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Evolution of the nano-scale mechanical properties of tribofilms formed from low- and high-SAPS oils and ZDDP on DLC coatings and steel

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The evolution of the nano-mechanical properties of tribofilms formed in steel/steel, steel/a-C:H and steel/Si-DLC contacts lubricated with two commercial oils containing different amounts of SAPS additives (E6 and E7 grade) and a mineral base oil containing ZDDP additive were examined in this investigation for two very different time periods. An atomic force microscope (AFM) was used in different modes to measure the topography, film thickness and stiffness, while the nano-hardness was measured with a nano-indenter. In addition, FTIR microscope was used on selected samples to explain some of the tribofilm's mechanical modifications with chemical changes. The results have shown that the tribofilm's evolution and growth are very much surface and additive dependent, and are different for steel and DLC coatings.

1. Introduction

Diamond-like-carbon (DLC) coatings are, due to their low friction, wear resistance, corrosion resistance, high hardness, chemical stability, etc., some of the promising types of hard coatings for various machine components. Their excellent low-friction and anti-wear properties have already been the subject of a number of studies and their properties have been investigated for different non-lubricated conditions [1–5] and lubricated conditions [6–10]. However, the interactions between the DLC surfaces and the lubricant additives have received less attention than for steel surfaces [11]. Nevertheless, several studies have already shown that tribochemical reactions do occur between additives and DLC coatings, and that protective tribofilms do form in the contacts [6,8,12–14]. Moreover, DLC coatings enable very good tribological behavior, even when only lubricated with base oils that do not contain any additives [15,16]. This suggests the possibility that DLC coatings might also have good performance with low-SAPS oils, since the interactions between the oil and the surface will probably be weaker than with conventional, strongly additivated oils, and thus similar to the base oil's behavior.

However, the interactions on surfaces and coatings in boundary-lubrication conditions are still not completely understood. The chemical reactions between the lubricant molecules and the surfaces are usually accompanied by the formation of a tribofilm [17]. This tribofilm is defined as a thin film generated as a result of a sliding contact, which is adhered to its worn parent surface, but has a different chemical composition, structure, and tribological behavior [18]. This indicates that the generation of tribofilms has a major influence on both the friction and wear. Indeed, it is well known that tribological performance is linked to the tribofilm's properties and, consequently, to the lubricating conditions [19–21].

A large number of studies have been conducted to describe and evaluate the properties of tribofilms, mostly on steel and also some on DLC coatings; however, these relate mostly to the film's chemical properties [16,22–28]. On the other hand, tribofilms' mechanical properties have not been studied in great detail, despite the fact that the mechanical properties are some of the most important parameters for effective films, and so the results are very scarce. Moreover, only a few authors have investigated the changes in the mechanical properties of tribofilms on steel as a function of time. In these studies, usually, only one or very few of the mechanical properties of the tribofilms were investigated, most often the hardness, modulus or morphology [19,21,24,29,30]. It was found that a ZDDP tribofilm's hardness properties evolve as a function of the tribological test's duration, with the early stages characterized by a tribofilm with a relatively low hardness, which increases in hardness as the test proceeds and eventually decreases in hardness as the wear debris removes some of the tribofilm that is present on the surface [24]. On the other hand, some studies [29] report that the indentation modulus and the hardness of the ZDDP tribofilm stay unaffected throughout the

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duration of the test, while the morphology evolves with time through a growth mechanism where, for shorter times, distinct segregated pads form, which then at longer times transform into a more uniform and morphologically smooth coating over the steel substrate. Moreover, contradictory results are also reported for the thickness of the tribofilm, where some reports state that the tribofilm's thickness does not change significantly with the rubbing time [30], while another report suggests that the tribofilm's thickness does increase with the rubbing time [21].

However, studies of the mechanical properties of tribofilms on DLC coatings [8,9,12,15,31–34] mostly evaluate only the topography and morphology of the tribofilms, while results relating to changes in the mechanical properties with time [13,35] are very rare. Some of the few available results about tribofilms on DLC coatings have shown that the morphology and thickness of the tribofilm vary with respect to time [13,35]. However, the limited information available about the mechanical properties requires further investigations about the growth and evolution of the tribofilm's properties on DLC coatings, and how these properties affect the tribological performance.

In our previous work on DLC [36] we investigated the DLC tribofilm's topography and mechanical properties with a number of nano-scale parameters to determine how they affect the macro-friction. However, in this work we have focused on the changes of the characteristic nano-mechanical parameters of the tribofilm with the sliding time and we evaluate how this affects the macro-friction.

The mechanical properties measured on the nano-scale and the changes in these properties with two different sliding distances have been examined. The tribofilm's nano-mechanical properties were evaluated with an atomic force microscope (AFM) and a nano-indenter. Steel and two types of DLC coatings (a-C:H and Si-DLC) with different surface energies were selected and lubricated with two fully formulated oils containing different amounts of SAPS, as well as with a base oil containing the ZDDP additive only. A selection of coatings and steel, as a reference, with different oils should answer the question as to how different surfaces influence the tribofilm's formation and growth, and how different additives influence the formation of tribofilms on the same surfaces. Moreover, the changes to the tribofilm's nano-mechanical properties were correlated with the macro-friction results.

2. Experimental

2.1. Materials

In our study, steel (AISI 52100/DIN 100Cr6) discs of 24-mm diameter were used, each with a hardness of 850 HV, which was measured with a microhardness tester (Leitz Miniload, Wild Leitz GmbH, Germany). The average surface roughness of the discs was Ra = 40–50 nm (Hommel Werke T8000, Jenoptik industrial Metrology Germany, GmbH). Standard steel (AISI 52100/DIN 100Cr6) bearing balls of 10-mm diameter with a roughness of 10 nm (reported by producer) were used as the counter body. Parts of the steel discs were coated with commercially available coatings, i.e., hydrogenated amorphous diamond-like carbon (denoted as a-C:H) and Si-doped hydrogenated amorphous diamond-like carbon (denoted as Si-DLC). All the coatings have the same sub-layers structure, i.e., adhesion to the substrate was achieved with a Ti-based adhesion layer, which was followed by a Si-based transition layer. The interlayers and coatings were deposited using a hybrid PVD/CVD process. For the a-C:H butane (C4H10, H/C ratio 2.5) was used as the precursor gas, while for the Si-DLC, butane (C4H10, H/C ratio 2.5) was also used as the precursor gas, but additionally a Si-based liquid component was evaporated and introduced into the deposition chamber. The total coating thicknesses were 1.8 ± 0.1 μm and 2 ± 0.1 μm for the a-C:H and Si-DLC coatings, respectively, with the DLC functional thickness being approximately 1 μm for both coatings. The detailed coating properties and chemical compositions are listed in Table 1, as reported by the producer (Oerlikon Blazers). The surface energies of selected steel and coated samples are 43.42 mJ/m^2 for steel, 40.47 mJ/m^2 for Si-DLC and 36.29 mJ/m^2 for a-C:H coating. Surface energies were calculated from measurements of contact-angle with three most commonly used and cited models, i.e. the Owens–Wendt–Rabel–Kaelble (OWRK) method, the van Oss method and the Wu method. The results of all three models are qualitatively the same and differ only in terms of the absolute values, by about 5–25%, depending on the method used. In this paper we used results obtained with OWRK method, which is probably also the most frequently used in the literature. The detailed procedure for surface energy measurements is explained in our previously reported study [37], where the same surfaces as in this study were used.

2.2. Oils

All the coatings were tested with three different oils: a commercially available, automotive E6 grade, low-SAPS oil [38]; a commercially available, automotive E7 grade, high-SAPS oil [38]; and a mineral base oil (Group III) with 1 wt% of secondary ZDDP additive. The properties of the selected lubricants are presented in Table 2.

2.3. Tribological tests

The tribological tests were performed using a tribometer (UMT-2, Bruker, CA, USA) with a pin-on-flat test geometry in a reciprocating motion. The steel balls were rubbed against DLC-coated discs immersed in a lubricant solution. As a reference material, steel discs were used in combination with all the selected lubricants. The tests were performed at an elevated temperature of 100 °C. The normal load was set to 10 N, which corresponds to 1 GPa of maximum initial Hertzian contact pressure, a frequency of 10 Hz and a stroke length of 5 mm, resulting in an average contact

Table 2
Viscosity values of E6, E7 and ZDDP oils.

Oil	E6	E7	ZDDP
Viscosity grade	SAE 10W-40	SAE 15W-40	/
Viscosity at 100 °C (mm^2/s)	13.95	14.57	12.30
Viscosity at 40 °C (mm^2/s)	85.99	108.7	76.59

Table 1
Properties of a-C:H and Si-DLC coatings.

Coating		Nanohardness [GPa]	Young modulus [GPa]	Total thickness [μm]	C [at%]	H [at%]	O [at%]	Si [at%]
a-C:H	Hydrogenated DLC coating	21.9 ± 1.8	163 ± 17	1.86	66.5	33.5	/	/
Si-DLC	Si doped DLC coating	17.4 ± 0.8	144 ± 5	2.1	44.6	34	7	14