TRIBOLOGICAL BEHAVIOUR OF W-DLC AGAINST AN ALUMINUM ALLOY IN LUBRICATED SLIDING

Sukanta BHOWMICK1, Anindya BANERJI1, Ahmet T. ALPAS1,*
1Mechanical, Automotive and Materials Engineering, University of Windsor, Canada
*Corresponding author: aalpas@uwindsor.ca

Abstract: Diamond like carbon (DLC) coatings mitigate aluminum adhesion and reduce friction under the ambient conditions but their tribological behavior under lubricated sliding need to be further instigated. In this study, tribological tests were performed to evaluate the friction and wear characteristics of W-DLC and H-DLC coatings sliding against an aluminum 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 lubricants incorporating sulfur 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. Raman spectroscopy indicated that the transfer layers formed during lubricated sliding of W-DLC incorporated tungsten disulphide (WS2).

Keywords: diamond-like carbon, H-DLC, W-DLC, tungsten disulphide (WS2), Al-Si alloys, friction, lubrication.

1. INTRODUCTION

Diamond-like carbon (DLC) coatings are known for their low coefficient of friction (COF) and low wear rate against aluminum compared to the other surface 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 minimize the interactions between covalent σ carbon bonds at the interface. Otherwise the interactions between the hydrogen free surface carbon atoms lead to high friction in vacuum as in the case of non-hydrogenated DLC (NH-DLC) coatings [11, 12]. 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 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] of Ti-6Al-4V pins tested against NH-DLC coatings 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.

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. The low COF was attributed to the weak Van der Waals forces between the two carbon surfaces passivated by OH groups initiating from the GMO lubricant. Matta et al. [17] performed similar 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. The studies suggest 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 behavior 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 a protective film. Podgornik et al. [19] studied the friction behavior of metal doped i.e. W containing DLC against itself in polyalphaolefin (PAO) oil with a sulfur 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 aluminum alloys in oil enriched with sulfur additive. The micromechanisms of wear and friction reduction are discussed with special emphasis on the role of tribolayer formation.

2. EXPERIMENTAL APPROACH

The H-DLC coatings were deposited on M2 steel substrates, with 0.10 μm thick Cr interlayer using an unbalanced magnetron sputtering system. The physical vapor deposition (PVD) system used had one chromium target and two graphite targets. First, a 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 in the coating structure 40 at. % of hydrogen content as confirmed 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-indenteter. 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 layer 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 % in the coating. 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 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 $5 \times 10^3$. The lubricants (LubriFluid, Vogel, Germany) that were 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 and 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 show the COF values of W-DLC and H-DLC coatings plotted as a function of number of revolutions under 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 extended to 4 × 10^3 revolutions during unlubricated sliding longer than that of the H-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 10^3 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.

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 Figure 2, and an average COF value of 0.14 ± 0.06 was measured.

The wear tracks formed on the H-DLC and W-DLC surfaces were examined using SEM and the representative SEI images are presented in Figures 3a and 3b. There wasn’t any notable aluminum transferred 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, higher wear accompanied by high running-in COF is shown in Figure 1.

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 the W-DLC (166 µm). The results indicate that the wear resistance of W-DLC was higher than that of the H-DLC under these testing conditions.
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 $0.31 \times 10^{-5}$ mm$^3$/Nm for unlubricated sliding, and $0.73 \times 10^{-5}$ mm$^3$/Nm under the lubricated condition. A higher wear, $0.51 \times 10^{-5}$ mm$^3$/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 $0.11 \times 10^{-5}$ mm$^3$/Nm was observed when this coating was subjected to lubricated sliding. This is consistent with the lowest observed COF for the W-DLC coating under the lubricated condition (Fig. 2).

The morphologies of 319 Al pin contact surfaces were also 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].

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

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
Figure 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 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-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 conceivably 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-

Figure 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 (d) are for (f) C, (g) W and (h) S transferred from the DLC and thus H-DLC has a lower running-in COF and shorter running-in period. The coatings had an excellent aluminum adhesion-mitigating property as well as low wear rates under unlubricated sliding. The relatively low COF and wear rates observed during steady sate were due to the establishment of the transfer layers on 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, at 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 being 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 of 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 (WS₂), whereas those formed in case of H-DLC consisted mainly of C and O, as shown in Figures 6b and 6c.

The low COF provided by tungsten disulphide is in agreement with the values reported in the literature, where formation of WS₂ film resulted in low COF of 0.15 [19]. The micro-Raman spectra presented in Figure 7 acquired from the transfer layer formed on the 319 Al pins after lubricated sliding revealed that the transfer layers in fact contained WS₂ as indicated by the presence of Raman peaks at 354 cm⁻¹ and 465 cm⁻¹ [26, 27]. It is conceivable that the W originated form the W-DLC contact surface which reacted with the S in the lubricating oil leading to WS₂ formation. Predictably WS₂ was not observed at the interface when lubricated tests involved H-DLC (Fig. 7).

Lastly, it is pertinent to consider some technological implications of the low COF of W-DLC. Machining applications such as deep hole drilling, metal tapping carried out without the use of lubricants may not particularly benefit from of W-DLC coated cutting tools due to a very high running-in COF values. For engineering components subjected to continuous sliding however the low COF of W-DLC could be advantageous when tribolayers incorporating WS₂ could develop on aluminum contact surface during continuous sliding motion. The use of W-DLC in lubricated contact would include trimming of aluminum 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. A WS₂ was detected at the interface tribolayer and its presence was the likely reason for the low COF of the W-DLC coating.

ACKNOWLEDGEMENT

Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC).

REFERENCES


