Jurnal Tribologi 18 (2018) 1-19

MYTRIBOS Malaysian Tribology Society

Jurnal Tribologi

Website : jurnaltribologi.mytribos.org e-issn: 2289-7232

The effects of oil additives and mating materials to the friction, wear and seizure characteristics of a-C:H coating

Mohd Taufik bin Taib [1,2,*], Noritsugu Umehara [1], Takayuki Tokoroyama [1], Motoyuki Murashima [1]

[1] Department of Micro-Nano Mechanical Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya-shi, Aichi 464-8603, JAPAN.
[2] Fakulti Kejuruteraan Mekanikal, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, MALAYSIA.
[*]Corresponding author: mtaufik@utem.edu.my

KEYWORD

DLC
a-C:H coating
Oil additives
Lubricants
Tribofilm
Mating materials

ABSTRACT

In this study, friction and wear behaviour of amorphous hydrogenated carbon (a-C:H) DLC coating slide against SUJ2, TiC and TiN mating material disks in Base and ZnDTP+MoDTC oils boundary lubrication is comparatively investigated to determine the most favourable DLC/mating material/lubricant and interrelated tribofilm formation mechanism on each mating mating materials. Tribological tests were executed by utilizing roller on disk friction tester, nano-indentation hardness test, 3D optical surface profiler, and EDS-SEM were used to characterize the tribofilm formed on both worn roller and disk surfaces. The results showed that the wear volume of a-C:H/TiC tribo-pair in ZnDTP+MoDTC marked a tremendous wear volume reduction compared to than that of in Base oil. EDS investigation on tribofilm element investigation revealed that SUJ2 and TiN mating material disk attracted high concentration of Molybdenum at% on its surface that later caused high wear volume on both roller and disk sliding surfaces. TiC mating material disk however, formed a low at% yet helpful tribofilm consisting of a fraction of Zn phosphate from ZnDTP attached on both roller and disk which assisted the reduction of wear volume.

Received 21 May 2018; received in revised form 13 June 2018; accepted 11 July 2018.
To cite this article: Taib et al. (2018). The effects of oil additives and mating materials to the friction, wear and seizure characteristics of a-C: H coating. Jurnal Tribologi 18, pp.1-19.

1.0 INTRODUCTION

It is estimated that over 30% of the chemical energy converted from engine fuel is to be transformed into friction between bearing parts under oil boundary lubrication conditions (Merlo, 2003). Deposition of diamond like carbon (DLC) to engine parts is one of the methods to scale down these losses so that higher fuel and engine efficiency can be achieved. With a combination of both sp2 and sp3 structures, DLC is one amorphous material that has the characteristics that is of low in friction, high hardness, chemically inert and highly wear resist (Bewilogua et al., 2009; Erdemir and Donnet, 2006; Kalin et al., 2008). However, before depositing DLC coating to engine parts, the problem of incompatibilities between DLC and lubricant additives needs to be solved first to avoid components or parts failure. This is because fully formulated commercial lubricants oils consist of various type of additives were designed to serve the interaction between metal to metal and not in between DLC and metal.

Progressive amounts of analytical investigations related to the friction and wear characteristic of DLC coatings under lubricated environments have been carried out over the past few decades (Forsberg et al., 2013; Kalin and Velkavrh, 2013; Neville et al., 2007). One of the study is the existence of self-lubricating MoS_2 sheets in friction modifier Molybdenum Dithiocarbamates (MoDTC) contained lubricant oil, enables the hydrogenated DLC coatings to gain ultra-low friction coefficient (de Barros' Bouchet et al., 2005; Yue et al., 2013). However, there are also studies reported that hydrogenated DLC coatings in lubricants with MoDTC marked higher wear rates than in Base oil lubrication (Sugimoto et al., 2013; Vengudusamy et al., 2012). (Haque et al., 2009; Kosarieh et al., 2013) manifested that the friction and wear of DLC coatings can further be reduced when boundary lubricated with MoDTC and Zinc Dialkyldithiophosphate (ZnDTP) contained lubricant oil. By means of tribochemical reactions, ZnDTP produces wear protective tribofilm on top of ferrous surface and has ever since been used extensively as anti-wear additive in lubricant oil (Spikes, 2004). There are some studies denoted that ZnDTP is incapable to play its role as anti-wear on DLC surface due to its chemical inertness property (Haque et al., 2007; Kalin and Vižintin, 2006) however, note that there are also studies claiming about the construction of thin ZnDTP tribofilm, on DLC coatings (Equey et al., 2008; Vengudusamy et al., 2011).

Apart from the utilization of Titanium Carbide (TiC) and Titanium Nitride (TiN) in extending the lifespan of cutting tools, both materials also used as a coating on machine elements such as sliding bearings, seals, and valves (Hogmark et al., 2000). (Guu and Lin, 1996; Guu et al., 1997) reported that in dry surface friction test, the wear rate of TiN coated specimen is lower than TiC coated specimen, however the friction coefficient is relatively higher than that of the TiC film. (Li et al., 2017) indicated that in PAO oil boundary lubrication friction test, the wear rate of a-C:H/TiC and a-C:H/steel tribo-pairs denoted the lowest wear rate compared to the other four tribo-pairs. Previous study by (Liu et al., 1999; Na et al., 2005; Suzuki et al., 2013) has demonstrated the effects of different mating materials in dry air environment to the friction and wear of diamond like carbon (DLC) by altering the types and hardness of the mating materials.

However, no attempt is made to investigate the effects of both lubricant additives and mating materials to DLC coating. In this study, tribological test between hydrogenated amorphous carbon (a-C:H) DLC slide against three type of mating materials of uncoated SUJ steel disk, Titanium Carbide (TiC) and Titanium Nitride (TiN) coated SUJ2 steel disk in Base and ZnDTP+MoDTC oils have been done, and their characteristics in terms of friction and tribofilm formation have been investigated.

2.0 MATERIALS AND METHODS

2.1 Hydrogenated DLC and lubricant oil additives

The hydrogenated amorphous carbon (a-C:H) coatings used in this study were supplied by Daido Metal Co. Ltd with a hydrogen content of 30 at%. They were deposited by a plasma enhanced chemical vapour (PECVD) method on the high carbon chrome steel (SUJ2) cylinder roller substrate with a thickness of 4.0 μm. The top surface of the DLC coating was polished during the finishing process to eradicate the droplets and particles possibly attached on the coating surface. Atomic force microscopy (SEIKO, Nanopics 1000) and Nanoindenter (NANOPICS 1000 Elionix ENT-1100a) was used to determine the surface roughness, hardness and Young's modulus of the DLC coating. Three variations of mating material disks used in this study were uncoated SUJ2 disk, and also Titanium Carbide (TiC) and Titanium Nitride (TiN) coated SUJ2 disks. Detailed properties of DLC coated roller and mating material disks are listed in Table 1.

Table 1: Properties of mating material disks and DLC roller.

Properties	**Roller**	**Disk**		
	a-C:H	**SUJ2**	**TiC**	**TiN**
Dimension (mm)	Ø5x5	Ø22.5x4	Ø22.5x4	Ø22.5x4
Substrate	SUJ2	-	SUJ2	SUJ2
Thickness (μm)	4	-	1	1

Two types of lubricant oil used in this study are non-additives added Base oil and anti-wear ZnDTP, anti-friction MoDTC included base oil which from this point forward will be referred as Base oil and ZnDTP+MoDTC oil.

2.2 Friction tester equipment

Figure 1 shows a schematic diagram of the roller-on-disk friction tester used in this research for the friction test against three types of mating material in two types of lubrication oils. In the friction test, four incremental-fixed loads of 10, 20, 30, 40 and 50 N (corresponding to maximum initial Hertzian contact pressures of 170, 240, 295, 340 and 380 MPa respectively for each load) were applied above the roller with the time interval of 20 minutes in between each load. The sliding speed of the two opposing surfaces was set at 100 rpm equivalent to 6.80×10^{-2} m/s at the centre of the roller. Therefore there is a linear distribution of velocity from 4.71×10^{-2} m/s to 8.90. $\times 10^{-2}$ m/s due to the radius range. The test temperature was set at 80°C. The tests were then repeated again 3 times for confirmation and reproducibility of results. Before and after the friction tests, all the mating materials and the a-C:H coated rollers were cleaned by acetone for 15 minutes. The above mentioned friction test experimental conditions were then summarized in Table 2.

2.3 DLC surface and tribofilm analysis equipment

In this research, nano-indentation hardness tester ENT-2100 manufactured by Elionix was used to execute the indentation hardness test on the mating material disks before and after friction tests. Surface morphology of tribofilm formed on mating material disks were studied using non-contact, three-dimensional, scanning white light interferometry (Zygo, Newview) and elemental study were done by utilizing the energy dispersive X-ray spectroscopy (EDS) to analyse the tribofilm chemical composition of the worn disk and roller surfaces.

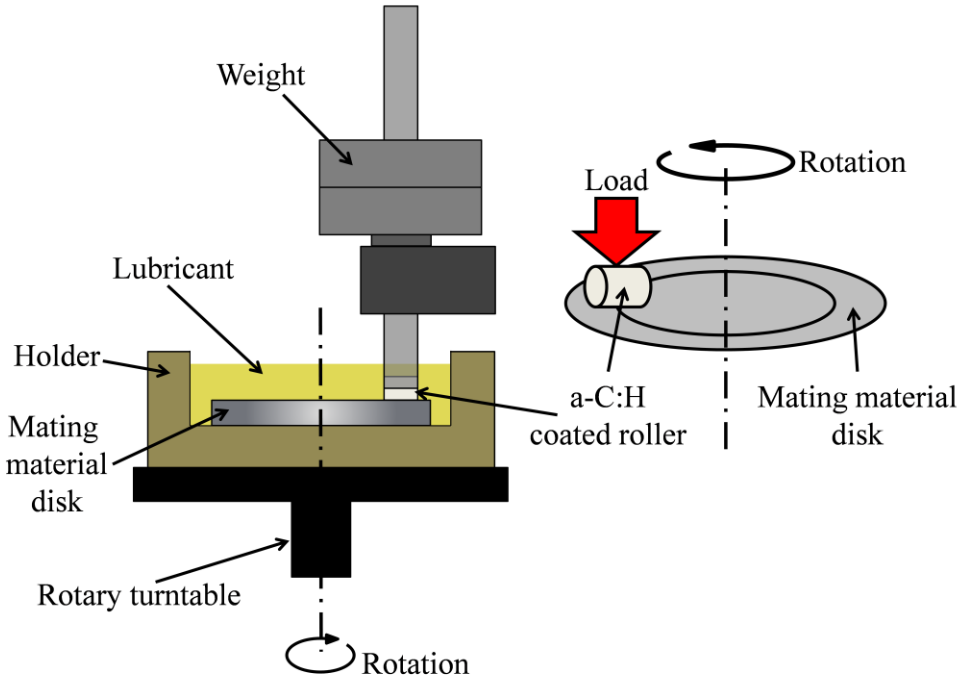

Figure 1: Schematics of roller-on-disk friction tester.

Table 2: Roller on disk friction test experimental conditions.

Roller	a-C:H
Disk	SUJ2, TiC, TiN
Lubricants	Base, ZnDTP+MoDTC
Load, N	10, 20, 30, 40, 50
Max. initial Hertzian contact pressure, MPa	170, 240, 295, 340, 380
Temperature, ^{o}C	80
Rotation speed, rpm	100
Sliding speed, m/s	6.80 x 10^{-2}
Duration, min	100 20 min/load

3.0 RESULTS AND DISCUSSION

3.1 Friction coefficient

Seizure test was conducted by applying incremental-fixed load, and seizure manifestation was observed in the form of large mass flow on the disc, steep accretion of friction coefficient, and uncommon noise and vibration originated from the roller on disk friction tester. Figure 2, 3 and 4 shows the typical test results of each a-C:H/SUJ2, a-C:H/TiC and a-C:H/TiN tribo-pairs in Base and ZnDTP+MoDTC oils.

Figure 2 shows the friction coefficient as a function of cycle numbers and applied force for a-C:H/SUJ2 tribo-pair under boundary lubrication condition. At the initial stage of friction test, the rapidly decreased friction coefficient reveals that the tribo-pair encountered a running-in period, and identical phenomenon appeared at every fixed load phases for both type of lubricant oils. As shown on the figure, friction coefficient decreased deliberately with the increment of applied force and number of sliding cycle. However, in comparison, the a-C:H/SUJ2 tribo-pair in Base oil showed lower friction coefficient of 0.05 than 0.08 in ZnDTP+MoDTC oil at the end of friction test.

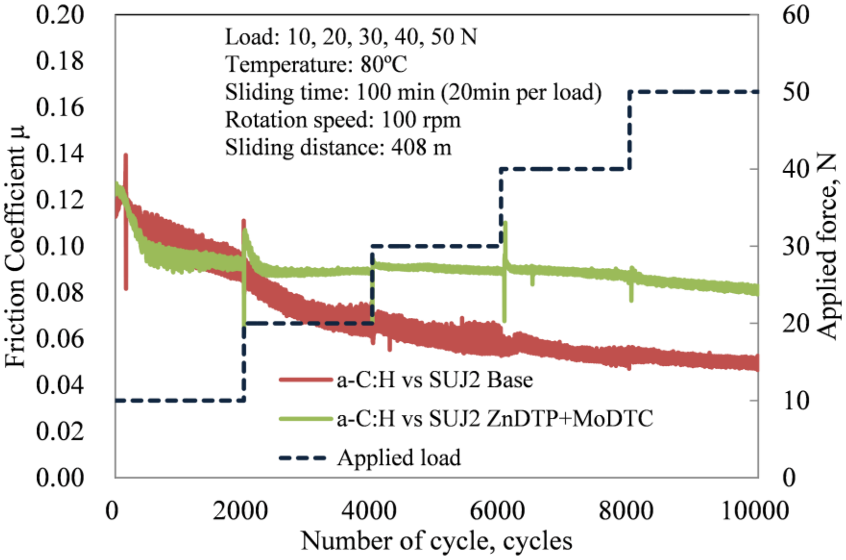

Figure 2: Friction coefficient of a-C-H-SUJ2 tribo-pairs in Base and ZnDTP_MoDTC oils.

Figure 3 exhibits the friction coefficient as a function of cycle numbers and applied force for a-C:H/TiC tribo-pair under boundary lubrication condition. It is revealed that there was no significant change of friction coefficient with the rising of incremental-fixed load for a-C:H/TiC tribo-pair in ZnDTP+MoDTC. The friction coefficient value stayed almost stagnant at 0.09 from start to the end of friction test. The friction coefficient of a-C:H/TiC tribo-pair in Base oil however was unstable and kept on fluctuating from the start of the friction test. During 40 N incremental-fixed load, as the usual running in phenomenon taking place, at 6500 cycle, the friction coefficient bounced and gradually increased. At 50 N incremental-fixed load, croaking noise and vibration was observed hence, the test was brought to a halt promptly.

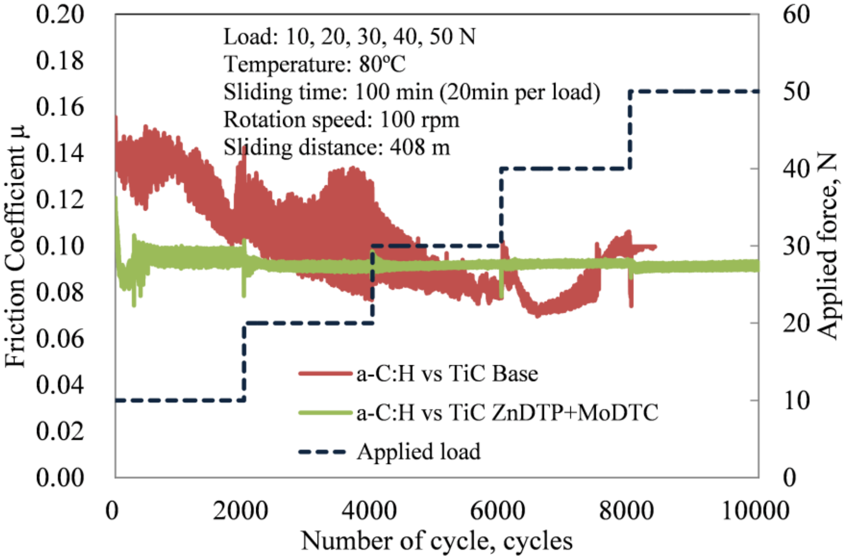

Figure 3: Friction coefficient of a-C-H-TiC tribo-pairs in Base and ZnDTP_MoDTC oils.

Figure 4 exhibits the friction coefficient as a function of cycle numbers and applied force for a-C:H/TiN tribo-pair under boundary lubrication condition. With uniform pattern of running-in cycles, friction coefficient of a-C:H/TiN tribo-pair in ZnDTP+MoDTC decreased gradually with the increment of applied force and number of sliding cycle. Although the friction coefficient of a-C:H/TiN tribo-pair in Base oil was unsteady and kept on fluctuating, no signs of seizure occurrence found.

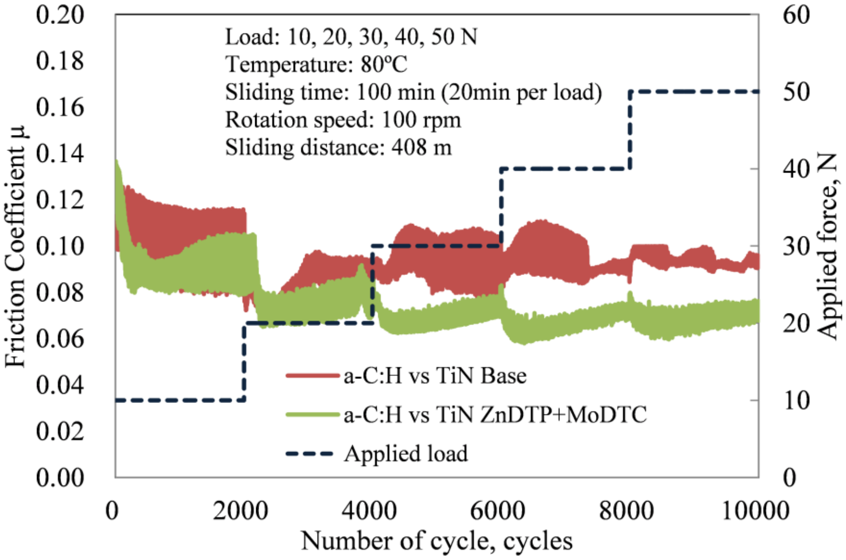

Figure 4: Friction coefficient of a-C-H-TiN tribo-pairs in Base and ZnDTP_MoDTC oils.

To make comparison of which lubricant oil gives the lowest and the highest friction coefficient, the results then concluded into one bar graph as shown in Figure 5 by taking the average of steady state friction coefficient between 4000 to 8000 cycles. As shown in the figure, a-C:H/SUJ2 tribo-pair in Base oil marked the lowest friction coefficient except for a-C:H/TiN tribo-pair in ZnDTP+MoDTC oil that recorded the second low friction coefficient, the rest tribo-pair in both type of oils logged the maximum value of friction coefficient of approximately 0.09.

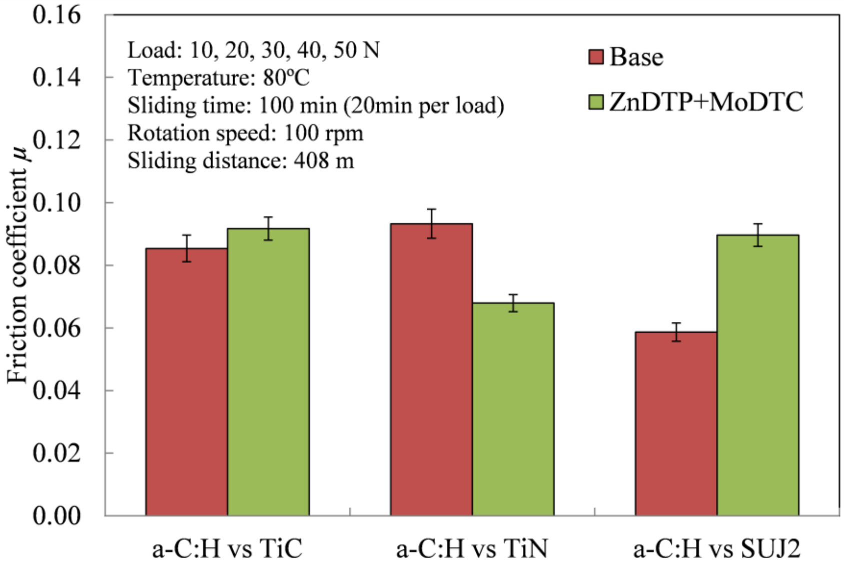

Figure 5: Friction coefficient of all three tribo-pairs in Base and ZnDTP_MoDTC oils.

3.2 Wear volume

Wear volume of a-C:H for each tribo-pair in Base and ZnDTP+MoDTC oils are shown in Figure 6. The highest and lowest wear volume of a-C:H is denoted by the same a-C:H/TiC tribo-pair in Base and ZnDTP+MoDTC oils respectively. The distinction between the two tribo-pair is compelling with 99.6% of reduction from Base to ZnDTP+MoDTC oil. Comparatively, a-C:H/TiN tribo-pair manifested high wear volume with significant 47.8% reduction from Base to ZnDTP+MoDTC oil. The a-C:H/SUJ2 tribo-pair wear volume however increased 44% higher from Base to ZnDTP+MoDTC oil.

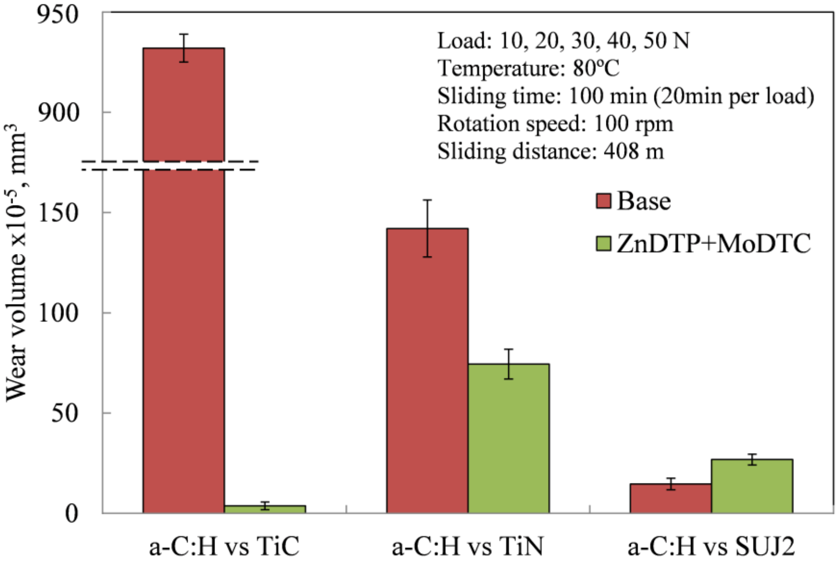

Figure 6: Wear volume of all three tribo-pairs in Base and ZnDTP_MoDTC oils.

3.3 Seizure occurrence observation on roller and disk

Figure 7 shows the optical microscope images of a-C:H/SUJ2, a-C:H/TiC and a-C:H/TiN tribo-pairs in Base oil. For the case of a-C:H/SUJ2 tribo-pair, the top surface of DLC roller wear has produced a polished mirror-like surface contributing to low friction coefficient. Because of the mating material was an uncoated SU2 steel, no sign of spalling from neither the roller nor the disk was observed. The finding suggests that no abrasive wear particles existed during the contact and as a result low wear volume obtained. Next, the arrangement of a-C:H/TiC tribo-pair disclosed the widest DLC wear width compared to the other tribo-pairs. Figure 7 (c) and (d) shows that the TiC coating on the disk peeled off and the DLC coating on the roller spalled and worn out. This led to metal to metal contact between both surfaces due to the excessive load imposed. Consequently, initial stage of seizure happened where irregular noise and vibration were noticed coming from the friction tester. TiN coated disk on the other hand, was the hardest mating material disks compared to the other two. Consequently, the DLC coating for the a-C:H/TiN tribo-pair wore heavily and spalled, causing the high wear volume of the DLC roller.

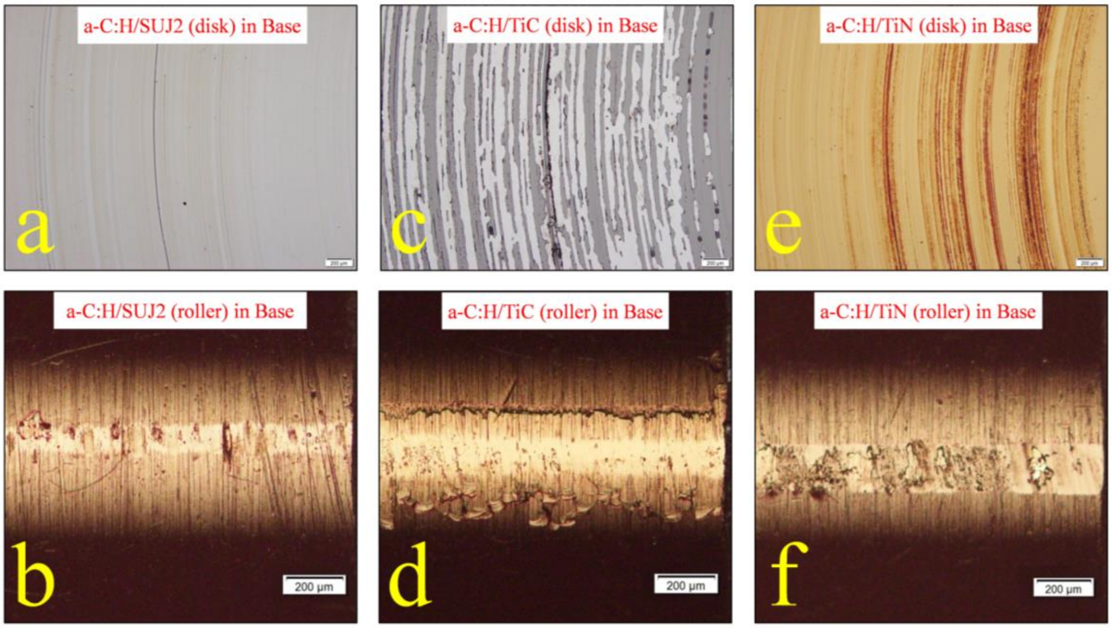

Figure 7: Optical microscope images of all three tribo-pairs Base oil.

Figure 8 shows the optical microscope images of a-C:H/SUJ2, a-C:H/TiC and a-C:H/TiN tribo-pairs in ZnDTP+MoDTC oil. As can be seen in the figure, all three tribo-pairs disk exhibited wear track with traces possibly tribofilms as a result of the rubbing between the two surfaces. And, all three tribo-pairs showed no spalling on the a-C:H rollers. Consistent with findings of past studies, wears of DLC/steel contact were especially high in MoDTC included lubricant oil (Sugimoto et al., 2013; Vengudusamy et al., 2012). This is reflected on the configuration of a-C:H/SUJ tribo-pair where high wear volume of a-C:H roller plus, blue and brownish wear pattern observed on the mating disk. High hardness of TiN disk further increased the wear volume of a-C:H/TiN tribo-pair with dark orange pattern formed on the disk wear track. a-C:H/TiC tribo-pair revealed the smallest a-C:H wear width with brownish wear pattern observed on the mating disk.

Seizure is basically attributed to exceptional micro-welding situated in the interfaces. It is inwardly overwhelmed by the nature of mating materials themselves and outwardly activated by applied stress instead of relative velocities (Ferrari and Robertson, 2000). In this study, all the three mating materials could administer seizure resistance particularly in ZnDTP+MoDTC lubricant oil. Although the Molybdenum inside the oil tends to cause high wear on DLC, it can suppress the effect of peeling off on both DLC and mating material coatings. Arrangement of a-C:H/TiC in Base oil however, came out to be the most unsuitable combinations due to the lack of anti-wear additives causing high wear and peeling off on both roller and disk coating materials that later led to the seizure occurrence.

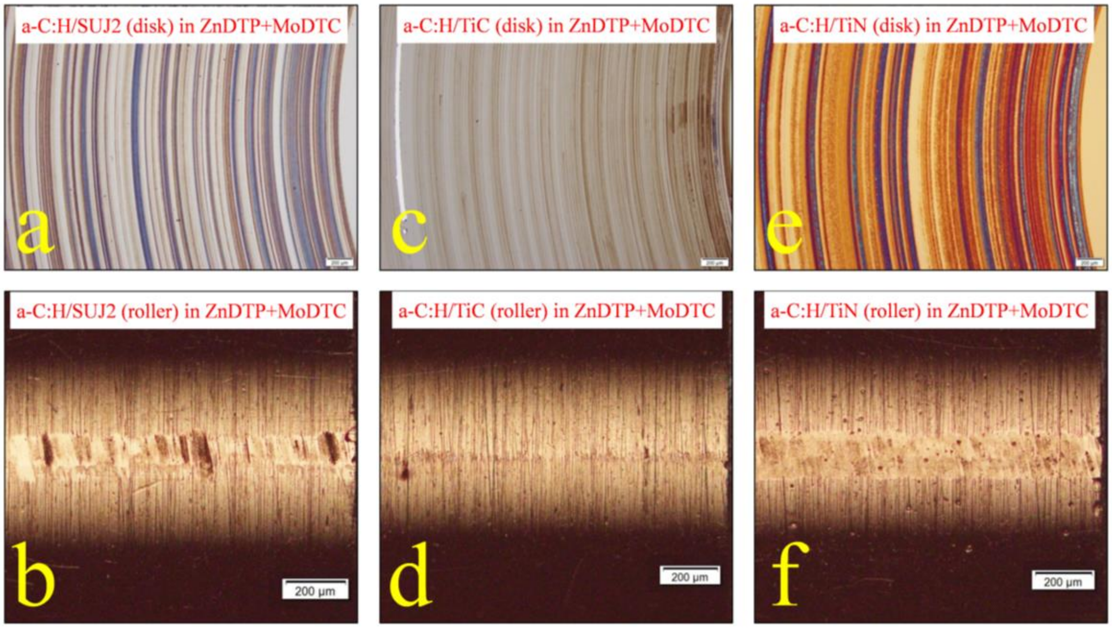

Figure 8: Optical microscope images of all three tribo-pairs ZnDTP_MoDTC oil.

3.4 Tribofilm elemental investigation

SEM element analysis area images of wear scar on roller and disk for each tribo-pair in Base and ZnDTP+MoDTC oils are shown as Figure 9 and Figure 10 respectively. An energy dispersive X-ray spectroscopy (EDS) was utilized to perform a qualitative element analysis of which elements of additives oils that appended on both roller and disk contact surfaces. Zinc, Phosphorus, Sulphur and Molybdenum were the main elements of ZnDTP and MoDTC lubricant additives. Common elements coming out from both oil additives and mating materials that were Carbon, Oxygen, Nitrogen and Iron were also monitored during the investigation. Atomic concentration values gained were then translated into bar graphs as shown in Figure 11 (a) and (b) also Figure 12 (a) and (b) to evaluate the differences in between each tribo-pair by observing the changes of lubricant additives' atomic concentration on both sliding surfaces. Oxygen atomic percentage on both roller and disk for each tribo-pair were about equal to each other and higher compared than that of Base oil. This indicates that Oxygen that coexisted in both ZnDTP and MoDTC further increased the Oxygen attachment on rollers and disks.

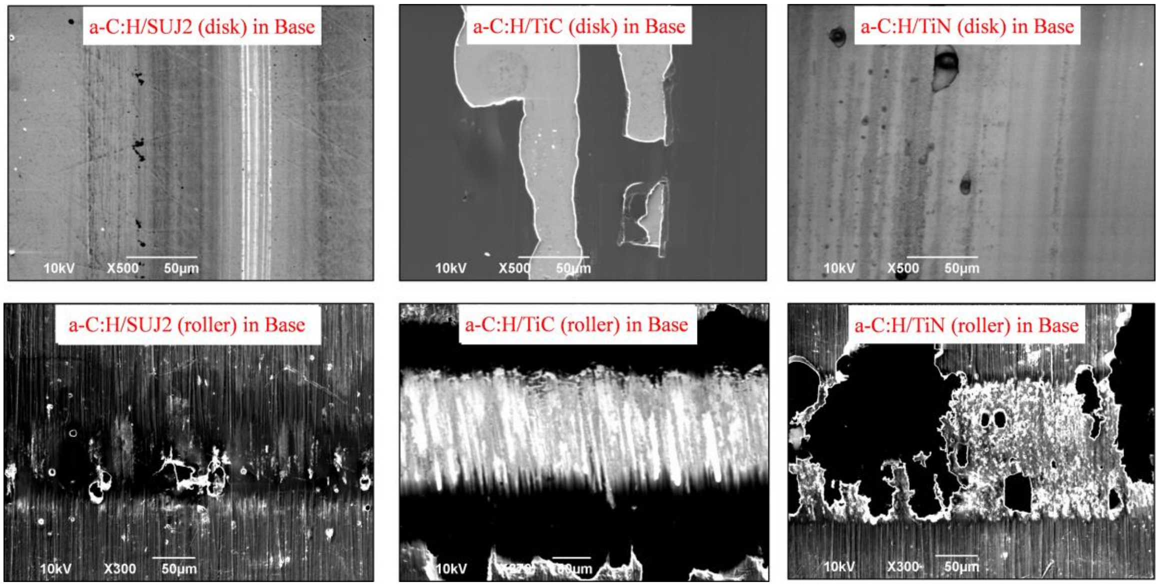

Figure 9: SEM images of EDS analysis area of all three tribo-pairs Base oil.

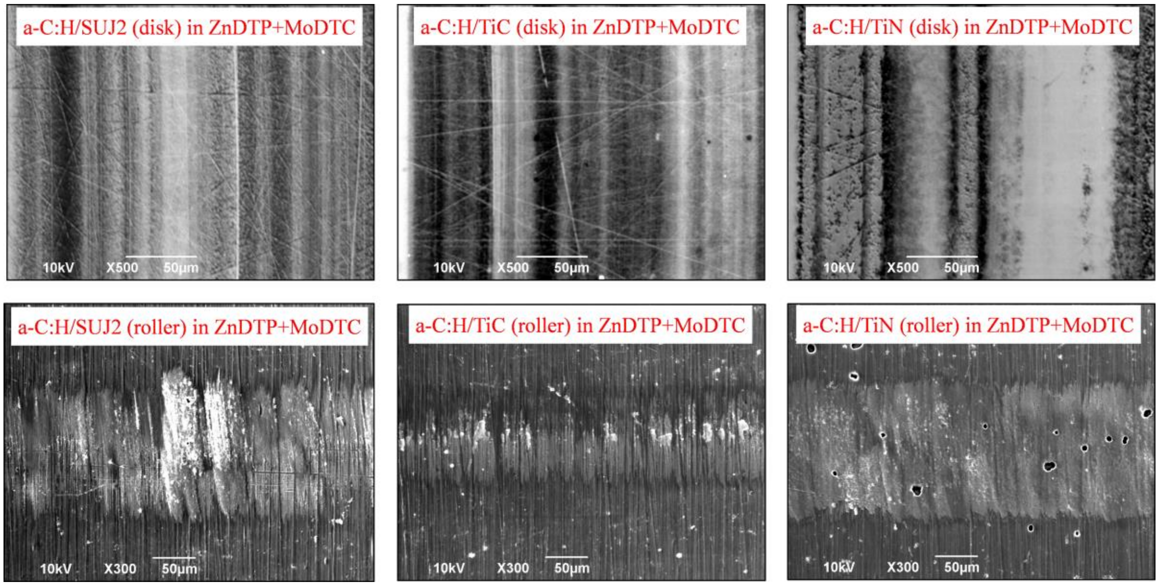

Figure 10: SEM images of EDS analysis area of all three tribo-pairs ZnDTP_MoDTC oil.

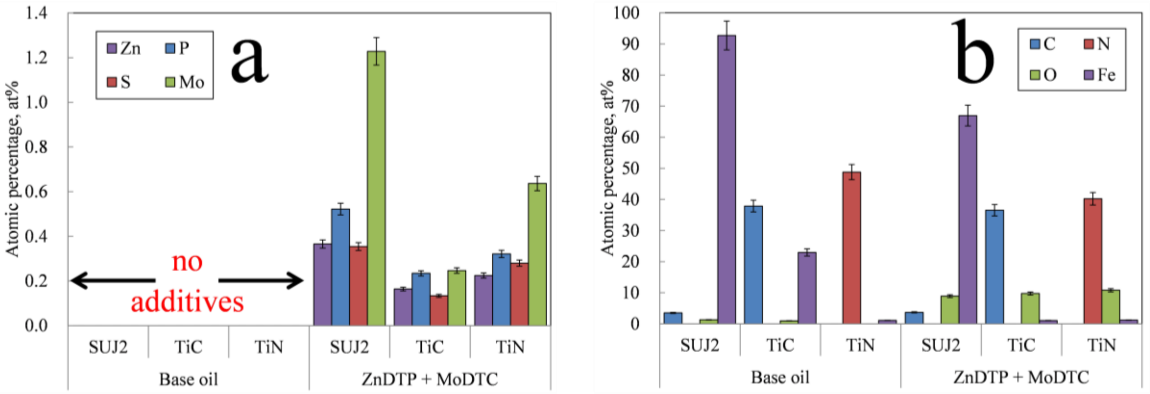

Figure 11: Lubricant additives elements analysis by EDS on mating material disks.

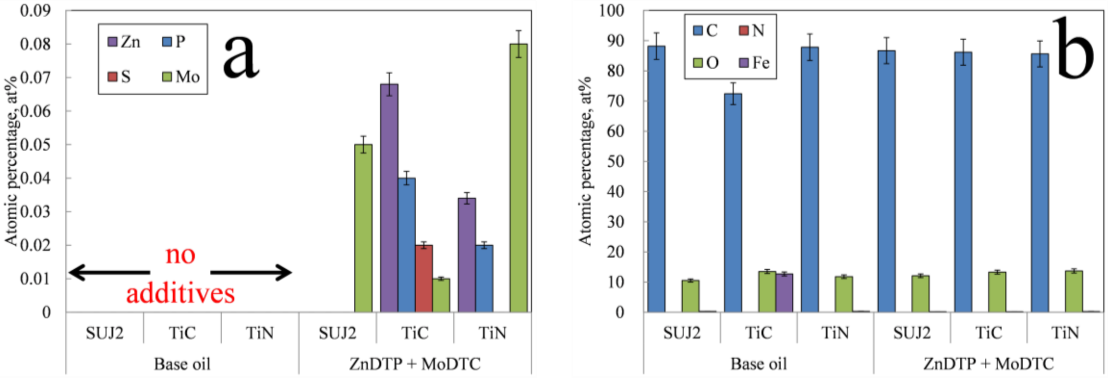

Figure 12: Lubricant additives elements analysis by EDS on a-C-H rollers.

For the case in Base oil, the findings suggest that high atomic percentage of Carbon, Iron and Nitrogen represents the value of a-C:H rollers and SUJ2, TiC and TiN disks main material atomic percentages. Generally, because of there was no lubricant additives included inside Base oil; there was no Zinc, Phosphorus, Sulphur and Molybdenum detected on each tribo-pairs disks and rollers for the case of friction test in Base oil. Oxygen detected on a-C:H/SUJ2 and a-C:H/TiC tribo-pairs roller and disk indicates oxidation occurred on both sliding wear surfaces. Except for a-C:H/TiN tribo-pair, Oxygen only discovered on DLC roller surface. Traces of Carbon possibly originated from a-C:H/SUJ2 tribo-pair DLC roller suggests that small transferred layer formed on SUJ2 disk. a-C:H/TiC tribo-pair exhibited high concentration of Iron on both roller and disk surfaces indicates that peeled TiC coating as well as worn out a-C:H coating have exposed the Iron substrate underneath both surfaces due to exponentially high wear volume for this a-C:H/TiC tribo-pair. There was also peeling off observed on a-C:H/TiN tribo-pair DLC coating but not as severe as in a-C:H/TiC tribo-pair. This was reflected by the detection of Iron on TiN disk which transferred from the DLC worn substrate particles to the TiN disk.

For the case in ZnDTP+MoDTC oil, a-C:H/SUJ2 tribo-pair signified the highest atomic percentage of Zinc, Phosphorus, Sulphur and Molybdenum on SUJ2 disk and intermediate amount of Molybdenum traced on the DLC roller. a-C:H/TiC tribo-pair on the other hand, disclosed the smallest atomic percentage of Zinc, Phosphorus, Sulphur and Molybdenum on TiC disk. The all four elements also found on the DLC roller with the least in Molybdenum and the highest in Zinc and Phosphorus. a-C:H/TiN tribo-pair marked the second highest atomic percentage of Zinc, Phosphorus, Sulphur and Molybdenum on TiN disk. Highest concentration of Molybdenum was also observed on DLC roller with traces of Zinc and Phosphorus.

Based on all the above results and description, the findings suggest that no beneficial tribofilm to reduce wear and friction produced on the sliding surfaces of the three tribo-pairs in Base oil. Because of that, a-C:H/TiC tribo-pair cannot withstand high load causing both roller and disk coatings were peeled under the given load. a-C:H/TiN tribo-pair DLC roller was also largely worn out due to the rubbings against harder TiN coated disk. a-C:H/SUJ2 appears to be the best candidate in Base oil with lower wear volume but relatively still high compared to a-C:H/TiC in ZnDTP+MoDTC. The wear of DLC under high load can further be reduced by finding the best match for a-C:H mating material in ZnDTP+MoDTC oil. The criterion is tribo-pairs that can dampen the wear accelerative effect of MoDTC and fully taking advantage on the presence of anti-wear ZnDTP inside the oil.

In ZnDTP+MoDTC, all mating material SUJ2, TiC and TiN can absorb the oil additives elements. a-C:H/SUJ2 and a-C:H/TiN tribo-pairs both revealed high atomic percentage of Molybdenum both on disk and roller which led to high wear volume on DLC roller. a-C:H/TiC tribo-pair on the contrary demonstrated smaller yet complete set of Zinc, Phosphorus, Sulphur and Molybdenum oil additives elements, found on both the roller and the disk. The finding provides evidence that TiC disk is able to accommodate a surface that attracts low concentration of oil additives elements on its surface and proved to be favourable to reduce wear of DLC coating.

3.5 Mating material coatings and tribofilms hardness and location

Because of no additives included inside Base oil, the observation and analysis of the effects of oil additives and mating materials to the formation of tribofilm was only done to the SUJ2, TiC and TiN disks in ZnDTP+MoDTC oil. Table 3 shows the results of hardness and Young's modulus of SUJ2, TiC and TiN mating material disks. All the three mating materials were subjected to indentation hardness test by a nano-indentation hardness tester to clarify the hardness of each mating material disks. The indentation load was set to 500 and 1000 µN. Lower 500 µN load was selected to verify whether the load can properly measure the hardness of the each mating materials disk surfaces. The same 500 µN was later used to determine the hardness of wear track formed on each mating material disks. The results suggest that both indentation loads can appropriately measure the hardness of each mating material disks with the highest hardness of 28 GPa for TiN, followed by TiC and SUJ2 with the hardness of 17 and 15 GPa respectively.

Figure 13 shows the nano-indentation location area of each mating material disks in ZnDTP+MoDTC oil. Ten selected indentation spot which are three on the bright spot of the wear track and the other seven on the darker spot of the wear track. The results of those ten hardness values were then converted into one single bar graph for both bright and dark spot hardness and shown in Figure 14. The results revealed that on the bright spot of the wear track, the hardness of each SUJ2, TiC and TiN were 14, 13 and 30 GPa which quite identical to the hardness values of the mating materials themselves. This suggests that on the bright spot of the wear track, there are no tribofilm formed on the area. On the darker area of the wear track however, the results varied from 3, 4 and 6 GPa for SUJ2, TiC and TiN accordingly. This indicates that the tribofilm on each wear track for each mating materials formed on darker area of wear track. Next investigation by 3D optical surface profiler was done to identify what basically these bright and darker areas of wear track represent, whether it is the ridges or grooves of the wear track.

Table 3: Hardness and Young's modulus of all three mating materials.

Mating material	SUJ2		TiC		TiN	
Indentation load, µN	500	1000	500	1000	500	1000
Hardness *H*, GPa	14.6	14.7	17.0	16.9	29.0	27.7
Hardness standard deviation, GPa	0.7	0.6	0.9	1.6	3.1	3.2
Young's modulus *E*, GPa	272.8	255.0	185.8	173.4	516.9	432.7
Young's modulus standard deviation, GPa	23.6	9.0	15.3	8.8	38.5	19.4

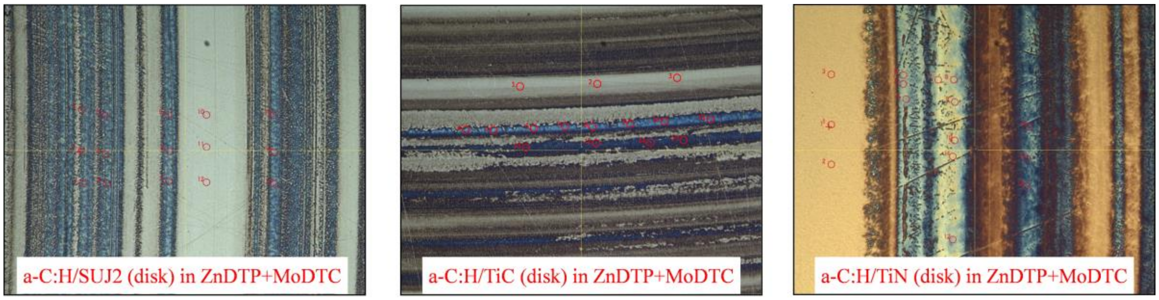

Figure 13: Nano-indentation analysis spots of all three tribo-pairs ZnDTP_MoDTC oil.

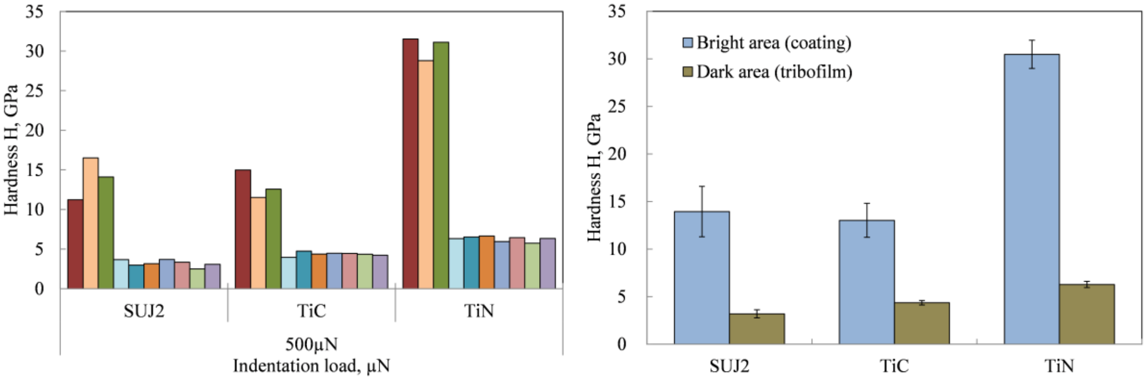

Figure 14: Hardness of tribofilm on mating materials bright and dark area.

3.6 Wear track surface morphology

Figure 15 and Figure 16 shows the 3D optical surface profiler images and surface profile graphs of SUJ2, TiC and TiN after friction test in ZnDTP+MoDTC oils respectively. Table 4 shows the SUJ2, TiC and TiN disks wear track ridge height and groove depth and also roughness gained from the surface profile graph. As shown in Figure 16 and Table 4, TiC disk wear track exhibited the lowest roughness but on the contrary, both SUJ2 and TiN disks show high roughness of wear track.

Figure 15 (a) and (c) 3D images show the high roughness and severely worn out SUJ2 and TiN disk surfaces. The above black and white wear track images revealed that the bright and dark curve represents the ridges and grooves of the wear track. TiC disk 3D image as shown in Figure 15 (b) however, exhibited low roughness and wear on its surface without no obvious ridges and grooves. The black and white wear track image evinced that the bright and dark curve formed uniformly on the smooth surface of the disk. By referring back to the hardness result in the previous section, the finding suggests that the tribofilm of ZnDTP+MoDTC oil formed on the grooves of the wear track for the mating materials of SUJ2 and TiN. TiC disk however, the composed tribofilm scattered consistently all over the smooth TiC disk surface.

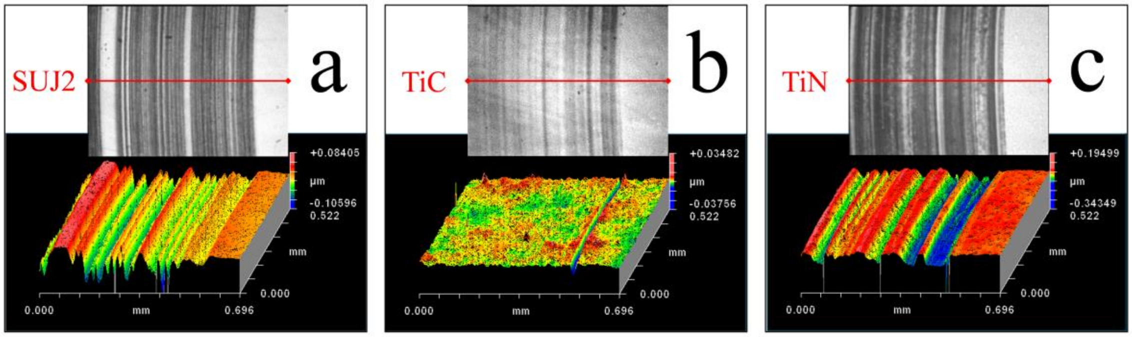

Figure 15: 3D optical surface profiler wear tracks images of all three mating material disks lubricated with ZnDTP_MoDTC.

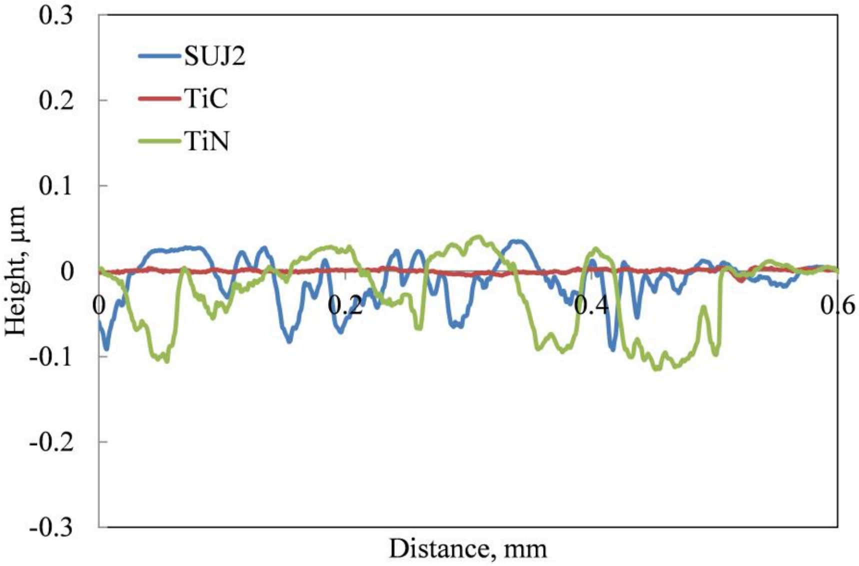

Figure 16: Surface profiles of all three mating material disks lubricated with ZnDTP_MoDTC.

Table 4: Wear track roughness of all three mating material disks lubricated with ZnDTP+MoDTC.

Mating material	SUJ2	TiC	TiN
Ridge height, nm	35.0	4.5	40.4
Groove depth, nm	92.2	11.6	115.0
Roughness, nm	23.0	2.0	37.0

3.7 Tribofilm formation mechanism on a-C:H/SUJ, a-C:H/TiC and a-C:H/TiN tribo-pairs

Previous study by de Barros' Bouchet et al. (2005) and Haque et al. (2007) claimed that ZnDTP anti-wear additive oil will decompose into several forms which are Zinc phosphate, ZnO and ZnS. The ZnDTP main wear reduction agent of zinc phosphate does not construct on high hydrogen content of hydrogenated DLC coatings, as it would only remained as ZnO/ZnS in the tribofilm. MoDTC on the other hand forms a low shear strength hexagonal MoS_2 layer that acts as multi-layer solid lubricant which gives low friction on both ferrous and nonferrous surfaces. MoO_3 also another type of tribofilm forms from MoDTC which caused high friction due to its abrasive sharp edge crystalline properties (Al Mahmud et al., 2014; Morina et al., 2003).

Figure 17 (a), (b), and (c) is illustrated to explain the mechanism of tribofilm formation on a-C:H/SUJ, a-C:H/TiC and a-C:H/TiN tribo-pairs. Figure 19 (a) indicates that higher friction coefficient and wear volume of a-C:H/SUJ2 tribo-pair in ZnDTP+MoDTC than in Base oil suggests that the tribofilm formed on both roller and disk consisted an abrasive MoO_3 that caused both sliding surface to wear out heavily. There was also Zn phosphate and ZnS present on the tribofilm however, the ability to reduce wear was not functional due to intensely high MoO_3.

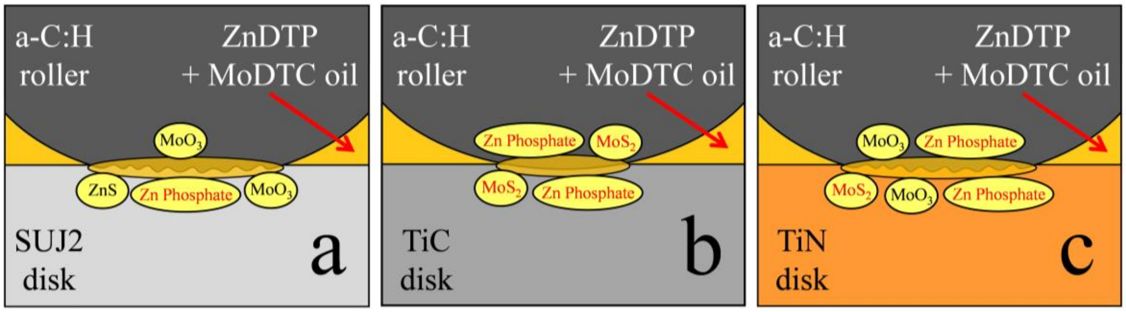

Figure 17: ZnDTP_MoDTC tribofilm formation mechanism on each mating material disks.

Although the wear pattern of a-C:H/TiN tribo-pair seemed similar to a-C:H/SUJ2 tribo-pair as shown in Figure 17 (c), the interaction was eminently different. This was due to the friction coefficient and wear volume of a-C:H/TiN in ZnDTP+MoDTC was lower than that of in Base oil. The findings suggest that tribofilm formed on roller and disk contained both MoO3 and Zn Phosphate therefore, the act of abrasive wear of MoO_3 was balanced out by the Zn phosphate. The MoS_2 found on the disk part of the tribofilm has helped to reduce the friction coefficient.

Figure 17 (b) shows the best scenario of a-C:H/TiC in ZnDTP+MoDTC oil which exhibited the least concentration of Molybdenum at% than the other two tribo-pairs. Compared to the a-C:H/TiN in Base oil, the wear of both roller and disk was remarkably low. The finding provides evidence that no MoO_3 and only MoS_2 derived tribofilm formed on both roller and disk. However, the too low concentration of MoS_2 cannot fully play the part of reducing the friction.

CONCLUSIONS

In this study, the friction characteristics of a-C:H DLC coating is evaluated by nano-indentation hardness test, 3D optical surface profiler, and EDS-SEM surface analysis equipment to understand the effect of mating materials SUJ2, TiC and TiN, and also additives added lubricant oils. The conclusions can be summarized as follows:

(a) ZnDTP+MoDTC lubricant oil is able to suppress seizure by concealing the effect of peeling off on both DLC and mating materials coatings. TiC comes out as the best material to be paired with DLC in ZnDTP+MoDTC with the lowest wear volume compared to the other tribo-pairs.

(b) a-C:H/SUJ2 and a-C:H/TiN tribo-pairs in ZnDTP+MoDTC absorbs high concentration of Molybdenum forming abrasive MoO_3 particles on both sliding surfaces causing high wear volume. a-C:H/TiC tribo-pair on the other hand formed both beneficial Zn phosphate and MoS_2 tribofilm that helps reduce the wear volume substantially and maintain the relatively low friction coefficient.

(c) The tribofilm of ZnDTP+MoDTC oil for a-C:H/SUJ2 and a-C:H/TiN tribo-pairs formed on the grooves of the wear track mating material disks. On a-C:H/TiC tribo-pair mating material disk however, the tribofilm that is useful to reduce wear scattered consistently all over the smooth TiC disk surface.

ACKNOWLEDGEMENTS

This work is supported by Council for Science, Technology and Innovation (CSTI), Cross ministerial Strategic Innovation Promotion Program (SIP), “Innovative Combustion Technology” (Funding agency: JST). The author (Mohd Taufik bin Taib) would also like to thank Universiti Teknikal Malaysia Melaka (UTeM) and the Ministry of Education Malaysia, for the financial support of his Doctoral study.

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