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Friction reduction mechanisms in cast iron sliding against DLC: Effect of biofuel (E85) diluted engine oil

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ABSTRACT

Parasitic friction losses during piston ring-cylinder liner interactions in an internal combustion (IC) engine consume large portions of the available fuel energy. This work investigates whether the tribological performance of grey cast iron (CI) cylinder liner would be improved using a piston ring coated with non-hydrogenated diamond-like carbon (NH-DLC) in comparison to uncoated CI and steel rings. Coefficient of friction (COF) values and volumetric wear losses of CI were determined using ball-on-disk type tests as a function of sliding distance. CI tested against itself during boundary lubricated sliding with synthetic engine oil showed a COF of 0.14 and a volumetric wear of 11.0×10^{-4} mm^3 after 6×10^5 cycles, whereas the use of NH-DLC coated counterface resulted in a COF of 0.11 and lesser wear of 0.5×10^{-4} mm^3. Dilution of the engine oil by ethanol containing E85 biofuel was beneficial as COF was further reduced to 0.08 for CI tested against NH-DLC while maintaining low wear of 0.2×10^{-4} mm^3. According to TEM and XPS analyses, an oil residue layer (ORL) formed on the CI contact surfaces as a result of sliding-induced degradation of zinc-dialkyldithiophospahte (ZDDP) additive in the oil. The ORL, which consisted of nano-crystalline particles of sulphides and phosphates of zinc (anti-wear components) embedded in an amorphous carbon matrix, was responsible for maintaining low wear. Ethanol dilution of the synthetic oil facilitated the formation of ORL. TEM/EELS studies of the NH-DLC counterface provided evidence for OH adsorption and passivation of carbon bonds at the surface that reduced the friction. It is anticipated that piston rings coated with NH-DLC run against CI liners would show low friction and wear during boundary lubricated sliding, an effect that could be enhanced when ethanol diluted oil is used.

1. Introduction

Sliding friction occurring during cylinder bore (liner)-piston ring interaction is a source of energy loss in internal combustion (IC) engines [1]. Traditionally, cylinder walls or liners are made of grey cast iron (CI) [2]. Buckley [3] tested CI against AISI 52100 steel counterfaces at 0.5 N load to investigate their wear and friction behaviour by altering the carbon content of cast iron. A direct relationship was found between carbon content and decreasing wear. Friction values were sensitive to the relative humidity (RH) of the system. On increasing the relative humidity from 0% RH (Ar atmosphere) to 50% RH the coefficient of friction (COF) reduced from 0.2 to 0.1. Unlubricated sliding under the ambient conditions led to CI contact surfaces being covered with a smeared graphite film which was responsible for the self-lubricating behaviour of cast iron [3,4]. Terheci et al. [5] performed unlubricated pin-on-disk tests on self-mated grey cast iron sliding pairs and found that under the ambient conditions a low COF between 0.33–0.37 was maintained on increasing the load from 2.0 N to 10.0 N. Riahi and Alpas [6] constructed a wear map for grey cast iron for unlubricated sliding (under ambient air) against AISI 52100 type steel. Three main wear regimes were identified consisting of severe, mild and ultra-mild wear, as the load and speed were reduced. In the ultra-mild wear (UMW) regime (<1.0 N, 1.0 m/s) low wear rates (10^{-6}–10^{-7} mm^3/m) were recorded with continuous iron oxide layers formed on both the steel counterface and the cast iron sample preventing direct metallic contact. In the UMW regime no plastic deformation at the contact surfaces was detected. At higher loads and high sliding velocities, mild wear regime was observed and characterised by discontinuous oxide layers and oxide debris formation. Another notable feature in the mild wear regime was the formation of the rosette type graphite flake morphology in the near surface region and fracture of these flakes and the matrix generated large-size debris. The transition from mild to severe wear occurred due to the local welding of the

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large-size cast iron debris that transferred to the counterface. The transferred material was found to be harder than the pristine cast iron and this was attributed to martensitic hardening. Thus, the unlubricated sliding experiments showed that friction and wear behaviour of cast iron is sensitive to the test atmosphere and the test parameters.

Normal engine operations could involve boundary lubricated sliding whereby transient lubrication conditions with asperity contact are experienced. Masjuki and Maleque [7] reported lower wear of cast iron pins tested against mild steel disks under boundary lubricated condition for tests in methyl ester blended with synthetic oil SAE 40 compared to tests in undiluted synthetic oil. It was suggested that the long chain esters formed a tribofilm by chemical adsorption between the polar end of the fatty acid molecules and the contact surfaces. De Silva et al. [8] tested grey cast iron cylinder liners against chromium coated piston rings under boundary lubricated conditions using ethanol+water blended synthetic oil (SAE 5W-30) and compared the results with tests in unmixed synthetic oil. The COF values reduced from 0.12 in synthetic oil to 0.07 in mixed oil and was attributed to changes in the additives (in oil) chemistry. Bench and dynamometer tests, performed on lightweight cylinder bore material namely Al-12% Si and Al-18.5% Si alloys, under boundary lubricated condition using synthetic oil SAE 5W-30 and analyzed using transmission electron microscopy TEM and spectroscopic methods have shown that a tribofilm was generated during sliding [9–11]. It was shown [12,13] that the tribolayers having antiwear properties could form as a result of zinc-dialkyldithiophospahte (ZDDP) degradation during sliding contact via an ion exchange reaction between the substrate and the lubricant. In summary, during boundary lubricated tests sliding induced degradation of additives in the oil could lead to the formation of a tribolayer, which reduced wear loss and presence of ethanol or fatty acids influenced the additive degradation chemistry.

The composition of piston ring coating is an important factor in determining the wear and friction behaviour of the cylinder liner-piston ring assembly. PVD deposited CrN, chromium plated film, WS_2 coating, sprayed molybdenum are among the few examples of wear resistant coatings deposited on piston rings [14–18]. A recent advance in piston ring surface engineering consists of the introduction of amorphous diamond-like carbon (DLC) coatings. Typically in a DLC coating sp^2 bonded graphitic clusters co-exist with sp^3 bonded carbon atoms. Electron Energy Loss Spectroscopy (EELS) and Raman spectroscopy were instrumental in determining the C bonding states in the DLC [19–21]. The hydrogen content of the coating has direct influence on the tribological properties of DLC coatings as demonstrated in previous studies [22–29]. The hydrogen atom terminated surfaces minimise interactions between covalent σ carbon bonds [22]. Hence, the hydrogenated DLC (40 at% H) coatings show low COF in vacuum and under inert atmospheres. Non-hydrogenated DLC (NH-DLC) coatings with $<2\%$ H recorded low friction in humid atmospheres [25,26]. OH groups (along with H) could be dissociated from the water molecules in the surrounding atmosphere [27] and passivated the carbon atoms on coating surfaces as well as the carbonaceous transfer layers formed on the counterface. A recent study [28] carried out on NH-DLC coatings tested against Ti-6Al-4V pins in ethanol showed a near complete elimination of running-in friction and low steady state COF emphasising the role of ethanol in passivating NH-DLC surface. It was also shown that NH-DLC coatings when used in combination with ester based oils would lead to low COF values [30]. Kano et al. [31] reported a COF of 0.03 for NH-DLC sliding against itself when tested in ester based lubricant glycerol mono-oleate (GMO). Using time-of-flight secondary ion mass spectroscopy ToF-SIMS, formation of an OH-terminated carbon surface was detected. The occurrence of low COF was attributed to weak Van der Waals forces between the two carbon surfaces passivated by OH groups originating from the GMO lubricant. Matta et al. [32] performed similar sliding experiments in which NH-DLC sliding against itself and lubricated with glycerol blended with hydrogen peroxide resulted in a COF of 0.03. X-ray photoelectron spectroscopy (XPS) and ToF-SIMS observations supported the earlier view that carbon surfaces were terminated by OH. This shows that lubricants such as GMO or glycerol/H_2O_2 that can provide OH groups are effective in reducing the friction. The effect of alcohol blended lubricants was explored by Hu et al. [33] where 2-ethylhexanol mixed with ZDDP additive in the engine oil was shown to increase its load-carrying capacity. The improved antiwear behaviour of 2-ethylhexanol (up to 8 wt%) and ZDDP (in base oil) mix tested against 52100 steel was attributed to the adhesion of polar hydroxyl groups to the metal surface and formation of a protective film although no spectroscopic evidence was provided for the same. ToF-SIMS studies performed on DLC/DLC (both hydrogenated and non-hydrogenated) and DLC/steel tested in zinc dialkyldithiophosphate (ZDDP) containing oil led to formation of ZDDP derived tribofilms on the DLC surfaces [34] in agreement with other studies [35,36]. In case of tests conducted on WC doped H-DLC against steel no tribofilm formation was found on the coating surface when tested in polyalpha-olefin (PAO) oil with extreme pressure additives [37,38]. The low friction ranging between 0.06–0.09 was attributed to the formation of a tribofilm on the steel counterface and steel substrate once the coating was worn. This tribofilm incorporated W and C from the coating and also S from the additive in the lubricating oil.

From the above review it becomes clear that during cylinder liner-piston ring interactions two factors are important for maintaining low friction and to reduce wear losses. These are i) formation of a tribolayer during boundary lubricated sliding comprising of ZDDP degraded antiwear components, and ii) in case of DLC coated counterfaces passivation of the carbonaceous surfaces by dissociated water molecules, or OH molecules from ethanol or similar additives in engine oil. Accordingly, the aim of this paper is to study the micromechanisms of tribolayer formation and surface passivation during sliding contact of a typical engine block material, type A cast iron, tested against a NH-DLC coated steel counterfaces. Tests were conducted under boundary lubrication sliding contact using synthetic oil and oil diluted by ethanol containing biofuel E85. Comparisons were made with cast iron and uncoated 52100 steels. Surface characterisation by electron microscopy and spectroscopic methods helped to delineate the mechanisms that control friction and wear.

2. Experimental

2.1. Materials and coatings

A typical engine block material, grey cast iron (CI) consisting of ASM type A graphite flakes [39] was used in the tribological tests. The microstructure of CI consisted of graphite flakes with an average length of 35.18 ± 8.2 μm that were embedded in a pearlite matrix (Fig. 1a and b). The bright-field TEM image of the pearlite with well-known lamellar microstructure consisting of alternate layers of ferrite and cementite is shown in Fig. 1c. The average width of the cementite lamellae was 53.7 ± 6.4 nm, while ferrite had an average width of 194.2 ± 28.6 nm. The Vickers hardness of the CI was determined as 202.9 ± 12 HV_{100}.

NH-DLC coatings were deposited on AISI 52100 steel balls of 6.0 mm diameter using an unbalanced magnetron sputtering system equipped with one chromium and two graphite targets. A 1.50 μm thick NH-DLC coating was deposited on a Cr interlayer to promote adhesion to the steel substrate. The hydrogen content,