Supporting information for

Macroscopic Superlow Friction of Steel and Diamond-Like Carbon Lubricated with a Formanisotropic 1,3-Diketone

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**State of the art**

Lubricants are additivated with special surface active substances (friction modifiers FM, extreme pressure additives EP) to improve the tribological performance of technical systems.\(^1\,\,^2\) But synthetic or mineral oils are in a particular area limited in terms of energy efficiency due to their physical and chemical properties. Therefore tribologists are searching for new materials (e.g. DLC\(^3\)) and lubricants (e.g. ionic liquids ILs\(^4\)), liquid crystals LCs\(^5\)) with beneficial properties. The conference symposium "Tribology and the liquid-crystalline state" (Washington, 1990) published by G. Biresaw gives an overview of insights and possible application in bearings for liquid crystals.\(^6\) In summary, interaction of liquid crystals with different surfaces and anisotropic properties (e.g. viscosity) due to molecular alignment were identified as crucial mechanisms to reduce friction and wear.\(^6\) Preliminary studies of the here presented 1,3-diketone showed the possibility to realize superlow friction in combination with steel surfaces at low contact pressure.\(^7\,-^\,^13\)

There are many types of different DLC coatings which are mainly classified in hydrogenated (a-C) and non-hydrogenated (a-C:H) amorphous carbon with a high fraction of meta stable sp\(^3\) bonding.\(^14\) A specific type of a-C, named tetrahedral amorphous carbon (ta-C), results at higher sp\(^3\) contents. The different types of possible DLC coatings are illustrated in the ternary C,H phase diagram.\(^15\) In addition, the DLC coatings can be alloyed with various metals. In the sp\(^3\) regions dangling bonds (unsaturated bonds) exist on the DLC surface\(^16\), which can react with OH- or O- groups.\(^17\) Erdemir et al. showed that the content of hydrogen strongly influences friction and wear.\(^18\) They found that a DLC coating derived from pure methane shows considerably worse tribological behavior than one derived from 25 % methane and 75 % hydrogen. Using a-C:H including more than 40 atomic % hydrogen in combination with steel or
the same DLC material super low friction property in an ultrahigh vacuum or in a dry inert gas atmosphere.\textsuperscript{19,20} These results illustrate the importance of the amount of hydrogen in the coating, but in combination with steel in addition the formation of a transfer layer on the counterbody seems to be a major mechanism to realize improved tribological performance.\textsuperscript{21} Thus it is suggested that the positively charged H-terminated carbon atoms and the weak van der Waals forces of the transfer layer generate a repulsive force which is responsible for the lower friction.\textsuperscript{22} Tasdemir et al.\textsuperscript{23} analyzed the friction and wear performance of DLC/DLC contacts lubricated with synthetic base Oil (polyalpha-olefin PAO) and found different tribological properties of the system depending on the used DLC coating (ta-C DLC, a-C:H, a-C:H:Si and a-C:H:Cr). For example ta-C DLC showed the lowest COF and a-C:H the highest wear rate. Dopant elements clearly influence the COF and enhance the durability of DLC coatings. Using Raman spectroscopy it was verified that graphitization only occurs using non-doped a-C:H coating. Therefore it is assumed that there is a link between the graphitization and the reduction of friction. But the fact that the tribological performance of the other coatings also differs has to be connected with additional influences like deposition methods, sp\textsuperscript{3} hybridization or hydrogen content. Tribological differences between non-doped, metal-doped (titanium Ti, tungsten carbide WC), and non-metal-doped (silicon Si) diamond-like carbon against steel under boundary lubrication was analyzed by Kalin and Vizintin.\textsuperscript{24} Different wear behavior was identified, whereat the non-doped DLC coatings showed the lowest wear. It was verified that the lower wear using non-doped DLC coatings arises from the absence of adhesion between the steel and the DLC coating. In addition, using additives adhesion between steel and doped-DLC contacts was also prevented. Jiang et al.\textsuperscript{25} measured in ambient air at dry conditions superlow friction using titanium/silicon codoped hydrogenated carbonfilm. Kržan et al.\textsuperscript{26} demonstrated the same
effect, insofar that for the friction reduction performance additives are not necessary using W-DLC coatings. Much effort in further research concerning the interaction of DLC in combination with different lubricants and additives was conducted. In this context zinc-free, zinc-containing (Zinc dialkyldithiophosphates, ZDDP), and molybdenum dialkyldithiocarbamate (MoDTC) containing anti-wear additives were tested. It was found lower COF using the additive in combination with Si-containing DLC film. The result of contact surface analysis using X-ray photoelectron spectroscopy (XPS) showed the formation of a boundary lubrication film including ZnO, ZnS, FePO₄, FeS and FeS₂. Due to the importance of the interaction of DLC coating with lubricant it is obvious that hydrogenated (a-C:H) and tetrahedral (ta-C) diamond-like carbon coating show different tribological characteristics. Mahmud et al. showed with SAE 40 lubricating oil that graphitization of the coating strongly influences COF and wear rate. In addition, as protective layer a polyphosphate glass is formed using ta-C that leads to a lower wear rate compared to a-C:H DLC.

There were also some tribological investigations using so called ‘biolubricants’, such as biodegradable synthetic esters and sunflower oil. In addition, it was found that the use of Canola oil improved the tribological properties of a-C:H coating due to the high amount of polar components. Another investigation from Kalin et al. also described the improved wear behavior of DLC/DLC contacts by using oils with more polar groups and non-saturated molecules. A review about the interaction of additives with different DLC coatings, the tribofilm formation and effective lubrication is given by Yazawa et al. Doping DLC coatings with reactive materials like tungsten (W) can enhance the tribofilm formation. It must be noticed that some additives support tribo-film formation (e.g. specific ILs), whereas others inhibit the formation of protective layers. In addition, the test environment changes friction and wear
properties of DLC coatings. In humid test environments hydrogen-free DLC operates, whereas hydrogenated DLC works better under dry and inert test conditions. But not only the chemical interaction plays an important role also the surface texture can affect the tribological behavior. The tribological behavior of DLC coatings was also characterized in combination with water-based lubricants. Tribological studies of a ta-C/ta-C friction pair lubricated with glycerol and glycerol monooleate (GMO) additive showed superlubricity. Simulations indicated that the OH-terminated groups of glycerol form a very smooth carbon surface layer ligated to the sp\(^1\) atoms which leads to a very flexible elastic response to sliding. In addition, Donnet et al. also verified that the interaction between hydrogen and diamond-like carbon films clearly influences tribological behavior. The interaction of friction modifiers with DLC was analysed by Minami et al. who found for hydrogen-free DLC an improved running-in performance and reduced wear. Such surface interactions also include further interfacial phenomena like wettability related to adhesion energy and interfacial tension of the lubricant. Investigations from Bobzin et al. showed that fore plasma coatings CrAlN and a-C:H the different wettability of mineral oil, polyalphaolefin, synthetic ester, polyether and polyglycol strongly influences the tribological behavior. The frictional behavior of self-assembled monolayers (SAMs) was measured using lateral force microscopy (LFM) by Choi et al. They found lower COF at SAM coated DLC compared to un-lubricated due to the hydrophopic character of the SAM surface. The formation of a surface layer on a hard coating, a so called hybrid tribo-film, maybe combines both advantages and will lead to low friction and low wear. The main challenge therefore consists of the difficulty of tribo-film formation on DLC coating. The Strubeck-curve characterizes the COF in dependency of the velocity and describes the different lubrication regimes: boundary-, mixed-, fluid-film-lubrication (elastohydrodynamic lubrication, EHL). Besides the importance of the
chemical interactions of the lubricant with the surface regarding boundary lubrication, the bulk properties of the lubricant play a major part of the tribological performance at mixed and especially at fluid-film-lubrication. Pioneer work concerning the reduction of COF with thin interface films was done by Bowden and D. Tabor.\textsuperscript{52} Novel research studies indicate that there is an additional transition lubrication regime between elastohydrodynamic lubrication and boundary lubrication which is called thin film lubrication (TFL). An overview on TFL of the state of the art and tribological mechanisms is given by Zhang et al.\textsuperscript{53,54} and Luo et al.\textsuperscript{55,56}. At TFL film thickness is reduced to some molecules, whereat it is assumed that these molecules form an ordered layer on the surface consisting of three regions: adsorbed film, ordered film and fluid film\textsuperscript{53}. Due to this orientation on the nanoscale the viscosity of the confined fluid gets obviously non-Newtonian\textsuperscript{57}. Xiang-Jun et al.\textsuperscript{58} found that the minimum COF appears at TFL regime. This behavior is explained with the change of viscosity, because of the orientation of molecules under high shear and confinement and secondary with the superimposed characteristics of fluid film and absorbed layer. For example the calculated viscosity for a six-layer dodecane film abruptly decreases at very high shear rates ($10^{11}$ s$^{-1}$).\textsuperscript{59} It was verified that this change is due to a nematic-like alignment of the molecules which goes along with a decrease of film thickness. Other calculations at high shear rate ($10^{9}$ s$^{-1}$) showed that bulk dodecane has a much higher viscosity than a shear aligned six-layer dodecane film.\textsuperscript{60} Luo et al. revealed that the initial viscosity of lubricant dictates the film thickness at which EHL changes to TFL\textsuperscript{56}. In addition, there could be even a transition at molecularly thin films under shear from liquid to solid\textsuperscript{57}.
Material and Methods

Figure S1. Technical drawing of the rotating ball-on-3-plates-friction-test (Co. Anton Paar MCR501 rheometer using tribological measuring cell)

Figure S2. Chemical structure of (1-(4-ethyl phenyl)nonane-1,3-dione (EPND-02/06) and its keto-enol tautomerism
**Figure S3.** Surface topography of the used materials using white light interferometry: (A) 100Cr6 plate; (B) DLC coated plate; (C) Si-DLC coated plate; (D) 100Cr6 ball; (E) DLC coated ball
**Results**

Lubricants The COF during 1st and 2nd conditioning at constant parameters are illustrated in Figure S4 and were carried out at 0.1 m·s⁻¹ to analyze the tribological behavior during mixed lubrication regime. Within the first conditioning run at constant testing parameters a running-in behavior is observable for the two material combinations 100Cr6/100Cr6 and 100Cr6/DLC using EPND-02/06 (Figure S4.A). But as can be seen in Figure S4.B at the second conditioning run all tested material combinations show a constant COF. It is remarkable that 100Cr6 has the highest COF with both lubricants by far. The lowest COF can be realized using EPND-02/06 in combination with DLC.

![Figure S4](image_url)

**Figure S4.** Friction values of EPND-02/06 and Optigear32 using rotating B3P (10 N; 100 °C; 0.1 m/s): (A) 1st conditioning; (B) 2nd conditioning
Table S1. Measured contact angles using sessile drop method of the different materials using three model liquids.

| Surface    | Contact angle [°] | Water* | Ethylene glycol** | Diiodomethane*** |
|------------|-------------------|--------|-------------------|------------------|
|            |                   |        |                   |                  |
| 100Cr6     | 76.9 ± 1.7        | 33.7 ± 1.0 | 47.4 ± 0.6        |
| DLC        | 84.4 ± 1.0        | 60.0 ± 1.7 | 45.3 ± 0.9        |
| Si-DLC     | 79.9 ± 2.0        | 57.3 ± 1.5 | 43.0 ± 0.7        |

* polar: 19.9 mN/m, dispersive: 52.2 mN/m; ** polar: 29.0 mN/m, dispersive: 19.0 mN/m; *** polar: 47.4 mN/m, dispersive: 2.6 mN/m

Figure S5. (A) Determination of surface tension using pendant drop method for water; Contact angle measurements using sessile drop method with water on steel 1.3505 (B), DLC (C) and Si-DLC (D).
Figure S6. Wear analysis using laser microscope after duration-tribotest (10 h, 20 N, 100 °C, 0.47 m/s) using EPND-02/06 and Optigear32 (left side: worn area on plate; right side ball). No wear scar on ball using DLC/DLC material combination.
Figure S7. Wear analysis using laser microscope after duration-tribotest (5 h, 20 N, 100 °C, 1.06 m/s) using EPND-02/06 and Optigear32 (left side: worn area on plate; right side ball). No wear scar on ball using DLC/DLC with EPND-02/06.
**Figure S8.** Raman-spectroscopy of the new and worn surfaces after duration-tribotests at 1.06 m s⁻¹ lubricated with EPND-02/06 and Optigear32: a) D and G bands on worn area of DLC using material combination 100Cr6/DLC; b) D and G bands on worn area of DLC using material combination DLC/DLC; c) Raman-spectra on worn area of Si-DLC using material combination 100Cr6/Si-DLC 100Cr6/Si-DLC; d) Slightly indicated D and G bands on worn area of 100Cr6 ball using material combination 100Cr6/Si-DLC with EPND-02/06 in contrast to Optigear32 (transfer layer).
Figure S9. XPS-analysis (depth profile) of new material: a) DLC; b) Si-DLC; c) 100Cr6; d) Depth profile of oxygen content.
Figure S10. XPS-analysis (depth profiles) after duration-tribotests at 1.06 m/s lubricated with EPND-02/06 and Optigear32.
Molecular Dynamic Simulations

A Gay-Berne potential (GB) was used to calculate dispersive interactions between EPND-02/06 molecules. As initial configuration of the GB-molecules a highly ordered smectic orientation was used (Figure 6.a). The GB-molecules are represented by rigid ellipsoids that interact via an anisotropic Lennard-Jones (LJ) potential. The pairwise interaction of two ellipsoids is calculated with respect to their orientation and relative position ($U_{GB}$, S1). A shifted LJ potential is used to determinate the distance dependency of the interactions ($U_r$, S2).

\[
U_{GB} = U_r(A_i, A_j, r_{ij}, \gamma) \eta_{ij}(A_i, A_j, \nu) \chi_{ij}(A_i, A_j, \hat{r}_{ij}, \mu)
\]

(S1)

\[
U_r = 4\epsilon_{GB}\left[\left(\frac{\sigma}{h_{ij} + \gamma\sigma}\right)^{12} - \left(\frac{\sigma}{h_{ij} + \gamma\sigma}\right)^{6}\right]
\]

(S2)

Whereas the maximum depth of the GB potential is given by $\epsilon_{GB}$, the mass centers of two particles by $r_{ij} = r_i - r_j$, the minimal distance between two ellipsoids by $h_{ij} = \min(|r_i - r_j|)$ and the empiric shift of the potential by the coefficient $\gamma$. The orientation of the GB ellipsoids is described using the values $A_i$ and $A_j$ ($3 \times 3$ rotational matrices) and the directional vector between two particles by $\hat{r}_{ij} = r_{ij}/|r_{ij}|$. The change of the potential energy due to the relative orientation of two ellipsoids is considered with $\eta_{ij}$ (S3). Here the empiric exponent $\nu$ gets introduced:

\[
G_{12}(A_1, A_2) = A_1^T S_1^2 A_1 + A_2^T S_2^2 A_2
\]

\[
\eta_{12} = \left[\frac{2s_1s_2}{\det[G_{12}(A_1, A_2)]}\right]^{\nu/2}
\]

\[s_i = \left[a_i b_1 + c_i^2\right]\left[a_i b_i\right]^{1/2}
\]

(S3)
\( \chi_{ij} \) takes the dependence of the energies of the relative positions of the two bodies into account\textsuperscript{62,63}. Here again an empirical exponent \( \mu \) is used:

\[
\chi(A_1, A_2, \hat{r}_{12}) = [2 \hat{r}_{12}^T B_{12}^{-1} (A_1, A_2) \hat{r}_{12}]^{\mu}
\]

\[
B_{12}(A_1, A_2) = A_1^T E_1 A_1 + A_2^T E_2 A_2
\]

\[
E_i = \begin{pmatrix} e_{ai}^{-1/\mu} & 0 & 0 \\ 0 & e_{bi}^{-1/\mu} & 0 \\ 0 & 0 & e_{ci}^{-1/\mu} \end{pmatrix}
\]

(S4)

\( e_{ai}, e_{bi} \) and \( e_{ci} \) are the potential depths of the in Figure S11 shown configurations FtF (face to face), StS (side to side) and EtE (end to end) of interaction between two identical GB particles with \( a_i = a_j, b_i = b_j \) and \( c_i = c_j \). By adopting \( a \leq b \leq c \) applies: \( e_{ai} = E_{\text{FtF}_i}, e_{bi} = E_{\text{StS}_i} \) and \( e_{ci} = e_{\text{EtE}_i} \).

The three energy parameters \( e \) are relative sizes based on \( e_{\text{GB}} \).

**Figure S11.** Relative orientation of two ellipsoids with identical semiaxis (\( a_i = a_j, b_i = b_j \) and \( c_i = c_j \) with \( a \leq b \leq c \)) for cases of face to face, side to side and end to end.
For the smallest distance $h_{12}(A_1, A_2, r_{12})$ between two molecules, the approximation of Perram et al.\textsuperscript{64} is used.

\[
\begin{align*}
    h_{12}^{GB}(A_1, A_2, r_{12}) &= r_{12} - \sigma_{12}(A_1, A_2, r_{12}) \\
    \sigma_{12}(A_1, A_2, r_{12}) &= \left[ \frac{1}{2} r_{12}^T G_{12}^{-1}(A_1, A_2) r_{12} \right]^{-\frac{1}{2}}
\end{align*}
\]

This approximation fails for two spheres of unequal radii, with $a_1 << a_2$ arises\textsuperscript{65}:

\[
\sigma_{12} = \sqrt{2(a_1^2 + a_2^2)} \approx \sqrt{2} a_2 > a_1 + a_2
\]

In this work, however, only the interactions of ellipsoids with ellipsoids with similar sizes are calculated. In these cases, the approximation is suitable.

It should be noted that the interactions between ellipsoids of various types directly arising from the structure of equation S1. It is calculated out of the shape (semiaxis) and the energy parameters $e$ of cases FtF, StS and EtE from the interactions between type $i$ with type $i$ and type $j$ with type $j$. There are no additional parameters for the interactions between GB-particles of different types available. There are only rules needed to create a common width $\sigma$ of the potential. The same depth $\varepsilon_{GB}$ can be chosen for all types. The information about the actual potential depth is in the energy parameters $e$ of cases FtF, StS and EtE. By tuning the empirical parameters $\varepsilon_{GB}$, $\sigma$, $\gamma$, $\nu$, and $\mu$ the potential of the molecule can be adjusted. These parameters were obtained from a fit to intermolecular potentials described by the universal force field as described by Li et al.\textsuperscript{11} The GB fluid (2304 GB particles) was confined between two solids with 1 GPa with a temperature of 360 °K. The solid surface is represented by the violet GB particles. The interaction strength of the green molecules was increased by a factor of 5 related to the GB fluid to make them solid-like. Based on the EtE-orientation shear bands are building at higher
shear rates than \( \dot{\gamma} = 10^{6.9} \) 1/s (Figure S12.A). The fat labeled particles were in a line at an earlier stage. It can be seen that the deformation occurs at two layers directly on the surfaces.

Figure S12. (A) System with shear bands at shear rates \( \dot{\gamma} > 10^{6.9} \) 1/s. The fat labeled GB0-particles were in a line without shearing. The deformation occurred near the surface; (B) Shear stress as function of shear rate for the EtE-oriented system with shear bands; (C) Viscosity as function of shear rate in the system with slip planes and adapted thereto function \( \eta_{pl} \) which describes the viscosity of a PL-fluid.

In Figure S12.B the shear stress is plotted as a function of shear rate. The out of shear resulting stress is shear rate-dependent in the system with sliding planes as it is expected for the viscous behavior. The shear stress is smaller than in the system without slip planes in which it is independent of the shear rate between 100 kPa and 400 kPa. The calculated viscosity is illustrated in Figure S12.C. The calculated values of viscosity are on a straight line in double logarithmic diagram. This behavior can be described by the relationship of Ostwald de Waele:
\[ \tau = K \dot{\gamma}^{n_{pl}} \]  

(Liquids for which the Ostwald de Waele relationship is valid are called powerlaw- fluids (PL). The viscosity of a PL-liquid can be calculated using:

\[ \eta_{pl} = K \dot{\gamma}^{n_{pl}-1} \]  

The function \( \eta_{pl} \) has been adjusted to the calculated values of the viscosity and is also shown in Figure S12.C. The parameters arise to: \( K = (4.5 \pm 1.8) \cdot 10^5 \text{ Pa} \cdot \text{s}^{n_{pl}} \) and \( \eta_{pl} = 0.21 \pm 0.02 \).

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