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The lubrication of both aluminium–silicon and model silicon surfaces with calcium sulphonate and an organic antiwear additive

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ABSTRACT

The lubrication of a line contact between an aluminium–silicon cylinder liner and a chromium steel piston ring, which operates under mild wear boundary lubricated conditions, has been investigated. The lubricant was synthetic six centistokes poly alpha olefin based, into which calcium sulphonate and an organic antiwear additive were blended. Calcium carbonate based tribofilms were generated exclusively on silicon grains within the aluminium alloy. Replication of the contact conditions using chromium steel pin on silicon plate generated larger scale tribofilms, which comprised small, interlinked pads; these were chemically identical to those on the aluminium–silicon alloy. The thickness and elastic modulus of the tribofilm generated on the silicon substrate were determined and the results compared against previous findings by the current author.

1. Introduction

Due to automotive emissions regulations dictated by the European Union [1] and other regulatory boards [2,3] becoming increasingly stringent, the need to minimise the concentration of certain chemicals within the exhaust emissions of passenger transport becomes paramount. The maximum level of sulphated ash derived from an engine oil is currently restricted by the European Automobile Manufacturers' Association (ACEA) [2]. Calcium based detergents contribute greatly to the sulphated ash level within an engine oil [4]. Thus, as emissions regulations become more strict, the concentration of the detergent in the lubricating fluid will need to decrease in order to meet the stipulated guidelines, potentially reducing the effectiveness of the additive. Therefore, in order to boost the performance of the metallic detergents, organic additives are being derived that are intended to work in conjunction with the aforementioned detergents but do not contribute to the emissions from passenger motor vehicles.

Hypereutectic aluminium–silicon alloys afford a reduction in mass compared to ferrous substrates due to their inherent low density [5]. On a macro-scale, the hardness and tensile strength of an aluminium–silicon alloy is similar to that possessed by a cast iron alternative [5–7]. Manufacturers are incorporating these alloys as substitutes for ferrous equivalents within engines [8,9], resulting in a reduction in emissions and the fuel consumed by a vehicle [9]. Furthermore, silicon grains are important constituents within aluminium–silicon alloys, since they are known to support the load in the contact [10–12] and facilitate zinc dialkyldithiophosphate [11] and overbased calcium sulphonate [13] tribofilm formation.

The preceding article [13] to this remarked upon the merits of overbased calcium sulphonate as a successful lubricant for aluminium–silicon alloys. The intention of this publication is to tribologically and tribochemically investigate the lubrication of the previously studied aluminium–silicon and silicon crystal tribosystems [13], but instead using a combination of calcium sulphonate and an organic antiwear additive as lubricant. Tribofilms were chemically evaluated using Secondary Ion Mass Spectrometry (SIMS) whilst Fourier Transform Infrared (FTIR) was additionally employed to analyse aluminium–silicon substrates. The topography of substrates was identified by Scanning Electron and Atomic Force Microscopy (SEM and AFM). The thickness and nanomechanical properties of tribofilms on silicon substrates were determined by AFM and nanoindentation.

2. Experimental

2.1. Materials

The materials used in this work are reported elsewhere [13]. Briefly, hypereutectic aluminium–silicon 83 mm diameter cylinder

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liners were machined into 7.0 mm × 7.0 mm × 3.5 mm (w × d × h) samples. The incident substrate to the cylinder liner was a martensitic chromium stainless steel (X105CrMo17 [14]) top compression piston ring, with external radius 85.3 mm and cut into 19 mm arc lengths. Both substrates were obtained from Elring Parts Ltd.

A single crystal silicon substrate was supplied by Pi-KEM Ltd, with dimensions 7.0 mm × 7.0 mm × 3.5 mm (w × d × h). Heat-treated high chromium martensitic stainless steel (X17CrNi16-2 [14]) pins of 6.0 mm diameter, 20.0 mm length and 90.0 mm radius of curvature, were supplied by Paterson Precision Ltd. All substrates were used in as-received form, with their respective surface root mean square roughness values stated in Table 1.

2.2. Methods

Lubricant C+OAW comprised PAO6 base oil, into which an organic antiwear additive (OAW) was blended at 0.5 mass%, together with 400 total base number (TBN) overbased calcium sulphonate (Table 2) at the maximum sulphated ash limit stipulated by the ACEA [2]. The base oil and additives were supplied by Lubrizol UK Ltd.

Tribological evaluation of the test oil was conducted using a *Cameron Plint TE77* reciprocating tribometer. The cylinder liner and piston ring interface was run in line contact arrangement using an uncompressed piston ring format, with the silicon crystal and chromium steel pin arranged in a point contact setup. Tribological experiments were conducted five times in line contact and three times in point contact arrangement.

The running and contact conditions for the two setups are described previously [13], but listed briefly in Table 3. These were devised such that the aluminium alloy was not overloaded and permitted the contact conditions experienced by silicon grains within the Al–Si alloy in the line contact to be replicated accurately by the silicon crystal and chromium pin tribosystem.

Table 1
Roughness of test substrates.

Substrate	R_q
Al–Si alloy	0.431 μm
Piston ring	0.179 μm
Silicon crystal	0.0139 μm
Chromium steel pin	0.353 μm

Table 2
Test lubricant.

Lubricant	Percentage in lubricant (mass%)		
	Overbased calcium sulphonate	OAW	PAO6 base oil
Lubricant C+OAW	0.94	0.5	98.56

Table 3
Experimental conditions.

Variable	Value
Applied load	10 N (line contact); 7 N (point contact)
Maximum contact pressure	85 MPa (line contact) [13]; 115 MPa (point contact) [13]
Stroke length	5 mm
Frequency	20 Hz
Time duration	2 h
Oil volume	10 ml
Oil temperature	100 °C

2.3. Region of surface analysis on Al–Si substrates

Uncompressed piston rings were utilised throughout this work since compressed piston rings were found, experimentally, to produce non-repeatable friction and wear in the line contact arrangement [15]. However, when incorporating an uncompressed piston ring, the resulting wear on each Al–Si sample, even though it was repeatable, would be of a non-uniform distribution across the substrate. Thus, a solution to this problem was found by physically and chemically analysing the outer edges of each cylinder liner exclusively [13], which therefore afforded comparisons to be made with other substrates.

2.4. Evaluation of worn Al–Si and silicon crystal surfaces

The methods by which worn aluminium–silicon and silicon crystal substrates were evaluated are documented in a previous publication [13]. Briefly, the topography of the substrates of interest was analysed using a *Philips*™ *XL30* SEM and a *Veeco Explorer*™ *SPM*. An average wear scar width from three positions on each worn silicon crystal substrate was determined using a *Reichert Jung Polyvar MET*™ light microscope.

Tribofilm thickness was determined by applying a small volume of an aqueous (distilled water) solution of ethylenediaminetetraacetic acid (EDTA) to the tribofilm; residual fluid was removed with paper towel [16,17]. Subsequently, following a process described previously [13], 100 μm × 100 μm regions, which incorporated the surface of the tribofilm and the freshly-exposed wear scar, were evaluated by AFM. The *SPMLab*™ software supplied with the apparatus was employed to determine the step height between the tribofilm and substrate; an average and standard deviation of the resulting tribofilm thickness was computed by comparing 10 separate areas of analysis. The reduced elastic modulus of the tribofilms on silicon crystal substrates was determined using a Micro Materials Ltd *NanoTest*™ *Platform One* device and a method previously reported [13].

The tribochemistry of the wear scars generated on both Al–Si and silicon crystal substrates was determined by using a *Millbrook Mini SIMS MC 300 MKII*™ device. Heptane was used to rinse all samples prior to SIMS analysis. Al–Si substrates were analysed using ~130 μm × 130 μm areas; the analysis area on silicon samples was ~70 μm × 70 μm [13]. Additionally, the aluminium alloy was evaluated using a *PerkinElmer*® *Spotlight 400* imaging FTIR apparatus [13] using an analysis area of 100 μm × 100 μm.

3. Results

3.1. Topography of Al–Si and silicon crystal substrates

3.1.1. Aluminium–silicon alloy

Tribofilms were generated exclusively on silicon grains within the aluminium alloy (Fig. 1A and B) and the surface honing of these regions had been removed. Indeed, whilst darkly shaded films were clearly evident on silicon regions within the alloy, the aluminium matrix was void of tribofilm generation but appeared undamaged. Silicon grains on the aluminium–silicon alloy were determined to protrude from the surface of the substrate by ~480 nm on average [15].

3.1.2. Silicon crystal

The tribofilm generated on silicon crystal by lubricant C+OAW is shown in Fig. 1. For reference, shown in Fig. 2 are SEM images of the tribofilm generated on silicon crystal using calcium sulphonate in PAO6 base oil as lubricant. At the scale of the herein reported AFM and SEM images, the lubricant C+OAW film did not contain