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.
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 on the bottom layer of the W-DLC coating. After that, the top layer of the W-DLC coating was synthesized. 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 7 A. 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 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 153 HV and surface roughness Ra = 4.13 nm. 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.

Table 1

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Current (A)</th>
<th>Temperature (°C)</th>
<th>Voltage (V)</th>
<th>Time (h)</th>
<th>Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion sulfuration</td>
<td>1–2</td>
<td>200</td>
<td>900</td>
<td>4</td>
<td>10–20</td>
</tr>
</tbody>
</table>

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.

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 (2θ = 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
bonding state of major elements. The XPS detailed spectra are shown in Fig. 3. It indicated that W, WC and WO2 are the main existing forms in W-DLC coating, while WS2 [19], WC and WO2 are in the sulfurized W-DLC coating as shown in Fig. 3(a). The chemical bonding state of S element is shown in Fig. 3(b). It confirmed the existence of tungsten sulfide in sulfurized W-DLC coating. The weak S spectrum implied the amount of sulfide is quite small. The analysis exactly verified the assumption of above XRD analysis result.

Fig. 4(a) shows the Gaussian fitting Raman spectra of W-DLC and sulfurized W-DLC coatings. It can be seen that both W-DLC and sulfurized W-DLC show typical amorphous carbon Raman characteristic peaks, consisting of a broad band D peak and a sharply peaked band G peak. As for W-DLC, the spectrum is composed of two bands centered at approximately 1562.5 cm\(^{-1}\) (G band) and 1390.8 cm\(^{-1}\) (D band). However, when it comes to the sulfurized W-DLC, the two bands are 1566.9 cm\(^{-1}\) (G band) and 1395.6 cm\(^{-1}\) (D band). The ratio ID/IG of sulfurized W-DLC coating increased from 2.46 to 2.48. It indicated that the sp\(^2\) content increased in sulfurized W-DLC coating due to the ion sulfuration treatment. In order to strengthen the Raman result, XPS analysis was taken into account, as shown in Fig. 4(b). It can be calculated that the sp\(^2\)/sp\(^3\) ratio changed from 1.88 to 3.66 after the low temperature ion sulfuration. It is confirmed that the graphitization occurred on the sulfurized coating.

3.2. Friction and wear behaviors

Fig. 5 shows the variations of friction coefficient of W-DLC and sulfurized W-DLC coatings with time under different lubrication...
conditions. The results showed that the friction coefficients of W-DLC and sulfurized W-DLC were the same under PAO lubrication except that the curve fluctuation of sulfurized W-DLC was in a narrower range. When MoDTC was added, the friction coefficients of both coatings obviously dropped, and the sulfurized W-DLC coating exhibited even lower friction coefficient. That means the sulfurized W-DLC coating showed a remarkably friction-reducing effect under MoDTC lubrication.

The calculated wear rates of all samples are shown in Fig. 6(a). It also can be found that the sulfurized W-DLC coating showed better wear resistance compared to W-DLC coating. When MoDTC was added, the wear rates of W-DLC and sulfurized W-DLC coatings increased compared to PAO lubrication. It means that MoDTC cannot improve the wear resistance of W-DLC coatings. Fig. 6(b) shows the wear rates of balls against W-DLC and sulfurized W-DLC coatings. In all cases, the wear rates of balls against sulfurized W-DLC coating were smaller than those against W-DLC coating. This indicated that the sulfurized W-DLC coating combined with MoDTC additive could lower the wear loss of the counterpart ball.

3.3. XPS analysis

The XPS spectra of the worn surface lubricated with MoDTC are given in Fig. 7. The binding energy values and the main components of the reference compounds are listed in Table 2. It can be seen that the chemical state of C 1s can be identified, the binding energies at 283.6 ± 0.2 eV, 284.5 ± 0.1 eV, 285.2 ± 0.1 eV and 286.6 ± 0.2 eV are corresponding to W–C, sp2-C, sp3-C and CO-contaminated. S 2p binding energy is usually corresponding to the sulfide, which was found on the sulfurized surface and on the worn scar with MoDTC lubrication. On W-DLC coatings, W 4f [19,20] presents mainly in the form of W, WC and WOx, while on the sulfurized W-DLC coatings in the form of WC, WS2 and WOx. When MoDTC was used, MoS2 and MoOx [2,11,12,18] were found in tribofilms on the worn scar. The binding energies of MoS2 are 229.5 ± 0.1 eV and 232.7 ± 0.1 eV. MoOx was detected at 228.5 ± 0.2 eV, 231.7 ± 0.2 eV, 232.3 ± 0.5 eV and 235 ± 0.5 eV.

3.4. Discussion

Low temperature ion sulfuration is a good way to obtain sulfide solid lubrication film, which usually shows high bearing capacity and low friction coefficient behaviors [14–16]. It can be seen from Fig. 5 that after the ion sulfuration treatment, the friction coefficient of sulfurized W-DLC coating lubricated with MoDTC was decreased compared with that of pure W-DLC coating under the same lubrication condition. This result can be attributed to the formation of metallic sulfide layer on W-DLC coatings. WSx can...
reduce friction due to its layered structure and prevention of the direct contact of the rubbing surfaces. Noshiro et al. [21] and our previous work [16,17] all presented that the sulfur compounds on DLC coating can improve the friction reducing property effectively. Moreover, it can be seen from Fig. 4 that graphitization occurred during low temperature ion sulfuration process. It is beneficial also to improve the friction reducing property.

The effects of sulfuration or graphitization on friction reduction were not obvious if MoDTC was not added. Thus it is important to understand the mechanism of MoDTC. MoDTC is a well-known friction modifier, which can reduce friction by forming a MoS₂-containing film on the tribological contact area [22–25]. During the friction and wear process, heat produced by friction promoted the decomposition of MoDTC. It can be seen

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**Fig. 7.** XPS detailed spectra of tribofilm formed on MoDTC lubricated worn surface: (a–d) W-DLC coating and (e–h) sulfurized W-DLC coating (a) C 1s, (b) W 4f, (c) Mo 3d, (d) S 2p, (e) C 1s, (f) W 4f, (g) Mo 3d, (h) S 2p.
from the XPS analysis (Fig. 7c and g)), MoS2 and MoOx (MoO2 or MoO3) are detected on the worn surfaces, while only MoOx (MoO2 or MoO3) exists outside the worn scar. That means MoDTC can be decomposed even when the tests were conducted at room temperature [13,18,26]. MoS2, one of the decomposition products of MoDTC, plays a major role of friction reduction. As well, its effectiveness depends also on the ratio of Mo sulfide/Mo oxide [18]. High fraction of Mo oxides in the tribofilm can weaken the effectiveness of Mo sulfide in reducing friction. The Mo sulfide/Mo oxide ratio can be calculated via the Mo 3d detailed spectra. The calculated ratio in worn surface of sulfurized W-DLC coating is 1.63, higher than 0.4 in worn surface of W-DLC coating. The main reason may be that WS2 provides more S2− to react with the decomposition products of MoDTC, which promotes more Mo2 formation in the tribofilm of sulfurized W-DLC coating. Besides, the sp2/sp3 ratio can be calculated via the C 1s detailed spectra. The calculated ratio of worn W-DLC coating changes from 1.88 to 2.4 due to friction, and from 3.66 to 8.8 for worn sulfurized W-DLC coating. More sp2-C content in the tribofilm is beneficial to friction reduction performance. It is implied that the lower friction coefficient for sulfurized W-DLC coating lubricated with MoDTC are attributed to the formation of WS2 and the higher ratios of Mo sulfide/Mo oxide and sp2/sp3 in the tribofilm.

Wear rate of pure W-DLC coatings did not decrease under MoDTC lubrication in this research, as shown in Fig. 6a. It is reported that despite its low friction coefficient, the CrC/a-C:H coating with 70 at% Cr content shows deep grooves and severe coating wear after friction test under oil with MoDTC [27]. It is suggested that the decomposition product from MoDTC (MoOx) will react with the amorphous component (C–H bonds and dangling bonds) in the DLC and promote its wear rate [28]. MoOx is believed to act as abrasive particles [24] and so they may enhance removal of tribofilms from the DLC coating [2,11]. Hence, it is suggested that the dominance of MoS2 and depletion of MoOx in the tribofilms formed on the sulfurized W-DLC coating surface provided better wear protection than pure W-DLC coating. The negative effect of MoDTC on wear could be prevented in some extent in the preparation of sulfide layer on W-DLC coating. Moreover, the low shear strength graphite-rich and sulfide composite top layer on contact zone and combining the support of the sublayer with a high hardness can provide better wear resistance for sulfurized W-DLC coating under both PAO and MoDTC lubrication.

4. Conclusions

Based on this research the following conclusions can be drawn:

(a) Sulfurized W-DLC coating can improve the tribological properties of W-DLC coating under boundary lubrication, especially the friction reduction performance under MoDTC lubrication.

(b) Sulfurized W-DLC coatings could lower the wear losses of the pure W-DLC coatings and the counterpart balls under both PAO and MoDTC lubrications.

(c) The improved tribological properties of sulfurized W-DLC coating lubricated with MoDTC are mainly due to the formation of WS2, and the higher ratio of Mo sulfide/Mo oxide and sp2/sp3 in the tribofilm.

Acknowledgments

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