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The Performance and Mechanisms of DLC-Coated Surfaces in Contact with Steel in Boundary-Lubrication Conditions - a Review

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The importance of hard coatings in mechanical applications has been increasing rapidly for more than 20 years. The development of novel coatings, such as improved ceramic, diamond-like-carbon and advanced nano-composites, has promoted scientific research in the field of tribology and surface engineering, and at the same time it has focussed attention on micro- and nano-technologies. Diamond-like-carbon (DLC) coatings are becoming one of the most promising types of hard coatings. Their main advantages are low friction, good anti-wear properties, and adhesive protection. However, due to their low surface energy their reactivity with conventional oils and additives is limited and remains unsatisfactory. For a qualitative step-change that would improve the performance and allow effective optimising and tailoring of boundary-lubricated DLC contacts for various mechanical systems it is necessary to understand the mechanisms of why, how, under which conditions, and with which types of DLC coatings and lubricants the actual boundary lubrication is possible. As a result of ten years of research in this field, a lot of data have been reported; however, due to the different types of coatings, lubricants and additives used in these studies, the results are often difficult to compare and are sometimes contradictory. As a result of the recent heavy demand from many industries to apply DLC coatings to lubricated systems, a much better understanding of these phenomena and their overall performance is required. Therefore, if we wish to see a more effective continuation of the research and a better understanding of the scattered results, an overview of the current state of the art of lubricated DLC contacts is needed. In this paper we analyse the performance and suggested boundary-lubrication mechanisms of DLC/steel contacts from already-published studies and we summarise our present understanding of the boundary lubrication in DLC/steel contacts, which complements our recent analyses of DLC/DLC contacts.

Keywords: diamond-like carbon coatings, boundary lubrication, base oil, additives, nanotribology

0 INTRODUCTION

The extensive research on diamond-like-carbon (DLC) coatings in the past ten years has made it possible for such coatings to become one of the most valuable and promising types of protective low-friction coatings for a variety of mechanical applications. During this period the improvements in the deposition parameters, the understanding of the coatings' structure and related properties, the operating contact conditions, and the wear and friction behaviours [1] to [7] were substantially improved.

Diamond-like-carbon materials can have different structures of sp^2- and sp^3-bonded carbon atoms, containing a substantial amount of hydrogen or almost none [8] to [10]. Figure 1 shows a ternary phase diagram of the sp^2, sp^3, and hydrogen contents of various forms of diamond-like carbon. With respect to their chemical structure, we can differentiate between "pure", i.e., non-doped-DLC coatings and "modified", i.e., doped-DLC coatings. Non-doped coatings consist of C and/or H atoms only, while the doped ones contain additional metal (Ti, W, Mo, etc.) or non-metal (Si, N, F, etc.) elements. DLC coatings can be further divided in two major groups, based on their hydrogen content: (i) non-hydrogenated DLC coatings that include amorphous (a-C) and tetragonal (ta-C) DLC coatings with a negligible hydrogen content, and (ii) hydrogenated DLC coatings that include amorphous (a-C:H) and tetragonal (ta-C:H) DLC coatings containing a substantial amount of hydrogen [11].

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Because there is such a wide variety of different DLC coatings, their physical and chemical properties can also be very different, which implies that DLC coatings are nowadays being used in various fields of industry, for example, automotive, aerospace, electronics, optics, as well as for medical equipment and many others. As a consequence many studies on the tribological performance of DLC for use in different mechanical applications can be found in literature, for example, for automotive valve-train applications [12] and [13], bearings [14] and [15], gears [16] and [17], piston rings [18] and [19], cam followers [20], spark-ignited, direct-injection fuel systems [21], cutting and forming tools [22] and [23], hydraulic systems [24], etc. For medical purposes, studies were performed primarily for the use of DLC in orthopaedic applications [25] and [26], while for applications in the computer industry, this is mostly related to the head-disk interface [27] to [30].

In the automotive industry, which is a strongly performance-driven field, there is an increased demand for the use of DLC coatings in various contacts and systems, and these are typically lubricated [31] to [33]. Due to an ever-growing demand to reduce oil consumption and thus the amount of oil in mechanical systems, but also because of the increased severity of the contact conditions, many of these systems need to operate under boundary- and starved-lubrication conditions [34] to [36]. Therefore, to achieve the appropriate performance under such conditions, some interactions between the coatings, the oils and the additives are necessary for long-term, low-friction and low-wear operation. However, DLC coatings

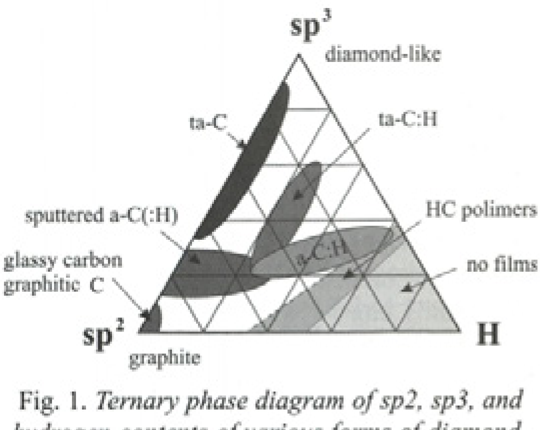


Fig. 1. *Ternary phase diagram of sp2, sp3, and hydrogen contents of various forms of diamond-like carbon*

are known as "inert" coatings with a low surface energy [37] and [38], and are therefore considered not to react with various oil additives and/or attract polar groups from the additives and the oil, which are the conventional mechanisms for the lubrication of steels and other metals [39] to [41]. Indeed, due to the early stage of research in this area, the chemical evidence and a definitive general mechanistic explanation of the boundary lubrication with DLC coatings was seldom provided [42] to [44], despite there being some excellent studies and frequently reported obvious empirical effects. This means that it is still questionable as to whether the lubricating mechanisms known from conventional steel (metal) surfaces are also valid for DLC coatings, or whether some other mechanisms are acting. In the ten years or so that there has been an interest in the boundary lubrication of DLC, a large quantity of empirical data has already been obtained, based on a variety of DLC coatings, base oils, additives, contact conditions, test devices, etc., which, in addition to providing new information, also makes understanding the behaviour and the performance of boundary-lubricated DLC coatings a complex task.

It is thus obvious that in order to improve and optimize the performance of DLC-lubricated systems, two specific requirements need to be fulfilled. Firstly, the real boundary-lubrication mechanisms of DLC coatings need to be revealed and understood from the mechanisms point of view, which means that studies have to be made in greater detail. Secondly, the results that were obtained so far, which are very scattered and poorly understood, need to be collected and compared, wherever this is possible. In this paper we attempt to summarize these previous results and analyse the behaviours that were reported during these studies. Due to the complexity and the variety of conditions and materials, only DLC/steel contacts are analysed in this paper. However, these are probably the most typical and often-used type of DLC contacts. This paper is thus complementary to our previous analyses of DLC/DLC contacts [45]. A presentation of the basic scheme of contacts using the different DLC coatings, additives and oils discussed in this paper is shown in Figure 2.

1 RESULTS

We have summarised the friction and wear results from already-published studies of lubricated DLC coatings in contact with steel [20], [32], [43],

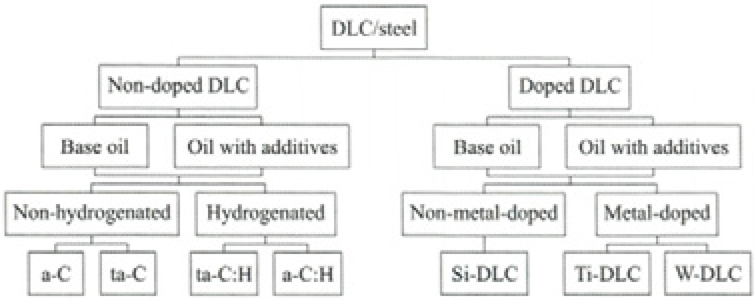


Fig. 2. *Schematic of the analysed contacts with respect to type of DLC and lubricants used*

[44], [46] to [57]. We then averaged all the values reported for specific coating/lubricant combinations with respect to the oils and the coatings shown in Figure 2. The presented results are shown as an average of the individual reported data, so that:

$$X = \frac{\sum_{j=1}^{n}\left[\sum_{j=1}^{p}\left(X_j+...+X_p\right)+...+\sum_{j=1}^{q}\left(X_j+...+X_q\right)\right]}{n} \quad (1),$$

where n represents the number of researches, $p...q$ represent the number of results taken from each study, and X stands for the analysed value, i.e., the coefficient of friction or wear rate.

Such an analysis was chosen in order to avoid the influence of the different number of results given by each study – having in mind that many studies present a list of results for specific material-lubricant combination, e.g., at various sliding intervals, velocities, loads, etc., which are impossible to fully consider empirically. However, where a large scatter of results showed a notable effect, this is pointed out and specifically commented on.

With regard to the scheme shown in Figure 2, we have separated the lubricants into base oils and oils with additives, in order to observe the influences of both separately. In Table 1 and Table 2 a list of analysed base oils and additives is presented.

In literature, it is more typical to report contacts as ball/disc, however, for the clarity of the discussed coating materials, we report in this paper the coating material first, although it is usually the disc. Consequently, contacts are throughout the paper reported as COATING/STEEL, irrespective whether the coating was a ball or a disc.

Table 1. *Denotations and specifications of analysed base oils*

Denotation	**Specification**
PAO	polyalphaolefin
M	mineral oil
S	sunflower oil
SE	saturated ester
UE	unsaturated ester

Table 2. *Denotations and specifications of analysed additives*

Denotation	**Specification**
EP	dialkyl dithiophosphate containing 9.3% P and 19.8% S or sulfurized olefin polysulfide
AW/EP	mixture of amine phosphates containing 4.8% P and 2.7% N
AW-mild	mixture of diamine monohexyl phosphate and amine dihexyl phosphate
AW	zinc dialkyldithiophosphate (ZDDP) or ZDDP-based anti-wear additive
FM	molybdenum dithiocarbamate (MoDTC)
FM+AW	molybdenum dithiocarbamate (MoDTC) + zinc dialkyldithiophosphate (ZDDP)
GMO	glycerol mono-oleate

1.1 Friction Results

1.1.1 Non-Doped DLC/Steel Contacts

Figure 3 shows the average coefficients of friction for a non-doped-DLC/steel contact lubricated with different oils and additives. In experiments involving only the base oils (without additives) the results with mineral and sunflower base oils generally have a higher friction (Fig. 3a) than the results with a polyalphaolefin (PAO) base oil (Fig. 3b). However, there is no significant difference in the friction between industrial base oils, i.e., mineral and sunflower base oils, while for the ester-type base oils (saturated or unsaturated) no results have been published so far.

Two types of additive effect can be seen in Figure 3, i.e., a friction increase and a friction decrease in comparison with base oils. Namely, the addition of AW/EP additives to mineral and sunflower oils generally caused an increase in the coefficient of friction. However, when the EP additives are added to base oils a decrease in the friction was observed for the sunflower oil, and an increase in the friction was observed for the mineral oil [46]. In both, the mineral and the sunflower base oils, the effect of the AW/EP additive was more pronounced than that of the EP additive. In one particular study [51], a decrease in the friction was observed when an anti-wear (ZDDP) additive was added to the mineral base oil, Figure 3a. However, the decrease was not as pronounced as one would expect from Figure 3a, because even with a base oil (in this particular study) the coefficient of friction was as low as 0.09 – i.e., much lower than the average of all the studies, as presented in the same diagram in Figure 3a. The decrease in the coefficient of friction in this case was about 0.02 during the running-in phase and about 0.01 for the steady-state value. When used in PAO base oil the AW additives (mild or strong) always increase the friction, although when a friction-modifier (FM) additive was present, the coefficient of friction decreased, Figure 3b.

The lowest coefficient of friction was found when using the formulated PAO (with the addition of MoDTC and ZDDP additives or with the GMO additive), while on the other hand, the highest levels of friction were obtained with the AW/EP formulated mineral and sunflower base oils.

In experiments with non-hydrogenated DLC coatings a generally lower friction was measured than with hydrogenated DLC coatings. All the friction data with non-hydrogenated DLC coatings

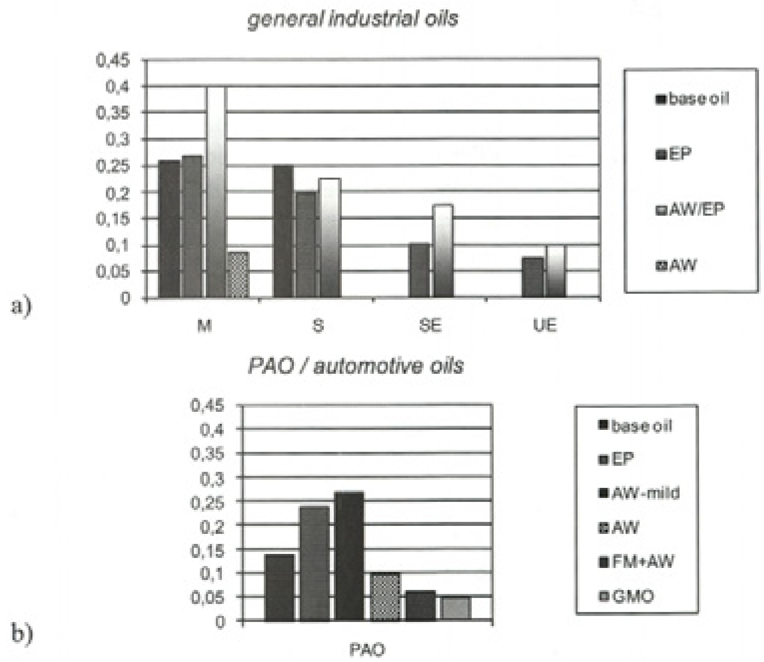


Fig. 3. *Average coefficient of friction for non-doped DLC/steel contact lubricated with (a) general industrial oils, and (b) PAO oils; with and without additives*

were lower than 0.1 – they were measured in (i) mineral oil with EP additives [50], (ii) PAO with MoDTC and ZDDP additives [43] and (iii) PAO with a GMO additive [20] and [44]. The lowest coefficient of friction (COF<0.05) among these was measured for the PAO with the GMO additive [44], which was also the lowest coefficient of friction found for a lubricated DLC/steel contact. With a-C:H coatings the coefficients of friction in the range 0.15 to 0.3 were measured using PAO with the EP or AW additives [52] and [53], and the amount of additive in the oil governed the friction behaviour. Sometimes an even higher friction was measured with the sunflower and mineral oils with the EP or AW/EP additives [46] and [49], which is also higher than in self-mated DLC/DLC contacts using the same oils and additives [58]. However, it should be made clear that these values are strongly test-dependent and are not just inherent contact properties.

1.1.2 Doped DLC/Steel Contacts

In Figure 4 the average friction is shown for doped DLC/steel contacts lubricated with different oils and additives. In tests with general industrial oils this friction was almost identical to the non-doped DLC coatings (Fig. 3). A similar situation could be inferred for the PAO/automotive oils. However, for the PAO oils a large scatter was calculated for the experiments with an EP additive. This is mostly the consequence of a substantial number of results reported for the EP additive with various concentrations mixed in base PAO oil in the contacts of W-DLC/steel, which, however, resulted in significantly different friction values. Namely, with some concentrations the friction increased, and with some it decreased [52] and [53]. This coating-lubricant combination (W-DLC/steel in contacts with EP additive) has also been studied for different test parameters, such as various temperatures, loads, sliding speeds, etc. [52], [53] and [55], and the EP additive was reported to have more influence on the friction than AW, particularly in the early stage of sliding. In some cases, when the EP additive was used, a significant reduction in the friction was reported after some period of sliding ("running-in"). Very similar results were reported for the mineral oils using the same additives [49], but the reduction of friction from the initial to the steady-state friction was found in

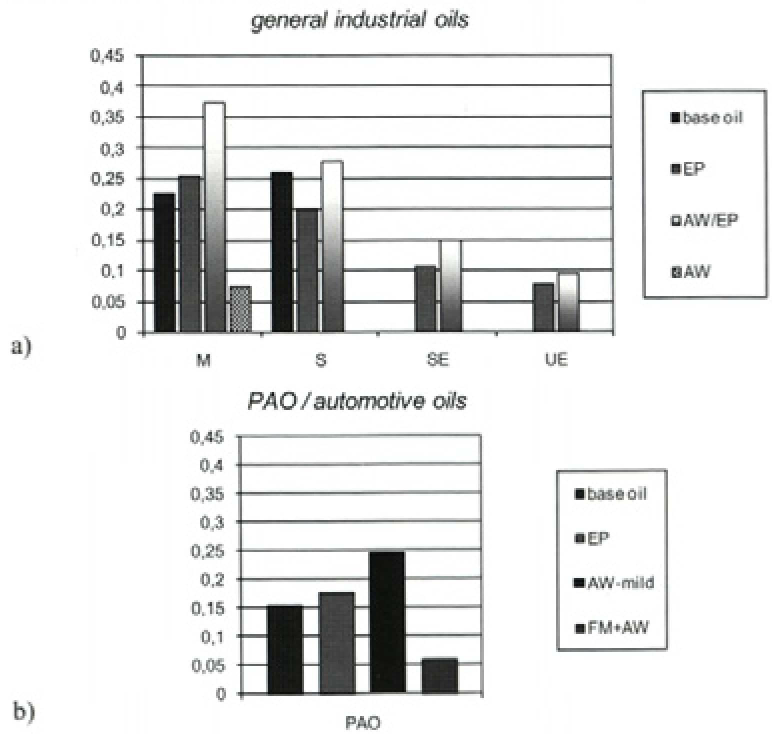


Fig. 4. *Average coefficient of friction for doped DLC/steel contact lubricated with (a) general industrial oils, and (b) PAO oils; with and without additives*

this case to be a consequence of coating removal and, therefore, the sliding of the steel ball over the Cr-interlayer (see Fig. 8), which resulted in a reduced friction [49]. In agreement with the latter conclusion, a complete removal of the coating (with some rare exceptions) was normally observed in these studies with additive concentrations lower than 2.5 % (typical conc. for formulations) – with mineral [49], but also with PAO oils [52], [53] and [55]. Therefore, this reduced friction was frequently found associated with excessive wear and coating removal, which is not a favourable tribological result for longer runs under such severe contact conditions.

From Figure 4a a decrease in the coefficient of friction with the use of the AW additive (ZDDP) in mineral oil [51] can be seen (last column at "M"). Si-DLC coatings were used in this particular study. It should be noted that the decrease was not so pronounced as it appears from this average value (single study), because even the base oil gave a rather low value compared to the average of many base-oil results that are encountered in the first column at "M". However, it is important to point out that the Si-DLC/steel contacts showed a larger decrease in friction than the non-doped DLC/steel combination. Furthermore, the friction decrease was shown to be dependent on the Si content in the coating – the highest Si/C ratio in the coating resulted in the greatest friction decrease when the AW additive was introduced into the base oil [51]. Another type of doped DLC coating that was investigated was the Ti-DLC coatings. The results showed that Ti-DLC coatings against steel result in the lowest friction and wear, even when tested with the PAO base oil only. This indicates that the interaction of the Ti-DLC with base oils is better and more protective than with other coatings. Namely, these results were even better than steel/steel, a-C:H/steel and a-C/steel [51], suggesting that this might be a promising coating/steel combination.

1.2 Wear Results

1.2.1 Non-Doped DLC/Steel Contacts

The interesting wear behaviour of non-doped DLC/steel contacts can be observed in Figure 5. A

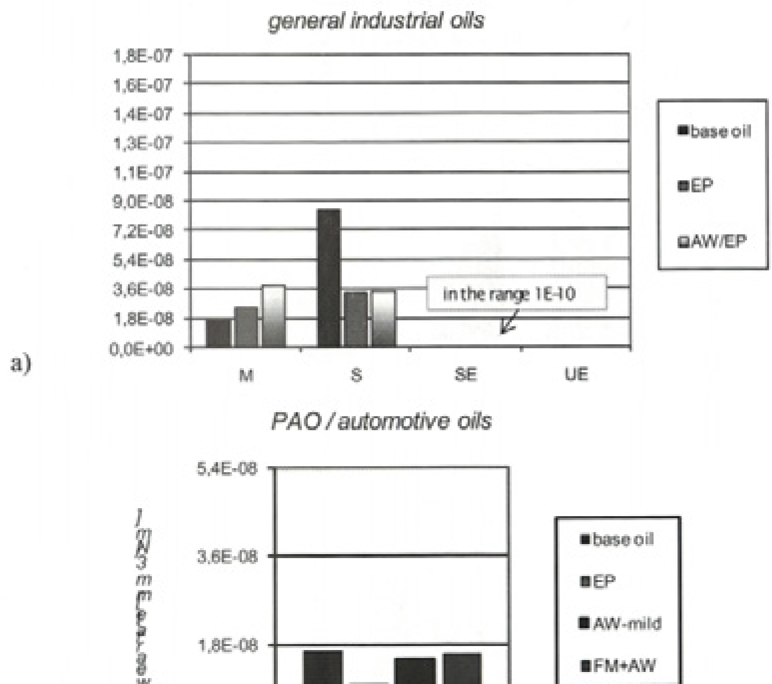


Fig. 5. *Average wear coefficient for non-doped DLC/steel contact lubricated with (a) general industrial oils, and (b) PAO oils; with and without additives*

huge difference in the wear rates can be seen for the general industrial oils, i.e., for the mineral and sunflower oils the wear was two orders of magnitude (100x) higher than that of the saturated and unsaturated esters, irrespective of whether additives were used or not. The wear rates in the PAO oils were generally slightly smaller, but in the same range as the mineral and sunflower base oils. Moreover, no significant effect of the additives was observed in the tests with PAO (Fig. 5b).

Two different responses were found for the a-C:H/steel contact with mineral and sunflower oils when additives were used. The inclusion of additives to mineral oil increased the wear of the steel ball and the highest wear was measured with the AW/EP additive. However, the inclusion of additives to the sunflower oil reduced the wear of the steel ball and the lowest wear was measured with the EP additive. Generally, the wear was slightly higher with the sunflower base oil than with the mineral base oil, which was also clearly visible from the SEM analysis of the worn surfaces that showed two different wear mechanisms for these oils [46]. Furthermore, when the AW/EP additive was used in mineral oil the sliding surface became soft and plastically deformed, while in sunflower oil the surface was brittle-like and contained small pits.

Another study was performed with a tungsten-carbide (WC) ball sliding against DLC. When the WC ball was tested against a non-hydrogenated (a-C) and hydrogenated (a-C:H) coating, and lubricated with a PAO-like oil (hydrogenated 1-decene homopolymer oil), the behaviour of the coatings was similar to that observed for the coatings tested in air, with only slightly lower wear of the coatings, indicating the positive influence of oil lubrication. The coating surfaces exhibited limited wear with a slight polishing-type wear, and with a specific wear rate of less than 6.4×10^{-9} mm^3/Nm [54].

1.2.2 Doped DLC/Steel Contacts

Most of results from Figure 6 require more discussion, as there are many specifics found in these studies, which affected the results. Namely, there are many more differences in the behaviour and more discrepancies in the results for doped

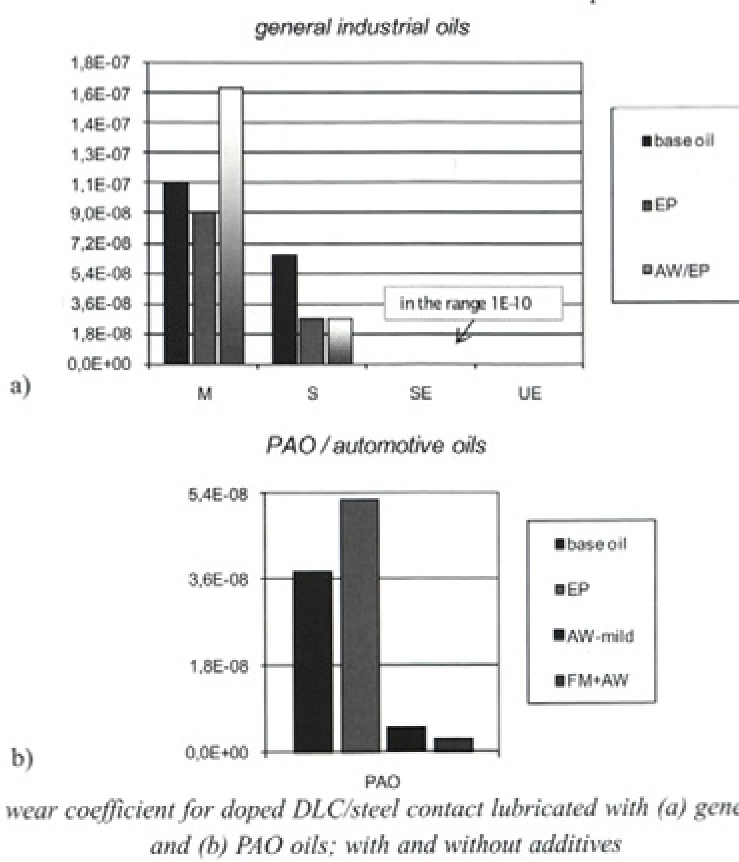


Fig. 6. *Average wear coefficient for doped DLC/steel contact lubricated with (a) general industrial oils, and (b) PAO oils; with and without additives*

DLC coatings against steel than can be seen from a diagram of the average values presented for several types of doped DLC coatings in Figure 6.

By using only mineral base oil, the W-DLC coating in contact with a steel counter-body suffered severe wear and was always worn through [46] and [49]. Other types of doped coatings (Ti-DLC, Si-DLC) showed better wear resistance, but the doped coatings always have higher wear, compared to non-doped coatings in contacts against steel, when tested with mineral base oil. When lubricated with sunflower base oil, the wear rate of these doped coatings was much lower, and this was true even for the W-DLC coating, where a three-times lower wear was measured for this combination. Moreover, with sunflower base oil, the wear of the W-DLC/steel was even smaller than that of the a-C:H/steel combination [46].

The additives generally reduced the wear of the doped DLC/steel contacts, Figure 6a. Most importantly, if the additives were successful in preventing the adhesion between the steel and the doped DLC, the wear was reduced compared to the wear with base oils, and was frequently lower than the non-doped DLC against steel (with additives). An exception was, however, found only for the W-DLC coating. Namely, the use of the AW/EP additive slightly reduced the wear of the W-DLC coating in the W-DLC/steel combination (still resulting in wearing out); however, the use of the EP additive resulted in higher wear. But, this case was unusual, because the coating was typically worn through and so severe adhesion could not be prevented. One of the reasons for this was explained in a study of mineral oils [49], where a clear formation of complex carbides, indicating the adhesion and dissolution of the WC (from the W-DLC) and the steel (from the ball counter-body) was found, as discussed and shown in Sections 1.3 and 1.4.

On the other hand, it was reported that when EP additives were used in PAO base oil, the additives improved the tribological behaviour of W-DLC/steel contacts, but this was strongly dependent on the concentration of the additive [52] and [53]. It was found that for concentrations from 0 to 1% of the EP additive, the W-DLC coating was removed from the surface. An increase in the EP additive concentration to the range from 2.5 % to 5 % gave excellent protection to the coated disc, almost eliminating its wear. However, at 10 % of EP in PAO oil, the effect of the additive was changed again; the friction increased and the surface layers became the same as with the steel/steel contacts, i.e., without any tungsten, but the wear was reported to remain very low. Presumably, the formation of a WS_2-containing layer is responsible for this beneficial effect, however, these results need to be further verified. Namely, the formation of WS_2 was found only for 0.5 % of the EP additive, for which the sliding actually led to a worn through coating [52]. Therefore, this explanation of a protective WS-type layer seems questionable and may even be used to support the opposing view, i.e., explaining how the coating was worn out due to the consumption of W from the coating at this low EP concentration. Moreover, the latter suggestion is in agreement with the high wear at 0.5 and 1 % of EP additive and another high-wear mechanism, i.e. the formation of complex carbides $W_{6-x}Fe_xC$ that were found in another similar study with 1 % of EP [49], and together they provide a reasonable explanation for such high wear and the wearing out of this coating in those severe boundary-lubricated conditions [49], [52] and [53].

When using PAO oil with MoDTC and ZDDP additives (i.e., FM+AW), the Ti-DLC/steel contacts showed very little wear, which can be seen in the results in the last column of Figure 6b [43]. Moreover, with the PAO base oil the wear of the steel counter body in the Ti-DLC/steel contacts was smaller than for the a-C:H/steel or a-C/steel combinations [43].

The wear was generally lower when both contact surfaces were coated with doped DLC [59] than when only one counter-body was coated, which was observed for different doped coatings in mineral oils [46] and [49], as well as for the Ti-DLC coating lubricated with additivated PAO [43]. Of course, this depends on the loads, the roughness, etc., and the amount of wear on the steel and the coated samples has to be evaluated separately. But, it should be noted that even if the coated surface tends to wear much less than the steel, the amount of wear on the steel side must also be evaluated, because steel is much softer than DLC coatings and thus it may became a critical part of the contact through various wear mechanisms (adhesion, abrasion, etc.) and sometimes even become unacceptable for the application.

1.3 DLC–Base-Oil Interactions

1.3.1 Non-Doped DLC/Steel Contacts

When experiments with PAO oils were considered, it was clear that the friction in non-doped DLC/steel contacts was higher, while the wear was lower than in self-mated non-doped DLC/DLC contacts. Among the non-doped DLC coatings in these DLC/steel contacts (with the base oil only), a higher coefficient of friction was measured with the hydrogenated a-C:H coating than with the non-hydrogenated a-C coating. But this was just the opposite to experiments with PAO that contained FM and AW additives (MoDTC and ZDDP) [43], where lower friction was found for the a-C:H coating than for the a-C coating. The wear in the contacts of the non-hydrogenated a-C coatings was, however, higher than the wear with the hydrogenated a-C:H coatings.

In agreement with this, in studies where mineral oils were used, almost no signs of wear could be found on the surfaces of the non-doped DLC. The major reason for this was the absence of any adhesion or transfer layers in these contacts [49], which is, however, the major difference in comparison to doped DLC coatings.

In some studies [20], [43] and [44] the coefficient of friction was much lower when using PAO base oil than when a mineral base oil was used [46], [49] and [50]. This discrepancy was so large that it hardly seems possible that it is a natural characteristic of the PAO base oil compared to the mineral oil. In order to evaluate this difference in the coefficient of friction, several additional tribological tests were conducted in our laboratory, including performing the tests with the PAO and a paraffin mineral base oil under exactly the same conditions: using the same tester and the same operating parameters. As can be seen from Figure 7, the results with the PAO and the mineral base oil were shown to be very close to each other, and this was true for non-doped and doped coatings, indicating that differences in literature, summarized

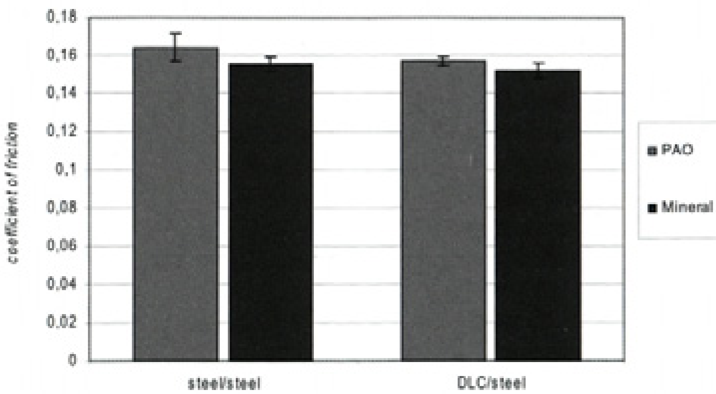


Fig. 7. *Coefficient of friction for steel/steel and DLC/steel contacts lubricated with PAO and mineral base oil*

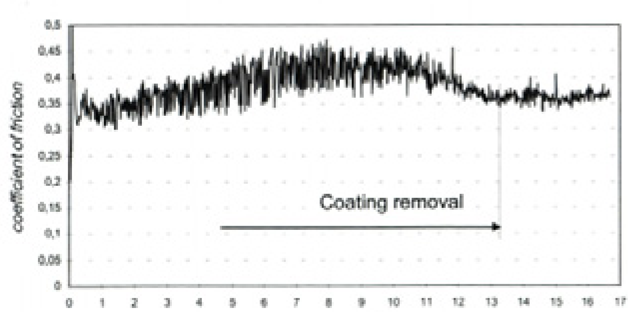


Fig. 8. *Coefficient of friction for W-DLC/steel contacts lubricated with a mineral base oil*

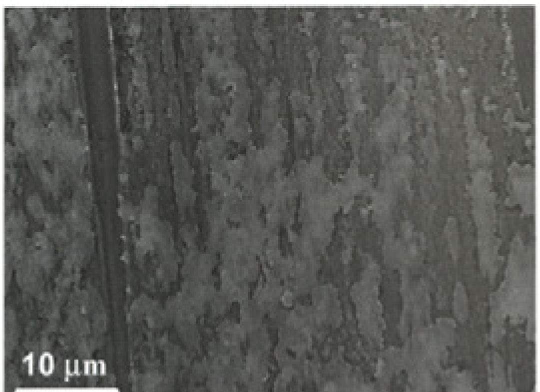
in Figure 3 and Figure 4, are most probably the consequence of different testing parameters and testing equipment used in different studies.

1.3.2 Doped DLC/Steel Contacts

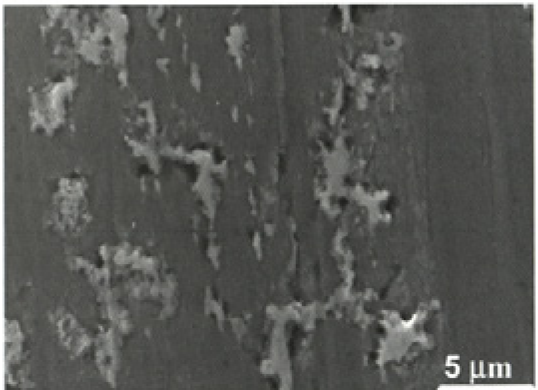
The most distinctive and studied contact of doped DLC coatings against steel in the presence of PAO base oils was the W-DLC coating. Generally, positive results with regard to friction are reported; however, these are somewhat contradictory compared to the wear behaviour. Namely, when sliding a steel ball against a W-DLC coated surface in PAO base oil, the transfer of the coating material from the W-DLC coated disc to the steel ball was observed. A transfer layer with WC particles was formed on the contact surface of the steel ball, which was reported to be responsible for the reduction of friction as compared to the steel/steel combination [52]. However, at the same time, the wear is high, obviously because of the transfer of the coating material. Thus, wearing through of the coating was reported. It is said that localized de-cohesion within the coating was followed by gradual wear, and eventually led to local exposure of the substrate [52]. This actually means that the coating was removed, although the friction was reduced.

Similarly, in another study of W-DLC/steel using mineral oil instead of PAO the coating was also always worn out [49]. Moreover, regarding the reduced friction, which also occurred after a certain sliding distance, it was shown that this friction reduction was measured at a time when the coating was worn through and the Cr interlayer was reached, thus leading to sliding between the steel and the Cr layer, which resulted in this friction reduction. This behaviour for the EP-added oil is presented in detail in [49], while Figure 8 shows very similar behaviour for the mineral base oil only. This finding seems to agree with the above observations of the PAO base oil reported in [52] and others. Moreover, in this comprehensive analysis using mineral oil [49], it was found that transfer and adhesion typically occur between the metal-doped DLC and the steel surfaces in the presence of a base oil only. This was obviously the case for both the Ti-DLC and the W-DLC. Furthermore, in the case of W-DLC/steel contacts, adhesion and substantial transfer layers were observed (Fig. 9a), including the formation of complex carbides (η-phase) $W_{6-x}Fe_xC$ in the form of dendrites (Fig. 9b). Thus, if adhesion is not prevented, the wear between the steel and the metal-doped DLC coatings could be very high. Accordingly, appropriate additives are obviously required for a reduced adhesion and the improved wear performance of these contacts.

Moreover, from a study comparing the tribological behaviour of W-DLC, Ti-DLC and Si-DLC coatings in contact with a steel counter-body [49] different wear mechanisms were found for the non-metal (Si) doped and metal (W, Ti) doped DLC coatings in contact with steel. Figure 10a shows an overview of a metal-doped Ti-DLC disk surface tested against a steel ball with mineral base oil without any additive. A relatively thick layer of adhered debris covered almost the whole wear surface, as seen from the corresponding EDS spectra



(a)



(b)

Fig. 9. *(a) Transfer of the doped W-DLC coating to the steel ball and (b) formation of complex carbides; i.e. dendrites*

in Figure 10b, while the transferred wear debris from the Ti-DLC were found on the steel balls. However, with additives in the oil, the adhesion of the Ti-DLC was successfully prevented, as seen from very limited material transfer in Figure 10c.

In contrast to the typical adhesion-based wear mechanisms found for metal-doped coatings (W-DLC and Ti-DLC), a non-metal-doped coating (Si-DLC) tested in mineral base oil against a steel counter body showed different wear behaviour, Figure 11. The amount of adhesion, even when using only base oil without additives, was negligible (Fig. 11a) compared to the Ti-DLC and W-DLC coatings. This suggests a limited chemical compatibility of the Si-DLC coatings with the steel surfaces, indicating that they are more like the non-doped DLC coatings than the metal-doped coatings. The observations of the ball surfaces were in agreement with the disc surfaces, as no sign of any transfer of the Si-DLC wear debris was found. The surfaces were mechanically damaged, showing poor lubricant protection, but no adhesion was present. Furthermore, when additives were added to the base oil, the surfaces changed their appearance, indicating that a thin and apparently soft layer formed on the Si-DLC surface, which might suggest that an interaction occurred between the additive, the steel and the coating, Figure 11b.

From this study [49] it is clear that in contrast to the non-metal-doped DLC coatings (Si-DLC), the metal-doped coatings (Ti-DLC and W-DLC) in contact with steel always experienced severe adhesive wear and mutual wear debris transfer if a mineral base oil without additives was used. Therefore, metal elements most probably induce metal-like behaviour of the metal-doped coatings, while the non-metal-doped coatings behave more like non-doped DLC coatings, which was also noted for self-mated DLC/DLC contacts [59]. On the other hand, the addition of EP additives was very successful on Ti-DLC, but this was not the case for W-DLC.

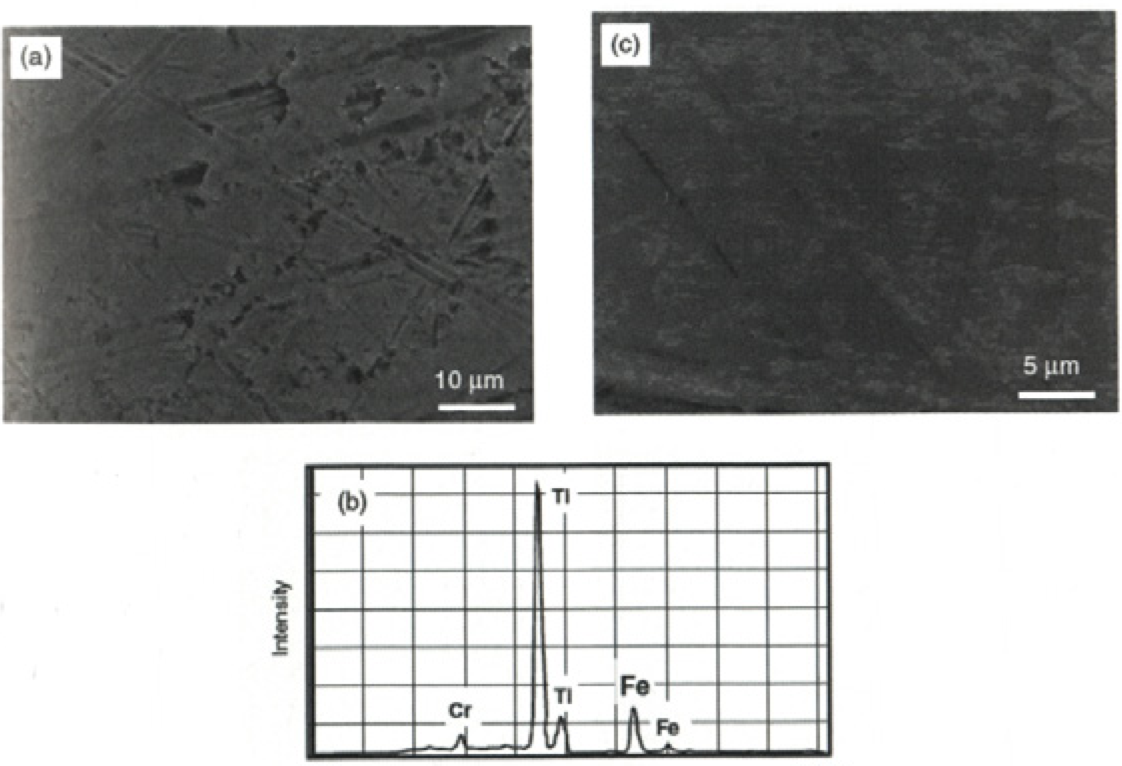


Fig. 10. *(a) SEM image of the Ti-DLC worn disc surface tested with mineral base oil and (c) mineral base oil with AW/EP additive. The figure in (b) corresponds to the EDS spectra of the layer from the figure in (a).*

1.4 DLC-Additive Interactions

1.4.1 Non-doped DLC/Steel Contacts

In a study of non-doped DLC coatings lubricated with mineral or sunflower oil containing the AW/EP additive no signs of tribofilm formation could be found on the worn DLC-coated surfaces using EDS analysis [46]. However, P-peaks were observed in the EDS spectra from the steel counter-body, indicating the formation of a tribofilm on the steel side of the contact, but not on the coating itself. Generally, the sunflower base oil showed less friction than the mineral base oil, and thus the effect due to the use of additives was also relatively smaller, while remaining distinct. The use of EP additives, however, always resulted in increased friction for both the sunflower base oil and the mineral base oil [46].

When the PAO base oil was used, with or without MoDTC (FM) and ZDDP (AW) additives, the hydrogenated a-C:H coating produced less friction than the non-hydrogenated a-C coating [43] in a contact with the steel counter-body. This positive effect of the hydrogen content on the lubrication properties of the DLC coating is similar to that observed in self-mated contacts with the same lubricants. Table 3 shows the elemental composition of the tribofilms formed in the contacts lubricated with the PAO oil containing the MoDTC and ZDDP additives, which formed on the hydrogenated a-C:H and non-hydrogenated a-C coatings after sliding in contact with a steel counter-body [43]. From the analyses it was found that the Mo3d (Mo(IV)) peak corresponds to MoS_2 and the Mo3d (Mo(VI)) peak corresponds to MoO_3. This shows that the MoS_2/MoO_3 ratio for the hydrogenated a-C:H coating is much higher than that of the non-hydrogenated a-C coating, which indicates the higher reactivity of these oils with hydrogenated DLC than with non-hydrogenated DLC. However, no significant effect of the steel counter-body on the chemical composition of the tribochemical layer was detected in this study.

In contrast to the above discussion on the effect of the hydrogen content in the presence of PAO with MoDTC and ZDDP additives, just the opposite behaviour can be concluded for the GMO additive. Namely, ultra-low friction was found with the non-hydrogenated ta-C coatings sliding against steel, when lubricated with PAO containing GMO [20,44], while with the hydrogenated DLC, the friction increased significantly. This difference in the friction behaviour due to hydrogen content in the DLC coating with different additives is schematically presented in Figure 12.

1.4.2 Doped DLC/Steel Contacts

In a study of sliding the steel ball against W-DLC-coated disks using PAO oil containing the EP additive, a tribofilm composed of the coating material (W and C) and sulphur (S) was formed on the steel surfaces (only) with EP concentrations from 0.5 to 5 %. Moreover, under a specific concentration of 0.5 % of EP additive, the WS_2 species were found using XPS analyses [52] and [55]. From "conventional" boundary-lubrication

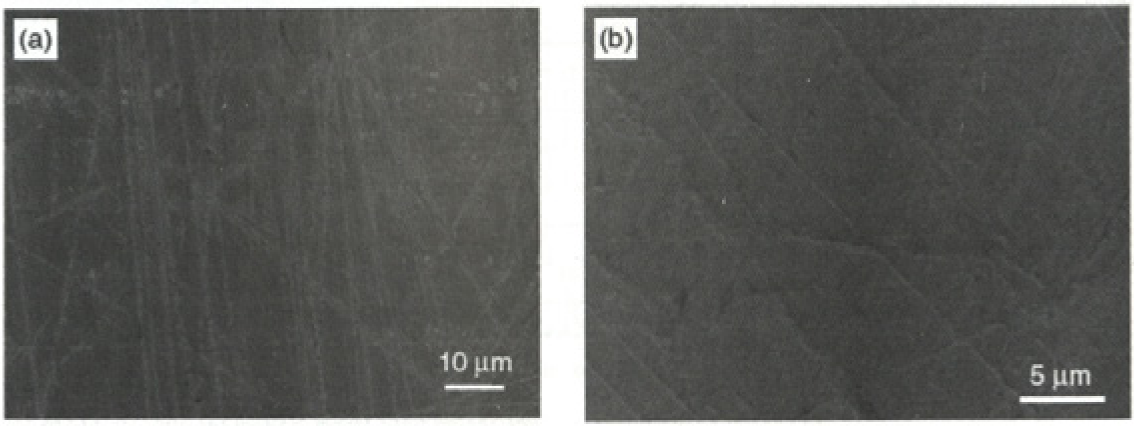


Fig. 11. *(a) SEM image of Si-DLC worn disc surface tested in mineral base oil and (b) mineral base oil with AW/EP additive*

Table 3. *Elemental composition (at. %) of tribofilms formed on a-C:H and a-C coating surfaces from DLC/steel contact using PAO with a mixture of MoDTC and ZDDP additives [43]*

Elements	Energy (eV)	Elemental composition (%)	
		a-C:H	a-C
C1s	284.8-285.5-287.6	94.6	92.4
O1s	531.0-532.8	3.1	5.2
S2p (sulphide)	162	0.8	0.9
Mo3d (Mo(IV))	229	0.4	0.4
Mo3d (Mo(VI))	232	0.1	0.9
P2p	133.2	≈ 0	≈ 0
Zn2p	10232.4	1.0	0.2

The data were obtained after the treatment of the XPS spectra.

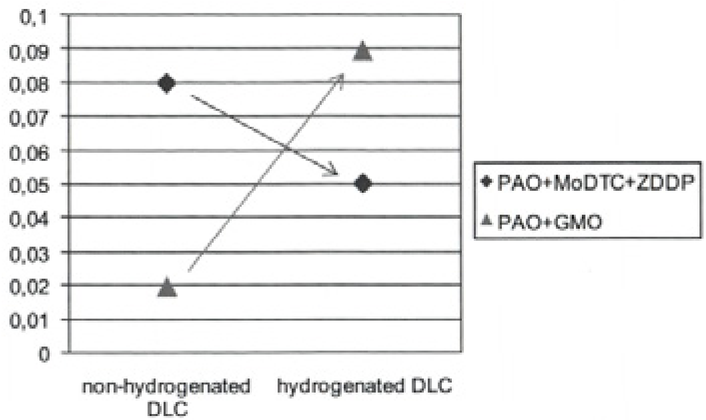


Fig. 12. *Effect of hydrogen content in the DLC coating on the friction coefficient using PAO oil containing (i) MoDTC and ZDDP and (ii) GMO additive. Schematic is designed from the data in [20], [43] and [44].*

practice it is known that the friction-reduction mechanism of the widely used MoDTC is based on the formation of nano-metric MoS_2 layers on the contact surfaces. Due to the fact that molybdenum (Mo) and tungsten (W) are chemically similar elements, it was proposed, based on the HSAB principle, that W transferred from the W-DLC coating to the steel counter-body, and in combination with the S-based EP additive, formed a lamellar WS_2-type tribofilm on the steel surface, which was further assumed to have similar tribological characteristics to that of MoS_2. Therefore, it was suggested that the tribofilm that contained the WS structures is similar to the MoS_2 films, and therefore it caused friction and wear reduction in the contacts lubricated with PAO oil containing from 2.5 % to 10 % of EP additive [52] and [55].

However, as discussed earlier, the explanation of the beneficial effect of a WS_2 layer appears questionable, because the WS_2 species were found by XPS only at 0.5 % of the EP additive (not at 2.5–10%), for which the sliding actually led to wearing out and removal of the coating [52] and [55]. Actually, this XPS evidence may suggest the opposite mechanism, i.e., how the coating was worn out so quickly at 0.5 % of EP, which occurred also at 1 % of EP, through the consumption of W from the coating. Thus, the only effect of WS_2 that was actually confirmed (at 0.5 % EP) is negative - not beneficial, because the coating was worn through and the friction was high at those conditions. Therefore, this result contradicts the explanation of the positive effect of using 2.5 to 10 % of EP, where low wear and friction were found, but the detailed chemical composition of the layer remained unknown. Therefore, it is not clear whether the same WS species, i.e. WS_2, are formed at concentrations of 2.5, 5 and 10 % of EP. What is more, at 10 % of EP, no W at all was found in the tribofilm that was, however, still rich in sulphur (the same as with the steel/steel contacts), but the wear was equally low as with 2.5 % or 5 % of EP [52]. Obviously, at 10 % of EP the mechanism for low wear and friction was not the same as with lower EP concentrations.

Furthermore, the lowest friction in that study was found for 2.5 % of EP, providing value of about 0.145, which is around 36 % lower than for PAO base oil (0.23). However, at 1 % of EP, where the coating was worn-through and removed, the friction of about 0.16 was measured, which is about 30 % lower compared to PAO base oil. Moreover, at 5 % and 10 % of EP, where the best tribological performance was reported, the friction was about 0.165 and 1.175 respectively, which is even higher than at 1 % of EP where coating was removed during steady state [52]. This shows that almost equally low or even lower steady-state friction as with optimal conditions at 2.5 % of EP can be maintained at very high wear rates even without the presence of the W-DLC coating (at 1 % of EP), or without W-containing tribofilm (at 10 % of EP). This conclusion agrees with another study of the same contact lubricated with paraffin mineral oil, where reduced steady-state friction was found as a consequence of W-DLC coating removal and sliding of steel ball over the Cr interlayer, as shown for 1 % of the same EP additive [49], as well as for the base oil only, see Figure 8.

Accordingly, three regions were identified with different wear behaviours depending on the EP concentration (0.5 to 1, 2.5 to 5 and 10 % of EP), while friction behaviour seems to be even more complex, suggesting that they cannot be governed by a single surface mechanism. Therefore, from the above discussion it follows to be very unlikely that the formation of the WS_2 layer could be the reason for the low wear (and friction) observed under the conditions of 2.5 to 10 % of EP in the oil, as suggested in [52] and [55]. On the other hand, the formation of complex carbides $W_{6-x}Fe_xC$ was found with the same contacts using 1 % of EP additive [49], which confirms the well-known high chemical compatibility and instability (dissolution) of the W–Fe–C system, which supports those results and provides a reasonable explanation for such high wear and wearing out of the coating that was typically found in all these studies [49], [52] and [55] – at concentrations lower than 2.5 % of EP, which is, however, already a very high concentration for any oil EP formulation. The W-DLC coating lubrication and interactions with additives, including the conditions to prevent its adhesion/dissolution with steel therefore need to be further clarified, but it seems obvious that the long-term performance of the W-DLC/steel contacts cannot be improved using the presently proposed mechanism with typical EP concentrations (around 1 %) if the coating has to be worn at such a high rate to provide "protective" and/or low-friction films. Moreover, in a thesis, where these tribofilms were in-depth investigated and analysed [60], it was concluded that to facilitate a long life of W-DLC coating in contacts with steel, more suitable S-based additives, and a process as well as the coating composition that allows deposition of thick coatings, are required because of the continuous high consumption of the coating and additive.

A very recent study [61] shows that similar metal-like adhesion behaviour of doped-DLC

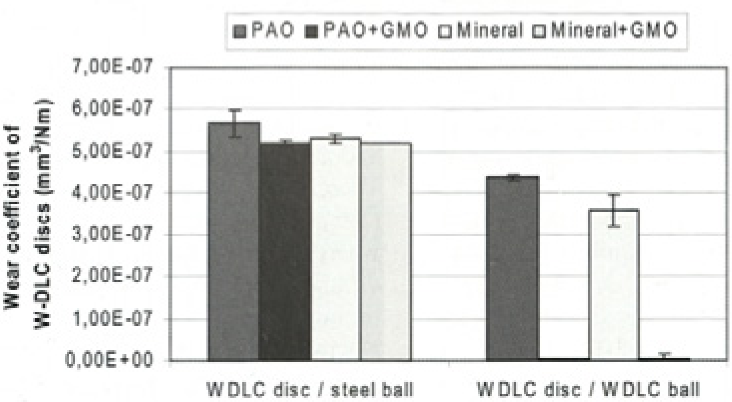


Fig. 13. *Wear of the W-DLC discs in W-DLC/steel and W-DLC/W-DLC contacts when tested with PAO and mineral oil, with and without GMO friction modifier*

against steel is obtained also with friction modifiers, such as GMO. Although GMO greatly improved the wear behaviour of W-DLC/W-DLC contacts, i.e. practically eliminated the wear of balls and discs, both in PAO and mineral oil, the wear of W-DLC/steel contacts was almost the same irrespective whether GMO was used or not, Figure 13. In a self-mated contact of Ti-DLC/Ti-DLC with another friction modifier, i.e. MoDTC, improved tribological behaviour was also found [43]. This shows that despite the obvious interactions of additives with metal-doped coatings [43], [45] and [59] and usually observed improvements, high chemical compatibility between these coatings (especially W-DLC) and steel is a critical parameter that determines their adhesion and wear, if the additives are not successful enough, as already suggested earlier [49].

2 DISCUSSION

Different friction and wear behaviours were observed depending on the different DLC-lubricant combinations presented in this paper (Fig. 2). In most reported studies the additives significantly affected the wear and friction of the boundary-lubricated DLC contacts; however, the extent of the change depends on the type of oils, the additives, coatings, etc. Different behaviours were observed for non-doped and doped coatings. Generally, it is suggested that metals, and possibly also other doping elements, provide sites for the coating-lubricant interactions in accordance with conventional metal-lubrication theories [39] to [41]. Such behaviour could be observed for Ti-DLC coatings, as well as for W-DLC coatings [49], [52] and [55]. However, this is not always plausible and can lead to severe wear if the adhesion between the doping elements and the steel counter-body is not prevented. Thus, appropriate additives need to be used or developed, but this challenge still remains for the future. Nevertheless, all these results confirm that in some cases even today's additives are relatively successful, which supports earlier findings on the reactivity between the DLC coatings and the additives [42] to [44]. The chemical structure of the coating seems to play the key role in the boundary-lubrication mechanisms of DLC/steel contacts as the differences between various, primarily doped, coatings are very large. However, also for the non-doped coatings, it is clear that the hydrogen content in the coating material, as well as the molecular structure of the base oil and the additives, play the key role in achieving the positive lubricating effect of the non-doped-DLC-–oil combinations. Finally, the contact conditions, especially the contact temperature need to be considered in much more in detail [62], as this can vary a lot in the temperature values [62] and [63] and the DLC response [42].

Several consistent trends and tribological behaviours were identified in this paper; however, some clear inconsistencies and discrepancies were also found. The main problem is that verified lubrication mechanisms that would indisputably explain certain behaviour are to a large extent missing. Accordingly, it is obvious that more results and more in-detail studies are required to better understanding DLC-coating/steel contacts, but the most obvious findings from the present analyses are summarized in the following section.

3 CONCLUSIONS

- Steel counter-bodies and their reactivity with oils and additives have an important effect on the friction in all the DLC/steel contacts. This is the reason for approximately the same friction values being measured for the doped and non-doped coatings under the same conditions.
- The addition of the AW/EP additive to the mineral base oil usually increases the friction. In contrast, the addition of the EP additive and friction modifier (GMO) to the mineral base oil decreased the friction.
- Non-hydrogenated DLC coatings typically have a lower friction than hydrogenated DLC coatings.
- With respect to the different oils, significantly lower friction was measured with PAO oils than mineral or other industrial oils, but this seems to be test-dependent rather than a property of the base oil (in combination with particular DLC coating).
- The lowest friction in the DLC/steel contacts was measured when friction modifiers were used.
- The wear of metal-doped DLC coatings is typically higher than that of non-doped DLC coatings, which is even more pronounced if the additive's efficiency is lower, and particularly with base oils.

- The wear of metal-doped-DLC/steel contacts strongly depends on the efficiency of the additives. If the additive protection is successful, wear can be reduced, otherwise the wear is very high due to the strong adhesion between the steel and the metal-doped DLC. Non-metal-doped DLC coatings appear to have a different wear behaviour compared to the metal-doped DLC coatings.
- The metal elements in DLC coatings most probably induce their metal-like behaviour, while the non-metal-doped coatings behave more like non-doped DLC coatings.
- For the performance of doped-DLC/steel contacts, it is clear that there is an important positive effect from additives possible, but it varies depending on the type of additives and coatings. Potential lubrication mechanisms remain uncertain due to inconsistencies and discrepancies in reported results. Presently suggested mechanisms for W-DLC coatings with EP additives are not appropriate for improved tribological performance due to high additive and coating consumption, i.e. wear.
- The hydrogen content in non-doped DLC coatings significantly affects their tribological performance. However, different friction behaviours were observed for different friction modifiers, depending on the hydrogen content. Some plausible mechanisms have already been proposed in the literature.

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