Deposition of anti-stick coatings to prevent hydrocarbon buildup on truck engines

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Abstract
The problem of buildup of hydrocarbon deposits on truck engine surfaces may reduce the fuel efficiency, in addition increasing the amount of unburned fuel as exhaust gases can lead to environmental risk. This problematic issue can be resolved by applying anti-stick coatings on engine pistons using physical vapor deposition (PVD) technique. In this work, broad range of coating substrate systems (Chrome based (CrN, CrAlTiN), Oxides (TiOx and ZrOx), Carbon based (Graphit-iC™ and Dymon-iC™) and special coating (TiB2), are investigated to determine their ability to act as anti-stick coatings. All the coatings investigated in this study, were applied on polished parts cut from engine piston cylinders. Characterizations were performed after applying droplets of engine oil and heat treating the surfaces up to 400 °C. Based on the evaluation of oil adhesion, surface energy, coating thermal stability, surface morphology, mechanical and crystallographic properties, the anti-stick performance ranking of coatings was suggested for truck engine piston application in order to improve their performance.

Keywords: PVD coatings; fuel efficiency; anti-stick; thermal analysis; performance ranking
1. Introduction

With the increase in petroleum prices and demanding environmental legislations, automobile and truck manufacturers are being forced to produce more fuel-efficient engines. Within the engine most of the friction related power losses occur inside piston-cylinder area, as estimated by Ürgen et al. [1] ~15% of the total frictional losses occur inside in all engine parts. In combustion engine, the explosion of the air/fuel mixture in the piston gives engine its power, in general, if more heat is generated, the more power the engine produces eventually. However, adherent, hard and abrasive carbon (the residual product of air/fuel reaction) layer deposits on the piston and cylinder surfaces due to burning of oil which ultimately decreases the overall performance of the engine (for example by increasing friction) [2-5]. Researchers are trying to find the main reasons for this carbon layer or (sometimes called) soot build-up in the automobile engines [2-5]. The change in engine design, controlling the gas chamber temperature and introduction of exhaust gas recirculation (EGR) minimizes the release of harmful oxides of Nitrogen (NOx) into the environment but in turn increases the soot build up on the engine parts [2]. This carbon or soot build up eventually results as a contacting or abrasive layer between two component parts (especially piston and cylinder) and results in abrading the parts due to friction, the oil viscosity increases due to soot build up and reduces oil pumps performance [2].

A possible solution to the build-up of the carbon layer is the deposition of an anti-stick coating on the cylinder surface using the physical vapor deposition (PVD) technique [6-19]. Physical vapor deposition (PVD) coatings are currently applied to engine components for combating wear and frictional losses mainly. An example is the use of PVD coatings on cylindrical roller thrust bearings investigated by Bobzin et al. [12] in which they concluded that anti friction and anti-wear properties of the coatings improved in the bearing systems due to fine grained structure of the coatings obtained by PVD techniques. Similarly, Fox-Rabinovich et al. [13] determined that the grain refinement is the major cause of enhanced wear properties of PVD coatings. Navinšek et al. [9] suggested that clean PVD coatings are better when compared with electroplating and electro-less processes, since latter processes cause environmental pollution because of their wastage. In addition, Erdemir and Holmberg [7] and Holmberg et al. [20] determined that PVD coatings are cost effective and exhibit lower surface roughness, higher hardness and increased wear resistance in comparison to electroplating. McConnell et al. [8] investigated the thermal stability of PVD coatings and they found a decreasing trend in wear performance of the coatings with increased temperature.
conditions. Thus, the main challenge is to develop suitable surface coatings to be able to withstand higher operating temperature of the engine and higher pressure contact.

Many researchers investigated PVD coatings for erosion and corrosion protection such as CrAlTiN and CrN [21,22] and they suggested that these multilayered coatings have huge potential for such applications due to their ability to tailor toughness and hardness by modifying the architecture of layer constituents and chemistry. Furthermore, the multilayered concept was also found beneficial in terms of frictional resistance as investigated by few more researchers [23,24], when they mixed CrN layers in Graphite like coatings (GLC) and AlTiN. However single layered PVD coatings were found useful as well in terms of wear and corrosion resistance due to better adhesion to the substrates and good crystallinity of such coatings [25-27]. The current work aims to investigate the potential of most common PVD coatings as anti-stick layer to avoid buildup of hydrocarbons in engine surfaces such as pistons. The following coating substrate systems are assessed in this study, (Chrome based (CrN, CrAlTiN), Oxides (TiOx and ZrOx), Carbon based (Graphit-iC™ and Dymon-iC™) and special coating (TiB2), because these coatings were investigated by several researchers for their enhanced anti-wear and anti-corrosion behavior such as CrAlTiN [21,22], CrN [23,24], ZrOx [17], TiOx [25], TiB2 [26], carbon-based coatings (Graphit-iC™ and Dymon-iC™) [27]. Carbon based and Chromium based coatings are well known for automotive applications and for the protection of engine parts however this is the first time that the oxide coatings and some special coatings are studied in detail for comparative purposes and thus this is the first time that all these significant coatings have been studied collectively for the anti-stick coating applications.

2. Materials and Methods

A commercial truck engine piston cylinder was obtained and test parts were cut from the cylinder wall, with sizes of approximately 1.5 cm x 1cm x 1 cm. These were then polished using progressively finer grit paper starting at grade 240 and finishing on the 1200 grade. They were then fine polished with 3 and 1μm diamond paste. The polished parts were uncontaminated using first methanol for 5 minutes and then acetone for 5 minutes in ultrasonic bath. Afterwards, ZrOx and TiOx coatings were deposited using a Teer Coatings UDP450 system (deposition parameters are provided in Table 1). CrAlTiN, CrN, TiB2, Graphit-iC™ and Dymon-iC™ used in this study were applied on the same substrate by commercial suppliers. All coatings were deposited by magnetron sputtering.
Thermal stability of the coatings is an important criterion to be used in truck engines. This was evaluated by heating the coated parts in air in a box furnace. Samples were heated at 30 °C/min up to temperatures of both 300 °C and 400 °C [28] and were maintained at this temperature for a period of 120 minutes before being allowed to cool. The anti-stick properties of the coated parts to carbon buildup is evaluated by applying a drop of heavy duty engine oil (Castrol GTX Diesel, 15W-40), onto the surface of the coatings was placed. The coated part with oil droplet was then fired in air in the box furnace. On removal from the furnace the adhesion of the ‘burnt oil’ was examined using an optical microscope. A scratch was also drawn through the residue using a diamond stylus of a scratch adhesion tester and the delamination of the burnt oil residue around this scratch using an optical microscope was examined in order to provide a qualitative assessment of adhesion of the residue to the surface.

The ball cratering device was utilized in order to determine the coating thicknesses. The spectroscopic ellipsometer measurements (Woollam M2000 variable wavelength ellipsometer) were carried out to verify the measured values. Sessile drop contact angle technique was used in order to measure contact angle and surface energy of the deposited coatings. For this purpose, a video capture apparatus from Dataphysics Instrument (OCA 20) was utilized. Surface free energy calculations were determined using three test liquids: deionized water, ethylene glycol and diiodomethane. A well-known, so called Owens, Wendt, Rabel and Kaelble (OWRK) method [29] was used to calculate polar and dispersive components of surface energies. Philips XRD (X-ray diffraction) system with PW 1711 detector and PW 3020 goniometer was utilized to measure crystallinity of the deposited coatings. A normal diffraction mode was used at 40 kV and 40 mA with Cu Kα radiation at a scan rate of 1°/min. Wilson Tukon microhardness tester (using 100 gm load) was used to measure micro-hardness of the deposited coating substrate systems. Rockwell C indenter with 100 Kgf load was employed to apply an indent on the coating substrate systems which was then assessed using optical microscopy to estimate adhesion quality of the coatings. This was done by comparing the indentation pattern with the standard scale (HF1: the best adhesion and HF6: the poorest adhesion) [30]. Surface roughness and top surface morphology of the uncoated and coated substrates was investigated by WYKO NT1100 Optical profilometer. An optical microscope was utilized to observe surface morphology, ball crater mark and Rockwell C indent. The adhesion of the coatings to the substrate was assessed using ST200 scratch adhesion tester (Teer Coatings). In this test, a Rockwell diamond tip travels across the coatings at a constant velocity of 10 mm/min and a constant loading rate of 100 N/min while an increasing normal force is applied on the tested
samples. The test was initiated at a starting load (normal force) of 5 N to recognize the start of the scratch track and it was stopped when load reached to 50 N. Finally, the critical load $L_c$ is detected at which the first failure in coatings is observed.

3. Results and discussion

3.1. Characterization of uncoated and coated piston cylinder test samples

Many pore defects were noticed in the piston cylinder substrate material prior to coating. However, the coated surface showed a reduction in the number of pores compared with the uncoated polished surface. The chemical analysis of the uncoated cylinder using Optical Emission Spectroscopy (with a spark source) determined the following elemental compositions: %C=0.46, %Si=0.26, %Mn=0.98, %P=0.02, %S=0.03, %Cr=1.04, %Ni=0.13, %Mo=0.21, %Cu=0.19, %As=>0.39. This analysis result classified the piston cylinder alloy as low alloy steel / medium carbon steel (similar to AISI 4142). These alloys exhibit lower corrosion resistance compared to high alloy steel such as 316L for example. The investigated coatings had thickness values from 0.6 to 2.5 µm. It should remain clear that while the thickness of the coating is not likely to have a significant effect on the anti-stick properties of the surface, it may however influence coating adhesion to the steel substrates because of internal coating stress [14], in addition, coating thickness may also influence surface morphology. Optical profilometry is used to monitor surface morphology in this study (Fig. 1). From all the coatings examined, TiOx and ZrOx surface exhibited the lowest surface roughness ($R_a \approx 5$ nm) and CrN and CrAlTiN the highest ($R_a \approx 15$ nm). It is appealing to note that in an earlier study which evaluated anti-stick properties of DLC (Diamond-like coating) coated die against aluminium, it was observed that adhesion of the coatings was poor for smoother die surfaces [31].

3.2. Evaluation of oil adhesion on uncoated and coated samples

In order to assess the anti-stick properties of the coatings to hydrocarbon deposits, contact angle and surface energy measurement were calculated on both the coated and uncoated cylinder parts (Table 2). As shown, coated surfaces exhibited a reduction in surface energy and an associated increase in contact angle, compared to uncoated piston cylinder sample. Amongst the coatings studied, CrAlTiN and TiOx exhibited the lowest and highest surface energies, at 29 mN/m and 41 mN/m respectively. It was observed that the surface free energy of the coatings was composed of higher dispersion component and lower polar component. The polar component of the surface free
energy determines adhesive characteristic of two opposite surfaces. The uncoated piston cylinder surface displayed highest polar component (9.8 mN/m) compared with all coatings (1.5-8.4 mN/m). The variation of contact angle and surface energy for different coatings is influenced by factors such as coating chemistry, structure, surface roughness etc. It is anticipated that both low polar component with low total surface energy surface are required for anti-stick applications, that lead to a lower adhesion to opposite surface [29]. From all the coatings tested, CrAlTiN surface exhibited both the lowest surface energy (29 mN/m) and polar component (1.5 mN/m). In order to assess the effect of engine oil adhesion on the coatings, contact angle tests were performed using the Castrol (GTX Diesel oil, 15W-40). As shown in Table 2, an increase in the oil contact angle was noticed for the coated sample compared to uncoated cylinder samples. With the CrAlTiN and CrN coatings exhibiting the higher oil contact angle of 29° and 27° respectively compared with 8° for the uncoated steel.

To evaluate the adhesion of hydrocarbon residues on the coated piston cylinder parts, tests were carried out involving heating the uncoated and coated parts with a drop of engine oil in a box furnace up to temperatures of 400 °C. The adhesion of the oil residue was then assessed using optical microscopy and using the scratch test technique described earlier. Scratch testing was carried out to help differentiate the oil residue adhesion to the test surfaces. The cracking pattern of the oil residue around the scratch formed by the scratch tester is given in Fig. 2. This test confirmed that Cr based coating exhibited the lowest level of adhesion to the oil residue as shown in Fig. 2a. For the Dymon-iC™ coating for example a carbon layer still visible within the scratch track of the coating, in contrast delamination and spallation of burned oil layer occurs along the scratch track edge of the CrAlTiN coating (Fig. 2b). This may be due to the lower surface energy of the CrAlTiN coating as detailed earlier.

### 3.3. Thermal stability of the coatings

For application in truck engines the requirement is that the PVD coatings should exhibit thermal stability up to temperatures 400 °C. The morphology of the deposited coatings before and after thermal treatment of both 300 and 400 °C were examined using optical microscopy. With the exception of the Dymon-iC™ coating, all the coatings tested exhibited an unchanged surface morphology before and after these heat treatments. The carbon based Dymon-iC™ coating partially degraded with the heat treatment since significant loss in coating adhesion was observed (Fig. 3). The color of the Graphit-iC™ and TiB₂ coatings changed after heat treatment may be because of
oxidation of the top surface of coatings (confirmed by XRD examination), as suggested by investigators as well [8,11,18].

The adhesion of the coatings substrate systems before and after heat treatment was measured using the Rockwell-C indentation test. In this test, the Rockwell C indent is compared to the adhesion quality chart, whereas in this chart HF1 represents good adhesion and HF6 represents total delamination [6,30]. Table 3 lists down the results, as coated CrAlTiN, CrN, TiOx and Graphite-IC coating were measured to have HF1 adhesion. After heat treatment, CrAlTiN and CrN coatings were measured to have HF2 adhesion, which indicate moderate adhesion. In contrast, even as coated Dymon-iC™ coatings behaved poorly in terms of adhesion quality and after heat treatment, their performance further deteriorated resulting in complete delamination of coatings (Fig. 4).

Coating adhesion was also assessed using the scratch test technique both before and after heat treatments of 300 and 400 °C (Table 4). Both Rockwell and scratch adhesion test result confirmed that Cr based coating such as CrAlTiN and CrN exhibited the highest thermal stability and Dymon-iC™, ZrOx and TiB₂ showed the lowest thermal stability.

The Vickers micro-hardness of the uncoated and coated piston cylinder samples was carried out before and after thermal treatment to analyze the mechanical stability of the coating-substrate composite system as shown in Table 5. The two oxide coatings exhibited the same hardness to that of the substrate. It should be noted that this hardness will be significantly influenced by the bulk hardness of the steel particularly for these lower thickness (<1 µm) oxide coatings. In contrast, the hardness values of the Graphite-IC and CrAlTiN coatings were found to be twice that of the uncoated steel. Among the coating studied in this work, CrAlTiN, TiB₂, CrN and Dymon-iC™ showed higher composite hardness compared with other coatings. A reduction of hardness value was observed for all coating after thermal treatment except for CrAlTiN coating, which as reported previously exhibits excellent thermal stability in the temperature range studied [32].

An XRD study was carried out in order to identify crystallography changes in the coating after thermal treatment. No peaks were observed from XRD spectrum of the as coated Graphit-iC™ coating, indicating the amorphous nature of the film (Fig. 5a). However, oxide peaks were found in the coating after subjecting it to thermal treatment
at 400 °C. This would indicate the formation of oxides and suggests partial coating decomposition at a temperature 400 °C [8]. No peaks were observed in the as coated TiOx sample spectrum thus demonstrating the amorphous nature of the deposited film. After heating to 400 °C however a number of diffraction peaks were observed. These peaks were similar to the reference indexed peaks with powder diffraction file (PDF) numbers 21-1272, indicated the formation of Anatase phase (TiOx) during the thermal treatment (vide supra). In contrast to the results obtained for Graphite-IC and TiOx, identical XRD peaks were observed for CrN, CrAlTiN, TiB$_2$ and ZrOx coatings both before and after thermal treatment. Cr based coatings mainly consist of the phases of Cr, Cr$_2$N and CrN before and after thermal treatment. This indicated that CrN and CrAlTiN coating thermally and mechanically stable at 400 °C (Fig. 5b), which is required temperature for the piston cylinder application [8]. Both TiB$_2$ and ZrOx coatings exhibited structural (phase) stability, however, they showed poor mechanical properties at 400 °C, indicating their unsuitability for the piston cylinder application.

4. Conclusions

In this study, a range of metal oxides and nitride coatings were deposited on parts cut from truck engine cylinders. The resulted surface energy of the coatings was lower than that for the uncoated steel. The thermal stability of the deposited coatings was monitored by heating the coated parts in air up to 400 °C. Based on an evaluation of the adhesion of oil and oil residue (after thermal treatment), coating thermal stability, surfaces morphology and mechanical performance, the following is the hydrocarbon ‘anti-stick’ ranking allocated to the coatings investigated: CrAlTiN > CrN > TiOx > ZrOx > Graphit-iC™ > TiB$_2$ > Dymon-iC™. It is clear from this assessment that the Cr based coatings such as CrAlTiN and CrN exhibit the highest anti-stick performance of all coatings investigated. While this initial study demonstrated the potential of these coatings; it will be necessary to further evaluate the effect of coating stoichiometry, thickness, etc. before practical applications.

Acknowledgments

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References


**Figure Captions**

**Figure 1.** 3D Optical profilometry image of the (a) uncoated sample (b) TiOx and (c) CrAlTiN coated polish piston sample

**Figure 2.** (a) Comparison of oil adhesion on (a) Uncoated, (b) CrAlTiN coated and (c) Dymon-iC™ coated piston samples by scratch test. (b) Comparison of oil adhesion on (a) Uncoated and (b) CrAlTiN coated piston samples by scratch test

**Figure 3.** Optical microscopy images of (a) the as coated CrN coating, (b) thermally treated CrN coating at 400 °C, (c) the as coated Dymon-iC™ coating and (d) thermally treated Dymon-iC™ coating at 400 °C.

**Figure 4.** The Rockwell-C indentation spot of (a) the as received CrN coating, (b) thermally treated CrN coating at 400 °C, (c) the as received Dymon-iC™ coating and (d) thermally treated Dymon-iC™ coating at 400 °C for adhesion evaluation.

**Figure 5.** The XRD patterns of (a) Graphit-iC™ and (b) CrAlTiN coatings (S = peak from steel work piece) obtained before and after thermal treatment at 400 °C.
Figure 3
Figure 4
Tables captions:

**Table 1.** Plasma cleaning and deposition conditions – (used for TiOx and ZrOx)

**Table 2.** Water and oil contact angle/surface energy measurement

**Table 3.** Evaluation of coating adhesion before and after thermal treatment using the Rockwell indentation test

**Table 4.** Assessment of coating adhesion using scratch tests before and after thermal treatments

**Table 5.** Microhardness measurements of coating-substrate composite (Error \(\approx 2\%\))
Table 1

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Table 3

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### Table 5

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