



## Wear behaviour of hydrogen free diamond-like carbon thin films in diesel fuel at different temperatures <sup>☆</sup>



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### ABSTRACT

In the present study, super hard, hydrogen free amorphous diamond-like carbons with a high fraction of sp<sup>3</sup> hybridised carbon were deposited by pulsed laser deposition. The tribological performance of DLC coatings was investigated by translatory oscillating relative motion of a 100Cr6 steel ball in diesel fuel or ambient air at 25 °C or 150 °C temperature. The structure of the coatings and the tribological worn surfaces were characterised by Raman spectroscopy and by scanning electron microscopy. Bio-fuel with a high fraction of unsaturated fatty acids has the potential to reduce friction in tribological systems with chemically inert DLC. Diesel blend with 10% bio-fuel reduces friction at 150 °C. If there is no diesel fuel, pre-oxidation at 450 °C for 8 h leads to the best wear resistance (↓ f & wear rate) at room temperature. Without diesel fuel, enhancement of temperature up to 150 °C during wear testing causes an increase of the coefficient of friction. Again the 450 °C pre-oxidised sample revealed the lowest friction. For this coating, Raman spectroscopy points to a small increase of the sp<sup>2</sup> C–C bonds. Diesel fuel seems to promote coherent coating failure under 150 °C wear, while pre-oxidation at 450 °C support adhesive coating ablation under higher loads or cyclic loading.

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### 1. Introduction

In many applications for automotive or airplane power train, diamond-like carbons (DLCs) play a key role for ensuring a friction reducing and sealing function [1–3]. Several millions of piston rings, engine valve-tappets or other engine parts are coated every year with diamond-like carbon films or carbon-based multilayers. For enhancing the effectiveness and reducing the emission of pollutants, the loading conditions in the power train need to be increased. Especially, temperature determines the tribological performance and life time of diamond-like carbon based films.

Higher efficiency of engines and low emissions correlate with higher temperatures and accurate process regulation during combustion. Amorphous carbon coatings are essential for smooth and low wear movement of articulating parts. Exact adjustment of the geometries of moving parts of pistons, pumps or fuel transportation systems depends on the surface modification by carbon coatings. However, these important coatings are very sensitive against temperature. Hard and damage tolerant carbon-based coating crucially improves wear resistance. Also, it implements some kind of sealing function. With increasing

demands on engine parts in terms of pressure and temperature, today's industrially applied DLCs come to a limit. There is a very strong need for improved coatings, which can fulfil both, wear resisting and sealing function. Hydrogen-free DLC offers improved temperature resistance in comparison to hydrogenated DLC. The present study takes up this topic. More temperature resistant tetrahedral amorphous and hydrogen-free carbon coatings were deposited by pulsed laser deposition (PLD). In order to simulate a longer practical use, a pre-oxidation was selected, because there is an alternation between combustion gases and wetting by diesel fuel.

Furthermore, the fraction of bio-fuel influences corrosion and wear behaviour of materials. Not only, the transfer film and the adsorbed functional groups on top of the DLC change with the addition of bio-fuel fractions, but the transfer of corrosion products from less chemically stable metallic parts in fuel transportation segments is higher as well. In any case, the tribological system is essentially influenced by higher temperatures and bio-fuel additions.

Commercial fossil diesel is derived from petroleum fuel oil, but fuel alternatives are gained from biological sources directly and called bio-diesel. As they grow as an agricultural product in the most cases, they are a renewable energy source and of immense importance for future energy delivery. Bio-diesel, bio-mass to liquid (BTL) or gas to liquid (GTL) diesel are increasingly being developed and adopted. In the present study, a commercially available diesel fuel, composed of petrofuel with a bio-diesel fraction is used as lubricant.

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## 2. Materials and methods

### 2.1. Testing of diesel fuel

There are a lot of different diesel blends. Even diesel from different batches can have a changed composition. In general, fossil diesel is gained by fractional distillation of crude oil between 200 °C and 350 °C at atmospheric pressure, resulting in a mixture of carbon chains. Typically, there are between 8 and 21 carbon atoms per molecule. Bio-diesel is produced by a chemical reaction of lipids from natural plants (i.e. rapeseed oil, palm oil or sunflower oil) with alcohol resulting in fatty acid esters.

An important performance figure of diesel fuel is the cetane number. It can be tested according to the standard DIN 51773. Fuel does ignite better with higher cetane number. The higher the cetane number, the better the readiness of the diesel to spread into hot compressed air. Fuels with a higher cetane number are best quality fuels, called “premium”. In the present study, a commercially available diesel fuel consisting of about 90% fossil and approximately 10% bio-fuel was used. The diesel blend was characterised according to the European standard DIN EN 590.

### 2.2. Coating deposition by PLD (pulsed laser deposition)

Hydrogen-free amorphous carbon coatings were deposited on polished 100Cr6 samples (down to 3 µm diamond paste) by laser deposition. The 100Cr6 flat samples were prepared according to DIN 51834-2 with a hardness of  $62 \pm 2$  HRC before coating deposition. The polished 100Cr6 samples were cleaned 5 min in ethanol in an ultrasonic bath. In the deposition chamber, argon ion bombardment (1 min,  $10^{-2}$  Pa working pressure, 700 eV energy,  $150 \mu\text{A}/\text{cm}^2$  current density at substrate) produced a further cleaning of the surface. As reported earlier [4,5], diamond-like carbon (DLC) films are produced by pulsed laser deposition (Fig. 1) from a polycrystalline graphite target with a purity of 99.9%. A KrF-excimer laser beam (248 nm) with maximum pulse energy of 1–1.2 J and pulse duration of 25–30 ns was used. Hereby, a maximum repetition rate of 50 Hz is possible. Energy density is in the range of between 2 and 8 J/cm<sup>2</sup>. Heavy accelerated carbon atoms, ions and other electrically charged or neutral species form a hydrogen-free carbon film with a fraction of sp<sup>3</sup>-hybridised C–C bonds of between 80 and 85% [5]. Due to the high fraction of sp<sup>3</sup>-hybridised C–C bonds, which results in a diamond-like tetrahedral short-range order, but no crystalline long-range order, the coatings were terminated as tetrahedral amorphous carbon (ta-C). The growth rate was  $120 \text{ nm} \times \text{min}^{-1}$ . Substrate temperature remains below 100 °C. Tetrahedral amorphous carbon coatings of 100 nm thickness were deposited and alternately stress released by laser radiation. The final thickness of the ta-C coating is 2.5 µm.

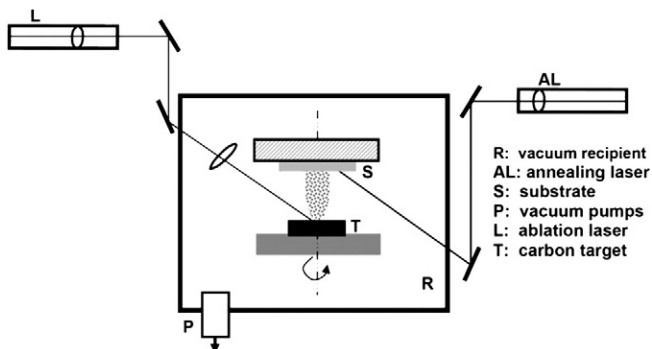


Fig. 1. Schematic drawing of the equipment for laser ablation of hydrogen-free diamond-like carbon coatings.

### 2.3. Coating pre-oxidation

In the initial stage, laser deposited ta-C coatings reveal high compressive stresses up to 8 to 10 GPa [5]. These stresses can be significantly reduced by in situ laser annealing without a significant reduction of hardness [5]. In practical use however, devices and components heat up entirely over longer periods. Carbon based coatings for automotive or airplane applications like pump components, piston rings or fuel injection systems experience cyclic and longer periods of heating. In order to simulate practical worse conditions under enhanced temperatures, laser deposited hydrogen-free diamond-like carbon coatings were annealed in air before testing the tribological properties in the present study. The conditions for pre-oxidation and the samples labelling are summarised in Table 1. Emphasis was placed in careful heating up with a rate of  $1 \text{ }^\circ\text{C} \times \text{min}^{-1}$  in order to avoid spallation of the coatings. The coatings adherence was classified according to VDI-guideline 3891 by indentation with a Rockwell HRC diamond.

### 2.4. Hardness and mechanical properties

The Martens hardness of the ta-C coatings was determined according to DIN EN ISO 14577:2002, parts 1 to 4 using ASMEC UNAT-M equipment with a Vickers type pyramid. The final load was 10 mN. At least 5 measurements were carried out for calculating the mean value and the standard deviation. Loading and holding times were 20 s. Hardness was measured after the wear test in not wear-free loaded centre positions of the sample. Therefore the hardness values can be deducted with the Raman spectra, which were taken at the same time.

### 2.5. Tribological tests

Wear tests were carried out according to DIN 51834, parts 2 and 3 using the translatory oscillation test machine SRV III with the software of SRV IV of the company Optimol Instruments GmbH, Germany. A standardised 100Cr6 ball according to DIN EN ISO 683-17 with a diameter of 10 mm was loaded with 10 N against the coated samples. A stroke length of 1.0 mm and a frequency of 10 Hz were used. The friction coefficient  $f$  was continuously recorded in order to observe the friction behaviour. According to the standard DIN 51834, part 3, all wear tests had a maximum duration of 120 min. The wear tests were carried out in a climate chamber. Relative humidity and temperature at the samples bottom can be recorded and regulated continuously. Tests were performed without and with diesel fuel at 25 °C or 150 °C. The testing parameters are summarised in Fig. 2.

Each single test was carried out with a new ball, while the coated flat sample was used for several tests, but in different areas. Before the single tests, the specimen was cleaned in an ultrasonic bath of ethanol.

According to DIN 51834-3:2008, the volumetric wear of the ball (Fig. 3) was determined according to Eq. (1).

$$W_{V,BALL} = \frac{\pi \cdot d_1^2 \cdot d_2^2}{64} \left[ \frac{1}{R} - \frac{1}{\bar{R}} \right] \quad (1)$$

Table 1  
Pre-oxidation conditions of the hydrogen-free diamond-like carbon coatings.

Sample	Pre-oxidation temperature/°C	Pre-oxidation time/min	Pre-oxidation atmosphere
ta-C, without pre-oxidation	–	–	–
ta-C, 350 °C, 8 h	350	480	air
ta-C, 450 °C, 8 h	450	480	air

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