Tribochemical interactions of piston ring coatings with molybdenum dithiocarbomate friction modifier

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In a typical tribosystem, the interactive behaviors of its three major elements - tribo-materials, lubricating oil basestocks and tribological additives, are critical to its tribological performances. Especially the effectiveness of the tribological additives is strongly dependent upon the tribo-materials [1, 2]. Research into the tribochemical interactions between the two basic elements in tribosystems can be beneficial to tribochemical design of the tribo-materials.

Molybdenum dithiocarbomate (MoDTC), one of the primary oil soluble organomolybdenum additives, is a very popular commercial friction modifier. Owing to its claimed superior friction performance, MoDTC has been widely investigated and are finding more and more applications. By investigating the effect of base stocks on the tribological behavior of MoDTC, Yamamoto et al [3, 4] found that when added into pure triaconthexaene (an advanced lubricating oil of low freezing point), MoDTC exhibited good friction-reducing and wear resistant performances at temperatures even up to 473 K. Stipanovic [5] concluded that the superior tribological behavior for MoDTC could be achieved when added into the base stocks with higher saturate content and aniline point. Yamamoto [6] also studied the effect of surrounding atmospheres, including air, oxygen, nitrogen and argon, on the tribological behavior for MoDTC and concluded that the atmosphere with higher O_2 content is essential to the formation of MoS_2 film decomposed by MoDTC on the worn surfaces. More recently, focus of numerous studies about MoDTC has been imparted to its interactions with other functional additives existing in the actual lubricants. It has been reported that a synergistic effect for friction-reduction and wear resistance could be obtained in the case of MoDTC and ZDTP combinations [7–9].

Obviously, up to now, there still lacks systematic tribochemical insights into the effect of tribo-materials on the tribological behaviors for MoDTC. In the current investigation, the tribochemical interactions of three typical gasoline engine piston ring coating materials with MoDTC were examined through X-ray photoelectron spectroscopy (XPS) analysis of chemical compositions and states of functional additive elements on the worn surfaces.

Tribological testing was carried out on an Optimal-SRV tribotester in air of about 15% relative humidity, with the contact geometry and interaction mode of the tribopair specimen shown in Fig. 1. Three kinds of coatings for gasoline engine piston rings, Mo-sprayed coating, Cr-plated coating and nitrided coating, were used as the upper specimens, and their hardness of working surfaces were 972 Hv, 1259 Hv and 634 Hv, respectively. The lower specimen mated with the three coatings was plain grey cast iron with a microstructure of pearlite + ferrite + graphite and a hardness of 234 Hv. The lubricant used was formulated by adding the MoDTC at 3 wt.% into a fully formulated mineral gasoline engine oil SJ/5W-30. For comparison, the crankcase oil SJ/5W-30 with no MoDTC was used and experimented as a baseline in the tribotest.

Tribological tests were run in two consecutive stages, as specified in Table I. For accuracy, each of the tests at the same conditions was run three times. Before each test run, ca. 40 μL lubricant was applied onto the contact region with a microsyringe.

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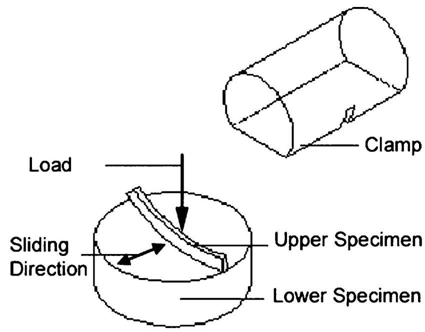


Figure 1 Geometry of friction pairs.

Frictional coefficient (μ) was recorded by the SRV tribotester. Wear rates of the specimens were deduced from the wear tracks. Worn morphologies of the specimens were observed by an Opton CSM950 type scanning electron microscopy (SEM). Examination of chemical status on the worn tracks was implemented on a PHI-5300 X-ray photoelectron Spectrometer(XPS) with excitation source of Al K_a, pass energy of 37.750 eV and internal reference standard of C1s at binding energy of 284.6 eV.

Fig 2 shows exemplarily the frictional behavior of the designated tribosystem as a function of time for the three tribopairs (Mo-sprayed, nitrided and Cr-plated coatings vs. the grey cast iron) lubricated by SJ/5W-30 engine oil with and without added MoDTC during one of the three test runs, since for the three runs, there shows a similar dependance of the frictional behavior on the testing time.

It can be observed that MoDTC can decrease frictional coefficient (μ) with its effectiveness depending heavily on the piston ring coating types. As for the starting time needed for the frictional coefficient (μ) to decline, for example, there needs approximately 48 min for the Cr-plated coating. This starting time is near 10 times longer than that for the nitrided coating, which indicates that, in the presence of the nitrided coating, MoDTC can exhibit its anti-friction performance in a more rapid way. This result suggests that much attention should be paid to the selection of tribo-materials in order to achieve the optimal frictional performance for the MoDTC friction modifier.

TABLE I Norms of tribological test

Test period	Load / N	Temperature/ °C	Time/ min	Note
Running-in	100	100	5	Frequency: 50Hz Stroke: 1mm
Running	250	125	55	Average speed: 0.16 m/s

The anti-wear performances for MoDTC are also greatly affected by the piston ring coating types. In Table II is presented the anti-wear measurements produced by MoDTC in the case of the three coatings. Rw, which represents the anti-wear effect for MoDTC, is defined as $Rw = \Delta W/W_M$ wherein ΔW stands for the change of wear rate due to MoDTC, i.e., $\Delta W = W_M - W_{MC}$, in which W_M and W_{MC} correspond to the wear rate when lubricated with and without added MoDTC, respectively. A positive value of the Rw means MoDTC has brought about anti-wear effect.

The data in Table II show that obvious anti-wear effect for MoDTC can be achieved for all the three coatings, and, comparatively, MoDTC can exhibit superior anti-wear effect in the case of the nitrided coating.

Fig. 3 displays the representative morphologies of the worn surfaces of the three piston ring coatings when lubricated with the lubricant of added MoDTC.

Clearly, the wear modes for the three piston ring coatings mated with the same grey cast iron material belong to abrasion. The wear severity, however, varies depending on the coating types. Comparatively, the ploughing grooves on the nitrided coating are slender and shallow, while the grooves produced on the worn Cr-plated surface are wider and deeper. As for the wear of the cast iron mated with these coatings, it can be seen from Fig. 4 that the wear mode and severity for the grey cast iron are different for the three types of mated piston ring coatings. When mated with the Cr-plated coating or the Mo-plated coating, the worn cast iron surface exhibits typical features of abrasion, and wider and deeper ploughing grooves can be observed on the worn surface mated with Cr-plated coating compared with those mated with the Mo-sprayed

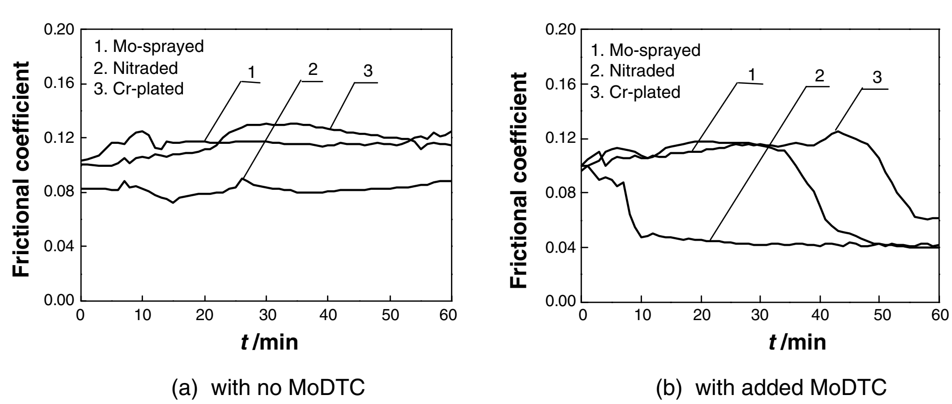
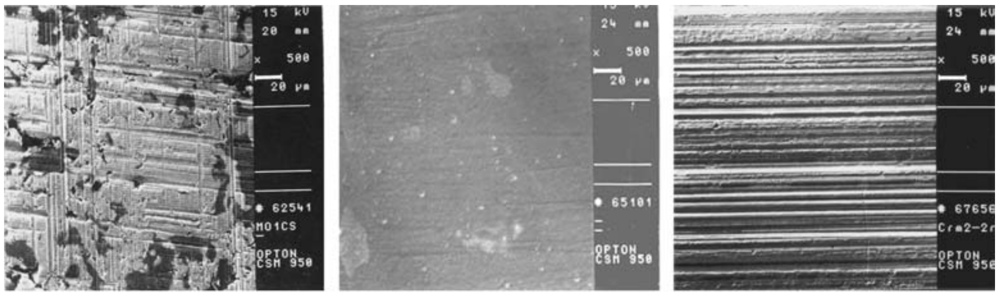


Figure 2 Temporal behaviors of frictional coefficient (μ) for the three tribopairs.

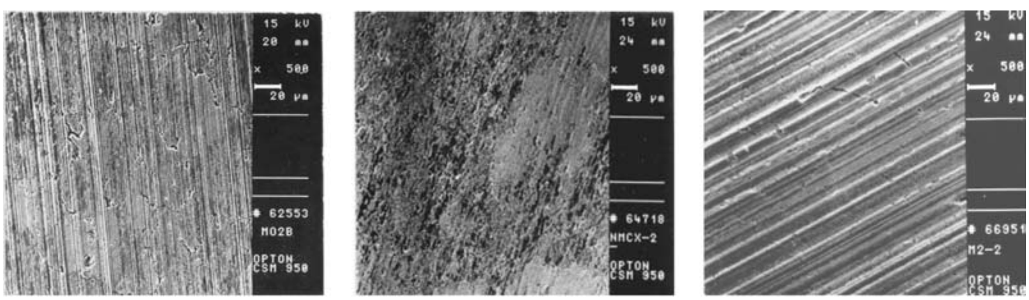
TABLE II Wear-resistant effect caused by MoDTC

	Rw / %							
	Coatings				Cast iron			
Coating types	1	2	3	average	1	2	3	average
Mo-sprayed coating	39.1	37.8	38.5	38.5	40.1	38.9	39.4	39.4
Nitrided coating	59.4	59.1	58.7	59.1	54.5	53.9	53.7	54.0
Cr-plated coating	14.5	14.9	14.8	14.7	39.1	40.2	40.1	39.8



(a) Mo-sprayed coating (b) Nitrided coating (c) Cr-plated coating

Figure 3 SEM images of worn surfaces of piston ring coatings in presence of MoDTC.



(a) Mated with Mo coating (b) Mated with Nitrided coating (c) Mated with Cr coating

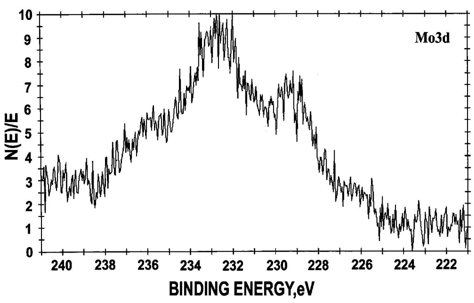
Figure 4 SEM images of worn cast iron surfaces mated with different piston ring coatings in presence of MoDTC.

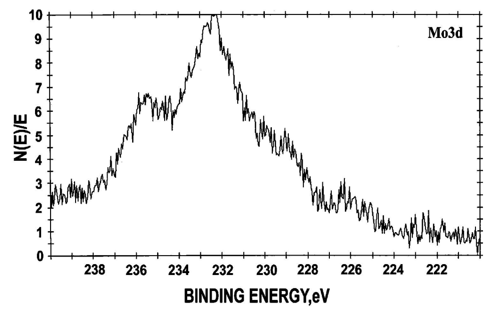
coating, which should be contributed to the higher hardness of the Cr-plated coating. As for the wear of the grey cast iron mated with the nitrided coating, a complex wear mode including corrosive and abrasive wear has been observed.

EDS examinations have shown that, there are few chemical species of Mo and S existing on the surface before the dip in friction takes place. However, on the worn surface after the friction coefficient begins to drop, there occurs much more Mo and S species. Since there contains no Mo and S in the crankcase oil SJ/5W-30 as well as in the grey cast iron composition, it can be deduced that these two elements are derived from the oil soluble organomolybdenum additive - MoDTC, and the dip in friction should be related to the existence of elements - Mo and S.

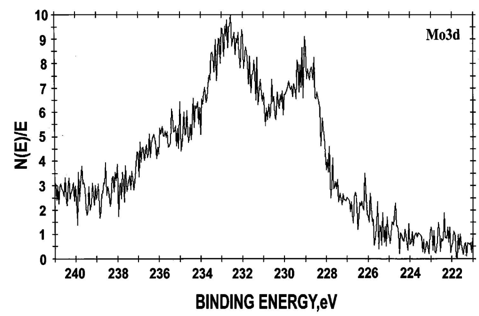
The chemical states of the elements Mo and S on the worn cast iron surfaces mated with the Mo-sprayed coating, nitrided coating and Cr-plated coating were analyzed with XPS, and their XPS spectra are presented in Figs 5 and 6, respectively.

Table III presents the calibration results for Mo_{3d} and S_{2p} peaks on the worn cast iron surfaces. From the data, it is clear that when lubricated with the MoDTC-containing lubricant, two chemical states for the element Mo, i.e. MoS_2 and MoO_3, can be detected on the worn iron surfaces mated with the Mo-sprayed, nitrided and Cr-plated coatings, respectively, which means the chemical state for the functional element Mo appears to be independent of the coating types. However, the proportion of MoS_2 and MoO_3, is affected by the type of piston ring coatings (e.g. 0.96 for Mo-sprayed coating, 1.16 for nitrided coating, and 0.77 for Cr-plated coating). This suggests that the piston ring coating type influences the relative content of the Mo species, but does not affect their chemical states. It is not the case with regard to the element S on the worn cast iron surfaces. In presence of MoDTC, in addition to MoS_2 and FeS, the only chemical state of element S on the worn surfaces mated with the Mo-sprayed and nitrided coatings, another chemical species $FeSO_4$ (another chemical state of element S) can be generated on



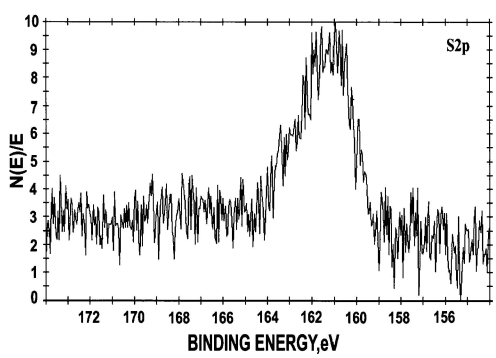


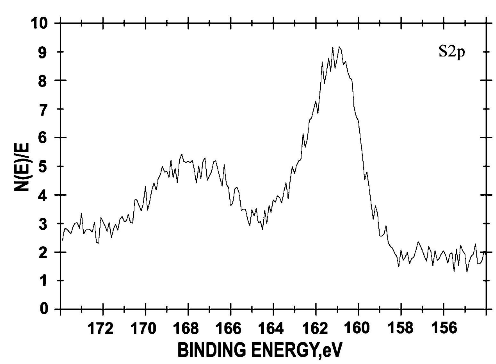
(a) mated with Mo-sprayed coating (b) mated with Cr-plated coating



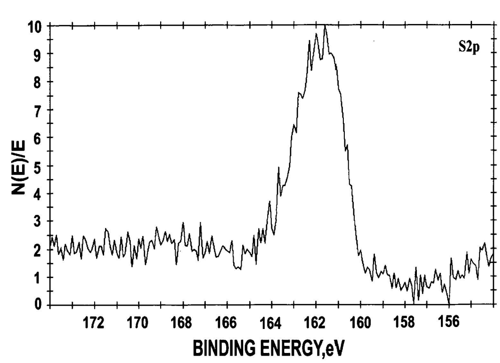
(c) mated with nitrided coating

Figure 5 XPS spectra for element Mo.





(a) mated with Mo-sprayed coating (b) mated with Cr-plated coating



(c) mated with nitrided coating

Figure 6 XPS spectra for element S.

TABLE III Calibration results for Mo_{3d} and S_{2p} peaks

Coating types	Chemical species of Mo and S / at.%			
	MoO_3	MoS_2	FeS	$FeSO_4$
Mo-sprayed coating	0.48	0.46	0.55	–
Nitrided coating	0.37	0.42	1.84	–
Cr-plated coating	0.35	0.27	0.40	0.75

the worn surface of the Cr-plated coating. Furthermore, the contents of the S species also vary with the type of tribocoatings.

Generally, MoO_3 and FeS are supposed to provide superior wear resistance [6, 10]. According to the data listed in Table III, for the three tribocoatings, the sumed contents of MoO_3 and FeS are quite different. Compared with those on the worn surfaces of Mo-sprayed and Cr-plated coatings, the highest sumed contents of these wear resistant constituents can be found on the worn surface of the nitrided coating, accounting for the best anti-wear effect caused by MoDTC (Table II and Fig. 3). This suggests that there probably exists a relevancy between the sumed contents of MoO_3 and FeS and the wear resistance in presence of MoDTC. One important fact should be noted that the contents of MoS_2 on the worn cast iron surfaces mated with Mo-sprayed and nitrided coatings are much higher than that on the worn cast iron surface mated with Cr-plated coating (Table III). In combination with the frictional coefficient curves shown in Fig. 1, it can be deduced that the antifriction effect of MoDTC is dependent on the contents of MoS_2 yielded on the worn cast iron surfaces.

In conclusion, MoDTC behaves tribologically different for the three piston ring coatings - Mo-sprayed coating, nitrided coating and Cr-plated coating. MoDTC can provide anti-friction and anti-wear performance for the three tribocoatings lubricated sliding against the cast iron cylinder bore, with the best tribological effect achieved in the case of the nitrided coating. When lubricated with a fully formulated petroleum based engine oil SJ/5W-30 containing MoDTC, wear of the Mo-sprayed, nitrided and Cr-plated coatings assumes the abrasion mode, and the wear severity appears to be related to the hardness of the tribocoatings concerned. In addition, the mode and severity for the wear of the cast iron are affected by the type of the mated coatings. Nature of the piston ring coatings possesses substantial influences on the chemical states and relative concentrations of the functional elements Mo and S on the worn cast iron surfaces. It is supposed that the difference in the tribological behaviors of the three different tribocoatings in presence of MoDTC can be attributed to the variations of the contents of MoS_2 and other wear-resistant species generated on the worn surfaces.

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