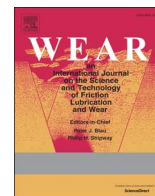




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Formation of interfacial molybdenum carbide for DLC lubricated by MoDTC: Origin of wear mechanism

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ABSTRACT

A large amount of research has been devoted to the effect of molybdenum dithiocarbamate (MoDTC) additives on the lubricating performances of carbon-based coatings, showing that a high wear rate is produced when the MoDTC is blended with the base oil. However, the mechanisms leading to the coating removal are not fully understood yet.

In this work, the friction and wear performances of an amorphous hydrogenated DLC coating doped with silicon and oxygen have been analysed when lubricated by MoDTC-containing oils. Tribological experiments have been conducted with DLC/steel and DLC/DLC contacts under boundary lubrication conditions using a ball-on-flat tribometer. To understand the wear mechanism, the chemical composition of the tribofilm formed on the steel ball counterpart was investigated by X-ray Photoelectron Spectroscopy (XPS). Transmission Electron Microscopy (TEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDX). A new DLC wear model has been proposed and validated.

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1. Introduction

Many recent works have shown that Diamond-like carbon (DLC) coatings provide an optimal combination of relatively high hardness, chemical inertness and low friction and wear rates [1].

In recent years, a large number of studies have been devoted to the improvement of DLC coating performance. Particularly, to enhance the properties of the DLC films, different chemical elements or compounds (nitrogen, silicon, titanium, tungsten, etc.) have been added into the coating [2,3]. Among them, amorphous hydrogenated silicon- and oxygen-doped DLC films (a-C:H:Si:O) have attracted special attention due to their ability to decrease the residual internal stress without sacrificing the hardness of the coating [4,5]. This is because the coating has improved resistance to oxidation and adhesion to metal alloys, steels and glasses, leading to better high temperature stability [6–8]. Due to these interesting properties, this type of DLC has been studied in the last few years for application in different fields. Great effort has been expended in the development of a carbon-based coating containing silicon and oxygen to be employed on automotive parts.

Therefore, it is extremely important to optimize the interaction between a-C:H:Si:O DLC and the additives present in modern engine lubricants to further reduce its already low friction coefficient. Molybdenum Dithiocarbamate (MoDTC) is a well-known friction modifier additive that basically decomposes during the tribo-test under heating, generating molybdenum disulfides (MoS₂) sheets and molybdenum oxide (MoO₃) species [9]. Although the exact mechanisms are not fully understood yet, it is well accepted that the low friction coefficient is brought about the interaction between MoS₂ lamellar sheets in the generated tribofilm [10].

The changes in the coating structure under lubrication with MoDTC-containing oil have been extensively investigated in recent years [11–13]. The antagonism between the DLC coating and the MoDTC friction modifier, causing a catastrophic high wear rate, has already been reported several times. On the other hand, although some wear models have been proposed [11,12], there is still a lack of understanding of the fundamental wear mechanisms. In fact, there are strong disagreements in the literature on this aspect: the DLC wear has been explained both by abrasive wear caused by MoO₃ hard particles [11] and by a graphitization process occurring on the top surface of the DLC [14,15]. Shinyoshi *et al.* [11] and Haque T. *et al.* [12] tried to justify the high wear obtained on the DLC sample when lubricated by MoDTC by the interaction

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between the coating and the molybdenum oxide derived from the additive decomposition during the tribotest. However, the relation between the MoO₃ and the wear rate of the DLC coating has already been rejected by different authors [16]. It has also been demonstrated experimentally [14,15] and using dynamic simulations [15] that the severe tribotest conditions (temperature, pressure and mechanical stress) can induce re-hybridization changes from sp³ to sp² in the electronic structure of carbon. This transformation can lead to a faster removal of the DLC top surface, causing the coating failure. So far, however, the evidence for a direct relation between the MoDTC and the chemical changes in the C-C bond has not been clearly explained yet.

In a previous study [17], preliminary results were reported for the first time, and a new wear model based on the formation of molybdenum carbide species has been proposed. In particular, tribological experiments combined with X-ray photoelectron spectroscopy (XPS) surface analyses have revealed the presence of Mo-C bonding on the steel counterpart. For this reason, it has been proposed that the main wear mechanism responsible for the DLC failure when lubricated by MoDTC-containing oil has a chemical origin. It was suggested that there is a chemical reaction between the molybdenum present in the tribofilm formed on the steel ball and the dangling carbon bonds of the DLC derived from the breaking of the carbon-silicon bonding.

This study provides strong support for the conjecture that the formation of a Mo-containing tribofilm material on the steel counterpart is at the origin of the mechanism governing the wear of DLC coatings. It remains, however, unclear whether such MoC_x species can cause such dramatic wear, and particularly if this is related to their structure and mechanical properties.

Although XPS analyses are able to detect the presence of MoC_x species on the rubbed surfaces, it is not possible to infer the underlying mechanism from analytical results alone. In the current work, after a brief summary of the most relevant results described in [17], we address the validation of the new proposed wear model using microscopic and mechanical tools.

A Transmission Electron Microscopy (TEM) study coupled with Energy Dispersive X-Ray Spectroscopy (EDX) and Selected Area Electron Diffraction (SAED) analysis has been employed to analyse the structure of the tribofilm formed on the steel ball to confirm the presence of molybdenum carbide. Furthermore, to evaluate if the MoC_x-containing tribofilm formed on the steel ball is much stiffer than the DLC coating, nano-indentation tests were performed on the tribofilm to demonstrate whether the DLC wear is caused by an abrasive mechanism. Finally, the key role of the steel counterpart in the proposed mechanism has been validated by considering the DLC/DLC contact configuration.

2. Materials and methods

2.1. Material

2.1.1. Lubricant

A standard mineral oil belonging to group III was used as a base lubricant. The kinematic viscosity of this base oil is 20 cSt at 40 °C. The chemical structure of the molybdenum dithiocarbamate (MoDTC) used as a friction modifier additive is shown in Fig. 1.

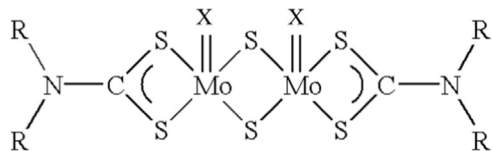


Fig. 1. Chemical structure of molybdenum dithiocarbamate (MoDTC).

Table 1

Principal properties for the steel and the DLC materials.

Properties of coating/ material	Uncoated steel sub- strate and steel counterbody	a-C:H:Si:O coated steel plate
Specification	AISI 52100	PACVD Si & O doped DLC with Ti adhesion layer
Thickness of the coating	–	ca. 2.0 μm
Thickness of Ti adhesion layer	–	ca. 0.3 μm
Hardness (GPa)	10	18–20
H% content (approximately)	–	25–35
Roughness	Ra < 0.05 μm	Ra < 0.05 μm

In the schematic formula, X can be S or O atom (although mainly S), while R is a mixture of C₈ and C₁₃ alkyl chains. The concentration of the MoDTC friction modifier is set to 1 wt%. The additive is blended with the base oil by heating and stirring the solution at 65 °C for 10 min. Tests were conducted at least three times using the oils, both with and without MoDTC.

2.1.2. a-C:H:Si:O DLC coating

An amorphous hydrogenated diamond-like carbon coating doped with silicon and oxygen (a-C:H:Si:O) was deposited on the polished AISI 52100 steel by plasma enhanced chemical vapour deposition (PECVD). An adhesion-promoting titanium sub-layer was first deposited on the steel plate. The material properties of the DLC coating and the steel are given in Table 1.

2.2. Methods

2.2.1. Tribotest

The tribological experiments were conducted using a reciprocating linear ball-on-flat tribometer on both the DLC/steel contact, i.e., with AISI 52100 steel ball (6.7 mm radius) against a DLC-coated flat coupon, and the DLC/DLC tribo-pairs.

The boundary condition is reached using a combination of parameters. A load of 8 N is applied resulting in a maximum contact pressure about 770 MPa. The average speed is 5 mm/s, with a stroke length of 5 mm. The duration of the test is 1 h at 100 °C. At this temperature, the calculated minimum EHL film thickness is less than 1 nm, much smaller than the composite roughness of the two surfaces. Therefore the lambda ratio is well below unity and the lubrication regime is boundary.

To remove any dust from the initial surfaces, both the coated flat coupon and steel ball samples were cleaned before each test using *n*-heptane solvent in an ultrasonic bath for 10 min.

The friction experiment has been repeated three times and the reproducibility is fairly good.

2.2.2. X-ray Photoelectron Spectroscopy (XPS)

The elemental composition of the top surface (typically depth of 10 nm) and the nature of the chemical bonds between the elements have been investigated by XPS. The apparatus is an PHI-ULVAC VersaProbe II, integrated with a monochromatized AlKα X-ray source (1486.6 eV). The X-ray beam can be focused on the wear scar of an area of 50 μm × 50 μm, probing a depth of only a few nm. The energy scale was calibrated with reference to the C1s line at BE=284.8 eV. First, XPS measurements were taken over a survey spectrum covering a range of 1200 eV, to identify all peaks and the presence of contaminants. Afterwards, a scanning of the individual peaks in more detail over a smaller range of 15–20 eV was undertaken. The detailed spectra of the elements identified were acquired to establish the different chemical states of the

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