



Tribological Behaviour of W-DLC against an Aluminium Alloy Subjected to Lubricated Sliding

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ABSTRACT

Diamond like carbon (DLC) coatings mitigate aluminium adhesion and reduce friction under the ambient conditions but their tribological behaviour under lubricated sliding need to be further investigated. In this study, tribological tests were performed to evaluate the friction and wear characteristics of W-DLC and H-DLC coatings sliding against an aluminium alloy (319 Al) under unlubricated (40 % RH) and lubricated sliding conditions. For unlubricated sliding, coefficient of friction (COF) values of H-DLC and W-DLC were 0.15 and 0.20. A lower COF value of 0.11 was observed when W-DLC was tested using lubricant oil incorporating sulphur while the H-DLC's COF remained almost unchanged. The mechanisms responsible for the low friction of W-DLC observed during lubricated sliding were revealed by studying the compositions of the coating surfaces and the transfer layers formed on 319 Al. Micro-Raman spectroscopy indicated that the transfer layers formed during lubricated sliding of W-DLC incorporated tungsten disulphide (WS₂).

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1. INTRODUCTION

Diamond-like carbon (DLC) coatings are known for their low coefficient of friction (COF) and low wear rate against aluminium compared to the other coatings (i.e. CrN, TiN) tested under the ambient conditions [1-6]. Studies showed that the hydrogen content of the DLC coatings influences friction and wear properties of DLC coatings [7-10]. The hydrogenated DLC (H-DLC) coatings show the lowest COF in vacuum, due to the hydrogen terminated surface carbon atoms that passivate carbon bonds at the interface. Otherwise the covalent σ carbon atoms lead to high friction in vacuum as in the case of non-

hydrogenated DLC (NH-DLC) coatings [11,12]. The NH-DLC showed low friction and wear in water [13], ethanol and humid atmospheres [14,15]. The dissociation of the water molecules in the surrounding atmosphere and OH passivation of the NH-DLC surface as well as the carbonaceous transfer layer formed on the counterface are the mechanisms that lead to the observed low COF. A recent study [14] on NH-DLC coatings tested against Ti-6Al-4V in ethanol showed an almost complete elimination of the running-in friction and generation of a low and steady state COF indicating that H and OH generated from ethanol dissociation would passivate NH-DLC surface effectively.

Kano et al. [16] reported a very low COF of 0.03 for NH-DLC sliding against itself during lubricated tests that used ester based lubricant glycerol mono-oleate (GMO). The formation of an OH-terminated carbon surface was detected by time of flight secondary ion mass spectroscopy (ToF-SIMS). The low COF was attributed to the weak Van der Waals forces between the two carbon surfaces passivated by OH groups derived from the GMO lubricant. Matta et al. [17] performed sliding experiments in which NH-DLC sliding against itself was lubricated with glycerol in the presence of hydrogen peroxide resulting in a COF value of 0.03. Similar to the previous studies it was found that carbon surfaces were terminated by OH. These studies suggested that lubricants that can provide OH (GMO or glycerol/H₂O₂) are capable of reducing friction by passivation of NH-DLC. The effect of alcohol blended lubricants was explored by Hu et al. [18] who showed that 2-ethylhexanol mixed with ZDDP additives in the engine oil increased its load-carrying capacity. The authors explained the improved anti-wear behaviour of 2-ethylhexanol (up to 8 wt. %) and ZDDP (in base oil) mix against 52100 steel by considering the adhesion of polar hydroxyl groups to the metal surface and formation of a protective film. Podgornik et al. [19] studied the friction behaviour of metal doped i.e. W containing DLC against itself in polyalphaolefin (PAO) oil with a sulphur based additive. The authors observed a low COF of 0.15, which was attributed to the formation of WS₂ in sliding interface. The DLC coated components are being considered for use in powertrain applications where lubricated sliding with Al-Si surfaces is important [20-22].

The current study investigates the friction and wear of a W-DLC coating sliding against an engine grade aluminium alloys in oil enriched with sulfur additive. The micromechanisms of wear and friction reduction are discussed with special emphasis placed on the role of tribolayer formation.

2. EXPERIMENTAL APPROACH

The H-DLC coatings were deposited on M2 type steel substrates, using an unbalanced magnetron sputtering system. The physical vapour deposition (PVD) system had one chromium

target and two graphite targets. First, a 0.10 µm Cr layer was deposited to promote adhesion with the steel surface. Subsequently the power to the Cr target was decreased gradually while increasing the power to graphite targets to obtain a 1.50 µm thick H-DLC coating. Butane precursor gas was used to incorporate 40 at. % of hydrogen determined by elastic recoil detection (ERD) analyses. The hardness and elastic modulus of the coating were measured using a Hysitron TI 900 triboindenter equipped with a Berkovich nano-indenter. Accordingly, the hardness and the elastic modulus of H-DLC were 11.40 GPa and 103 GPa.

The W-DLC coatings were deposited on M2 steel coupons using a cathodic arc PVD system. The substrate surfaces were first cleaned by Ar glow discharge, and then a Cr interlayer was deposited. The hardness of the W-DLC coating was 8.70 GPa, and its elastic modulus was 104 GPa. The W content of the coating was 20 % and the H was kept < 2 %. The details of coating microstructure can be found in [23].

Sliding wear tests were conducted using a pin-on-disk type tribometer. Pins with a 4 mm radius, made from the 319 Al (Al-6.5% Si) alloy were tested against both H-DLC and W-DLC coated coupons. Sliding tests were carried out under unlubricated condition in an ambient air (40 % RH) as well as under boundary lubricated condition, at 0.12 m/s linear speed and a constant normal load of 5.00 N for sliding cycles up to 5000. The lubricants (LubriFluid, Vogel, Germany) used in sliding tests contained sulfur (S) and phosphorus (P) additives, as determined by a JEOL 300MHz nuclear magnetic resonance (NMR) spectrometer.

Following the sliding tests, the 319 Al pin contact surfaces were examined by SEM and their compositions were analyzed using energy dispersive spectroscopy (EDS) and micro-Raman spectroscopy. The EDS spectra were recorded using an FEI Quanta 200 FEG SEM equipped with an EDAX SiLi detector spectrometer. The Raman spectra of the transfer layers were obtained using a 50 mW Nd-YAG solid state laser (532.00 nm excitation line) through the 50 × objective lens of a Horiba Raman micro-spectrometer. The volumetric wear losses of the coatings were calculated from the volume of the removed material by measuring the cross-sectional area

at eight different locations along the wear track by an optical surface profilometer (Wyko NT 1100).

3. RESULTS

Figure 1 shows the COF values of W-DLC and H-DLC coatings plotted as a function of number of revolutions for unlubricated sliding. COF values for lubricated sliding are plotted in Figure 2. During unlubricated sliding, the COF of W-DLC initially increased to a high value of 0.62, then decreased to a low value of 0.19 for a few cycles. Following this running-in period a low average value of 0.20 ± 0.01 was attained. The duration of the running-in period for H-DLC was 4000 revolutions during unlubricated sliding longer than that of the W-DLC. The COF of H-DLC rose to 0.27 and then decreased to a low COF of 0.15 ± 0.01 for the last 1000 revolutions. In summary, the H-DLC showed both lower running-in and steady state COF values compared to the W-DLC during unlubricated sliding tests.

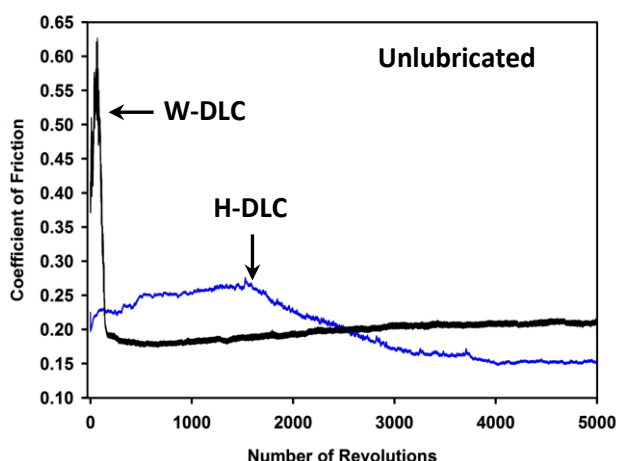


Fig. 1. Variations of coefficient of friction values with the number of revolutions for H-DLC and W-DLC coatings tested against 319 Al under ambient conditions.

Running-in COF values decreased during lubricated tests for both H-DLC and W-DLC as expected. However, for W-DLC a further 25 % decrease in both running-in and steady state COF values were observed in comparison to the H-DLC, Fig. 2. The COF of W-DLC initially increased to 0.13 at the 1st cycle and then decreased to 0.11 at the 64th cycle. The COF once more rose to 0.13 at the 425th cycle and maintained an average value of 0.11 ± 0.01 for the last 3000 revolutions.

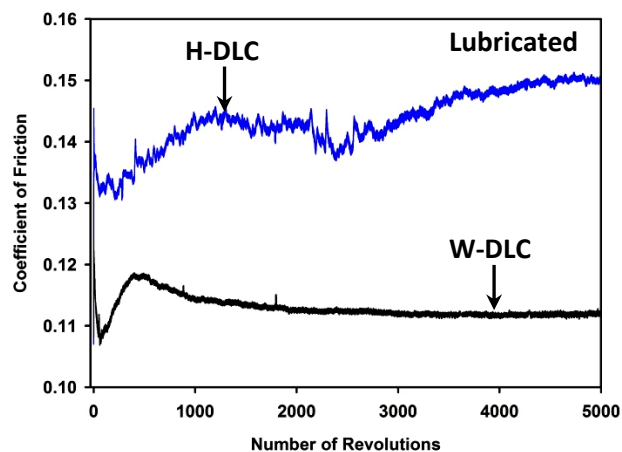


Fig. 2. Variations of coefficient of friction values with the number of revolutions for H-DLC and W-DLC coatings tested against 319 Al under lubricated condition.

The COF observed for H-DLC was not only higher but also less stable compared to W-DLC. Higher variations of COF values for the entire test range are noted in Fig. 2, and an average COF value of 0.14 ± 0.06 was measured.

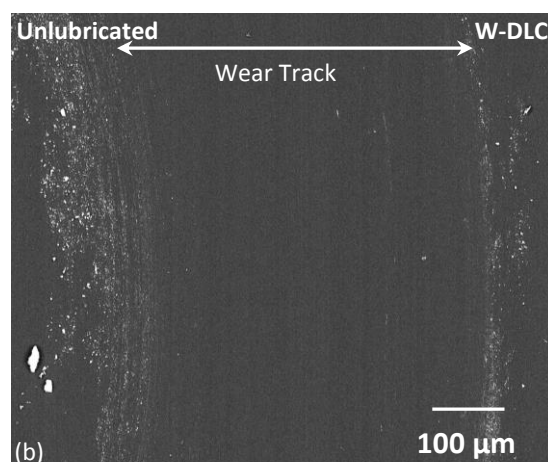
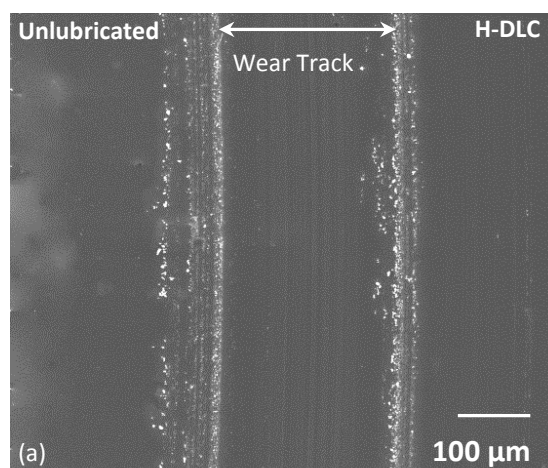


Fig. 3. Typical secondary electron images of wear tracks formed on: (a) H-DLC and (b) W-DLC surfaces when tested against 319 Al during unlubricated sliding.

The wear tracks formed on the H-DLC and W-DLC surfaces were examined using SEM and the representative SEI images are presented in Figs. 3a and 3b. No notable aluminium transfer occurred either to H-DLC or W-DLC during unlubricated sliding. However, a wider wear track of 536 μm was observed for W-DLC compared to the 251 μm wide wear track formed on the H-DLC surface. Thus, for W-DLC higher wear accompanied by high COF during unlubricated.

An opposite trend was observed when the lubricated tests were considered (Figs. 4a and 4b). The H-DLC's wear track was wider (321 μm) than that of the W-DLC (166 μm).

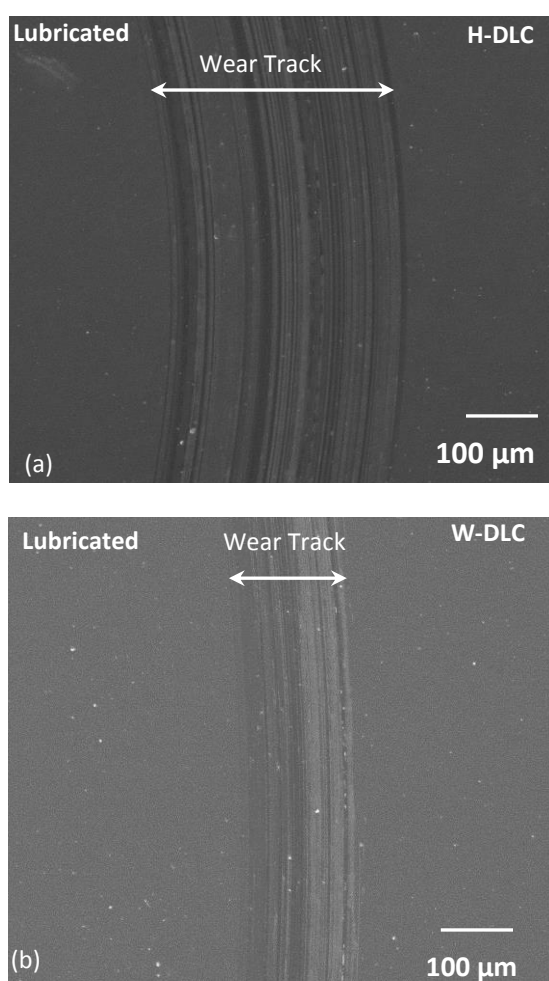


Fig. 4. Typical secondary electron images of wear tracks formed on the (a) H-DLC and (b) W-DLC surfaces when tested against 319 Al during lubricated sliding.

The wear rates of H-DLC and W-DLC coatings were measured using an optical surface profilometer. For H-DLC, the normalized wear rate was $0.31 \times 10^{-5} \text{ mm}^3/\text{Nm}$ for unlubricated sliding, and $0.73 \times 10^{-5} \text{ mm}^3/\text{Nm}$ under the

lubricated condition. A higher wear, $0.51 \times 10^{-5} \text{ mm}^3/\text{Nm}$ was observed for W-DLC compared to the H-DLC for unlubricated sliding. However, a drastic reduction in wear rate of W-DLC to $0.11 \times 10^{-5} \text{ mm}^3/\text{Nm}$ was observed when this coating was subjected to lubricated sliding. This is consistent with the low COF of the W-DLC coating under the lubricated condition (Fig. 2).

The morphologies of 319 Al pin contact surfaces were examined by SEM and their composition was determined by EDS. It was observed that the tips of the pins were covered with patches of transferred materials. Figure 5a shows the sliding surface of 319 Al pin for the unlubricated test conducted against H-DLC. It can be seen that the tip was covered by a transfer layer. The corresponding EDS elemental maps show the distributions of C and O (Figs. 5b and 5c). It can be concluded that the transfer layer was rich in C (Fig. 5c) such that a carbonaceous layer was formed [24,25].

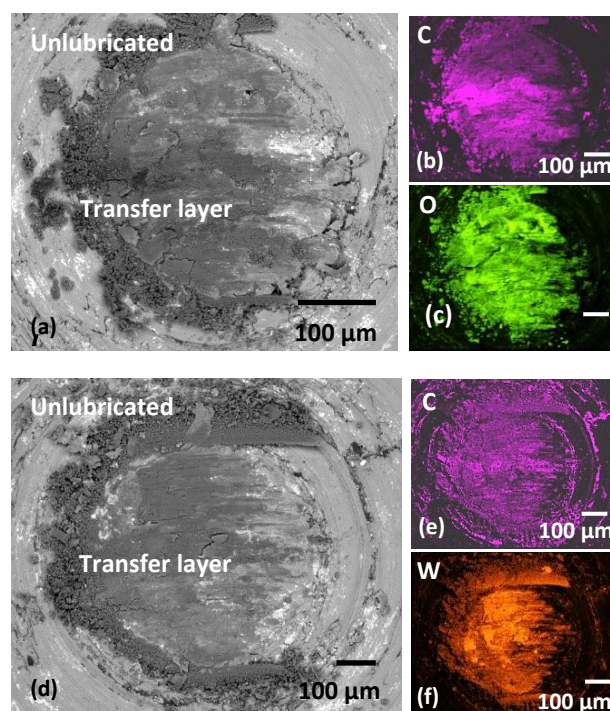


Fig. 5. (a) Secondary electron image of the 319 Al pin surface taken after unlubricated sliding against H-DLC coating; The elemental EDS maps taken from (a) are for (b) C and (c) O (d) Secondary electron image of 319 Al pin surface after the unlubricated sliding against W-DLC coating; The elemental EDS maps taken from (d) are for (e) C and (f) W.

A transfer layer (Fig. 5d) was also observed when the tests were conducted against W-DLC. In addition to C (Fig. 5e) and O (not shown), a

significant amount of W was observed in the transfer layer on the counterface in contact with the W-DLC coating (Fig. 5f).

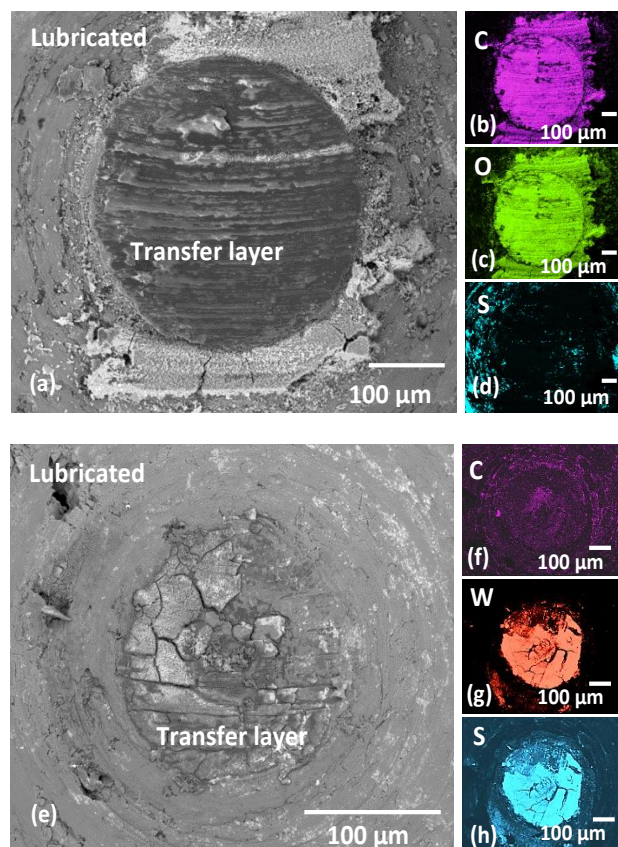


Fig. 6. (a) Secondary electron image of the 319 Al pin surface taken after lubricated sliding against H-DLC coating; The elemental EDS maps taken from (a) are for (b) C, (c) O and (d) S (e) Secondary electron image of 319 Al pin surface after the lubricated sliding test against W-DLC coating; The elemental EDS maps taken from (e) are for (f) C, (g) W and (h) S.

Figure 6a shows the sliding surface of 319 Al pin after a lubricated test conducted against H-DLC. A C and O-rich transfer layer was formed on the 319 Al pin (Figs. 6b and 6c). Furthermore there was evidence of sulfur as indicated by the S map, mostly towards the periphery of the contact area (Fig. 6d). A carbonaceous transfer layer enriched in W was observed on the sliding surface of 319 Al tested against W-DLC in lubricated conditions as shown in Figures 6e to 6g. Presence of S was the notable feature of the transfer layer on the counterface run against W-DLC during lubricated tests. This observation suggested the possibility of formation of WS_2 compound on the counterface as discussed in Section 4.

4. DISCUSSION

Both H-DLC and W-DLC coatings exhibited rather low COF values under unlubricated sliding despite the fact that a high running-in COF was observed for W-DLC. This period coincides with the formation of a transfer layer on the counterface. The layer would need time to become passivated by OH dissociated from moisture [12-15]. The transfer layer on the counterface in contact with H-DLC would already be passivated by H- transferred from the DLC and thus H-DLC has a lower running-in COF and a shorter running-in period. The coatings had excellent aluminium adhesion-mitigation capacities as well as low wear rates under unlubricated sliding. The relatively low COF and wear rates observed during steady-state were due to the establishment of the transfer layers during the running-in. These layers were rich in carbon as confirmed by the Raman studies [10,12,23]. As both layers were passivated by H and OH, by the end of the running-in period, the C-C interactions between the layers and the sliding interface were minimized and a low friction regime occurred subsequently, with H-DLC having the lower COF coating at high cycles.

The COF of W-DLC was 25 % lower and more stable than that of H-DLC during the lubricated tests. The improvements in the tribological performance were due to the change in the composition of transfer layers as observed in Figure 6e. The transfer layers formed on 319 Al slid against W-DLC consisted of tungsten disulphide (WS_2), whereas those formed in case of H-DLC consisted mainly of C and O, as shown in Figs. 6b and 6c.

The low COF provided by tungsten disulphide is in agreement with the values reported in the literature, where formation of WS_2 film resulted in low COF of 0.15 [19]. The micro-Raman spectra presented in Fig. 7 acquired from the transfer layer formed on the 319 Al pins after lubricated sliding revealed that the transfer layers in fact contained WS_2 as indicated by the presence of Raman peaks at 354 cm^{-1} and 465 cm^{-1} [26,27]. It is conceivable that W in the transfer layer originated from the W-DLC's contact surface which reacted with the S in the lubricating oil leading to WS_2 formation.

Predictably WS_2 was not observed at the interface when lubricated tests involved H-DLC (Fig. 7).

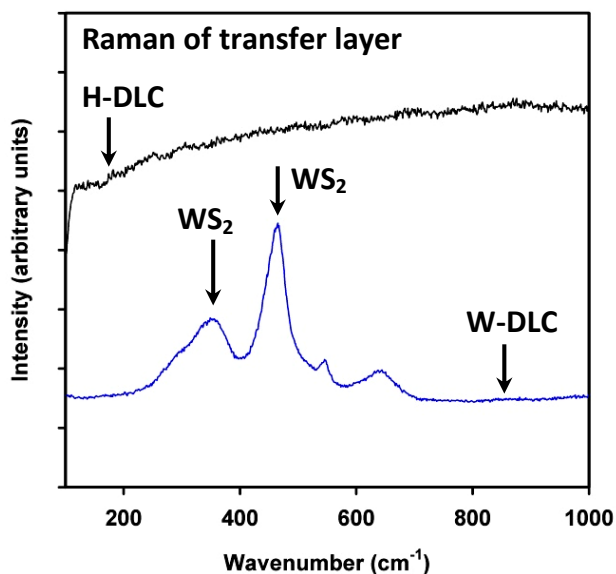


Fig. 7. Micro-Raman spectra of the transfer layer formed on 319 Al counterface subjected to lubricated sliding contact against H-DLC and W-DLC coatings.

Lastly, it is pertinent to consider some technological implications of the low COF of W-DLC. Machining applications such as deep hole drilling and metal tapping carried out without the use of lubricants may not particularly benefit from W-DLC coated cutting tools due to a very high running-in COF values of this coating. For engineering components subjected to continuous sliding however the low COF of W-DLC could be advantageous when tribolayers incorporating WS_2 could develop on aluminium contact surface during continuous sliding motion. The potential use of W-DLC in lubricated contact could include trimming of aluminium sheets and also as counterfaces such as piston rings in Al-Si lightweight engines.

5. CONCLUSIONS

The sliding of H-DLC and W-DLC coatings against 319 Al (Al-6.5% Si) alloy provided low COF values of 0.15 and 0.20 when tested in ambient air.

A 25% reduction in COF was observed in case of W-DLC sliding against 319 Al when compared to H-DLC under the boundary lubricated condition.

The low and stable COF of W-DLC coating was attributed to the formation of a tribo-film which is rich in both W and S. Formation of WS_2 was detected at the interface tribolayer and its presence was the likely reason for the low COF of the W-DLC coating.

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