1. Introduction

Diamond-like carbon (DLC) coatings have been extensively researched in recent years to further our understanding of their properties and increase the efficiency in their use to reduce energy toward a sustainable society. Their properties (such as high hardness, low friction coefficient, wear resistance and chemical inertness (Clausing et al., 2012; Erdemir, 2006; Robertson, 1992; Tasdemir, 2013)) or their tribological behaviors with different oil additives (Costa et al., 2011; Kosarieh et al., 2016; Renman, 2012) have been investigated over the years. Among additives for lubricating oils being used since 1920s, some are chemical compounds known to be able to absorb and/or react with the sliding surfaces to produce low-shear-strength tribochemical reaction layers that prevent direct contact between the sliding surfaces and are often used to reduce wear in the boundary-lubricated regime. The most common antiwear additive is a zinc, sulfur and phosphorus containing compound called ZnDTP (zincdialkyldithiophosphate) that has been the most widely used oil additive, especially in engine oils (Renman, 2012; Sabbatini, 2014). Equey et al. investigated the ZnDTP tribofilm formation on hydrogenated amorphous carbon (a-C:H) DLC surfaces, and concluded that the tribofilm formed on DLC surfaces had a different structure and weaker adhesion than that found on steel surfaces (Equey et al., 2008a). Tasdemir et al. also reported that there is an effective tribofilm formation on DLC surfaces, and depending on the type of DLC coating, the shape of the tribofilm and the friction behavior of the DLC coating differ. His results show that the patchy-like ZnDTP tribofilm formed on tetrahedral amorphous carbon (ta-C) DLC shows lower friction coefficient than the pad-like ZnDTP tribofilm formed on other types of DLC which he studied (Tasdemir et al., 2014).
The aim of this study is to characterize the shape of the ZnDTP tribofilm depending on the type of DLC coating. We also investigated the relation between the shape of the tribofilm and the friction behavior of DLC coatings. Friction behaviors of DLC coatings and topography parameters of ZnDTP tribofilm have been investigated in this research.

2. Experimental Details

2.1. Material characterization and lubricants

In this study, four types of DLC coatings were tested against self-mated DLC coatings: non-hydrogenated amorphous carbon (a-C) coating, non-hydrogenated tetrahedral amorphous carbon (ta-C) coating, hydrogenated amorphous carbon (a-C:H) coating, and silicon-doped hydrogenated amorphous carbon (Si-DLC) coating. Tested DLC coatings were deposited on disks and pins of high carbon chrome bearing steel (JIS SUJ2), which have an average hardness of 62 HRC. DLC coated pins were 5mm in diameter and 5mm in length, and DLC coated disks were 22.5 mm in diameter and 4 mm in thickness. A thin metal interlayer was used for all coatings to increase the adhesion between the coating and the steel.

The hardness and Young’s modulus of all DLC coatings were determined by nano-indentation at 1000 µN load with a Berkovich indenter (Elionix, ENT-1100). Surface roughness was evaluated by atomic force microscopy (AFM; Nanopics 1000, SEIKO instruments, Japan). Hydrogen content in the coatings was measured using Elastic Recoil Detection Analysis (ERDA) using N+ monovalent as the irradiation ion, with 500 keV irradiation ion energy. Important characteristic properties of tested DLC coatings are shown in Table 1.

The base oil used in this study was a synthetic poly-alpha-olefin (PAO) having a 19 mm²/s viscosity and a 17.08 GPa⁻¹ pressure-viscosity coefficient at 40 °C. Secondary type ZnDTP additive was used at 0.08 wt.% concentration.

| Material | Hardness (GPa) | Young’s Modulus (GPa) | Roughness Ra (nm) | Hydrogen (at.%) | Thickness (µm) | Deposition method | sp²/sp³ ratio | Surface energy (mJ/mm²) |
|----------|---------------|----------------------|-------------------|----------------|---------------|-----------------|--------------|------------------------|
| a-C      | 15 ± 3        | 192 ± 10             | 5 ± 3             | <1             | 1             | M. S.           | 1.01         | 46.8                   |
| ta-C     | 75 ± 5        | 900 ± 50             | 17 ± 5            | <1             | 1             | FCVA            | 0.81         | 32.6                   |
| a-C:H    | 26 ± 3        | 203 ± 15             | 12 ± 4            | 19             | 1-2           | PECVD           | 1.57         | 40.9                   |
| Si-DLC   | 24 ± 3        | 189 ± 12             | 14 ± 4            | 27             | 1-2           | PECVD           | 3.66         | 28.8                   |

2.2. Tribological experiments

Boundary lubrication friction tests were carried out using standard pin-on-disc type unidirectional tribotester illustrated in Figure 2.2.1. For each type of coating, the DLC-coated circular cylindrical pin was loaded and rubbed against the self-mated DLC-coated disc under pure sliding condition. The pin was located 6mm in diameter from the center of the disc and fixed to prevent it from rotating. A load of 5 N was applied (corresponding to a maximum initial Hertzian contact pressure of 150 MPa) with 0.1 m/s entrainment speed. Both pin and disc were totally immersed in the lubricant. The theoretical minimum film thickness (h_min) and dimensionless lambda (Λ) ratio were calculated using Eqs. (1) and (2) respectively to ensure a boundary lubricated regime (Hamrock et al., 2004).

\[ h_{min} = 3.63RU^{0.68}G^{0.49}W^{-0.073}(1 - e^{-0.68k}) \]  
\[ Λ = \frac{h_{min}}{\sqrt{R_{q,a}^2 + R_{q,b}^2}} \]

Where R is the radius of the pin, U is a dimensionless speed parameter, G is a dimensionless material parameter, W is a dimensionless load parameter, R_{q,a} is the surface roughness of the pin and R_{q,b} is the surface roughness of the disk. The calculated lambda parameter was 0.36 which states that lubrication regime was boundary lubrication.

Tests were performed at 80 °C with 0.1 m/s average linear speed. The average speed was calculated in accordance with the middle of the line contact. The oil temperature was controlled by thermocouple which is fitted to just below
the holder. Test duration was 1 hour and total sliding distance was 405 m. Before and after the friction tests, all samples were rinsed in benzene and washed with acetone in an ultrasonic bath (unless otherwise stated) to remove contaminants and oil species and provide initial condition that do not affect the final shape of the tribofilm.

3. Surface analysis

Prior to the surface analyses, samples were ultrasonically cleaned successively with benzene and acetone, in order to remove the excess lubricant. Surface analyses were performed using Field Emission Scanning Electron Microscopy (FESEM; JEOL, JSM-7000FK) and Surface Roughness Analysis three-dimensional Scanning Electron Microscope (ERA-9000 Semi-lens 3D SEM). Surfaces of rubbed DLC disks were investigated with FESEM to confirm whether or not ZnDTP tribofilm was formed on DLC surfaces. In cases where this was true, we checked to confirm whether the structure was the same as that reported by Tasdemir et al (Tasdemir et al., 2014). In this case, we also used 3D SEM to investigate the shape of the formed tribofilm.

4. Bearing area parameters

The bearing area curve or Abbott-Firestone curve has been used to evaluate surfaces since its introduction in 1933 by Abott and Firestone (Jamison, 1976; Stewart, 1990). It gives significant information to characterize the measured profile. The topography of a surface is characterized by the bearing area parameters (also call topography parameters) using the bearing area curve. Figure 4.1 shows a typical surface roughness profile and its bearing area curve along with its bearing area parameters. The bearing area of a surface roughness is divided into three parts: one part describes the peaks (first region of contact); another part describes the valleys (lubricant retention region); and another part describes the core roughness of the surface (working region). The bearing area curve being obtained by computing the surface area at each level of the surface profile, starting at the highest peak to the deepest valley, provides information about the surface area of the three parts of the bearing area described above. The bearing area parameters consist of the height of the peak zone, the height of the core roughness, the depth of the valley zone, and the material surface area corresponding to each of the three parts.

To obtain those parameters from the bearing area curve, a line segment called "Equivalent straight line", representing at least 40% of the surface area axis (horizontal axis), is moved over the curve as shown in Figure 4.1. The equivalent straight line is extended to intercept the height/depth axis (vertical axis) at 0% and 100% of the surface area axis. Interceptions of the equivalent straight line and the height/depth axis represent the height of the peak zone and the depth of the valley zone. The difference in height denotes the height of the core roughness. Next, two horizontal lines are drawn from interception points of the equivalent straight line and the height/depth axis to meet the 1. The projection on the surface area axis of interception points between those two horizontal lines and the bearing area curve give the material surface area of the peak zone the core roughness and the valley zone as shown in Figure 4.1.
5. Results

5.1. Friction results

Figure 5.1 shows the friction coefficient curves of self-mated DLC/DLC tribopairs as a function of sliding cycles. The friction curve of Si-DLC shows some fluctuations during the running-in period before stabilizing at an average value of 0.0751. The friction curve of a-C DLC shows a small increase during the running-in period before decreasing and stabilizing at an average value of 0.0708. The friction curve of a-C:H DLC shows immediate friction reduction in the early stages of sliding before increasing slowly to a stable value of 0.0615. The friction curve of ta-C DLC shows continuous decrease from the running-in period, and it kept decreasing up to an average value of 0.0126. The lowest friction coefficient is obtained with ta-C DLC followed by a-C:H DLC, a-C DLC, and the highest friction coefficient is obtained with Si-DLC. Those results strongly agree with friction results reported by other researchers where ta-C DLC generates the lowest friction for DLC/DLC contact in PAO+ZnDTP lubrication system (Tasdemir et al., 2014; Vengudusamy, 2013; Yazawa et al., 2014). Friction behaviors of DLC coatings in base oil plus oil additives are often reported to be correlated to tribofilm formation on DLC surfaces during rubbing process. Investigation of ZnDTP tribofilm observe in this study will be presented in the next sections.

5.2. FESEM observation

ZnDPT tribofilm formation on DLC surfaces has been investigated extensively. Some research reported no tribofilm formation on the DLC coatings (Kalin et al., 2004) while others reported that tribochemical interactions of ZnDPT with DLC coatings result in the formation of a tribofilm with either a patchy-like or pad-like structure (Zahid et al., 2015).
Investigation by FESEM revealed that some tribofilm were present at the surface of disk samples investigated in this work after the tribological tests in PAO + ZnDTP oil. The observed tribofilms were similar in appearance to results reported previously by Tasdemir et al. (Tasdemir et al., 2014). Figure 5.1.1 shows a clear formation of a white pad-like tribofilm on a-C DLC, a-C:H DLC and Si DLC while a white patchy-like tribofilm was observed on ta-C DLC.
5.3. 3DSEM observation

After we confirmed that the ZnDTP tribofilm was formed on tested samples, DLC surfaces were further investigated in order to characterize the shape of the formed tribofilm. Using 3D SEM, observed surfaces covered with tribofilm (figures 5.3.1a to 5.3.1d) were scanned and digitized in numerical data to reveal their real shape. Statistical analyses were performed on obtained data sets by R programming to reproduce digitized surfaces (figures 5.3.2a to 5.3.2d). In order to separate data related to the tribofilm from the non-tribofilm data, numerical images were converted into grayscale and then converted in binary matrices. A Hadamard product was then performed using the binary matrices and original digitized surface matrices. The Hadamard product is the product element by element of two matrices of the same dimensions, thus, all data that are "0" in the binary matrix will remain "0" in the final result, and all data that are "1" in the binary matrix will keep the value of the original digitized surface matrix. Obtained results are shown in figures 5.3.3a to 5.3.3d where we can observe a relatively good separation of the tribofilm related data set for each type of DLC coating. The shape of obtained tribofilm remains very random from one DLC type to another. Thus, the most accurate way to characterize the shape of the tribofilm appears to be the bearing area curve or Abbott-Firestone curve. The bearing area curve is the relation between depth and surface area. It gives the ratio of material total surface area at any level, starting at the highest peak, called the bearing ratio or material ratio, as a function of level. Figure 5.3.4 shows the bearing area curve of each type of DLC coating. We can observe that the patchy-like tribofilm formed on ta-C DLC coating exhibits a wide surface area with a maximum height of about 0.03 μm, which is thinner than the pad-like tribofilm formed on other DLC coatings for which the height goes higher than 0.035 μm. The thicker tribofilm is observed on a-C:H DLC coating with a maximum height of about 0.047 μm, and also exhibit smaller surface area than other DLC coatings.
Figure 5.3.1 3DSEM images of ZnDTP tribofilm formed on (a) a-C DLC, (b) a-C:H DLC, (c) Si DLC and (d) ta-C DLC, after friction test in PAO+ZnDTP oil at 80°C.

Figure 5.3.2 Images of digitized surfaces covered with ZnDTP tribofilm formed on (a) a-C DLC, (b) a-C:H DLC, (c) Si DLC and (d) ta-C DLC, after friction test in PAO+ZnDTP oil at 80°C. The measurement unit is µm.
Figure 5.3.3 Digitized ZnDTP tribofilm formed on (a) a-C DLC, (b) a-C:H DLC, (c) Si DLC and (d) ta-C DLC, after friction test in PAO+ZnDTP oil at 80 ºC. The measurement unit is µm.

Figure 5.3.4 Bearing area curves of ZnDTP tribofilm formed on different DLC coatings after friction test in PAO+ZnDTP oil at 80 ºC

6. Discussion

6.1. Relationship between friction coefficient and shape of ZnDTP tribofilm

A correlation between the bearing area curve and the friction coefficient on Figure 5.3.5 shows that the wide and thin patchy-like tribofilm (height of 0.03 µm) formed on ta-C coating shows low friction (friction coefficient inferior to 0.02) while narrow and thick pad-like tribofilms (height superior to 0.035 µm) formed on other DLC coatings show high friction (friction coefficient superior to 0.06). Such interpretation strongly agrees with Yazawa et al. who reported that formation of ZnDTP-derived thin white layer on ta-C DLC generates the lowest friction for DLC/DLC contact (Yazawa et al., 2014). ZnDTP oil additive is known to form strong adhesion tribofilm on ferrous surfaces but not on DLC surfaces (Equey et al., 2008a, 2008b; Yazawa et al., 2014). The thin tribofilm formed on ta-C coating can be explained by the weakness of the tribofilm which cannot efficiently agglomerate in the range of 0.02 and 0.03 µm thus the tribofilm spread over the surface of the coating. On the other hand, the thick tribofilm formed on a-C:H DLC and other types of DLC coatings can be explained by a stronger tribofilm that can agglomerate higher than 0.035 µm. Such interpretation strongly agrees with Vengudusamy et al. who investigated the durability of ZnDTP tribofilms formed in DLC/DLC contacts and conclude that ZnDTP tribofilms formed on Si-DLC and a-C:H DLC surfaces were more strongly adhered than ta-C DLC (Vengudusamy et al., 2013). Thus, we can understand the relationship between the shape of the tribofilm and the friction coefficient in two points:

- In the case of ta-C DLC, the tribofilm agglomerate better at low height, providing a low roughness film that reduce the friction coefficient.
- In the case of a-C:H DLC and other DLC coatings, the tribofilm agglomerate thicker than ta-C DLC, providing a rougher film that increase the friction coefficient.
Figure 5.3.5 Correlation between the bearing area curve and the friction coefficient: Wide and thin patchy-like tribofilm (height of 0.03 µm) formed on ta-C coating shows low friction (friction coefficient inferior to 0.02) while narrow and thick pad-like tribofilm (height superior to 0.035 µm) formed on other DLC coatings shows high friction (friction coefficient superior to 0.06)

6.2. Bearing area parameters evaluation

In our study, the method described in section 4. was used to evaluate the bearing area parameters characterizing the surface topography of ZnDTP tribofilm observed on investigated DLC coatings as shown in Figure 6.2.2. Obtained results are shown in Figure 6.2.3, where a comparison between bearing area parameters of the ZnDTP tribofilm formed on a-C:H DLC that shows high friction coefficient and bearing area parameters of the ZnDTP tribofilm formed on ta-C DLC that shows low friction coefficient reveals that ZnDTP tribofilm formed on ta-C DLC has:

1. shallower valley
2. smaller core
3. smaller peak
4. narrower valley void
5. wider core material surface area coverage
6. narrower peak material surface area coverage

We can then understand that a tribofilm that fulfils the above-mentioned conditions will likely show low friction coefficient. To verify that, a comparison with ZnDTP tribofilm formed on other types of DLC coatings show that:

- the tribofilm on a-C DLC shows smaller peak than the tribofilm on ta-C DLC but deeper valley and higher core material;
- the tribofilm on Si DLC shows almost the same core material height and peak material height as tribofilm on ta-C, but deeper valley;
- the tribofilm on Si DLC shows narrower peak material surface area and wider core material area than tribofilm on ta-c DLC, but wider valley void.

ZnDTP tribofilm formed on other types of DLC coatings don't fulfill the above-mentioned conditions, and show higher friction coefficient than the ZnDTP tribofilm formed on ta-C DLC. This verify that the tribofilm showing lower friction coefficient fulfills the above-mentioned conditions. We could not verify that a tribofilm that fulfils identified 6
conditions will show low friction coefficient, but we can conclude that such tribofilm will likely show lower friction coefficient than a tribofilm that doesn’t fulfill all the above-mentioned conditions.

Figure 6.2.2 Evaluation of bearing area parameters of ZnDTP tribofilm observed on DLC coatings

Tribofilm on ta-C DLC shows lower Valley depth
Tribofilm on ta-C DLC shows lower Core Material height
Tribofilm on ta-C DLC shows lower Peak Material height
7. Conclusion
The effect of ZnDTP tribofilm's morphology on friction behaviors of DLC coatings in boundary lubrication was investigated in this work. Results show that:

- as reported by previous researches, ta-C DLC exhibited the lowest friction coefficient while other tested DLC coatings exhibited higher friction coefficient.
- the formation of ZnDTP pad-like or patchy tribofilms was observed on investigated DLC coatings by means of FESEM and 3D SEM analysis.
- 3D SEM investigation on the tribofilm revealed, through bearing area curve analysis, that the patchy-like tribofilm formed on ta-C DLC coating was wider and thinner (about 0.03 µm height) than the pad-like tribofilm formed on other DLC coatings which were narrower and thicker (more than 0.035 µm height).
- bearing area parameters analyses demonstrated that compared to the ZnDTP tribofilm formed on other tested DLC coatings, the ZnDTP tribofilm formed on ta-C DLC has shallower valley, smaller core, smaller peak, narrower valley void, wider core material surface area coverage and narrower peak material surface area coverage.

These evidences suggest that the tribofilm formed on ta-C DLC is weaker than those formed on other tested DLC coatings, and thus spread wider on the surface of the coating, leading to a topography that promote lower friction coefficient.

Acknowledgements
The authors would like to thank ELIONIX INC. for its valuable assistance 3DSEM measurements.

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