Friction and Wear Behavior of Thin-Film Ceramic Coatings under Lubricated Sliding Contact

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Abstract

Thin film ceramic coatings are increasingly being used in lubricated tribological components. Unfortunately, lubricants formulated with functional additives such as anti-wear and friction modifiers, are usually designed to interact with ferrous material to form tribochemical surface films. When this lubricants are applied to coated surfaces, the effectiveness of the additives is still largely unknown. In this study, we evaluated the friction and wear behavior of several commercially available thin-film ceramic coatings when lubricated with unformulated and fully formulated synthetic oils to assess the impact of lubricant on such coatings. A variety of

behaviors were observed for different coatings which can be explained in terms of the differences in tribochemical film formation and properties on the coatings surfaces.

Keywords: ceramic coatings, wear, friction, lubricant additives, tribofilms.

1 Introduction

Tribological components in machinery, such as gears, bearings etc., are usually lubricated either with oil or grease. Most of these components operate under severe sliding or rolling contact conditions and hence, adequate lubrication is essential for optimal operation and prevention of failure. Lubricants used in various tribological applications are usually formulated with additives for optimal performance [1, 2]. The commercial oil lubricants consist primarily of a basestock and an additives package. The basestock can be mineral-oil based or synthetic-oil (such as poly-alpha-olefin (PAO), ester or polyol) based. Additives normally accounts for 4-10% of the total weight in fully formulated lubricants. Most of the efforts in term of lubricant formulation are devoted to producing the right combination of basestock and additives with a particular or desirable functionality. Although there are many different types of additives, they can be divided into four major functional categories: (1) Additives for lubricity; such as antiwear additives used to reduce wear, friction modifier additives used for friction control and extreme pressure additives used to prevent catastrophic failure under high severity contact conditions. (2) Additives to control chemical breakdown; such as antioxidant additives to retard the degradation of the oil by air via oxidation, corrosion inhibitor additives used to retard oxidation of the metallic surfaces in contact, and detergent

additives used to clean and neutralize oil impurities. (3) Additives for contaminant control; this group includes dispersant additives to keep contaminants suspended in the oil and prevent them from coagulating. (4) Additives for viscosity control: such as viscosity modifier additives used to keep viscosity higher at elevated temperatures.

In lubricated tribological contacts, different regimes of lubrications occur depending on the severity of the contact and the properties of the lubricant. In hydrodynamic regime the surfaces of the two components in contact are completely separated by lubricant fluid film. In elasto-hydrodynamic (EHD)/ mixed regime there is some limited interaction between the surface materials of the tribological contacts. The interactions are mostly elastic in this regime, hence it is called EHD. Boundary regime is characterized by high severity contacts and extensive interaction between the surface materials, the so-called metal-to-metal contact. In this regime, friction and wear are higher than in other regimes and the lubricant additives play an important role. Additives in the lubricant interact with the surface material to produce a tribochemical film also known as boundary film. Depending on the nature of the additives, the resulting film can have different properties (e.g. low friction, wear resistant, etc...). Under hydrodynamic and EHD lubrication regimes, friction and wear are mostly determined by the lubricant fluid film properties. Under boundary lubrication regime, friction and wear are determined by the simultaneous shear of the fluid film, boundary film and the near surface material.

Structural ceramic materials have a combination of properties that can result in excellent tribological properties. These include high hardness, high temperature stability and low density. However, the relatively low fracture toughness and relatively high cost of part

fabrication are barriers to the widespread use of ceramic tribological components.

Nevertheless, ceramic materials are being used in tribological applications that involves high temperature and aggressively hostile environments. Current applications includes bearings, mechanical seals, machining tools, dies and medical prostheses [3-6]. Development of ceramic coatings deposited on metallic substrates provided a pathway for a cost-effective approach to take advantage of desirable properties without the low fracture toughness problem. There are numerous commercially available ceramic coatings currently in use. These coatings can be deposited by a variety of techniques, such as the different variants of physical vapor deposition (PVD), chemical vapor deposition, etc.

Existing lubricants additives are usually formulated for ferrous materials because most of the lubricated tribological components are made of steel or cast iron. However, over the last decade or so, thin film ceramic coatings are increasingly being used to enhance the performance of tribological components [7-12]. Most often they are used to solve persistent tribological problems or failures occurring with typical components.

Currently, there is very limited knowledge about the role of lubricant additives in tribological performance of ceramic coated surfaces. Since the ceramic coatings are relatively thin, they are usually applied to existing components with minimal changes to the system, including lubrication. The question of the nature of interaction between lubricants and thin film ceramic coatings on tribological performance has to be addressed. The interaction between the two technologies could be synergistic, antagonistic or has no effect at all. In order to effectively integrate these two technologies (i.e. lubricant additives and ceramic coatings), adequate understanding of the interaction between them is needed. Hence the goal of the

present study is to assess the impact of thin-film ceramic coatings on friction and wear behavior on lubricated contacts, paying special attention to the formation of tribochemical boundary films.

2 Experimental Details

2.1 Coatings

Four commercially available thin film ceramic coatings from Ionbond™, namely: titanium nitride (TiN) Ionbond™ 01, titanium carbon nitride (TiCN) Ionbond™ 10, titanium aluminum nitride (AlTiN) Ionbond™ 20 and metal-doped (Me-DLC) amorphous (a-C:H:W) diamond like carbon coating Ionbond™ 40 were used for the present study. The performance of the coatings was compared to baseline uncoated case-carburized and hardened 4120 steel material, which is also the substrate for the coatings. Thin-film hard ceramic were deposited on steel flats of dimensions 38 mm x 5.1 mm x 6.3 mm by physical vapor deposition technique to a thickness ranging between 1-5 microns. Uncoated case carburized steel flat substrate has a hardness of 6.8 GPa (60 HRC) and surface roughness of 19 nm R_a. Some relevant properties of the coatings and the uncoated steel substrate; such as thickness, hardness and surface roughness are summarized in table I.

The coating thickness shown in table I, was measured by the standard calowear technique. This involves the creation of a crater by a rotating ball of known diameter through the coating into the substrate. The coating thickness measured by this technique is consistent with the estimate from cross-section SEM characterization of the coatings shown in Fig. 1. The nanoindentation technique was used to measure the hardness and elastic modulus of the

coating tested using a Hysitron TI-950 nano-indenter system using a Berkovich diamond indenter to a depth of 100 nm. The results of hardness and modulus measurements measurement are shown in table I.

2.2 Friction & Wear Testing

Oil-lubricated friction and wear tests were conducted with a roller-on-flat contact configuration in reciprocating sliding. The counterface roller is made of 4370 steel alloy ($\varnothing$ 6.3 mm, 10 mm length) with surface roughness of 200 nm R_a and hardness of 6.1 GPa (56 HRC). Tests were conducted with three different synthetic lubricants: basestock poly-alpha-olefin (PAO10) without additives and two fully formulated commercially available lubricants. Lubricant A (Optimol Optigear BM 220) is a commercially available mineral base high performance gear oil from Castrol and contained an additives package that was optimized for friction control, while lubricant B (Roadranger SAE 50) is an Eaton commercially available synthetic transmission lubricant and has an additives package optimized for wear protection. Some of the lubricants properties as provided by the manufacturer are summarized in Table II. Adequate amount of lubricant was applied to cover the flat surface completely at the start of the test. Periodic replenishment of lubricant was done during the duration of the test. In all cases, enough oil was on the surface at the end of test. Tests were conducted at 150N normal load (which imposes a 0.33 GPa Hertzian contact pressure), 0.5 Hz reciprocating frequency (30 rpm.), 10mm stroke length (equivalent average linear speed of 10mm/s) and for a duration of 180 minutes. The flat specimen was heated to 100 °C with a heater cartridge located below the sample holder. Friction coefficient was continuously measured during the testing. Wear

volume on both counterface materials, flats and rollers, were measured at conclusion of the test using white light interferometry. Worn surfaces were characterized by optical and scanning electron microscopy (SEM) (Quanta 400F ESEM) equipped with energy dispersive analysis X-ray (EDAX) operating at 10kV, in order to evaluate the surface damage and wear mechanisms.

3 Results

The friction behavior for the different coatings and the uncoated substrate when tested with basestock PAO without additives is shown in Fig. 2A. The friction coefficients varies with time for some of the materials tested (TiN, TiCN, and AlTiN coatings) and are nearly constant for the duration of test for other materials (uncoated substrate and the Me-DLC coating). Most of the variation in the friction at the early part of the tests can be attributed to the run-in process. After this initial period that can take 30-60 minutes, the frictional response for most of the materials reach a steady state with values typical for boundary lubrication regime ($\mu \sim 0.13-0.15$). AlTiN coating showed the largest decrease on its friction coefficient during the run-in process; starting with a value of $\mu \sim 0.3$ the friction decreased to 0.18 in the first hour of testing and finally reached a value of $\mu \sim 0.15$ after 3 hours of testing. It should be noted also that the friction coefficient is highest for the AlTiN coating for the duration of the tests. TiN coating also showed considerable variation in friction with time. Although the friction coefficient at the beginning ($\mu \sim 0.19$) and to the end of the test ($\mu \sim 0.13$) didn't differ much, there was a significant reduction in the early stage of test, followed by an increase until steady state was finally reached towards the end of the test. The variation in frictional response for TiCN coating was somewhat similar to TiN, but lower in magnitude and much

less noisy. Starting with a value of $\mu \sim 0.17$, the friction coefficient fell to 0.13 before increased and reached a steady value of $\mu \sim 0.15$. For Me-DLC coating the friction behavior was constant for the entire duration of the test with the lowest value of friction ($\mu \sim 0.1$). Also the uncoated substrate displayed an almost constant frictional response with a friction coefficient of $\mu \sim 0.15$ except for the very first minutes of run-in.

Results of the frictional behavior of different coatings and uncoated steel tested with fully formulated synthetic lubricant A are shown in Fig. 2B. When tested in this lubricant, all materials showed a reduction in friction within the first 5-30 minutes of the test and reached a steady state friction coefficient. Because the friction reduction is much more than what was observed in the test with the basestock lubricant, the friction behavior in lubricant A is attributed to combined effect of run-in and interaction of the lubricant additives with the surface materials to form tribochemical films. With the exception of AlTiN, the steady state friction coefficient with values between 0.04-0.065 is considerably lower than typical boundary lubrication regime friction ($\mu \sim 0.1$ -0.15). In ferrous materials, such low friction value under boundary lubrication regime is normally indicative of the formation of a low friction boundary films. Although the largest reduction in friction was observed for the uncoated steel substrate (from $\mu \sim 0.125$ to $\mu \sim 0.04$), some of the coatings also experienced a significant decreased in friction in the presence of this formulated oil: Me-DLC (from $\mu \sim 0.1$ to $\mu \sim 0.05$); TiN (from $\mu \sim 0.2$ to $\mu \sim 0.055$) and TiCN (from $\mu \sim 0.15$ to $\mu \sim 0.065$). Less friction reduction was observed in test with the AlTiN coating. After an initial decrease (from $\mu \sim 0.2$ to $\mu \sim 0.1$), very early in the test, friction coefficient became noisy and showed a somewhat

gradual increase for the rest of the test. Although, lower friction coefficient was observed in all the tests with lubricant A (which was optimized for friction control) when compared to tests with the PAO basestock, the presence of coatings seems to reduce the effectiveness of the additives as the uncoated baseline steel exhibited the lowest friction coefficient of the materials tested.

Fig. 2C shows the frictional behavior for different coatings and uncoated steel substrate tested with fully formulated synthetic lubricant B. Friction showed only a slight decrease after a run-in (10-15 minutes) and similar friction behavior was observed for all the coatings and uncoated steel substrate after the run-in period. A steady state friction coefficient was reached for all materials ($\mu \sim 0.09-0.10$). Again, the only exception to this frictional behavior is the AlTiN coating in which the test started with a friction coefficient that was substantially higher (about 0.2) than the remaining coatings. There was a gradual decrease in friction coefficient until a steady state value ($\mu \sim 0.115$) was reached half the way into the test. Except for AlTiN, the coating material appears to have no effect on friction in tests with this lubricant. Other than the time needed to reach the steady state value, all the coatings and the uncoated steel substrate tested showed a similar steady state friction coefficient ($\mu \sim 0.09-0.12$).

At the conclusion of each test, the wear tracks of both the steel roller counterface and the flat surfaces were characterized by optical, 3D interferometry and scanning electron microscopy. Because most of the wear was produced in the softer counterface (roller), and wear on the flats was minimal (not measurable), an assessment of wear was conducted by measuring the wear in the roller for each test. A summary of wear volume in the rollers at the conclusion of

the tests is shown in Fig. 3. It is clear that wear in rollers tested against most of the coatings was higher than wear in rollers tested against the uncoated steel. Wear in rollers tested against Me-DLC coating was the only one lower than roller wear against uncoated steel. Formulated lubricants were more effective than basestock (PAO) in reducing roller wear when rubbed against uncoated baseline steel. Wear produced on the roller by the different coating seems to be independent of the type of lubricant, whether formulated or not. Except for Me-DLC, all other coatings produced substantially more wear to counterface steel roller. (Note the log scale for wear axes in Fig. 3).

4 Discussion

In friction and wear tests with basestock PAO that contains no additives, a range of frictional behavior was observed depending on the coating. The operating lubrication regime under the test conditions used for the present study is boundary. Under such conditions, extensive interaction is expected between the contacting materials through the lubricant fluid film. Sliding against the DLC coating resulted in lower friction, because of the inherent low friction attributes of the coating. The other coatings showed higher friction and more variability as the contact dynamic changes with the occurrence of wear during the duration of test. Wear measured in the steel roller counterface is higher when sliding against all coatings compared to the uncoated steel flat specimen; except for the DLC coating. The higher hardness of the coatings is responsible for more wear in the relatively softer steel counterface (roller). In the peculiar case of DLC coating, this material is known to protect the counterface surfaces under dry condition. This could be due in part to the transfer of a carbon layer from

the DLC coating unto the counterface body, as has been reported in other studies under dry lubrication [13, 14]. Although the current study is lubricated, DLC also reduced wear in the counter-face as indicated in Fig. 3. Evidence of a possible transfer of surface film from the coating into the roller was observed as shown in Fig. 4. The mechanism by which this transfer takes place is not fully understood yet.

With fully formulated lubricant A, optimized for friction control, different friction behaviors were also observed for the different materials tested. For the uncoated substrate (baseline) the friction coefficient started at 0.12 and decreased to a value of 0.04 due to the formation of a tribochemical film as shown in Fig. 5a. EDAX spectrum of this film is shown in Fig. 5b, which indicates the presence of elements that are usually present in lubricant oil additives, such as O, Zn, Mg, P and S. This film fully covers the contact area and is responsible for the sustained and constant low friction behavior. Again, since the test conditions for this study invokes boundary lubrication regime, the oil additives are expected to react with the contact surface to produce a protective tribochemical surface film i.e. the boundary films. Because the lubricant is formulated for ferrous surfaces and optimized for friction reduction, the observed low friction in the test with uncoated surface is expected. For TiN and TiCN coatings, the friction trend is similar to the baseline, with a significant reduction in friction with time and reaching values for the friction coefficient of 0.055 and 0.065 respectively. There is evidence of limited localized tribochemical film formation and some metal transfer from the steel roller unto the coating surface, both present in the same areas, indicative of higher severity of contact in the localized areas (Fig. 5c and Fig. 5d).

Although the oil additives are not expected to react with the ceramic coating surface, the coincidence of metal transfer and the limited tribofilm formation on this two coatings may suggest the lubricant additive can indeed be effective on ceramic coated surfaces if there is adequate ferrous material transferred into the coating surface. For Me-DLC coating, friction started at a lower value (0.095) and decreased to a steady state friction coefficient value of (0.05). There is minimal film formation on the coating (Fig. 5e) but some evidence of film formation on the roller. It is unclear if this film is transferred carbon film or tribochemical reaction film. In tests with AlTiN coating, friction coefficient started at a much higher value (0.2) and remained high until the end of the test (0.12). Extensive metal transfer from the roller (softer counterface) onto the coating was observed (Fig. 5f). It appears that excessive and perhaps continuous metal transfer into the ceramic coating surface may interfere with tribochemical film formation, making the additive ineffective.

For fully formulated lubricant B, optimized to minimize wear, similar friction behavior and values were observed for all coated and uncoated samples. For the uncoated steel substrate (baseline) the original surface topography was preserved (with no wear) and there was minimal tribochemical film formation; hence the friction remained constant (Fig. 6a). TiN, TiCN and AlTiN coatings showed similar friction behavior and different degree of metal transfer and tribochemical film formation. They all produced more wear on the counterface steel roller but minimal to no wear in the coating themselves (Fig. 6b, 6c and 6d, respectively). For DLC coating, only slight decrease in friction with time was observed. There was no evidence of film formation on the coating, but evidence of some films was

present on the roller wear track (Fig. 6e). Recall that with unformulated PAO, minimal wear was observed in the roller because of the carbon transferred to protect the counterface. With fully formulated lubricants wear is observed in the roller. This may be due to the additives interfering with carbon transfer to counterface when sliding against DLC coating, thereby inhibiting the wear protection provided by the carbon transfer from the coating.

5 Conclusions

Based on the experimental results from the present study, lubricant formulation with additives was effective in reducing friction and/or wear in steel-on-steel lubricated contact through the formation of surface tribochemical films as expected. The presence of thin-film ceramics coatings on one of the sliding surfaces sometimes has no effect and sometimes is detrimental to the effectiveness of tribochemical films produced from lubricated additives. Me-DLC coating has beneficial effect by reducing both friction and wear in contacts lubricated with un-formulated basestock oil. In fully formulated lubricants, the DLC was not as effective, although still beneficial. TiN and TiCN coatings both have minimal effect on friction behavior of wear optimized formulated and unformulated lubricants, but produced more wear on the counterface. In friction optimized lubricant, there is evidence of possible tribofilm formation and the consequent reduction in friction. AlTiN coating showed higher friction and wear of counterface in all the lubricants tested. There is no evidence of tribofilm formation on the coating.

Much more research work is needed to develop adequate understanding of the interactions between lubricant additives and thin-film coatings. This will facilitate the

development and design of robust tribological components that can effectively integrate lubricant and ceramic coating technologies for optimal performance.

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Table I: Properties of thin-film hard ceramic coatings

Table II: Properties of the lubricants

Fig. 1: Coatings cross-section SEM micrographs: a) TiN, b) TiNC, c) AlTiN, d) Me-DLC coating.

Fig. 2: Friction coefficient variation with time for the different coatings and uncoated steel substrate lubricated with: a) basestock-PAO10, b) lubricant A- friction optimized, c) lubricant B - wear optimized

Fig. 3: Roller wear volume after sliding against steel substrate and different thin-film coatings.

Fig. 4: Carbon transfer film on steel roller slid against Me-DLC coating in PAO.

Fig. 5: Micrographs of flat specimen surfaces tested with lubricant A: a) steel substrate, b) EDAX spectrum of tribochemical film, c) TiN, d) TiCN, e) Me-DLC and f) AlTiN,

Fig. 6: Micrographs of flat specimen surfaces tested with lubricant B: a) steel substrate, b) TiN, c) TiCN, d) AlTiN and e) steel roller tested against Me-DLC.

Coatings	Deposition method	Type	Thickness (μm)	Nano Hardness (GPa)	Elastic Modulus (GPa)	Roughness (nm)
TiN	PVD	Monolayer	3.7	29.5 $\pm$ 2.5	371 $\pm$ 22	87
TiCN	PVD	Monolayer	0.9	39.2 $\pm$ 3.8	337 $\pm$ 20	49
AlTiN	PVD	bilayer	2.4	34.5 $\pm$ 2.1	291 $\pm$ 10	19
Me-DLC	PVD	multilayer	3.5	14.7 $\pm$ 1.3	164 $\pm$ 13	56

Table I: Properties of thin-film hard ceramic coatings

Lubricant	PAO	Synthetic A	Synthetic B
Viscosity 40°C (cSt)	71.1	233.5	132
Viscosity 100°C (cSt)	10.70	18.7	17.5
Viscosity Index	-	92	146
Flash point (°C)	272	235	221
Pour point (°C)	-51	-15, 5	-45

Density (kg/m ³) at 15.6C	837	905	860
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Table II: Properties of the lubricants.

Fig 1

Fig 2a

Fig 2b

Fig 2c

Fig 3

Fig 4

Fig 5

Fig 6