

On the Tribochemical Action of Engine Soot

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Abstract

The tribological behaviour of soot was studied by means of a pin-on-disk tribometer coupled to a high resolution wear measurement system (RNT). The soot particles were characterized by high-resolution transmission electron microscopy (HRTEM), energy electron loss spectroscopy (EELS), electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS). The surfaces of the tribometer disks were analyzed by atomic force microscopy (AFM), Auger electron spectroscopy (AES) and prepared with focused ion beam (FIB) for high-resolution transmission electron microscopy (HRTEM). Our results show that wear does not depend on the mechanical properties of different soot particles, but is closely related to their reactivity and the amount of defect sites. A new wear model for Otto soot is proposed.

Keywords: Soot; Wear; Diesel and Otto engine; Oil; Tribochemistry

1. Introduction

Whether soot particulate emissions have a detrimental effect on the life of internal combustion (ic) engines, and how pronounced this effect is, has been disputed for a long time and continues to be of high interest to car manufacturers. Many conflicting, incomplete ideas and explanations about the properties and effects of soot particulates on the wear mechanism have been published. Rounds et al. [1, 2] showed that soot is not abrasive but adsorb anti-wear additives, thus diminishing anti-wear properties. Ryason et al. [3], however, concluded that soot particles are abrasive because they were found to generate grooves and breakouts in metal surfaces. The same idea was held by Nagai et al. [4] who showed that soot particles are very hard and act abrasively on metal surfaces. The authors also found that intensified exhaust gas recirculation (EGR) raises the soot concentration in oil, thus enhancing wear. Ratoi et al. [5] showed that dispersed Carbon Black rapidly abraded zinc dialkyldithiophosphate (ZDDP) reaction films. Gautam et al. [6] found more wear with soot contamination of the oil than without. Moreover, it was seen that higher soot concentrations in oil generates more wear whereas a higher concentration of phosphorus in the oil leads to less wear. Soejima et al. [7], Yamaguchi et al. [8], and Aldajah et

al. [9] found that the presence of soot particles reduces the thickness and extension of anti-wear films and are abrasive. Truhan et al. [10] concluded that the chemical activity of soot particles and their reaction with ZDDP prevents the formation of liquid boundary layers on metal surfaces.

Part of the controversy found in the literature arises from the fact that the properties of soot particulate emissions very much depend on the thermodynamics of combustion in the engine and, consequently, on the final structure of carbonaceous matter, such as the average primary particle and aggregate sizes and size distributions, polydispersity, and the degree of graphiticity. This determines the rheological properties. The structural complexity of soots varies depending on the type of engine and its operating conditions. The same holds for experiments with well-defined industrial carbon black varieties which were used for controlled modification of the rheological properties of engine oils modified by adding specific quantities of a specific grade of carbon black. A wide variety of synthetic carbon black very different in size and structure are commercially available. Comparability of the findings about the influence of carbonaceous matter on oils makes it imperative that the same grade of carbon black is used in the experiments.

It must also be noted that the properties of soots vary, as is shown by comparing soot collected from the exhaust system of a passenger car with and without catalytic converter, on the one hand, with soot collected from the piston and the oil, on the other hand. In this study, this uncertainty is avoided by focusing on particulates collected right from the oil under identical conditions [11].

It can be concluded from the literature that the wear mechanism induced by the presence of soot is not fully understood yet. More fundamental knowledge is needed. Thus, the properties of soot and their influence on wear were in the focus of our studies.

This study examined the effect of different types of soot on the wear of cam and cam follower materials. A pin on disk test was employed because this tribo-system has unidirectional motion. A variety of analytical techniques were employed to measure soot morphology and chemical properties, friction, wear and chemical reactions on the wear surfaces.

2. Experimental Details

2.1. Materials and Oils

In all tribological experiments, (Fig. 1), a case-hardened pin (16MnCr5) 5.2 mm in diameter eroded from the K-cam of a camshaft was run against a nitrided disk (bucket tappet); various fully formulated

commercial lubricants (Fuchs Titan 5W30) were used.

Fig. 1. Camshaft from K-cam eroded pin, pin fitting and bucket tappet.

The oils used for the tribological tests were fresh oil, Carbon Black oil, Carbon Black centrifuged oil, and two oils which were loaded with soot by dynamometer engine tests and sampled at different running times. One set of oil samples were aged using a spark ignition internal combustion (ic) engine which uses the thermodynamic Otto cycle and one set which was generated by an auto ignition ic engine in a Diesel cycle. We will refer to these oils in short as Otto and as Diesel engine oil. Carbon Black oils were obtained as concentrates (MIRA CORP.) and then diluted with fresh oil. The concentration of soot in the oils is shown in Table 1.

Table 1

Soot concentration in oils used for wear tests

Name	Soot concentration [wt.%]	phosphor [mg/kg]	silicium [mg/kg]	sulphur [mg/kg]
Fresh oil	0.00	641	<10	2100
Carbon Black (CB)	1.01	628	8	2170
CB centrifuged	0.01	630	3	2090
Diesel engine oil	2.61	542	59	1560
Diesel engine oil	4.72	970	26	1990
Otto engine oil	0.54	469	41	1540
Otto engine oil	0.94	582	41	1950

2.2. Pin-on-disk Tribometer

A custom-built pin-on-disk tribometer (Fig. 2) was employed for the tribological experiments. Wear was measured continuously by the radionuclide wear measurement technique [12]. The nominal contact pressure in all experiments was 13 MPa; the sliding velocity 0.3 m/s; the oil temperature was kept constant at 120°C; and the duration of all experiments was 40 hours.

Fig. 2. Schematic representation of the setup for the pin-on-disk wear testing machine.

2.2. Analytical Methods

High-resolution transmission electron microscopy (HRTEM; Jeol 2010F) was used to study the nanostructure and the surface structure of soot particles as well as the surface structure of the tribometer disks on the first nanometer of the surface. HRTEM was accompanied by electron energy loss spectroscopy (EELS) to obtain information about the binding of carbon atoms to their nearest neighbours. EELS spectra supplied additional information about the morphology and elemental composition of the soot samples.

Electron spin resonance (ESR) furnished information on the number of unpaired electrons within the soot particles. The spectra were recorded by an ELEXSYS 500-10/12 spectrometer with a frequency of 9.5 GHz at 77K and room temperature.

X-ray photoelectron spectroscopy (XPS; Leybold MAX 100) was conducted to study the chemical composition and chemical states in the topmost atomic layers of soot particles.

Atomic force microscopy (AFM; Veeco Dimension 3100) was used to analyze the topography of the wear track.

Depth profiles of the elemental composition on the first 100 nanometers of the disks were measured by Auger electron spectroscopy (AES; Auger Nanoprobe PHI 680).

In addition to AFM and AES, lamellae of the tribometer disks for high-resolution transmission electron microscopy (HRTEM) were prepared by the focused ion beam technique (FIB; FEI Strata FIB 205).

3. Results

3.1. Pin-on-disk Tribometer

In all tests, the friction coefficient was found to decrease as a function of the sliding time after passing through a peak in the first few minutes of non-transient behavior (running-in). This trend is particularly visible for

the oils with 4.7 wt.% (Fig. 3 (a)) and 2.6 wt.% (Fig. 3 (b)) of Diesel soot. Increased soot concentration was found to decrease the friction coefficient. Surprisingly, the dependence of wear on the soot concentration is inverted - at a high Diesel soot concentration (Fig. 3 (a)), the amount of wear increases very fast, the wear rate equaling up to 2000 nm/h within the first 10 hours. After 15 hours of running time, the wear rate levelled off, reaching a constant level of 40 nm/h. Lowering the soot content resulted in faster running-in (Fig. 3 (b)). Here, the wear rate is constant after only 6 hours of running time. As a result, total wear is lower at the end of the test.

Fig. 3. Wear and friction as a function of time in samples tested with Diesel soot (a) 4.7 wt.%, (b) 2.6 wt.%.

Significantly different wear characteristics were observed for Otto soot compared to Diesel soot and CB oils. Both oils containing 0.9 wt.% soot (Fig. 4 (a)) and those containing 0.5 wt.% soot (Fig. 4 (b)) showed constant wear rates without running-in for 40 hour of 1200 nm/h (Fig. 4 (a)) and 700 nm/h (Fig. 4 (b)), respectively, within the test time. Thus, the total amount of material removed at the end of the tribological test for both varieties of Otto soot oils is significantly higher than in the case of Diesel soot despite the much lower soot concentration.

Fig. 4. Wear and friction as a function of time for samples tested with Otto soot (a) 0.9 wt.%, (b) 0.5 wt.%.

Low total wear was found for Carbon Black (CB) (Fig. 5 (a)). As in the experiments with Diesel soot oil, pronounced running-in and low wear rates were found. The general trend of the friction coefficient is also comparable to that found for Diesel soot oil.

Fig. 5. Wear and friction as a function of time for sample tested with (a) 1.0 wt.% Carbon Black, (b) centrifuged Carbon Black, (c) fresh oil.

Unlike the sooted oils (Diesel and Otto), fresh oil (Fig. 5 (c)) shows low total wear. Towards the end of the experiment, the wear rate has a constant level of 1 nm/h. This result is comparable to centrifuged CB oil (Fig. 5 (b)) where a wear rate of 1.3 nm/h was found after 12 hours of running-in time. However, the friction coefficient

measured with fresh oil is higher than in the latter case.

Figure 6 is an overview demonstrating the effect of the soot concentration and type of soot on wear behaviour. Fresh oil and centrifuged CB oil produce comparable low total wear levels.

Using Carbon black resulted in a long running-in time but, ultimately, the lowest wear rate and total wear.

Diesel sooted oils showed pronounced running-in characteristics with high wear rates which decrease after the running-in time. Total wear for 4.7 wt.% Diesel soot oil amounted to 51,000 nm and, for 2.6 wt.% Diesel soot oil, to 24,000 nm.

Fig. 6. Wear as a function of time for all tested oil samples.

Surprisingly, Otto soot showed an almost linear wear trend and a constant wear rate. Total wear for 0.9 wt.% Otto soot was found to be 51,000 nm and, for 0.5 wt.% Otto soot 36,000 nm.

Fig. 7 shows the total wear as a function of the soot concentration in oil for the used oils.

Fig. 7. Wear as a function of soot concentration for all oil samples.

As observed in previous studies [4, 9, 10], a significant increase in wear due to the presence of soot in oil was found.

However, it should be noted that engine soot does not increase wear more than CB. When Carbon Black was removed by centrifuging, results were as good as in the case of fresh oil.

In summary we find that it is not possible relate the oil properties or more precisely the soot concentration with the total wear and the wear rate. That means that other properties of soot particles which we will address at a later point in this article may be more relevant for the wear behaviour.

3.2. HRTEM

The structures of the different soot particles were examined by High Resolution Transmission Electron Microscopy. Figure 10 shows the nanoscale morphology of Carbon Black. Primary particle diameters range between 50 and 60 nm (Fig. 8 (a)). CB particles are larger than the Otto and Diesel soot particles. The paracrystalline Carbon Black species shows some disorder in the graphite structure (Fig. 8 (b)).

Fig. 8. HRTEM images of Carbon Black. (a) primary particle size, (b) fine structure inside a primary particle.

The level of graphitization is low. Only the boundary area showed structures with a higher level of graphitization (see arrows).

Fig. 9 shows TEM images of Diesel soot particulates. The primary particle diameters are smaller here than those of CB, ranging between 15 and 25 nm.

Fig. 9. HRTEM images of Diesel soot. (a) primary particle size, (b) fine structure inside primary particles.

The primary particles also show a notably higher degree of graphitization (Fig. 9 (b)) mainly in the boundary area. The structure resembles concentric graphite-like spherical entities and ring-like structures and flat or smooth surface structures (see arrows) and detached damaged areas (discontinuity of spherical graphite structures).

Finally, the primary particle diameters of Otto soot are larger (30-40 nm) than those of Diesel soot (Fig. 10 (a)). The structure of Otto soot appears to be similar to that of CB, i.e. was paracrystalline, disordered and partly amorphous, respectively. A preferred orientation or pronounced graphitization was not detected.

Fig. 10. HRTEM images of Otto soot. (a) primary particle size, (b) fine structure inside of primary particle.

The particle surface (Fig. 10 (b)) is very coarse with many small randomly arranged graphite particles and shows a high degree of turbostratic disorder. Compared to Carbon Black (Fig. 8 (b)), no significant indications were found of pronounced graphite-like structures in the boundary area.

3.3. EELS

In addition to the HRTEM analysis, electron energy loss spectroscopy measurements were performed to study the sp^2/sp^3 -character of the carbons. Analysis was focused on the characteristic fine structure at the K-absorption edge (Fig. 11) of carbon, which provides information about the chemical bonding state of the carbon atoms.

Fig. 11. EELS results of soot samples, Carbon Black, synthetic diamond, and C₆₀-fullerene soot.

Figure 11 shows differences in fine structure of the absorption edge. Significant features are the energy losses in the range of 288 to 290 eV (three fold carbon bond: π^* -band, sp^2 -hybridized carbon), and in the range of 295 to 320 eV (four fold carbon bond: σ^* -band, sp^3 -hybridized carbon). In order to evaluate the EELS spectra of engine soot, we compared them with synthetically grown diamond particles consisting only of sp^3 -hybridized carbon atoms. Therefore, no π^* -band peaks can be observed, only a σ^* -band peak at higher loss energies can be seen. An additional peak is observed between 308 and 310 eV which can be explained by the three-dimensional diamond crystal structure. In addition, also EELS spectra of C₆₀-fullerene soot (Alt-Hoechst, gold grade quality) were measured which should be representative of well-ordered structures. Comparatively small σ^* -band peaks and, based on the spherical aromatic morphology, a small pronounced π^* -band peak were visible.

On the other hand, the spectra of the paracrystalline or partly amorphous structures found in Otto soot show broadened peaks. The flat σ^* -band peak in the range of 300 to 320 eV is indicative of high disorder and remnant of sp^3 -hybridized carbon (see also Fig. 10 (b)). The relatively low-energy π^* -band at 290 eV shows that significant amounts of sp^2 -hybridized carbon (graphite) exist. We conclude that the structure of Otto soot is mainly not adamantite but graphitic.

For the Diesel soot particulates the small π^* -band peaks are more pronounced than for Otto soot particulates and for Carbon Black. As is illustrated in Figure 9, the sp^2 -character is enhanced.

Finally, Carbon Black particles show a pronounced π^* -band peak and a flat σ^* -band zone at higher energy loss levels (308 - 310 eV). These result from paracrystalline carbon species of turbostratic disorder and broken graphite structures caused by sp^3 -fragments.

In summary, the energy loss fine structure at the K-edge indicates that soot particulates are a heterogeneous material. Generally, soot particulates can be understood as a composition of sp^2 - and sp^3 -hybridized carbon. Yet the energy loss spectra reveal very different fractions of threefold and fourfold bonded carbon atoms. The more pronounced the π^* -band, the larger is the contribution of graphite-like entities. On the other hand, differences in the σ^* -area are due to disorder, incomplete graphitization, and sp^3 -type components.

3.4. ESR

Electron spin resonance was performed for two engine soot samples. Figures 12 and 13 show the results of electron spin measurements of Diesel and Otto soot. The broad peaks observed in the spectra for Diesel soot (Fig. 13) at $g' = 2.013$ most probably stem from iron oxide contamination. The signal at $g' = 2.013$ is characteristic of Fe^{3+} while the deep field peak ($g' = 8.827$) may also be due to a ferromagnetic mixed valency oxide species. In

the Otto soot (Fig. 12) samples, however, contamination was very low (broad signal at $g' = 2.013$) and detectable only at room temperature.

Fig. 12. Overview, spectrum of Otto soot measured at 77 K and room temperature (300 K).

Fig. 13. Overview, spectrum of Diesel soot measured at 77 K and room temperature (300 K).

Figure 14 shows the detailed ESR signals caused by C-radicals (area around $g' = 2$).

Purely paramagnetic behavior, without any magnetic interaction among the radicals of the sample, theoretically should produce an intensity ratio of the signals at 77 K and 293 K of 3.8.

However, we measured $I(77\text{ K})/I(293\text{ K}) = 2.75$ for Otto soot, which is significantly lower. Hence the conclusion is that an antiferromagnetic interaction occurs between neighbouring spins, which is not present when the radical concentration is high enough.

Fig. 14. Radical signal of the samples measured at 77 K and room temperature (Otto soot) and at 77 K (Diesel soot).

Another effect is seen for Diesel soot (cf. Fig. 14). The radical signal nearly disappears at room temperature, which implies short relaxation times. This effect is known from highly condensed graphite (i.e. conducting) structures. In this case, the unpaired electrons form no non-localized radicals but a conduction band. The signal is caused by the so-called conduction electron spin resonance (CESR) and can be detected only at low temperatures.

3.5. XPS

XPS analysis shows that not only the nanostructures of different engine soots (Fig. 8-10) but also the surface chemistry of Otto and, Diesel soot and CB are different (Fig. 15 and Table 3).

Table 2 contains typical reference values of the binding energies of various functional groups of carbon, oxygen, and sulphur.

In Fig. 15 Otto soot shows the highest surface concentration of oxygen-bearing surface functional groups (5.16 at.%) and, accordingly, the lowest carbon concentration (91.6 at.%) of all types of carbons investigated here, as well as the largest amount of aliphatic carbon (285.1 eV, Table 3). In addition, the oxygen signals show the comparatively largest relative number of C=O-type surface groups (about 71.4 at.%, signal contribution approx. 532 eV). The total oxygen contents on the surfaces of Diesel soot and CB were 0.44 at.% and 0.30 at.%, respectively. These samples show higher surface concentrations of C-OH functional surface groups: 78.9 at.% (Diesel soot) and 40.3 at.% (CB) compared to 28.6 at.% (Otto soot).

Fig. 15. Results of the evaluation of XPS measurements: surface concentrations of the elements on Diesel and Otto engine soot and on CB as isolated from engine oil.

Table 2

Typical reference levels of binding energies of different chemical states of carbon, oxygen, and sulphur [13, 14, 15, 16, 17, 18].

Carbon (C1s-signal)	Binding energy [eV]
	Ca.
Carbodic carbon	281-283
Graphitic carbon	283-284.6
Aliphatic carbon	284.6-285.3
Hydroxyl groups (C-OH)	285-286
Carbonyl groups (C=O)	287-288
Carboxyl groups (COOH)	288-289
Carbonates	289-290
Plasmon loss features or $\pi\pi^*$ transitions	291-293
Oxygen (O1s-signal)	
Inorganic oxygen (lattice bonding)	529-530
Carbonyl groups (C=O) and C-O-C groups	530-532

Hydroxyl group (C-OH)	532-533
Adsorbed humidity	534-535
Sulphur (S2p-signal)	
Sulphides	161-162
Sulphane-S	163-164
Elemental sulphur	164
Sulphites	165-166
Sulphates	168-170

Table 3

Quantitative analysis of measured XPS signals

	Carbon Black		Diesel soot		Otto soot	
	eV	at.%	eV	at.%	eV	at.%
C 1s	285	69.2	284.9	80.4	284.8	32.1
	285.4	30.8	285.5	19.6	285.1	63.1
					287	4.7
O 1s	532.2	59.7	531.9	21.1	532	71.4
	533.6	40.3	532.5	78.9	532.4	28.6
S 2p	162.7	100	163.1	64.1	162.9	85.4
			168.9	35.9	168.6	14.6

Sulphur concentrations in Otto and Diesel soots are identical (0.06 at.%). However, the sulphane-sulphur content is higher (85.4 at.%) in Otto soot than in Diesel soot (64.1 eV), where the amount of sulphates/sulphonates is enhanced (approx. 35.9 at.% as against approx. 14.6 at.%). The spectra of CB were dominated by sulphane-sulphur (0.04 at.%). Therefore, the differences in the S2p-signal mainly relate to the oxidation state of sulphur, and not to the surface concentration.

3.6. AFM

Figure 16 (a) shows the surface of the tribometer disk prior to the tribological tests. The topography is made

up of grooves produced when the disk was finished, and an additional roughness component on a smaller scale caused by surface nitriding.

Fig. 16. AFM images (a) of a new surface and (b) after test with fresh oil.

After the tests with fresh oil (Fig. 16 (b)) and CB centrifuged oil (Fig. 17 (b)), several asperities are reduced in height compared to a new disk surface.

Fig. 17. AFM images: surface after testing with (a) Carbon black oil and (b) Carbon black centrifuged oil.

CB oils (Fig. 17 (a)) were found to have the smallest effect on disk topography, as can easily be seen from the fact that manufacturing grooves are still present.

Fig. 18. AFM images: surface after testing with (a) 2.6 wt.% Diesel soot oil and (b) 0.5 wt.% Otto soot oil.

The surface topographies obtained after experiments with 2.6 wt.% Diesel (Fig. 18 (a)) and 0.5 wt.% Otto soot (Fig. 18 (b)) show similarities; higher surface regions look highly polished, the number and depth of manufacturing grooves being reduced. However, there are also deep grooves in the direction of running (RD) caused by the sliding pin.

Fig. 19. AFM images: surface after testing with (a) Diesel soot (4.7 wt.%) and (b) Otto soot (0.9 wt.%).

Also the surfaces of the tribometer disks show similar characteristics after the experiments with 4.7 wt.% Diesel (Fig. 19 (a)) and with 0.9 wt.% Otto soot (Fig. 19 (b)). Large areas of the disks are very highly polished, manufacturing grooves are barely present. Also in this case we find grooves in the direction of running.

3.7. AES

The chemical composition of the new disk (Fig. 20 (a)) shows a carbon and nitrogen signal in the range of 10 at.%, which is a result of the nitriding process. Surface contamination by elemental carbon was also observed. Moreover, formation of an oxide layer to a depth of 30 nm was seen.

Fig. 20. Depth profile determined by Auger electron spectroscopy: (a) new sample and after tests with (b) fresh oil, (c) Carbon Black oil, (d) Carbon Black centrifuged oil, (e) Diesel soot (2.6 wt.%) oil, (f) Otto soot (0.5 wt.%) oil, (g) Diesel soot (4.7 wt.%) oil, (h) Otto soot (0.9 wt.%) oil.

After the experiment with fresh oil (Fig. 20 (b)) high concentrations of sulphur and calcium in excess of 10 at.% as well as zinc, phosphorus and oxygen were found. Hence, it can be concluded that a 30 nm oxide layer with embedded engine oil additives, such as calcium, sulphur, zinc and phosphorus has formed. The depth profile for centrifuged CB oil (Fig. 20 (d)) is very similar. However, no phosphorus was detected, and the calcium concentration was lower than that of fresh oil. This could be an effect of centrifuging if the removal of Carbon Black would include additive elements, e.g. phosphorus, calcium, zinc, and sulphur.

After the experiments with CB oil we noticed that the high oxygen concentration (Fig. 20 (c)) decreased within the first 10 nm depth underneath the surface. In comparison to fresh oil we found a thinner oxide layer with a low concentration of calcium, sulphur and zinc.

Fig. 20 (e) shows the depth profile of the tribometer disk after the test with 2.6 wt.% Diesel soot. Again we noted the formation of an oxide layer of approx. 20 nm thickness which, however, did not contain zinc and phosphorus.

At a higher concentration of Diesel soot (4.7 wt.%) the oxide layer had grown to 50 nm thickness, and the concentration of oxygen increased as well (Fig. 20 (g)).

However, the AES depth profile of the sample after the test with 0.5 wt.% Otto soot (Fig. 20 (f)) shows a low oxygen concentration. Again, no phosphorus was detected, and the zinc and calcium concentrations were found to be very low. When the concentration of Otto soot in the oil was increased, the oxide layer grew in thickness as in the case of Diesel soot but with a lower oxygen concentration.

3.8 TEM FIB

Finally, TEM measurements were performed on disk material prepared by FIB. The nitriding process caused a high degree of porosity also leading to roughness. After the experiment with fresh oil (Fig. 21 (b)), the topmost zone of the disk was seen to be more compact, producing a continuous layer of differently oriented grains. The microstructure of the disk tested with centrifuged CB oil is very similar (Fig. 22 (b)), and also the CB oil (Fig. 22 (a)) and Diesel soot (Fig. 23 (a)) lead to a compacted zone with fewer pores. However, it is more difficult in these cases to identify separate grains (Fig. 23 (a)). Moreover, the containing Diesel soot oils produce a thicker layer of 200 nm, which is more or less in agreement with the AES depth spectra.

Fig. 21. High-resolution micrographs of (a) new sample and (b) after the test with fresh oil.

Fig. 22. High-resolution micrographs of samples after (a) the CB oil test and (b) the test with CB centrifuged oil.

As with Carbon Black (Fig. 22 (a)), the test with Diesel soot (Fig. 23 (a)) shows a continuous layer structure. Remarkably enough, no compacted zone but a microstructure similar to the new sample was found after the experiment with Otto soot (Fig. 23 (b)). Considering the high wear rate, a compact layer may not have been produced because it was quickly removed during sliding.

Fig. 23. High-resolution micrographs of samples after tests with (a) Diesel soot oil and (b) Otto soot oil.

4. Discussion

The analytical methods employed here to characterize engine soot and artificial CB revealed clear differences in morphology and surface structure of different types of soot. RNT also clearly distinguished the tribological effects of different types of soot in terms of friction, wear rate, and running-in time. Moreover, different

types of soot and the frictional energy dissipated during contact caused different third bodies to be produced between the sliding structures. Hence we conclude that the tribological behavior observed is caused by mechano-chemical reactions between soot particles and the sliding surfaces. In the following we discuss possible tribochemical mechanisms that could explain the observed effects. With fresh oil and centrifuged oil containing Carbon Black the additives were detected on the surface of the tribometer disk where they can actively reduce wear. The additives are incorporated in the near surface as a result of high activation at the moment of mechanical intervention. A new system of local anti-wear layers and a third body is being formed during running-in.

In contrast Carbon Black has a morphology similar to that of Otto soot, though with different surface functions and elemental bonds to the soot matrix. The total wear of Carbon Black is low compared to engine soot and the running-in is finished after a few hours. As a result of low polarity, weak binding of elements to the soot matrix and the absence of free radicals, a thick oxide layer without additives is generated after running-in.

A similar behavior is observed for Diesel soot. Compared to experiments with fresh oil at the beginning of the experiment, a lot of material is worn away. After prolonged running-in, wear slows down to a lower rate. A thick oxide layer without additives is present after this period. Diesel soot shows a comparatively higher degree of surface graphitization and a more “even” surface topography. Only a few defect sites for the binding of reactive species are present on this surface.

CB and Diesel soot have in common that the appearance of graphite-like structures in the outer region of the carbon particles leads to fewer reactions of soot with the engine oil chemistry [21, 22].

4.1 A New Wear Model for Otto soot

Based on the differences observed for the species of soot investigated here, a new tribochemical model is postulated below which may explain the high wear caused especially by soot generated by spark ignition engines (Otto soot). While the surface of Diesel soot particulates (Fig. 24 (b)) shows a high degree of graphitization and relatively few defects, Otto soot particulates (Fig. 24 (a)) have paracrystalline or partly amorphous structures with comparatively more open graphitic ends and defects producing a rugged surface structure.

Fig. 24. Morphology of (a) Otto soot and (b) Diesel soot.

The pronounced disorder on the surface of soot leaves many electrons unpaired (dangling bonds) and with higher reactivity, as indicated by the ESR spectra [23]. Therefore, the surface of Otto soot offers more reactive sites for chemical reactions [24]. Figure 25 shows a schematic diagram of the new wear model proposed. Initially, the sliding surfaces may possess a boundary film. Otto soot particulates, with primary particles carrying unpaired reactive electrons (dangling bonds), act as an interlayer (see Fig. 25 (a)).

Fig. 25. A new wear model for Otto soot.

An established view is that mechanical activation by (Fig. 25 (b)) removes boundary films from sliding surfaces. Thus, reactive sites will be left on the nascent metal surfaces allowing for polar binding of either soot particulates or polar additives to the metal surface at active sites. Based on our analytical results we speculate that soot particles win this competition over anti-wear additives although the latter are also surface active. Hence, less oil additive elements are able produce a new protective layer, become part of a third body and will reduce wear [25, 26]. From oil analysis we can rule out that soot lead to a significant depletion of additives in the oil. According to various authors, tribochemical reactions may be induced also by emitted electrons [19, 20]. Therefore also exo-electrons emitted from the metal surface may play a role to initiate chemical reactions with soot particulates. From our experiments such a mechanism can neither be confirmed nor discarded.

Due to unprotected surfaces (Fig. 25 (d)), near surface material will be removed continuously at high rates, which may speed up the reaction of soot particulates in the subsequent rubbing process. Consequently, no typical running-in characteristics and third-body formation are observed. In the case of Diesel soot and CB, however, fewer reactive sites on the surface of soot particulates seem to allow the formation of a tribolayer and third bodies.

This model is in contrast to earlier concepts by Ryason et al. [3], Aldajah et al. [9], and Yamaguchi et al. [8], which suggested abrasive action caused by soot particulates. The present study focused in term of materials and sliding conditions on cam/follower systems but we expect that the general wear behavior can be also found for cylinder liner and piston rings.

5. Conclusions

The findings made in this study show soot particulates to have a significant effect on wear. For the types of soot particulates studied it is safe to conclude that the wear rate increases with the soot particulate concentration. However, it is also seen that wear properties cannot be deduced only from the soot particulate concentration;

morphology, surface chemistry, and reactivity of the soot particulate species being more important factors. This is because particulates are not abrasive but offer reaction sites for mechano-chemical interaction. Depending on the type of soot particulate, the adsorption and chemisorption mechanisms of oil additives on sliding surfaces are modified, which can greatly increase materials abrasion. An important practical consequence is that the use of model soot particulates such as Carbon Black, may falsify the outcome of engine wear tests. Recent experiments by Joly-Pottuz [27] showed that carbon nano-onions have better tribological properties than graphite powders. This fits well to the results that we have obtained for different types of soot; carbon nano-onions have a well-ordered graphite shell structure and therefore should have very few dangling bonds. Because of this, lower wear rates than with Otto and Diesel soot can be expected.

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