Wear 311 (2014) 1–13

Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

# Effect of bio-fuel (E85) addition on lubricated sliding wear mechanisms of a eutectic Al–Si alloy

A. Banerji, A. Edrisy, V. Francis, A.T. Alpas [*]

*Department of Mechanical, Automotive and Materials Engineering, University of Windsor, 401 Sunset Avenue, Windsor, ON, Canada N9B 3P4*

## ARTICLE INFO

*Article history:*
Received 27 August 2013
Received in revised form
2 December 2013
Accepted 11 December 2013
Available online 22 December 2013

*Keywords:*
Bio-fuels
E85
Al–Si alloy
Engine wear
Tribolayer
Ultra-mild wear

## ABSTRACT

The effect of addition of bio-fuel blend consisting of 85% ethanol and 15% gasoline by volume, E85, on lubricated sliding wear of a eutectic Al–12.6% Si alloy was investigated. The alloy was tested under the loading conditions that promoted ultra-mild wear (UMW), using a mixture composed of equal proportions of E85 fuel and synthetic engine oil, designated as E85/oil (1:1) blend. UMW occurred in three stages when the E85/oil (1:1) blend was used: initially wear was limited to the Si particles that subsequently fractured and/or sunk into the Al matrix; this was followed by a running-in period of higher wear of Al matrix, and then a low steady state wear stage was reached, due to the formation of a protective tribolayer on the sliding surface—called an oil-residue layer (ORL). The ORL was supported by embedded Si particles and a subsurface microstructure consisting of nanocrystalline Al grains that formed as a result of severe local plastic deformation during sliding. The composition of the ORL incorporated nanocrystalline regions of Al, Si, ZnS and ZnO surrounded by amorphous regions consisting of carbon and possibly phosphates. Compared to the ORL formed on samples tested using unmixed engine oil (without E85) the E85/oil (1:1) blend generated higher proportions of Zn, S and P compounds in the ORL. It was proposed that the hydroxyl groups in ethanol molecules facilitated ZDDP degradation, thus leading to an ORL that was richer in anti-wear compounds and consequently lower volumetric wear was observed when the E85/oil (1:1) blend was used.

## 1. Introduction

Reduction of vehicle mass by increasing the use of lightweight Al–Si alloys in engine components has been a key area of focus for the automotive industry over the past decade [1,2]. This has stimulated research on tribological behaviour of cylinder bores made of Al–Si alloys during piston ring contact. The wear resistance provided by Al–Si alloys arise from the specific surface preparation techniques and near-surface microstructural evolution during sliding contact [3–11]. Slattery et al. [3,4] investigated the micro-mechanisms of wear in linerless engine block made of a near eutectic Al–Si alloy (with Ni and Cu as alloying elements) subjected to dynamometer testing. After nearly 300 h of testing, the engine showed negligible wear, which was attributed to the combined effects of Si particle exposure (by honing [4]), formation of oil deposits on the contact surface during sliding and generation of a near-surface zone with ultra-fine aluminium grains [3–5,11]. The very low wear rates (few nanometers of material removal per hour) corresponded to a wear regime described as ultra-mild wear (UMW) [5–7]. The mechanisms responsible for very low wear rates that occur under UMW conditions have been simulated under the laboratory testing conditions for both hypereutectic alloys [8,9] and near-eutectic Al–Si alloys [10,11].

### 1.1. Micromechanisms of UMW in Al–Si alloys

In an engine grade hypereutectic Al–18.5% Si alloy [8], UMW damage was found to be restricted to the top surfaces of large Si particles that acted as load bearing ‘asperities’ on which a contact pressures as large as 1080 MPa were applied (at 2.0 N) [9]. For alloys with smaller Si particles like a spray deposited Al–25% Si alloy [5], the Si particles experienced higher contact pressure of 1680 MPa resulting in sinking-in of particles into the Al matrix. An Al–11% Si alloy [5,10] with a similarly low aspect ratio ( ~ 1.5) but lower particle volume fraction experienced 60% higher contact pressure [5]. Consequently an earlier transition occurred, from the first stage of UMW where the protruded particles mitigated the matrix wear, to the UMW II stage where the Si particles were sunken in the matrix and hence UMW II stage defined a running-in period where high volumetric wear occurred. For high sliding cycles a reduction in wear rate was observed (UMW III stage). This was attributed to the formation of a tribolayer called as an oil residue layer (ORL) that covered the wear tracks [5,11]. Underneath the ORL evidence was found for localized severe plastic

---

[*] Corresponding author. Tel.: +1 519 253 3000x2602; fax: +1 519 973 7085.
*E-mail address:* aalpas@uwindsor.ca (A.T. Alpas).

0043-1648/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.wear.2013.12.011

deformation [12] that manifested itself by the formation of a nanocrystalline Al grain structure [5,11] that was harder than the initial surface and thought to support the ORL. Thus, once the ORL was established, it acted as an antiwear layer allowing the near-eutectic Al–Si alloys to operate at near zero wear rates similar to the hypereutectic grades.

Details of chemical composition of the ORL formed under boundary lubricating conditions when using synthetic engine oil (containing zinc dialkyldithiophospahte, ZDDP, additives) are yet to be clarified. The ORL on eutectic Al–Si alloys tested at 25 °C consisted of amorphous carbon (detected using EELS) as well as Zn, S, P and Ca [5,11] compounds. Grun et al. [13] studied the damage mechanisms of a hypereutectic Al–Si alloy sliding against steel discs lubricated by ZDDP (1.5 wt%) in base oil. Formation of patches of protective tribofilm (tribopads), comprising of P, O, Zn and S, on hard phases like Si, intermetallics (with Cu) and steel counterface were detected. For the ferrous alloys (AISI 52100 grade), Fujita and Spikes [14] provided evidence that the tribolayers having antiwear properties could form as a result of ZDDP degradation during sliding contact at room temperature. Tribolayers formed on A2 grade steel [15] during sliding at 100 °C were shown to consist of polyphosphate chains with shorter length compared to the antiwear films formed thermally at 200 °C and had lower sulphur content. Pereira et al. [16] found that the antiwear layer formed on Al–25% Si alloy tested with ZDDP (in base oil) heated at 100 °C had similar chemical composition and Young's modulus to those formed on steel surfaces tested at similar temperature. In ORL formed on tops of Si particles in an Al–12.6% Si alloy tested at 100 °C, using fully formulated synthetic oil (containing ZDDP), nano-crystals of zinc sulphide [17] and zinc polyphosphates with short chain lengths were identified [18]. It was also noted that the tribolayers may act as an energy-absorbing entity and possibly delay Si fracture [19]. The ZDDP degradation mechanism is complex and involves several steps [14–19,20,21]. Willermet et al. [20] proposed that ZDDP degradation would start with a ZDDP adsorption process and a reaction with the metal substrate that would lead to the formation of Zn terminated phosphate compounds. Nicholls et al. [21] suggested that antiwear layers produced on Al 319 (Al–7% Si) alloys placed in sliding contact with steel at 60 °C involved formation of a linkage isomer that was absorbed on the metal surface leading to the formation of zinc polyphosphates as well as sulphur species in their reduced form (sulphides).

### 1.2. *Effect of E85 mixed fuel on wear*

The motivation for using ethanol based bio-fuels in modern powertrains is to provide a clean energy source with reduced carbon and sulphur content and consequently decreasing atmospheric emissions [22]. A common ethanol–gasoline blend that consists of 85% ethanol and 15% gasoline, E85, is known to improve fuel quality by increasing its octane value [23]. Combustion properties of ethanol-gasoline blends have been studied [23–25]. As ethanol has a high latent heat of vaporization and moderately high boiling point (78 °C) it can easily reach the cylinder walls (as well as the crankcase lubrication reservoir) [25]. Ethanol is corrosive to Al due to the presence of azeotropic water. Thus, freshly formulated ethanol fuel blends should contain neutral dry-ethanol having little corrosive effect on Al. A stagnant ethanol-fuel blend would absorb moisture from the atmosphere posing corrosion related problems that may contribute to surface degradation [22]. There are only few studies in the literature detailing the effect of ethanol on the friction and wear in a piston-cylinder (cast iron) assembly. De Silva et al. [25] reported around 20% reduction in friction of grey cast iron cylinder liner tested

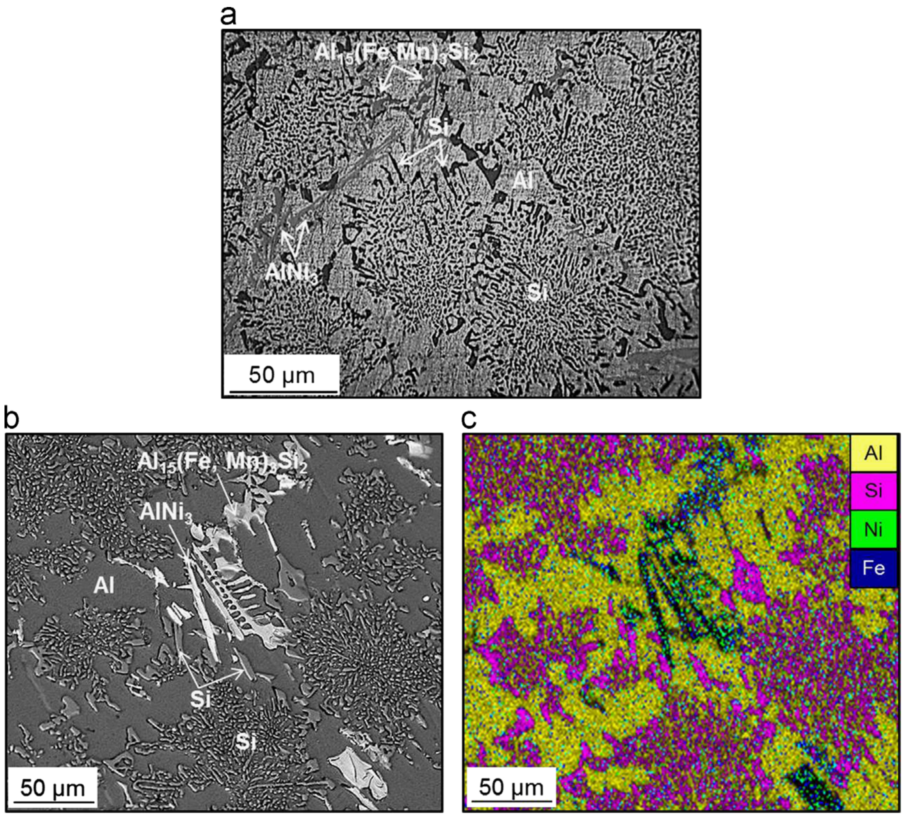

**Fig. 1.** (a) Optical micrograph showing the microstructure of Al–12.6% Si alloy etched with 10% NaOH solution. (b) Backscattered electron image (tilted at 45° to the beam) of etched Al–12.6% Si alloy. (c) EDS map of image (b) showing the distribution of Si and Ni, Fe in intermetallic phases.