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Synergistic effects between sulfurized W-DLC coating and MoDTC lubricating additive for improvement of tribological performance

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ABSTRACT

Low temperature ion sulfuration technology was used to obtain sulfurized layer on W doped diamond-like carbon (W-DLC) coating. The tribological behaviors of the pure W-DLC and sulfurized W-DLC coatings were investigated under PAO and MoDTC lubrication conditions. It shows that sulfurized W-DLC coatings can obviously improve their tribological performances under PAO with MoDTC lubrication. The primary reason is due to the formation of WS_x on the surface of sulfurized W-DLC coating, the decomposition of additives for formation a higher ratio of Mo sulfide/Mo oxide and the graphitization for a high ratio of sp^2/sp^3.

1. Introduction

Owing to the increasing demand of low emissions and fuel economy in automotive industry, the reduction of friction and wear of tribocomponents is of great importance [1,2]. Fortunately, this can be achieved by the development of the materials science and lubrication technologies. In recent years, diamond-like carbon (DLC) coating becomes increasingly attractive due to its excellent performances, such as high hardness, low friction and high wear-resistance [3–6]. MoDTC is a well known friction reducing additive which has been used in formula lubricating oil. Accordingly, many researchers have focused on the effects between various DLC coatings and MoDTC. The good anti-friction performance of DLC coatings lubricated by MoDTC is primarily attributed to the formed metal sulfide. DLC coatings in several different tests exhibited an improvement in friction reduction property by forming MoS_2-containing tribofilm on the contact area when MoDTC was used [7–9]. However, wear resistant properties were seldom taken into consideration, especially the comparison between PAO and MoDTC. Vengudusamy et al. [10] investigated the tribological behaviors of several types (a-C, a-C:H, WC-DLC, Si-DLC, etc.) of DLC coatings for MoDTC solution in DLC/steel contacts. It showed that the wear rates of DLC coatings lubricated with MoDTC were even higher than those under PAO lubrication. The reason may be a larger amount of MoO_3 formed in the tribofilm. MoO_3 is believed to act as abrasive particles and so they may enhance removal of tribofilms from DLC coatings and cause high wear losses. Haque et al. [11] pointed out that higher MoS_2/MoO_x ratio provided better wear protection. Thus, it is important to find a way to obtain high MoS_2/MoO_x ratio. S atom was reported to promote the formation of MoS_2 [12,13], meaning a higher MoS_2/MoO_x ratio. By increasing the content of S in MoDTC solution, or adding S-containing additive, higher MoS_2/MoO_x ratio could be obtained. However, this is against with the principle of environmental protection that low sulfur in the lubricating oil is required. Another approach is the use of surface modification technology, which can produce a sulfide film on metallic surfaces [14,15]. Our previous study showed that the sulfurized W-DLC coating showed better tribological performances under dry condition compared with pure W-DLC coating [16,17]. Hence, it is supposed that sulfide layer prepared on the DLC coating could exhibit good tribological behaviors itself and promote more MoS_2 forming, which may achieve a better tribological performances.

In the present paper, Me–DLC coatings with tungsten as metal content (W-DLC) was selected which can offer an active surface chemistry to the additive. A combined tribological system of sulfurized W-DLC coating and MoDTC was investigated aiming at further deeply understanding the mechanism of synergistic effects.

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2. Experimental details

The substrate sample was made from 316L steel, with a hardness of 153 HV and surface roughness Ra = 4.13 nm. W-DLC (the content of W is 27.7%) and sulfurized W-DLC coatings were compared in this investigation. The W-DLC coatings were prepared by using ASM600DMTG multi-functional coater. A functional graded Cr/CrN/CrCN/CrC interlayer was deposited by ion beam arc evaporation of Cr target first. After the deposition of the graded interlayer, W-DLC coating was deposited by ion beam deposition (the inlet gas into the ion source was the mixture of argon and ethyne) combined with DC magnetron sputtering of W target. During the deposition of W-DLC coating, the DC magnetron sputtering current is gradually decreased, while the discharge voltage of the sputter target was 250 V and the ion beam deposition conditions were unchanged, so a graded W-DLC coating was synthesized. The DC magnetron sputtering current of W target for the top layer of the W-DLC coating was 7A. The detailed parameters of deposition were described in reference [17]. The total thickness of W-DLC coating was about 2.6 μm. The sulfurized W-DLC coating was produced in a LDM2-15 model plasma low temperature ion sulfuration furnace. Table 1 shows the process parameters of low temperature ion sulfuration technology.

Friction and wear tests were performed on a MS-T3000 model ball-on-disc tribo-tester, with 4 mm diameter 52,100 steel balls (hardness of 770 HV) against coated stationary disc. The test was conducted at a load of 10 N (corresponding to the Hertz mean contact stress of 1.29 GPa), linear speed of 0.125 m/s and test duration of 30 min in ambient temperature. The lambda ratio of EHD film thickness over the composite surface roughness can be used to evaluate the lubrication regime. The lambda ratios for both W-DLC and sulfurized W-DLC coatings are 0.4, showing that the lubrication was just in the boundary lubrication regime. Prior to testing, all samples were ultrasonically cleaned in ethanol and petroleum ether, then, a thin layer of oil was spread over the surface of the disc. Poly-alpha-olefin (PAO-4) oil, with a viscosity of 16.68 mm^2/s at the temperature 40 °C, was used as a base oil. Friction modifier MoDTC (Mo 10 at% and S 11 at%) was chosen as the additive. The adding content was 1.0 wt%. Each test was repeated three times under the same conditions in order to check the repeatability of the measurements.

During the tests, the coefficient of friction was monitored and recorded continuously by the computer. Nano Map-D dual mode 3D profilometer was used to observe the worn surfaces. The roughness of samples and wear volumes were calculated also by the software affiliated with the 3D profilometer. The phase composition of W-DLC and sulfurized W-DLC was measured with an X-ray diffractometer (XRD). JSM-6460LV scanning electron microscope (SEM) was utilized to observe the surface morphologies. ESCALAB 250Xi X-ray photoelectron spectroscope (XPS) was employed to identify the valence state of some typical elements on the worn surfaces after etching 10 nm. The instrument used a high-power rotating anode and monochromatised X-ray of Al Kα source. The binding energy of 284.5 eV for C 1s was selected as a reference for charge correction. Prior to XPS analysis, the samples were immersed in the mixed solution of ethanol and petroleum ether to eliminate the residual lubricant. Casa XPS software [18] was used to analyze the XPS curves obtained from long scans to confirm the chemical composition. All fitted spectra subsequently underwent a Shirley background subtraction. The value of slope was changed to obtain the desired background. The position and full-width at half-maximum (FWHM) were constrained in order to obtain information with the most appropriate chemical meaning.

Table 1
Process parameters of low temperature ion sulfuration technology.

Treatment	Current (A)	Temperature (°C)	Voltage (V)	Time (h)	Pressure (Pa)
Ion sulfuration	1–2	200	900	4	10–20

3. Results and discussion

3.1. Characterization

Fig. 1 shows the surface morphologies of W-DLC and sulfurized W-DLC coatings. It can be seen that the coatings are smooth and dense, but there exist some particles and pit defects. This phenomenon may usually happen during the preparation of metal buffer layer. The increasing number of evaporated metal particles led to the formation of metal droplets on the surface, while parts of the droplets fell off forming the pits. The nano-hardness of sulfurized W-DLC coating was 18.7 GPa, a little lower compared to 19.3 GPa of W-DLC coating due to the sulfuration treatment [16]. The roughnesses of the W-DLC and sulfurized W-DLC coating are nearly the same, 11.4 nm and 12.0 nm, respectively.

Fig. 2 shows the phase composition of W-DLC and sulfurized W-DLC coatings. Only WC phase ($2\theta = 35.60°$) was detected on the coatings. S-contained phase was not found in sulfurized W-DLC coating after ion sulfuration treatment. The reason may be that the generated amount of sulfide was less than the detection range of XRD.

To further understand the chemical composition of W-DLC and sulfurized W-DLC coatings XPS was used to measure the chemical

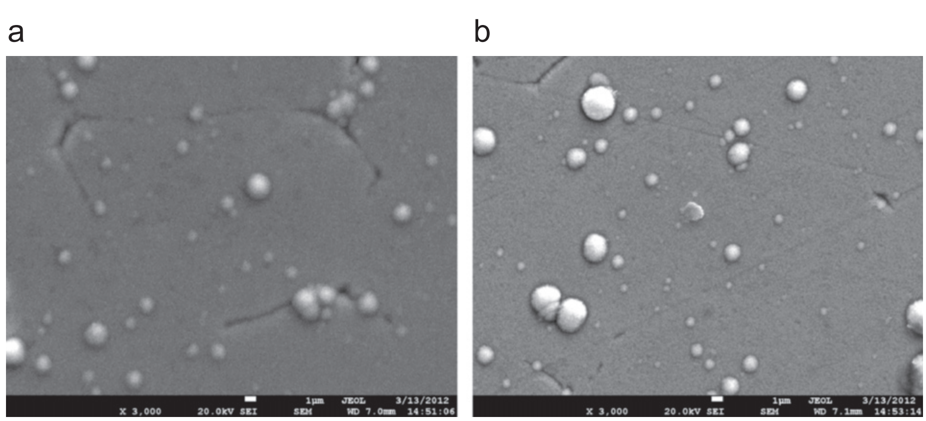

Fig. 1. Typical SEM images of W-DLC and sulfurized W-DLC coatings: (a) W-DLC and (b) sulfurized W-DLC.