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Tribological response of MoS_2 Coated and oxy-nitrided samples with alternative extreme pressure (EP) and anti-wear (AW) additives

Thawhid Khan[1)*], Yukio Tamura[2)], Hiroshi Yamamoto[2)], Anne Neville[1)] and Ardian Morina[1)]

[1)] Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, United Kingdom
[2)] Materials Technical Centre, Development Division, Komatsu Ltd., Kanagawa 254-8567, Japan

*Corresponding author: T.A.Khan@leeds.ac.uk

Oxy-nitriding (QPQ) and MoS_2 coatings are widely used surface modification techniques in industry to improve the friction and wear characteristics of components and interacting surfaces. To ensure optimum performance of components within tribological environments it is crucial to ensure compatibility between surfaces and lubricants, as the break-down of the lubricating film could lead to seizure between interacting components. This study analyses the interaction of extreme pressure and anti-wear additives with two modified surfaces. The friction and tribofilm formation behaviour were investigated using a Mini Traction Machine (MTM2) fitted with a 3D Spacer Layer Imaging Method. The chemical composition of the species formed after testing was analysed using X-ray Photoelectron Spectroscopy (XPS). This study found that the properties of the modified surfaces and their interaction with the various lubricant additives impact their tribological performance. With the oxy-nitrided samples no real effect on friction was observed when using the Sulphurised Olefin (SO) or Tricresyl Phosphate (TCP) additives, mostly due to lack of interaction with the less reactive iron nitride layer and their roles as anti-wear additives. However when using the SO additive with the MoS_2 coated sample, a significant reduction in friction was observed with time. This was mostly likely due to the combined effect with formation of FeS and MoS_2 within the tribofilm.

Keywords: tribology, tribochemistry, coatings, heat treatments, additives

1. Introduction

Hydraulic motors/pumps are key components within hydraulic systems, but they are hindered by their inefficiency which in some cases can be up to 15% [1]. High friction between interacting components can cause excessive wear and may also initiate seizure and complete failure of the motor/pump [2].

The application of heat treatments and coatings on steel surfaces is an effective way to improve the tribological properties of steel. This improvement can be further enhanced through ensuring the compatibility between the treated surface and lubricants within tribological environments. The role of surface protective additives is crucial with severe operating conditions and moving components in the boundary lubrication regime. Through the tribochemical reaction of the additives at the contact a protective film can be formed. The nature of this film and the regeneration of the protective layer are dependent on the presence of the additive package [3, 4, 5]. There is still much to be learnt about surface/lubricant interactions when the surfaces have been exposed to heat-treatment or surface engineering.

The use of various extreme pressure and anti-wear additives to base lubricants is a common and effective method to reduce friction and wear. The lubrication behaviour of the additive is influenced by the properties of the interacting surfaces, the environmental atmosphere and the properties of additive itself. Zinc dialkyldithiophosphate (ZDDP) is one of the most successful and effective anti-wear and extreme-pressure additives commonly applied to hydraulic fluids. The formation of a glassy sacrificial phosphate film at interacting contacts helps determine the effectiveness of the wear reduction though preventing adhesion between surfaces and reducing stresses caused by surface asperities. The interaction of ZDDP with solid surfaces often leads to the formation of different compounds such as iron sulphide or zinc/iron phosphate which could further impact the wear and friction behaviour of the tribofilm [6]. On steel samples, the tribofilms can grow to a thickness >100 nm and have an uneven pad-like structure [7]. Previous work showed oxy-nitrided (QPQ) samples performed tribologically better than untreated and coated samples during tribometer tests in terms of friction and wear, when fully formulated hydraulic oil was used as a lubricant [6].

Alternative extreme pressure and anti-wear additives to ZDDP include sulphurised olefin (SO) and tricresyl phosphate (TCP), which are both widely used within industry. The effectiveness of SO as an extreme pressure additive is due to the formation of a film of sulphide covering the metal surface [8]. FeS is softer than the metal surface and behaves as a solid lubricant. Sulphur additives are deemed highly effective in the most severe operating conditions and help to mitigate scuffing [9].

TCP demonstrates good anti-wear behaviour due to its chemical reaction with iron to form an iron phosphate and iron oxide film. Phosphorous containing compounds are effective anti-wear additives under moderate friction conditions and allow the application of higher loads [8]. Several researchers [10] have indicated that the effectiveness of SO and TCP additives are determined by the presence of oxygen in the testing atmosphere.

The aim of this project is to investigate the chemical interactions with various EP additives and treated surfaces in different lubrication regimes. The interaction between an oxy-nitrided and MoS_2 coated steel surface and hydraulic oils containing alternative EP and AW additives will be investigated. By using two alternative lubricant mixtures which were composed of either sulphur or phosphorous containing additives, allowed the investigation of the effect of both elements on the tribological behaviour of the treated surfaces individually. The goal of the project is to achieve sustained low friction and wear behaviour through the optimisation of these additive packages with a modified surface.

2. Experimental Methodology

The treated samples were lubricated with the different oil additives; two extreme pressure and anti-wear additives widely used in industry – sulphurised olefin and tricresyl phosphate. The use of sulphur and phosphorous based additives respectively would allowed the investigation in to the interaction mechanisms of the treated samples with the different additives.

2.1 Tribometer Testing

A Mini Traction Machine (MTM2) tribometer (Figure 1) was used to measure the friction and wear properties of the surface treatments with the oils containing different additives, with the generation and composition of the tribofilms being investigated using the 3D Spacer Layer Imaging Method (MTM-SLIM). The MTM tribometer allows the imaging of the formation of a tribofilm with time on two different treated surfaces which have either been coated or heat treated. It also allows the application of a sliding contact interacting within different lubrication regimes which closely represents the movement occurring between components within a hydraulic motor.

Using a Mini Traction Machine (MTM2) with a ball-on-disc configuration to represent the sliding conditions of interacting components, the friction and wear behaviour of the treated samples could be investigated. This set-up featured a ¾ inch ball made from nitriding steel and treated as described above. The counter face was a 46 mm diameter disc composed from spheroidal graphite cast iron which had been gas nitrided (650-670 HV_1). New specimens (balls and discs) were used for each test and were cleaned with solvents in an ultrasonic bath for 15 minutes prior to testing. During testing, the temperature was kept constant at 80°C and a load of 36N was applied corresponding to an initial Hertzian contact pressure of 1 GPa. The sliding-rolling ratio (SRR), defined as the ratio of the sliding speed (U_b-U_d) to the entrainment speed (U_b+U_d)/2 (where U_b and U_d are the speed of the ball and the disc, with respect to the contact) was 150% [7]. Yamaguchi [11] states the piston and cylinder component within the piston pump is a pure sliding contact, but for this study a percentage of rolling contact will be applied to replicate the rotation of the pistons within the cylinder block. The MTM2 is fitted with 3D Spacer Layer Imaging Method (SLIM) attachment, which enables in situ capture of optical interference images of the tribofilms on the steel ball. Using these images the behaviour of the formation of a tribofilm on the different treated surface can be understood.

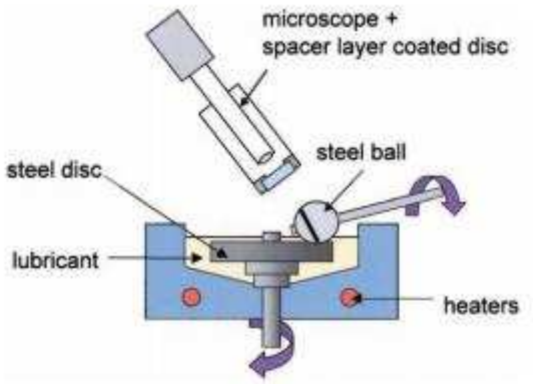


Figure 1. Diagram of MTM-SLIM set up [7]

The tribological tests were split into three alternative stages which were carried out at fixed time intervals, with an overall two hour testing period. The first stage, known as the conditioning phase, included rubbing the ball and disc together at a fixed slow entrainment speed in the mixed lubrication regime to encourage the formation of tribofilm on the ball and disc wear track. This was then followed by applying the Stribeck curve parameters, starting at a high speed - 2 m/s (mixed regime) and continued towards the lowest speed value - 0.01 m/s (boundary regime). The final stage involved halting the test and the ball sample was loaded against the spacer layer-coated window, where an image was captured which would allow the measurement of the tribofilm. Table 1 summarises the conditions used with the tribometer within this study.

Table 1. Test conditions used with MTM2 - SLIM

Conditioning Phase	
Temperature	80°C
Load / Hertzian Contact Pressure	36 N / 1 GPa
Entrainment Speed	0.1 m/s
Sliding-rolling Ratio	150%
Stribeck Curve Phase	
Temperature	80°C
Load / Hertzian Contact Pressure	36 N / 1 GPa
Entrainment Speed	2 to 0.01 m/s
Sliding-rolling Ratio	150%

2.2 Materials and lubricants

The material used for this investigation is nitriding steel, generally used for components subjected to high friction and wear. The ball shaped samples had a hardness of ~300HV$_1$ prior to treatment. To carry out the oxy-nitriding heat (QPQ) treatment on the samples, it involved using a cyanide/cyanate bath at 400-600°C to form a ~19 µm nitride layer ($Fe_{2-3}N$ & Fe_4N), followed by using a specialised nitrate – nitrite cooling salt bath to form a 0.5 µm oxide layer (Fe_3O_4) on top, which acts as a protective running-in coating (800-830 HV$_1$) – the process is highlighted in *Figure 2* [12]. Polishing and finishing are used to achieve a smooth surface finish - R$_a$ – 30 nm.

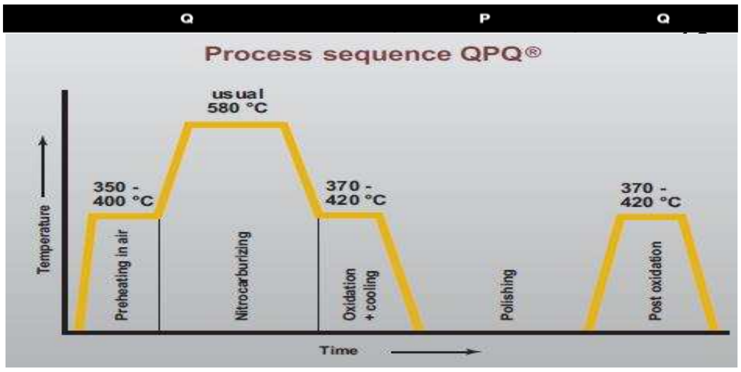


Figure 2. Salt bath nitriding (QPQ) heat treatment process [12].

The alternate treatment applied within this study involved using a gas-nitrided hardened ball sample, on which a 9 µm molybdenum disulphide (MoS_2) running-in coating was sprayed on top (750-780 HV$_1$). This coating is typically used in systems where lubricants are deemed ineffective. After treatment the ball samples had a surface roughness – R_a – 680 nm. The key processes to the application of the coatings are highlighted in Figure 3 [13].

The spheroidal graphite cast iron counter discs were gas nitrided and this treatment was kept constant for all counter surfaces, leaving the sample with a surface finish - R_a – 50 nm. The wear on the plate samples post-experiments were negligible so surface analysis mainly focussed on the treated ball samples.

The base oil (BO) used was a group I mineral oil with a viscosity of 5.2 cSt at 80°C. Lubricant one and two were a mixture of BO and SO or TCP respectively (Table 2).

Table 2. Lubricants tested

1.	BO + SO (1.5%)
2.	BO + TCP (0.25%)

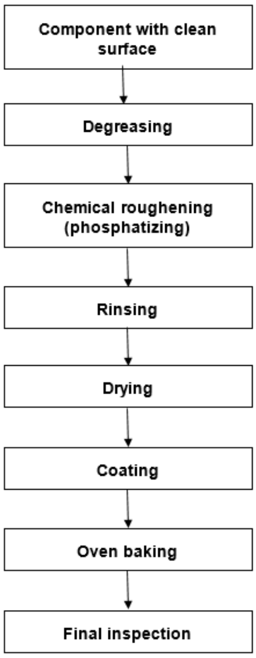


Figure 3. Schematic diagram for the application of the MoS_2 coatings [13].

2.3 Morphology and Topography Analysis

The changes in surface topography of the different samples were analysed using a Leica optical microscope and a Taylor Hobson Talysurf Profilometer, which allows the measurement of the depth of the wear scars formed on the ball samples.

2.4 Tribofilm Chemical Properties

Post experimental surface analysis included carrying out X-ray Photoelectron Spectroscopy (XPS) on the worn surfaces of the pin samples to identify the chemical species present in the tribofilms formed which could essentially affect friction and wear. A monochromatized Al Kα X-ray source was used to carry out high resolution scans for specific peaks. The beam line was focused in the centre of the wear scar in an area of 200 μm × 200 μm. The tribofilm was also etched (0.2 min) and the charging effects in the results were corrected by fixing the C1s peak (adventitious carbon) at 284.8 eV. Casa XPS software which applies a Shirley algorithm to construct a background, through a curve fitting procedure, which is applied to the peaks identified. To accurately determine the chemical species present the peak's area and full-width at half-maximum (FWHM) were constrained.

3. Results

3.1 Surface Characterisation

Microhardness measurements have been carried out with Micro Vickers microhardness tester using a load of 9.81 N (1 kg) across the samples cross-sections. The results are presented in Figure 4. Figures 5 & 6 show the SEM morphologies through the cross-section of each treated samples (QPQ and MoS_2. The Taylor Hobson Form Talysurf was employed to measure the surface roughness of the samples.

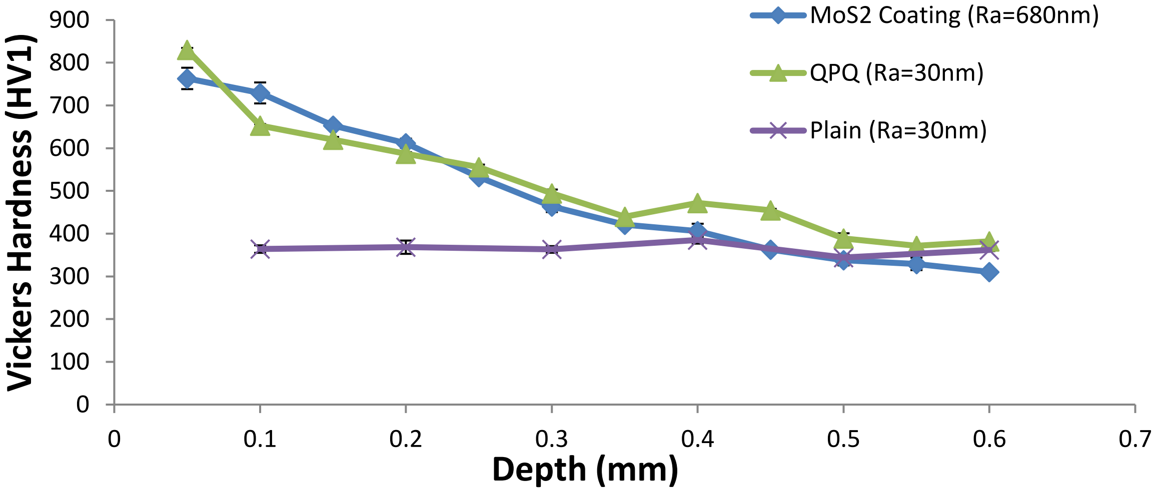


Figure 4. Comparison of the hardness through each of the treated samples cross-section and also their surface roughness.

The plain (untreated) samples were shown to mainly be composed of pearlite and ferrite matrices. For the QPQ samples (*Figure 5*) three distinctive layers are detected; on the very top surface a very thin black oxide layer of ~0.5 µm thickness is present. Underneath this layer is a ~19 µm thick compound layer of a porous constitution. The final visible layer was a diffusion zone of approximately ~250 µm thickness.

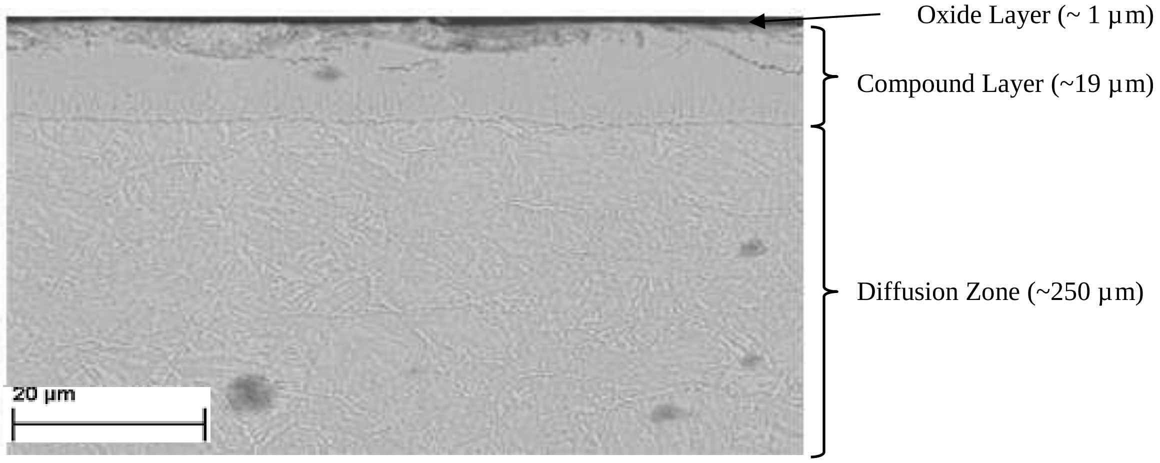


Figure 5. SEM image profile through the cross-section of a QPQ ball sample.

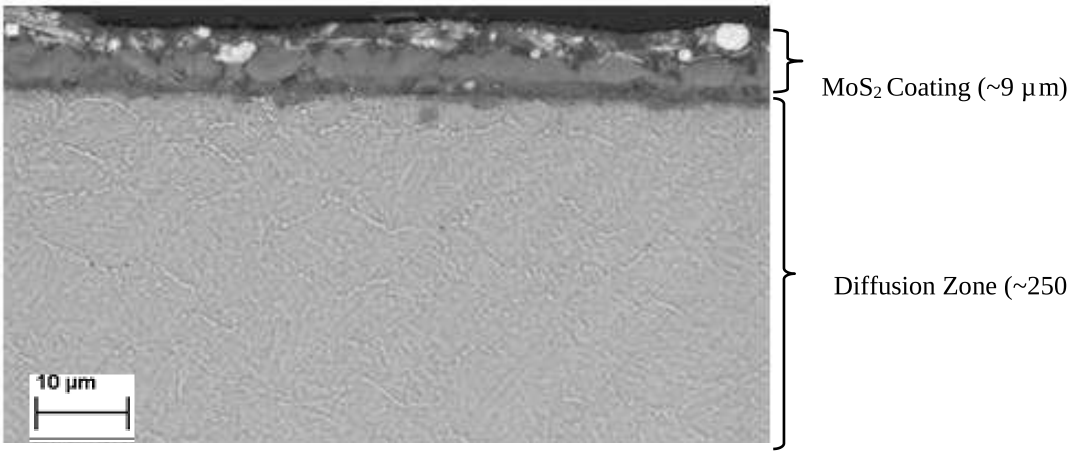


Figure 6. SEM image profile through the cross-section of a MoS_2 coated ball sample.

Compared to the QPQ samples, on the balls coated with MoS_2 (Figure 6) it is possible to see a thick layer (~9µm) followed by a diffusion zone formed by the original gas nitriding of the sample. The sample was originally hardened using the gas nitriding process before the formed nitride layer was removed, leaving the diffusion zone.

3.2 Tribofilm Formation from MTM SLIM Tests

Figures 7-20 show a series of Stribeck friction curves measured during a 2-hr rubbing test using BO+SO & BO+TCP. They highlight the dynamics of the different treated surfaces with the lubricant throughout the mixed and boundary lubrication regimes. On each graph the change from boundary (1-100 mm/s) to mixed lubrication (100-10000 mm/s) is highlighted by a dashed red line These graphs are combined with a series of optical interference images of the tribofilms formed on the surface of the treated balls, which would be indicated by dark areas. The sliding direction in all these images is from left to right. Due to the roughness of the ball samples and in some cases the relative thinness of the formed tribofilm, it was not possible to quantify the film thickness accurately.

3.2.1 BO+SO - Friction & Wear

Figure 7 shows the friction coefficient as a function of entrainment speed for the SO additive with the QPQ treated sample. As the entrainment speed is reduced friction steadily increases. In the mixed lubrication regime from 100 mm/s – 2000 mm/s, it is possible to see that friction begins to reduce with time until the entrainment speed reduces below 100 mm/s (boundary regime) where friction remains constant for the 2-hr rubbing period at the lower speeds. The optical interference images (Figure 8) show virtually no tribofilm was formed during the duration of the test. The optical interference images show that the wear of the sample increased with time, shown by the distortion of the wear track in the SLIM image.

A different trend is observed with the MoS$_2$ coated sample (Figure 9), where at all entrainment speeds with an increase in time the friction coefficient is seen to reduce steadily. The reduction in friction after the two hour testing period at the different entrainment speeds ranged from 20-40%. The MoS$_2$ coated surface was significantly more sensitive to the SO additive than the QPQ samples. The SLIM images (Figure 10) showed the formation of a thin tribofilm and the exposure of a rougher surface than that observed when using QPQ samples (Table 2). Once again the wear of the sample increased with the duration of the test as shown by the distortion of the wear track from the SLIM images.

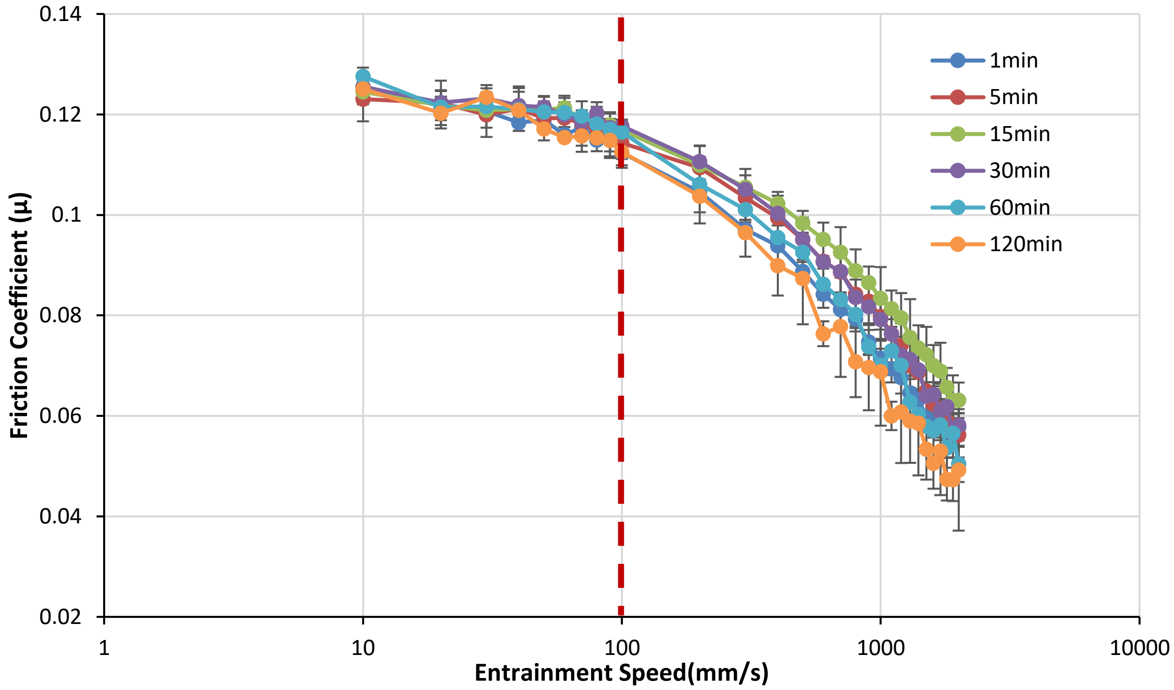


Figure 7. Series of Stribeck curves when using a QPQ ball and gas nitrided disc with BO+SO lubricant

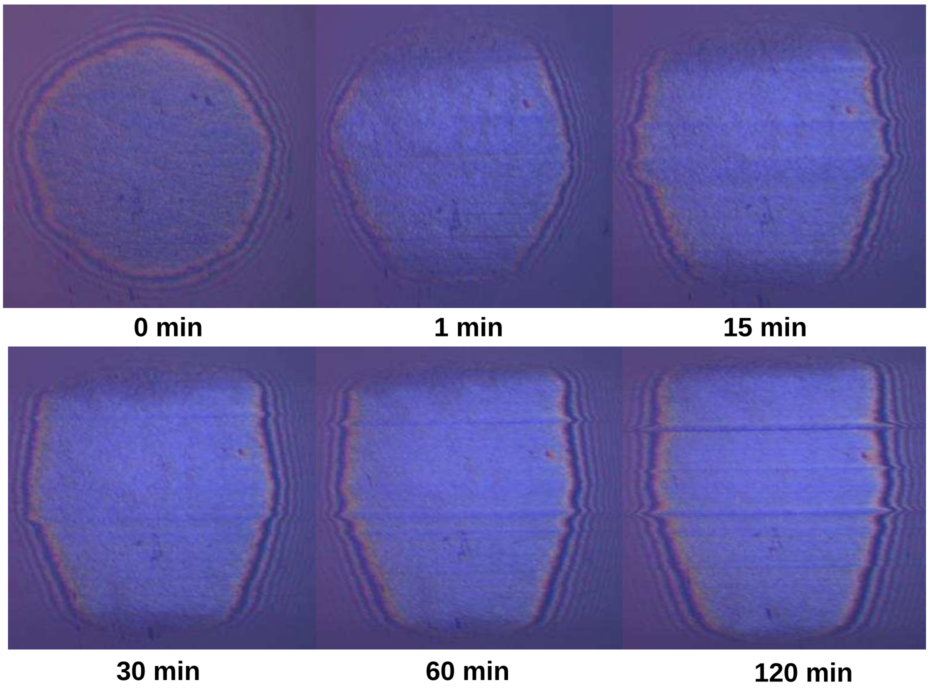


Figure 8. Optical interference (SLIM) images of the tribofilm formation on QPQ samples with BO+SO lubricant

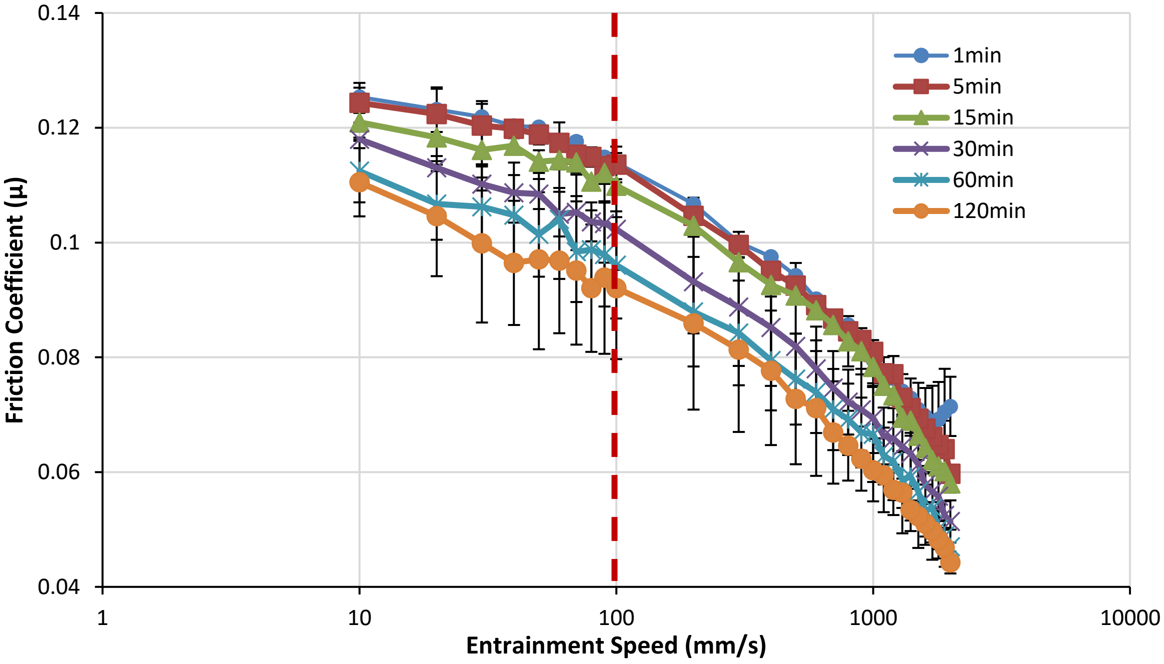
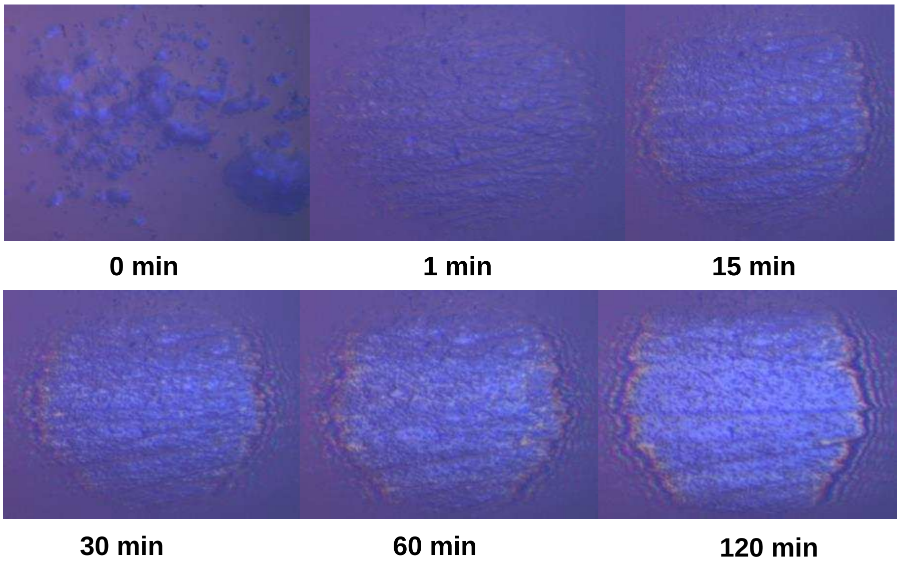


Figure 9. Series of Stribeck curves when using a MoS_2 coated ball and gas nitrided disc with BO+SO lubricant



0 min 1 min 15 min

30 min 60 min 120 min

Figure 10. Optical interference (SLIM) images of the tribofilm formation on MoS_2 coated samples with BO+SO lubricant

Table 2. The roughness (R_a) of the treated ball samples pre and post testing when using the SO additive

	R_a (µm) Pre-test	**R_a (µm) Post-test**
QPQ Ball Sample	0.03	0.22
MoS_2 Ball sample	0.68	1.71

When comparing the friction performance of the two treated samples, Figure 11, after 2hrs it is possible to see that the MoS_2 coated sample performed better in both boundary and mixed regime, producing lower friction values. The values at higher entrainment speeds merge; indicating that the nature of the surface at this point is having less effect than at lower entrainment speeds. The MoS_2 samples showed a higher variation in repeatability in comparison to the QPQ samples, however the lower friction trends are still evident.

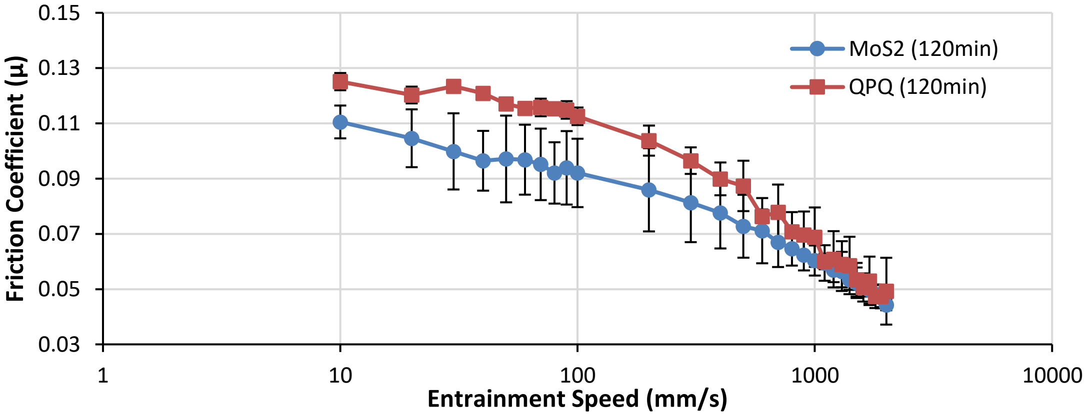


Figure 11. Comparison of the Stribeck curves after 2hr rubbing test for QPQ and MoS_2 coated samples and gas nitrided disc with BO+SO lubricant.

Optical images of the worn area of the QPQ MTM ball samples (Figure 12(a)) after testing showed the removal of the oxide layer (~ 1 µm) and the exposure of a porous compound layer. There are signs of scoring across the surface. No clear tribofilm is identified on the worn surface.

However with the MoS_2 ball samples (Figure 12(b)) the worn surface shows the almost complete removal of the MoS_2 coating (~ 9 µm), with only remnants of it being observed in the wear scar. Scoring in observed across the surface alongside the presence of a uniform tribofilm covering the worn area.

In terms of wear (Figure 13), the MoS_2 coated samples had greater wear depths and penetration than the QPQ samples. The wear scar images and depth analysis indicate the MoS_2 coating was removed during testing.

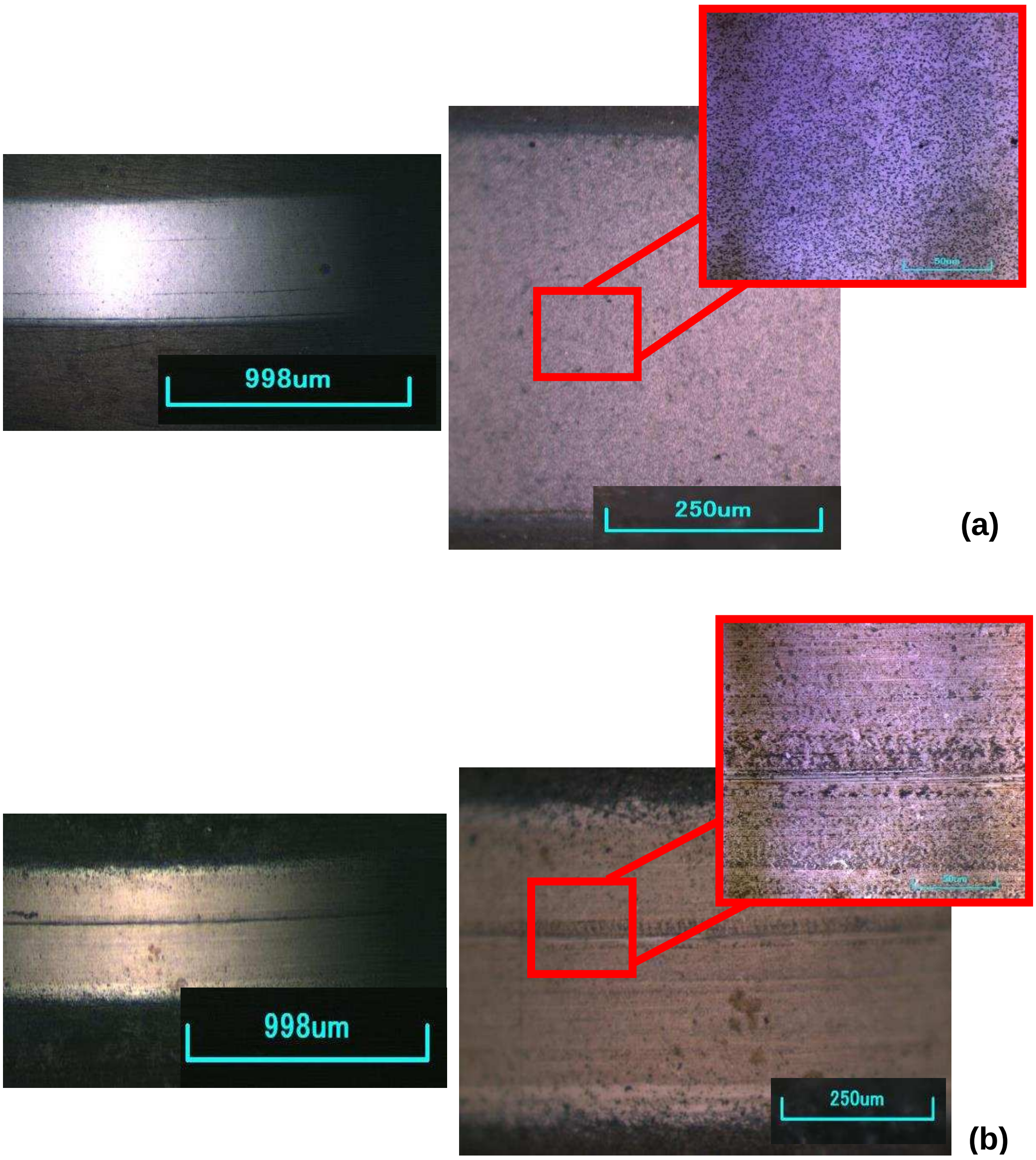


Figure 12. Optical images of wear scar regions of the MTM ball samples with the SO additive – (a) QPQ ball (b) MoS_2 ball.

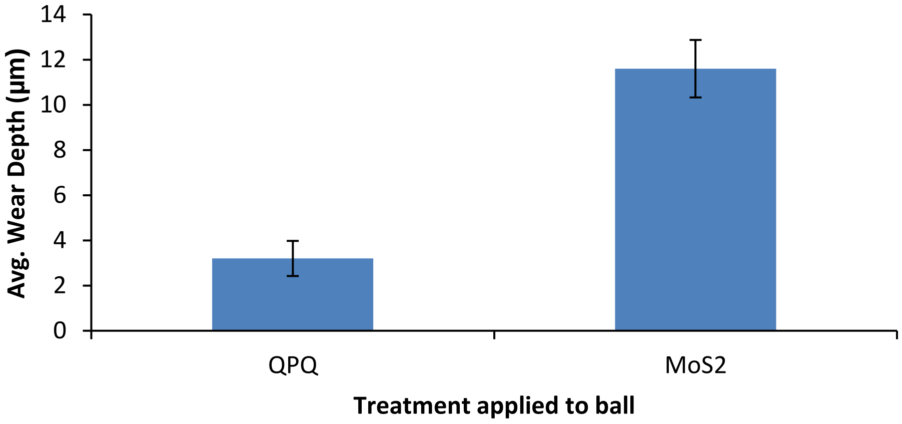


Figure 13. Comparison of the wear depths of QPQ & MoS_2 coated ball samples when using BO+SO.

3.2.3 BO+TCP - Friction & Wear

Figure 14 shows the friction coefficient of TCP additive with the QPQ treated sample. As the entrainment speed is reduced friction steadily increases. In boundary condition it is possible to see that friction is constant throughout the two hours of the test. In the mixed regime friction begins to reduce slightly with time. However taking into consideration statistical error the change does not seem significant. The SLIM images are similar to those from the SO oil tests and no clear tribofilm is formed. However at 60 and 120 minutes a thin tribofilm seems to be present as highlighted in Figure 15.The SLIM images show less distortion of the samples wear track with time compared to using the SO additive, suggesting lower wear is occurring.

With the MoS_2 coated sample, in boundary regime there seems to be no change in friction during the duration of the two hour test (Figure 16), there is a slight reduction in friction within the mixed regime with time however the behaviour is similar to that seen with the QPQ sample and the change is not significant. The optical interference images show the formation of a tribofilm on the wear track (Figure 17), composed of non-uniformly distributed patches elongated along the sliding direction developing in thickness with the duration of the test. The images also show the shape of the wear track is maintained during the test. The wear scar shows signs of adhesive wear and the surface is once again rougher than using the QPQ sample (Table 3).

Even with the formation of a tribofilm on both sample variants there was no real impact on friction. This indicated that the properties of the tribofilm formed when using the TCP additive were different to that observed when using the ZDDP additive which lead to an increase in friction as observed by Yue et al [6].

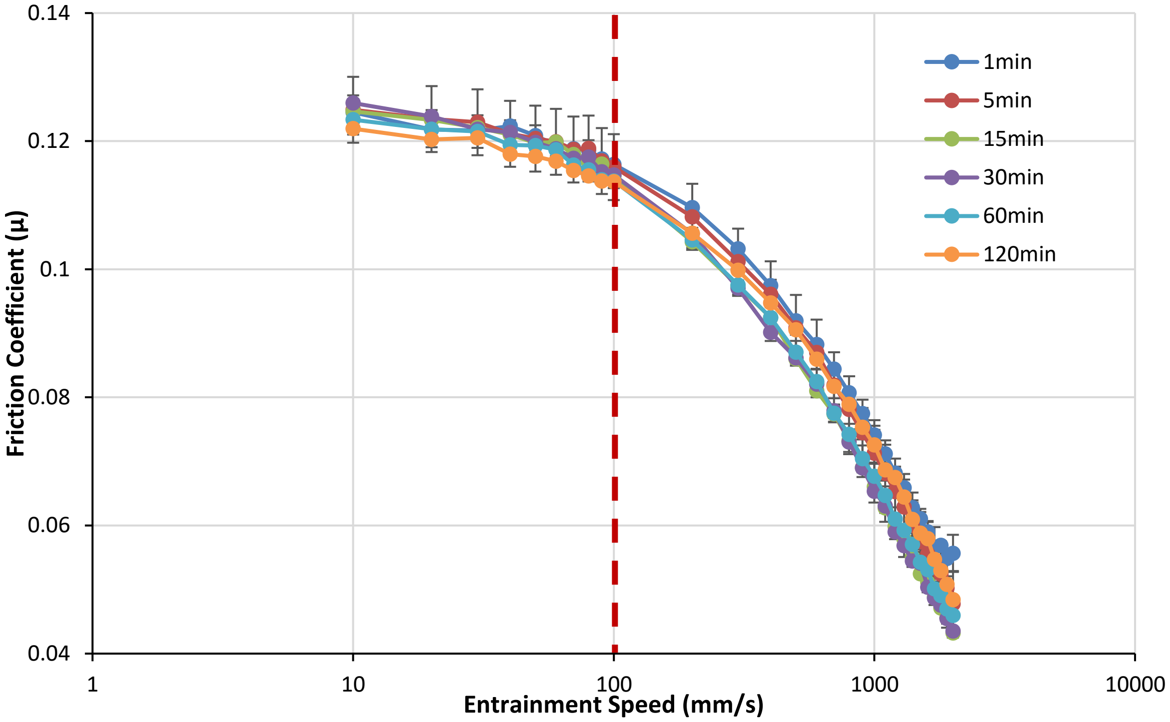
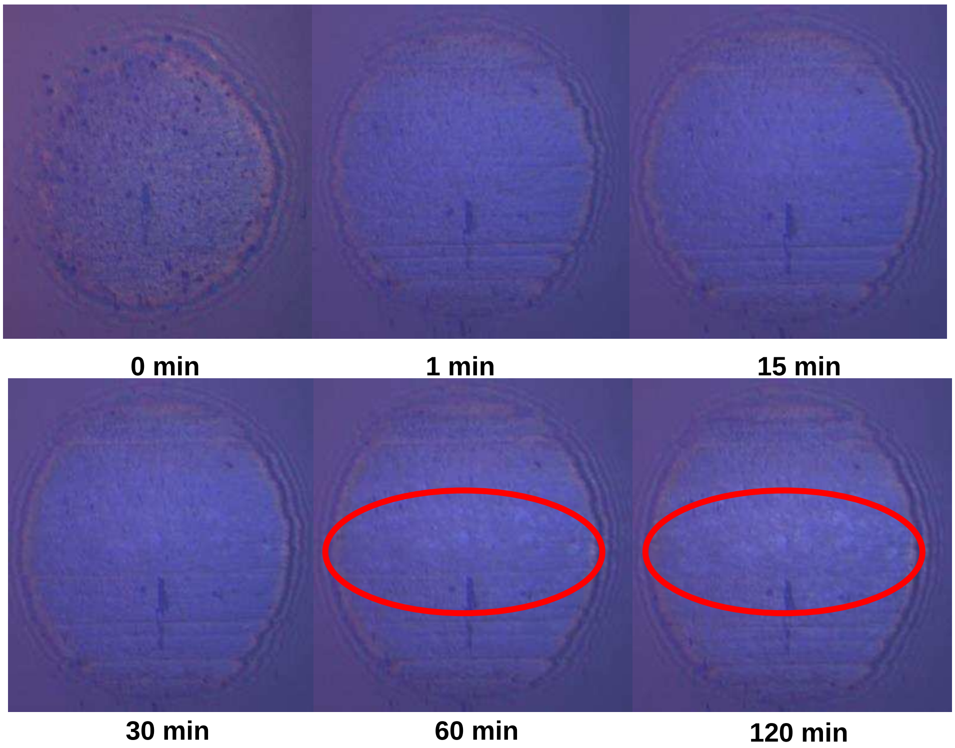


Figure 14. Series of Stribeck curves when using a QPQ ball and gas nitrided disc with BO+TCP lubricant.


0 min 1 min 15 min

30 min 60 min 120 min

Figure 15. Optical interference (SLIM) images of the tribofilm formation on QPQ samples with BO+TCP lubricant

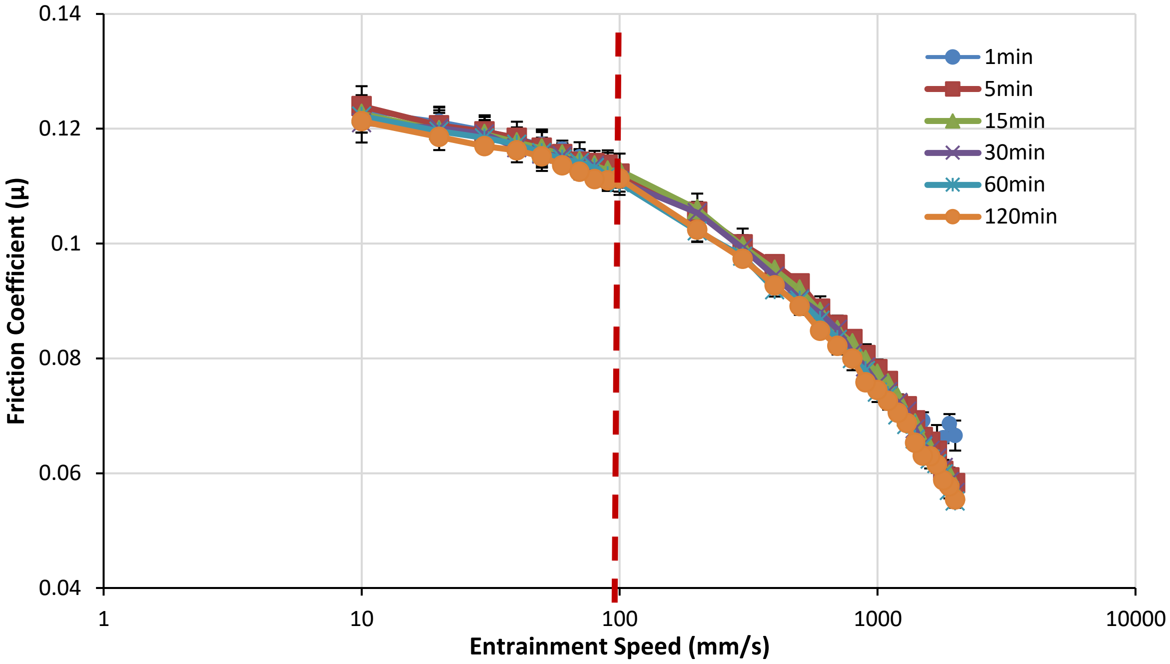


Figure 16. Series of Stribeck curves when using a MoS_2 coated ball and gas nitrided discs with BO+TCP lubricant.

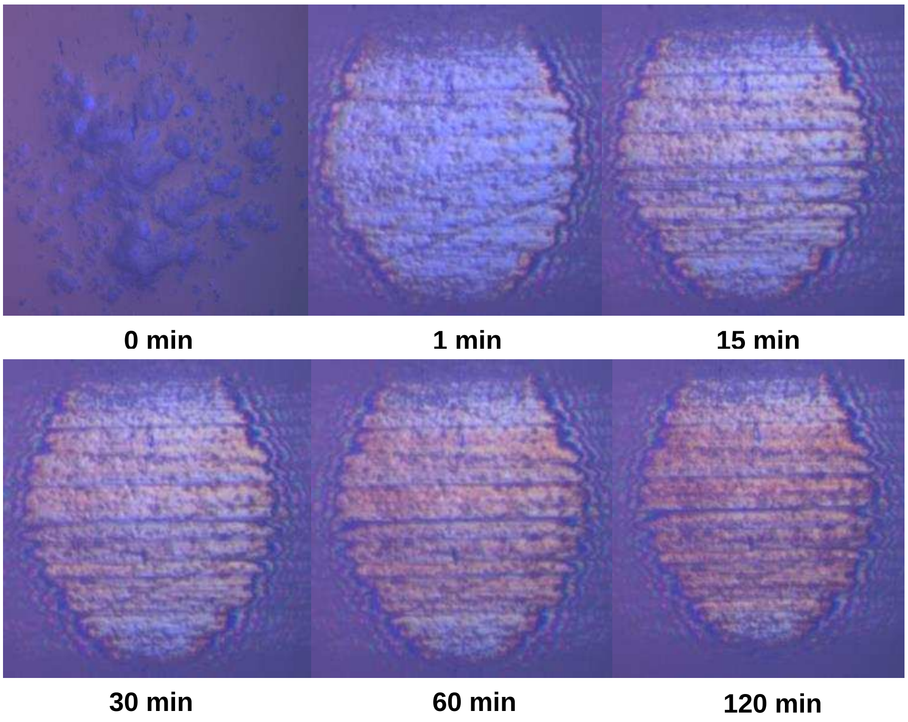


Figure 17. Optical interference (SLIM) images of the tribofilm formation on MoS_2 coated samples with BO+TCP lubricant

Table 3. The roughness (R_a) of the treated ball samples pre and post testing when using the TCP additive

	R_a (µm) Pre-test	**R_a (µm) Post-test**
QPQ Ball Sample	0.03	0.14
MoS_2 Ball sample	0.68	1.35

When comparing the friction performance of the two treated samples, Figure 18, after 2hrs it seems the friction response of the two treated samples are almost identical.

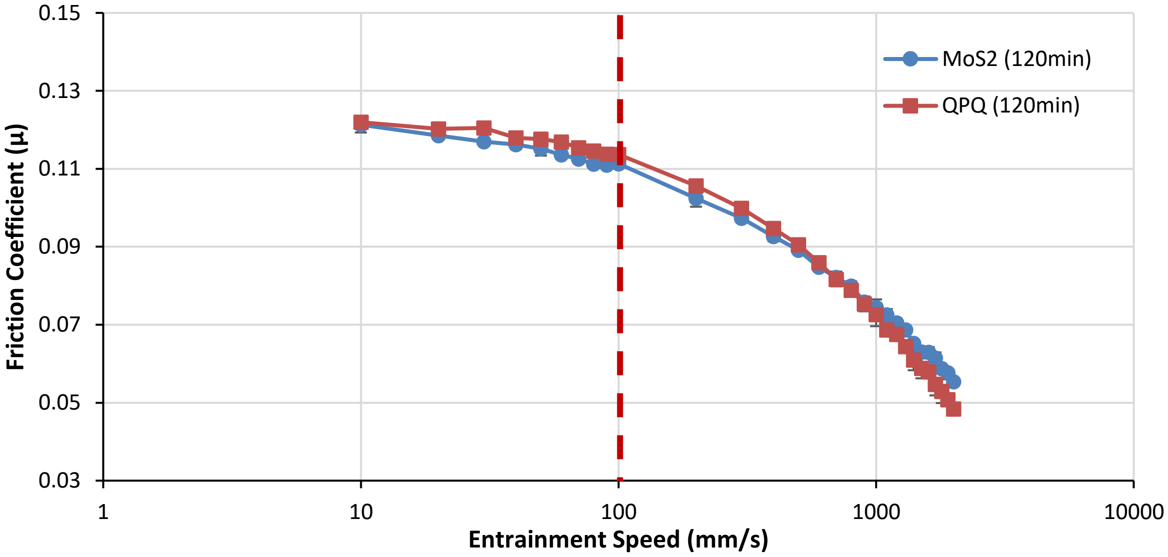


Figure 18. Comparison of the Stribeck curves after 2hr rubbing test for QPQ and MoS_2 coated samples gas nitrided discs with BO+TCP lubricant.

The wear track of the QPQ MTM balls (Figure 19(a)) with the TCP additive showed the partial wearing of the Fe_3O_4 oxide layer in contrast to using the SO additive (Figure 12(a)), where the layer was completely removed. Even though the Fe_3O_4 layer survived the test, sections of it were worn through. When using the TCP additive the presence of a tribofilm can be observed on the worn surface which was not the case when using the SO additive.

Similar to when using the SO additive, the MoS_2 coating was worn away with the TCP additive (Figure 19(b)) with only remnants present within the contact. A thicker tribofilm is observed to form on the surface.

However in terms of wear, once again the MoS_2 coated samples had greater wear depths than the QPQ samples (Figure 20). The wear analysis of the QPQ samples indicated wear was less than 1µm, suggesting the oxide layer survived testing as supported by the optical images (Figure 12(a)). With the MoS_2 samples wear depths were similar to the thickness of the coating, which may explain the presence of remnants of the MoS_2 coating as observed by the optical images (Figure 19(b)).

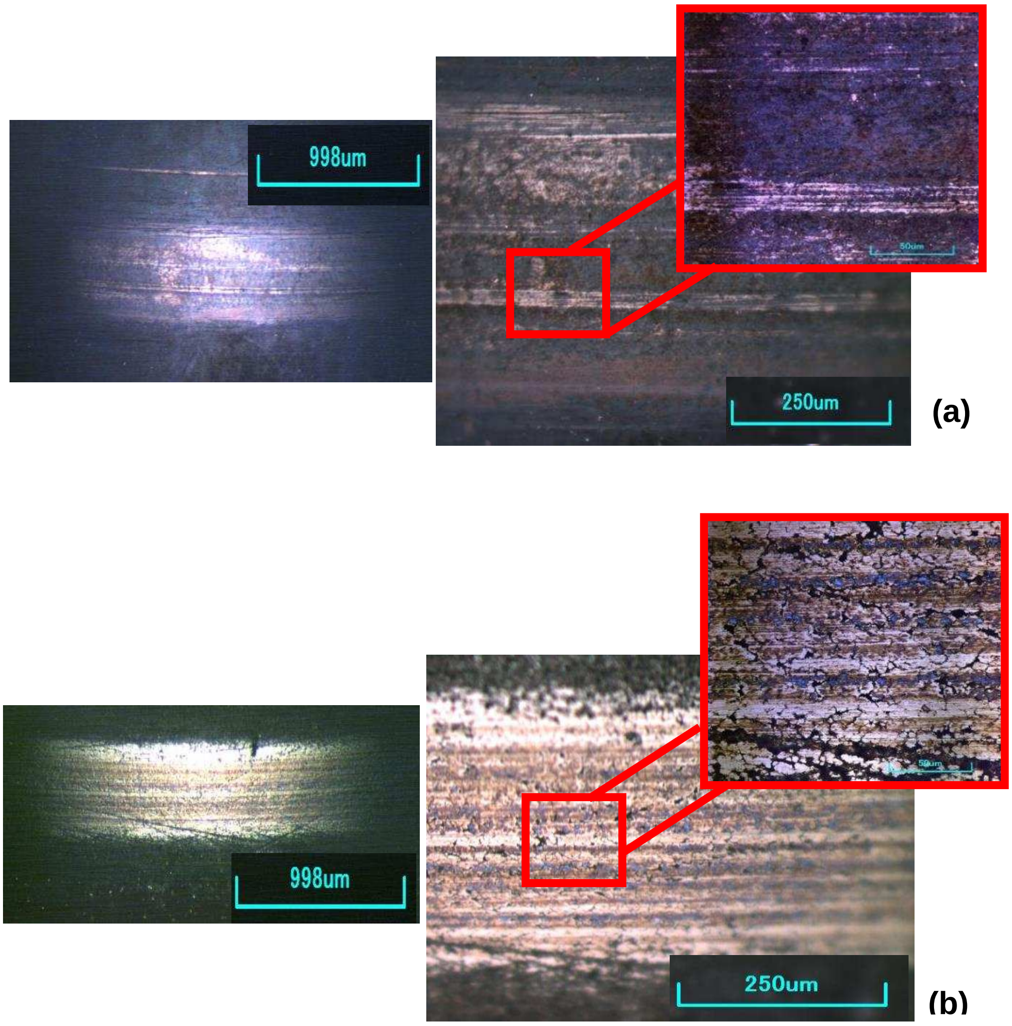


Figure 19. Optical images of wear scar regions of the MTM ball samples with the TCP additive – (a) QPQ ball (b) MoS_2 ball.

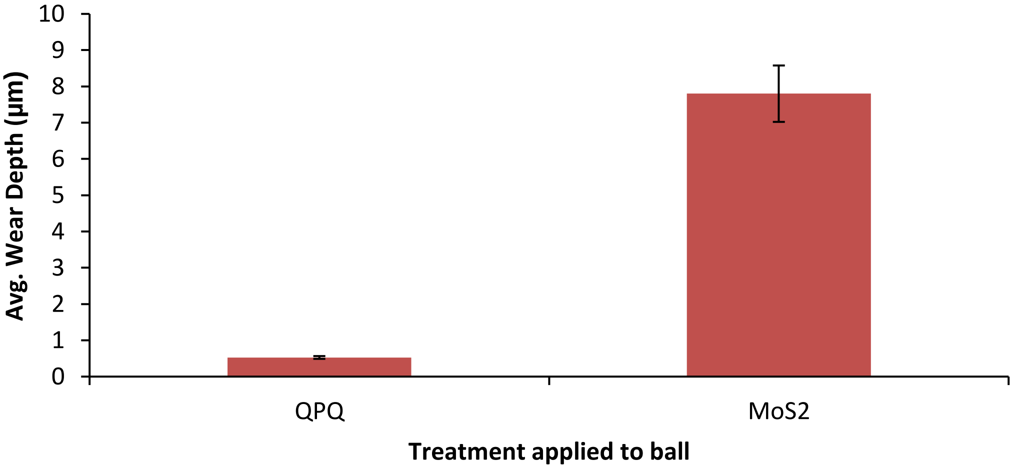


Figure 20. Comparison of the wear depths of QPQ & MoS_2 coated ball samples when using BO+TCP.

3.2.3 Effect of additives on treated samples

Using Figure 21 to compare the friction response of the two additives with the QPQ samples, it is possible to see the friction trends are almost identical and the differing additives have no real affect when compared to each other. There is a stark comparison when analysing the effect of the different additives on the wear loss of the sample (Figure 22), the wear depth when using the TCP additive is significantly smaller than using the SO additive. The figure also shows that with both additives the wear never penetrated past the compound layer and into the substrate. The SLIM also showed the formation of a thin tribofilm with the TCP additive (Figure 15) whereas nothing was formed when SO (Figure 8) was used.

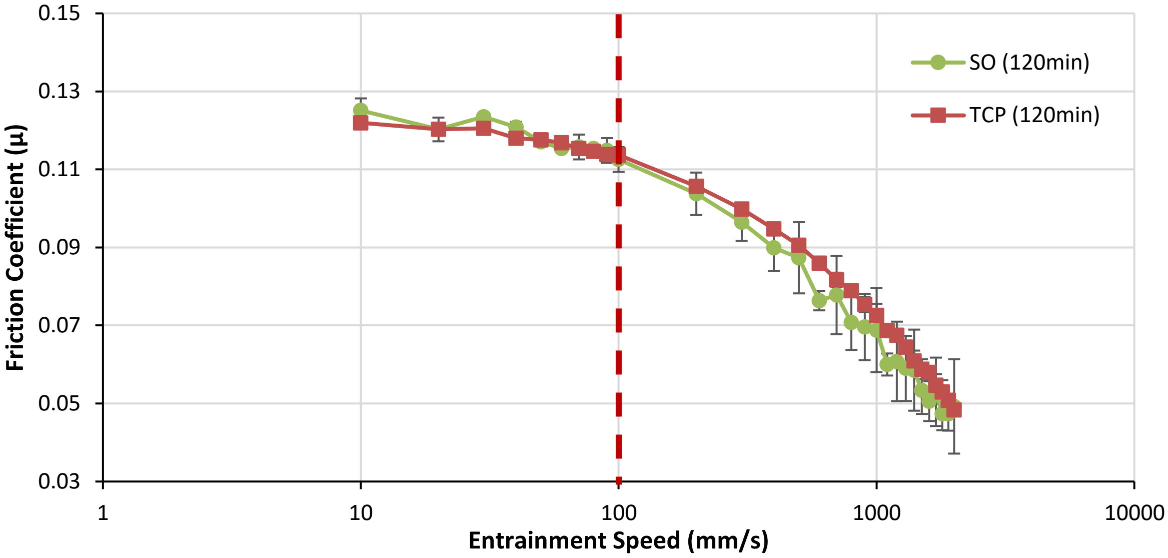


Figure 21. Comparison of the Stribeck curves after 2hr rubbing test for QPQ samples with gas nitrided discs when using BO+SO & BO+TCP lubricants.

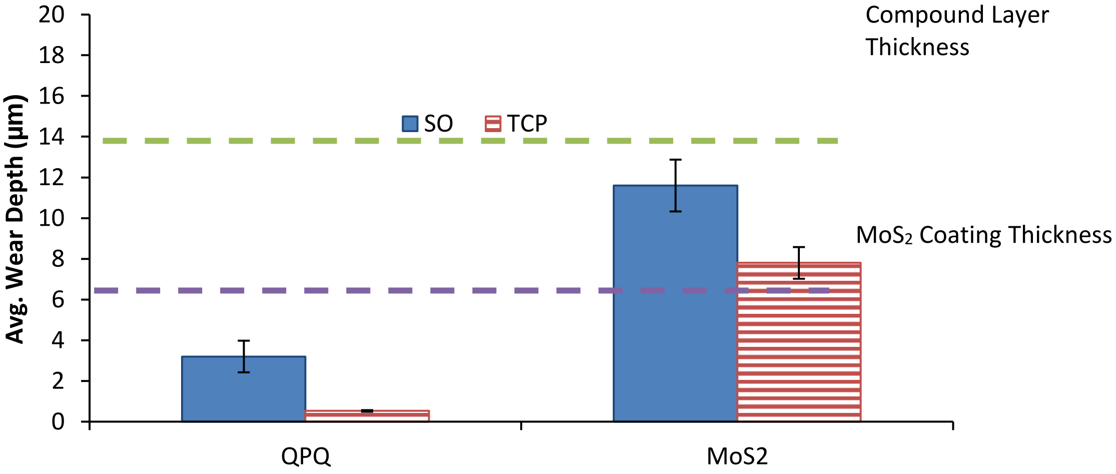


Figure 22. Comparison of the wear depths of QPQ & MoS_2 coated ball samples when using BO+SO & BO+TCP lubricants.

Analysing the effect of the different additives with the MoS_2 coated sample using Figure 23, the SO additive has a clear and effective impact on friction compared to the TCP additive. The SO additive produces significantly lower friction results in mixed and boundary conditions. However there is a different trend observed when comparing the depth of the wear scars on the ball, where the trend follows that seen with the QPQ sample. The samples tested with the TCP additives have smaller wear penetration (Figure 22), but for both oils it seems the coating did not survive the tests with the wear depth penetrating past the applied coating and into the substrate material. This is most likely due to the relative softness of the MoS_2 coating. It had also been observed that a clear thicker tribofilm was formed when using the TCP additive, whereas it was thinner when using the SO additive.

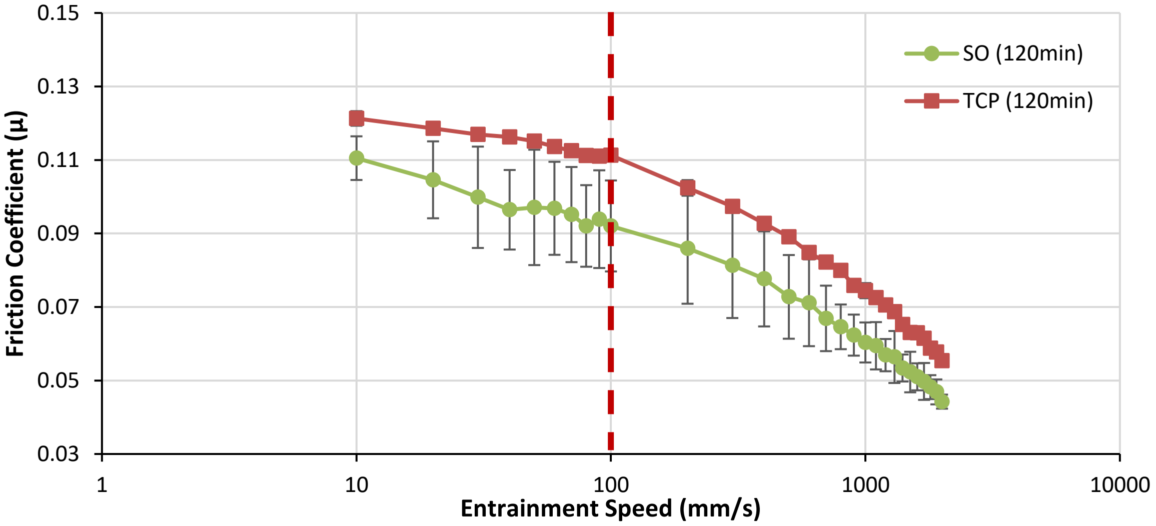


Figure 23. Comparison of the Stribeck curves after 2hr rubbing test for MoS_2 coated samples and gas nitrided discs when using BO+SO & BO+TCP lubricants.

3.3 XPS analysis on worn surfaces of MTM balls

XPS analysis was carried out to analyse the changes in chemical species formed in the tribofilms on the surface of the oxy-nitrided (QPQ) & MoS_2 coated samples when using the two different lubricant additives, which vary in elemental composition. Table 4 and Figures 24-27 highlight the key species formed on the worn surface of the two sample types when using different additives. Table 4 shows the species present at a 1.33 nm etching depth, alongside confirming the presence of a tribofilm with all the additives in this study. The XPS peaks show a higher intensity sulphur and phosphorous presence within the MoS_2 coated sample indicating a thicker layer has been formed. When using the SO additive with QPQ samples (Figure 24), there is a formation of FeS (~712.1 eV) and iron oxides. However when using the TCP additive (Figure 26) the key species identified are $FePO_4$ (~712.4 eV) and iron oxides. The same species formations were observed when using the MoS_2 coated samples (Figures 25 & 27), however when using the SO additive no traces of MoS_2 from the coating were detected in the wear scar. With the QPQ samples organic nitrogen species (~399 eV) were detected, which can be attributed to absorbed nitride complex [13].

Table 4. General binding energy values for compounds relevant to the tribofilms formed on the worn surface of the QPQ and MoS_2 samples when using the different EP additives at 0.2min etching time.

Sample Type	Additive	Element	B.E / eV (±1eV)	Chemical state
QPQ	**SO**	N 1s	399.0	Organic Species
		S 2p	162.3	Sulphide
		Fe 2p	712.1	FeS
			709.5	Fe_3O_4
	TCP	N 1s	398.1	Organic Species
		P 2p	133.4	Phosphate
		Fe 2p	712.4	$FePO_4$
			709.3	Fe_3O_4
MoS_2 coating	**SO**	S 2p	161.9	Sulphide
		Fe 2p	711.9	FeS
			709.0	Fe_2O_3
	TCP	P 2p	133.7	Phosphate
		Fe 2p	712.4	$FePO_4$
			710.3	Fe_2O_3

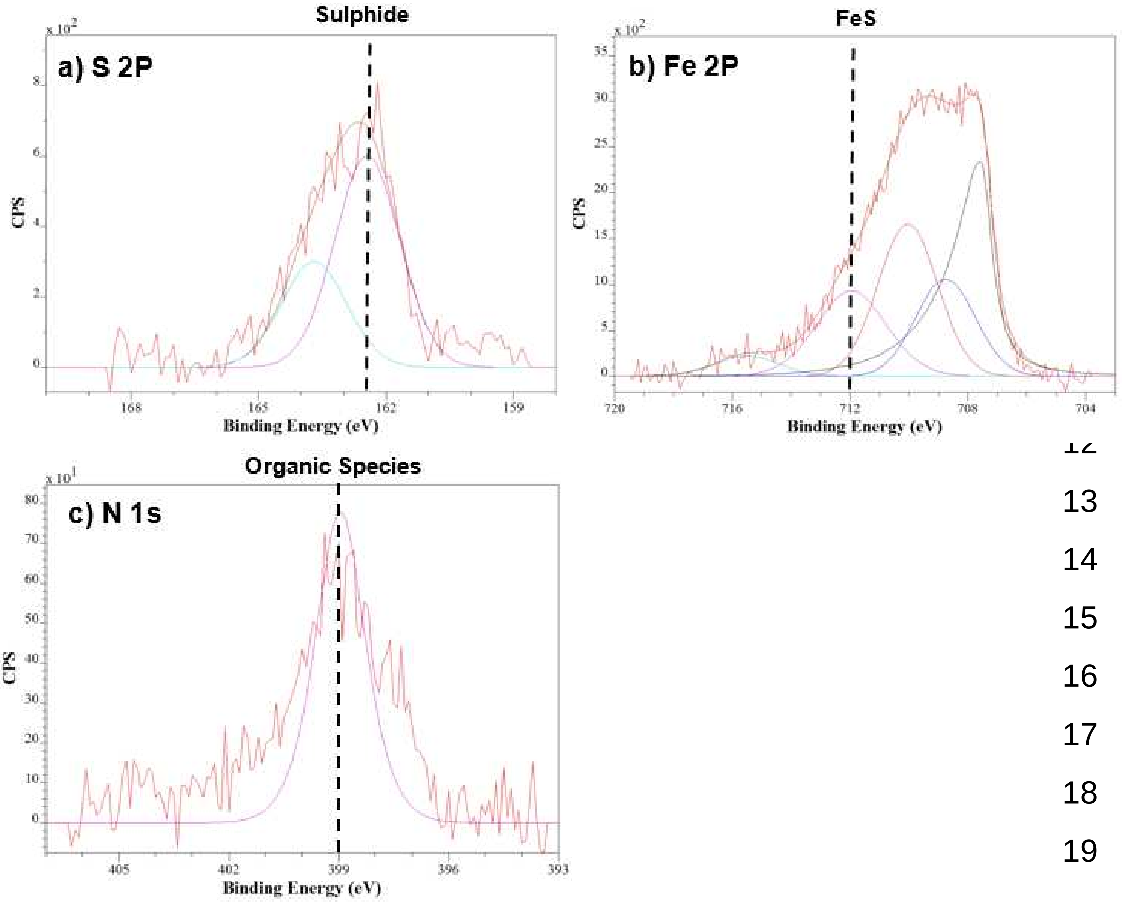


Figure 24. XPS spectra of S 2p, Fe 2p & N 1s on worn surface of the QPQ MTM ball samples at 1.33 nm etching depth with SO additive.

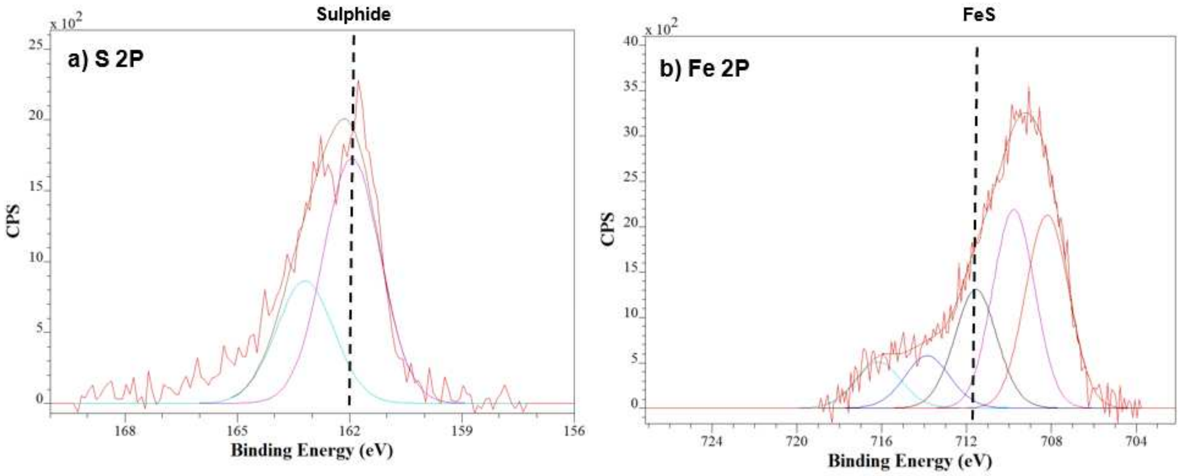


Figure 25. XPS spectra of S 2p & Fe 2p on worn surface of the MoS_2 coated MTM ball samples at 1.33 nm etching depth with SO additive.

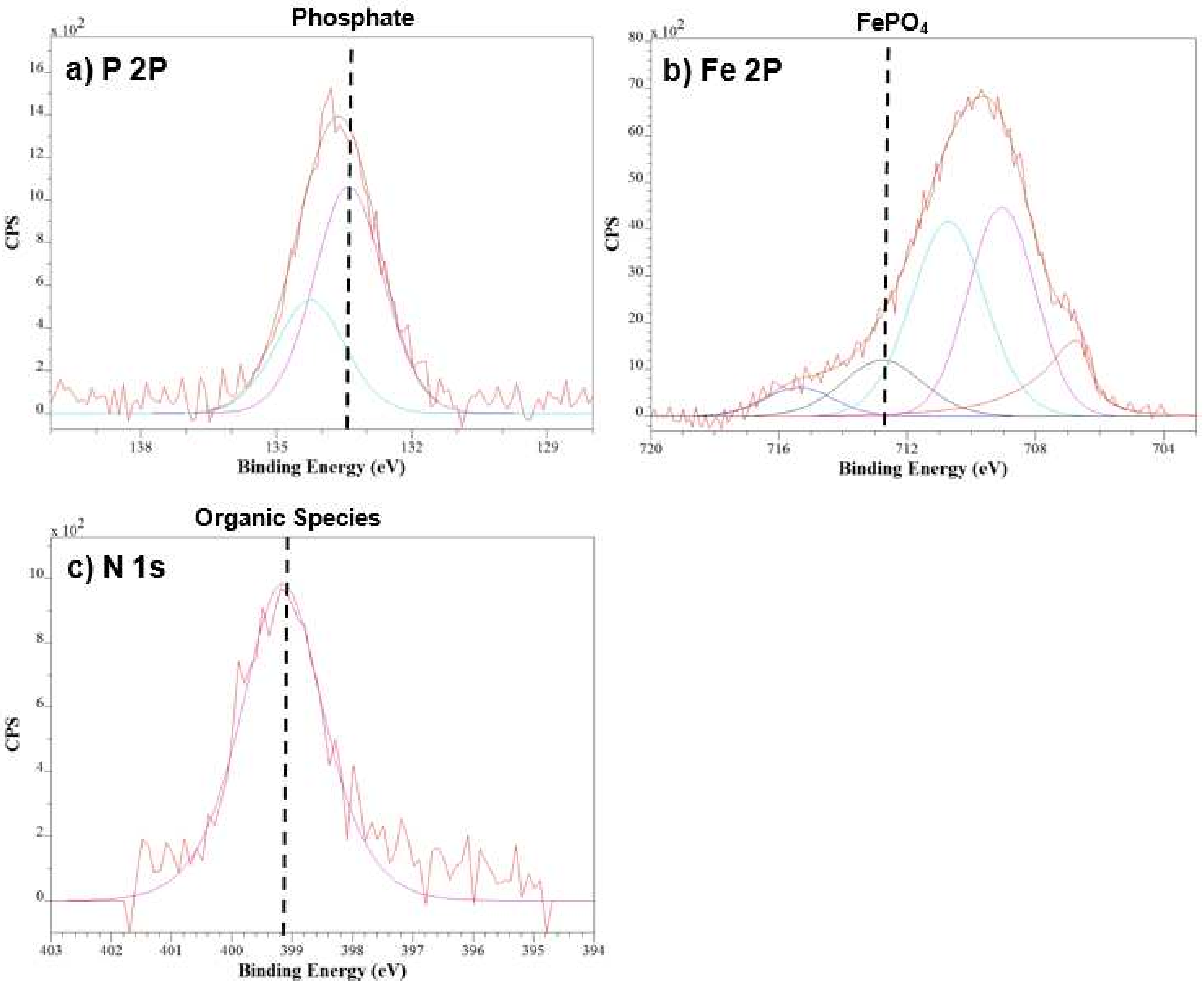


Figure 26. XPS spectra of P 2p, Fe 2p & N 1s on worn surface of the QPQ MTM ball samples at 1.33 nm etching depth with TCP additive.

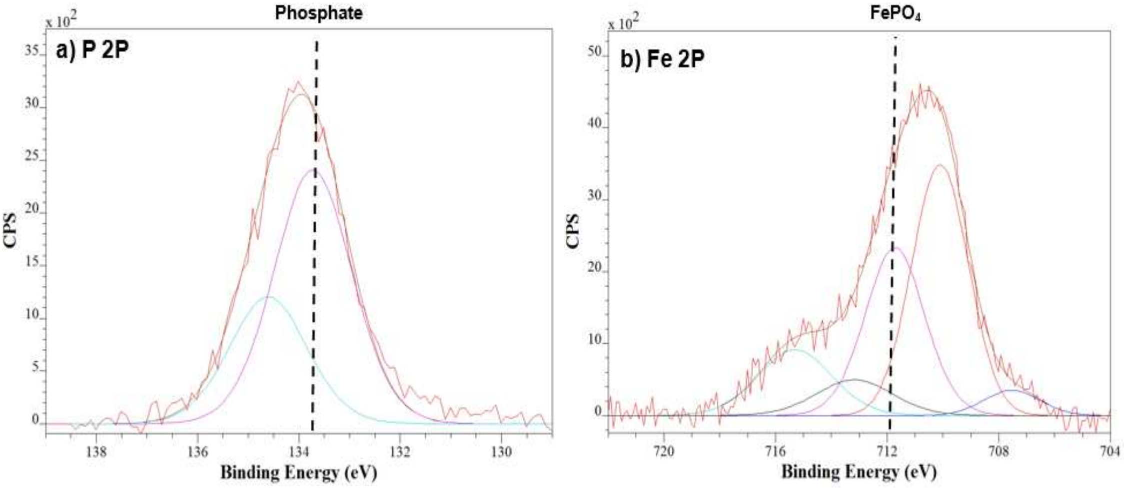


Figure 27. XPS spectra of P 2p & Fe 2p on worn surface of the MoS_2 MTM ball samples at 1.33 nm etching depth with TCP additive.

4. Discussion

The tribological behaviour observed with the different treated samples is due to a combination of factors such as the mechanical properties and surface characteristics alongside tribochemical interactions with the lubricants used.

4.1 Friction and Wear

A common trend observed with the QPQ and MoS_2 treated samples with both additives was the reduction of friction with time. This may be due to a number of factors such as the removal of asperities of the ball's surfaces, which would allow greater entrainment of lubricant between two surfaces and hence a reduction in friction is observed with time or the drop in contact pressure due to the wearing of contacting surfaces. In some cases friction within boundary regime remained constant over time with both samples and additives; this may be due to the inability to form effective friction reducing tribofilm.

The wear depths of the MoS_2 coated samples were significantly higher than the QPQ balls, with the diffusion zone being exposed in all experiments (Figure 28). Bonded coating manufacturer Kluber [14] states that MoS_2 coatings are usually used as a running-in coating, with the durability of the coating being relatively short and once is has been worn through it cannot be replenished. The exposure of the diffusion zone suggests the coating is easily removed during testing and is of a softer nature, compared to the layers produced by nitriding. The properties of nitrided layers produced play a significant role in the tribological performance observed. Qiang et al [15] reported that the formation of a ε-phase composed compound layer with inter-metallic/ceramic properties makes it difficult for metallic counterparts to adhere with. This combined with a lamellar close packed hexagonal microstructure, which is easy to slide and to run in along the base plane would help to reduce the heat produced by friction. With the MoS_2 coated sample the rougher metallic diffusion zone surface (Tables 2 & 3) is exposed when using both additives, allowing it to adhere with the nitrided counter face in comparison to the QPQ sample where its ceramic layer interacts with that of the counter disc. The metallic surface interaction of the MoS_2 sample and counter disc led to adhesive wear occurring at the contact surface, which was not seen with the QPQ samples.

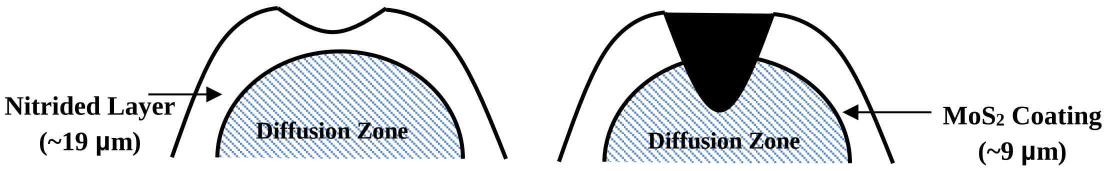


Figure 28. Cross-sectional scheme of treated MTM ball samples worn surfaces

The impact of the properties of the modified surfaces on tribological behaviour are highlighted in Figure 22 where the QPQ samples are shown to have greater wear resistance than the MoS_2 coated samples. The figure also importantly shows that not only can the surface impact behaviour but so can its interaction with the additives in the lubricant, which is investigated further in the next section.

4.2 Surface Tribochemistry

The interaction of the different additive-containing lubricants with the treated samples played a significant role in the tribological behaviour observed. It can be difficult to form a tribofilm on a treated surface in some cases due to the reduction in reactivity with the lubricant additives compared to a steel surface [3]. SLIM images when using the QPQ samples (Figures 8 & 14) show no tribofilm presence when using SO and a very thin formation when using the TCP additive. The compound layer present on the QPQ samples is known for its inert/inter-metallic properties [16, 17] and with the absence of nascent iron in this layer, it is not surprising that no or a very thin tribofilm is formed.

Using XPS to etch the worn surface of the QPQ samples it was possible to confirm the presence of a thin tribofilms and to characterize the formed protective layers. With the presence of the SO additive FeS is seen to form within the tribofilm of the QPQ samples. However due to the inert properties of the nitride layer this may have prevented the formation of sufficient concentration of FeS to impact the friction response of the system.

When TCP was used, there is a slight formation of a visible tribofilm and using XPS $FePO_4$ was detected alongside phosphates which would improve the anti-wear behaviour of the sample, with Figure 22 showing lower wear penetration compared to using SO. Overall the TCP additive had no impact on friction but only on wear behaviour. Ma et al [8] believed the presence of a film formed when using a TCP additive would improve the samples anti-wear and load carrying properties whereas when using SO only the load carrying ability would be enhanced. Kawamura et al [18] states that the crystal structure of FeS compounds formed when using the SO additive would substantially affect the samples wear properties, hence this is possibly the reason for why high wear is observed compared to when using TCP with both types of samples. Even though the reduced reactiveness of the compound layer [16, 17] limits the formation of a thick tribofilm, the type of additive present within the lubricant can still greatly impact the friction and wear performance as observed.

The key difference between the QPQ and MoS_2 samples was the absence of a less reactive compound layer which was replaced with a MoS_2 layer with the latter sample. Figure 22 shows that the applied MoS_2 coating is almost completely removed during testing with both lubricant variants and the nascent iron rich diffusion zone was exposed. This allowed the formation of tribofilms containing higher concentrations of key compounds which could impact the tribological behaviour. With MoS_2 coated samples and TCP additive combination a thick tribofilm is seen to form (Figure 17), however the friction response of both samples (MoS_2 & QPQ) with the TCP additive were identical (Figure 18), supporting the assumption that the additive has no impact on friction. Instead wear resistance is improved due to the formation of a thick compact boundary lubrication film composed of $FePO_4$.

Even though a thin tribofilm is formed when using the SO additive (Figure 10), the MoS_2 coated sample demonstrated a significant friction reduction response even when compared to the QPQ sample. XPS showed the formation of FeS within the tribofilm formed, this combined with the remnants of the MoS_2 coating would greatly influence the friction behaviour of the sample. A similar response was observed within Wang et al's [19] work with MoS_2/FeS multilayer films under lubrication (Figure 29), where the friction decreased and was lower than steel with an FeS film. Wang et al [19] proposed this was due both compounds possessing a close packed hexagonal crystalline structure allowing easy slip along the close-packed plane. With the formation of FeS on the worn MoS_2 coated surface, this multilayer film would be subject to plastic deformation creating a plastic flow layer over the worn surface which help to reduce friction within the system. However the relative softness of both compounds would have a detrimental effect on the wear rate of the sample.

The interactions of the SO and TCP additives with the MoS_2 coated samples again show the interaction of additive with modified surface can greatly impact the tribological performance as observed when using the SO additive.

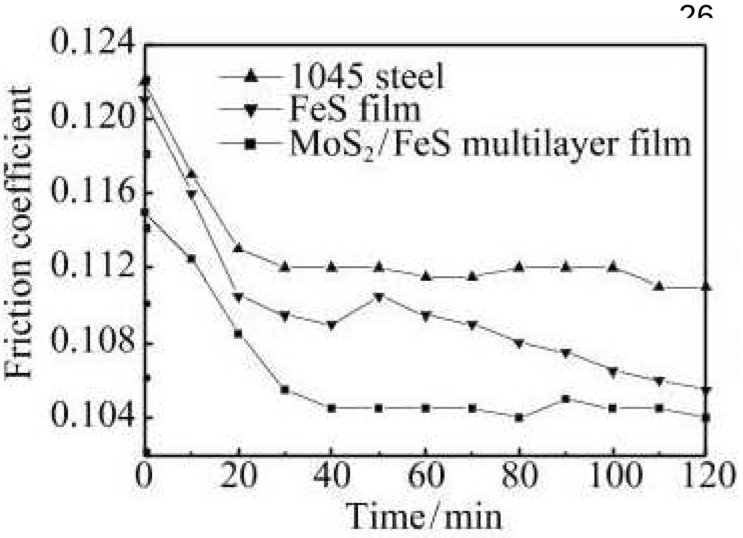


Figure 29. Friction behaviour of MoS_2/FeS multilayer, FeS film and steel under oil lubrication [19].

Ma et al [8] stated that the effectiveness of SO & TCP additives are determined by the presence of oxygen in the testing atmosphere. With the presence of an oxide layer on the QPQ sample surfaces it is assumed this would enhance the tribological performance of the samples.

When using the TCP additive significantly low wear was observed with the QPQ samples (Figure 22), believed to be due to the interaction of the additive with the oxide layer. Guan et al [20] believed that the mechanism of decomposition of TCP on an oxide layer involved a chemical mechanism of decomposition with an initial P=O bonding of intact TCP to the surface. This results in increased polarisation and activation of the P=O bond, followed by nucleophilic attack of residual H_2O or surface O^{2-} onto the P-atom. Ultimately this results in the formation of the metal phosphate or polyphosphate layer.

5. Conclusions

The effectiveness of extreme pressure and anti-wear additives on improving the friction and wear characteristics of an oxy-nitrided and MoS_2 coated sample was investigated. This study successfully highlighted that tribological performance can be influenced not only by the properties of modified surfaces but also the lubricant additives used. The study allowed the investigation of the interaction of sulphur and phosphorous containing additives with the modified surfaces individually. The following was concluded:

(a) The properties of the layers produced after surface treatment can impact tribological performance as seen with QPQ samples which showed lower wear penetration in comparison to the alternative sample. The interaction of the surface with various lubricant additives can further influence behaviour.
(b) XPS showed that when using the SO additive, FeS is formed, whereas with TCP $FePO_4$ is detected to be present within the tribofilm. The presence of both compounds could impact friction and wear behaviour.
(c) The SO & TCP additives respectively made minimal impact to modifying the friction behaviour of the QPQ samples. The relative thinness of the FeS containing tribofilm when using SO may have led to no impact on friction behaviour. The TCP also made no change to friction reaction as expected but it significantly improved the anti-wear and load carrying abilities of the surface.
(d) With TCP additive with the MoS_2 coated samples made no improvements to the friction response of the sample however similarly to the QPQ sample there was a drastic improvement to its anti-wear behaviour. When using the SO additive a significant reduction in friction with time is observed due to the synergistic effect of the FeS formed within the tribofilm and the MoS_2 coating.
(e) Even with the reduced reactiveness of the QPQ sample the interaction of certain additives can greatly impact the tribological performance of the surface.
(f) With MoS_2 coated samples with both additives the formation of a visible tribofilm is observed however with QPQ samples there is not. This is most likely due to the reduced reactiveness of the compound layer of the QPQ sample preventing the formation of a thicker tribofilm.

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6. References

[1] Manring, N.D., *Friction Forces Within the Cylinder Bores of Swash-Plate Type Axial-Piston Pumps and Motors.* Journal of Dynamic Systems, Measurement, and Control, 1999. **121**(3): p. 531-537.

[2] Nilsson, D. and B. Prakash, *Investigation into the seizure of hydraulic motors.* Tribology International, 2010. **43**(1–2): p. 92-99.

[3] Yazawa, S., et al., Reducing Friction and Wear of Tribological Systems through Hybrid Tribofilm Consisting of Coating and Lubricants. Lubricants, 2014. p.90-112.

[4] Wang, Y. and S.C. Tung, Scuffing and wear behavior of aluminum piston skirt coatings against aluminum cylinder bore. Wear, 1999. **225–229, Part 2**(0), p. 1100-1108.

[5] Neville, A., et al., Compatibility between tribological surfaces and lubricant additives—How friction and wear reduction can be controlled by surface/lube synergies. Tribology International, 2007. **40**(10–12), p. 1680-1695.

[6] Yue, W., et al., Synergistic Effects between Plasma-Nitrided AISI 52100 Steel and Zinc Dialkyldithiophosphate Additive under Boundary Lubrication. Tribology Transactions, 2012. **55**(3), p. 278-287.

[7] Ratoi, M., et al., The Impact of Organic Friction Modifiers on Engine Oil Tribofilms. RSC Advances, 2014. **9**, p.4278-4285.

[8] Ma, Y., et al., The synergistic effects of EP and AW additives with oxynitrided surface of steel. Tribology International, 1995. **28** (5), p.329-334.

[9] Khorramian, B.A., et al., Review of anti-wear additives for crankcase oils. Wear, 1993. **169** (1), p.87-95.

[10] Tomaru, M., et al., Effect of some chemical factors on film failure under EP conditions. Wear, 1977. **41**, p.117-140.

[11] Yamaguchi, A. “Tribology of Hydraulic Pumps,” in Tribology of Hydraulic Pump Testing, Totten, G.E., Kling, G.H. and Smolenski, D.J., eds. American Society for Testing and Materials, 1996. p. 49-61.

[12] Boβlet, J. *Tufftride/ QPQ Process.* http://www.durferrit.de/media/pdf/Tenifer_QPQ_eng.pdf. [cited 2016 June]

[13] Xia, Y., et al., *Remarkable friction stabilization of AISI 52100 steel by plasma nitriding under lubrication of alkyl naphthalene.* Wear, 2010. **268**(7–8): p. 917-923.

[14] Klueber Lubrication Munchen, *Bonded coatings for all metal surfaces.* p.1-16.

[15] Qiang, Y.H, et al, *Microstructure and tribological properties of complex nitrocarburized steel.* Journal of Materials Processing Technology, 2000. **101**, p.180-185.

[16] Leite, M.V., Wear mechanisms and microstructre of pulsed plasma nitrided AISI H13 tool steel. Wear, 2010. **269**, p.466-472.

[17] Basso, R.L.O., Effect of Carbon on the Compound Layer Properties of AISI H13 Tool Steel in Pulsed Plasma Nitrocarburizing. Plasma Processes and Polymers, 2007. **4**, p.728-731.

[18] Kawamura, M., et al., Organic sulphur and phosphorous compounds as extreme pressure additives. Wear, 1981. **72**, p.45-53.

[19] Wang, H., et al., Micro and nano sulfide solid lubrication. [Online]. Berlin: Springer, 2011. [Accessed 25 January 2016]. Available from: https://www.vlebooks.com/vleweb/Product/Index/678751?page=0

[20] Guan, B., B.A. Pochopien, and D.S. Wright, The chemistry, mechanism and function of tricresyl phosphate (TCP) as an anti-wear lubricant additive. Lubrication Science, 2016. **28**(5): p. 257-265.