Wear of hydrogenated DLC in MoDTC-containing oils

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1. Introduction

Diamond-like carbon (DLC) coatings on steel substrates have been widely applied in machine components to reduce friction. One way to reduce friction in crankcase engines is to blend a friction modifier additive such as molybdenum dialkyl-dithiocarbamates (MoDTCs). While MoDTCs can greatly reduce boundary friction, many studies have reported that MoDTC can cause high wear of DLC coatings, especially of the hydrogenated amorphous carbon (a-C:H) type [1]. It is important to note that this high wear is seen only when DLC is rubbed against a steel counterface and is not observed when DLC is rubbed against DLC. Although the precise mechanism of a-C:H DLC wear in MoDTC oil has not been unambiguously determined, several studies have suggested that this wear is related to the formation of MoO_3 from MoDTC in the DLC/steel tribocontact [2]. This study aims to understand whether informed lubricant formulation can control the deleterious impact of MoDTC on a-C:H DLC wear and to determine the underlying mechanisms involved. In order to achieve this, the influence of various lubricant additives on wear of a DLC-coated component rubbed against a steel counterpart in MoDTC-containing oil has been investigated.

2. Test methods

2.1 Test conditions and procedures

A mini traction machine (MTM) was employed to observe DLC wear and tribofilm growth during tests using a spacer layer imaging method (SLIM). MTM tests were controlled to an initial theoretical lambda ratio of less than 0.2, thus providing boundary lubrication conditions.

2.2 Test lubricants

MoDTC was studied at a concentration of 300 ppm of Mo in polyalphaolefin base oil (PAO 4). A range of other additives commonly used in engine oils were blended individually with this MoDTC solution in PAO such as ZDDP, detergent and dispersant.

3. Results

3.1 DLC disc wear

Worn DLC disc surfaces after MTM tests were observed by optical micrography and WLI. The wear volumes of DLC discs over the areas (400 μm × 600 μm) are summarized in Fig. 1. The wear volume from tests in PAO alone was obtained from the region without DLC delamination. Rubbing the steel ball against DLC disc in PAO alone, without any additives, resulted in delamination of the DLC coating over approximately half of the track, with the remainder showing 0.9×10^3 μm^3 volume of predominantly abrasive wear. By contrast, PAO+Mo oil generated a high level of quite even wear of 3.7×10^3 μm^3 wear volume. The addition of all surface-active additives alleviated this DLC wear to varying extents.

3.2 Tribofilm formation on steel balls

Fig. 2 shows the evolution of film thickness during the tests. PAO alone formed dark coloured films on the wear track of 26 nm thickness at the end of the 3 h test. Given wear on the DLC disc and no additives in the lubricant, these dark coloured film may be attributed to carbon transferred from the DLC disc to the steel ball. PAO+Mo formed a lighter coloured film of 19 nm thickness. This film may consist of MoDTC tribofilm and/or transferred carbon from the DLC disc, since the latter experienced high wear in

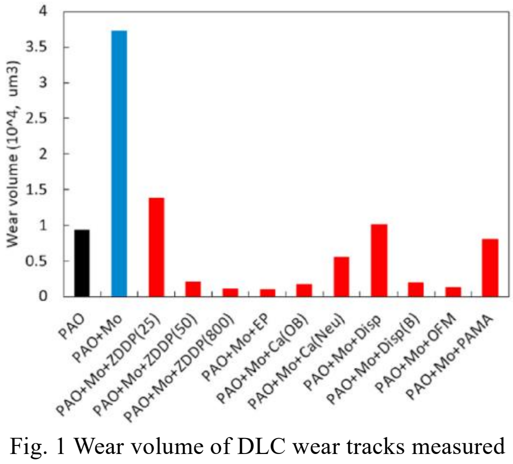

Fig. 1 Wear volume of DLC wear tracks measured

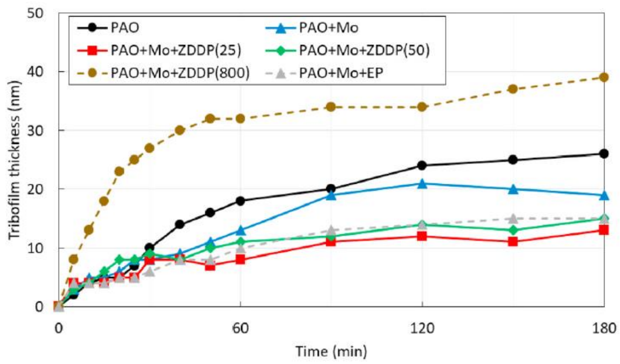

Fig. 2 The evolution of tribofilm thickness on the steel balls during the tests

this oil. The addition of ZDDP(800) resulted in thicker tribofilms than just PAO+Mo whereas the oils with ZDDP(25), ZDDP(50), EP formed thinner tribofilms, approximately 10 nm, than PAO+Mo. These results suggest that films on the steel balls are composed of one or both of transferred carbon and tribofilms produced by adsorption or reaction of the various lubricant additives.

3.3 Friction behaviour

The evolution of friction coefficient during the MTM tests was measured as shown in Fig. 3. For PAO alone, friction coefficient decreased from 0.08 to 0.07 at the beginning of test, and then increased after 10 min rubbing to reach 0.09–0.11 at the end of the test. Friction also showed relatively high fluctuations. Given the apparent carbon films on the steel ball, the reduction of friction coefficient in the first 10 min may result from this transferred carbon films as reported. After this, the DLC coating probably started to be severely delaminated with an increase of surface roughness, resulting in high friction coefficient. PAO+Mo showed lower friction coefficient during the test than PAO alone, reaching 0.06 after 5 min, and then increased to 0.08. The addition of ZDDP(800), to an MoDTC solution gave lower friction coefficient than PAO+Mo, that slightly increased towards the end of the tests to reach 0.07. By contrast, friction coefficient in the oils with ZDDP(25), ZDDP(50) and EP remained at a low level, 0.03–0.06.

3.4 Mechanism by which lubricant additives reduce DLC wear

It is evident from the above results that, while wear of a-C:H DLC against a steel contact is promoted by MoDTC, such wear is mitigated to a greater or lesser extent by the addition of several commonly-used, surface-active engine oil additives to the MoDTC/base oil solution. Based on the mechanism of DLC wear against steel, three possible reasons why DLC wear was reduced by the addition of surface-active additives to PAO+Mo can be suggested; (i) formation of thick antiwear tribofilm (ii) increase of MoS_2/MoO_3 ratio in the MoDTC tribofilm (iii) reduction of MoDTC tribofilm formation. Fig. 12 plots the wear volume against Mo^{4+}/Mo^{6+} ratio and, based on tribofilm thickness measurements and Raman analyses, maps the regions over which these mechanisms may be active. Thick tribofilms appear to suppress DLC wear very effectively without the need for increasing MoS2:MoO3 ratio, while increasing MoS_2:MoO_3 ratio without forming a thick tribofilm is also quite effective at suppressing wear.

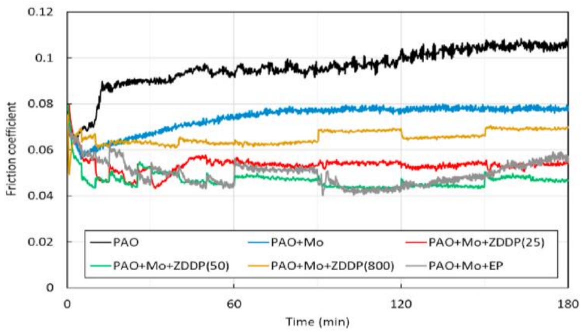

Fig. 3 The evolution of friction coefficient during the tests.

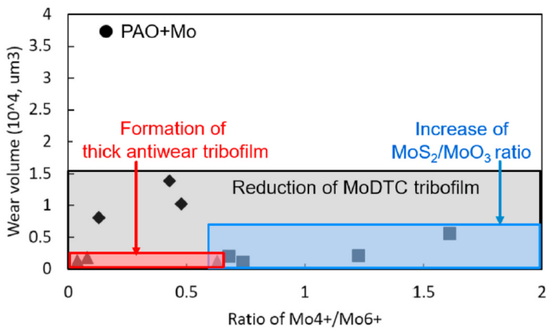

Fig. 4 The relationship between Mo^{4+}/Mo^{6+} and wear volume of DLC disc.

4. Conclusions

This study has used an MTM ball on disc tribometer, combined with SLIM and surface analysis based on TEM, STEM-EDX, Raman and XPS in order to understand the relevant mechanisms by which the addition of other surface-active additives improves a-C:H DLC wear of DLC against a steel contact rubbed in an MoDTC solution. The addition of all these additives reduces DLC wear to some extent, and in such a fashion that there appears to be more than one wear-reducing mechanisms, DLC wear in PAO+Mo can be reduced by the presence of other surface-active additives in three ways. Firstly, asperity contact between DLC and steel can be mitigated by forming thick antiwear tribofilms. Secondly, other additives can increase the ratio of MoS_2:MoO_3, reducing the amount of wear-enhancing MoO_3 in the tribofilm. Thirdly, the amount of MoDTC tribofilm including MoO_3 can be reduced by the competitive adsorption of other surface-active additives. This study was published in Wear [3].

5. Reference

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