

Ultralow friction of DLC in presence of glycerol mono-oleate (GMO)

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This paper presents a unique tribological system that is able to produce no measurable wear of material combination and that reduces friction markedly in the ultralow regime under boundary lubrication. Ultralow friction (0.03) was obtained by sliding hydrogen-free Diamond-Like-Carbon ta-C against ta-C lubricated with Poly-alpha Olefin base oil containing Glycerol Mono-Oleate (GMO) additive. The origin of ultralow friction in these conditions has been investigated by surface analysis techniques. Results are in agreement with the formation of a OH-terminated carbon surface. This new surface chemistry might be formed by the tribochemical reaction of alcohol function groups with the friction-activated ta-C atoms. The origin of low friction could be due to the very low-energy interaction between OH-terminated surfaces.

KEY WORDS: ultra-low friction, boundary lubrication, tribochemistry on DLC coatings

1. Introduction

1.1. Low friction limit under boundary lubrication

The traditional Amontons friction law $F = \mu W$ relates the friction force F to the normal load via the friction coefficient μ . The Bowden and Tabor model of friction provides a good starting point for understanding how a thin interface film (or a so-called third body) can drastically reduce the friction coefficient [1]. The friction coefficient is assumed to depend on the normal load W , the real contact area A and the shear strength S of the interfacial tribofilm (or film transfer) as:

$$\mu = S \cdot \frac{A}{W} \quad (1)$$

The shear strength S of solids at high pressure has been observed to have a pressure dependence, which can be approximated by [2]:

$$S = S_0 + \alpha P \quad (2)$$

According to the Hertzian contact theory (below the elastic limits), and in the sphere-on-plane configuration, the friction coefficient μ depends of three variables as [3]:

$$\mu = S_0 \pi \left(3 \frac{R}{4} E \right)^{\frac{2}{3}} W^{-\frac{1}{3}} + \alpha \quad (3)$$

where E is the composite elastic modulus of the contacting materials and R is the radius of the sphere. This simplified model assumes that the real contact area corresponds to the Hertzian zone, as calculated in equation (3). This assumption is verified in the case of soft and very thin interface films leading to a good accommodation in the contact geometry. Therefore, friction measurements at different normal loads can be useful to determine S_0 and α values in a given tribological system. However, equation (3) indicates that the minimum friction coefficient value is α and then that friction cannot vanish completely.

In the case of MoS₂ coatings for example, many friction experiments have been performed under different atmospheres, and α values as 0.001 have been determined. On the other hand, if the shear strength of the interface is very low, say 25 MPa, μ is calculated and predicted to be a few thousandths. By definition it is proposed that the friction coefficient can be divided in three levels (i) low friction with $\mu < 0.1$, (ii) ultralow friction where $0.01 < \mu < 0.1$ and (iii) superlow friction if $\mu < 0.01$. It is to be noticed that measurements of superlow friction is very difficult and that most of mechanical devices measuring the friction tangential force and the normal load simultaneously have a limited accuracy. So, in practical situations, superlow friction is generally found to lie in the range 0.001

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$< \mu < 0.01$ because friction measurement under $\mu < 0.001$ is not accurate enough.

In the case of very thin interface films such as H-terminated surfaces on carbon materials, or very thin tribofilms whose thickness is below 2 nm, it is not sure that equations (2) and (3) are still valid and the existence of a limiting value to the lowest friction attainable remains questionable.

1.2. Survey on superlubricity of MoS₂ and DLC coatings

Superlubricity refers to the vanishing of friction force. Superlubric conditions were theoretically predicted by Hirano and Martin [4] in 1991 based on frictional anisotropy between uncommensurate crystal surfaces. This prediction was verified experimentally by some of the authors [5–9]. It was experimentally found in 1993 that the friction coefficient on pure molybdenum disulphide (MoS₂) coatings became unmeasurable (i.e., fell below 0.002) in an ultrahigh vacuum (10 nPa). High-resolution transmission electron microscopic (TEM) investigations showed that the superlow friction behaviour was probably due to frictional anisotropy between rotated MoS₂ nanocrystals in the contact area. In 2000, Chhowalla and Amaratunga [10] reported similar findings concerning the ultralow friction and wear performance of a new fullerene-like MoS₂ nanoparticle material. It was later discovered by several authors independently that some hydrogenated diamond-like carbon (DLC) coatings exhibited the same superlow state with a friction coefficient lying in the millirange. The superlow friction property was obtained when sliding a-C:H surface containing a large amount of hydrogen (more than 40 atomic %) on steel (or the same DLC material) in an ultrahigh vacuum or in a dry inert gas atmosphere [11,12]. Previous results indicate that hydrogen plays a dominant role in the friction behaviour of a-C:H films. Also the formation of a transfer film on the steel counterface seems a necessary condition [12]. The resulting topcoats are thought to interact through weak van der Waals forces. When H-terminated, superlow friction of carbon surfaces is attributed to C—H/C—H low binding energy of 0.08 eV per bond. According to the model previously described, the shear strength can be calculated to be in the range of 10 MPa, corresponding to a steady-state friction coefficient lower than 0.01 [13]. Finally, atomic scale friction can be studied by using molecular dynamics calculations. The simulation reproduces atomic stick-slip motion and low friction coefficients. It has been shown that friction of graphite flakes can produce superlow friction if dangling bonds of the crystal edges have been passivated [14].

These earlier results are certainly of interest in tribological issues for space applications. To the best of our

knowledge, friction values below 0.04 have never been reported under the boundary lubrication conditions used in most industrial machines with steel components.

2. Experimental

2.1. DLC coatings

The ta-C coating was applied to the polished carburized steel disc and the hardened steel pins to a thickness of 0.5 μm from a graphite target by arc-ion plating, a physical vapour deposition (PVD) process, and did not contain hydrogen [15]. The hydrogen-containing DLC (a-C:H) coating was applied to the polished carburized steel disc and hardened steel pins to a 1.0-micron thickness by a plasma-assisted chemical vapour deposition (CVD) process from hydrocarbon gas. It contained about 20 at.% of hydrogen [15]. This hydrogen content was estimated by SIMS analysis and comparison with a hydrogen content well-known standard sample. The surface roughness of these two kinds of coatings was in the 20–40 nm range.

2.2. Tribological conditions

The pin-on-disc sliding tests were conducted in the following manner. The pins, measuring 5 mm in diameter and 5 mm in length, were made of hardened bearing steel (AISI 52100) and polished to a surface roughness of Ra 0.05 μm . The disc measured 35 mm in diameter and 2.5 mm in thickness and was made of carburized steel. The three pins were secured to prevent them from rotating and were pressed against the toric sliding surface of the rotating disc at a position that was 20 mm in diameter from the center of the disc. Contact at the sliding interfaces was in the shape of lines under high Hertzian pressure of 700 MPa due to a normal force of 500 N. Lubrication was provided by an oil bath heated to 353 K. The sliding speed was varied in a range of 0–1 m/s for the tribological experiments and the sliding time was 60 min. The SRV sliding tests were performed with a reciprocating, needle-pin-on-flat-disc tribometer that was lubricated before the test by wetting it with several droplets (5 cc) of the test oil heated to 80 °C. The pins, measuring 18 mm in diameter and 22 mm in length, were made of hardened steel and polished to a surface roughness of Ra 0.05 μm . The disc measured 24 mm in diameter and 7.9 mm in thickness and was made of carburized steel. The reciprocating pins were pressed against the stationary disc by a force of 400 N that generated 270 MPa of pressure. The length of the track was 3.0 mm and the reciprocating time was 15 min at 50 Hz.

At the end of the tests, the flat samples were washed in *n*-heptane and *n*-propanol to eliminate all the

residual oil, gel-like species and contaminants and permit accurate surface analyses.

2.3. Nanoscratch measurement

Nanoscratch measurements were obtained in a constant-force nanoscratching process using a conical diamond tip as a stylus for scratching. The nanoscratching process consisted of applying a constant normal force by pressing the diamond stylus on the sample surface and then displacing the stylus to induce a lateral scratch on the surface. By detecting the lateral force and normal displacement, the friction coefficient relative to the scratch depth was determined on the basis of the ratio of the lateral force to the normal force.

2.4. Surface analyses

X-ray Photoelectron Spectroscopy (XPS) analyses were performed with a non-monochromatized source that had a dual anode for Mg K_{α} or Al K_{α} irradiation. The size of the X-ray probe was set at 500 μm so that a spatially resolved analysis could be achieved inside the tribofilms with a good signal/noise ratio. The thickness probed in the XPS analyses was about 5 nm with exponential decay. Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) experiments were performed with a ToF-SIMS IV apparatus (ION-TOF, Münster, Germany). The size of the probed area was about 100 \times 100 μm^2 and the diameter of the spot was smaller than 1 μm in order to obtain average information. The sampling depth probed by ToF-SIMS was less than 1 nm.

3. Results and discussion

3.1. Steel/DLC tribological systems lubricated by Glycerol Mono-Oleate (GMO)

We have evaluated the friction properties of more than 50 different kinds of DLC coating materials, including hydrogen-containing DLC (a-C:H), metal-containing DLC (Me-C:H) and hydrogen-free DLC (a-C and ta-C) under boundary lubrication conditions in normal engine oil. In this work, we are mostly interested in comparing the performance of two DLC coatings: a hydrogenated one (a-C:H) and a non-hydrogenated one (ta-C). The ta-C material is mainly composed of carbon in the sp^3 hybridization, as studied by XANES spectra in figure 1. This result is in agreement with the high hardness and Young modulus values measured by nano-indentation, respectively 65 and 650 GPa. SIMS profiling showed no hydrogen in the bulk (data not shown here). In the C–H phase diagram of Robertson, it then belongs to a tetrahe-

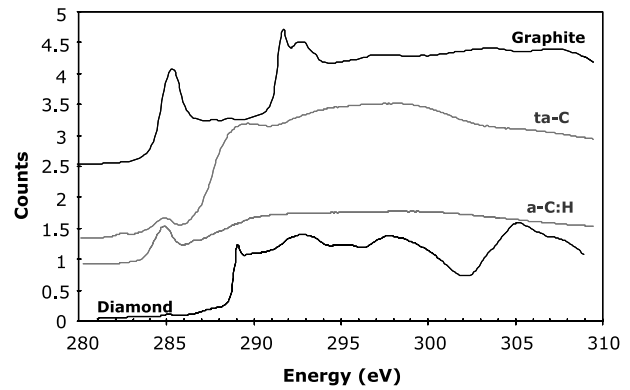


Figure 1. XANES spectra recorded on ta-C and a-C:H materials. XANES spectra of diamond and graphite materials are also reported on the figure for the comparison.

dral amorphous carbon ta-C. Because automotive engine oil contains many kinds of additives, it was difficult to identify the interactions between the friction modifiers and the ta-C coating. Many types of friction modifier additives were examined, including amine, amide and ester. We evaluated the effect of the GMO friction modifier additive on the friction property of ta-C, when used with a poly-alpha-olefin (PAO) based oil. First, tribological tests were conducted using a pin-on-disc type machine consisting of three fixed pins sliding on a rotating disc. Different tests were performed with steel/steel, ta-C/steel and a-C:H/steel friction pairs and different lubricants: 5W-30 engine oil, PAO and PAO+GMO (1% by weight of Glycerol Mono-Oleate). For pure PAO, only ta-C/steel combination was tested. Results are shown in figure 2. When lubricated with typical API SG 5W-30 engine oil, friction of ta-C/steel combination was reduced to 0.08 compared to 0.125 for the steel/steel pair, that is a 40% reduction. Interestingly, friction of a-C:H/steel lubricated with engine oil showed a higher value of 0.105. As shown in figure 2, when GMO is used as additive in PAO it was found the ta-C/steel friction pair gave an ultralow friction coefficient of 0.02 instead of 0.07 with pure PAO. On the contrary, a-C:H/steel and steel/steel pairs displayed a much higher friction coefficient of 0.09 and 0.1 with GMO containing PAO. Generally, it was found that the lower is the hydrogen content of DLC, the lower is the friction coefficient of this combination [15]. This tribofilm is known to form on sliding steel surfaces as a result of complex tribochemical reactions, and shearing of the tribofilm often increases the friction level [16–18]. Therefore, it is thought that a low-shear-strength tribofilm resulting from reactions with the friction modifiers contained in the engine oil presumably formed on the hydrogen-free ta-C surface and is responsible for the substantially lower friction coefficient observed for this material in figure 2.

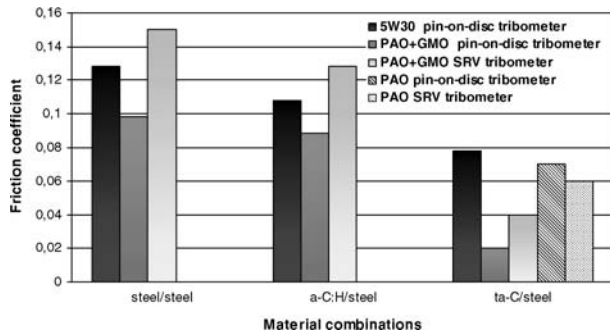


Figure 2. Friction coefficients of steel counterpart on tested materials lubricated with different oils measured in pin-on-disc sliding tests and SRV sliding tests. The sliding speed was 0.03 m/s and the sliding time was 60 min for the pin-on-disc tribometer. The friction coefficient was measured at 60 min. Oil temperature was 80 °C for both test machines. The pins and cylinders were made of hardened steel AISI 52100. SCM415 was carburized steel. ta-C material was applied by a PVD coating process. a-C:H material was applied by a CVD process. 5W-30 was API SG standard engine oil. PAO was a poly-alpha-olefin oil that had the same viscosity at 80 °C as 5W-30 oil. PAO + GMO contained 1 mass % of glycerol mono-oleate.

Although the uppermost sliding surface and the underlying area are thought to control macro-scale friction behaviour, it is experimentally difficult to estimate shear strength and friction behaviour as a function of depth on a nanometer scale [19–22]. Recently, however, we have developed a novel nanoscratch method to elucidate the macro-scale effect of reduced friction in relation to the nanoscale tribological properties [23]. In figure 3, nanoscratch measurements reveal that the sliding area of the ta-C coated steel disc, exhibiting ultralow friction in standard pin-on-disc tests, displays also low shear strength and low friction coefficients at nano-scale. Figure 3 also shows the evolution of nanoscale friction coefficient as a function of scratch depth for inside and outside wear scar area and this for the three surface conditions. The first one was a non-cleaned surface after the sliding test, the second one was a cleaned surface subjected to supersonic cleaning in a hexane solvent and the third one was a hexane-cleaned surface rewetted with PAO + GMO oil. The sliding area displayed a lower friction coefficient than the non-sliding area and exhibited an obvious reduction particularly near the surface within a depth of less than 5 nm. This result suggests that a very thin tribofilm with low shear strength formed on the sliding surface of the ta-C disc lubricated with PAO + GMO lubricant. The tribofilm was the reason for the ultralow friction observed for this material combination in the sliding tests.

To confirm this ultralow friction property, the ta-C/steel friction pair lubricated with PAO + GMO was evaluated using another sliding test rig, the SRV test machine, which is commonly used to evaluate the boundary lubrication properties of engine oil. The ta-C/steel couple showed a friction coefficient of 0.04

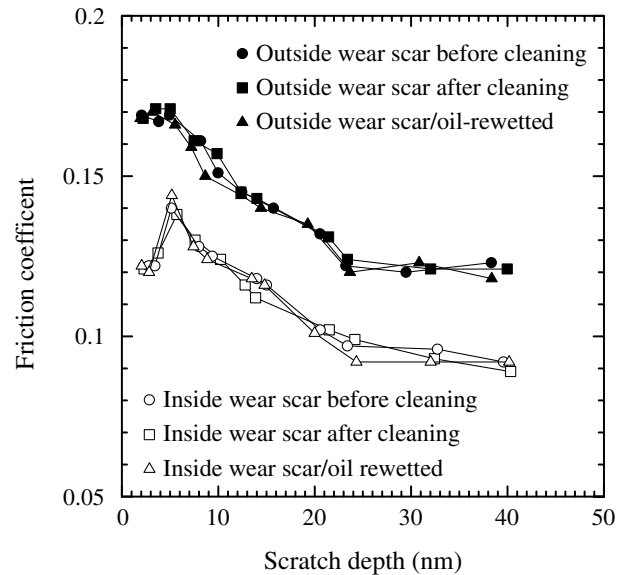


Figure 3. Nanoscratch measurements obtained for three surface conditions in a constant-force nanoscratching process using a conical diamond tip as a stylus for scratching. One was a non-cleaned surface after the sliding test, a second was a supersonic cleaned surface using a hexane solvent and the third was a surface rewetted with PAO + GMO oil after hexane cleaning. The circles and squares were measured on the non-sliding and sliding areas, respectively.

compared with the value of for that 0.02 measured in the pin-on-disc test (see figure 2). The reason for this discrepancy is that the SRV value was actually averaged with those measured during reciprocating motion, including the high values at the reciprocating points. Nevertheless, friction of ta-C/steel was much lower than the friction coefficient exhibited by the a-C:H/steel couple and the steel/steel one, both of which showing a higher friction level than the pin-on-disc-test results in figure 2. So, ultra-low friction property of the ta-C/steel couple lubricated with PAO + GMO was observed in the two different testing machines.

As a final step, friction properties were evaluated in a pin-on-disc test as a function of the sliding speed for the ta-C/steel pair lubricated with PAO + GMO and compared with those of the a-C:H/steel pair. Moreover, the sliding friction data were compared with the results found for a needle bearing, a a-C:H/steel pair and a ta-C/steel pair lubricated with 5W-30 engine oil. The results are shown in figure 4. Data show that friction coefficients of the ta-C/steel pairs are much lower than those of the a-C:H/steel pairs. The most notable result here is that the ta-C/steel pair lubricated with PAO + GMO exhibited a superlow friction coefficient of 0.006 at sliding speeds over 0.1 m/s (100 rpm), which was comparable to the friction coefficient of the needle bearing under pure rolling. In order to evaluate how much of that superlow friction is due to EHD or hydrodynamic lubrication, the λ ratio was determined for these experiments. For the both lubricants, the λ

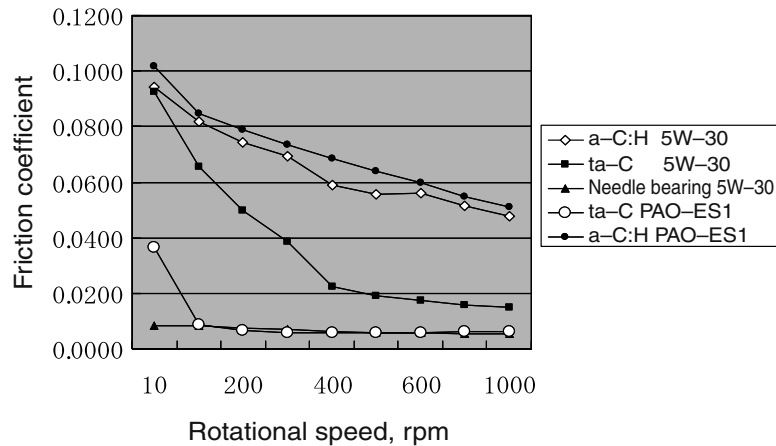


Figure 4. Friction properties of the ta-C/steel pair lubricated with PAO + GMO as a function of the sliding speed compared with those of a needle bearing.

ratio varies between 0.12 and 0.89 when sliding speed is increased from 0.05 m/s (50 rpm) to 0.9 m/s (900 rpm). This superlow friction performance demonstrates for the first time that the rolling contact friction level of needle bearings can be obtained in sliding contact under a boundary lubrication condition.

3.2. DLC/DLC tribological systems lubricated by GMO

Friction properties of DLC couples lubricated with PAO + GMO were also evaluated in the SRV test to make clear the reason for ultralow friction. Figure 5 shows the friction coefficients of different kinds of material combinations lubricated with PAO + GMO. Amazing results were obtained for the ta-C/ta-C combination. The friction coefficients of the ta-C couples were substantially lower than those of the a-C:H ones and that of the ta-C/steel combination (see figure 2). These results strongly suggest that the ultralow friction phenomenon was obtained by the interaction between the ta-C coating and the ester-containing oil and is

certainly due to the formation of a very thin and low-shear-strength tribofilm on the ta-C sliding surface.

3.3. Low friction mechanism as studied by surface analyses

To understand the origin of the ultralow friction observed for PAO + GMO-lubricated ta-C coatings in boundary lubrication, we investigated the chemical nature of the tribofilm generated at the sliding surface of ta-C couples by surface sensitive chemical and molecular analysis techniques: XPS and (ToF-SIMS). Spectra were recorded inside and outside the tribofilm area (wear track) in order to clarify the material change on the ta-C surface under friction. First, XPS analyses (not shown here) revealed the presence of C and O elements both inside and outside the tribofilm area. The C—O and C=O bonds were detected in lower proportion outside the tribofilm area than inside. This would seem to indicate that some GMO was adsorbed on the ta-C surface before the friction process. The molecular transformations of GMO under friction were further investigated by ToF-SIMS (see figures 6 and 7). The positive ion spectrum of standard GMO between masses 235 and 360 (figure 6(a)) is compared with the spectra obtained outside and inside the tribofilm area in figure 6(b) and (c), respectively. The detection of the characteristic masses of GMO (dots) clearly demonstrates the presence of GMO molecules on the unworn ta-C surface. We calculated the ratio between the higher mass ion fragment $C_{21}H_{39}O_3$, which is characteristic of GMO molecule, and the lower mass ion fragments $C_{19}H_{37}O_3$, $C_{19}H_{35}O_3$, $C_{17}H_{33}O_3$, $C_{18}H_{33}O$, $C_{16}H_{31}O$ and $C_{16}H_{29}O$. This ratio was found to be twice lower inside the wear scar, suggesting a more advanced state of GMO tribochemical decomposition. It was also

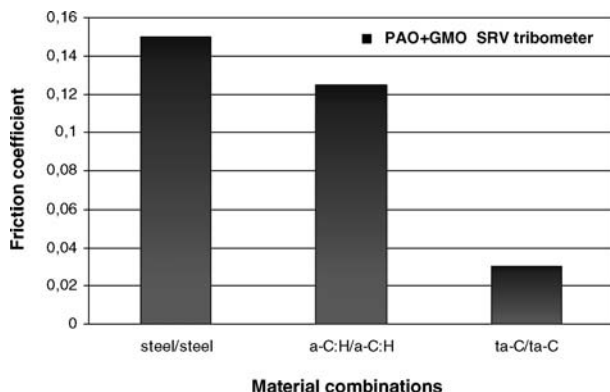


Figure 5. Friction coefficients obtained in SRV tests of steel/steel and DLC/DLC couples lubricated with PAO + GMO oil.

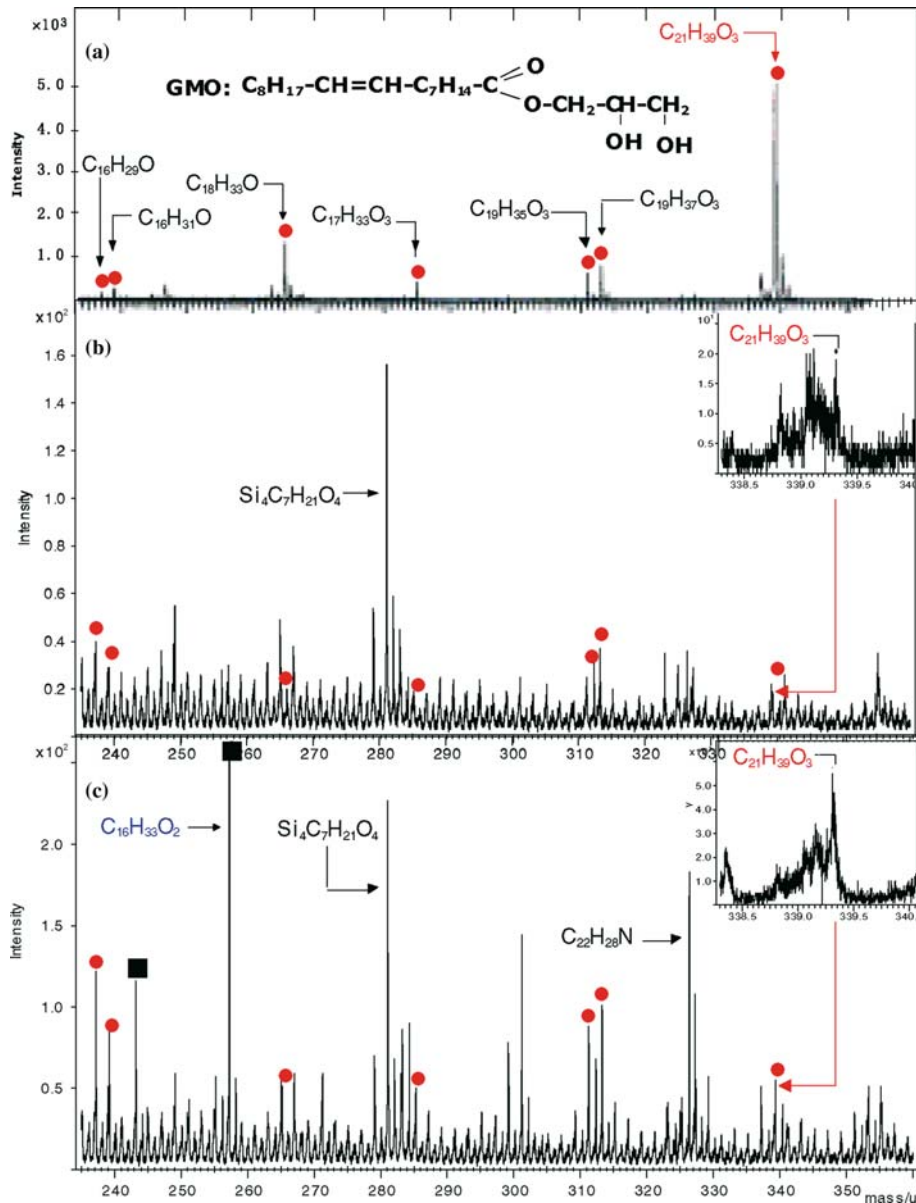


Figure 6. ToF-SIMS surface analyses. (a) The positive ion spectrum of GMO is compared with spectra obtained (b) outside the wear track and (c) inside the wear track.

observed that the mass fragments attributed to the PAO hydrocarbon base oil ($\text{C}_n\text{H}_{2n-3}$ to $\text{C}_n\text{H}_{2n+1}$) did not appear in the spectra obtained on the ta-C surface. Moreover, new masses attributed to palmitic acid fragments (squares in figure 6(c)) were also found inside the wear scar. The static SIMS data indicate a relative increase of the quantity of alcohol groups (as OH^-) in the tribofilm area (see figure 7). Figure 7(a) presents the negative SIMS spectrum recorded on a virgin DLC surface, showing the absence of the characteristic GMO ions fragments (dots). Figure 7(b) and (c) which respectively show the corresponding SIMS spectra recorded outside and inside the tribofilm reveal the presence of GMO ions fragments. From the figure 7(b) and (c), it clearly appears that the ratio between OH^-

peak intensity and the GMO ions fragments peaks intensities has increased inside the tribofilm area compared to outside the tribofilm. These overall SIMS results strongly support the formation of a friction-induced tribofilm exhibiting ultralow friction. Thus, the tribochemical degradation of GMO generates OH species on the friction surface especially by reaction with the carbon dangling bonds. The origin of superlubricity in these conditions might be attributed to the low energy Van der Waals interaction between two sliding hydroxylated carbon surfaces (OH-terminated carbon film surface) Schematic view in figure 8 shows the formation of friction-induced hydroxylated-terminated carbon surfaces in agreement with the different static SIMS data.

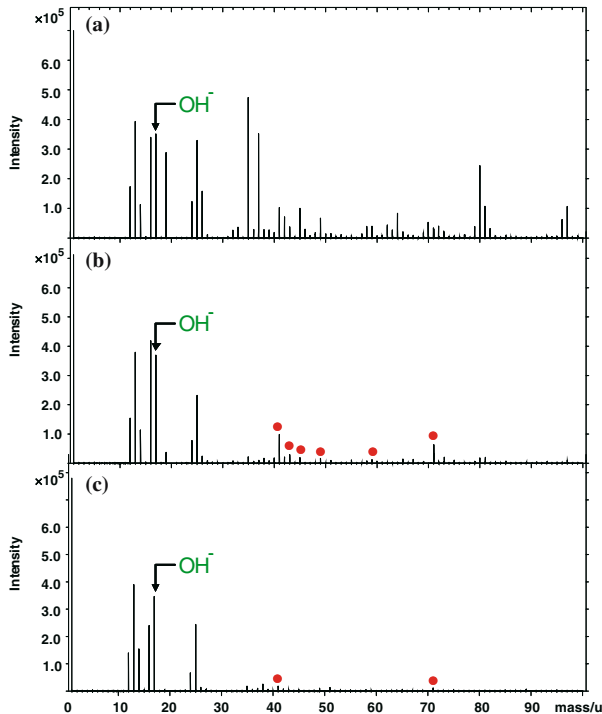


Figure 7. ToF-SIMS surface analyses. (a) The negative ion spectrum of virgin ta-C surface is compared with spectra obtained (b) outside the wear track and (c) inside the wear track.

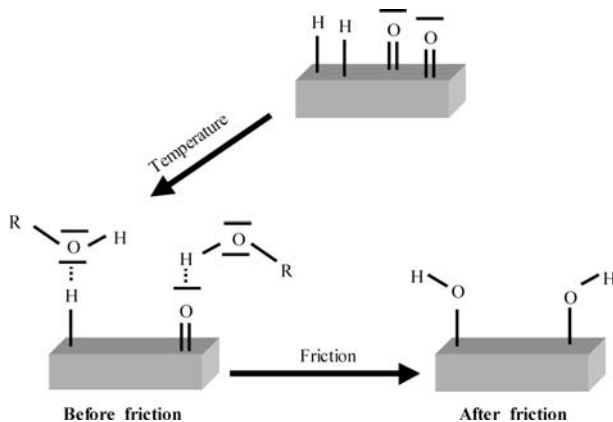


Figure 8. Schematic view of friction-induced hydroxylated-terminated carbon surfaces.

4. Conclusion

Ultralow friction coefficient of 0.03 was obtained by sliding the ta-C/ta-C pair lubricated with PAO-GMO. The origin of ultralubricity in these conditions has been investigated by ToF-SIMS analysis on wear surfaces, and especially by comparing analyses performed inside and outside the wear scar. Our results are in agreement with the formation of a OH-terminated carbon surface after a short sliding induction period. This new surface chemistry is formed by the tribochemical reaction of lubricant alcohol function groups with the

friction-activated ta-C atoms (hydroxylation of carbon). The thickness of the tribofilm is lower than 2 nm, as indicated by SIMS profiling. This surface is quite similar to the superlow friction H-terminated surface formed in the case of hydrogenated DLC coatings (a-C:H) sliding in an ultrahigh vacuum. The origin of this new kind of ultralubricity could be due to the very low-energy interaction between OH-terminated surfaces sliding on each other. However more analytical work is necessary to confirm this fact.

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