Tribology in Industry

Effect of Substrate Surface Roughness on the Tribological Properties of DLC-H Coatings on Tappet Valve

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A B S T R A C T

DLC-H coatings are increasingly used in automobile engine application at high temperatures, especially the reduction of friction and wear in sliding contacts. It is therefore important to determine the best substrate surface roughness on which DLC-H coatings will perform best at 200ºC (extreme engine temperature). In this work, we examined DLC-H coatings on different substrate surface roughness all deposited on tappet valve by plasma enhanced chemical vapour deposition (PECVD) under similar conditions. Microstructure, structure, mechanical properties, and tribological behaviour of the coatings were examine. The film had an approximate hydrogen content of 19 %. It was observed that the hardness and elastic modulus reduced as the surface roughness increased. The coatings deposited on tappet valve of 0.3 µm substrate surface roughness possessed excellent tribological properties at 200 ºC. The smoothness of the substrate aided in providing good adhesion of the coating on the substrate surface, which provided resistance to wear at 200 ºC. It was revealed from the tribological behaviour and Raman analysis that the films were protected by the contact of the tribo-layer on the surface of the DLC-H coating.

1. INTRODUCTION

The wide application of hydrogenated diamond-like carbon (DLC-H) films are due to the fact that they possess excellent tribological properties. DLC-H has hardness values 5 to 40 GPa and low coefficient of friction (<0.1) [1]. However, DLC coatings are faced with the challenge of low adhesion when dealing with metallic substrate mainly because of the presence of high internal stresses and high difference in thermal expansion coefficient between the DLC coating

and metallic substrate, causing film delamination from the substrate. In addition, the presence of dirt and rough surface substrate can lead to poor adhesion to metallic substrate [1,2]. Consequently, to improve upon the adherence of DLC films to metallic substrate, interlayers (silane and chromium) has been used to serve as intermediates between the metallic substrate and the DLC coatings [2], the use of argon cleaning has made it possible to remove all forms of dirt in the deposition reactor [3]. Substrate surface roughness also need to be controlled within a certain range to ensure optimum adhesion to metallic substrate [4]. Authors, have recommended that in order for DLC coatings to exhibit proper adhesion to metallic substrate, the substrate surface roughness should not be lower than 263 nm or higher than 0.93 μm [4,5]. However, there may be a difference when making use of different deposition technique, resulting in different adhesion properties and affecting both wear and friction properties of the DLC coating on the metallic substrate [5]. Uhure et al. (2007) used various substrate roughness (ground, super-finished, 1000 grit, 220 grit and 1 mm diamond finish) to study effect of surface roughness on the mechanical properties of diamond-like carbon coatings [6]. Studies have showed how wear of a counter body could be affected by rougher substrate [4]. Diverse research has been carried out on how the substrate surface roughness affects the tribology of DLC coatings [4, 7-9]. Wear debris generated can be increased when the degree of wear is increased [10-12]. Miyoshi et al. (1993) [12] studied friction and wear behaviour of diamond-like carbon films deposited by a plasma assisted depositor which revealed that an increase in the substrate surface roughness significantly increases the wear rate of the diamond-like carbon film notwithstanding the sliding conditions. Substrate surface roughness can affect measurements of DLC elastic modulus during nano-indentation penetration test [6,13]. Likewise, the tribological behaviour of the DLC coatings itself can be affected by the DLC's final roughness after been deposited on a substrate because the substrate surface roughness will have a significant influence on DLC roughness [14]. In this present work, the effect of substrate surface roughness on the tribological properties of hydrogenated DLC on tappet valve at 200 °C for automobile applications was studied. Wear experiments were performed for the DLC-H film at 200 °C for different surface roughness (0.3, 1 and 2 μm), under dry conditions using Optimol SRV tribometer (ball on disk). The hardness and young modulus of the coating were measured before and after the wear test. Scratch and Rockwell C indentation test were carried out to understand the effect of substrate surface roughness on the adhesion properties of the DLC-H coatings. Raman spectroscopy was also used to assess the nature of bonding structure which occur before and after the wear test on the DLC-H film coated on different substrate surface roughness. SEM/EDS and Optical microscope was used to access the microstructure of the DLC-H coatings on different substrate surface to explain the variation in tribological properties of the different films.

2. EXPERIMENTAL

Commercial tappet valve (AISI 52100) was polished and cleaned and DLC-H coatings was then deposited on the polished tappet valves with different substrate surface roughness (0.3, 1, 2 μm) using PECVD in an Ar/C_2H_2 atmosphere (see Fig. 1). Argon was first introduced into the chamber at a pressure of 2.0 mTorr and bias -600V for 40 mins, then followed by the deposition of the interlayer by introducing silane at a pressure of 2.9 mTorr and bias -800V for 15 mins and lastly, the DLC-H was deposited by introducing acetylene at a pressure of 3.3 mTorr and bias -800V for 2 hours. The deposition parameters are presented in Table 1. DLC-H bonding structure was analyzed by Raman Spectroscopy (Horiba scientific Lab) before and after wear (centre of the wear track). A 120° conical Rockwell C adhesion test according to VDI 3198 was performed under an applied load of 150 Kgf, thrice on each coating surface. Scratch test (CETR UMT-2M-110 tribometer) was performed in a linear reciprocated mode with an applied load varied from 1 to 50 N and sliding speed of 0.1 mm/s for 90 secs. The tribological performance of these coatings were analyzed at 200 °C using reciprocating sliding tester - SRV (ball-on-disc configuration) using a load of 5 N, frequency of 10 Hz and stroke length 5 mm during a period of 30 min, the experiment was carried out in triplicates. The counterpart used was AISI 52100

steel ball and the wear volume were determined using 3D CCI – Taylor Hobson profilometer. The specific wear rate (Ws) was calculated using equation 1 [15,16]. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) was used to obtain microstructural images of the scratch and wear tracks. The hardness and elastic modulus of the DLC-H coating before and after tribological test was performed using nano-indentation (Hysitron Ti950 triboindenter, having a Berkovich type diamond tip).

Table 1: Deposition process parameters.

	Argon etching	Interlayer	a-C:H
Pressure (Torr)	2.9×10^{-3}	2.9×10^{-3}	3.3×10^{-3}
Time (min)	40 min	15 min	2 hours
Precursor	Ar	SiH_4	C_2H_2
Flow rates (sccm)	8	3.5	10
Bias (V)	-600	-800	-800
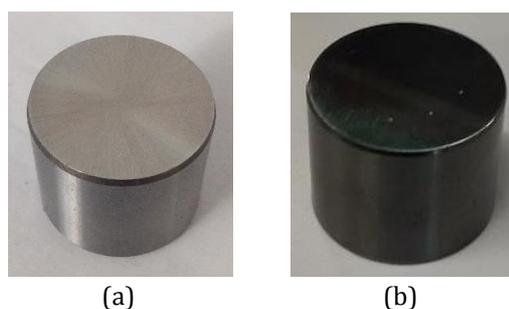
Fig. 1. Tappet valve (a) without coating, (b) with DLC-H coated.

The specific wear rate (Ws) was calculated using equation (1).

$$W_s = \Delta V / F_n \times S \qquad (1)$$

where ΔV is wear volume, F_n is normal load and S is the sliding distance [15,16].

3. RESULTS AND DISCUSSION

3.1 Structure characterization of DLC-H film

Figure 2(a-d), presents the Raman spectra of the coated tappet valve at different substrate surface roughness before and after wear test. Which is the most used technique to analyse the bond structure of DLCs [17,18]. Figure 2a, reveals Raman spectra for DLC-H before wear test, with Raman active mode at 1369 and 1570 cm^{-1} representing the D and G peaks, respectively [19]. The D band is related to closed sp^2 structures (aromatics), while

the G band is associated with either closed or open (olefinics) sp^2 structures [20]. Figures 2b, 2c and 2d are Raman spectra for DLC-H after wear test. In Fig. 2b, υ-(Si-O-Si) was identified at 432.41 cm^{-1}, while υ-(CC) alicyclic, aliphatic chains vibration were present at 1057.60 and 1310.16 cm^{-1} (D band) and υ-(C=C) was found at 1587.22 cm^{-1} (G band) [21]. Fig. 2c, showed lattice vibrations in crystals peak at a Raman position 215.25 cm^{-1}, δ-(CC) aliphatic chains at 284.39 cm^{-1}, υ-(Si-O-Si) was observed at 411.92 and 497.61 cm^{-1}, υ-(CC) alicyclic, aliphatic chains vibration was present at 659.73 and 1319.70 cm^{-1} (D band) and υ-(CC) aromatic ring chain vibration was found at 1600.72 cm^{-1} (G band), while υ-(C=C) and υ-(C=O) was identified at 1801.48 cm^{-1} and lastly, υ-(C=C) was found at 1981.13 cm^{-1} [21]. Fig. 2d, showed δ-(CC) aliphatic chains at 252.74 and 388.96 cm^{-1}, υ-(Si-O-Si) was observed at 582.76 cm^{-1}, υ-(CC) alicyclic, aliphatic chains vibration was present at 1286.14 cm^{-1} (D band), while υ-(C=C) at 1630.41 (G band) and 1872.66 cm^{-1} and υ-(C=O) was identified at 1770.63 cm^{-1} [21]. Results are like those reported in literature for DLC-H/SiH$_4$ interlayer [22].
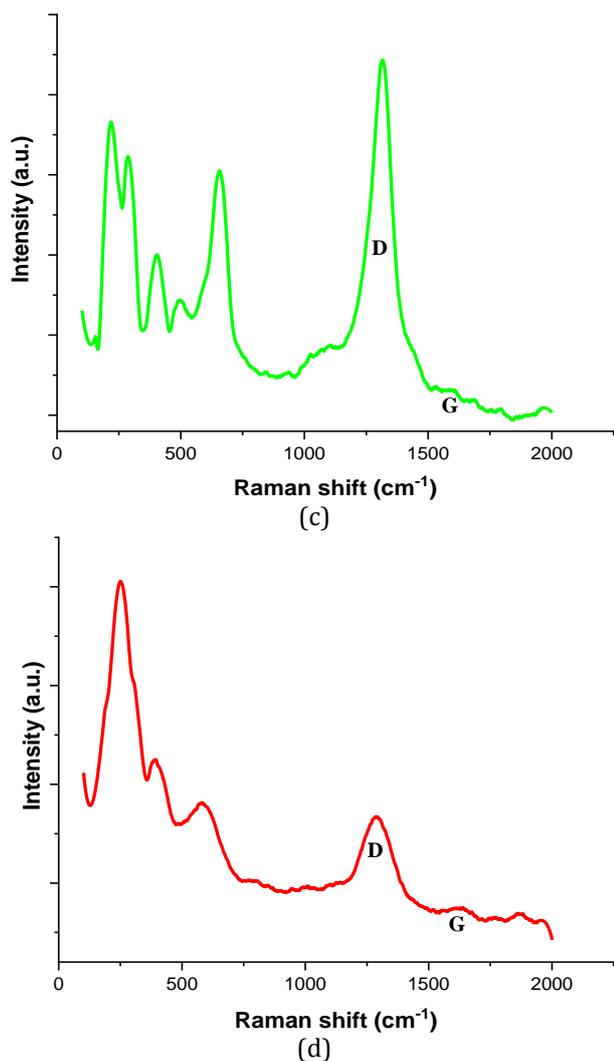

(a)

(b)

(c)

(d)
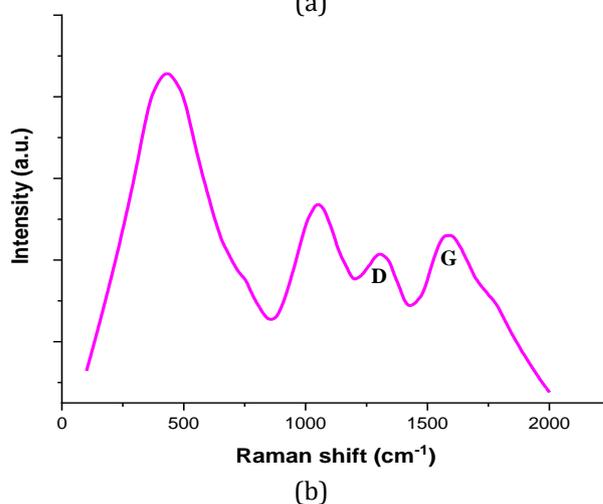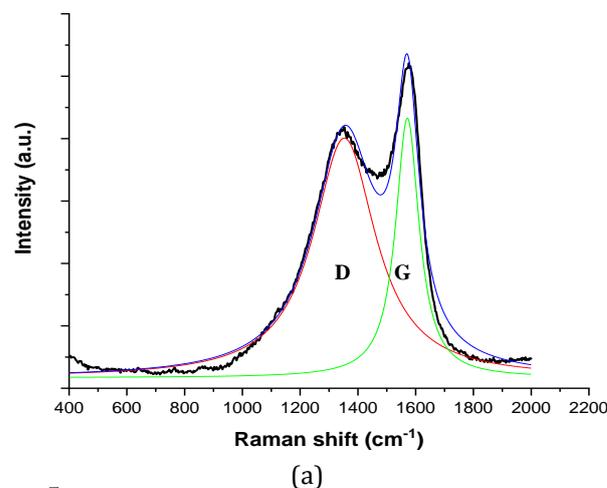
Fig. 2. Raman spectra of the DLC-H coating on tappet valve a) before subjected to wear test b) surface roughness of 0.3 μm coated with DLC-H after wear test c) surface roughness of 1 μm coated with DLC-H after wear test d) surface roughness of 2 μm coated with DLC-H after wear test.

Figure 3 presents SEM images and EDS results of as-deposited DLC-H films on the tappet valve with substrates surface roughness of 0.3, 1 and 2 μm. DLC-H films on substrates surface roughness with 0.3 and 1 μm had a good coverage as seen in Figs. 3a & 3b. While tappet valve with substrates surface roughness (Ra - 2 μm) showed poor adhesion to DLC-H coating (Fig. 3c). The images in Figs. 3a, 3b & 3c correlates EDS results (Fig. 3a1, b1 & c1). The EDS results presence C from the DLC-H, Si from the interlayer. Fe, Cr and Mn were obtained from the tappet valve substrate, while the presence of Ar was due to the Argon etching carried out at the beginning of the deposition process. The EDS results reveals that Fig. 3c1 had higher Fe content that Fig. 3a1 & b1, this is simply due to the poor adhesion of DLC on the substrate with highest surface roughness (2 μm), thereby exposing the substrate.

3.2 Scratch test

The plot of COF of DLC-H film on substrates surface roughness with 0.3, 1 and 2 μm are presented in Fig. 4. Figure 5 is the SEM image of the scratch track of the DLC-H. The plot revealed a steadily increase in the COF as the load increased for 1 and 2 μm, however, it was totally different for 0.3 μm, which remained constant except for regions with small radial cracking of the DLC-H coating at short intervals, leading to tiny irregular peaks, this is referred to as spallation. It reveals that roughness of the substrate before deposition has significant effect on the adhesion of the DLC coating. This agrees with the findings of Sheeja et al. (2002) [23] who found a decrease in adhesion with higher substrate surface roughness.
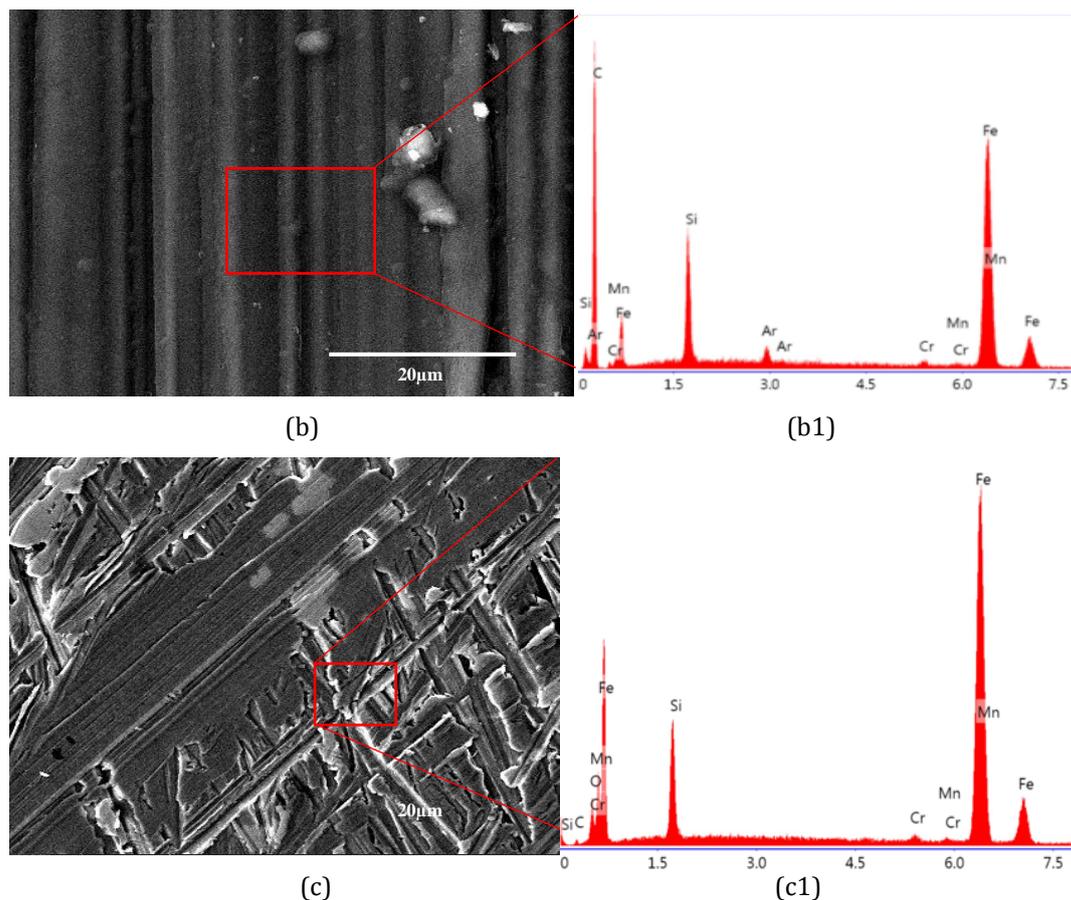

(a)

(a1)

(b)

(b1)

(c)

(c1)
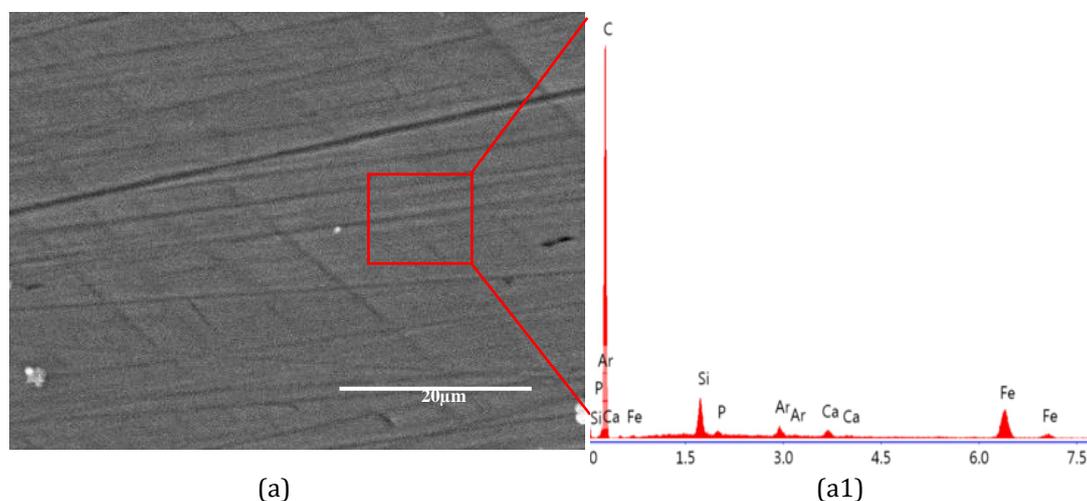
Fig. 3. SEM/EDS results of DLC-H film with substrate surface roughness (a-a1) 0.3 μm, (b-b1) 1 μm, (c-c1) 2 μm.
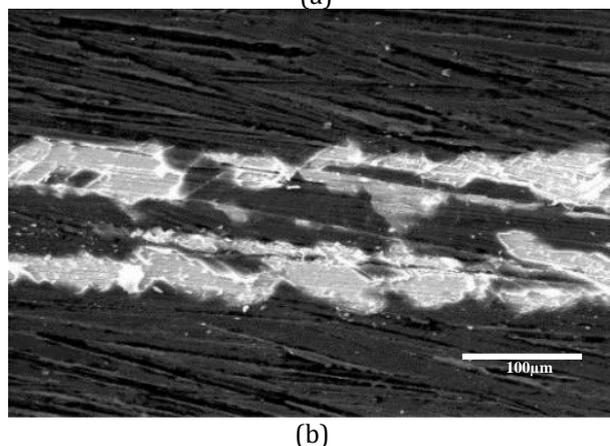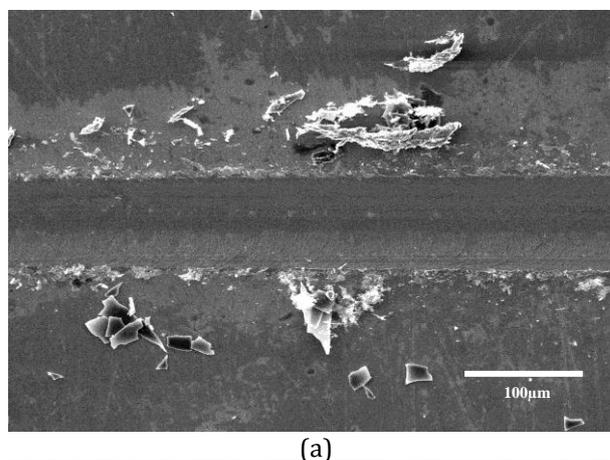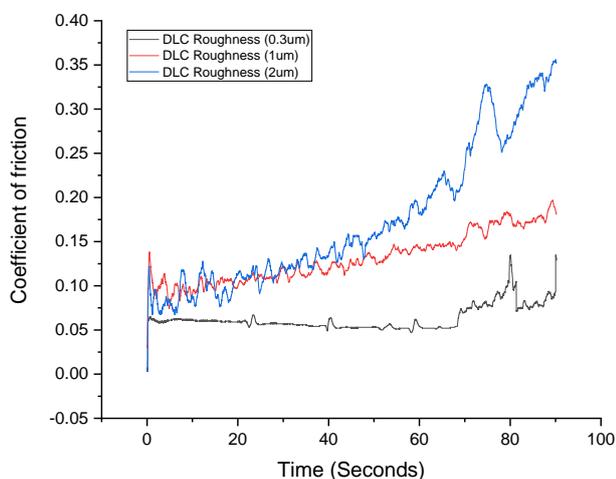

Fig. 4. Coefficient of friction for DLC-H coating on different substrate surface roughness.

The failure modes observed in Figs. 5a-5c, with spallation at the border of the scratch track increasing as the substrate surface roughness increased. For the sample with the highest substrate surface roughness of 2 μm, coating failure occurred throughout the coating surface, giving rise to delamination all through the track width along the peaks, leading to severe failure.


(a)

(b)
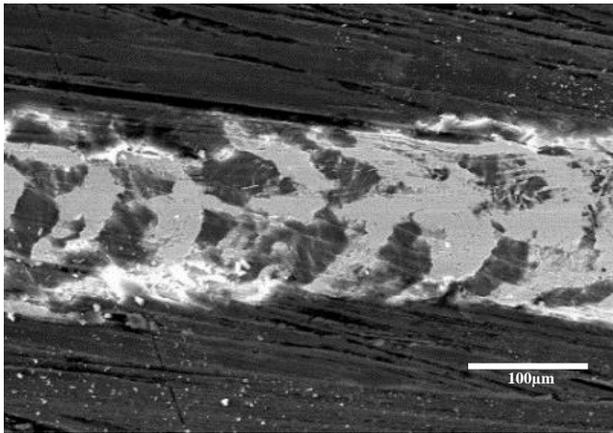
(c)

Fig. 5. SEM of scratch track of DLC-H film with substrate surface roughness (a) 0.3 μm, (b) 1 μm, (c) 2 μm.

3.3 Rockwell C indentation test

Figure 6 presents images of the DLC-H surface indented using Rockwell C under an applied load of 1471 N on the DLC-H coating for different substrate surface roughness [24]. The indented coating was classified based on VDI 3198 standard [24]. The coatings showed good adhesion and absence of delamination for the DLC-H coating on 0.3 μm substrate surface roughness. However, the DLC-H coated on substrate surface roughness with 1 and 2 μm had delamination, even though the substrate surface roughness with 1 μm had lesser delamination and better adhesion to the tappet valve substrate as compared to the substrate surface roughness of 2 μm. Rockwell C indentation test confirms good adhesion for Figs. 6a & 6b and using the VDI 3198 standard it shows that DLC-H coated on substrate surface roughness with 0.3, 1 and 2 μm can be classified as HF-1, HF-4 and HF-5 respectively.
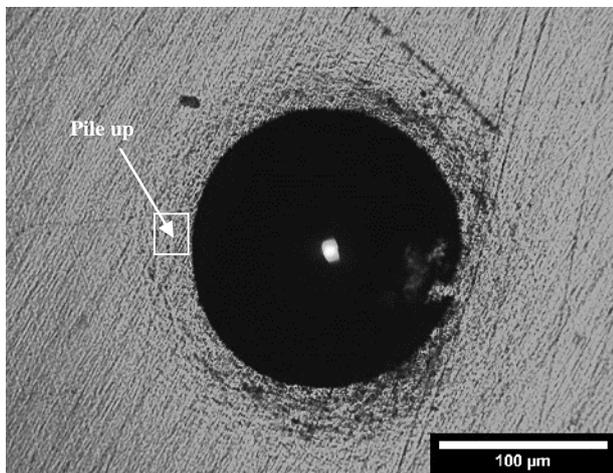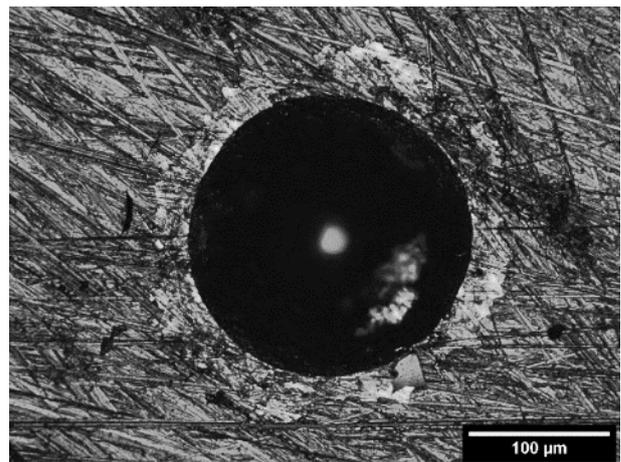
(b)
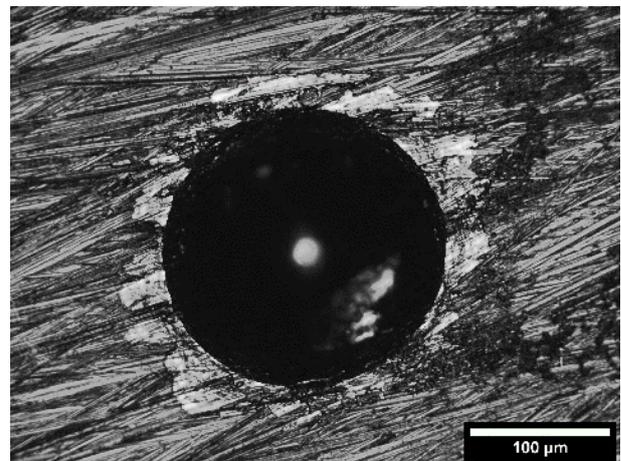
(c)

Fig. 6. Rockwell-C adhesion test of DLC-H film with substrate surface roughness (a) 0.3 μm, (b) 1 μm, (c) 2 μm.

Therefore, 0.3 and 1 μm, are regarded as acceptable failures, DLC-H coated on substrate surface roughness with 0.3 μm had no crack at all, only a region of pile up (Fig. 6a). While 2 μm is regarded as an unacceptable failure (Fig. 6c), because of the level of delamination, hence it has poor adhesion. Good adhesion will protect the coatings from wear and spalling.

3.4 Mechanical properties of DLC-H coatings before and after wear

Figure 7a, presents the result of hardness and elastic modulus on different substrate surface roughness before and after wear test at 200°C. The DLC-H film has a hardness of 18.77±0.1, 18.42±0.22 and 17.58±0.19 GPa for 0.3, 1 and 2μm respectively and a Young's modulus of 150.07±1.2, 149.10±1.9 and 147.33±1.55 GPa for 0.3, 1 and 2 μm respectively (Table 2), which is in agreement with hardness and young's modulus values reported in the literature for DLC-H films

(a)

deposited by PECVD [25]. Hardness and elastic modulus decreased slightly with increasing substrate roughness as seen in Fig. 7a and was confirmed by Joslin and Oliver, (1990) [26].

Table 2. Hardness and Young modulus of DLC before and after wear.

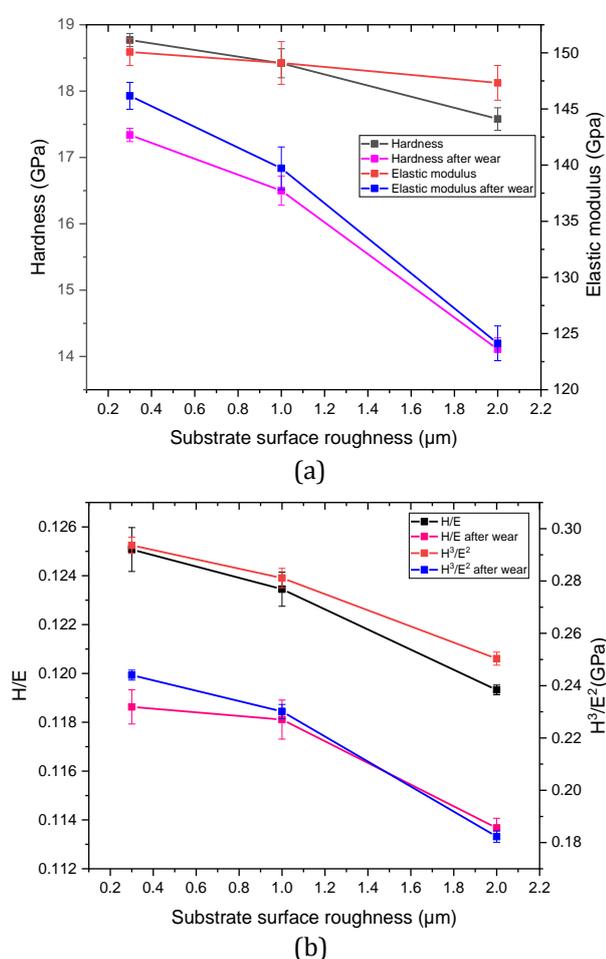| Surface rough. (μm)	Hardness (GPa) Before wear	Hardness (GPa) After wear	Young modulus (GPa) Before wear	Young modulus (GPa) After wear
0.3	18.77±0.10	17.34±0.11	150.07±1.20	146.17±1.10
1	18.42±0.22	16.50±0.20	149.10±1.90	139.72±1.50
2	17.58±0.19	14.11±0.17	147.33±1.55	124.13±1.50

(a)

(b)

Fig. 7. (a) Hardness and young's modulus, (b) H/E and H^3/E^2.

Furthermore, it can be observed from the plot that the DLC-H film after wear has a hardness value of 17.34±0.11, 16.50±0.20 and 14.11±0.17 GPa for 0.3, 1 and 2μm respectively and a Young's modulus of 146.17±1.1, 139.72±1.5 and 124.13±1.50 GPa for 0.3, 1 and 2μm respectively (Table 2) there was significant reduction in the hardness and elastic modulus values after wear test at 200°C was

performed. The reduction in hardness value before wear was performed is related the effect of substrate surface roughness that causes poor adhesion as the roughness increases. Furthermore, the decrease in hardness and modulus value after wear at 200 °C can be attributed to the combine effect of substrate surface roughness, mechanical deformation and thermal transformation from sp^3 (diamond-like) to sp^2 (graphite-like) [27]. The ratio H/E and H^3/E^2 related to the plastic deformation resistance of the coatings is shown in Fig. 7b. As the substrate surface roughness increases from 0.3 to 2 μm, there is a slight reduction in the ratio of H/E and H^3/E^2 revealing there is not much difference in the toughness as the substrate surface roughness increases. However, for coatings subjected to wear at 200 °C there is a significant decrease in the toughness indicating a disadvantage in the use of high substrate surface roughness for DLC-H coatings for high temperature application.

3.5 Tribological behaviour of DLC-H coatings at 200 °C

3.5.1 Wear rate of different substrate surface roughness

The specific wear rate of the coating tested on different substrate surface roughness at 200°C are shown in Fig. 8. At 0.3 μm substrate surface roughness had the lowest specific wear rate, followed by the 1μm, which was slightly higher. However, there was a rapid increase in the specific wear rate for the 2 μm which was due to poor adhesion of DLC-H at higher substrate surface roughness.
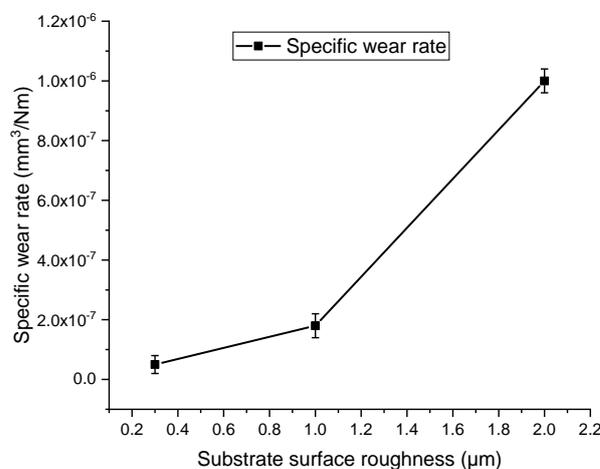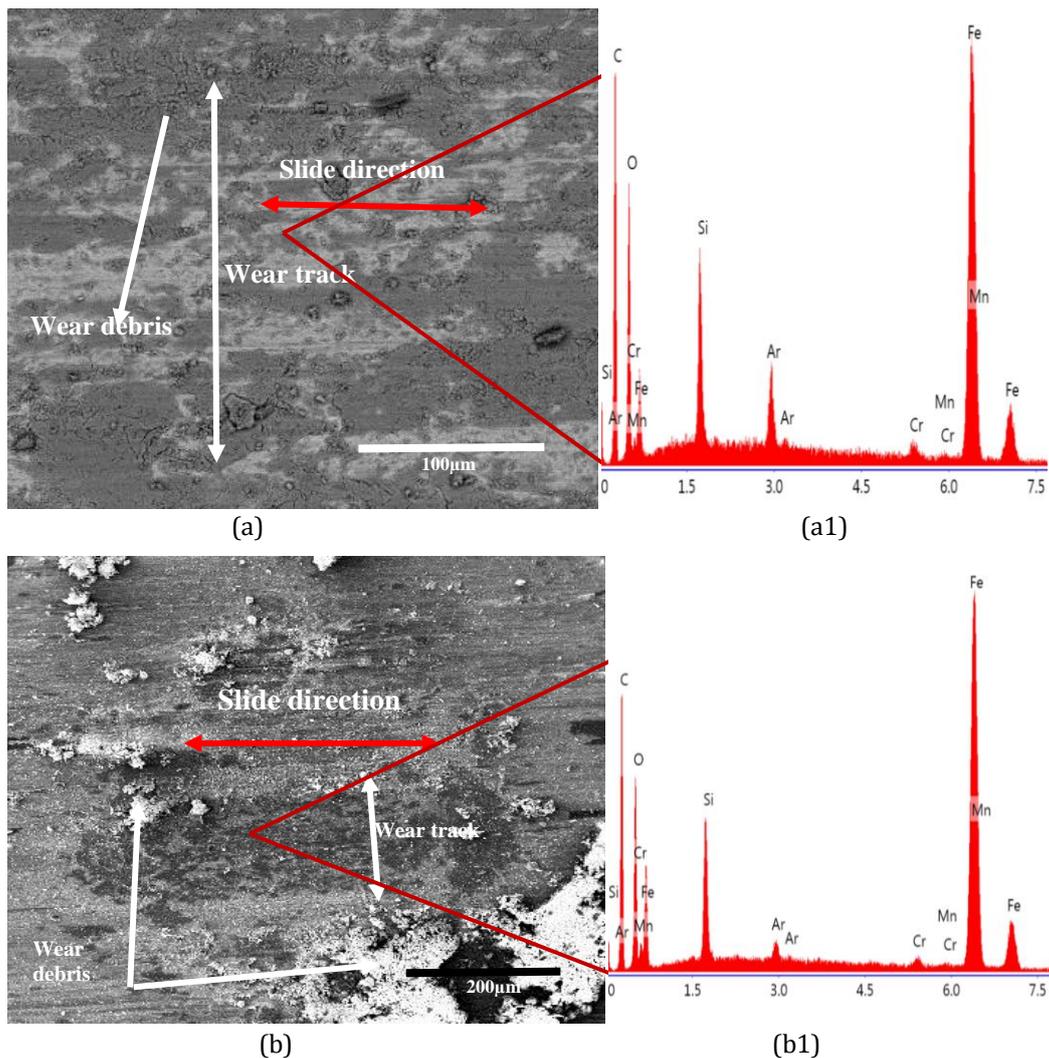

Fig. 8. Plot of substrate surface roughness against wear volume wear rate.

Also, at 200 °C, it is expected that the coating will experience softening due to graphitization and an increased wear rate caused by easy removal of the coating, thereby reducing its ability to resist wear. Although, the wear rate values are similar to those in literature with similar chemical properties [27]. This was as a result of the tribo-films formed by the abrasive particles on the DLC-H coatings. The total wear rate on the surface of the DLC-H film was due to combine effect of high temperature and abrasive contact of the contact body; the low wear was due to the combine effect of the hardness and good adhesion of the DLC-H coating. The wear volume and wear rate presented in this study shows good thermal stability of the DLC-H film deposited on tappet valve with substrate surface roughness of 0.3 µm, which was due to effect of the hardness and SiH_4 interlayer (which may have generated Si-O-Si due to oxidation at high temperature) and C-C as seen from the Raman spectra (2b-d) serving as tribo-films.

3.5.2 Wear mechanisms and surface analysis of the wear scar.

Figure 9 presents the SEM/EDS results of the coatings wear scar after tests performed at 200 °C. The DLC-H coatings on the 0.3 µm substrate surface roughness presented a very clean wear track with only little debris, suggesting the occurrence of abrasion wear mechanism. Looking closely at the scars, film debris being detached from the DLC-H surface can be observed (Fig. 9a). The wear scar analysed by EDS consists mainly C, O, Si, Fe, Mn, Cr and Ar obtained from the DLC-H coating and the tappet valve substrate. The wear scars for the DLC-H coatings on the 1 µm substrate surface roughness was similar; it depicts partially smooth wear scar; however, very shallow and narrow scars are visible at the centre. In addition, the coatings on the 2 µm substrate surface roughness had more severe wear scars (Fig. 9c).
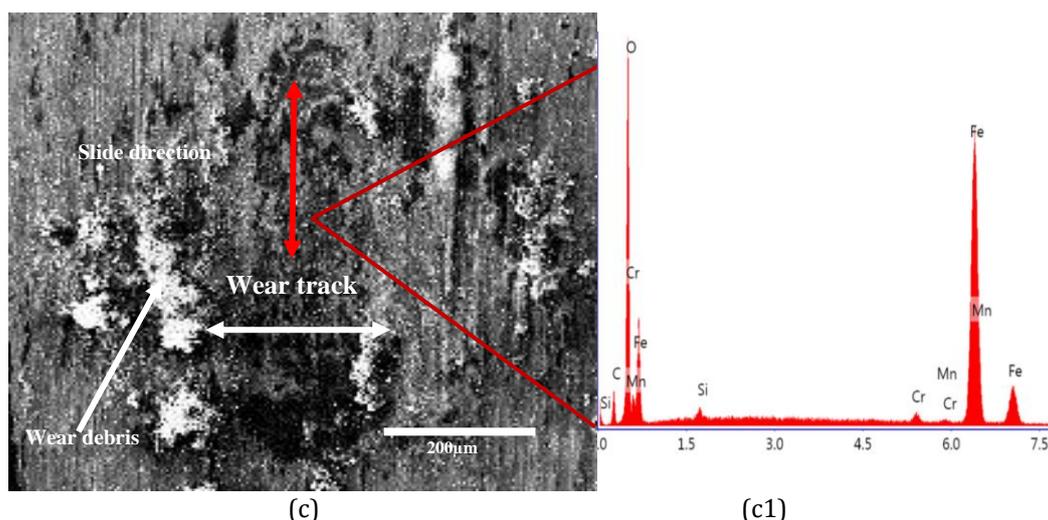

(a)   (a1)

(b)   (b1)

Fig. 9. SEM image and EDS results of wear at 200 °C on tappet valve of DLC-H film with substrate surface roughness (a-a1) 0.3 μm, (b-b1) 1 μm, (c-c1) 2 μm.

EDS analysis of the debris revealed major elements such as C, Si, O (Figs. 9a1, 9b1 & 9c1) which serves as abrasive particles and were obtained from both the DLC-H coatings and SiH_4 interlayer causing higher wear rate. The presence of oxygen was due to the oxidization of the DLC-H coatings that occurred at 200 °C. Debris on the coating surface and wear tracks can be observed from the SEM in Figs. 9a, 9b & 9c. Both mechanical stress and thermal degradation may cause micro-wear under sliding contact [6,27]. Increase in transformation to sp^2 significantly decreases the mechanical strength, which eventually, leads to critical failure or engine parts malfunction.

4. CONCLUSION

In this work, we examined DLC-H coatings on different substrate surface roughness all deposited on tappet valve deposited by PECVD under similar conditions. The properties of the coatings were used to examine on different substrate surface roughness at high temperature. The coatings deposited on tappet valve of 0.3 μm substrate surface roughness possessed the excellent tribological properties during wear test at 200 °C. The tappet valve of 0.3 μm substrate surface roughness showed higher hardness. Smoothness of the substrate aided in providing good adhesion of the coating on the substrate surface and avoided detachment of particles, which provided resistance to wear of the DLC-H coatings at 200 °C. It was observed that as the substrate surface roughness increased, there was a reduction in the hardness, elastic modulus and wear resistance of the DLC-H coatings. Although, coatings on the tappet valve with substrate surface roughness of 1 μm, experienced a little delamination it fell within the acceptable failure under the Rockwell C adhesion test, but for 2 μm it was not classified as acceptable failure and showed the highest wear rate at 200 °C. It was revealed from the tribological behaviour and SEM/EDS results that the films were protected by the contact of the tribo-layer formed.

Acknowledgement

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