ELSEVIER

Tribology International 38 (2005) 257–264

TRIBOLOGY INTERNATIONAL

www.elsevier.com/locate/triboint

Boundary lubrication mechanisms of carbon coatings by MoDTC and ZDDP additives

M.I. de Barros'Bouchet*, J.M. Martin, T. Le-Mogne, B. Vacher

Ecole Centrale de Lyon, UMR CNRS 55 13, 69134 Ecully, Cedex, France

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 MoS_2 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 fulfil 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

* Corresponding author. Fax: +33 4 78 43 33 83.
E-mail address: maria-isabel.de-barros@ec-lyon.fr (M.I. de Barros'Bouchet).

0301-679X/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.triboint.2004.08.009

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 −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(dialkyldithiocarbamate)] 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.

Table 1
Composition and properties of the diamond-like carbon films

Coating	Thickness (μm)	Surface roughness (Ra) (nm)	Hardness (Hv)	Young modulus (GPa)	Hydrogen content (at. %)	Ti content (at. %)
a-C:H	3	20–40	1600	≈150	≈50	≈0
Ti-C:H	3	20–40	1000	≈80	≈35	Ti≈2
a-C	3	40–60	2000	≈200	<5	≈0

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 $5\times 8\ mm^2$. 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

Atthe 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