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Effects of molybdenum dithiocarbamate and zinc dialkyl dithiophosphate additives on tribological behaviors of hydrogenated diamond-like carbon coatings

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ABSTRACT

The tribological behaviors of hydrogenated diamond-like carbon (DLC) coatings under varied load conditions lubricated with polyalpha olefin (PAO), molybdenum dithiocarbamate (MoDTC) and zinc dialkyl dithiophosphate (ZDDP) additives were investigated in this paper. Hydrogenated DLC coatings were synthesized through the decomposition of acetylene by the ion source. The tribological performances were measured on a SRV tribometer. The morphologies and chemical structures of the DLC coatings were investigated by the scanning electron microscope (SEM), Raman spectrometer (Raman) and X-ray photoelectron spectroscope (XPS). It was shown that the low friction and high wear were achieved on the hydrogenated DLC coating under MoDTC lubrication, while low wear was found on the hydrogenated DLC coating lubricated by ZDDP. The primary reason was attributed to different tribofilms formed on the contact area and the formation of graphitic layer. Both factors working together leaded to quite different tribological behaviors.

1. Introduction

The diamond-like carbon (DLC) coatings are increasingly used as protective surfaces for the mechanical parts to offer excellent tribological performances [1–4]. Most mechanical parts usually work under lubrication conditions. The tribofilm could separate two friction pairs under boundary lubrication regime, which would be beneficial to the further improvement of the tribological performances. The friction modifier Molybdenum dithiocarbamate (MoDTC) and the antiwear additive zinc dialkyl dithiophosphate (ZDDP) are the most commonly used lubricating oil additives in the fully formulated engine oil for ferrous surfaces. Boundary lubrication properties in the presence of anti-wear and anti-friction additives are mainly governed by the formation of tribofilms [5]. For ferrous substrate, the decomposition of MoDTC provides low friction MoS_2 tribofilm at the contact areas [6–8]; ZDDP forms zinc phosphate to provide antiwear performance [7–9] and the chain lengths of phosphate greatly influence the tribological behavior of the tribofilms [10]. However, for DLC coatings, the research results usually contradicted with each other.

In general, DLC coatings with different compositions deposited by physical vapor deposition (PVD) or chemical vapor deposition (CVD) could affect the chemical structures and mechanical properties of the tribofilms and graphitization degree, which may finally lead to the contradictory results. Recently, the high wear performance of DLC coating under MoDTC lubrication in the DLC/steel contact has been reported [11–16], as well as the graphitization of the DLC followed by the formation of hard Mo compounds result in high wear rate on the DLC film [13–15], whereas the graphitization was not detected in Ref. [16] and it was not mentioned in Ref. [11,12]. It was reported that ZDDP can form tribofilms on DLC coatings [17–21], whereas no tribochemical reaction between DLC coating and additive was found in Ref. [22–23]. Moreover, Vengudusamy et al. [17] recognized that graphitization occurred on W-DLC coatings, while Kalin et al. [18] pointed out no significant C–C structural changes of Ti-DLC coating appeared during the tribological tests.

The previous work [24,25] showed that the wear rates of DLC coatings under dry conditions are 1.5×10^{-14} $m^3/(Nm)$ while they decreased to 3×10^{-17} $m^3/(Nm)$ to 1.7×10^{-16} $m^3/(Nm)$ when lubricated by base oil with additives. MoDTC decreased the friction coefficients to 0.07, but increased the wear rate. ZDDP can slightly reduce the friction coefficient and improve the wear resistance.

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However, whether these phenomena would be affected by loads and how the tribochemical reactions and graphitization effects the tribological properties of DLC coatings are still not clear so far. To further understand the interrelation between the tribological performances of DLC coatings and the experimental conditions is all-important.

In this paper, the tribological behaviors of hydrogenated DLC coating lubricated by polyalpha olefin (PAO) with MoDTC and ZDDP under three load conditions were investigated. The friction and wear data of DLC coatings under different load conditions were compared. The tribofilms and graphitization layers were characterized, and the tribological mechanisms were discussed. It aims to further understand the tribofilms affecting the friction and wear behaviors of DLC coatings. It would be beneficial for selecting the experimental details and materials, providing support for more complex mechanism analysis and designing the lubricating oil of automotive engines.

2. Experimental details

2.1. Coating deposition

The hydrogenated DLC coatings (10–15 at.% hydrogen) were prepared by using ASM600DMTG multi-functional coater. The experimental material was 316L steel with a hardness of 153 HV, whose chemical composition is as follows: C $\leqslant$ 0.08, Si $\leqslant$ 1.00, Mn $\leqslant$ 2.00, P $\leqslant$ 0.035, S $\leqslant$ 0.03, Ni: 10.0–14.0, Cr: 16.0–18.0, Mo: 2.0–3.0. The substrate samples were 3 mm in thickness and with a roughness of 4.13 nm. Prior to deposition, all samples were ultrasonically cleaned in ethanol and petroleum ether. The vacuum deposition chamber was evacuated to a base pressure of 1.0×10^{-2} Pa. Pure argon (99.99 vol.%), nitrogen (99.99 vol.%) and acetylene (99.99 vol.%) gases were successively fed into the chamber to act as working gas. First of all, a functional graded Cr/CrN/CrCN/CrC interlayer was deposited by ion beam arc evaporation of Cr target. After that, DLC coating was deposited by ion beam deposition. The deposition parameters for DLC coatings were as follows: the discharge voltage of the ion source was 330 V, the discharge current of the ion source was 5 A, the input fluxes of argon and ethyne were 160 sccm and 60 sccm respectively, and the total pressure was 0.2 Pa. Finally, the total thickness of DLC coating was about 2.6 μm, and the DLC layer was about 1 μm.

2.2. Lubricants

Poly-alpha-olefin (PAO-4) synthetic oil was selected as the base oil, whose kinematic viscosity was 16.68 mm^2/s at 40 °C. Friction modifier MoDTC (Mo 10 at.% and S 11 at.%) and extreme antiwear additive ZDDP (Zn 10 at.%, P 8 at.% and S 15 at.%) were used as additives. The additive content (mass fraction) in the base oil was fixed at 1.0 wt.%.

2.3. Tribological tests

The experiments were carried out on an Optimol-2 SRV oscillating friction and wear tester in a ball-on-disc contact configuration. The upper balls were made of AISI 52100 steel with a diameter of 10 mm and hardness of 770 HV. The lower stationary samples (12 mm $\times$ 12 mm) were made of DLC coated 316L steel. The experimental parameters of friction and wear tests were shown as below, load: 20 N, 50 N and 100 N (corresponding to Hertz mean contact stress of 0.8 GPa, 1.09 GPa and 1.37 GPa), test duration: 60 min, frequency: 50 Hz, sliding distance: 1 mm, temperature: 100 °C. The lambda ratio of EHD film thickness over the composite surface roughness can be used to evaluate the lubrication regime. The lambda ratios for DLC coatings at the load of 20 N, 50 N and 100 N are 0.45, 0.42 and 0.4 respectively, which present that all lubrication conditions are just in the boundary lubrication regime. The morphologies of wear DLC coated samples were observed by NanoMap-D profilometer and the wear scar diameters of balls were measured by optical microscope. The wear volumes were then calculated by the NanoMap-3D controlled software. Finally, the wear rates of DLC coated samples and upper balls were calculated by the following equation:

$$A = \frac{\Delta V}{F \times S}$$

(F = 20 N, 50 N and 100 N; S = 360 m.

For the balls: $\Delta V = \frac{\pi h(3r^2+h^2)}{6}$, $h = R - \sqrt{R^2 - r^2}$, R = 5 mm, r is the wear scar radius).

Three repeated measurements were performed under the same conditions in order to check the repeatability of the measurements. The averaged value was adopted in this paper.

2.4. Surface analysis

All samples were further degreased in ethanol and petroleum ether to eliminate all the remaining oil and contaminants before the surface analysis. The surface morphologies were observed through the JSM-7001F Scanning Electronic Microscope (SEM). Microscopic Confocal Raman Spectrometer RM2000 with 514.5 nm wavelength of Ar laser was used as an effective approach to identify the structures of carbon and the degree of graphitization. ESCALAB 250Xi X-ray photoelectron spectroscope was used to investigate the chemical states of the typical elements in the worn surfaces, using Al Kα radiation as the excitation source, and the binding energy of C 1s (284.5 eV) was chosen as a reference for charge correction. Casa XPS software [26] was used to analyze the XPS curves obtained from long scans to confirm the chemical composition.

3. Results and discussion

3.1. DLC coatings

Fig. 1 shows the SEM morphologies and 3D images of hydrogenated DLC coating. The coating was quite smooth and dense with a roughness of 21.4 ± 1.0 nm. Some particles and pit defects could be found on the coating, which were formed during the preparation of metal buffer layer. The increasing number of evaporated metal particles resulted in the formation of metal droplets on the surface, and the pits were formed due to falling off of the droplets. The nano-hardness and elastic modulus of the hydrogenated DLC coating was about 17 GPa and 175 GPa respectively [24,27].

3.2. Behaviors of friction and wear

The mean coefficients of friction and wear rates of hydrogenated DLC coatings and counterparts under PAO, MoDTC and ZDDP lubrication at different loads are presented in Fig. 2. The friction coefficients of hydrogenated DLC coatings were around 0.11–0.12 when only PAO is used. Under ZDDP lubrication, there was no improvement in friction reducing of hydrogenated DLC coatings. The friction coefficients remained at 0.11–0.13. However, when the coatings were lubricated with MoDTC, the friction coefficients dramatically dropped to 0.06–0.07. It indicates that the friction reducing property of hydrogenated DLC coating could be improved by MoDTC additive. In addition, higher load did not show any effect on the friction coefficients of DLC coatings under the same lubrication condition.