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ORIGINAL PAPER

Tribological Behaviors of Different Diamond-Like Carbon Coatings on Nitrided Mild Steel Lubricated With Benzotriazole-Containing Borate Esters

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Abstract Three synthesized benzotriazole-containing borate esters were separately added into poly-alpha-olefin (PAO) as additives, using molybdenum dithiocarbamate (MoDTC) as the comparison. The friction and wear behavior of Ti-DLC and Ti/Al-DLC coating on nitrided AISI-1045 steel sliding against AISI 52100 steel under the lubrication of PAO containing various additives was evaluated using a reciprocating ball-on-disk friction and wear tester. The morphology and chemical feature of the worn surfaces of the DLC coatings were observed and analyzed using a three dimensional (3D) surface profiler, a scanning electron microscope (SEM), and an X-ray photoelectron spectroscope (XPS). Results show that the three kinds of benzotriazole-containing borate esters as additives in PAO had much better tribological properties than MoDTC; the wear resistance of Ti/Al-DLC coating was better than Ti-DLC coating.

Keywords Antiwear additives · Boundary lubrication · XPS · DLC coating · Friction and wear

1 Introduction

Borate esters, as a new generation of lubricating additives, have attracted much attention because of their excellent properties including excellent anti-wear and friction-reducing, oxidation inhibition and low toxicity properties [1–7]. The synthesis and tribological properties of various B- and N-containing additives have been extensively focused on. For instance, using boric acid, hexadecanol, and Schiff base as the starting materials, Zheng et al. [8] synthesized several borate esters containing nitrogen and found that the synthetic borate esters had good hydrolytic stability and friction-reducing properties. Jia et al. [9, 10] investigated friction and wear properties of several borate esters as additives in PAO on DLC coating. Results show that the borate esters gave much better friction-reduction and wear resistance properties for DLC coating/steel and DLC coating/DLC coating sliding pairs than MoDTC and ZDDP. On the other hand, benzotrizole-containing additives showed many important properties, including excellent load-carrying capacity, good wear resistance properties, good antioxidative properties, good anticorrosive properties, high thermal stabilities, and so on [11]. Li and Ren [11, 12] synthesized three S-(1H-benzotriazole-1-yl) methyl *N*,*N*-dialkyldithiocarbamates and investigated their tribological behaviors. The three compounds exhibited excellent load-carrying capacity, and produced the protective film containing Fe, N, S elements on the worn surface. Farng et al. [13–15] claimed several patents for preparing benzotriazole-containing polymers and found that the synthesized compounds had excellent tribological properties. However, few have been reported on the tribological behaviors of the benzotriazole-containing borate esters.

On the other hand, DLC coating was one of the most promising functional coatings, which possess many important characteristics such as extremely high hardness, high thermal and chemical stability, and excellent tribological properties [16–21]. Some investigators [22, 23]

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suggested that the addition of Cu or Al into the TiC coating resulted in a remarkable reduction of stress while its hardness was decreased slightly. Pang [22] found that the Ti–Al–C coatings possessed low friction coefficient and long wear life under dry sliding conditions. Moreover, it is interesting to investigate the tribological behavior of Ti-DLC and Ti/Al-DLC coatings under boundary lubricated conditions, although the friction and wear behavior of DLC coatings in the presence of MoDTC or ZDDP additives has been investigated [24–26]. In this article, plasma nitriding was applied as a pre-treatment to enhance the mechanical properties of the substrate, for example, hardness and tribological properties, then the Ti- and Ti/Al-DLC coatings were deposited on the nitride steel by magnetron sputtering. Three benzotriazole-containing borate esters were added into PAO as additives in the present research. The friction and wear behavior of the Ti-DLC coating and Ti/Al-DLC coating on plasma nitrided AISI 1045 steel sliding against AISI 52100 steel balls under boundary lubricated conditions was investigated with a reciprocating friction and wear tester. At the same time, a comparative investigation was carried out using MoDTC as the reference additive. The tribochemical characteristics and action mechanisms of the benzotriazole-containing borate esters lubricated with the DLC coatings were investigated based on the analyses of 3D profiler, SEM, and XPS.

2 Experimental Details

2.1 Plasma Nitriding of AISI-1045 Steel and Deposition of DLC Coating

AISI 1045 steel discs [ϕ24 mm × 7.8 mm, chemical composition (wt%): 0.42 C, 0.17 Si, 0.5 Mo, 0.035 P, 0.035 S, 0.025 Cr, 0.30 Ni, 0.25 Cu, and balance Fe] were polished to mirror finish (Ra < 0.03 μm) before nitriding. The polished mild steel discs were then nitrided in a pulsed plasma nitriding furnace (LDM2-25 DL, China) at an applied voltage of 0–1000 V, using NH_3 as the source gas [9]. Finally, DLC coatings (Ra < 0.03 μm) with Ti- and Ti/Al-interlayer were deposited on the polished nitrided mild steel by magnetron sputtering. During the film deposition processes, the medium frequency (20 kHz) magnetron sputtering target was kept at constant current of 2.2 A with the voltage less than 600 V. The deposition system is a multifunctional equipment designed at our lab, and the details of the system are described elsewhere [27]. The hardness of Ti-DLC coating (15.6 GP) and Ti/Al-DLC coating (13.8 GP) were measured using nanoindentation testing (NANOTEST 600, Micro Materials Ltd, UK). The 3D profiles of the Ti-DLC coating and Ti/Al-DLC coating were determined by MICROXAM-3D surface profiler (ADE Inc., America) (see Fig. 1). A scratch tester (MFT-4000) was employed to measure the adhesions between DLC coatings and substrates. The scratch test was carried out under the conditions with a load rate of 50 N/min, an end load of 50 N and a scratch length of 5 mm.

2.2 Lubricants

The molecular formula of the three synthesized benzotriazole-containing borate esters (brown liquids at room temperature), are shown in Fig. 2. The three borate esters and MoDTC (provided by AIST, Japan) were separately added to PAO (dynamic viscosity at 40 °C: 66 mm^2/s) at a concentration of 2.0 wt%, and the borate esters possess good stability in PAO. The thermogravimetric (TG) of borate esters was carried out on Netzsch STA499 simultaneous thermal analyzer at a heating rate of 10 °C min^{-1} under N_2.

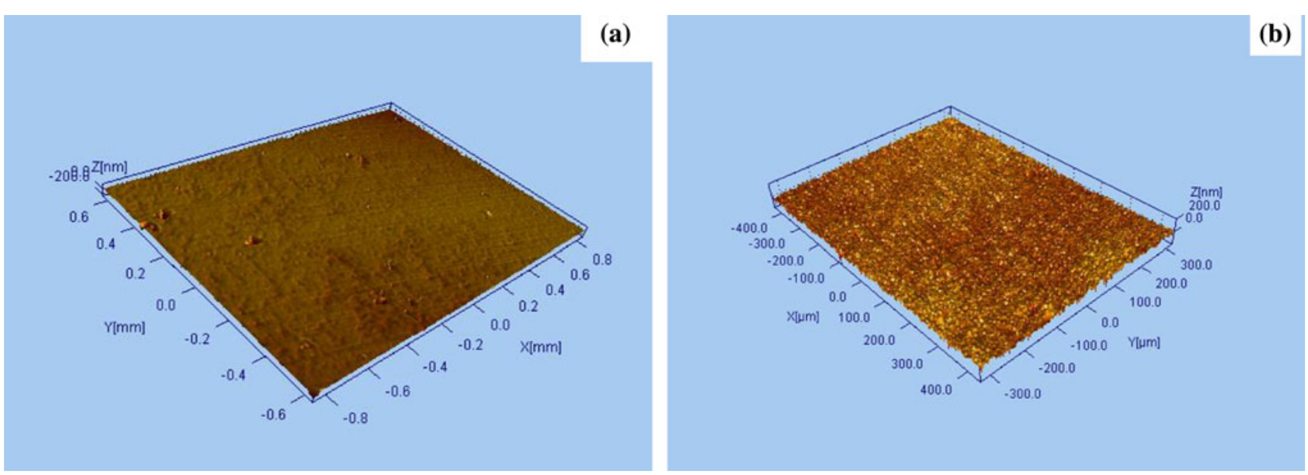
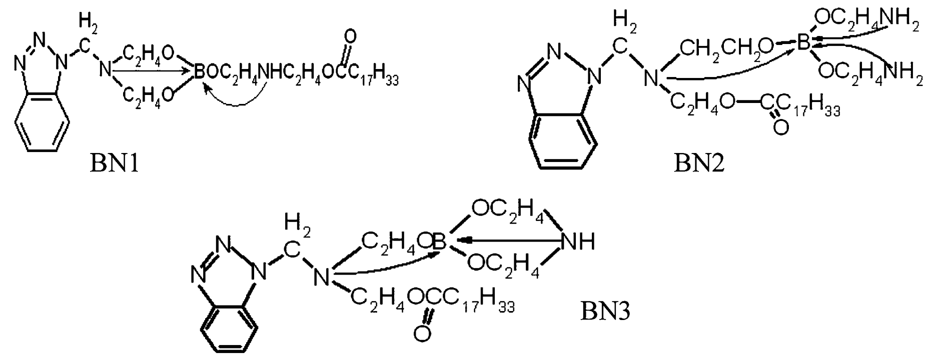


Fig. 1 Three dimensional (3D) profiles of **a** Ti-DLC coating and **b** Ti/Al-DLC coating on nitrided AISI 1045 steel

Fig. 2 Molecular formula of the three borate esters



2.3 Friction and Wear Test

The tribological properties of the benzotriazole-containing borate esters in PAO were investigated using a reciprocating friction and wear tester (Optimol SRV, Germany). The sliding tests of the DLC coatings on nitrided mild steel against AISI 52100 steel ball (ϕ10 mm) were executed at an amplitude of 1 mm, test time of 30 min, load of 20 and 80 N (contact Hertz pressure 0.77 and 1.22 GPa, respectively), and reciprocating frequency of 10, 20, 30, 40, and 50 Hz. The details of the friction and wear tester are described elsewhere [9]. The friction coefficient was automatically recorded using a PC connected to the tester. The wear volume loss of the DLC coating specimen was determined using MICROXAM-3D surface profiler, and the wear volume loss was transformed to wear rate after being divided by load and sliding distance. Three repeat measurements were conducted under each of pre-set testing conditions. And the averaged values of the three repeat tests are reported in this paper.

2.4 Analysis of the Worn Surface of DLC Coatings

At the end of each sliding test, the lower DLC coating specimen was ultrasonically cleaned in acetone to remove residue oil and contaminants on the surface. The cleaned DLC coating specimen was then used for measurement of X-ray photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics Inc., USA), and analysis of wear volume loss and scanning electron microscopy (SEM, JSM-6500LV, Jeol, Japan), aiming to reveal possible tribochemical reactions and tribological properties of the additives. The XPS analysis, with a resolution of ±0.1 eV, was carried out with monochromatized AlK_α excitation source, using the binding energy of contaminant carbon (C1s: 284.6 eV) as the reference [28]. The SEM observation, with a resolution of about 0.35 nm, was conducted at an accelerating voltage of 20 kV.

3 Results and Discussion

3.1 Thermal Stability and Corrosion-Inhibiting Performance

The thermogravimetric curves for the three borate eaters are shown in Fig. 3. The first break-up temperature of borate eaters is about 170 °C, and the BN1 and BN2 are decomposed entirely at 420 and 450 °C, respectively. The results show that these esters possess a relatively high thermal stability if temperature exceeds 200°C.

3.2 Friction and Wear Behavior of DLC Coating

The friction coefficient and wear rate of the Ti-DLC coating sliding against 52100 steel at a load of 20 N and under the lubrication of PAO containing different additives are shown in Fig. 4. It is obvious that the Ti-DLC coating lubricated with PAO containing the three kinds of benzotriazole-containing borate esters had a higher friction coefficient than that lubricated with PAO-MoDTC at high frequency. At the same time, the friction coefficient of the Ti-DLC coating in the presence of the borate ester

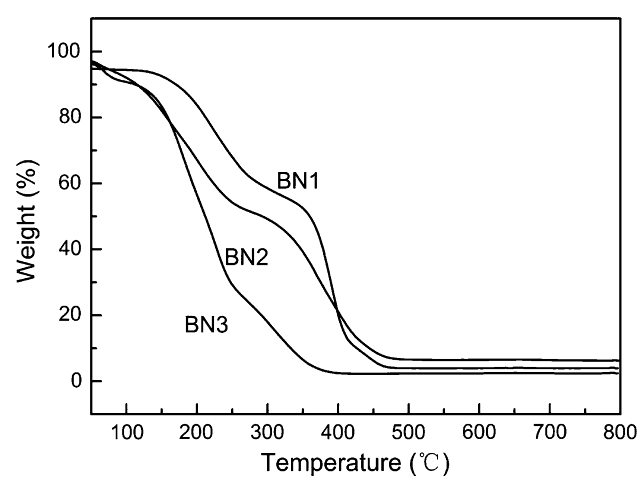


Fig. 3 Thermogravimetric curve for the three borate esters

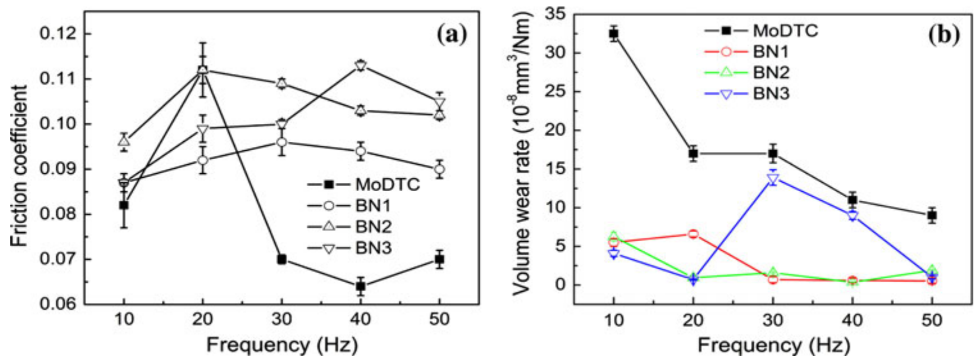


Fig. 4 Friction coefficient (**a**) and volume wear rate (**b**) of Ti-DLC coating sliding against 52100 steel at 20 N for 30 min

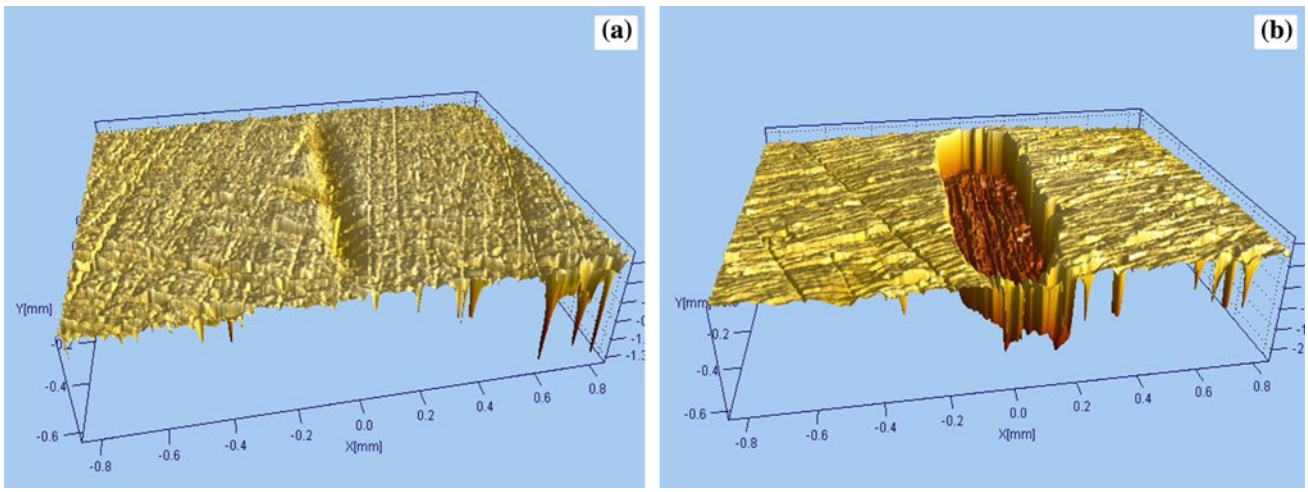


Fig. 5 3D profiles of the wear tracks of the Ti-DLC coating lubricated with PAO-BN1 (**a**) and PAO-MoDTC (**b**) at 20 N and 50 Hz for 30 min

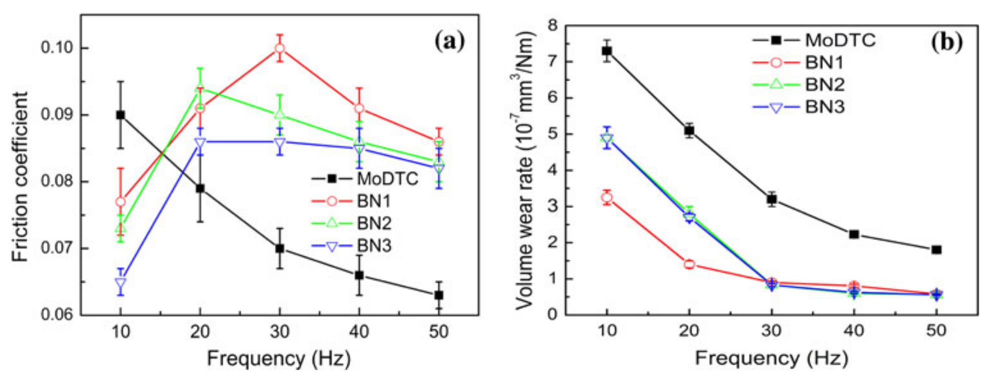


Fig. 6 Friction coefficient (**a**) and volume wear rate (**b**) of Ti-DLC coating at 80 N for 30 min

additives was almost unchanged at different frequencies. Moreover, as shown in Fig. 4b, the wear resistance of Ti-DLC coating lubricated with PAO-borate esters was better than that with PAO-MoDTC. For example, at a frequency of 50 Hz, the wear rate of the Ti-DLC coating lubricated with PAO-borate esters was only one-seventh of that lubricated with PAO-MoDTC. The wear rate of Ti-DLC coating indicated that the synthesized benzotriazole-containing borate ester additives had much better antiwear ability for Ti-DLC coating/steel pair than MoDTC. This is also confirmed by the 3D wear track profiles of the Ti-DLC coating under the lubrication of various lubricants (see Fig. 5).

When the load was increased to 80 N, the three kinds of benzotriazole-containing borate ester additives still showed better antiwear ability than MoDTC for the Ti-DLC coating/steel pair (see Fig. 6). As for the friction coefficient of the four lubricants, the coefficient of Ti-DLC coating lubricated with PAO-MoDTC is lower than that with PAO containing the three borate esters under high frequency. At a frequency of 10 Hz, the friction coefficient of PAO-MoDTC was 0.09, being higher than other three lubricants.

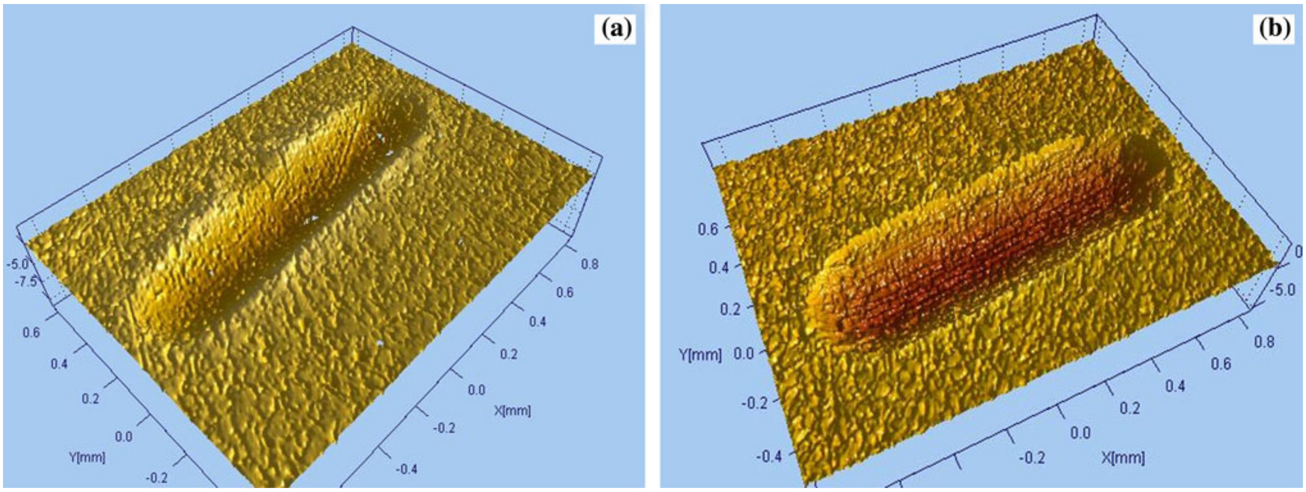


Fig. 7 3D wear track profiles of the Ti-DLC coating at 80 N and 50 Hz for 30 min lubricated with PAO-BN1 (**a**) and PAO-MoDTC (**b**)

Fig. 8 Friction coefficient and volume wear rate of Ti/Al-DLC coating at 80 N for 30 min

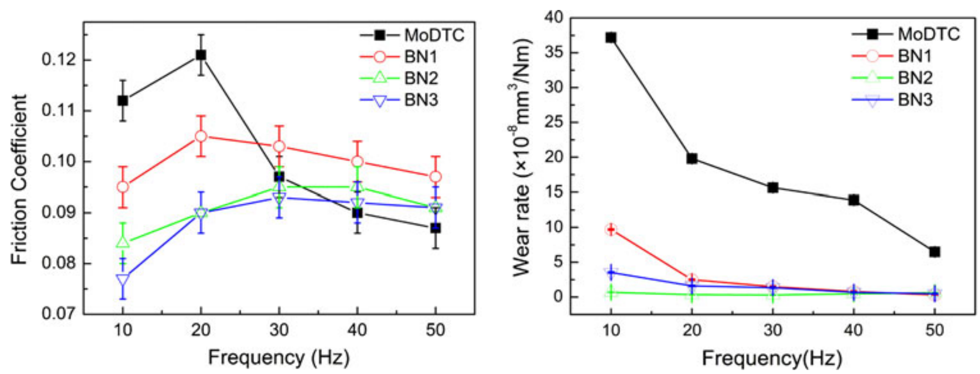


Figure 7 shows the 3D wear track profile of the Ti-DLC coating lubricated with PAO-BN1 and PAO-MoDTC at 80 N as an example. The Ti-DLC coating was dominated by mild wear when lubricated with PAO-BN1 at an increased load of 80 N, but the wear track was wider and deeper than that of 20 N, which is naturally attributed to enhanced deformation and damage of the coating at a higher load. As for PAO-MoDTC, the wear track at 80 N was also wider and deeper than that at 20 N.

On the other hand, Fig. 8 shows the friction coefficient and wear rate of the Ti/Al-DLC coating sliding against AISI 52100 steel at a load of 80 N under the lubrication of the four lubricants. The Ti/Al-DLC coating lubricated with PAO containing the three borate esters had a more constant friction coefficient than that lubricated with PAO-MoDTC under all frequencies. For instance, at a frequency of 20 Hz, the coefficient of friction of 0.12 was recorded for PAO containing MoDTC, and it decreased to 0.087 for PAO containing BN2. However, at a frequency of 50 Hz, the coefficient of friction of PAO-MoDTC was 0.085, which was lower than other three lubricants. The wear rate of the Ti/Al-DLC coating lubricated with PAO-MoDTC is much larger than that with borate esters. Comparing the two kinds of coatings, the Ti/Al-DLC coating showed better wear resistance than Ti-DLC coating under the lubrication of the four lubricants. For example, at a frequency of 50 Hz, the wear rate of the Ti/Al-DLC coating lubricated with PAO containing borate esters was only one-fifth of that of the Ti-DLC coating.

3.3 Analysis of the Worn Surfaces of DLC Coating by SEM and XPS

Figure 9 shows the SEM photographs of the worn surfaces of the Ti-DLC coating lubricated with PAO-BN1 and PAO-MoDTC at the frequency of 50 Hz. Obviously, the Ti-DLC coating experienced less wear damage at 20 N than that at 80 N (see Fig. 9a, b). Figure 9b showed that severe micro-fracture and peeling-off occurred when lubricated with PAO-MoDTC under 80 N. Moreover, the DLC coating was broken during the first few minutes of sliding at 20 N when lubricated with PAO-MoDTC (see Fig. 9d). This is different from the mild wear and damage of the Ti-DLC coating lubricated with PAO-BN1 at 80 N load (see Fig. 9c). These SEM observations agree well with the corresponding wear rate shown in Figs. 4 and 6.

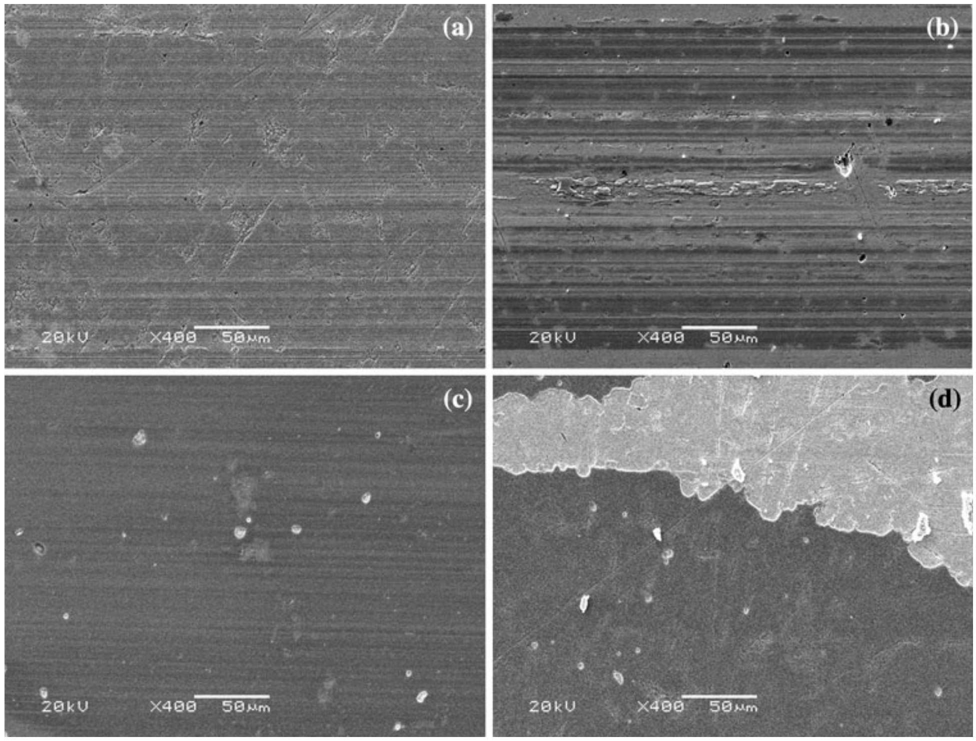


Fig. 9 SEM photographs of the worn surfaces of the Ti- DLC coating lubricated with **a** PAO-MoDTC, 20 N, 30 min; **b** PAO-MoDTC, 80 N, 30 min; **c** PAO-BN1, 80 N, 30 min; and **d** PAO-MoDTC, 20 N, 3 min

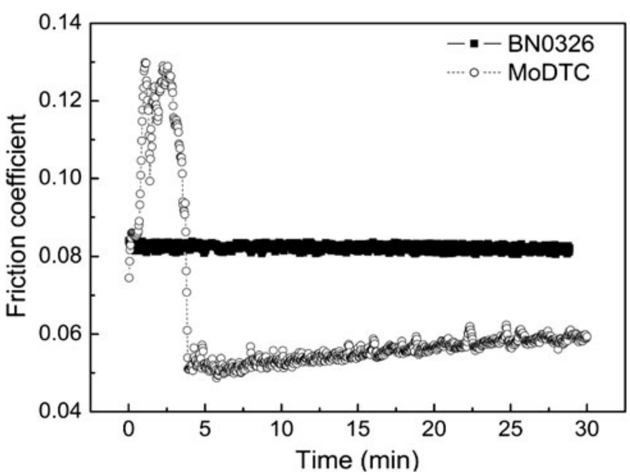


Fig. 10 Friction coefficient *vs*. time curves of Ti-DLC coating/steel pair lubricated with PAO-BN1 and PAO-MoDTC under 80 N and 50 Hz

Figure 10 shows the evolution of the friction coefficient of PAO-BN1 and PAO-MoDTC lubricated Ti-DLC coating at 50 Hz and 80 N. The friction coefficient of PAO-MoDTC increased rapidly at the first few minutes of sliding and then sharply dropped to a very low value. Comparing to what has been reported elsewhere [29], it might be reasonably assumed that the freshly exposed metal on the worn surface reacted with MoDTC during sliding, forming friction-reducing film thereon. This supposition could be well supported by the corresponding XPS analysis of the worn surface. On the other hand, the coefficient of PAO-BN1 was unchanged during the whole sliding process, showing excellent friction stability.

Figure 11 shows the SEM imagines of the wear tracks of the Ti/Al-DLC coating lubricated with PAO-BN1 and PAO-MoDTC at a frequency of 50 Hz. The worn surface of the Ti/Al-DLC coating under the lubrication of PAO-BN1 is smoother and shows almost no signs of scuffing and/or adhesion wear as compared with that under the lubrication of PAO-MoDTC. Moreover, the Ti/Al-DLC coating showed less wear damage than the Ti-DLC coating under the same condition (see Figs. 9, 11).

Figure 12 shows the XPS spectra of B_{1s}, N_{1s} and Fe_{2p} on the worn surface of the Ti-DLC coating lubricated with PAO-BN1 at 20 N for 30 min (The XPS data for PAO-BN2 and PAO-BN3 at 20 N are similar and not shown here). The B_{1s} peak located at 189.2–191.8 eV indicates that BN and B_2O_3 were present on the worn surface. Prior investigators suggested that the tribochemical decomposition of borate ester happened during sliding and B atoms were permeated into the sub-layer of the DLC coating because of their small atomic diameter [8, 9]. The broad peak of N_{1s} from 398.9 to 400.8 eV could be assigned to N-containing organic compounds on the worn surface. It is likely that the benzotriazole and other N-containing groups, derived from borate ester additives, were adsorbed on the worn surface forming protective film to improve the tribological properties [12]. Moreover, almost no signal of Fe_{2p} was detected on the worn surface of the DLC coating, implying that the DLC coating on the nitrided mild steel

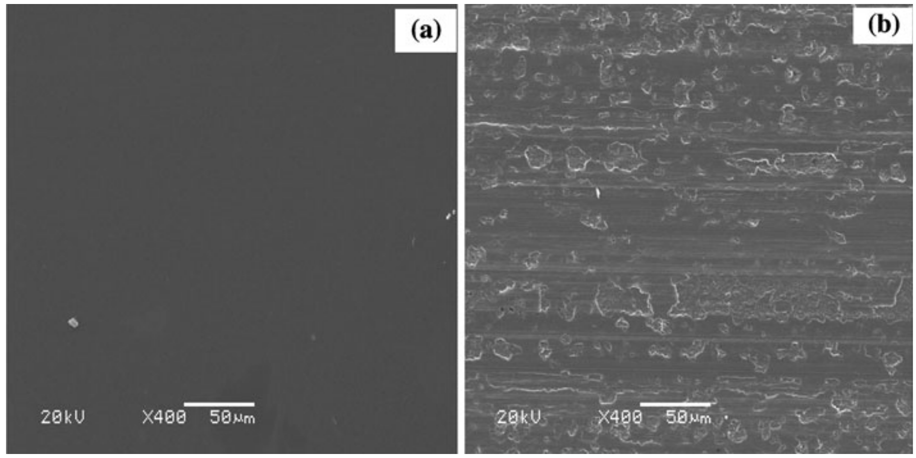


Fig. 11 SEM photographs of the worn surfaces of Ti/Al-DLC coating lubricated with PAO-BN1 (**a**) and PAO-MoDTC (**b**) at 80 N load for 30 min

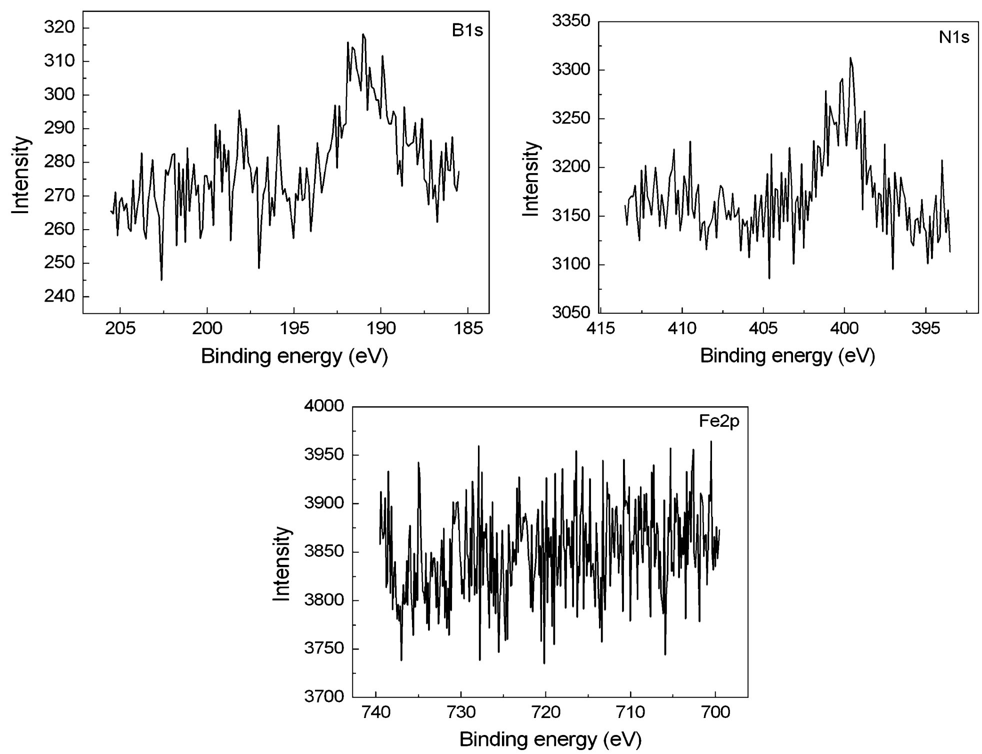


Fig. 12 XPS spectra of the worn surface of the Ti-DLC coating lubricated with PAO-BN1 under 20 N for 30 min

substrate experienced little wear and damage. The above observation agrees well with the SEM images of the worn surfaces shown in Fig. 9. Figure 13 shows the XPS spectra of B_{1s}, N_{1s} and Fe_{2p} on the worn surface of the upper ball of Ti-DLC/steel pair lubricated with PAO containing BN1. The broad peak of B_{1s} from 189.9 to 192.1 eV is attributed to BN and B_2O_3. The broad peak of N1 s peak from 398.3 to 401.5 eV might be assigned to adsorbed N-containing organic compounds. The peak of Fe_{2p} at 711.1 eV can be attributed to Fe_2O_3.

Figure 14 shows the XPS spectra of Mo_{3d}, S_{2p}, N_{1s} and Fe_{2p} on the worn surface of the Ti-DLC coating lubricated with PAO-MoDTC at 20 N for 30 min (The XPS data for the DLC coating lubricated with PAO-MoDTC at 80 N are similar to that at 20 N and not shown). The peak of Mo_{3d} centered at 229.1 eV corresponds to MoS_2 and Mo-oxides. The broad peak of S_{2p} at 163.3 eV can be assigned to MoS_2 and FeS [30, 31], where FeS can also be identified from the Fe_{2p} peak at 712.0 eV [28]. The broad peak of N_{1s} within 398.9–402.1 eV can be assigned to N-containing organic groups and NH_3 possibly originated from the source gas for nitriding and N-containing compounds. Prior investigators [9, 25] stated that all the elements derived from MoDTC were hardly detected on the worn surface, and the MoDTC was little active on the DLC coating. Possibly, there is no reaction between the lubricants and the DLC coatings at the

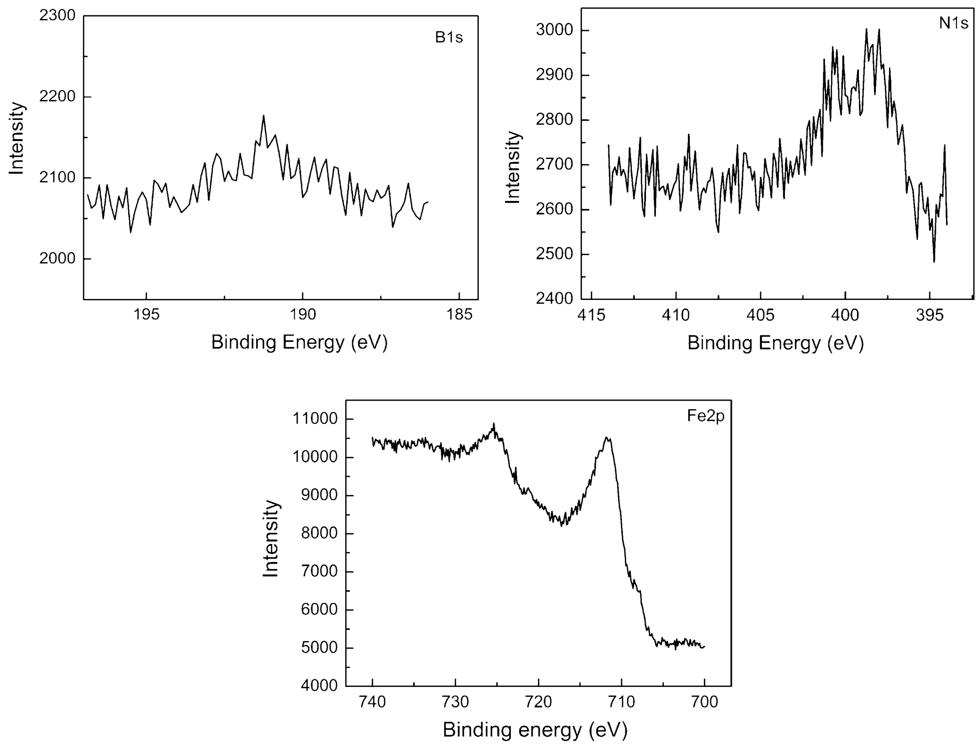


Fig. 13 XPS spectra of the worn surface of the upper ball of the Ti-DLC coating/steel sliding pairs lubricated with PAO-BN1 under 20 N for 30 min

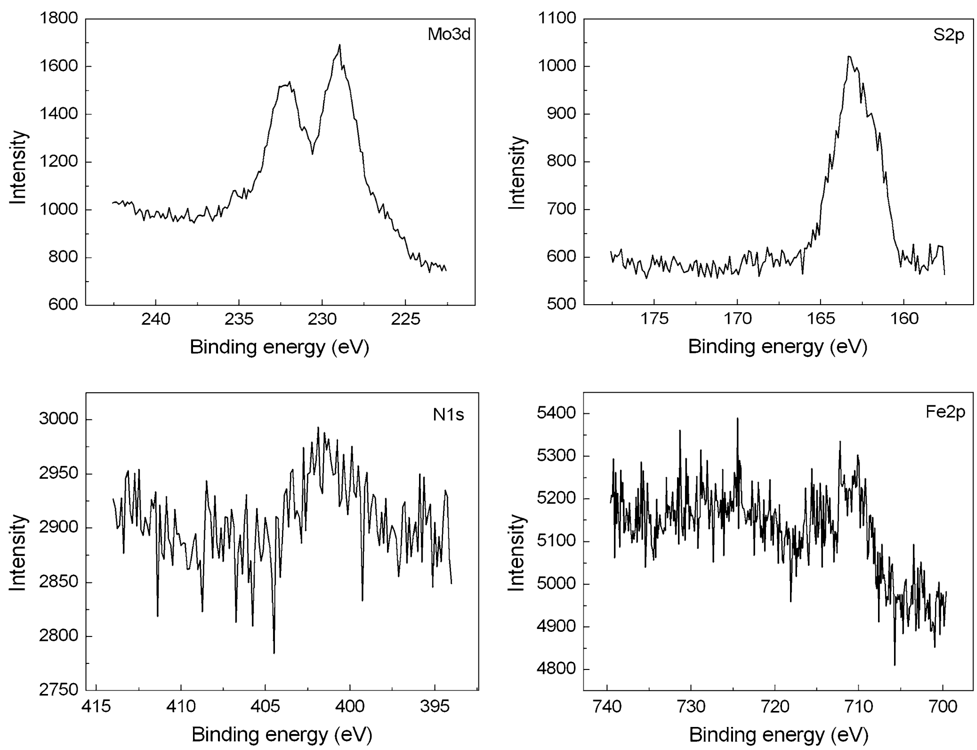


Fig. 14 XPS spectra of Ti-DLC coating lubricated with PAO-MoDTC under 20 N for 30 min

first few minutes, and Mo-oxides come from the degradation of MoDTC during sliding. Mo-oxide destroyed the DLC coating and the organic S-containing compounds react with Mo, and newly exposed Fe on the worn surface. All these compounds formed a protective tribofilm leading to a very low friction coefficient (see Fig. 10) along with sliding [30]. The XPS data for the worn surface of the upper ball of Ti-DLC/Steel pair lubricated with PAO-MoDTC showed that the tribofilm containing Mo, S and Fe elements existed on the worn surface of the upper ball.

4 Discussion

DLC coatings have attracted particular attention because of their excellent high hardness, low friction coefficient and chemical inertness. But, the large internal compressive stress in the film limited the usage of the DLC coating [27]. Many methods have been used to solve the problems of the high internal stress and poor adhesion of DLC films and metallic substrate. For example, element doping and/or interlayer (such as Ti, Si, W and others) between DLC coating and substrate are often used to resolve these difficulties [27, 32]. On the other hand, the friction and wear properties of ionic liquid borate esters and other borate esters have been investigated for DLC/steel and DLC/DLC pairs, and the result showed that tribofilm containing B and N existed and played an important role during sliding [9, 10].

Under boundary lubrication, the Ti/Al-DLC coating possesses a better tribological property than Ti-DLC coating under the same condition. The EDS analysis of the wear track of the Ti-DLC coating and Ti/Al-DLC coating was executed to get some clues for their difference on tribology. Table 1 shows the atomic concentration of the Ti-DLC coating and Ti/Al-DLC coating with PAO-BN1 at 80 N load for 30 min. Interestingly, the atomic concentration (%) of B and N on the worn surface of Ti/Al-DLC coating and Ti-DLC coating was 22.18, 2.62 and 17.10, 1.57, respectively. Some researchers [8–10] believed that borate esters degraded during sliding and produced B_2O_3, BN and N-containing compounds. The boron elements penetrated into the sublayer of surface due to its small atomic diameter. The N-containing compounds adsorbed on the worn surface of the pair because of the existence of B and triboplasma. The tribofilm containing B and N existed and played an important role on reducing friction and increasing wear resistance. The Ti/Al-DLC coating showed better than the Ti-DLC coating, possibly because of the higher atomic concentration of B and N on the worn surface of Ti/Al-DLC coating. Moreover, the hardness of the Ti-DLC coating and Ti/Al-DLC coating were 15.6 and 13.8 GP, respectively. It is more reasonable to conclude that more B atoms were permeated into the sub-layer of the Ti/Al-DLC coating than that of Ti-DLC coating because of its relatively lower hardness, and more N atoms were adsorbed on the worn surface of the Ti/Al-DLC coating because of the B atoms [8]. It is reasonable to presume that the excellent wear resistance of the Ti/Al-DLC coating is attributed to the increasing of the B and N atoms on the worn surface. On the other hand, prior investigator suggested that the hard film can improve the surface load bearing capacity and the soft film can decrease shear strength [33]. As for the adhesions between DLC coatings and substrates, the critical loads of Ti-DLC coating and Ti/Al-DLC coatings were 26 N and 31 N, respectively. Prior researchers suggested that a relatively high adhesion strength considerably improved the tribological behaviors of DLC coatings [22]. Possibly, the Ti/Al-DLC coating exhibited an excellent tribological property also because of the relatively higher adhesion and lower hardness than Ti-DLC coating.

Table 1 The atomic concentration (%) of different DLC coatings lubricated with PAO-BN1 at 80 N load

	C	O	B	N	Fe	Ti	Al
Ti-DLC worn surface	26.09	2.63	17.10	1.57	16.61	35.99	
Ti-DLC unworn surface	50.84	0.90			47.89	0.36	
Ti/Al-DLC worn surface	37.63	1.89	22.18	2.62	12.54	15.36	7.78
Ti/Al-DLC unworn surface	49.78	1.00			48.97	0.05	0.19

5 Conclusions

From the above experimental results, the following conclusions can be drawn:

(1) The Ti-DLC coating and Ti/Al-DLC coating on plasma nitrided mild steel exhibited much better friction-reducing and antiwear ability when sliding against 52100 steel under the lubrication of PAO containing synthesized benzotriazole-containing borate ester additives than under the lubrication of PAO-MoDTC. At a frequency of 50 Hz, the wear rate of the Ti-DLC coating lubricated with PAO-borate esters was only about one-seventh of that lubricated with PAO-MoDTC. The wear rate of the Ti/Al-DLC coating lubricated with the four lubricants is smaller than that of the Ti-DLC coating. At 20 N, the coefficient of friction of the Ti-DLC/steel pair lubricated with PAO containing BN1 is lower than the other two BN-containing additives under all frequency. The wear rate of the Ti-DLC/steel pair lubricated with PAO containing BN2 is the lowest among the three borate esters at 20–40 Hz. At 80 N, the wear rate of Ti-DLC/steel pair lubricated with BN1 is smaller than the other two borate esters at 10–20 Hz, and there is no significant difference at high frequency. As for Ti/Al-DLC coating, the wear rate of BN2 is the lowest among the three borate esters at 10–30 Hz, and there is no difference at other frequencies.

(2) Ti-DLC coating sliding against AISI 52100 steel under the lubrication of PAO-MoDTC was seriously

damaged and failed during the first few minutes of sliding at 20 N. However, it only experienced mild wear and damage when sliding against the steel counterpart under the lubrication of PAO-BN1 even at an increased load of 80 N, implying that the synthesized benzotriazole-containing borate ester additives had better friction-reducing and anti-wear abilities for the Ti-DLC coating/steel sliding pair than MoDTC.

(3) During sliding of Ti-DLC coating against steel in the presence of MoDTC in PAO, active S element and Mo-oxides were generated from the decomposition of MoDTC. The decomposed species chemically reacted with each other or freshly exposed Fe of the steel sliding surface, forming tribofilms containing Mo, S, and N-containing group, and subsequently reduced friction after the DLC coating was worn through. The atomic concentration (%) of B and N on the worn surface of the Ti/Al-DLC coating was larger than that of Ti-DLC coating, which possibly improved the wear resistance of the DLC coating. Possibly, the relatively higher adhesion and lower hardness of the Ti/Al-DLC coating also supplied better tribological properties than the Ti-DLC coating.

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