2	Stable value decreased greatly	Decreased greatly
PBII with N_2 then glow discharge deposition with C_2H_2 plus H_2	Decreased slightly	Without obvious change
PBII with C_2H_2 then glow discharge deposition with C_2H_2 plus H_2	Increased	Decreased

of the counterbody (ball) with number of wear cycles are displayed. The steeper the curve looks, the lower wear resistance it reflects. The figure indicates under the changed test conditions (counterbody Ti-6Al-4V, load 5 N, speed 0.03 m/s), wear resistance of samples increases in the order of: those unmodified, those only implanted with nitrogen (mode 1), those coated with TiN + TiC + Ti(C, N)/DLC (mode 4), and that of those coated with TiC/DLC (mode 8) and those coated with TiN/DLC (mode 6) are no higher than that of those unmodified. That is, the wear resistance for those coated with TiN + TiC + Ti(C, N)/DLC remains the highest. Similar changes in tribological behavior might also happen when load or other test condition(s) is changed.

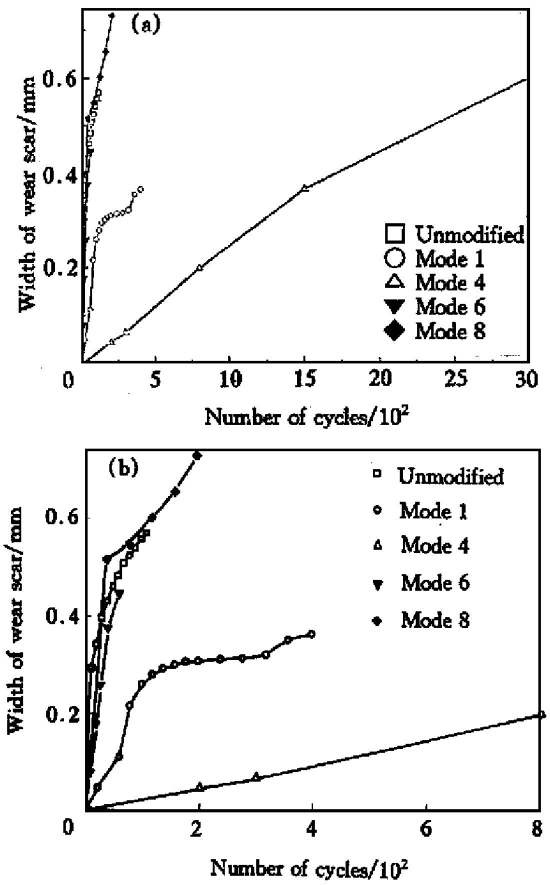

Fig.2 Variations in width of wear scar of counterbody (ball) with number of wear cycles ((b) is partial magnification of (a))
(counterbody Ti-6Al-4V load 5 N; speed 0.03 m/s)

The changes of results caused by test conditions are considered mainly due to a combined action of the following elements: 1) Some of the TiN, carbide, carbonitride, DLC films and their multilayers may has their own preferred counterface(s) (such as friction against some kind(s) of metal, alloy or nonmetal). 2) For different film or multilayer, there may exist a different critical contact load. When the contact load exceeds this critical value (turning point), tribological behavior such as friction coefficient will show significant changes. Whether the critical load is high or low depends to a large extent on the film-substrate adhesion status of the coating(s). 3) The change in test conditions may cause different changes in the counterface status (such as temperature at the contact points, existing status of transition films, composition and morphology of the transition films, etc.) for the different coating(s). But the detailed mechanism remains to be investigated.

Wear dynamic resistance profiles are displayed in Fig.3. Wear dynamic resistance increases and "peak" is more obviously observed with the increase of nitrogen implantation dose or when counterbody AISI 52100 was changed to Ti-6Al-4V, as shown in Fig.3 (a). Wear dynamic resistance decreases to a very small value which is slightly over zero after breakthrough happened. For samples coated with TiN + TiC + Ti(C, N)/DLC, however, when counterbody AISI 52100 was changed to Ti-6Al-4V, the "peak" becomes lower and nearer, as shown in Fig.3(b). For samples coated with TiC/DLC, initial wear dynamic resistance increases with the increase of carbon implantation dose (time) as shown in Fig.3(b). For samples coated with TiN/DLC, wear dynamic resistance profiles with sharper gradient are observed at a higher load (5 N). Owing to insulativity of the DLC layers, the DLC coated samples have much higher wear dynamic resistance compared with the samples only implanted with N_2. The appearance of "peaks" in the profiles might be due or correspond to the process of formation and breaking apart of transition films (transferred from the disc to ball).

SEM photomicrographs of worn surfaces of discs are exhibited in Fig.4. It can be seen that the wear of all discs presented is mostly abrasive dominated. The wear by sliding grooves was alleviated after implantation with N_2, and further alleviated after im-

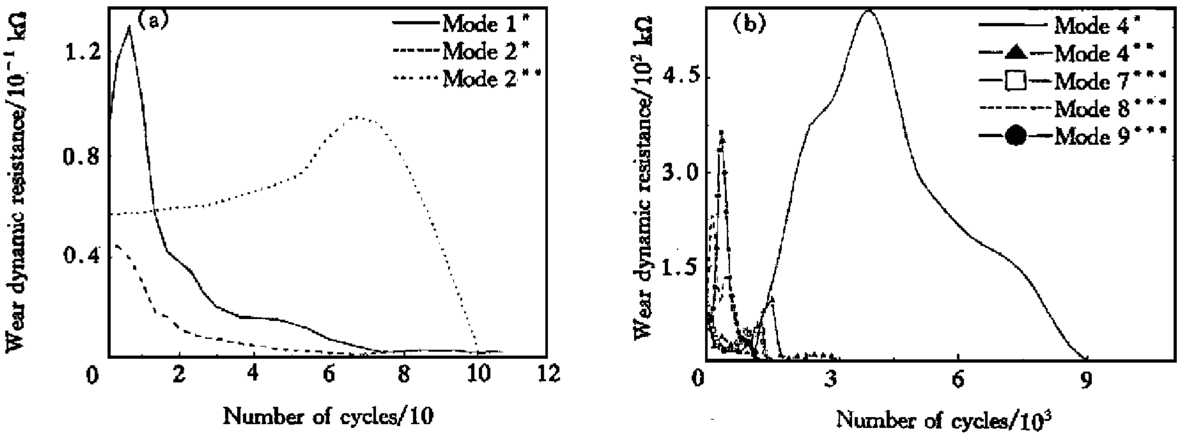

Fig.3 Wear dynamic resistance profiles
(* Ball AISI 52100, load 5 N, speed 0.04 m/s; * * Ball Ti-6Al-4V, load 5 N, speed 0.03 m/s;

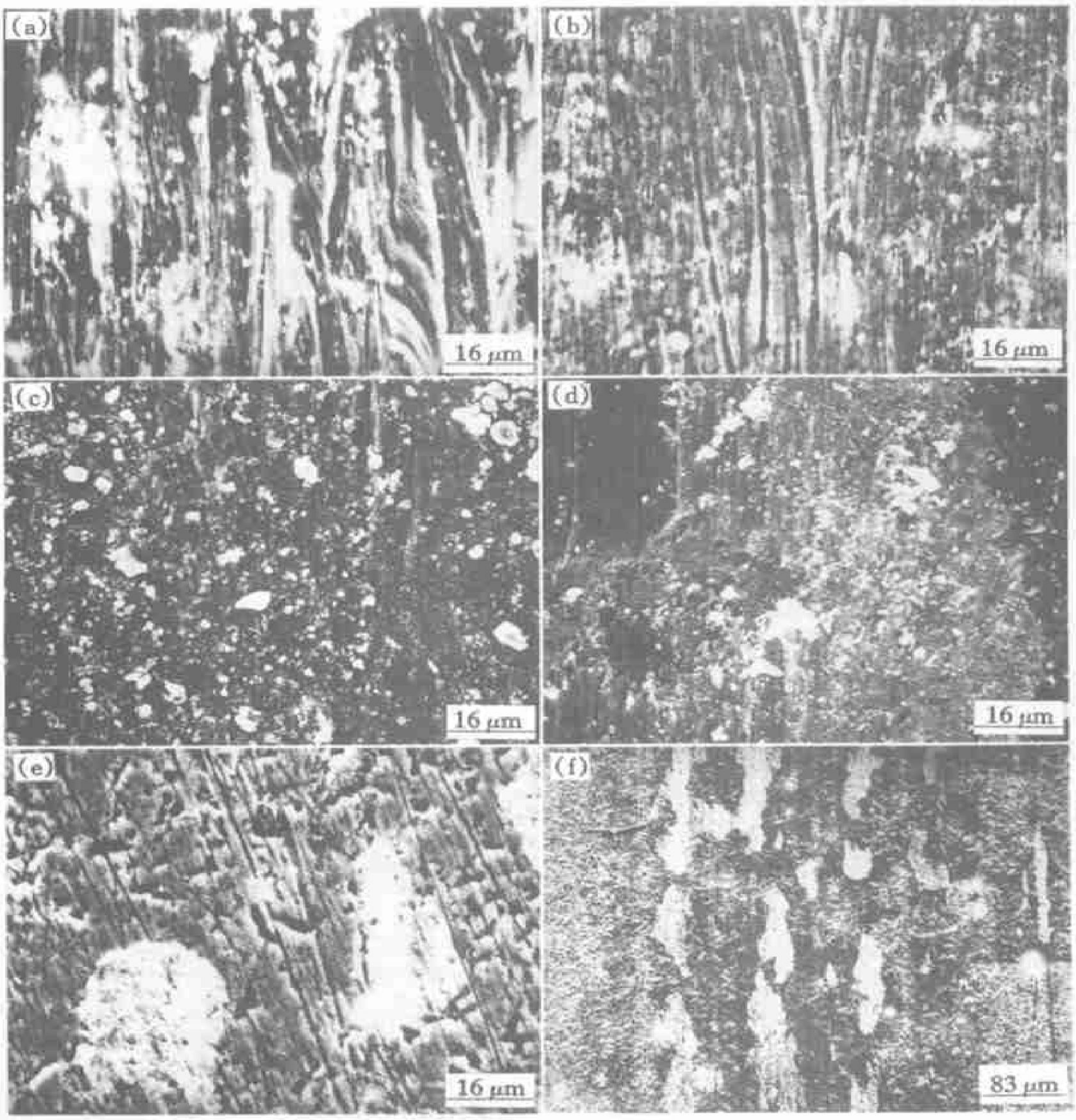

Fig.4 SEM micrographs of worn surfaces of discs
(a) —Unmodified; (b) —Mode 1; (c) —Mode 6; (d) —Mode 8; (e), (f) —Mode 3
(Ball AISI 52100; load 1 N; speed 0.05 m/s; after 400, 400, 7600, 1520 and 25500 cycles for (a), (b), (c), (d) and (e) —(f) respectively)

plantation with N_2 then C_2H_2 plus H_2. Under a low load (1 N), another way of breakthrough was also observed for the TiN + TiC + Ti(C, N)/DLC coated samples; that is, the breakthrough started from partial worn out, and ended with joined piece dilamination, as shown in Fig.4(e) and (f). This process might take place much earlier for the TiN/DLC or TiC/DLC coated samples. The debris pieces dilaminated were crushed to more and finer wear debris particles, as shown in Fig.4(c) and (d). The transition films were observed on all counterbodies AISI 52100. The formation and transferring of the transition film were discussed elsewhere[7~9]. It is considered that film structure, microhardness and film-substrate adhesion etc. are all important elements which affect or determine tribological behavior of the modified samples. When counterbody AISI 52100 was changed to Ti-6Al-4V, the wear of most modified samples was changed from only disc to both disc and ball abrasive dominated.

4 CONCLUSIONS

1) Under the test condition of counterbody AISI 52100, load 1 N, speed 0.05 m/s, the initial friction coefficient increases for samples in the order of those deposited with DLC (about 0.04), those implanted with DLC (about 0.1), those only implanted with N_2(about 0.14), and the unmodified (about 0.23). There are low stable friction stages with increasing cycles for samples in the order of those coated with TiC/DLC, those coated with TiN/DLC, and those coated with TiN + TiC + Ti(C, N)/DLC. This stage does not exist for the unmodified, and is not obvious for those only implanted with N_2. Wear life increases, hence tribological properties improve for samples in the order of those only implanted with nitrogen, those coated with TiC/DLC, those coated with TiN/DLC, and those coated with TiN + TiC + Ti(C, N)/DLC. Tribological behavior (including wear dynamic resistance profile) is affected by not only conditions of surface modification but also conditions of triboexperiments, and different surface modification methods lead to different response to the change of counterbody, etc. But among all the modification methods used, the best effect remains for the PBII with nitrogen then acetylene plus hydrogen.

2) The appearance of "peaks" in the wear dynamic resistance profiles may be due or correspond to the process of formation and breaking apart of transfer films. The breakthrough of the DLC coated samples can start from partial wearing out, and end with joined piece dilamination. There are transition films on all counterbodies AISI 52100 whether tested against the modified or unmodified discs. When counterbody AISI 52100 is changed to Ti-6Al-4V, wear of most modified samples will be changed from only disc to both disc and ball abrasive dominated.

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(Edited by YANG Bing)