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ZDDP and MoDTC tribofilm evolution on a hypereutectic Al-Si alloy lubricated in the boundary regime

Xin Xia[1], **Ardian Morina**[1], **Anne Neville**[1], **Martin Priest**[1], **Rupesh Roshan**[1], **Chris P. Warrens**[2] and **Marc J. Payne**[2]

[1]School of Mechanical Engineering, University of Leeds, LS2 9JT, UK

[2]Castrol Limited, Technology Centre, Whitchurch Hill, Pangbourne, Reading, RG8 7QR, UK

Abstract

The tribolochemical performance of a cast iron/Al-Si alloy system lubricated in the boundary regime using lubricants containing Zinc Dialkyldithiophosphate (ZDDP) and Molybdenum Dialkyldithiocarbamate (MoDTC) additives has been investigated. Tests were conducted on a Plint TE 77 reciprocating tribometer in contact conditions comparable to the conditions in a piston ring/cylinder liner system of the internal combustion engine. Tests were performed for 4 different time durations, from 1 minute to 3 hours, to investigate the tribofilm evolution formed on the Al-Si alloy surfaces. Surface sensitive analytical techniques such as atomic force microscopy (AFM) and secondary ion mass spectrometry (SIMS) have been used to determine the nature of the surface topography as well as the chemical nature of the tribofilms formed on the Al-Si material. The additive effect on the tribofilm formation as well as tribological performance is discussed. It is shown that the MoDTC additive, blended into a ZDDP-containing lubricant, improves the effectiveness of friction and wear reduction by providing an interface in the tribofilm that can be easily sheared, thus protecting the ZDDP-derived phosphate film from high shear stress. Tribofilms formed on all the Al-Si test surfaces after short times and the lubricant also affected the physical nature of the Al-Si microstructure. The tribofilm evolution processes for different lubricants is discussed in relation to recent literature and hypotheses of tribofilm evolution on Al-Si material are proposed.

***Keywords**:* Friction; Wear; ZDDP; MoDTC; Tribofilm, Al-Si alloy

1. Introduction

Lubrication science and materials technologies are shown to be two key areas with the short/mid term potential to facilitate the increase of fuel economy of automotive engines and reduce their harmful emissions. This can be achieved mainly by reduction of mechanical losses due to friction (energy efficient lubricants and low friction/durable surface coatings) and by engine weight reduction (low density materials). Intensive efforts have been made to reduce the weight of engine components by reducing or replacing cast iron content in the engine with low density materials, one of them being the hypereutectic Aluminium-Silicon alloy. High strength-to-weight ratio, high thermal conductivity and low machining cost of these alloys have made this material a cost-effective replacement for heavy cast iron in engine blocks [1]. The high silicon content of these alloys (>13%) improves the wear resistance and increases the overall strength of the aluminium matrix (ref).

The study of Al-Si alloys against steel lubricated by commercial engine oils under boundary lubrication conditions has been reported occasionally since the 1960s and 1970s [2, 3], with research focused mainly on the tribological performance of Al-Si alloys lubricated by zinc dialkyl dithiophosphate (ZDDP) [4-6]. The challenge in understanding fully these interactions lie mainly in the research being performed using different Al-Si alloys and under different testing conditions. As a result, the performance of Al-Si alloys in boundary lubricated systems is still not fully understood. It is particularly important to understand the performance of these alloys when lubricated with oils that contain additives known to effectively work on steel surfaces, such as Zinc Dialkyldithiophosphate (ZDDP) and Molybdenum Dialkyldithiocarbamate (MoDTC). It is only through doing this that strategies for efficient lubrication of Al-Si alloys with new generation lubricants can be developed.

ZDDP is known as a versatile additive, due to its extremely effective performance as an antioxidant and through providing wear protection of iron-containing materials. Performance of this additive in maintaining low wear is due to its interaction with the ferrous material resulting in formation of a layered phosphate/sulphide tribofilm at the interface. Formation of the ZDDP tribofilm in Al-Si alloys has been recently studied [4-6] and, although the findings are still not conclusive, an insight on the interaction between this additive and the Al-Si alloy has started to develop. It is demonstrated that polyphosphates form on both Al and Si material [6] while the higher Si content promotes formation of the polyphosphates from the ZDDP additive [4].

With regard to friction reduction, effectiveness of the MoDTC additive on Al-Si surfaces, and its interactions with the ZDDP, still remain to be studied. MoDTC is known as a good friction modifier for steel tribocouples lubricated in the boundary regime due to its decomposition to form MoS_2 sheets in the interface. In the case of Al-Si alloy surfaces, XANES [7] has shown that MoS_2, ZnS and sulphate form on the Al-Si plate wear scar when fully formulated oil is used for lubrication. The detailed friction and wear performance as a function of time, additive concentration and testing conditions remains to be understood. In a previous paper Xin *et al.* [8] reported how the lubricant additives could affect the resulting Al-Si surface structure in boundary lubricated contacts. How these structures develop as a function of rubbing time and the rate at which the additives affect the surface are very important.

In terms of wear mechanisms, there are principally two Al-Si alloy wear models which have recently been proposed by different research groups. Nicholls *et al.* **[4]** presented the hypothesis of ZDDP tribofilm formation on an Al-Si surface as the top phase of Al-matrix is removed physically and only Si grains remain in the uppermost Al-Si alloy layer. The newly generated nascent Al and adsorbed linkage isomers (LI) and ZDDP react with the nascent Al and form aluminium oxide, aluminium phosphide and sulphur species under an oxygen sufficient environment. The nascent Al can also react with P to form AlP under an oxygen starved environment **[4]**. The new tribofilm is formed predominantly on the remaining Si grains. The schematic image of this wear model is shown in Figure 1.

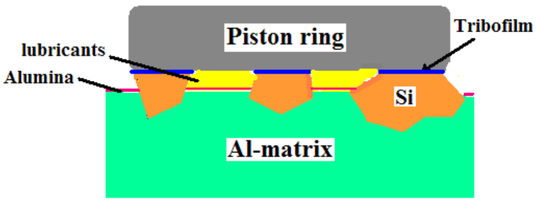


Figure 1. Schematic of Nicholls *et al.* [4] proposed wear model

The second wear model, recently proposed by Dienwiebel *et al.* **[9]** is described in Figure 2. It is reported that the Si grains and wear debris from various sources are embedded into the adjacent soft Al-matrix and form a new contact surface on both sides. The surface layer formed is shown to contain carbon, oxygen, calcium and phosphorus and it is suggested that this film physically decreases the friction force.

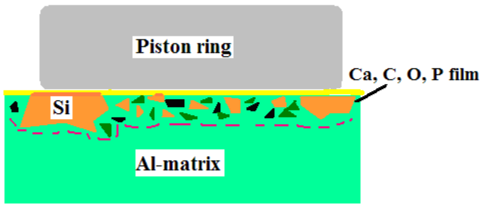


Figure 2. Schematic wear model of Dienwiebel *et al. [9]*

Xia *et al.* [8] performed tribological tests on a cast iron/Al-Si alloy system lubricated in the boundary regime using lubricants containing ZDDP and ZDDP with two different concentrations of MoDTC and observed the two types of wear models reported by Nicholls *et al.* [4] and Dienwiebel *et al* [9] depending on the lubricant. In addition, they reported that when the ZDDP was used alone, a composite transfer/reaction film was formed which contains silicon wear debris, additive components (Zn, P, S) and transfer of material (Fe) from the pin formed on the Al-Si alloy surface. The structure of the tribological surface was found to be dependent on the oil such that the three oils with ZDDP above ZDDP and low MoDTC and ZDDP and high MoDTC gave structures shown in Figure 3 a-c respectively. (SEM images)

Mosey *et al.* **[10, 11]** proposed a cross-linking theory to be useful to interpret functionality and formation of ZDDP anti-wear films formed on Al-based materials. Based on this theory, due to the different hardness between the two contact surfaces, substantial wear of the substrate may occur under rubbing contact. Since the hardness of the tribofilm is higher than that of the Al matrix, the ZDDP tribofilm may sink and embed into the Al matrix. However, this theory does not take into account the complex chemical interactions between surface/additive and additive/additive in tribofilm formation on Al-Si alloys.

As can be seen from the review of literature, the picture of how the ZDDP and MoDTC additives perform in lubricating the Al-Si alloys in boundary/mixed regime is still at best patchy. It is still unclear how the substrate properties of Al and Si affect the tribofilm formation from these two additives and if this tribofilm is as effective as it is when lubricating iron-containing tribosystems. In this study the tribological performance of ZDDP and MoDTC containing oils, wear mechanisms and tribofilm formation and its evolution with rubbing time in Al-Si alloys are assessed.

2. Experimental

2.1 Tribological test

A high frequency reciprocating pin-on-place friction tribometer (TE 77) was employed to simulate the tribological conditions of the piston ring/liner engine interface. The pin was mounted in a holder on the movable arm. The flat specimen was mounted in a heated shallow tray containing the lubricant with a thermocouple for temperature control. The EN 1452 cast iron pins were 20mm in length; 6mm in diameter and the ends of the pins were machined to a

40mm radius of curvature. The Al-Si alloy plates were cut from $38\times15\times4mm^3$ to $7\times7\times3mm^3$ to enable surface analysis with minimal handling of the samples after the test. Taylor-Hobson 5-120 profilometer and Indentec 8187.5 LKV universal hardness tester were used to measure sample surface roughness and hardness before test. The Young's modulus and passion ratio of those materials were cited from Matweb – online material information resource **[12]**. The composition and the physical characteristics of the test materials are shown in Table 1 and Table 2, respectively.

Wt%	**Fe**	**Si**	**C**	**O**	**Mo**	**Mn**	**Al**	**Mg**	**Zn**	**Cu**	**Ti**
CI pin	84.9	1.9	9.3	2.7	0.4	-	-	-	-	-	-
Al-Si plate	0.7	16-18	-	-	-	0.2	Balance	0.6-0.7	0.2	4 -5	0.2

Table 1. Test samples chemical composition

	Pin (CI)	**Plate (Al-alloy)**
Young's Modulus	122.5GPa	81.2GPa
Poisson Ratio	0.26	0.3
Hardness	373 HV	135 HV
Initial surface roughness (Ra)	0.7-0.9 μm	0.7-0.9 μm

Table 2. Test samples physical characteristics

These testing conditions are determined to simulate the severe end of lubrication conditions in piston ring/liner system, since in these conditions the lubricant chemistry functionality will be most emphasized.

A blend of polyalphaolefin synthetic base oil PAO6, ester, ZDDP and MoDTC additives was used as a lubricating oil. Two concentrations of MoDTC which were adopted for conventional commercial lubricants were used to assess the effect of additives in Al-Si lubrication. The lubricant dynamic viscosity at 100 °C was 5.8 mm^2/s. Ester was used in these simple lubricant formulations to ensure the additives were fully soluble in the base fluid. There was no significant change in base oil viscosity when the additives were blended into the base oil. The chemical compositions of different model lubricants (Oil A, Oil B1 and Oil B2) used to perform the tests are shown in Table 3.

	Base oil	**Ester (wt%)**	**ZDDP (wt%)**	**MoDTC (wt%)**
Oil A	Balance	10	0.8	-
Oil B1	Balance	10	0.8	1.2
Oil B2	Balance	10	0.8	0.22

Table 3. The lubricants chemical compositions (wt %)

Pin samples were mounted to ensure proper alignment by checking perpendicularity of load and a level-reciprocating arm. Approximately, 10 ml of lubricant was used to immerse the flat plate. All tests were conducted with a 5mm stroke at 20Hz and at a constant bulk lubricant temperature of 100 ºC. In order to reach a realistic value of the contact pressure, similar to cylinder liner/piston ring working conditions, the normal load in this test was chosen as 10N for the Al-Si/CI tribocouple. Other working conditions are shown in Table 4.

Working Conditions	**Al-Si/CI**
Normal Load	10N
Maximum contact pressure	151MPa
Average linear speed at the contact surface	0.2 m/s
Test duration	1min, 10mins, 1 hour, 3 hours

Table 4. Testing conditions

New components were used for each test. They were initially cleaned in an ultrasonic bath using acetone for 10 minutes to remove any impurities from the surface before each test. After the test, the pins and plates were dipped in heptane for 1–2 seconds to remove excess oil from the surface, in preparation for surface analysis **[13]**. Ex-situ analyses were performed on the pin and plate samples to understand the formation, wear performance and the chemical characteristics of the tribofilm formed during tribological testing.

2.2 Surface analysis techniques

An optical profile projector and 3-D Talysurf profilometer were used to obtain the topography and wear measurements. A Nikon V-16D optical profile projector was used for measuring the diameter of the wear scar of the pin and the volume loss of the pin was calculated by equation (1).

$$V_{pin} = \frac{1}{6}\pi h(3r^2 + h^2) = \frac{1}{2}\pi h r^2 \qquad (h << r) \qquad (1)$$

where, $h = R - \sqrt{R^2 - r^2}$, R is tip radius of pin (mm), r is radius of the wear scar measured after test (mm), h is height of the spherical tip of pin after wear test and V_{pin} is volume loss of pin (mm^3) .

The wear volumes of the plates were measured by a Taylor-Hobson 5-120 profilometer. Five measurements were taken across each wear scar to calculate plate wear volume loss and the variation was small. The dimensional wear coefficient *k* quoted in units of $mm^3N^{-1}m^{-1}$ was calculated using the Archard equation (Equation (2)) **[14]**.

$$V = klw \qquad (2)$$

where ‘V’ is the wear volume, ‘l’ is the sliding distance and ‘w’ is the normal load.

The atomic force microscopy (AFM) was applied to probe the microstructure features of the tribofilm after the tribological test. The Scanning Probe Microscope (SPM) used in this work was a Topometrix TMX 2000 Explorer. The maximum scan range in the x, y, z direction of $100 \times 100 \times 8$ μm^3. Scanning was performed in contact mode with a Si_3N_4 cantilever, with a nominal speed of 0.04N/m. All measurements in this work were all conducted in this condition.

2D topographic analyses are scanned in several different places across the wear scar to observe uniformity of the microstructure. The images shown in this work are representative of the structure found. Figure 3 shows the typical AFM 2D and 3D topographic images taken from the sample before test. From the image, it can be seen the distinct height difference between Al matrix and Si grains which is around 2µm.

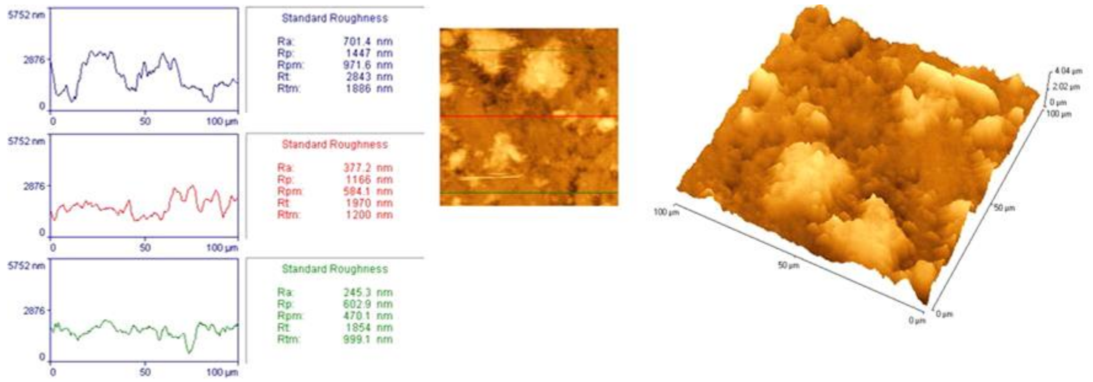


Figure 3. Microstructure of the Al-Si sample before the test obtained with AFM

The tribofilms formed on the plates were chemically analysed using a desktop quadrupole version Milbrook MiniSIMS. This technique was used due to its high surface sensitivity (up to ppm level) and depth resolution (up to 2nm). The instrument has a liquid metal ion source; the primary beam (Ga+ 6KeV, 3nA) is focused and moved in a controlled raster. Two types of data were obtained in this study:

- Mass spectra – to identify the chemical species in the wear scar. The scanning details are: 300×300 µm area; amu= 2-200; step=0.2 and dwell = 0.01.
- Depth profile – to obtain information on film thickness

3. Results and Discussion

3.1 Tribological performance

3.1.1 Friction results

Figure 5 shows the friction coefficient versus time obtained testing Al-Si/CI tribocouples with the three oils. The repeatability of results was good and final values of friction coefficients were within 5% for replicate tests. Representative results are presented in Figure 4.

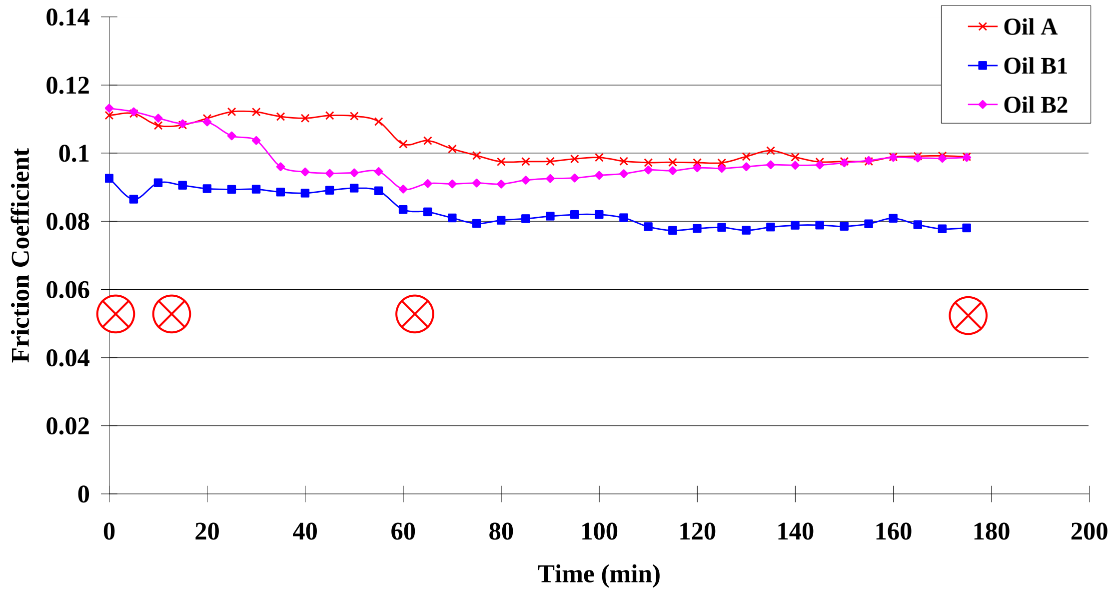


Figure 4. Friction versus time plots for all three oils tested. Crossed circles indicate the times for which tests were performed to follow the evolution of the tribofilm.

The friction values at 1 minute, 10 minutes, 1 hour and for the last 1 hour average value of the 3 hours test are given in Table 5.

	1 min	10min	1h	3h
Oil A	0.11	0.11	0.11	0.10
Oil B1	0.09	0.08	0.08	0.08
Oil B2	0.11	0.10	0.09	0.10

Table 5. Friction coefficient at the end of different rubbing time tests

Higher concentration of the MoDTC additive (Oil B1) resulted in friction reduction at the end of the test while the low concentration of the MoDTC did not have any effect on the friction compared to the ZDDP only oil (Oil A). Friction reduction with Oil B1 is seen after the first minutes of rubbing and was stabilised after the first hour of the test. From Figure 5, it can also be observed that there is no distinctive induction time (i.e. time prior to instantaneous friction drop) for the MoDTC-containing lubricants as has been seen when MoDTC-containing oils are used to lubricate steel [15, 16]. However, for Oil B1 the friction dropped and stabilization occurred after 1 hour. The reason friction reduction step is reduced compared to the 0.05 step often seen in ferrous systems and this could be due to the mild loading conditions used in the current tests; the contact pressure is shown to be an essential input in order to obtain low friction from MoDTC oils [17].

3.1.2 Wear performance

Table 6 shows the average values of dimensional wear coefficients for the plate and pin samples obtained after 1 minute, 10 minute, 1 hour and 3 hour tests.

Al-Si plates wear (mm^3/Nm)	**1min**	**10min**	**1h**	**3h**
Oil A	340 E-07	41 E-07	3.4 E-07	5.0 E-07
Oil B1	520 E-07	20 E-07	3.7 E-07	2.2 E-07
Oil B2	290 E-07	37 E-07	4.0 E-07	2.8 E-07

Table 6. Dimensional wear coefficients of Al-Si plates as a function of lubricant and rubbing time

As expected, for all three oils the highest wear is seen after short time tests due to the running-in period. The wear coefficients after 1h and 3h tests, for all three oils, remain at similar level indicating the steady state lubrication which also resulted in steady friction coefficient. The wear scar cross-sections obtained with the Focused Ion Beam (FIB) milling has shown that Al matrix around the Si grains is deformed indicating the Si grain displacement in the matrix as a result of testing contact pressure [18]. Hence, in Al-Si alloys a large degree of the “volume loss” could be as a result of the Si grains being pushed into the Al-matrix under the testing conditions. Considering the Al-Si plate wear coefficients values of after 3 hours tests, the performance of the three oils can be ranked as:

Oil A > Oil B2 > Oil B1.

Where > is that friction and wear "are higher than".

Interestingly the ZDDP oil offers the least wear protection to Al-Si sample and the paper focuses on why this is and follows the tribofilm and surface structure evolution.

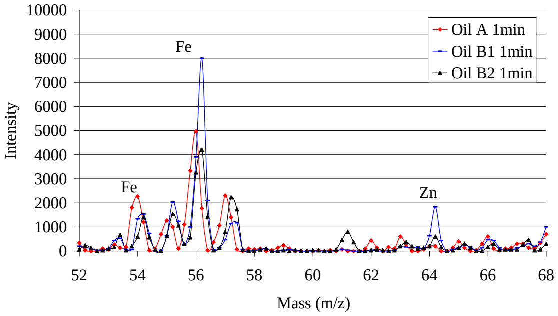
Table 6 wear results indicate that Oil B1, although initially giving the highest wear, gave the lowest wear coefficient after 3 hours. It appears that the ZDDP in Oil A is effective in wear reduction during the running in period, and is comparable to Oil B1, but as time elapses this protection is lost and both friction and wear achieve relatively high values. This suggests that the ZDDP additive cannot form a stable and durable tribofilm on Al-Si alloys. The MoDTC at higher concentration, (oil B1), together with the ZDDP provided the highest wear protection in the Al-Si/CI tribocouple, in agreement with other published research [7]. After 10 minutes the wear coefficient was the lowest of the three oils. Wear values as a function of time (Table 6) clearly indicate that the chemistry in the oil is important for the steady state wear performance of the Al-Si/CI system.

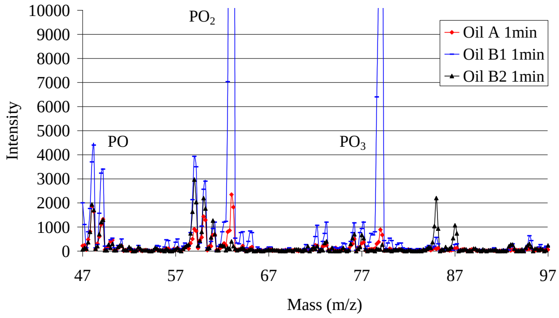
3.2 Surface Analyses

Analyses of the surface chemistry and of the surface microstructure and topography as a function of the rubbing time are obtained in order to understand the evolution of the tribofilms and the role of tribochemistry during the rubbing process.

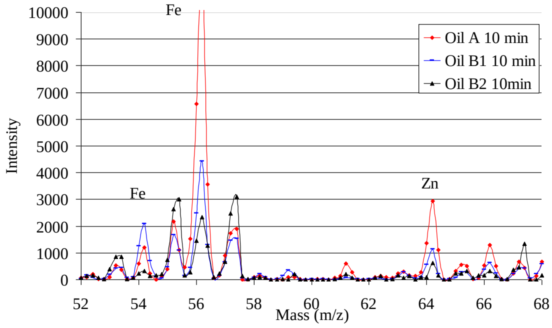
3.2.1 Surface chemistry

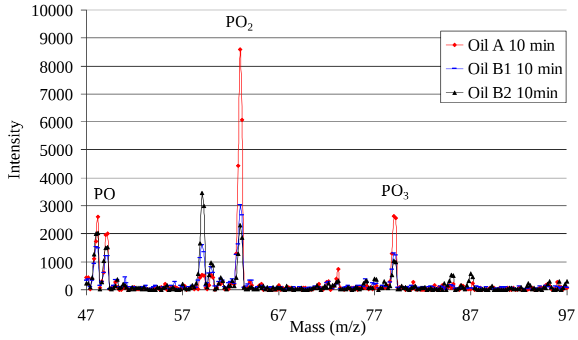
Figure 5 shows SIMS analyses obtained from the middle of the Al-Si plate wear scars which resulted from different rubbing time tests using the three oils. The SIMS analysis depth is extremely small (around 1nm) and, as such, the analysis is without doubt of the tribofilm top layer. It is also taken over a relatively large (300µm x 300µm) area of the surface.



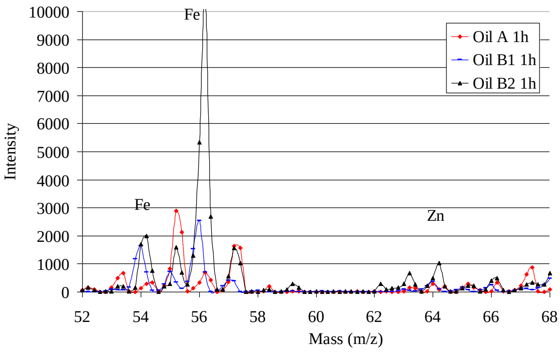


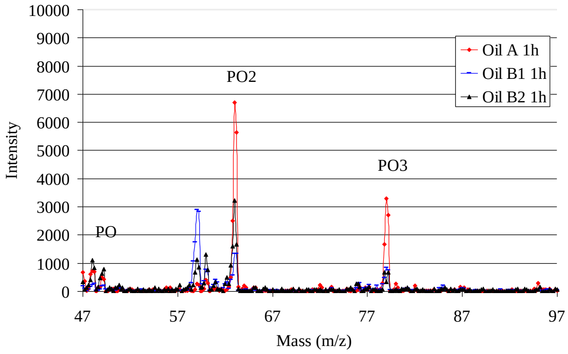
a) 1 min test - SIMS positive ion spectra SIMS negative ion spectra



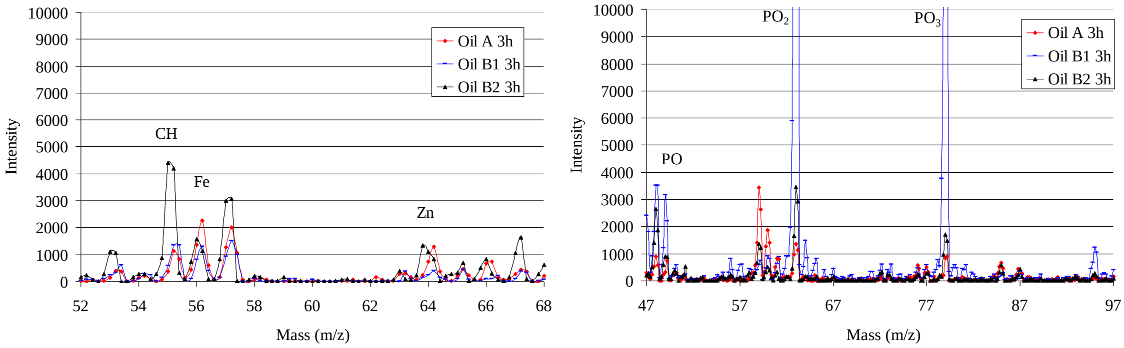


b) 10 min test - SIMS positive ion spectra SIMS negative ion spectra





c) 1h test - SIMS positive ion spectra SIMS negative ion spectra



d) 3h test - SIMS positive ion spectra SIMS negative ion spectra

Figure 5. SIMS positive and negative ions spectra obtained from the wear scars produced from tests with Oil A, B1 and B2 after a) 1 minute, b) 10 minute, c) 1 hour and d) 3 hour tests

All the three oils tested formed a tribofilm even after a short time of rubbing. The film formed from Oil A is shown to contain Zn, SO, PO_2, PO_3 and P_2O_2H species. This is in agreement with the study by Nicholls *et al.* [4] which showed formation of phosphates, in conjunction with the undecomposed ZDDP, even after two minutes rubbing. In the short time tests (1min and 10min), the iron peak is seen to correlate with the PO_2 peak to the lowest values seen. At these short times the wear is still high due to the surfaces breaking-in and it appears that the iron phosphate is formed on the pin and transferred to the Al-Si surface. The highest intensity of PO_2 and PO_3 SIMS peaks is obtained from the Oil B1, 3h test wear scar, indicating a uniform layer formed. For this oil at this time, both friction and wear were reduced to the lowest values seen.

Figure 6 shows the change of the PO_2 intensity with etching. Interpretation of these data assumes that the phosphate is uniformly distributed across the 300μm x 300μm scan area. AFM images shown later can be used to provide further discussion around this. A higher PO_2 peak therefore is consistent with a greater PO_2 concentration in the tribofilm and important information regarding the concentration as a function of depth can be obtained.

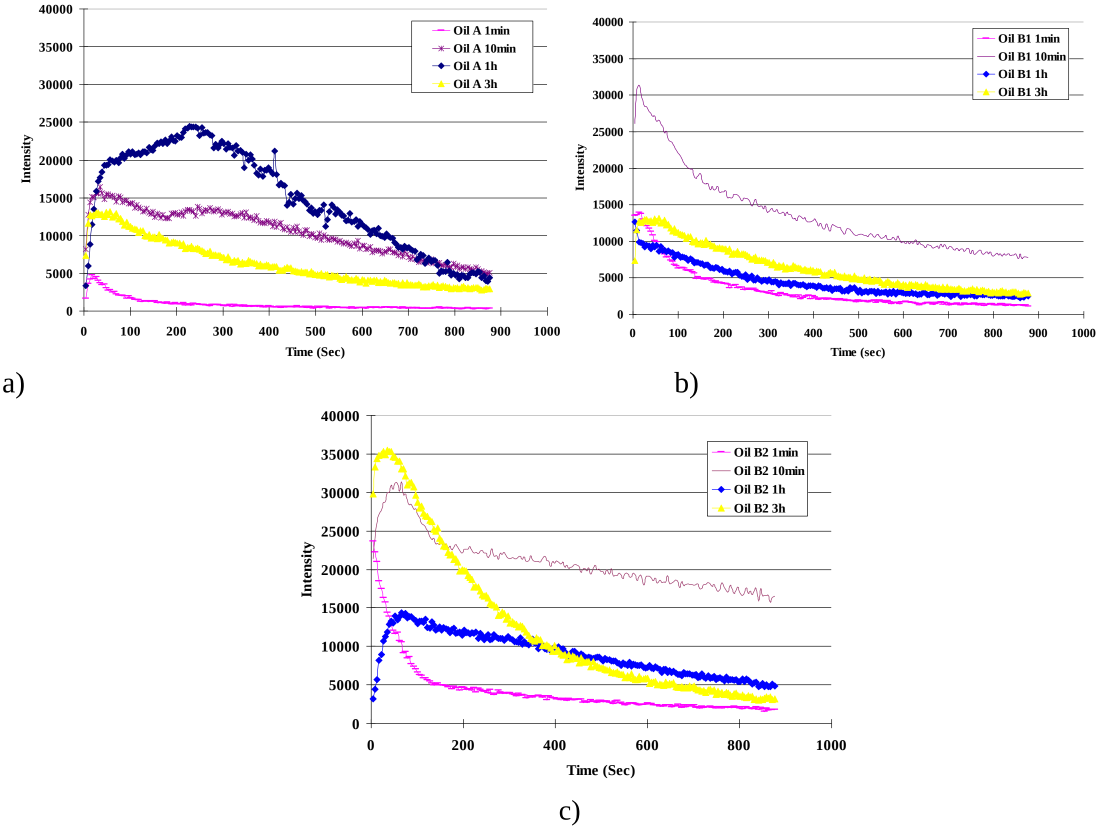


Figure 6. PO_2 SIMS peak depth profiling, a) Oil A tribofilm, b) Oil B1 tribofilm and c) Oil B2 tribofilm

Analysing the PO_2 content at the near surface and as a function of etching gives a fairly complicated picture of the evolution of the tribofilm. As expected, in isolation, analysis of the PO_2 peak intensity does not give definitive information about the tribofilm influence on friction and wear but some interesting trends emerge. A summary of the main features of the PO_2 evolution from SIMS is presented in Table X.

- In all surfaces and at all times there is an emergence of a PO_2 peak. It's intensity is maximum in the near surface region (at low etching times) and is reduced significantly deeper into the film.
- There is no universal correlation between PO_2 concentration and the level of wear but it can be seen that for oil B1 a stable PO_2 level is reached after 1 hour and this links to the stabilization of the wear coefficient values

In all cases the PO_2 peak is reduced at 3 hours compared to the earlier periods suggesting that the phosphate film formed is not stable and in the presence of MoDTC it is evident that the Mo-species are also present at the surface. It is therefore suggested that it is their presence in the case of Oil B1 that dominates both friction and wear behaviour. The evolution of the Mo peak and the change as a function of depth are presented in Figure 7. In both cases the Mo intensity after 3 h was greatest and for oil B1, consistent with the PO_2 results a steady state was reached after 1 h where Mo was maximum.

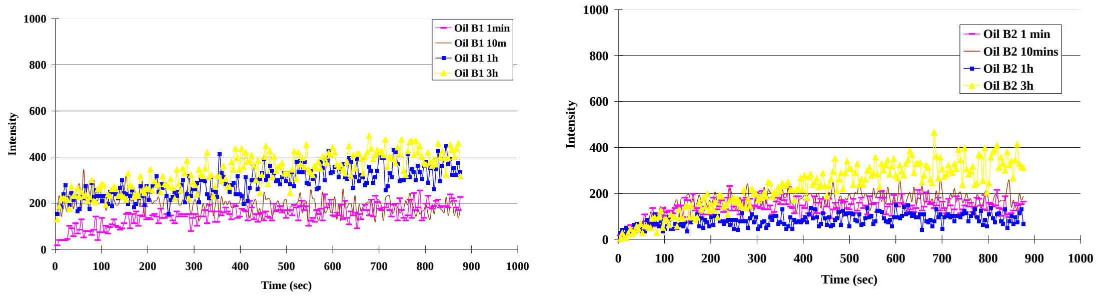


Figure 7. SIMS depth profiling of the Mo peak

Figure 8 gives the RAMAN spectra of the surface films formed from Oil B1. This technique probes up to 1 μm of the surface analysed, thus giving useful information of chemical composition of the bulk tribofilm. RAMAN peaks at 405 cm^{-1} and 379 cm^{-1} are observed at the wear scar formed after the test, indicating formation of the MoS_2 in the wear scar [19]. Rinsing with heptane removed the hydrocarbons from the wear scar but not the MoS_2 film. This film is seen to form on both Al and Si phases of the alloy.

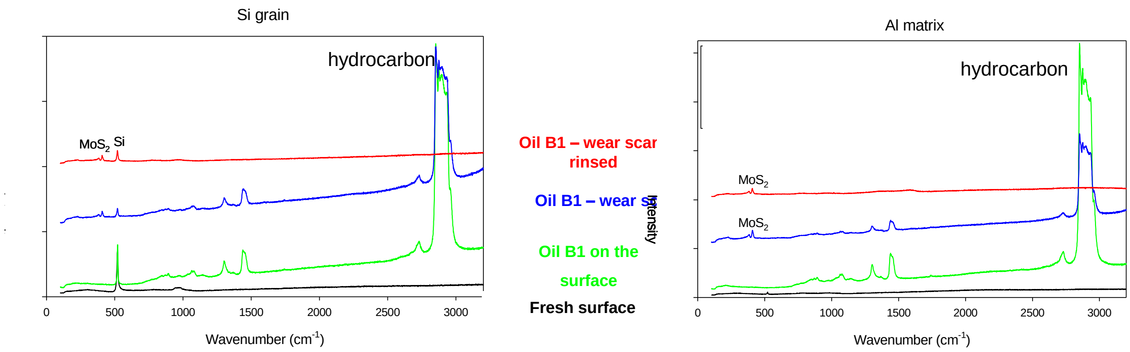


Figure 8. RAMAN spectra from the fresh Al-Si surface, Oil B1 dispersed on the Al-Si surface, Oil B1 wear scar and Oil B1 wear scar after rinsing with heptane

Formation of the MoS_2 in the Al-Si wear scar from Mo-containing fully formulated oil has been shown in a study by Pereira *et al*. [7] using the XANES surface technique. The current study confirms this and shows that the MoS_2 formation is not dependent on the substrate properties but mainly on the MoDTC concentration in the oil and the rubbing process.

3.2.2 Wear scar microstructure as a function of rubbing time

The 3 hour test Al-Si wear scar microstructure has been extensively discussed in previous work [8] and the resulting microstructures of the surfaces from SEM were presented in Figure 3. To improve our understanding of the effect of oil chemistry on the friction and wear performance of Al-Si surfaces with rubbing time, it is crucial to look at the physical surface structure intermediate stages between start and end of the 3h test.

Figure 9 and Figure 10 show how the wear scar microstructure changes depending on the oil used and the rubbing time. Roughness values of three lines in the sliding direction are also shown.

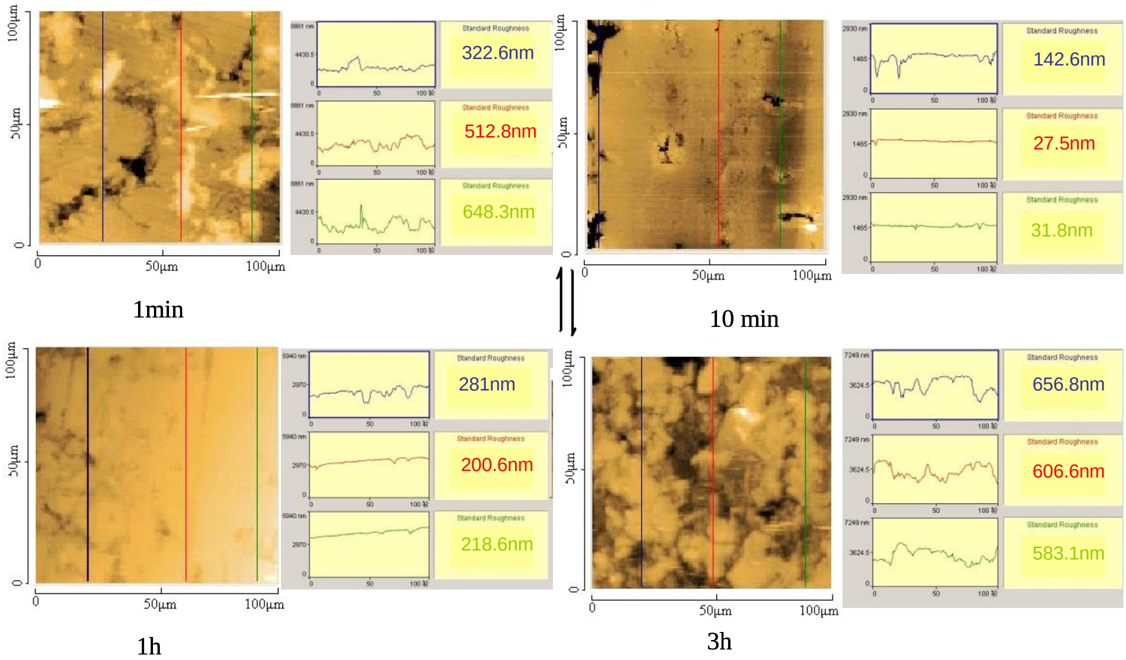


Figure 9. AFM images, line profiles and their R_a values obtained from the Al-Si wear scar after the test with Oil A at different rubbing times. Sliding direction is in vertical direction.

At 1min rubbing, the AFM imaging still showed a structure similar to the starting surface although in these conditions the wear coefficient measured is the highest and the SIMS analyses showed PO_2 and PO_3 peaks in the surface. Further rubbing, 10min and 1h, resulted in wear scars with smoother surface where the Al-Si phases were not visible, indicating a layer of film covering the surface. This is also supported by the SIMS data of the PO_2 film thickness shown in Figure 6, where it can be seen that the thickest film is formed at 10min and 1h wear scars. This film was disrupted with further rubbing and as a result, after the 3h test, a highly damaged wear scar is observed. This was also shown with the increase of line roughness values with rubbing.

In the case of oil B1, a uniform wear scar is observed after the 10min test and this was seen to last even after the 3h test.

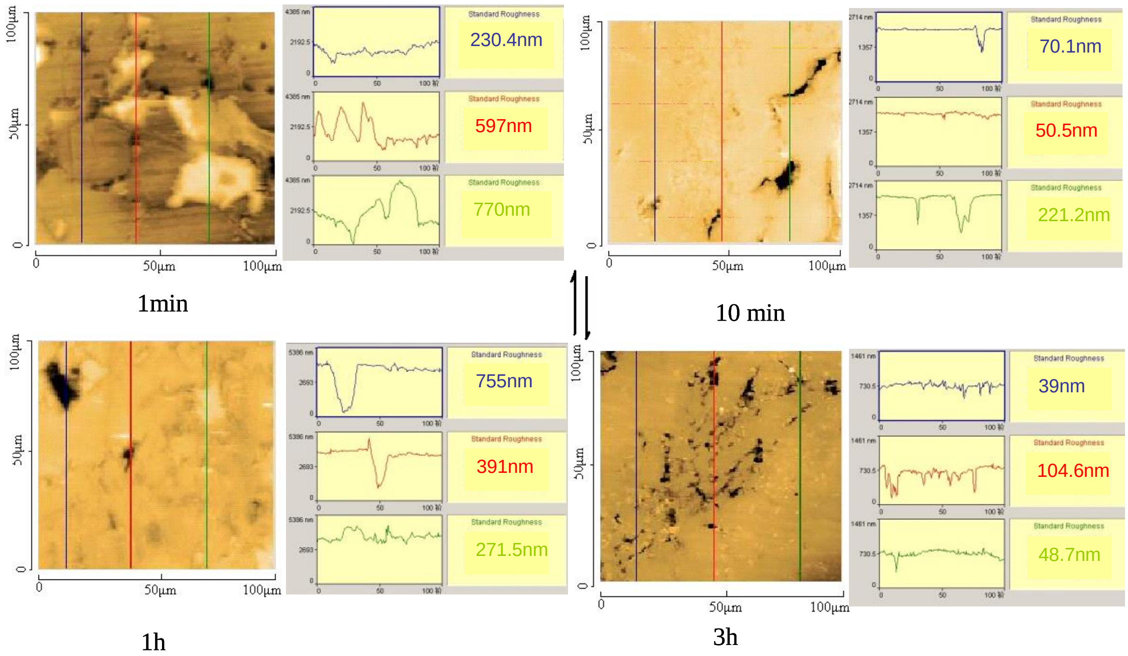


Figure 10. AFM images, line profiles and their R_a values obtained from the Al-Si wear scar after the test with Oil B1 at different rubbing times. Sliding direction is in vertical direction.

The presence of high concentration of MoDTC additive resulted in a uniform tribofilm formed throughout the sliding process. Topographical analyses of the wear scar in the sliding direction show a reduction of line roughness after the initial rubbing, which was maintained throughout the test.

3.3 Linking surface characteristics to friction and wear: the effect of additives

Tribological test results and the chemical analyses of the wear scar show that the lubricant chemistry influences significantly the tribological performance of the Al-Si alloys when lubricated in the boundary regime by formation of the tribofilms. The presence of the high concentration MoDTC and ZDDP additives in the lubricant resulted in the formation of a uniform phosphate film and MoS_2 from the MoDTC additive which covered the Al-Si phases. This led to the friction and wear reduction. It appears that the MoS_2 tribofilm formed in the wear scar will also influence the wear performance, mainly through the friction reduction.

Although a phosphate film formed from the ZDDP oil (Oil A) in the Al-Si wear scar, the wear obtained after 3h test was the highest from the lubricants tested. In Al-Si alloys, the ZDDP tribofilm is not effective in wear reduction as it is in Fe-based materials. This is also observed by Pereira *et al*. [6] where it is suggested that this is due to the low tenacity of the film to the Al-Si material. The reason for the low tenacity is because the Al-Si material can not provide thick oxide layer on the surface, therefore the ZDDP film is unable to bind to the surface via oxide as it does on the steel surface. The process of the tribofilm formation is a dynamic process which involves formation and removal of the tribofilm during rubbing process. This study indicates that the balance between removal and formation of the phosphate film changes with rubbing. After 1h test with Oil A, the removal rate is higher than formation rate of the phosphate film resulting in continuous wear while with Oil B1, low friction tribofilm improved this balance resulting in low wear and friction.

4. Conclusions

The tribological performance of Al-Si/CI tribocouple lubricated by ZDDP and ZDDP with MoDTCs has been studied. The chemical properties of tribofilms formed on Al-Si plates as well as the resulting wear mechanisms as a function of the rubbing time have been investigated. The main conclusions from this work are:

- A ZDDP additive show to form a phosphate tribofilm after the first rubbing strokes but its role in protecting the Al-Si surface from wear is small.
- Durability of the ZDDP film formed was seen to be improved when a low friction MoS_2 film is formed.
- MoDTC showed to form the low friction MoS_2 in both Al and Si phases of the Al-Si alloy. This resulted in lower friction and controlled wear.
- The wear scar microstructure is highly dependent on the lubricant chemistry. Low

friction tribofilm forms a uniform tribofilm which protects the alloy from the high wear.

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