Wear 302 (2013) 890–898

Contents lists available at SciVerse ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

The effect of MoDTC-type friction modifier on the wear performance of a hydrogenated DLC coating

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ARTICLE INFO

Article history:
Received 15 September 2012
Received in revised form
19 December 2012
Accepted 28 December 2012
Available online 11 January 2013

Keywords:
Diamond-Like Carbon coating
MoDTC
ZDDP
Fully formulated oils
Wear

ABSTRACT

The application of Diamond-Like Carbon (DLC) coatings for automotive components is becoming a promising strategy to cope with the new challenges faced by automotive industries. DLC coatings simultaneously provide low friction and excellent wear resistance which could potentially improve fuel economy and durability of the engine components in contact. The mechanisms by which a non-ferrous material interacts with a variety of lubricant additives is becoming better understood as the research effort in this area increases however there are still significant gaps in the understanding. A better understanding of DLC wear may lead to lubricant additive solutions being tailored for DLC surfaces to provide excellent durability (wear) as well as similar or increased fuel economy (low friction). In this work, the wear and friction properties of DLC coating under boundary lubrication conditions have been investigated.

A pin-on-plate tribotester was used to run the experiments using HSS steel plates coated with 15 at% hydrogenated DLC (a-C:15H) sliding against cast iron pins. One type of fully formulated oil with and without ZDDP and two levels of a MoDTC type friction modifier (Mo-FM) was used in this study. The friction and wear response of the fully formulated oils is discussed in detail. Furthermore, Optical Microscope and Scanning Electron Microscopy (SEM) were used to observe the wear scar and obtain wear mechanisms. Energy-Dispersive X-ray analysis (EDX) and X-ray Photoelectron Spectroscopy (XPS) analysis were performed on the tribofilms to understand the tribochemical interactions between oil additives and the DLC coating. A nano-indentation study was conducted to observe the changes in the structure of the coating, which can provide a better insight into the wear mode and failure mechanism of such hard coatings.

In the light of the physical observations and tribochemical analysis of the wear scar, the wear behaviour of a hydrogenated DLC (a-C:15H) coating was found to depend on the concentration of the MoDTC friction modifier and the wear performance is much better when ZDDP is present in the oil. The tribochemical mechanisms, which contribute to this behaviour, are discussed in this paper.

1. Introduction

Diamond-Like Carbon (DLC) coatings have become an attractive surface engineering solution in the automotive industry as they offer excellent tribological performance including low coefficient of friction, high wear resistance [1,2] and outstanding running-in properties [2]. Diamond like carbon coatings have similar properties to diamond but are amorphous carbon coating consisting network of sp^2 (graphite-like), sp^3 (diamond-like) and hydrogen bonds.

Commonly used lubricant additives are designed to form tribofilms on ferrous-base surfaces. It is therefore essential to optimise coating and lubricant compatibility to enable additive solutions to be tailored to DLC surfaces. The properties of DLC coatings depend extensively on the sp^2/sp^3 ratio as well as hydrogen content, which in return, depends on the deposition process and applied parameters [3]. Thus, the interaction between lubricant additives and DLC depends significantly on the type of DLC used.

Molybdenum Dithiocarbamates (MoDTC) and Zinc Dialkyldithiophosphates (ZDDP) are well-known friction modifier and antiwear additives respectively, used for ferrous surfaces. Having low shear strength, MoS_2 low friction crystals, derived from MoDTC decomposition, provide low friction at the tribological contacts in boundary lubrication conditions [4–6]. ZDDP offers antiwear properties by forming sulphide- and phosphate-containing tribofilms at ferrous surfaces [5–7]. It has also been suggested that the presence of ZDDP could promote MoS_2 formation and that ZDDP may

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0043-1648/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.wear.2012.12.052

enhance durability of the MoS_2 sheets [8,9]. In addition, MoDTC has been found to improve the wear resistance of the ferrous surfaces by forming N-containing species in the tribofilm [5].

Different researchers have started to evaluate interactions between lubricant additives with various types of non-ferrous DLC coatings under boundary lubrication. DLC coatings have been reported to be chemically inert using a steel pin sliding against DLC-coated disks lubricated in oil containing MoDTC and/or ZDDP [10]. In contrast, molybdenum-based friction modifiers and ZDDP antiwear have been reported to form low friction MoS_2 sheets and/or ZDDP-derived compounds respectively, on the DLC coating providing low friction and better wear performance under boundary lubrication conditions [11–17].

Recently, the effect of MoDTC in increasing wear of a DLC coating in a DLC/steel contact has been reported [16,18–23]. Haque et al. [16] showed that DLCs rubbed against steel in the presence of a MoDTC-containing base oil gave extremely high wear but that the addition of the antiwear additive ZDDP terminated this effect [16]. Sugimoto [20] also reported the higher wear of DLC in a DLC/steel system when lubricated in MoDTC-containing fully formulated oil. In contrast, Tung et al. [24] showed that MoDTC can reduce the wear of a DLC coating lubricated in fully formulated engine oil which could be due to the fact that ZDDP was present in his oil and could suppress the effect of MoDTC on promoting wear of DLC coatings reported by others. Recent literature on the harmful effect of Mo-containing friction modifier in promoting high wear of DLC is summarised in Table 1.

The origin of “MoDTC induced wear” on DLC is not fully understood and previous studies mainly used single additive solutions rather than realistic fully formulated oils. Furthermore, the addition of ZDDP to the lubricant has been shown to cancel or reduce the effect of MoDTC in promoting wear on DLC coatings, but it has not been reported whether other surface active additives in the oil could provide similar protection. Therefore, a comprehensive understanding of the DLC/MoDTC interaction is still to be clearly produced. The main objective of this work is to study the effect of a MoDTC-type friction modifier (Mo-FM) concentration on the wear performance of 15 at% hydrogenated DLC coating (a-C:15H) under boundary lubrication conditions using fully formulated oils.

2. Experimental details

2.1. Pin-on-plate tests

Tests were conducted using a reciprocating pin-on-plate tribometer under boundary lubrication conditions. The samples were cleaned prior to the start of the test using acetone. The tests temperature was set at 100 °C and the contact point of the plate and the pin was lubricated under a static volume of oil (3 ml). The average linear speed was 20 mm/s (stroke frequency of 1 Hz). A load of 390 N was applied providing an initial Hertzian contact pressure of 0.7 GPa resembling a pressure range to a typical cam/follower contact gasoline engine. The duration of the tests was 20 h and the friction force data was recorded every second. For a more precise evaluation of the friction performance, each type of test was repeated at least three times and the average repeatability was found to be less than 0.007 for the friction coefficient in the steady state region (i.e. last hour of the tests).

2.2. Materials

Tests were carried out in the pin-on-plate tribotester using Cast Iron (CI) pins and coated HSS M2 Grade steel plate. The dimensions of the CI pin were 20 mm in length, diameter 6 mm and the ends of the pins had a 40 mm radius of curvature. The geometry of the plate was 15 mm × 6 mm × 3 mm. The physical properties of the substrate, coatings and pin are given in Table 2.

A hybrid unbalanced magnetron sputter ion plating/PECVD deposition system was used to deposit the a-C:15H coating on the steel plate. First the substrates were cleaned by Ar^+ plasma ion etching using pulsed DC bias followed by deposition of a thin adhesion promoting Cr layer by DC magnetron sputtering with a pulsed DC bias. A CrN intermediate layer was then deposited by introducing nitrogen gas into the chamber. Finally, by adding a hydrocarbon gas, a layer of the a-C:15H coating was deposited using a Plasma Enhanced Chemical Vapour Deposition (PECVD) technique, where a pulsed DC bias was applied on the substrate and a discharge enhancing electrode with a 13.56-MHz RF generator was used.

Table 1
Summary of the literature on the effect of MoDTC on promoting high wear of DLC coatings.

Author(s)	System	Type of DLC	High wear for DLC coating observed with:			Wear Mechanism
			Model oils		Fully formulated oils	
			MoDTC	ZDDP +MODTC		
Tung et al.,[24]	DLC/CI	Not mentioned	–	–	No	A protective tribofilm produced by MoDTC with ZDDP, which acts to reduce wear.
Shinyoshi et al.[19]	DLC/ steel	Not mentioned	Yes	–	–	Oxidative wear due to the reaction of MoO_3 with the DLC active sites.
Haque et al.[16,18]	DLC/CI	a-C a-C:15H	Yes (Multiple sources)	No	–	In the absence of ZDDP, high pressure exerted by small third body particles could go beyond the endurance limit of the coating.
Vengudusamy, B., et al.[21]	DLC/ steel	a-C a-C:H	Yes	–	–	“Pro-wear process must involve the presence of the steel counterface”
	DLC/DLC	Si-DLC	No	–	–	
Sugimoto [20]	DLC/ steel	a-C:H	–	–	Yes	Graphitization of the DLC followed by the formation of hard Mo compounds on the steel counterpace accelerating the wear on the DLC plate.