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Tribological performance of DLC coatings deposited by ion beam deposition under dry friction and oil lubricated conditions

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ABSTRACT

Understanding the reaction between lubricant additives and diamond-like carbon coatings is imperative for the improvement of the friction and wear properties of mechanical parts with diamond-like carbon coatings. Diamond-like carbon coatings were deposited with ion beam deposition and the influence of lubricant additives on the friction coefficients and wear rates of diamond-like carbon coatings under the lubricated conditions was studied. It was revealed that the wear rates of diamond-like carbon coatings under unlubricated conditions are 1.5×10^{-14} $m^3/(Nm)$ while they are decreased to 3×10^{-17} $m^3/(Nm)$ to 1.7×10^{-16} $m^3/(Nm)$ when lubricated by PAO-4 base oil with three additives. The addition of molybdenum dithiocarbamate in PAO-4 base oil decreases the friction coefficients of diamond-like carbon coatings to 0.07, but increases the wear rate of diamond-like carbon coatings. The addition of zinc dialkyl dithiophosphate to PAO-4 can slightly decrease the friction coefficient of diamond-like carbon coatings and improve the wear resistance of diamond-like carbon coatings. The addition of amine sulfuric-phosphate diester in PAO-4 can greatly decrease the wear rate of diamond-like carbon coatings to 3×10^{-17} $m^3/(Nm)$ but has a negligible effect on the friction coefficients of diamond-like carbon coatings.

1. Introduction

Wear is one of main reasons of failure of mechanical parts, being attended by substantial economic losses. Therefore, improvement of tribological performance of mechanical parts is a prerequisite of the development of modern machine design and manufacturing. Diamond-like carbon (DLC) coatings are widely used to protect the mechanical parts from wear due to their excellent physical and chemical properties such as high hardness, excellent tribological performance including low friction coefficients and low wear rates, high corrosion resistance, and high chemical stability [1,2].

Under unlubricated conditions, the friction coefficients and the wear rates of DLC coatings are greatly affected by environment [3–5], and the wear resistance of DLC coatings decreases with increasing friction temperature [5]. If DLC-coated samples are used under lubricated conditions, the lubricant can isolate the coatings from the air, which inhibits the untoward effect of environment on the tribological performance of the coatings; furthermore, the flowing liquid lubricant takes away the heat generated during friction and lowers the temperature at the contact surface, which is beneficial to the further improvement of the tribological performance of DLC coatings. Ban M. et al. found that lubrication can greatly decrease the friction and wear of DLC coatings [6]. Most of the currently used lubricant additives are designed to interact with ferrous-based surfaces [7], but for a proper selection of lubricant additives one must know the synergistic action of lubricant additives and coatings materials. Although many components are usually used under lubricated conditions [8], there still exists some indistinction concerning the tribological behaviors of DLC coatings under lubricated conditions [9–11]. In order to optimize the lubricated condition and effectively improve the performance of the mechanical parts with DLC coatings, understanding the correlation between the tribological performances of DLC-coated mechanical parts and the lubricated conditions is all-important.

Polyalpha olefin synthetic oil (PAO-4) is a kind of widely used base oil of engine lubricants [12], so studying the tribological performance of DLC coatings lubricated by PAO-4 with various lubricant additives is necessary for the application of DLC coatings in machines and mechanisms. In this paper, three widely used lubricant additives, including an antiwear and antioxidant additive of zinc dialkyl dithiophosphate (ZDDP), a friction modifier additive of molybdenum dithiocarbamate (MoDTC), and an extreme pressure and anti-wear

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additive of amine sulfuric-phosphate diester (T307) were added in PAO-4; and the influence of the lubricant additives on the tribological performance of DLC coatings under PAO-4 was studied.

2. Experimental

2.1. Sample preparation

DLC coatings were deposited on polished S31600 stainless steel plates and silicon wafers by ion beam deposition in a multifunctional ion plating device (ProChina, AS600DMTG). After the substrates were ultrasonically cleaned in metal cleaning agent/water solution, deionized water, next in ethanol, and dried in hot air. After the vacuum deposition chamber was pumped to a base pressure of 1.0×10^{-2} Pa, the sample surface was etched with argon ions produced by a linear anode layer ion source for 50 min. DLC coatings were deposited by ion beam deposition (the inlet gas into the ion source was the mixture of argon with a purity of 99.99% and methane with a purity of 99.99%). The ion beam deposition parameters for DLC coatings were as follows: the discharge voltage of the ion source was 300–400 V, the discharge current of the ion source was 4–6 A, the input fluxes of argon and methane were 160 sccm and 60 sccm respectively, and the total pressure during deposition was 3×10^{-1} Pa. The total thickness of the coatings was controlled at 2.3 μm. The roughness R_a of DLC-coated S31600 stainless steel samples is was 0.01.

In order to improve the adhesion between DLC coatings and the substrate, before the deposition of the DLC coatings, a gradual transition layer was deposited by ion beam assisted magnetron sputtering following depositing a Cr adhesion layer using vacuum arc ion plating.

2.2. Characterization

The surface morphology of DLC coatings was observed using scanning electron microscopy (JEOL, JSM6400). The chemical composition of DLC coatings was measured with Auger electron spectroscopy (PHI 700). The chemical bonding structure of the coatings was determined by X-ray photoelectron spectroscopy (PHI Quantera) and Raman spectroscopy (Renishaw, RM2000, the wavelength of the incident laser beam was 514.5 nm). The hardness of DLC coatings was evaluated by nano-indentation (MTS XP) with a load of 200 mN and using continuous stiffness mode. The film-substrate adhesion of DLC coatings was obtained by scratch test (Lanzhou Institute of Chemical Physics, MFT-4000) with a load rate of 100 N/min and a scratch length of 5 mm respectively.

The tribological performance of DLC coatings under unlubricated conditions and lubricated conditions was evaluated using a ball-on-disk wear tester (Lanzhou Institute of Chemical Physics, MS-T3000). The samples were placed on the disk with a rotary movement at a speed of 400 rpm. The counterparts for all wear tests were Si_3N_4 balls of 4 mm diam. The diameter of the circular wear track was 6 mm. The load was 1.96 N under unlubricated conditions and 9.80 N under lubricated conditions. The average value was obtained from three results.

PAO-4 was chosen as the base oil of the lubricant. The kinematic viscosity at 40 °C and the viscosity index of PAO-4 was 16.68 mm^2/s and 124 respectively. The widely used lubricant additives, ZDDP, MoDTC, and T307 were added in PAO-4 base oil at a concentration of 1 mass%.

3D optical surface profiler (Zygo, Micro XAM-3D) was used to measure the profiles of the wear tracks and the wear volumes were calculated from the profile. Scanning electron microscopy (JEOL, JSM6400) was applied to observe the worn surface of DLC-coated S31600 stainless steel.

3. Results and discussion

3.1. Surface morphology

The surface morphology of DLC films is shown in Fig. 1. It can be found that there exist a number of macroparticles on the surface of DLC coatings, and their size is less than 10 μm. The measurements by Auger electron spectroscopy (Fig. 2) revealed that the surface composition of the macroparticle is similar to that of the flat zones and no metallic inclusions have been found in the DLC coatings, which means that the macroparticles are not produced during the deposition of top layer of DLC coatings and have a negligible effect on the tribological performance of DLC coatings.

3.2. X-ray photoelectron and Raman spectra

C 1s spectrum of DLC coatings is indicated in Fig. 3. C 1s peak can be deconvoluted into three peaks which are attributed to sp^2-C (284.4 eV), sp^3-C (285.1 eV) and CO-contaminated carbon (287.4 eV) respectively. The concentration of sp^3 hybridization can be estimated by the ratio of the area of sp^3 peak to the sum areas of sp^3 and sp^2, which shows that the concentration of sp^3 hybridization in the deposited DLC coatings amounts to about 47%.

The Gaussian peak fitting of the Raman spectrum of the coatings is shown in Fig. 4. The spectrum consists of two peaks centered at 1389 cm^{-1} (D band) and 1560 cm^{-1} (G band) respectively. The D band is attributed to bond angle disorder in the graphite-like micro-domains affected by sp^3 bonds, and the G band is attributed to the symmetric E_{2g} C–C stretching mode in graphite-like materials [12]. The broadening of the lines is attributed to an amorphous structure of the films.

3.3. Mechanical properties

The measurement results of the nano-indentation test of DLC-coated samples are shown in Fig. 5. The change of the measured value for the indentation depth less than 100 nm is attributed to the effect of the surface roughness while the decrease of the measurement values with the indentation depth beyond 300 nm is caused by the substrate effect [11], and the stable measurement value for the hardness and elastic modulus for the depth from 100 nm to 300 nm can be taken as the hardness and elastic modulus of DLC coatings. The hardness and elastic modulus of DLC coatings is 17 ± 2 GPa and 170 ± 17 GPa respectively.

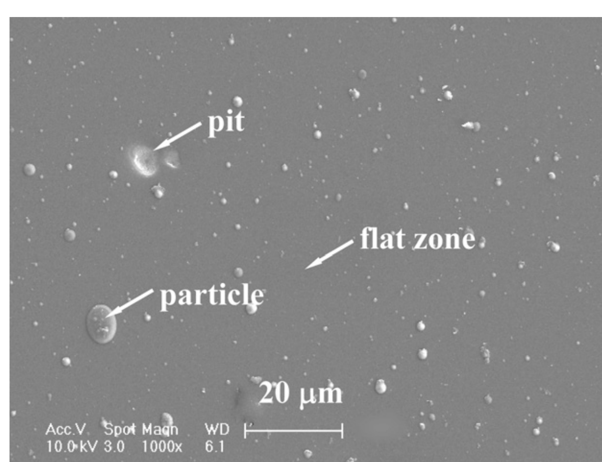

Fig. 1. Surface morphology of DLC coatings.

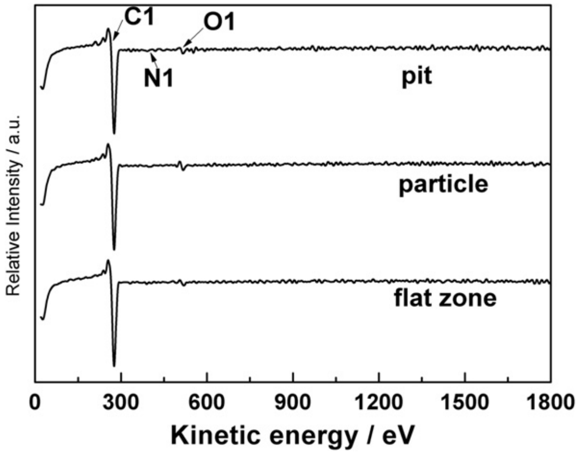

Fig. 2. Auger electron spectra in different zones on the surface of DLC coatings.

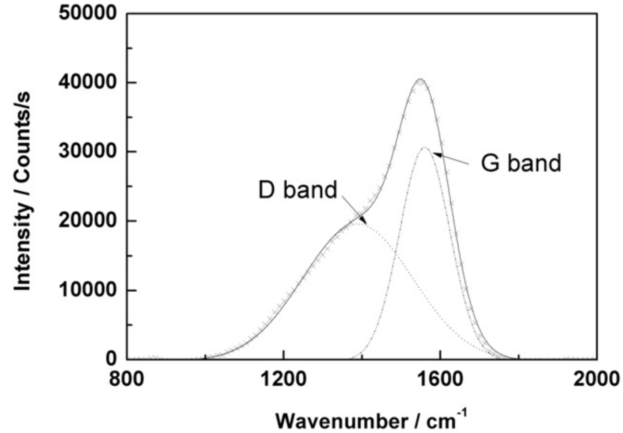

Fig. 4. Raman spectrum of DLC coatings.

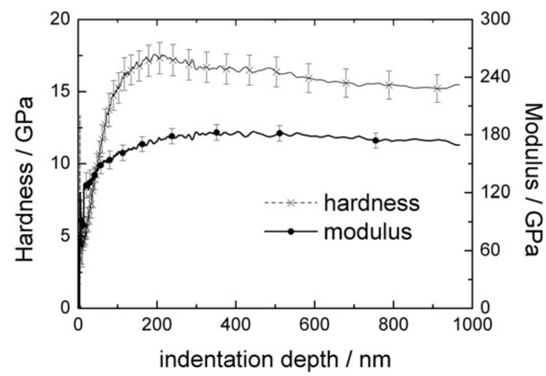

Fig. 5. Hardness and elastic modulus of DLC coatings.

A good adhesion between the coatings and their substrates is very important for the reliability of the wear resistant coatings on the mechanical parts working under a heavy load and an alternating load [13]. For hard coatings, a critical load of above 60 N is usually considered as an acceptable value for industrial application [14]. The scratch test showed that a good adhesion between DLC coatings and the substrates with a critical load of 85 N, which means that the fabricated DLC coatings could be used even under severe tribological conditions.

3.4. Tribological performance

The friction coefficients of DLC coatings against Si_3N_4 lubricated by PAO-4 with three additives are indicated in Fig. 6. The friction coefficients of DLC coatings lubricated by PAO-4 solution (0.07–0.11) are appreciably lower than those under dry friction (0.12). The introduction of T307 in PAO-4 has an unobvious effect on the friction coefficients of DLC coatings. The friction coefficients of DLC coatings can be decreased to 0.07 at the start but they are gradually increased with friction duration when MoDTC is introduced into PAO-4. The friction coefficients of DLC coatings lubricated by PAO-4 can be decreased to 0.09 when ZDDP is added into the PAO-4.

The wear rates of DLC-coated S31600 stainless steel samples lubricated by PAO-4 with three additives are shown in Fig. 7, in which PAO-4 with ZDDP, MoDTC, and T307 is denoted as PZ, PM, and PT respectively. The wear rates of DLC-coated samples under lubricated conditions are in the range from 3.8×10^{-17} m^3/(Nm) to 4.6×10^{-16} m^3/(Nm), which are much lower than those under dry friction (1.5×10^{-14} m^3/(Nm)). The addition of T307 and ZDDP in PAO-4 can reduce the wear rates of DLC coatings lubricated by PAO-4 solution from 1.0×10^{-16} m^3/(Nm) for those lubricated by pure PAO-4 to 8.2×10^{-17} m^3/(Nm) and 3.8×10^{-17} m^3/(Nm) respectively, and the improvement efficiency of wear rates of DLC coatings by T307 is more obvious than that by ZDDP. However, the addition of MoDTC in PAO-4 increases the wear rates of DLC coatings to 4.6×10^{-16} m^3/(Nm).

The surface morphology of the worn surface of DLC coatings under various lubricated conditions is shown in Fig. 8. It can be

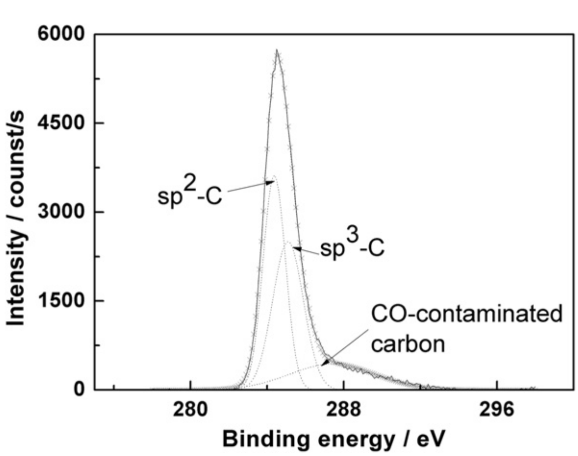

Fig. 3. C 1s spectrum of DLC coatings.

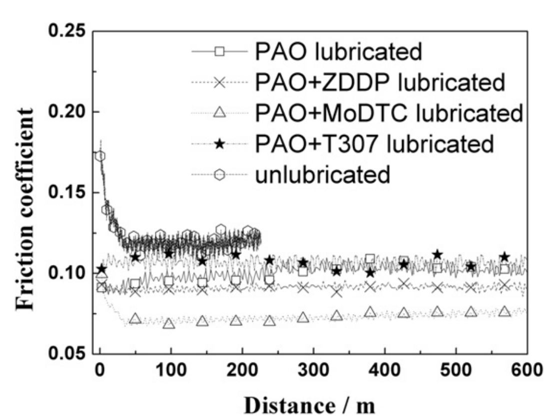

Fig. 6. Friction coefficients of DLC coatings under unlubricated and lubricated conditions.

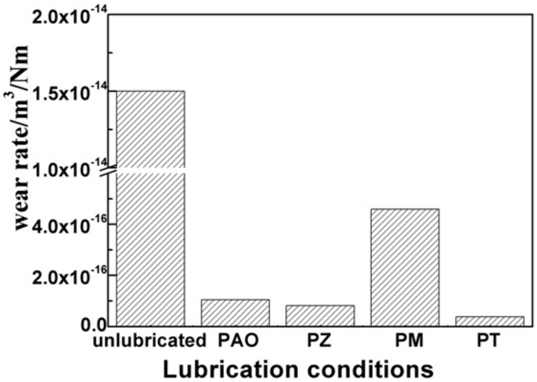

Fig. 7. Wear of DLC coatings of DLC coatings under unlubricated and lubricated conditions.

found that DLC coatings undergo a serious deformation under unlubricated conditions due to high Hertzian stress, while the fracture takes place only at a small part on the surface of DLC coatings under PAO-4 lubricated conditions. And the area of the fracture on the worn surface under PAO-4+MoDTC lubrication is larger than that under the others lubricated conditions.

The rubbing surfaces are often covered with a transfer layer, and the tribological performance of DLC coatings is closely related to chemical and physical nature of the transfer layer [15]. Under unlubricated conditions, the transfer layer is mainly composed of carbon-rich interlayer with a low shear strength, which can be transferred repeatedly back and forth between the two contact surfaces and contributes to low friction and wear rate [16,17].

Under lubricated conditions, a layer of lubricant films formed on the contact surfaces restrains the direct contact of the two counterparts and lowers the stress on the coatings surface, which makes the deformation of the coatings surface under lubricated conditions (shown in Fig. 8b–e) much less than that under unlubricated conditions (shown in Fig. 8a); and the shear strength of the liquid lubricant films is lower than that of carbon-rich transfer layer, which decreases the friction coefficient.

MoDTC is an additive containing Mo and S. When lubricated with MoDTC solution, Mo compounds containing sulphides and oxides formed on the contact surfaces due to the decomposition of MoDTC molecules during friction, and the MoS_2 formed on the surface of

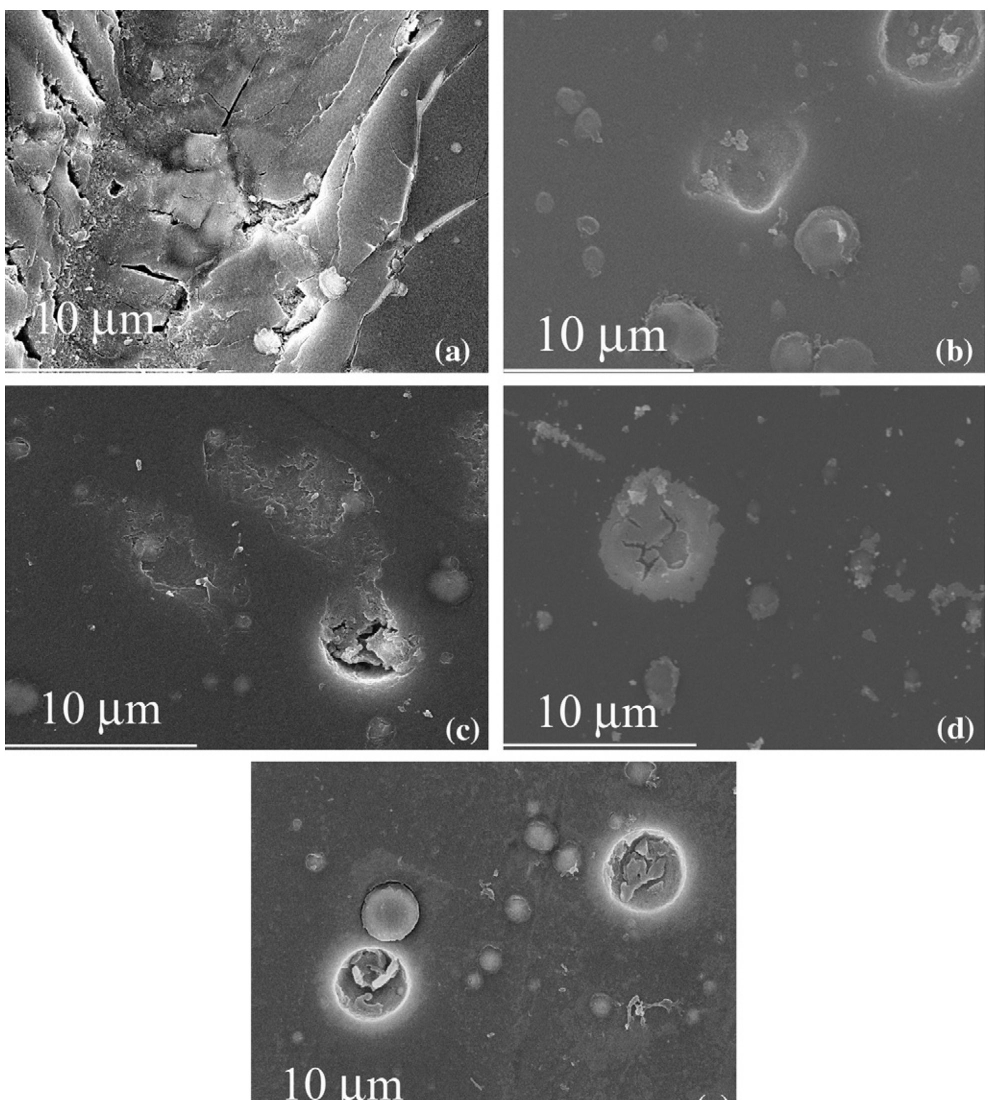

Fig. 8. Surface morphology of the worn surface of DLC coatings under (a) unlubricated conditions, and lubricated by (b) PAO-4, (c) PAO-4+MoDTC, (d) PAO-4+ZDDP, and (e) PAO-4+T307.

DLC coatings can reduce the friction coefficients [18,19]. The concentration of MoDTC in the lubricant is decreased with the decomposition of the MoDTC molecules, and the sulphides in the tribofilms are progressively oxidized into Mo oxides. When MoS_2 is gradually replaced by Mo oxides, the low boundary friction is lost, which makes the friction and wear increased [18,19]. Therefore, high wear rates are found for DLC coatings lubricated by PAO-4+MoDTC and the friction coefficient of DLC coatings lubricated by MoDTC solution is gradually increased with friction duration.

Zn, P, and S are found at the pads on the worn surface of DLC coatings by EDX, which implies that the tribofilms to improve the friction and wear performance are formed from ZDDP on the worn surface of DLC coatings. So the friction coefficients and wear rate of DLC coatings can be decreased by the introduction of ZDDP into PAO-4.

T307 is a kind of extreme-pressure and anti-wear additive containing S, P, and N to improve the wear resistance under high load or high velocity; the effect of S and P is realized through the formation of the tribofilms while N improves the tribological performance mainly by the physical adsorption and chemical adsorption [20]. Since the adsorption is not so dependent on the reaction between worn surface and lubricant additives, the contact between friction pairs can be segregated by the absorbed layer even when the tribofilms cannot be formed. The insufficiency of tribofilm formation due to the inert properties of DLC coatings can be counteracted with the formation of the absorbed layers. Therefore, the addition of T307 obviously improves the wear resistance of DLC coatings lubricated with PAO-4.

4. Conclusions

The wear rates of the DLC coatings lubricated with PAO-4 are much lower than those under unlubricated conditions, and the friction coefficients of DLC coatings can be reduced by PAO-4 lubrication. The introduction of MoDTC into PAO-4 is beneficial for reducing the friction coefficients of DLC coatings however it decreases simultaneously the wear resistance of the coatings. The friction coefficients and wear rates of DLC coatings lubricated with PAO-4 can be reduced by the addition of ZDDP in PAO-4. The addition of T307 in PAO-4 improves the wear resistance of DLC coatings however it has a negligible effect on the friction coefficients of the coatings.

Acknowledgments

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