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Friction, Wear, and Surface Film Formation Characteristics of Diamond-Like Carbon Thin Coating in Valvetrain Application

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The friction and wear characteristics of thin diamond-like carbon (DLC) coatings have been investigated extensively in recent years mostly in laboratory bench tests. These coatings are known to provide significant friction reduction in the absence of lubricants. In the presence of lubricants, the friction benefits of these coatings are not clearly demonstrated. The current investigation is focused on exploring the friction reduction potential of a DLC coating obtained from a supplier in laboratory bench tests and in a motored valve train test. The DLC coating was deposited on the bucket tappet. In laboratory bench tests, results showed significant friction reduction in the absence of any lubricant but not in the presence of engine oil. In motored valve train tests a significant reduction in friction torque was observed when compared against a slightly rougher uncoated bucket, but no reduction was observed when compared against uncoated bucket tappet with comparable surface finish. Under boundary lubrication conditions, no lubricant-derived surface films were present on the DLC-coated surface. However, under mixed lubrication conditions, evidence of patchy antiwear surface films could be observed on DLC-coated buckets. The antiwear film appears to be primarily composed of calcium phosphate.

KEY WORDS

DLC Coating; Friction; Wear; Valvetrain; Boundary Lubrication; Mixed Lubrication

INTRODUCTION

Diamond-like carbon (DLC) coatings are well known for their very low sliding friction coefficient coupled with high hardness and wear resistance, making them a suitable candidate material for engineering components involved in sliding motion. The

friction-reducing property of diamond-like carbon coatings was first noticed in the early 1970s (Aisenberg and Chabot (1)), when friction coefficients as low as 0.01–0.02 were reported in dry sliding contact against steel. Similar results were also reported at low partial pressure of water vapor (Enke, et al. (2)). However, interest on this thin coating did not pick up until the early 1990s, when vacuum methods for making this material became widely available. In the late 1980s, a lot of research resources were directed toward development of thin diamond (not DLC) coatings for cutting tools and other engineering applications for friction reduction. However, diamond coatings could not be successfully deposited on steel substrates because of high deposition temperatures. Also, low friction was only achieved under dry sliding when both sliding surfaces were coated with diamond (Bowden and Young (3); Bowden and Hanwell (4); Jahanmir, et al. (5); Samuels and Wilks (6); Gangopadhyay and Tamor (7)). When only one surface was coated, the friction coefficient was high, causing high wear on the uncoated surface, primarily due to high surface roughness of as-deposited films (Gangopadhyay and Tamor (7)).

This led to increased research on DLC coatings primarily because the coatings were amorphous and the as-deposited coatings were significantly smoother than diamond coatings. Essentially, the roughness of DLC-coated materials was similar to the roughness of the underlying substrate. However, the early coatings were susceptible to moisture degradation (Kokaku and Kitoh (8); Kim, et al. (9)) and had high residual compressive stress, limiting the thickness of coatings to less than a few micrometers. Incorporation of nitrogen (Franceschini, et al. (10)) and metals like tungsten, silicon (Miyake, et al. (11)), tantalum, etc., reduced the residual compressive stress. Incorporation of silicon in the coating also made it insensitive to moisture (Gangopadhyay, et al. (12)). Friction coefficients as low as 0.05–0.010 are routinely observed in sliding contacts with steel in the absence of any lubricant, compared to 0.5–0.7 for uncoated steel sliding against steel. Sliding friction coefficients of 0.01 or less have also been reported under certain test environments (Donnet, et al. (13)). A low friction coefficient is also associated with



Fig. 1—(a) Scanning electron micrograph through the cross section of the coating and (b) a crater on the coated surface showing various composition bands.

low wear of the steel counterface compared to uncoated steel and extremely low wear of the DLC-coated substrate (Koskinen, et al. (14); Oguri and Arai (15)).

The low friction coefficient of DLC coatings is believed to be due to the formation of a transfer layer on the opposing surface. At the start of sliding there is a strong interaction between steel and the DLC coating, resulting in a high friction coefficient. However, as sliding continues, there is cohesive failure in the DLC coating, leading to transfer of DLC wear particulates to the opposing surface. This leads to DLC-coated substrate sliding against a DLC coating, resulting in a marked friction coefficient reduction (Gangopadhyay, et al. (16)). Based on analysis of wear surfaces using Raman spectroscopy, Oguri and Arai (17) proposed that in the absence of moisture the DLC coating transformed to a graphite-like state by the sliding action, resulting in low friction. In the presence of moisture, the low friction coefficient of silicon-containing DLC coatings was attributed to formation of a silica-sol. Erdemir, et al. (18) also attribute the low friction of DLC coatings to formation of graphite-like material at contact areas.

Recent tribological investigations on DLC coatings are directed more toward understanding the effect of lubricants and the interaction of DLC coatings with lubricant additives, in particular with antiwear additives and friction modifiers. Under boundary lubrication conditions in pin-on-disk tests, DLC coatings did not show any friction reduction. This result was attributed to the lack of formation of any transfer film on the counterface material (Gangopadhyay, et al. (19)). Broda and Bethke (20) evaluated the friction coefficient of three different DLC coatings in the presence of three different oils with varying amounts of Mo-based organic friction modifier. DLC coatings showed 40% reduced friction coefficient compared to uncoated steel parts in the presence of low to medium level of Mo-based friction modifier in the oil and also in the absence of any additives. In the oil with high Mo, the friction coefficient of the uncoated steel part was low

and the difference between uncoated and DLC-coated parts was small. Kano, et al. (21) measured a friction coefficient as low as 0.006 in the presence of polyalphaolefin-based oil containing glycerol mono-oleate (GMO) friction-reducing additive. Shinyoshi, et al. (22) reported that the wear of DLC coatings increased in the presence of molybdenum dithiocarbamate (MoDTC) in the oil. The decomposition of MoDTC produced MoO_3 , which interacted with the DLC coating, resulting in increased wear. Haque, et al. (23) observed that the low friction of hydrogenated DLC coatings is due to the transfer of a carbon layer from the DLC-coated part to the counterbody. However, they did not find any zinc dialkyldithiophosphate (ZDDP)-derived antiwear films on the DLC-coated surface, and Mo-dimer and Mo-trimer friction modifiers interacted with DLC coating to form MoS_2 and MoO_3 compounds. They observed that the higher the ratio of $\text{MoS}_2/\text{MoO}_3$, the lower the friction coefficient. Podgornik, et al. (24) reported similar results: when the DLC-coated steel and an uncoated steel interface were lubricated with polyalphaolefin oil, a low friction coefficient was observed, which was attributed to transfer of DLC coating to the uncoated steel surface. However, when an extreme pressure additive or a ZDDP antiwear additive was added to polyalphaolefin oil, they did not observe any interactions between the DLC-coated surface and the additives. In a motored valve train where the cam lobe slides against a bucket, significant friction reductions have been reported when DLC coating was deposited on the bucket (Schamel, et al. (25)). Equey, et al. (26) observed the formation of about 100-nm-thick tribofilm on DLC-coated surfaces following sliding tests using a high-frequency reciprocating rig (HFRR) under mixed lubrication regime. The tribofilm contained Zn, P, and S, the elements from the additive, ZDDP. But the authors claimed that it was a weakly bonded film because it could be removed by ultrasonic cleaning in cyclohexane. However, a hydrogen-free DLC coating containing Ta could not be lubricated satisfactorily by MoDTC-containing oil. An ashless friction modifier was developed for

effective lubrication, suggesting the need for an appropriate friction modifier for lubricating DLC-coated components (Okuda, et al. (27)).

It could be observed from the above discussion that the lubrication characteristics of diamond-like carbon coatings have been widely investigated. The interactions of additive compounds with DLC coating vary widely depending on lubrication regimes, additive chemistry, and the chemistry of the coating. The objectives of this investigation are to understand the friction and wear reduction potential under boundary and mixed lubrication regimes and to understand the interactions of lubricant additives with DLC coating.

EXPERIMENTAL DETAILS

Material

The diamond-like carbon coating was deposited on steel substrates by a supplier using a chemical vapor deposition technique. Figure 1a shows a cross section of the coated steel, where the bottom portion is the steel substrate and the narrow white band on top is the DLC coating. The coating appears to be about $1\ \mu\text{m}$ thick. Examination of the white band at higher magnification indicates that the coating is very dense with no columnar structure. The material on top of the white band is the epoxy material on which the steel sample was mounted. In order to understand the coating composition and the interlayer between the coating and the substrate to promote adhesion, a circular crater was formed by spinning a steel ball coated with diamond paste on the DLC-coated tappet (see Fig. 1b). This allowed the analysis of each distinct composition band without interference from the layer underneath. The composition of each band was analyzed with auger electron spectroscopy. The analysis showed that it is a multilayer coating starting with a chromium-rich layer adjacent to the steel substrate, followed by a titanium- and tungsten-rich layer, and finally finished with a thin layer of silicon containing diamond-like carbon coating. The purpose of depositing a multilayer coating is to improve adhesion on the steel substrate and tribological properties.

Friction and Wear Evaluation

The friction and wear properties of DLC coatings were evaluated in two different test rigs.

Laboratory Bench Rig

The boundary friction and wear characteristics were determined using a Plint TE77 rig (Phoenix Tribology, UK) (shown in Fig. 2) where a 6.35-mm-diameter, 12-mm-long polished cylinder reciprocated against a steel flat at 5 Hz under a constant load of 240 N (corresponds to maximum Hertzian contact stress of 0.48 GPa) and stroke of 15 mm. The long axis of the cylinder was in contact with the flat, which was made of the same material as production bucket tappets used in the engine valvetrain. The test duration was 1 h. The flat was coated and the cylinder was not. Tests were conducted both in the presence and absence of lubricants. In lubricated tests, the contact area was submerged in SAE 5W-20 viscosity grade GF-4 engine oil maintained at 40, 80,



Fig. 2—The Plint test machine used for friction and wear evaluation under boundary lubrication conditions.

100, and 120°C . The kinematic viscosity of the lubricant was 47 and 8.6 cSt at 40 and 100°C , respectively. Under these test conditions, the minimum oil film thickness was $0.002\ \mu\text{m}$ using Dowson and Higginson's equation (Peterson and Winer (28)). The composite surface roughness was $0.317\ \mu\text{m}$, which leads to specific film thickness value of 0.007, much less than 1. Therefore, the contact operates in the boundary lubrication regime. The materials, hardness, and surface roughness of tribo-pairs used in this investigation are described in Table 1. A surface roughness (Ra) of $0.15\ \mu\text{m}$ is a production representative value. An Ra value of $0.54\ \mu\text{m}$ was selected to assess whether there would be an increase in friction coefficient.

Motored Valvetrain Rig for Friction Evaluation

A motored valve train rig was constructed using a 3.5-L V-6 right-hand cylinder head from a 3.5-L engine as shown in Fig. 3 for friction evaluations in the mixed lubrication regime. Analytical modeling estimated minimum oil film thickness in the range



Fig. 3—The motored valve train rig for friction evaluation.

TABLE 1—THE PROPERTIES OF MATERIALS TESTED IN THE PLINT MACHINE AND THE MOTORED VALVETRAIN RIG

	Material	Hardness	Surface Roughness, Ra
Plint tests			
Cylinder	AISI 52100 steel	82 HRA	0.28 μm
Flat	16MnCr5 steel	58 HRA	0.54 μm , 0.15 μm
DLC coating	a-C:Si	–2000 Hv	0.54 μm , 0.15 μm
Motored valvetrain tests			
Camshaft	Chilled cast iron	73 HRA	0.10 μm
Bucket tappet	Carbonitrided steel	76 HRA	0.04 μm

of 0.2–0.3 μm for the camshaft speed range used in this investigation. The composite surface roughness of the cam lobe and tappet is about 0.14 μm . This leads to lambda values (the ratio of minimum oil film thickness to composite surface roughness) in the range 1.4–2.0, indicative of a mixed lubrication regime. The cylinder head was mounted at a 60° angle on an aluminum support to represent the actual vehicle-installed position of this engine. This engine had four camshafts, one intake and one exhaust in each head. One intake camshaft made of chilled cast iron was used for this investigation, and it was driven by an electric motor through a flywheel and a set of couplings. An in-line torque meter measured the average torque. Each camshaft contained six cam lobes, which slid against six tappets. SAE 5W-20 GF-4 engine oil, the same as used for Plint testing, was run at multiple temperatures. Engine oil was heated externally in a sump to maintain oil galley temperature in the range 80–120°C and then pumped into the engine inlet from where it flowed through the original channels to lubricate the cam and tappet contact. The lubricant pressure was maintained at 40 psi. The coolant was also heated in an external sump about 5°C above the oil set temperature and then pumped into the engine inlet from where it flowed through the original channels just like the engine oil. The circulation of hot coolant assisted in bringing the cylinder head to the required temperature quickly.

Prior to evaluation of each surface modification, it was important to ensure that the surfaces of the cam lobes and bucket tappets were adequately broken in. The break-in of a new camshaft and new bucket tappets was conducted to ensure stable friction

by monitoring friction torque as a function of time. The break-in procedure consisted of running the system at 300, 500, 700, 800, 900, 1,100, 1,300, 1,500, 2,000, and 2,500 rpm, with more time spent at lower speeds. The oil temperature was maintained at 100°C. The system was considered broken in when a stable friction was reached at each rpm, which was typically about 150–200 h. A new camshaft and a set of six bucket tappets were used for each test while ensuring that the lash between the cam lobes and the bucket tappets were maintained within the specified limit. The surface roughness of the cam lobes and bucket tappets were measured using a stylus profilometer (Talysurf 10, Taylor–Hobson, UK) before and after tests. The bucket tappets were DLC-coated and the camshaft was not.

RESULTS AND DISCUSSIONS

Laboratory Bench Tests

Figure 4 shows the friction characteristics of DLC coatings (deposited on polished flats, Ra = 0.15 μm) as a function of test time. The friction coefficient of DLC coating under nonlubricated condition was initially high probably due to the higher affinity of carbon on steel. It then slowly dropped to a lower value with continued sliding, probably due to the formation of a transfer film on the opposing surface. During the last 30 min of sliding, the friction coefficient remained relatively stable at about 0.08. In the presence of the engine oil, the initial friction coefficient was lower than that observed in the nonlubricated condition and continued at that level for the test duration. The steady-state friction coefficient under the nonlubricated condition appeared to be lower than that of lubricated condition. The friction coefficient of steel sliding against steel under the nonlubricated condition is also plotted for comparison.

Figure 5 shows the friction coefficients of DLC coatings as a function of engine oil temperature compared with data from uncoated steel flats. The reported friction coefficients are the average of the last 15 min of two tests, which were very reproducible (friction coefficient values only differed in the third decimal point). The friction coefficients increased slightly with the engine oil temperature and the friction coefficients of DLC coatings were a little higher than those observed with uncoated steel flats. Also, there was very little difference in friction coefficients when the surface roughness (Ra) changed from 0.54 to 0.15 μm .

Figure 6 shows the wear scar width on the cylinder as a function of temperature when the flat surface roughness was 0.15 μm Ra. In the case of the uncoated flat, wear scar width increased with oil temperature. The wear of the cylinder in contact with

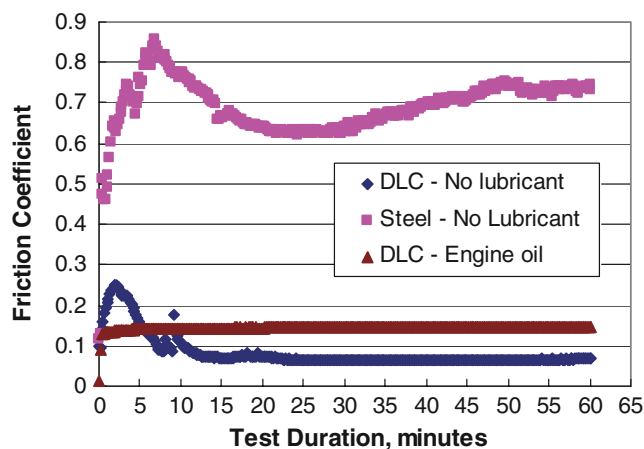


Fig. 4—The friction characteristics of DLC films as a function of test duration using polished flats.

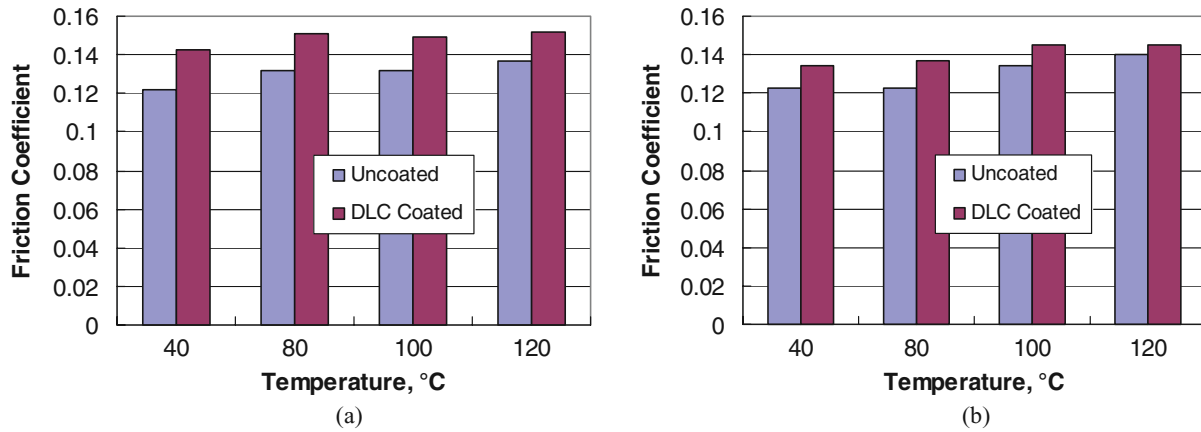


Fig. 5—The friction characteristics of DLC coatings as a function of engine oil temperature when the surface roughness of the flat is (a) $0.54 \mu\text{m}$ and (b) $0.15 \mu\text{m}$.

DLC-coated flats was much higher than that for uncoated flats. This could be due to increased surface hardness of the flat due to deposition of coating and/or the lack of formation of lubricant-derived antiwear films as described later. The wear scar width of the cylinder against an uncoated polished flat was 1.25 mm when no lubricant was present. There was no measureable wear on uncoated and DLC-coated flats.

Figure 7 shows 488 nm Raman spectra taken from the wear scar regions of the DLC-coated flats from lubricated and unlubricated tests as well as a spectrum from an unworn area. The Raman spectrum (Fig. 7a) from the unworn region shows a broad peak centered at around $1,550 \text{ cm}^{-1}$, which is known as the G peak, and a small broad band at 870 cm^{-1} . The latter band may be due to a vibration between carbon (C) and one of the elements comprising the film. DLC coatings that contain no metals did not have this band. Tamor and Vassell (29) demonstrated that the width, position, and intensity of the G peak are related to the coating deposition conditions and film properties. Following a lubricated test at 100°C , the Raman spectrum from the wear scar area showed a broader G peak and a more noticeable D peak cen-

tered at around $1,350 \text{ cm}^{-1}$, as shown in Fig. 7b. The D peak became more prominent following the unlubricated test, as shown in Fig. 7c. The appearance of the D peak is an indication of a change in the microstructure of the DLC coating. In the unlubricated test, the localization of frictional heat may have contributed to this change more than in the lubricated test, where heat is carried off by the lubricant flow.

Figure 8 shows scanning electron micrographs of worn and unworn regions of a DLC-coated flat following lubricated test at 100°C . There is very little difference in the coating morphology between the worn and unworn regions. The worn region appeared untouched, although several tiny, flat regions were created as a result of sliding. This is a reflection of the hard, wear-resistant surface created by the deposition of DLC coating. These flat regions are believed to have carried the load. The worn area also contains tiny white spots, which appear as topographical defects in the SEM image. However, auger spectroscopy found the elemental composition in this region to be identical to the surrounding region. It is not clear whether these regions were created as a result of sliding. Auger electron spectra were taken from one of these flat regions to understand the interactions of lubricant additives with the coating. Auger electron spectra were also taken from worn regions of an uncoated flat tested with the lubricant at 100°C for comparison. Figure 9a shows the elemental distribution through the thickness of the lubricant-derived surface films. The film contained low levels of Zn, S, and P, which are primarily from the interactions of antiwear and antioxidant compound ZDDP. The film surface was rich in O and Ca, and with continued sputtering the concentration level decreased slowly. The source of Ca was from the detergent and generally deposited on the surface as calcium carbonate (Giasson, et al. (30)). The general distribution of elements on the film was typical of an uncoated steel flat sliding against another steel counterpart in the presence of engine oil and in general was responsible for antiwear protection. In contrast, the worn DLC-coated surface, as shown in Fig. 9b, did not contain any of the elements from the lubricant additives. Instead, the worn surface contained C and Si, the components of the DLC coating. This result suggests lack of any interactions between the lubricant additives and the DLC coating.

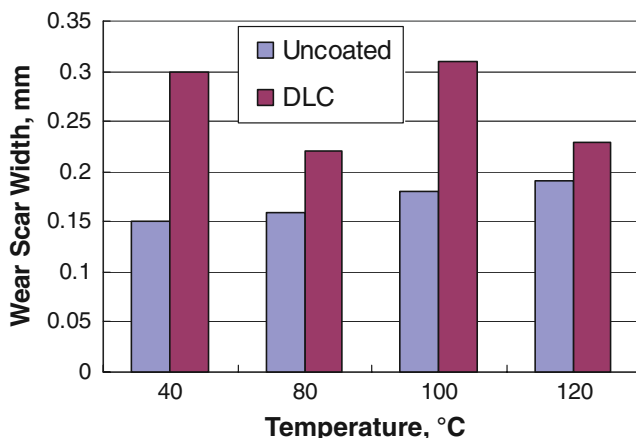


Fig. 6—Wear scar width of cylinders in contact with DLC-coated polished flats.

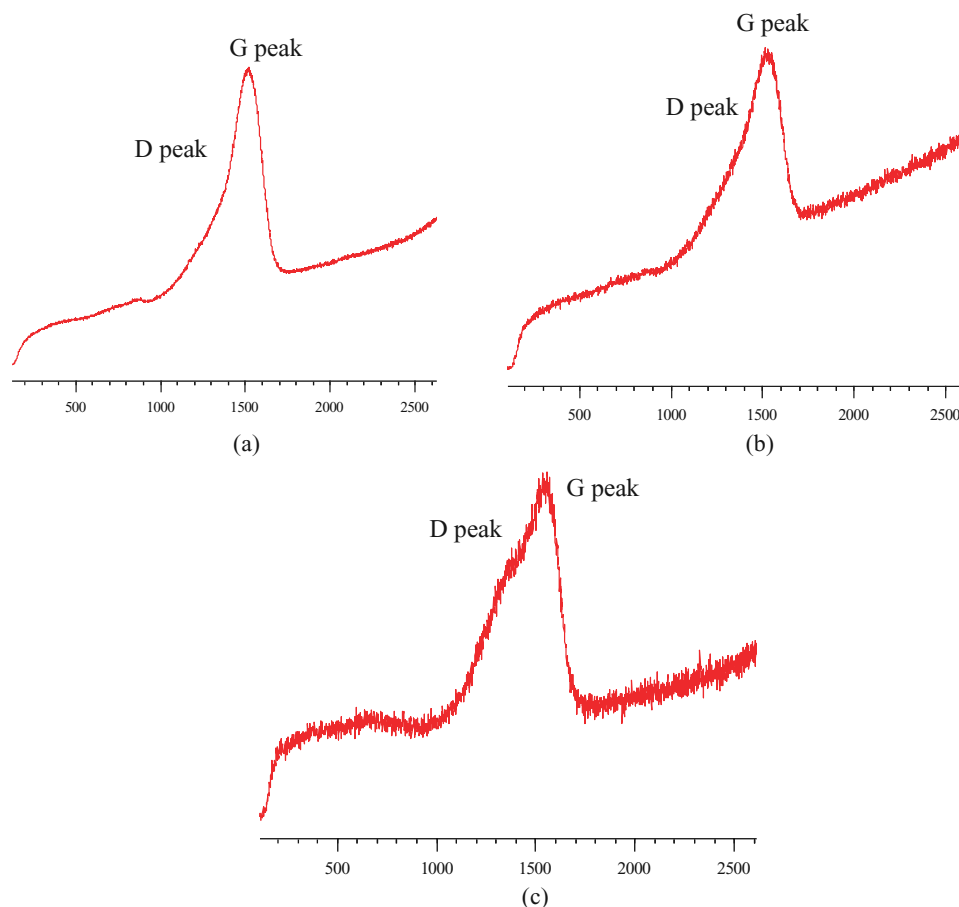


Fig. 7—Raman spectra from an (a) unworn region, (b) worn area from a lubricated test at 100°C, and (c) worn area from an unlubricated test using DLC-coated flats.

Therefore, the antiwear protection was enabled through the wear resistance characteristics of the DLC coating and not from the lubricant additives.

Motored Valvetrain Friction

Figure 10 shows friction torque obtained at 100°C oil temperature with DLC-coated bucket tappets, production buckets,

and polished buckets having the same surface roughness as DLC-coated buckets. The friction torque decreased as speed increased, suggesting that the system operates in a mixed lubrication regime. The polished buckets showed substantial friction reduction at all speeds, confirming the importance of surface roughness. The friction benefit observed with polished buckets compared favorably to DLC-coated buckets. Because the surface roughness of polished and DLC-coated buckets is the same, the data suggest

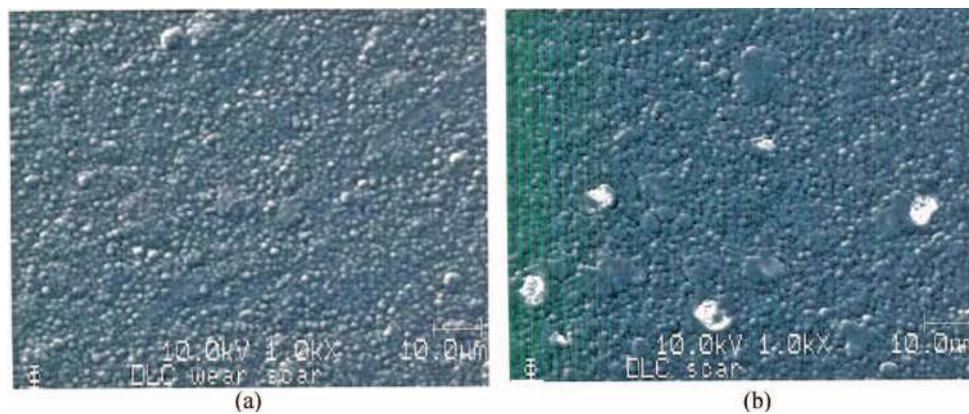


Fig. 8—Scanning electron micrographs of (a) an unworn region and (b) worn regions of DLC-coated flat after a lubricated test at 100°C (from Plint tests).

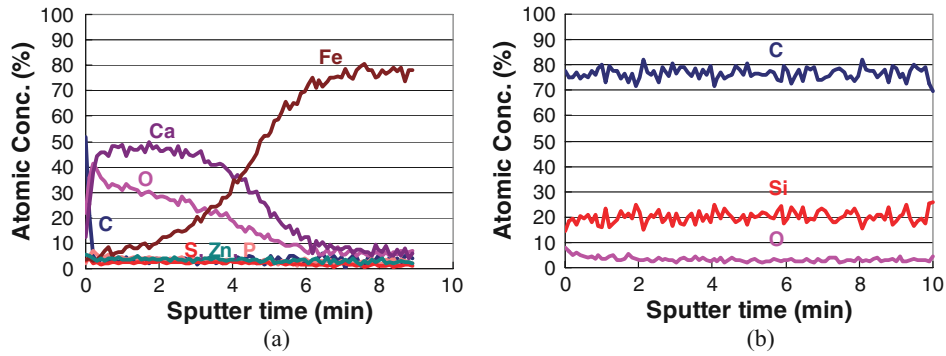


Fig. 9—Auger depth profile through surface films formed on (a) uncoated and (b) DLC-coated steel flat in the presence of lubricant at 100°C (from Plint tests).

that the DLC coating did not offer any additional friction reduction benefit. Testing at 80 and 120°C oil temperatures showed similar results.

The surface of one of the DLC-coated buckets was analyzed using scanning electron spectroscopy to determine whether any lubricant-derived film formed on the surface due to operation in a mixed lubrication regime. Examination of the wear surface showed random distribution of patchy films throughout (Fig. 11a). The lubricant-derived film appeared white in the scanning electron micrograph and could be identified distinctly on the DLC coating background, which appeared dark as shown in Fig. 11b. The micrograph also showed parallel lines indicating abrasive wear marks.

Auger electron spectra taken from the light and dark regions of Fig. 11b are shown in Figs. 12a and 12b, respectively. Auger electron spectra from the light region show high concentrations of O and Ca on the surface. The concentration of these elements dropped as sputtering continued. It took almost 10 min for complete removal of the film. There was also some Zn, S, and P, the elements from ZDDP, on the surface. The concentrations of C and Si, which are elements of the DLC coating, were low on the surface but increased with continued sputtering as the lubricant derived films were removed. The auger spectra from the darker

regions did not contain any of the lubricant-derived elements but primarily contained C and Si as shown in Fig. 12b.

Figure 13a shows a scanning electron micrograph from another region of the wear surface, showing similar light and dark regions along with Ca (Fig. 13b) and P (Fig. 13c) maps. The Ca and P maps are practically superimposed on each other, which shows that both elements are present in the lubricant-derived films. Examination of another bucket tappet showed similar results. Figure 14a shows an infrared reflectance absorbance spectrum from a DLC-coated bucket tappet. A spectrum from a polished bucket is also shown in Fig. 14b for comparison. The infrared reflection-absorption spectra represent the composition of the deposited film in a 2-mm-diameter circle on the bucket tappet. Because the deposited material is not a continuous film, the spectra obtained are averages over the spot examined and over the entire thickness of the films. The peak intensities of spectra taken from various locations varied depending on where spectra were obtained, but the composition remained the same. In Fig. 14b, the strong peak at around 1,150 cm^{-1} is associated with phosphate-type inorganic compounds, and the peaks at 1,441 and 1,511 cm^{-1} are associated with carbonate material deposited due to interactions of detergents with the surface. The broad band centered at 3,000 cm^{-1} is indicative of -OH groups and is involved in hydrogen bond-type interactions. Phosphate bands at 1,133, 1,094, and 908 cm^{-1} were also found on the DLC-coated buckets (Fig. 14a). The carbonate peak was present on the uncoated bucket but was absent on the DLC-coated bucket. Combining these results with the auger results suggests that the lubricant-derived film on the DLC-coated bucket is primarily calcium phosphate. This is significantly different from the mixed phosphate and carbonate films found on uncoated steel buckets in past evaluations of lubricant-derived films on steel substrates (Gangopadhyay, et al. (31); Lindsay, et al. (32); Willermet, et al. (33)).

Figure 15 shows a 244-nm (UV) Raman spectrum obtained from the surface of the DLC-coated bucket, which showed the characteristic carbon peak of DLC coating at 1,571 cm^{-1} . In addition, the peak at 988 cm^{-1} is typical of phosphate films, further confirming that the surface film on DLC coating is phosphate containing. No peak for carbonate was seen.

The surface analysis results clearly showed the formation of patchy lubricant additive-derived tribofilm on the bucket surface from the motored valve train rig, which primarily operated in the

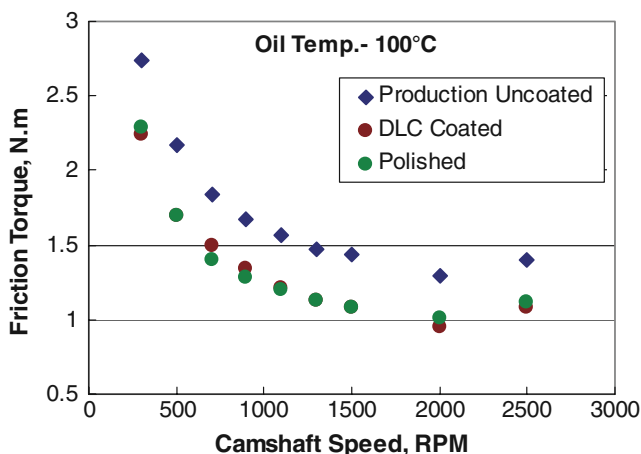


Fig. 10—Friction torque as a function of camshaft speed at 100°C oil temperature.

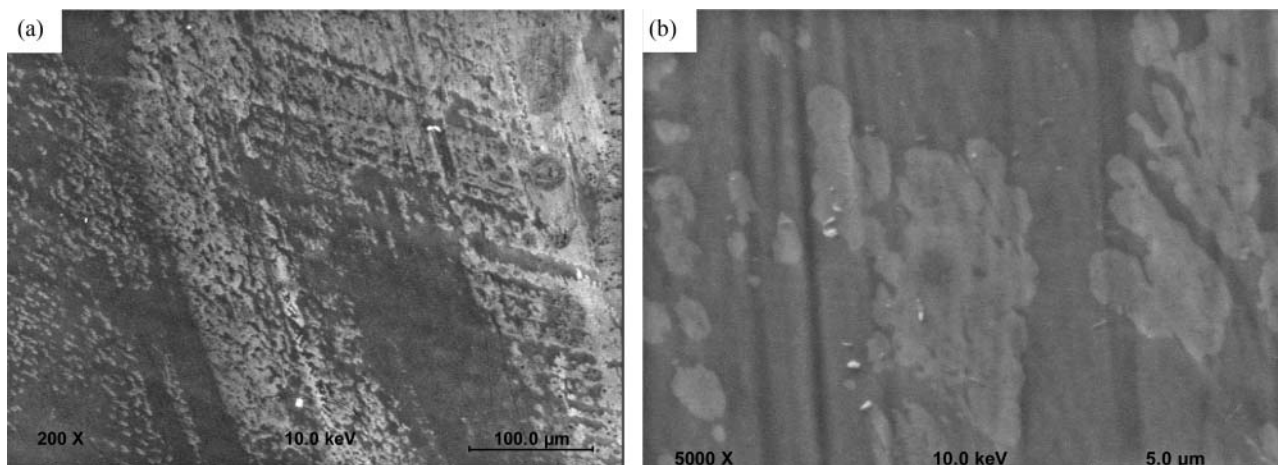


Fig. 11—Scanning electron micrograph of worn region (a) at low magnification showing the distribution of films and (b) at higher magnification showing film morphology on the DLC-coated bucket tappet.

mixed lubrication regime. However, no such tribofilms could be observed on the flat samples used on the Plint test. This is somewhat unexpected because the latter test was run under boundary lubrication conditions, where there were a lot more asperity interactions. It is possible that the contact stress was not high enough to make a tribofilm. The contact stress with a 240 N load in Plint, which is near the maximum capability of the machine, was about 0.48 GPa. This is nearly half of the peak contact stress seen in the valvetrain rig. Another difference between the two tests was the test duration. The Plint test was limited to 1 h, whereas the motored valve train test was nearly 250 h. It has been observed that the formation of a lubricant-derived film and its thickness varies with the rubbing time, concentration of ZDDP, and temperature (Fujita, et al. (34); Miklozic, et al. (35)). In our experience, we have observed tribofilm formation on ferrous surfaces in Plint tests under similar conditions. The relative chemical inertness of the DLC surface compared to a ferrous surface may explain the lack of film formation on DLC-coated samples in these Plint tests.

It is often asked whether any special lubricant additive is required for diamond-like carbon coatings. The authors believe

that it is too early to predict whether any changes in additive chemistry would be needed for DLC-coated surfaces, given the wide variation observed in the chemistry of DLC coatings; that is, hydrogenated vs. nonhydrogenated, ratio of sp^2 to sp^3 content, presence of metals in the film, and so on. The necessity for any special additive chemistry for DLC coatings can be divided into two parts: (a) friction requirements and (b) wear requirements. Regarding friction requirements, in this particular investigation we see evidence of lubricant-derived tribofilms on DLC-coated surface in the presence of GF-4 oil. This particular DLC coating did not offer any additional friction advantage. Renondeau, et al. (36) explored the effects of an antiwear additive, detergent/dispersant, and a GF-4 oil on the friction coefficients of various DLC-coated surfaces. They observed that friction response varied depending on the additive components present in the engine oil. They also observed that some of the DLC coatings responded to engine oil chemistry and some did not. Okuda, et al. (27) reported that the presence of an MoDTC friction modifier did not exhibit a friction-reducing effect on hydrogen-free DLC coating. This led to the replacement of MoDTC with an ashless

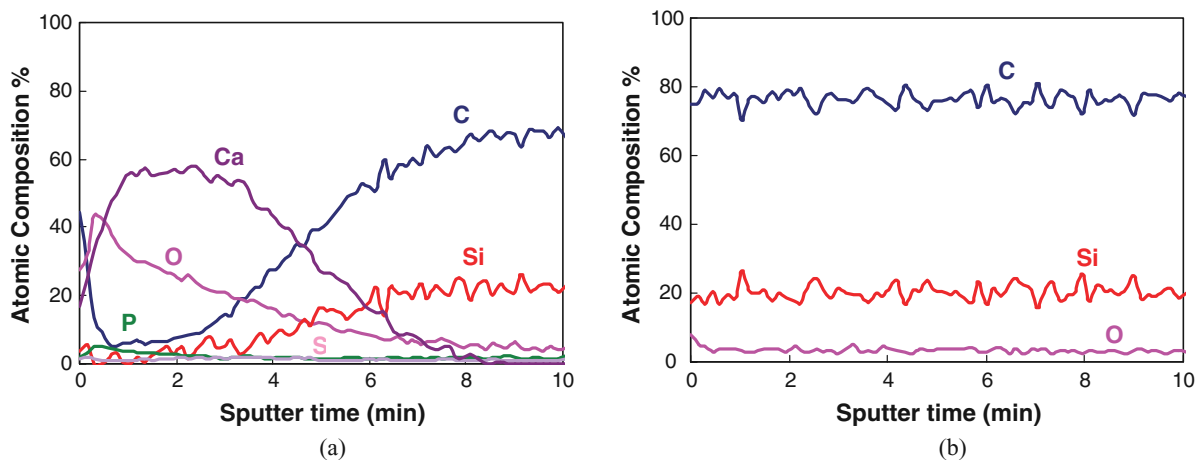


Fig. 12—Auger electron spectra of (a) light region and (b) dark region on DLC-coated bucket tappet surface.

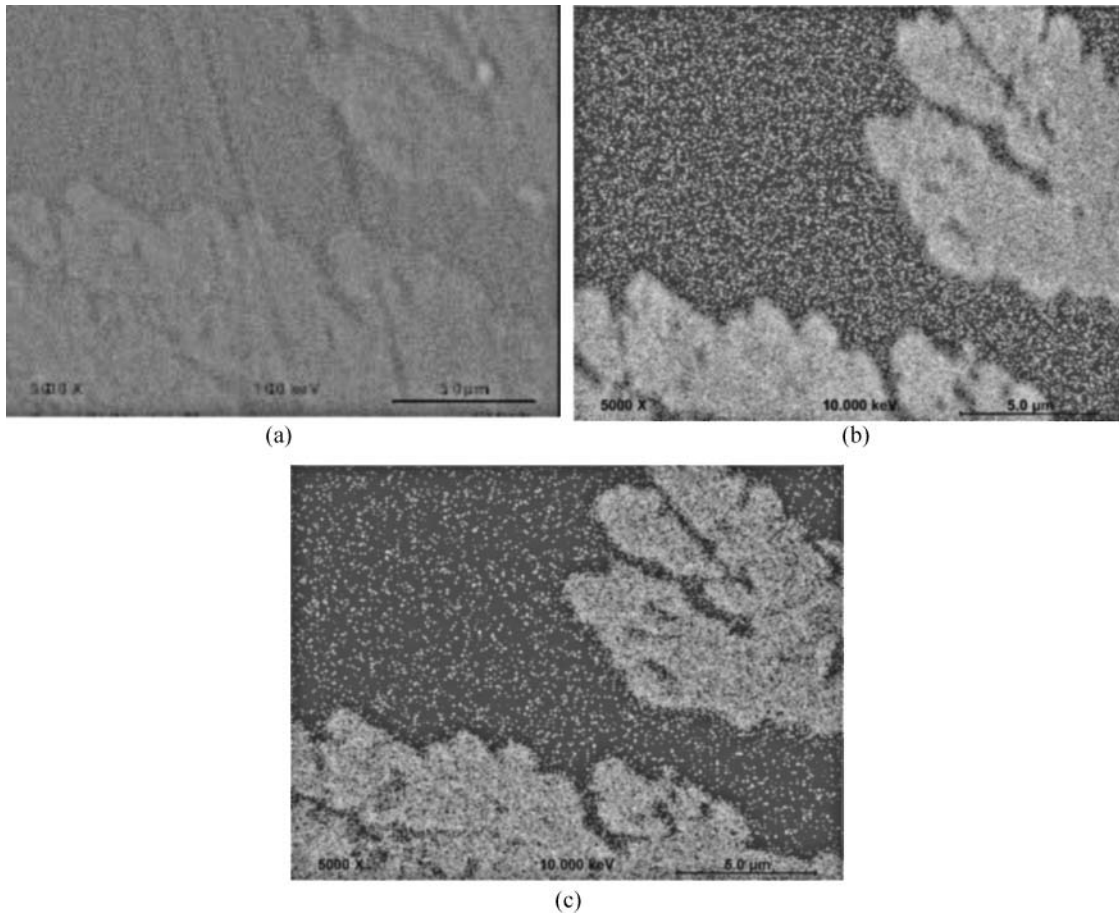


Fig. 13—(a) Scanning electron micrograph, (b) Ca map, and (c) P map of a wear region on DLC-coated bucket surface.

friction modifier. Similarly, Broda and Bethke (20) reported that the friction responses of DLC coatings varied depending on the DLC coating formulation as well as engine oil formulation. Regarding wear requirements, DLC coatings have intrinsic wear resistance compared to uncoated steel due to their high hardness. Therefore, additional wear protection from lubricant additives may not be necessary for the DLC-coated parts. However, one needs to be careful that additives present in the engine oil do not increase wear. Shinyoshi, et al. (22) showed an increase in wear

of DLC coating in the presence of molybdenum dithiocarbamate friction modifier in the engine oil. Therefore, further research is necessary before the question can be answered definitively.

CONCLUSIONS

In unlubricated sliding tests, the DLC coating investigated in this study showed significant reduction in friction coefficient compared to steel sliding on steel, possibly due to the formation of a transfer film. However, in the presence of engine oil, the

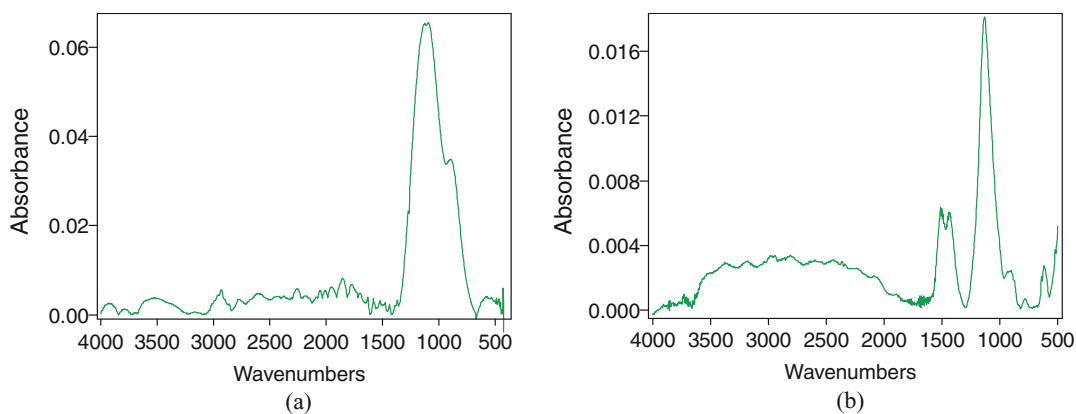


Fig. 14—Infrared reflectance-absorbance spectra of (a) polished DLC-coated bucket and (b) polished uncoated bucket.

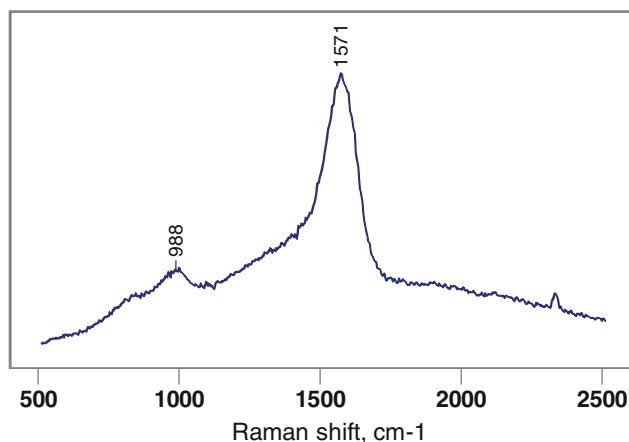


Fig. 15—Raman spectrum of tribofilm on DLC-coated bucket.

friction coefficient was slightly higher than that observed in the absence of the engine oil, possibly due to the lack of a transfer film formation.

In boundary lubrication conditions, the wear of the counterface steel cylinder in contact with a DLC-coated flat was higher than that against uncoated steel flats, probably because of high hardness of DLC coating and also because of the absence of any lubricant-derived antiwear films on the coated substrate.

In unlubricated sliding conditions, Raman spectroscopy data suggest a transformation in the microstructure of the DLC coating. This transformation was less evident under lubricated sliding.

In motored valvetrain tests, under mixed lubrication conditions, both polished and DLC-coated steel bucket tappets showed lower friction torque than the production bucket tappets. However, no significant difference was observed between the polished and the DLC-coated buckets, suggesting no friction advantage of DLC coating in this application.

Under boundary lubrication conditions, no additive-derived antiwear film could be observed on the DLC-coated surface, possibly due to the short duration of tests and relative chemical inertness compared to a ferrous surface. However, under a mixed lubrication regime in motored valvetrain tests, patchy additive-derived antiwear films could be observed. Based on IR, auger, and Raman spectroscopy results, the film appears to primarily consist of calcium phosphate, which is different from the mixture of phosphate-type inorganic compounds and carbonates previously observed on uncoated steel surfaces.

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