Boundary lubrication mechanisms of carbon coatings by MoDTC and ZDDP additives

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Abstract

Fuel economy and reduction of harmful elements in lubricants are becoming important issues in the automotive industry. An approach to respond to these requirements is the potential use of low friction coatings in engine components exposed to boundary lubrication conditions. Diamond-like-carbon (DLC) coatings present a wide range of tribological behavior, including friction coefficients in ultra-high vacuum below 0.02. The engine oil environment which provides similar favourable air free conditions might lead to such low friction levels.

In this work, the friction and wear properties of DLC coatings in boundary lubrication conditions have been investigated as a function of the hydrogen content in the carbon coating. Their interaction with ZDDP which is the exclusive antiwear agent in most automotive lubrication blends and friction-modifier additive MoDTC has been studied. Hydrogenated DLC coatings can be better lubricated in the presence of the friction-modifier additive MoDTC through the formation of MoS2 solid lubricant material than can non-hydrogenated DLC. In contrast, the antiwear additive ZDDP does not significantly affect the wear behavior of DLC coatings. The good tribological performances of the DLC coatings suggest that they can contribute to reduce friction and wear in the engine, and so permit the significant decrease of additive concentration.

Keywords: Boundary lubrication; DLC coatings; Tribochemistry

1. Introduction

In the new millennium, the long-term impact of lubricants and additives components will become design and marketing issues based on such concerns as the environment, toxicity and fuel economy. Development of lubricant additives directly from renewable natural materials and new mechanical components for combustion engine (lightweight body structures, direct-injection systems for gasoline engines...) [1–3] will play a far more important role than in the last for improving fuel economy and environment protection. However, the replacement of extreme-pressure additives such as zinc dialkyldithiophosphates (ZDDP) will present a challenge in terms of being found in nature and the development of mechanical components has several disadvantages such as its high cost and design limitations.

Another approach to respond to these economical and environmental requirements is the potential use of low friction and wear resistant coatings in mechanical components submitted to boundary lubrication conditions. Diamond-like-carbon (DLC) coatings which have been extensively studied as surface films to protect hard brittle materials from cracking [4] and ductile metal surfaces from adhesion [5] may fulfill this role. Depending on their properties which are in turn dependent on the deposition procedure, these coatings present a wide range of tribological behavior, including friction coefficients in ultra-high vacuum below 0.02 [6–8]. In boundary lubrication, the engine oil environment which provides similar favourable air free conditions may lead to such low friction levels.

In this work, we study the friction and wear properties of DLC coatings under boundary lubrication conditions. Additivated and non-additivated lubricants have been investigated. Low-cost multifunctional additive ZDDP, used for over 50 years in the lubricant industry in engine oils, and friction modifier molybdenum dithiocarbamate (MoDTC) later introduced into automotive crankcase
lubricants to improve the fuel efficiency have been tested. A multi-technique approach coupling X-ray Electron Spectroscopy (XPS) surface analyses and TEM/EELS observations has been employed to gain an understanding of the boundary films structure formed from the additive decomposition products. Different tribochemical reactions occur in boundary lubrication between DLC materials and additives depending on the hydrogen content and mechanical properties of DLC coatings.

2. Experimental details

2.1. DLC coatings

Different DLC coatings materials were deposited on polished AISI 52100 steel substrates, including hydrogen-containing DLC (a-C:H), titanium-containing DLC (Ti-C:H) and hydrogen-free DLC (a-C) coatings. The surface roughness of polished AISI 52100 steel substrates before deposition was about 10 nm in Ra. Hydrogen-containing DLC and titanium-containing DLC were prepared by hybrid technique of magnetron sputtering and d.c. plasma enhanced chemical vapor deposition (PACVD) performed in the same reactor. Substrates were cleaned by a bias etching at chemical vapor deposition (PACVD) performed in the same technique of magnetron sputtering and d.c. plasma enhanced chemical vapor deposition (PACVD) performed in the same reactor. Substrates were cleaned by a bias etching at 200 V for 10 min prior to film deposition. The substrate temperature during the deposition process was lower than 200 °C. Hydrogen-free DLC (a-C) films were prepared by arc-ion plating. The thickness of the diamond-like carbon based films are reported in Table 1 with other characteristics like surface roughness. We notice that all kinds of coatings display a surface roughness varying in the 20–60 nm range. The coatings deposited by PVD method do not have a surface finish significantly rougher. The hydrogen-containing DLC and titanium-containing DLC were, respectively, characterized by forward recoil elastic scattering (FRES) and Rutherford back-scattering spectroscopy (RBS) to determine the composition. The film thicknesses were measured by cross-sectional micrographs. The mechanical properties were determined by microindentation.

2.2. Lubricants

Lubricants comprise a base fluid and additives. The base fluid was a mixture of synthetic poly-alpha-olefin (PAO) 4 and 6. Zinc dithiophosphate (ZDDP) was added to the base fluid to enhance its oxidation resistance and to impart antiwear performance. The ZDDP is a C3/C6 secondary zinc di-alkyl dithiophosphate. Friction modifier molybdenum dithiocarbamate (MoDTC) was also added to the base fluid to reduce the friction and make smooth transition from static to dynamic conditions. The MoDTC is mainly composed of di-sulfide-bis [oxo(dialkylthiocarbamate)] molybdenum. It contains impurities consisting of 10% atomic thiuram disulfide. The alkyl chains are C8 (2-ethylhexyl) and C13. The S/Mo ratio (weight %) is equal to 1.3. The two additives were obtained from Asahi Denka Kogyo (Japan). First, we examined the tribological properties of each coating under base fluid lubrication and then additivated MoDTC and ZDDP+MoDTC lubricants. Previous works [9] have shown that equi-molar concentration of ZDDP and MoDTC in base fluid yields optimum friction-reduction results. Therefore, the lubricant concentration of MoDTC and ZDDP was adjusted to that value which corresponds to 700 ppm of zinc and 200 ppm of molybdenum in base fluid.

2.3. Tribological tests

A Cameron–Plint friction machine with a reciprocating cylinder-on-flat configuration was used to generate a relatively large area of tribofilms in mild/severe tribological conditions. The DLC coatings were systematically deposited on the plane counterface. The films were also deposited on the AISI 52100 steel cylinder counterface to check whether or not the tribological behavior depends on the lubricant interaction with coatings, in comparison to the deposition on the plane only. The diameter and length of the steel cylinders were 6 and 5 mm, respectively. The DLC coated steel flat was immersed in the oil solution. The friction tests were performed at 373 K (100 °C) with a sliding speed of 0.2 m s⁻¹ under a normal load of 350 N (maximum initial contact pressure 0.6 GPa) for 1 h. The normal load was increased progressively up to 50 N and maintained to this value during 5 min for a running in effect. Then, it was increased to 350 N. Each test was repeated four times under the same conditions in order to check the reproducibility of the measurements. The solid tribochemical film (tribofilm) formed during the tests covers a rectangular area of 5×8 mm². After the tribological experiments, the worn surfaces were examined by optical microscopy. The final worn volumes of the flat and the cylinder were evaluated from cross-sectional images of the wear tracks, and from the width of the wear scars, respectively.

2.4. TEM/EELS observations

At the end of the test, some wear particles were picked up with care from the flat samples. They were rinsed in the n-heptane and deposited on a copper grid, covered by a very
thin carbon film (approximately 5 nm thick) for the Transmission Electron Microscopy (TEM) observations. The wear particles were observed in an analytical Transmission Electron Microscope (PHILIPS 420EM) equipped with Electron Energy Loss Spectroscopy (EELS). This microscope produces loss energy spectra giving information on the elementary composition of the wear particles which is related to the tribofilms composition.

2.5. XPS analyses

The flat sample was further degreased in an ultra-sonic bath of n-heptane to eliminate all the residual oil, gel-like species and contaminants, prior to XPS analysis. The tribofilm was then analyzed by a micro-spot XPS (VG 220I apparatus). XPS was performed with a non-monochromatized AlKα X-ray source. The size of the analysed area was set at 500 μm so that spatially resolved analysis can be achieved inside the tribofilm on the flat specimen. XPS is a very surface sensitive technique probing from mono-layer to a few nanometers (5 nm). Special attention has been paid to the peak fitting of Zn2p, S2p, O1s, Mo3d, C1s and Fe2p photopeaks and Auger Zn LMM lines. Before etching, such a surface is generally contaminated with carbon and possibly oxygen but this does not hinder the detection of the elements of the additive. Argon etching (Ar⁺, 5 keV) was not performed because of possible irradiation damage to sulfur species before XPS analysis. Then the thickness of the tribofilms formed during the friction tests has not been accurately estimated.

3. Results

3.1. Tribological test data

3.1.1. DLC/steel

Fig. 1 shows the steady-state friction coefficients of the DLC-coated flat/steel cylinder couples tested under different lubricated conditions. The DLC coatings with PAO lubrication exhibit a similar low steady-state friction coefficient in the 0.08–0.1 range. The friction tests performed with MoDTC and ZDDP additivated base fluid show lower friction coefficients ranged between 0.05 and 0.06 for hydrogenated DLC coatings (a-C:H and Ti-C:H), a highest value, 0.08, is obtained with the hydrogen-free DLC. This coating exhibits also the higher wear of the steel counterface as shown by Fig. 2 which reports the final wear rates measured in the steel cylinders. No significant production of wear particles is observed in the wear track of the plane, which remains difficult to visualize. It should be noted that similar wear rates are obtained under PAO and additivated PAO lubricated conditions for all DLC coatings. However, hydrogenated DLC coatings display slightly better friction and wear behaviors than those of steel/steel couple in the same conditions.

3.1.2. DLC/DLC

Tests with the films deposited on both the plane and the cylinder were also performed for the hydrogenated DLC coatings. In this configuration, the lubrication with MoDTC additivated fluid base is also investigated. As shown in Fig. 3, the additional deposition of the film on the cylinder
diminishes slightly the steady-state friction level, in comparison to the film deposited only on the plane. Figs. 4 and 5 detail the evolution of the average friction coefficients in the different lubricated conditions, versus the sliding distance, for the a-C:H and Ti-C:H coatings, respectively. First, we observed that the influence of additives appears much more significant on the friction behavior of the higher hydrogenated coating a-C:H. However, the friction level during the running-in period stays higher for the a-C:H coating, in the 0.08–0.2 range, than for the Ti-C:H coating, in the 0.05–0.08 range, whatever the conditions of lubrication. As shown in Figs. 4 and 5, the friction-modifier additive MoDTC provides the better running-in effect whatever the coatings. No significant production of wear debris was observed in the wear tracks of both the plane and the cylinder after the friction tests with MoDTC and ZDDP additivated lubricant, contrary to the case of PAO which produced to the scratches formation on the plane and severe wear of cylinder. For the MoDTC additivated lubricant, the Ti-C:H coating do not present significant wear in comparison to the a-C:H coating which displays some scratches. The final wear rates measured in the DLC-coated cylinders are presented on Fig. 6. As shown by Figs. 2 and 6, the additional deposition of the film on the cylinder improved significantly the anti-wear behavior of hydrogenated DLC coatings under MoDTC and ZDDP lubrication, in comparison to the film deposited only on the plane.

3.2. XPS analyses and TEM/EELS observations

3.2.1. DLC/steel

After the friction experiments, TEM/EELS observations and XPS surface analyses were performed on the surface of the complete set films to elucidate the origin of the friction improvement of hydrogenated DLC coatings under MoDTC + ZDDP lubrication, in comparison to the hydrogen-free DLC coatings. The advantage of XPS is to provide semi-quantitative elementary analysis, which permits to calculate the stoichiometry of the tribofilm compounds. XPS analyses were also carried out outside the tribofilms to clarify the material change occurring under the friction process. Table 2 shows the elementary composition of the MoDTC + ZDDP tribofilms (wear track) formed on the hydrogenated DLC (a-C:H) and hydrogen-free DLC (a-C) coatings surfaces after the friction tests against steel.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Energy (eV)</th>
<th>Elemental composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>284.8–285.5–287.6</td>
<td>a-C:H 94.6  a-C 92.4</td>
</tr>
<tr>
<td>O1s</td>
<td>531.0–532.8</td>
<td>a-C:H 3.1  a-C 5.2</td>
</tr>
<tr>
<td>S2p (sulfide)</td>
<td>162</td>
<td>a-C:H 0.8  a-C 0.9</td>
</tr>
<tr>
<td>Mo3d (Mo(IV))</td>
<td>229</td>
<td>a-C:H 0.4  a-C 0.4</td>
</tr>
<tr>
<td>Mo3d (Mo(VI))</td>
<td>222</td>
<td>a-C:H 0.1  a-C 0.9</td>
</tr>
<tr>
<td>P2p</td>
<td>133.2</td>
<td>a-C:H ≈0  a-C ≈0</td>
</tr>
<tr>
<td>Zn2p</td>
<td>1022.4</td>
<td>a-C:H 1.0  a-C 0.2</td>
</tr>
</tbody>
</table>

The data were obtained after the treatment of the XPS spectra.
counterfaces. First of all, it can be noticed that zinc, molybdenum and sulfur elements derived from MoDTC and ZDDP additives were detected on both DLC surfaces in low proportion, typically a few atomic percent. No iron is found in both tribofilms indicating that the DLC films were not delaminated during the test and no major wear debris transfer from the pin occurred. As shown in Table 2, both tribofilms are strongly depleted of phosphorous when compared to the initial ZDDP molecule which presents a P/Zn ratio of 2. The Zn2p XPS spectra obtained from these two surfaces are broader than those of the standard compounds ZnO, ZnS and ZnSO4, and then it is difficult to correctly assign the zinc to chemical components. The S2p photopeaks show one contribution at 162 eV indicating that sulfur is essentially involved in metal sulfide (molybdenum sulfide and/or zinc sulfide). From the study of Mo3d photopeaks, molybdenum sulfide solid lubricant might be present in the whole tribofilms. The decomposition of Mo3d photopeaks of the top surfaces analysis is compared with pure MoS2 (229.7 eV) and MoO3 (232.7 eV) in Fig. 7. As reported in Table 2, the MoS2/MoO3 ratio for the hydrogenated DLC is more five times greater than that obtained for the non-hydrogenated DLC. It is also interesting to compare with the outside tribofilms analysis in Fig. 7(e). Results show the presence of the MoO3 compound and a new contribution which can be attributed either to Mo(V) (331 eV) which is effectively present in the MoDTC molecule, or oxisulfide species MoSxO(y−x). It appears more reasonable that some residual MoDTC is present on the surface of the DLC coatings. No nitrogen is detected from the N1s photopeak, but we note that interferences exist between the N1s and Mo3p lines, so that a few percent of nitrogen would be hardly visible in these conditions. The comparison of Mo3d XPS photopeaks obtained inside and outside tribofilm clearly demonstrates that molybdenum sulfide was in situ generated by the friction process between DLC-coated surfaces and steel counterfaces.

3.2.2. DLC/DLC

To verify that the build-up of molybdenum sulfide interfacial material takes place directly on the surface of hydrogenated amorphous carbon coatings, without transfer from a steel counterface, XPS analyses were carried out on the hydrogenated DLC-coated flats which have been tested against hydrogenated DLC-coated cylinders. No iron was found in the tribofilms formed on DLC surfaces indicating that no delamination and/or excessive wear of carbon material occurs. Fig. 8(a) and (b) present the Mo3d photopeaks recorded inside the tribofilms formed on the richer hydrogenated DLC coating a-C:H after the friction tests carried out, respectively, with MoDTC/ZDDP additivated lubricant and MoDTC additive. For binary mixture, Mo3d XPS spectrum show two main contributions MoS2 (Mo (IV)) and MoO3 (Mo (VI)) unlike to the Mo3d XPS spectrum obtained with MoDTC additive which
displays a third peak at about 231 eV (Mo(V)). This Mo3d photopeak clearly indicates the incomplete decomposition of the MoDTC molecule during the friction and the strong presence of molybdenum oxide in comparison with molybdenum sulfide (1.3 at.% of MoO3 and 0.4 at.% of MoS2) for MoDTC additive. Also, the S2 s photopeak at 226 eV is very weak in this case. The presence of MoS2 bonding strongly visible on the MoDTC+ZDDP derived surface (2.5 at.% of MoS2 and 2.5 at.% of MoO3) is corroborated by the sulfide form of sulfur (S2p at 162.3 eV) and a quantitative ratio S/Mo of about 2.1. These data indicate that the presence of ZDDP promotes the formation of MoS2 in the tribofilm. Moreover, the comparison of the Mo3d XPS photopeaks obtained inside (Fig. 8a) and outside (Fig. 8d) the tribofilm clearly shows that molybdenum sulfide material was in situ generated by the friction process between two hydrogenated amorphous carbon surfaces. These both results have already been observed on steel substrates [10].

The TEM micrographs of typical fragments of the tribofilms obtained on the a-C:H coating after the friction tests carried out with MoDTC+ZDDP additivated lubricant and MoDTC additive are shown, respectively, in Fig. 9(a) and (b). For the binary mixture, X-ray analysis (not shown) revealed few phosphate zones, containing phosphorous, oxygen and zinc. Dispersed inside this phosphate matrix, we can observe a few MoS2 single sheets which have already been formed. These sheets are recognized as MoS2 because of the basal plane distance of h-MoS2 crystal lamellar structure (0.7 nm) which can be observed in some places. The length of the sheets is variable, from 2 to 10 nm, and they appear in a very disperse and diluted form (Fig. 9(a)) contrary to that observed in the case of MoDTC additive in Fig. 9(b) where the MoS2 sheets form bundles. These bundles are embedded in a carbon, oxygen and iron rich matrix.

XPS analyses of the tribofilms formed on the titanium-containing DLC coatings Ti-C:H after the friction tests carried out with MoDTC+ZDDP additivated lubricant and MoDTC additive were also performed. All the elements derived from additives were hardly detected inside both tribofilms which appear similar, the amounts of S, Zn and Mo were less than 1 at.%. It can be stated that MoDTC and ZDDP additives are less active on the titanium-containing amorphous carbon surface than on the richer-hydrogenated amorphous carbon surface. Although the weaker reactivity, the comparison between the Mo3d photopeaks of MoDTC+ZDDP derived surface on Ti-C:H (Fig. 8c) coating and the Mo3d photopeaks of MoDTC+ZDDP derived surface on a-C:H (Fig. 8a) might indicate that molybdenum sulfide formation is more energetically favourable and/or faster in the case of richer-hydrogenated amorphous carbon surface.

4. Discussion

The present study shows that selected hydrogenated amorphous carbon surfaces can be lubricated by usual MoDTC and ZDDP additivated lubricants. The tribochemical reactions between amorphous carbon coatings and additives of lubrication depend on the coating properties. Relationships between hydrogen content and improvement of tribological behavior under lubricated conditions are evidenced. More work is needed to understand the interactions between MoS2 and carbonaceous surfaces. At the moment, only assumptions can be made on the basis of the chemical hardness approach (HSAB principle) [11]. During the friction process, hydrogen-terminated surface of DLC coatings is disrupted and the species present in the lubricant can react with the dangling bonds of the nascent surface. From the chemical hardness point of view, hydrogenated carbon materials are soft bases and will preferentially interact with soft acids, like Mo4+, involved in the formation of MoS2. Hydrogenated-free carbon materials might be ‘intermediate bases’ which also react
with hard acids, like Mo$^{6+}$, involved in the formation of MoO$_3$ compound. This can explain why hydrogen-containing carbon materials promote the MoS$_2$ formation to the detriment of MoO$_3$.

On the other hand, in the light of both XPS and TEM investigations and previous works on the tribochemistry of additives on steel surfaces which show that ZDDP additive increases the formation MoS$_2$ [10,12], we can suggest the following hypotheses (Fig. 10) for the in situ tribochemical formation of MoS$_2$ in presence of MoDTC and ZDDP binary lubricant mixture. The MoS$_2$ units come from degradation of MoDTC in the contact by the tribochemical reaction. From a chemical point of view, electron transfer occurs on the Mo–S chemical bonding in MoDTC molecule, which leads under friction mechanical process to the formation of free radicals, one oxysulphide corresponding to the core of MoDTC molecule and the others to the chain ends. Chain ends radicals then recombine to form thiuram disulfide, whereas the oxysulphide decomposes into MoS$_2$, which crystallizes into sheets, and MoO$_2$. These sheets can oxidize in the presence of O$_2$. The role of ZDDP is principally to provide the sulphur atoms to complete the sulfuration of the oxysulphide. If the concentration in ZDDP is sufficient, then a lot of MoS$_2$ units are formed and can diffuse in the phosphate matrix. These units can easily meet together and a two-D lamellar sheet can progressively grow and cover the asperity tip and reduce efficiently the friction. In these conditions, MoS$_2$ sheets are present in the contact with a few molybdenum oxide. If the ZDDP concentration is low, the sulfuration is reduced and also the presence of molybdenum oxide is predominant in the contact. In this last case, the MoS$_2$ sheets form isolated and compact bundles in a carbon and oxygen rich matrix which can easily be ejected from the contact and then not reduce efficiently the friction.

5. Conclusion

MoDTC and ZDDP additives react directly on amorphous carbon surfaces. They seem to be more active with selected hydrogenated amorphous carbon surfaces. The friction and wear performances are improved by coating both counterfaces. XPS analysis show the formation of MoS$_2$ in the contact area only. The presence of zinc phosphate has been detected by EDX in the wear debris collected inside the tribofilm. On amorphous carbon surfaces, the role of antiwear ZDDP agent seems to be principally to enhance the formation of MoS$_2$ sheets. The composition of tribofilm appears similar to that of tribofilm obtained on steel surfaces in the same lubrication conditions. It is interesting to notice that tribochemical reactions can occur without the presence of iron catalyst element in the tribo-system.

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Appendix. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.triboint.2004.08.009

References