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Influence of hydrogen and tungsten concentration on the tribological properties of DLC/DLC contacts with ZDDP

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ABSTRACT

Diamond-like carbon (DLC) coatings are becoming potential candidates for automotive engine parts because of their excellent friction and wear resistance properties. It is important to understand their film-forming, friction reduction and wear resistance mechanisms. This paper studies the influence of hydrogen and tungsten concentration in DLCs on friction and wear by comparing the behaviour of one a-C, five a-C:H and four a-C:H:W coatings in DLC/DLC contacts lubricated with base oil and a ZDDP solution. a-C show lower boundary friction than the other types. W-DLCs experience higher wear compared to the other coatings. Over the range of concentrations studied, hydrogen and tungsten contents do not affect friction greatly but have a marked effect on adhesion, film-forming and wear properties.

1. Introduction

In recent years diamond-like carbon (DLC) coatings have become attractive for automotive parts because of their excellent friction and wear resistance properties. There are many different types of commercially-available DLC coating, varying in deposition technique, doping elements in the coating, doping element concentration, hydrogen content, sp^3 content, *etc*. These different types have different properties, tribological behavior and interactions with lubricant additives. Lubricant manufacturers must be aware of these differences and be able to produce oils able to be effective with many types of DLC coating. In the current study the impact of varying DLC hydrogen and tungsten concentration on the friction and wear properties of DLCs in both base oil and zinc dialkyldithiophosphate (ZDDP) solution is explored.

Although there have been some studies on DLCs with ZDDP or other antiwear/extreme pressure (AW/EP) additives in recent years [1–14], the findings are quite contradictory. Some studies have reported that ZDDPs form tribofilms on DLC coatings [1–4,6,11–14] while some have reported they do not and/or that no tribochemical reaction occurs between DLC and additive [5,7–10]. In order to understand why such contradictory results were observed, it is important to note the differences in the DLCs studied. These differences are summarised in Table 1. Only DLCs relevant to this paper are listed (a-C, a-C:H and a-C:H:W) and it should be noted that most a-C:Hs studied had hydrogen contents ranging from 14 to 50 at% and exhibited quite different results over this range.

It is interesting to note that although [4] and [5] studied very similar commercially-available a-C:H coatings, their results were contradictory, the former reporting a tribochemical reaction between DLC and additive but the latter no such reaction. Also, studies by Haque et al. reported that ZDDP-derived tribofilm formed only on DLCs having 14–16 at% H [6] and not on more highly hydrogenated DLCs having 30 at% H [5], while a similar study by De Barros Bouchet et al. [11] on highly hydrogenated DLC having 50 at% H reported the formation of ZDDP-derived tribofilms. It is clear from these studies that although contradictory results have been reported on similar DLC types, the concentration of hydrogen plays an important role in the film-forming properties of DLC coatings.

Similarly contradictory results were reported for W-DLCs studied by [14] and [7], the former reporting a tribochemical reaction between DLC and additive but the latter none. It is not clear why such diverse results have been observed when studying similar, commercially-available DLCs.

In order to obtain a good comparison and better understanding of the influence of hydrogen and tungsten concentration on the tribological properties of DLCs, this paper describes tests carried out on a range of DLCs under the same test

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conditions in the same test rig. A wide range of DLCs have been obtained from several manufacturers, including one a-C, five a-C:Hs having different hydrogen concentrations (17, 18, 20, 22 and 25 at%) and four a-C:H:Ws having the same hydrogen content (~15 at%) but varying tungsten concentration (12, 14, 18 and 21 at%). The tribological responses of these DLCs in both hydrocarbon base oil and ZDDP solution have been investigated.

2. Materials and experimental details

DLC coatings were deposited on the steel test specimens generally used in the mini-traction machine (MTM), *i.e.* AISI 52100 steel balls and discs, of hardness 760 HV and root mean square roughness, R_q of 10 nm. Hardness and elastic modulus, chemical composition, hydrogen content and sp^3% of all DLC coatings were measured using Fischerscope HM2000, SEM/EDX, ERD and Raman spectroscopy, respectively.

Ten different DLCs were studied and their properties are listed in Table 2. The coatings were deposited by different techniques as presented in table 2 and thicknesses ranged from 3 to 5 μm. The AFM topography images of all DLCs before testing are shown in Fig. 1. The scale is the same for all of these AFM images, which indicates that there are considerable differences in the structures of the various DLC coatings. All tests were conducted on DLC/DLC tribopairs. The base fluid used in this study was an API group III oil having density 0.78 g/cm^3, viscosity 3.32 cP and effective pressure viscosity coefficient 16.3 GPa^{-1} at the test temperature of 100 °C. The ZDDP additive had a primary alkyl structure and was used at a concentration that gave 0.08 wt% P in the base oil solution.

Friction tests were carried out using an MTM. This is based on a rotating ball-on-disc configuration, where a 19 mm diameter DLC-coated ball is loaded and rubbed in rolling-sliding conditions against a DLC-coated disc immersed in lubricant. The friction test conditions used in this study were: applied load = 31 N, corresponding to a contact pressure of ca 1 GPa; entrainment speed = 0.1 m/s; slide-roll ratio = 0.5; temperature = 100 °C; test duration = 2 h. The entrainment speed is defined as $(u_b+u_d)/2$, where u_b and u_d are respectively the speed of the ball and disc with respect to the contacting surfaces, while the slide-roll ratio SRR is defined as the ratio of sliding speed $|u_b-u_d|$ to entrainment speed. The calculated lambda ratio (ratio of calculated elastohydrodynamic lubricant film thickness to composite

Table 1
A review of DLC coatings studied by other researchers in ZDDP/AW/EP solutions.

Ref.	DLCs studied	DLC combination	H (at%)	Testing temp. (°C)	ZDDP/AW/EP (wt%)	DLC—additive interaction/ tribofilm formation
[1]	a-C:H	DLC/DLC and DLC/steel	20	100	0.08%P	Yes
						Yes
[2]	a-C:H	DLC/DLC	25	80	1	Yes
[3]	a-C:H	DLC/DLC	–	80	–	Yes
[4]	a-C:H	DLC/DLC	40	100	0.08% P	Yes
	a-C		–			Yes
[5]	a-C:H	DLC/CI	30	100	0.64	No
[6]	a-C:H	DLC/CI	14–16	100	0.64	Yes
[7]	W-C:H	DLC/DLC and DLC/steel	–	–	–	No
[8]	a-C:H	DLC/steel	–	20–200	0.01–10	No
	W-C:H		–			No
[9]	W-C:H	DLC/DLC and	–	–	–	No
	a-C:H	DLC/steel	–	–		No
[10]	a-C:H1		30	80	9.3% P	No
	a-C:H2		30			No
	a-C:H:W		–			–
[11]	a-C:H	DLC/DLC and	~50	100	700 ppm	Yes
	a-C	DLC/steel	< 5		Zn	Yes
[12]	a-C:H1	DLC/DLC	–	80	9.3% P	Yes
	a-C:H2		–			Yes
	a-C:H:W		–			Yes
[13]	a-C:H	DLC/DLC	–	20, 80, 150	9.3% P	Yes
[14]	a-C:H:W	DLC/DLC	–	80	9.3% P	Yes
	a-C:H		30			Yes

Table 2
List and details of DLC coatings investigated.

No.	Materials	H %	W %	sp^3%	No. of layers	Interlayer/inclusions*	R_q (nm)	Hardness (HV)	Elastic modulus (GPa)	Deposition technique
1	a-C	1	–	15	1	–	16	2465 ± 135	198 ± 3	PECVD/PACVD
2	a-C:H 1	17	–	35	2	Cr	14	2365 ± 87	197 ± 5	PECVD
3	a-C:H 2	18	–	35	2	Cr	22	2500 ± 76	200 ± 6	PVD/PECVD
4	a-C:H 3	20	–	25	1	–	12	2460 ± 145	175 ± 7	PECVD
5	a-C:H 4	22	–	35	3	Si	11	2500 ± 60	183 ± 2	PECVD
6	a-C:H 5	25	–	38	1	Si	14	2372 ± 140	172 ± 7	PECVD
7	a-C:H:W 1	15	12	20	3	Cr	18	1183 ± 80	135 ± 5	Sputtering
8	a-C:H:W 2	15	14	25	3	Cr	35	1250 ± 80	140 ± 7	Combined
9	a-C:H:W 3	15	18	15	4	*Graphite	14	1318 ± 35	165 ± 3	sputtering
10	a-C:H:W 4	15	21	20	2	–	66	1190 ± 60	118 ± 6	PVD/PECVD PVD/PECVD
11	AISI 52100 Steel	–	–		–	–	10	760 ± 10	210 ± 5	–

* Inclusions present in the coating.