Chemical characterization and nanomechanical properties of antiwear films fabricated from ZDDP on a near hypereutectic Al–Si alloy

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X-ray absorption near edge structure (XANES) spectroscopy was used to monitor the products formed during the breakdown of the engine additive ZDDP during its action as a protective tribochemical agent. This investigation examines the film formed under various physical conditions on a near hypereutectic Al–Si alloy. For the first time, tribochemical films (tribofilms) formed on a high silicon weight content alloy, with virtually no ferrous component have been studied. Phosphorus K- and L-edge spectroscopies show that under typical engine operating conditions, the tribofilms have similar chemical composition over a range of different test conditions. X-ray photoelectron emission microscopy (X-PEEM) reveals that the polyphosphate glasses formed vary in chain length within localized regions. The mechanical properties of the substrate and the tribofilms were acquired using a Triboscope\textsuperscript{TM} from Hysitron Inc. The elastic moduli can be extracted from the indentation curves and show that the tribofilms' mechanical properties are similar to those of the tribofilms which form on steel under similar conditions.

KEY WORDS: ZDDP, XANES, X-PEEM, nanoindentation, polyphosphate, mechanical properties, tribofilm

1. Introduction

Due to the continuous effort in the automobile industry to reduce costs, to improve car design, and to increase fuel economy, there is a considerable incentive to reduce or replace the cast iron content in engines in order to reduce weight and frictional forces between surfaces which ultimately leads to wear.

Aluminum itself is a poor alternative to replace steel due to its inadequate wear resistance, and thus aluminum alloys have been introduced, that offer better wear protection, higher strength and fracture toughness, high specific rigidity, good thermal and electrical conductivity, and easy machining [1]. Alloying aluminum with silicon can increase the strength of aluminum as it is known to form a separate hard phase in an aluminum matrix.

One such alloy that has been developed and is currently used by DaimlerChrysler\textsuperscript{TM} is manufactured by PEAK Werkstoff GmbH\textsuperscript{TM} and is marketed under the name Silitec 5\textsuperscript{TM}. This alloy is currently used in many vehicles as a cylinder sleeve. It is prepared by a spray-compaction method (Osprey process) [2] which generates a high silicon weight content (23–26 wt.%) [1,3] alloy, in which the silicon grains resemble a hypereutectic two phase microstructure [4–6]. This process leads to very small silicon grain size with a narrow distribution. The walls of the cylinder liner are chemically etched to expose the primary silicon grains on the surface, ideally to provide a load bearing surface [1,3]. Other advantages of the Silitec 5\textsuperscript{TM} alloy over conventional die cast two phase alloys includes easier machinability, and etching this near hypereutectic alloy with such a unique microstructure is a very small but uniformly distributed volume, which provides a reservoir for oil retention thus reducing the amount of oil consumed by around 30% [3].

The lubrication demands are expected to be different for steel and aluminum alloys as the microstructure and chemical properties are not similar. A great deal of research has been carried out on the dry-sliding wear response of many Al–Si alloys [7–13], however little research has been carried out on the lubrication of these alloys. Currently, the most important antiwear and antioxidant additive that is added to engine oils is a class of molecules called zinc dialkyl dithiophosphates (ZDDPs) [14]. Antiwear films generated from ZDDPs are known to protect rubbing surfaces in engines, acting as sacrificial films when being rubbed that are constantly regenerated in a rubbing environment [15]. Studies have shown that the breakdown products of ZDDPs, and not the ZDDPs itself, provides the antiwear protection needed to lubricate sliding steel surfaces within a simulated and actual engine environment [16,17]. Several studies show that ZDDPs decomposes upon rubbing to form a protective film (tribofilm or antiwear film), however thermal decomposition has also been the accepted major mechanism of the antiwear film formation [18–20]. It is well known that these films are comprised of an amorphous polyphosphate glass structure.

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The mechanism for antiwear film formation has been proposed [18,21], however these studies, using X-ray absorption near-edge structure (XANES) from a synchrotron source, have been thus far conducted on steel. This is the first characterization of tribofilms formed on the Silitec 5<sup>TM</sup> alloy with virtually no iron content.

XANES is a very good technique for acquiring detailed spatially averaged chemical information pertaining to a material or a thin film. However, for sub-micron local resolution of a specific species, X-ray photoelectron emission microscopy (X-PEEM) has made great advances with the advent of synchrotron radiation [25–28]. Recently, X-PEEM has been carried out on chosen features of the antiwear film formed from ZDDP on steel [24,29], and on a ferrous Al–Si alloy, A390 (16–18% Si, ~1.3% Fe) [30].

Morphological and topographical surface characterization plays an essential role in examining the antiwear films formed, which has been the subject of numerous studies [24,31–36]. The thickness of the tribofilms has been described as a key attribute for the antiwear performance, as the film acts as a sacrificial layer and minimizing the asperity contact between surfaces [36].

The mechanical properties of the antiwear pads have also been the subject of numerous studies [24,30,31,36,37], as it is believed that the mechanical response of these films are the primary reason for the antiwear performance. The indentation modulus values have been acquired through nanoindentation. The indentation modulus found on antiwear pads formed on Si from the A390 alloy was ~76 ± 7 GPa [30].

In this paper, a spatial chemomechanical analysis of the antiwear films formed on the Silitec 5<sup>TM</sup> alloy was performed. Many variables that mimic operating conditions in an automobile engine were compared. The antiwear films that are formed were examined using XANES spectroscopy and X-PEEM to gain chemical information. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to gather topographical and morphological insight, while imaging nanoindentation was performed to acquire the mechanical properties of these films.

2. Experimental

2.1. Sample preparation

The aluminum-based Silitec 5<sup>TM</sup> alloy (~25% Si, ~4% Cu, ~1% Mg, < 0.3% Fe) was machined into disks with dimensions of 17 mm ± 0.5 mm radius and 3.5 ± 0.5 mm thickness. The disks were mechanically polished using 0.3 µm, 0.06 µm alumina slurry suspensions and finally using a 0.03 µm alumina paste. A weak caustic etching step using 5% NaOH was applied, which selectively dissolved away the aluminum matrix, at room temperature. This alloy is etched for commercial use so that the embedded silicon grains stand proud of the aluminum rich matrix [1].

Commercial ZDDP consisting of secondary butyl groups (85%) and n-octyl groups (15%) in MCT-10 base oil was obtained from Imperial Oil (Esso) of Canada. ZDDP solutions were prepared by mixing ZDDP concentrate in MCT-10 base oil.

Antiwear films were made on the Silitec 5<sup>TM</sup> alloy disk using steel pins in a Plint high frequency wear tester. The Silitec 5<sup>TM</sup> disks and cylindrical 52100 steel pins were cleaned in an ultrasonic bath using a light hydrocarbon solvent, and then placed in the Plint high frequency wear tester. The ZDDP solution was placed in the Plint wear tester and the steel pin was laid flat against the disk (cylindrical face in contact with the surface). The frequency used to generate the tribofilms was maintained at 25 Hz. The influence of various experimental parameters was studied independently changing one variable at one time, versus the standard conditions (see table 1). Parameters such as etching time of the substrate, rubbing time, temperature, ZDDP concentration, and applied load were tested. After each experiment, excess oil was removed from the disks using tissue paper and then the samples were rinsed in hexane.

A grid consisting of indented marks was created using a Vickers hardness tester using loads of 100 and 500 g which made indents ~25 µm and ~100 µm across respectively. The grid allowed for relocation of the same region with multiple techniques. The wear tests were made in duplicate.

2.2. Morphology and topography data acquisition

AFM topography images were compiled for all the samples in air using a Nanoscope IIIa equipped with a Multimode<sup>TM</sup> head (Digital Instruments, Santa Barbara, CA). The images were collected in contact force mode with a V-shaped silicon nitride cantilever possessing a spring constant of 0.12 N/m.

The SEM data were collected using a Hitachi S4500 SEM equipped with an EDAX<sup>TM</sup> light element EDX microanalysis system. Images were acquired with a 5 kV acceleration electron beam voltage, 17 mm working distance, and 30° tilt in the field emission mode.

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<th>Table 1. Variations in the physical parameters studied.</th>
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<td>Experimental parameters</td>
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<td>Temperature (°C)</td>
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<td>Applied force (N)</td>
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<td>ZDDP concentration (wt.% in MCT-10 base oil)</td>
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