

Friction and Wear Mechanisms of Cu/ta-C Coatings Under PAO-4 and PAO-4 with MoDTC Lubrication

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ABSTRACT

The tribological behavior of various types of DLC coatings in formulated and non-formulated lubricants are needed for proper usage of these coatings. In this research, the friction and wear mechanism of four different DLC coatings in poly-alpha-olefin type 4 (PAO-4) with and without MoDTC were investigated using ball-on-disc tribometer. One ta-C (tetrahedral amorphous carbon) and three Cu/ta-C (copper doped ta-C) with different sputter power of 50 W, 150 W, and 200 W coatings were deposited on silicon wafers by using FCVA (filtered cathodic vacuum arc) technique for this research. The results indicate that ta-C coating on silicon wafer has the lowest average friction coefficient (CoF) and better wear resistance than Cu/ta-C coating when lubricated under PAO-4 oil with MoDTC. Cu/ta-C with sputter powers of 150 W and 200 W exhibited the highest average friction coefficient under PAO-4 oil with MoDTC. Meanwhile, the average CoF for all samples were similar under PAO-4 base oil. In terms of wear, ta-C coating showed the highest wear rate under PAO-4 base oil then followed by Cu/ta-C with sputter power of 50 W. Nonetheless, Cu/ta-C with sputter powers of 150 W and 200 W exhibited significantly low wear rate under PAO-4 base oil compared to PAO-4 oil with MoDTC.

Keywords: Friction; Wear; Cu/ta-C coating; PAO-4; MoDTC; FCVA.



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1. Introduction

In order to deliver greater wear resistance, coating materials with high hardness were developed to fulfil the demand for increased durability of mechanical components used in harsh environments. This type of coating has been demanded extensively for various engineering applications.

Diamond-like Carbon (DLC) coating is a coating that possesses properties of natural diamond with mechanical properties such as high wear resistance, high hardness, and a low coefficient of friction under dry conditions. DLC coatings are constructed by a network of different fractions of sp² and sp³ hybridized C–C and C–H bonding and are usually amorphous [1].

Plasma Enhanced Chemical Vapour Deposition (PE-CVD) is an amorphous film used to coat a protective layer from gas state to solid state on a substrate. The deposition pressures influence the structures and properties of coatings. The average thickness of the coating increased as the deposition pressure increased. According to X. Wang et al. [2], in order to promptly deposit DLC coating, a pipeline is used directly as a deposition chamber by exciting carbon-containing source gas. DLC coating has excellent properties which is a good prospect in the field of inner protective coating. Application of coatings is one of the most widely used route in order to tailor wear performance, surface morphology, fatigue strength and adhesion of substrate material without altering bulk properties of the substrate.

Many coated DLC parts are used in bigger tribological system where steel-steel contacts still exist hence the coating

performance under lubricated conditions becomes an important factor. DLC coating can be used for a variety of applications due to the modifications that can be done and its properties such as chemical inertness, infrared transparency, high electrical resistivity, high wear resistance and low friction coefficients that can be adjusted by choosing the right deposition method.

There are many deposition methods of DLC films. Filtered cathodic vacuum arc (FCVA) is one of the deposition processes used to deposit thin films for a variety of applications. This technique can filter the macroparticle during the deposition process by using the magnetic filters in order to produce tremendously high quality of ta-C coatings with 87% of sp³ bonding fraction. Hence, producing coatings with outstanding properties and are suitable to enhance the performance in corrosion and wear resistance [3].

However, the number of industrial utilisations of DLC films is limited due to their low toughness that causes the films to become brittle. Many have used metal doping to modify the microstructure of the DLC films to solve this problem. Copper is known to be a ductile metal and non-carbide former which can be used as the doping element to enhance the friction and wear mechanisms of DLC coatings under lubrication [4]. In this research, Cu was doped into ta-C films with different concentration by changing the sputter power.

Moreover, Molybdenum Dithiocarbamate or well known as MoDTC is a complex additive package that can be mixed into the base oil for better performance of lubricants.

Poly-alpha-olefin (PAO-4) base oil is one of the synthetic hydrocarbon liquids with low comparatively short molecular

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lengths and side branch densities that were established as high-performance base-stock oils for automotive and industrial applications. Thereby, this research paper aims to investigate ta-C and Cu/ta-C with different sputter power coatings on silicon wafer under PAO-4 oil with MoDTC and PAO-4 base oil lubrications.

2. System Design

In order to successfully execute the experiment, a set of systematic method is required to be set as a standard. The methods for data collection are included as well as the concepts and theories which underline the methods. The experiments procedures, concepts and theories are described in detail for further understanding on the experiment.

2.1 Deposition Process

In order to systematically study ta-C films under lubrication, one set of ta-C and three sets of Cu doped ta-C with different sputter power coated silicon wafer samples were designed. Three main deposition processes which are etching, sputtering and arc deposition were performed to fabricate the coated samples.

The silicon wafers undergo etching process by using the linear ion source (LIS) for 10 minutes to remove the impurities on the surface of the silicon wafers beforehand. Argon gas is used as the reactant gas with a flow of 18 sccm. The voltage supply used was 1.7kV which yielded a 260 mA of current.

After the etching process, it was then continued with the sputtering of Cu for 30 minutes to deposit a buffer layer on the surface of the substrate to enhance the adhesion strength of the coating layer. Argon gas was used as the reactant gas with a flow of 25sccm and a power supply of 250W.

Then, as for the coating layer, two types of coatings were designed which are ta-C and Cu doped ta-C coatings in this research. There were two processes involved in this coating process which are arc deposition and sputter processes. Both coatings have the same thickness which are 1 μ m but different deposition time. Arc deposition process was used to deposit the ta-C film on the substrates, meanwhile, arc deposition and sputter processes were used simultaneously to produce Cu doped ta-C film. The arc deposition process was conducted under duct bias voltage of 10 V with a reference current of 60 A in a 45°-bend magnetic FCVA system for both types of coatings.

For the Cu doped ta-C coating, it was conducted with argon gas as the source of reactant gas with a flow of 25 sccm. The power supply used varies for the Cu doped ta-C coating as there were three different samples designed. There are four samples that were designed with their own specific condition where one sample is for ta-C coating and the other three samples are for Cu/ta-C coating with variation of sputter power as shown in Table 1 below which reveals the coating layer structure of the substrate.

Table 1 The Type of ta-C and Cu Doped ta-C Coatings

Thickness	Sample #1	Sample #2	Sample #3	Sample #4
1 μm	ta-C	Cu/ta-C (50W)	Cu/ta-C (150W)	Cu/ta-C (200W)
0.3 μm	Cu Buffer Layer			
Silicon wafer (100)				

2.2 Tribological Test

The sliding friction test was carried out by using a ball-on-disk tribometer to determine the friction and wear properties of the coating film.

The counter specimen used was silicon nitride (Si₃N₄) ball of 4 mm radius. Prior to the experiments, the ball was cleaned in an ultrasonic bath using ethanol for 3 minutes to remove surface contaminants on the ball. The zig used to hold the silicon wafer was also cleaned by using ethanol. Then, the silicon wafer was attached to the zig with a glue.

Four types of samples with different deposition parameters were used for this experiment. The ball is reciprocated for 1 hour and 39 minutes against the sample with an applied load of 20 N, a linear speed of 84 mm/s and a stroke length of 4 mm at ambient temperature of 18-23 °C with humidity of 10-20 % for a total distance of 502654.82mm of 20000 cycles under two types of lubrications which are PAO-4 base oil and PAO-4 oil with MoDTC.

The coefficient of friction (CoF) was monitored as a function of the number of cycles. The results of friction coefficient were obtained by referring to the real time display of test information in computer software of tribometer. The average friction coefficient of each tested sample was computed and plotted in a graph for both lubrications. The wear rate for each tested sample was also recorded and plotted in a graph. Then, the images of the wear scar of the counterpart material and the wear track on the coating surface were observed by using confocal microscopy.

3. Results and Discussions

The results and discussions are presented in four subsections according to coating characterization, friction behavior, wear behavior and surface analysis.

3.1 Coating Characterization

The coating characterization was distinguished by comparing results from the previous study. Fig. 1 shows the Cu concentration and the average growth rate of the films as a function of the sputtering current of the magnetron sputtering unit. The Cu concentration increased with the sputtering current. In this research, the sputtering power was adjusted to control the Cu concentration in films. The sputtering current increased with the sputtering power, indicating that the Cu concentration increases when higher sputtering power is used.

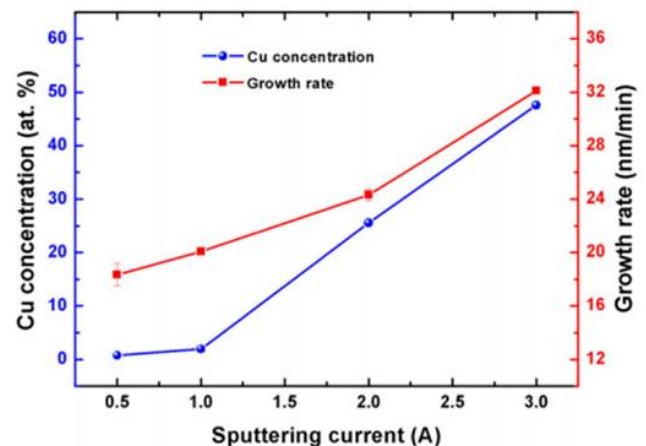


Fig. 1 Cu concentration and growth rate of the Cu-DLC films as a function of the sputtering current. (Source: [4])

Moreover, the residual stresses of the films were measured as a function of the Cu concentration, as shown in Fig. 2. Based on previous study, pure DLC film has higher residual stress which is about 2.7 GPa while the residual stress for Cu-DLC film is lower with 1.4 GPa when Cu 0.74 at.%. The residual stress of the films increases with increasing Cu concentration and starts to reduce when Cu concentration is 25.6 at.% which can be seen from Fig. 3. Thereby, it is believed that the residual stresses in this research study are similar to the previous study whereas it increases as the sputtering power increases.

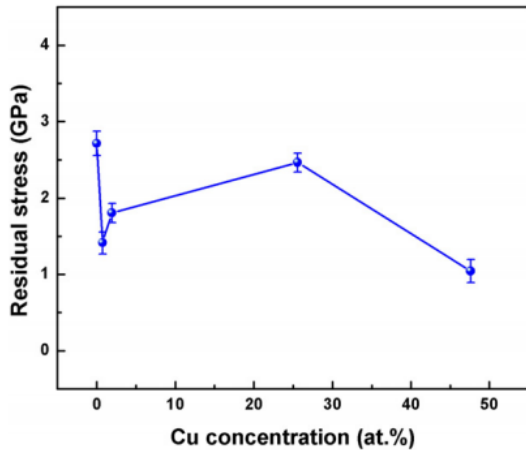


Fig. 2 Residual stress of the Cu-DLC films as a function of Cu concentration. (Source: [4])

The graph pattern of the film hardness and elastic modulus at different Cu concentrations were similar to the residual stress as both the mechanical properties and residual stress of the DLC films were highly dependent on the sp³-C bonding structures [4]. The film shows lower hardness compared to pure DLC at lower concentration of Cu. This result is homogenous to the previous research conducted by Hojun Ryu et al. [5], which showed that those N-doped ta-C films have lower hardness than that of non-doped ta-C film. Thus, it can be concluded that non-doped ta-C has higher hardness compared to Cu-doped ta-C in this study.

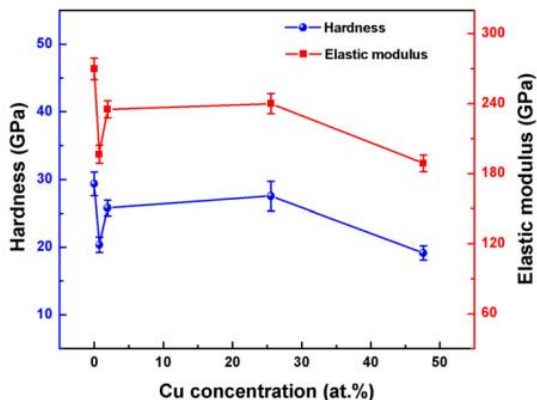


Fig. 3 Hardness and elastic modulus of the Cu-DLC films as a function of Cu concentration. (Source: Dai et al. 2015)

3.2 Frictional Behaviors Under PAO-4 Base Oil and PAO-4 Oil with MoDTC Lubrications

This sliding friction test was carried out by using ball-on-disc tribometer to determine the friction and wear properties of the coating film under two different types of lubrication which are PAO-4 base Oil and PAO-4 Oil with MoDTC.

Normally, PAO is known to have better lubricity hence the reduced friction coefficient. Moreover, the friction reduction might be due to the formation of MoDTC derived tribofilms MoS₂ and surface graphitization [6], [7]. The addition of MoDTC further improve the friction performance. According to Zahid et al. [8] the surface energy is improved when DLC coatings are doped with metals as the chemical reactivity of the coating with lubricant is increased due to formation of active sites.

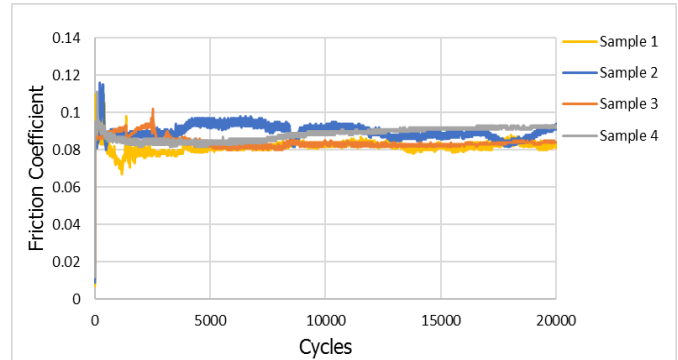


Fig. 4 Frictional behavior of ta-C and Cu-doped ta-C coatings under PAO-4 Base Oil

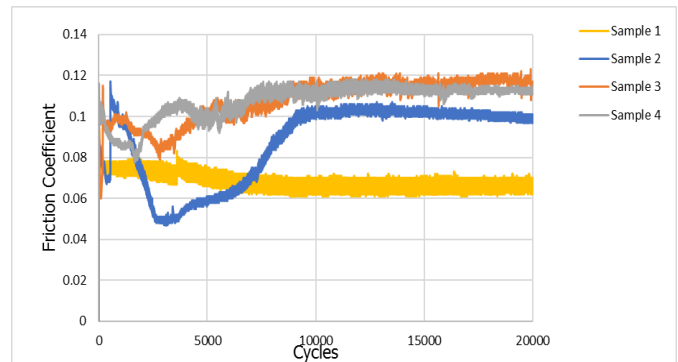


Fig. 5 Frictional behavior of different type of ta-C and Cu-doped ta-C coating under PAO-4 with MoDTC

Fig. 4 shows the behavior of the CoF for ta-C and Cu doped ta-C coating in PAO-4 base oil lubrication. In the case of ta-C coating, the coefficient of friction was the lowest and showed stable behavior, but it was confirmed that the coefficient of friction was lowered as the UBM (Unbalanced Magnetron) power for Cu doping increased. This is due to the high hardness characteristics of the ta-C coating film, and it is believed that the contact area is relatively smaller than that of Cu doping ta-C. The mechanical properties of the ta-C coating used in the experiment can be confirmed from the previous results [9]. In addition, the Cu-doped ta-C coating exhibits a high coefficient of friction behavior when contacting the mating material with the two materials ta-C and Cu during friction.

In addition, as shown in Fig. 5, when PAO-4 base oil with MoDTC was used, the ta-C coating still showed the lowest coefficient of friction, but the Cu doping ta-C showed a high friction behavior of 0.08 ~ 0.1 or more. However, it can be seen that the friction coefficient characteristics increase as the Cu sputter power increases.

The Cu sputter power of 50 W showed the lowest coefficient of friction among Cu-doped ta-C, which is believed to be due to the doping of a small amount of Cu compared to 150 W and 200 W.

3.3 Wear Behaviors Under PAO-4 Base Oil and PAO-4 Oil with MoDTC Lubrications

The wear behavior of disk and counter materials was investigated based on the analysis of frictional behavior of ta-C coating and Cu doped ta-C coatings. Fig. 6 and Fig. 7 show the amount of wear of the disk and the counter materials (Si₃N₄) used in the PAO-4 base oil and PAO-4 oil with MoDTC lubrications.

In the case of ta-C coating, the wear of disk and Si₃N₄ ball was highest in PAO environment. This is believed to be due to the simultaneous wear of the counterpart material and disk during friction due to the high hardness characteristics of the ta-C coating without the chemical effect of oil. In addition, it can be understood that carbon-based particles wear due to abrasion have a lubrication effect at the contact interface, so that the amount of wear is high, but the coefficient of friction is low.

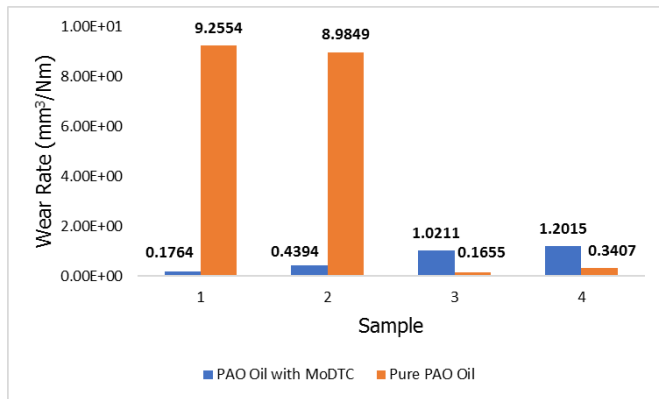


Fig. 6 To compare with wear rate of coatings under the PAO-4 base Oil and PAO-4 with MoDTC

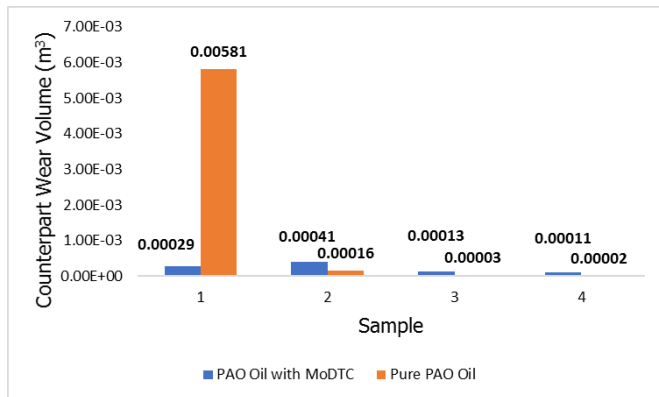


Fig. 7 To compare with wear volume of Counter materials (Si₃N₄ ball) under the PAO-4 base Oil and PAO-4 with MoDTC

However, in the case of Cu doped ta-C coatings, when the Cu sputtering power was 50 W, the disk wear decreased slightly, but at 100 W and 200 W, the wear of the counterpart material decreased sharply. This phenomenon shows that the coating with higher sputter power has better wear resistance when lubricated with PAO-4 base oil.

More interestingly, in the PAO-4 oil with MoDTC lubrication, low wear amount was observed in Cu doped ta-C coatings including ta-C coatings and counterpart materials. In addition, as the Cu sputtering power increases, the amount of disk wear increases, and the lowest disk wear behavior is seen in the general ta-C coating. This might be due to tribo-chemical reaction in Si₃N₄ that resulted in low wear under the boundary lubrication [10].

In this research, the addition of MoDTC in PAO-4 base oil showed positive effects on the wear performance. The wear rate in both ta-C/Si₃N₄ and Cu/ta-C/ Si₃N₄ contacts displayed similarly same behaviour as it resulted low wear under PAO oil with MoDTC lubrication. The wear rate for all types of DLCs in PAO oil with MoDTC are low suggesting that even with the presence of MoDTC, the wear rate is rather controlled by the nature of the DLC itself than the MoDTC [8].

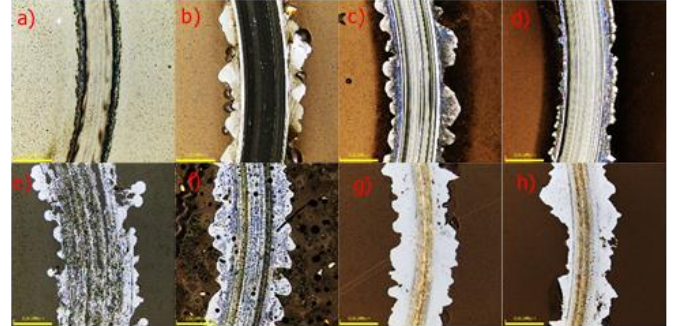


Fig. 8 Wear track of coatings for a) ta-C b) Cu-doped ta-C (50W) c) Cu-doped ta-C (150W) and d) Cu-doped ta-C (200W) under PAO-4 Oil with MoDTC and e) ta-C f) Cu-doped ta-C (50W) g) Cu-doped ta-C (150W) and h) Cu-doped ta-C (200W) under PAO-4 Base Oil

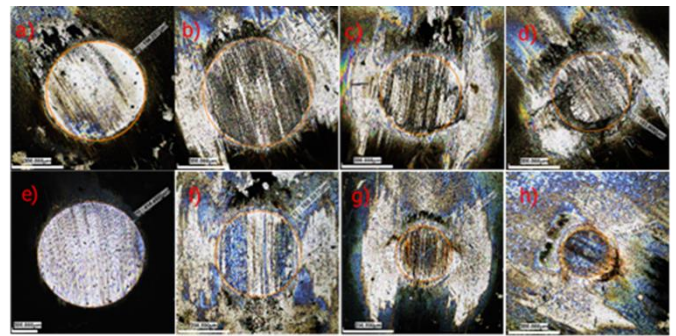


Fig. 9 Wear scar of the counterpart material for a) ta-C b) Cu-doped ta-C (50W) c) Cu-doped ta-C (150W) and d) Cu-doped ta-C (200W) under PAO-4 Oil with MoDTC and e) ta-C f) Cu-doped ta-C (50W) g) Cu-doped ta-C (150W) and h) Cu-doped ta-C (200W) under PAO-4 Base Oil

3.4 Surface Analysis

The wear track image (Fig. 8) on the coating surface and the wear scar of the counterpart material (Fig. 9) were observed by using the laser scanning confocal microscope. It can be observed that the wear tracks on the coating surface of all samples are severely damage when lubricated with pure PAO oil. The wear width of Sample 1 (ta-C coating) in pure PAO oil is significant due to abrasive wear. This evidence of abrasive wear can be evidence in the friction and wear phenomena of the ta-C coating as mentioned above.

Meanwhile, the wear track on the coating surface of Sample 1 (ta-C coating) is the smoothest when lubricated under PAO oil with MoDTC. This might be due to less formation of wear debris in ta-C coating than Cu/ta-C coating. In Fig. 10 and Fig. 11, the size of wear scar of the counterpart material reduced as the sputter power increased in Cu/ta-C/Si₃N₄ contacts for both types of lubrications. It can be observed that the size of wear scars of counterpart material for Samples 2 (Cu/ta-C, 50 W), 3 (Cu/ta-C, 100 W) and 4 (Cu/ta-C, 150 W) are smaller under pure PAO oil lubrication compared to PAO oil with MoDTC. This might be

due to the formation of tribo-film on the counterpart ball. However, it is the opposite in ta-C/Si₃N₄ contacts whereas size of wear scar of counterpart material is smaller under PAO oil with MoDTC lubrication compared to pure PAO oil.

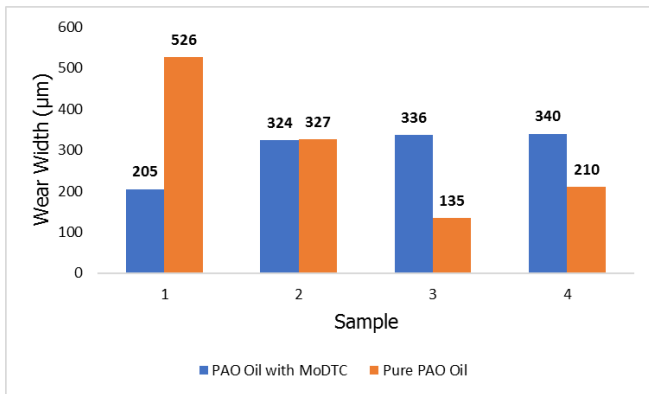


Fig. 10 Width of wear track of the coatings

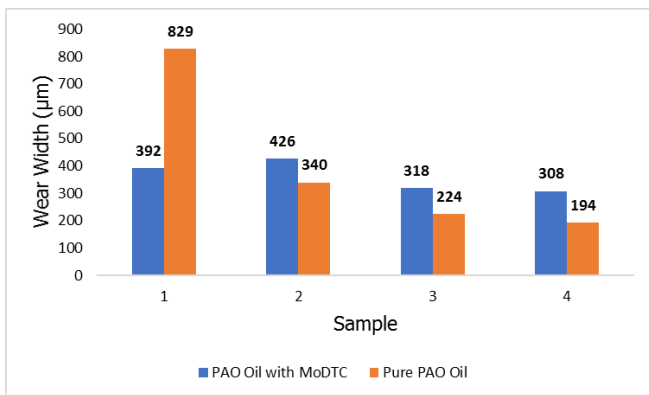


Fig. 11 Width of wear scar of the Si₃N₄ balls

4. Conclusion

In this research, silicon wafers were coated with ta-C and Cu/ta-C coating with different sputter power. The sputter powers of 50 W, 150 W and 200 W were used for the Cu/ta-C coatings. All samples were examined for its frictional and wear behaviour when lubricated with two types of lubrications which are PAO-4 base oil and PAO-4 oil with MoDTC.

The results show that:

- i. Cu/ta-C coating with lower sputter power has smaller friction coefficient but ta-C coating has the smallest when lubricated under PAO-4 oil with MoDTC.
- ii. Cu/ta-C coating with higher sputter power has better wear resistance under PAO-4 base oil lubrication.
- iii. The size of wear scar of the counterpart material reduced as the sputter power increase in Cu/ta-C/Si₃N₄ contacts for both types of lubrications.

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