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Investigation of the tribological and tribochemical interactions of different ferrous layers applied to nitride surfaces.

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Nitriding is a widely used industrial process aiming to improve the tribological properties and performance of components. Previous studies have shown the effectiveness of the treatment with friction and wear performance but very few have focussed on the influence of different ferrous layers formed by variant nitriding treatments on tribological and tribochemical behaviour. The influence of an oxide (Fe_3O_4) and sulphide (FeS) layer on friction and wear performance alongside tribochemical formation were investigated when using a fully formulated hydraulic lubricant. The tribological behaviour of the variant nitride samples were analysed using a tribometer and surface profiler. Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX), Electron probe micro analysis (EPMA) and X-ray Photoelectron Spectroscopy (XPS) were employed to identify the morphologies and chemical compositions of the treated surface before and after testing. No real effect on friction or wear was observed with the presence of an oxide (Fe_3O_4) layer, even though the formation of FeS_2 was observed within the tribofilm. However the formation of a sulphide (FeS) layer after sulphur nitriding produced the lowest friction and wear in –comparison to the alternative nitride variants. This was due to the lubrication properties of the FeS layer. The study effectively demonstrated that the type of ferrous layer could impact tribological & tribochemical properties of nitride samples.

Keywords: Oxy-Nitriding, Sulphur nitriding, Nitriding, Tribo-chemistry, Zinc Dialkydithiophosphate

1. Introduction

Hydraulic systems are hindered by inefficiencies of up to 15% from components such as hydraulic motors and pumps [1]. Seizure and excessive wear of the interacting components with the motor/pump can be caused by high friction [2]. Surface engineering techniques have been quickly developed for improving the tribological behaviours and lengthening the service life of machine parts. Among them, salt bath nitriding and sulphur-nitriding are effective and widely used surface treatment techniques in industry [3].

Nitriding or nitrocarburizing are thermochemical surface treatments used to improve surface and tribological properties such as wear and corrosion resistance alongside increasing the hardness of the material [4]. Ferritic nitriding is carried out between 400-580°C, forming two distinctive layers – an outside compound layer and an inner diffusion layer. The compound layer is usually composed of γ'-Fe4N and ε -Fe2-3N, where γ'-Fe4N have a lower hardness but have a good toughness [5]. γ -phases are seen to dominate the compound zone after nitriding, whereas ε-phases are almost solely seen after nitrocarburising due to the greater influence of the presence of carbon [6-9].

With the sulphur nitriding process, the sulphides in the bath can react with components being treated to form iron sulphide on the outer surface layer [10, 11]. The presence of sulphur within the treatment bath stabilises the formation of primarily ε-phase within the compound layer and a very shallow finely porous zone [12]. An iron sulphide layer is a good solid lubrication film that shows significant friction-reducing and anti-scuffing properties, but the thin solid lubrication film can be quickly worn away if the substrate is not hard enough to support it [3].

The selection of lubricating oil and additives is potentially another important problem for improving the tribological properties of key machine parts [3]. There has been little research carried out on the tribochemical interactions between the layers deposited upon nitrided steel surfaces and the additives within the lubricating hydraulic oil.

The lubrication behaviour of an additive is influenced by the properties of the interacting surfaces, the environmental atmosphere and the properties of the additive itself. Zinc dialkydithiophosphate (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 due to interacting contacts helps determine the effectiveness of the wear reduction though preventing adhesion between surfaces. The interaction of ZDDP with solid surfaces can lead 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. On steel samples, the tribofilms can grow to a thickness >100 nm and have an uneven pad-like structure [4, 13, 14].

The aim of the current study is to investigate and understand the tribological impact of different ferrous layers formed on a relatively inert nitride surface, and how they influence formation and effectiveness of lubricant additive tribofilms.

2. Experimental Methodologies

2.1. Materials and lubricants

The material used for this investigation is alloyed nitriding steel, generally used for components subjected to high friction and wear. The pin shaped samples had a 10 mm sliding radius for the pins.

The three pin samples used in this study were treated by variants of the salt bath nitriding heat treatment. The Isonite samples are produced using a cyanide/cyanate bath at 400-600°C to form a nitride layer (15µm), due to the formation of carbonate during the process both nitrogen and carbon diffuse in to the surface hence this process is recognised as nitrocarburising. The QPQ treatment involved using a specialised nitrate – nitrite cooling salt bath to form an oxide layer (0.5 µm) on the Isonite samples. Figure 1 highlights the different stages of the Isonite and QPQ process.

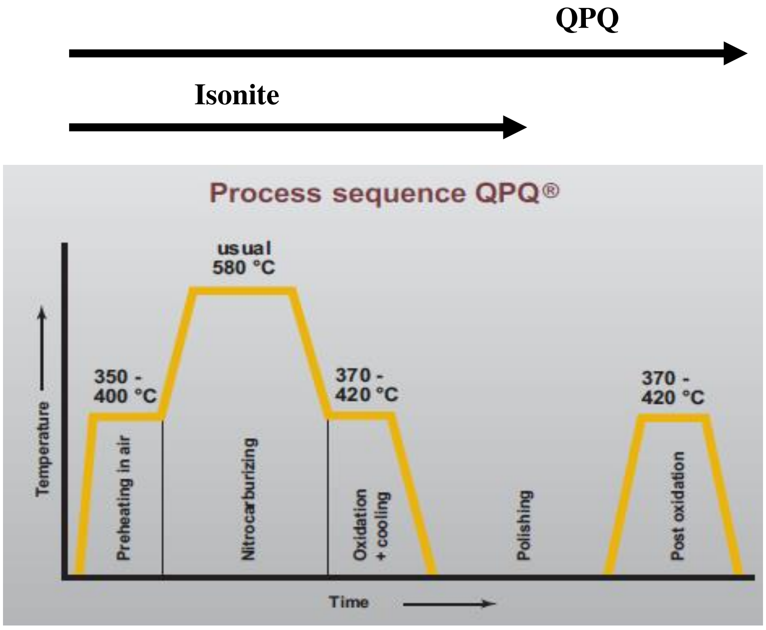


Figure 1. Salt bath nitriding heat treatment process stages for Isonite and QPQ variants [7].

The Sursulf (SN) process is a low polluting, cyanide free nitriding salt bath treatment which uses sulphur as accelerant. The bath is composed of a mixture of cyanates and carbonates of lithium, sodium and potassium along with small amounts of potassium sulphide (K_2S). The cyanate is used as the source for nitrogen and sulphide (K_2S) is the source for sulphur. At the surface the cyanate catalytically decomposes at the surface of the steel components being treated, to liberate carbon monoxide and nascent nitrogen diffuses in to the material of the sample being treated to form a compound layer. The sulphides in the bath also react with components being treated to form iron sulphide on the outer surface layer and filling the porosity present on this surface of the treated component.

Another variant of the nitriding process was applied to the counter face plate samples. The 7mm x 7mm x 3mm plates were made from spheroidal graphite cast iron which were then gas nitrided. The treatment applied to the plates was not varied and the wear after testing was minimal so it is not reported in this paper. The coupling of steel pins to cast iron plates represents friction pair components within a hydraulic motor. In this study three nitride variant samples are used (Table 1), with two of the samples having a ferrous layer variant present on the nitrided surface.

Table 1. Summary of the layers present with the different nitride variant treatments.

Sample	Composition
Isonite Pin	Nitride layer
QPQ Pin	Oxide layer + nitride layer
SN Pin	Sulphide layer + nitride layer
Gas Nitrided Plate	Nitride layer

The microstructure of the treated pin samples through their cross-sections have been examined using Scanning Electron Microscopy (SEM). Microhardness measurements were carried out with Micro Vickers hardness tester using a load of 9.81 N (1 kg) on the treated pin samples (Figure 2). The hardness of the original material prior to treatment was ~300 HV_1. The Isonite and QPQ samples hardness's are almost identical through their cross-sections, however with the SN sample a different trend is observed. The hardness through the cross-section for 0.15mm from the top surface matched the alternative samples, however after this depth a sharp drop is observed until the substrate material is reached. This indicates a lower case depth with the SN samples.

This study used a fully-formulated hydraulic oil, with a full additive package which includes detergent, dispersant and the anti-wear additive ZDDP.

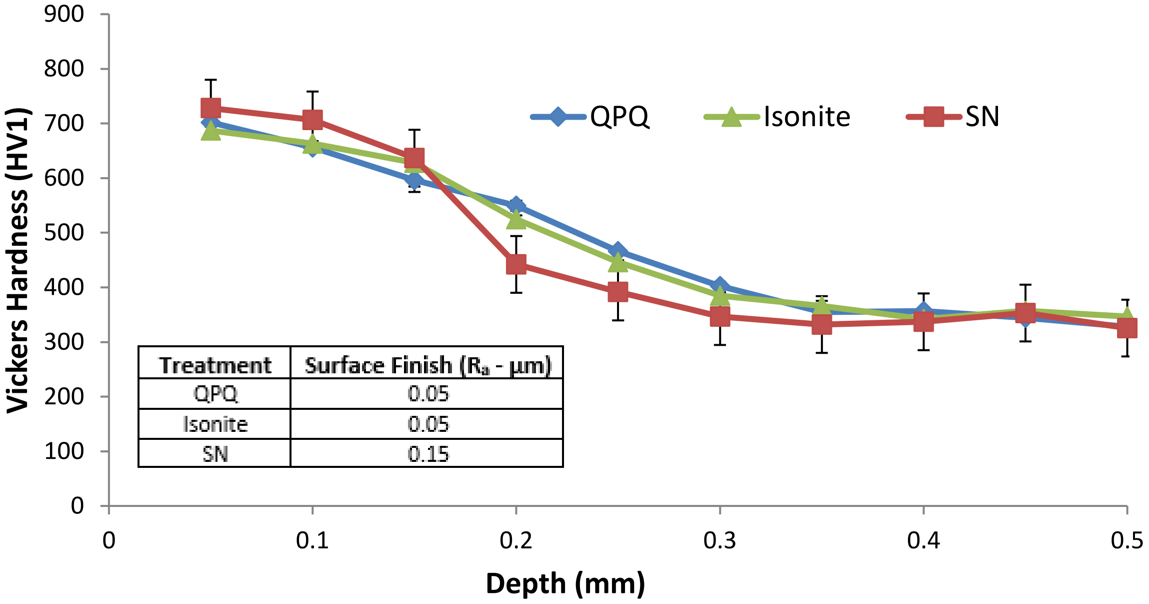


Figure 2. Comparison of the hardness through the Iso, QPQ and SN pin sample cross-sections and the surface finishes.

2.2 Tribometer Tests

Using a Cameron Plint TE77 reciprocating tribometer with a pin-on-plate configuration to represent the sliding conditions of interacting components, the friction and wear behaviour of the treated samples could be investigated. In operation, the pins were the nitriding steel samples and the plates were composed from graphite cast iron, the treatments applied to both sets of samples are described above. The testing conditions are given in Table 2 and were derived from those used to mimic the operational conditions of a hydraulic motor.

Table 2. TE77 test conditions

Set up	Conditions
Stroke Length	7 mm
Sliding Speed	0.17 m/s (12Hz) & 0.35 m/s (25Hz)
Hertzian Contact Pressure	0.92 & 1.19 GPa
Dynamic Viscosity (100°C)	~0.030 Pa.s
Lubricant Temp.	80°C
Testing Time	2 h

The TE77 using a force transducer and program produces a data file of the friction force every 300 seconds for a duration of 2 hours. Each data file is composed of 1000 measurements which were taken every 0.3 seconds. The friction coefficient results were calculated when the system has reached steady state and were based on the last 30 minutes steady friction data. The lubricant was heated to 80°C using heating elements attached to the bath in which the samples were clamped down and flooded in lubricant.

The tests are carried out under the boundary lubrication regime which was defined by calculating the lambda ratio:

$$\lambda = \frac{h_{min}}{\sqrt{R_{q1}^2 + R_{q2}^2}} \qquad (1)$$

Where h_{min} is the minimum film thickness determined using the Dowson/Hamrock equation and R_{q1} & R_{q2} are the roughness of the interacting surfaces. For the lubrication regime to be within the boundary lubrication condition.

After testing the samples were washed in heptane to remove excess oil and contaminants. All tests were repeated to achieve a good repeatability for the friction and wear behaviour.

2.3 Morphology and Topography Analysis

Wear measurements of the diameter and depths were carried out using a Leica optical microscope and a Taylor Hobson Talysurf profilometer.

2.4 Tribofilm Chemical Properties

Energy dispersive X-ray analysis (EDX) was the technique used to identify the elemental and chemical composition of the different treated samples or an area of interest. The EDX system is integrated within a secondary electron microscope (SEM), and when the specimen surface is being bombarded with electrons, the energy of the X-ray signal released is measured which is then used to identify the atom which released it. This analysis technique was used to analyse the surface chemistry after testing allowing the characterisation of any tribofilms formed.

Electron probe micro analysis (EPMA) was combined with EDX to establish the composition of small areas on the specimens. A beam of accelerated electrons is focussed on the surface of a specimen using a series of electromagnetic lenses, and these energetic electrons produce characteristic x-rays within a small volume (1-9 µm^3) of the specimen. The x-rays are analysed by energy dispersive detectors, where the resulting energy spectra allows the identification of the qualitative elemental composition of the sample. The characteristic x-rays are detected at particular wavelengths, with quantitative analysis being carried out using their intensity. Locally resolved analysis becomes possible due to the ability of the diameter of the exciting electron beam spot to be focussed below 1 µm [15]. The advantages of this technique are its high spatial resolution and sensitivity, where in some cases individual analysis can be extremely short.

Post experimental surface analysis also 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. A monochromatized Al Kα X-ray source was used to carryout high resolution scans for specific peaks. The beam was focused in the centre of the wear scar in an area of 200 µm × 200 µm. The tribofilm was also etched 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 areas and full-width at half-maximum (FWHM) were constrained.

3. Results & Discussion

3.1 Surface characterisation

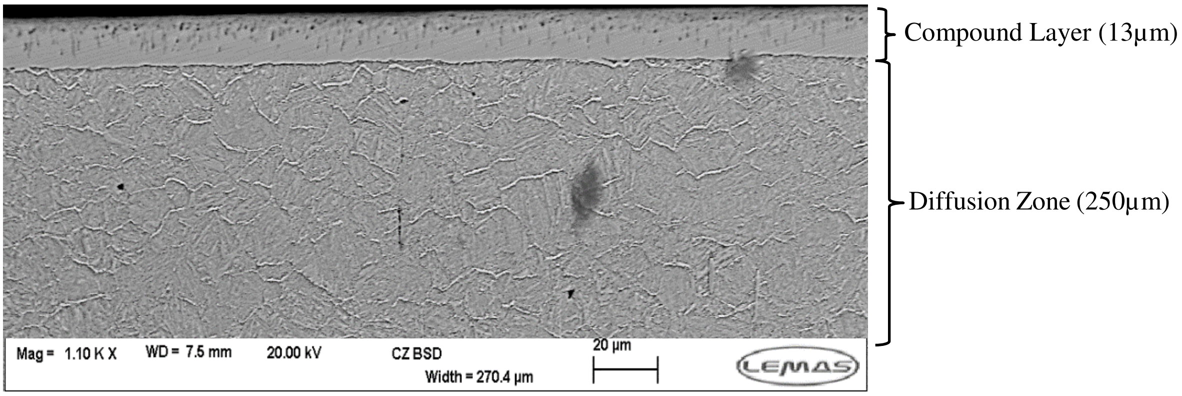


Figure 3. SEM image profile through the cross-section of an Iso pin sample.

Figure 3 is an SEM image of a cross-section of the Isonite treated pin sample. Two distinctive layers are detected. A 13 µm thick compound layer of a porous constitution, followed by a diffusion zone of approximately 250 µm thickness.

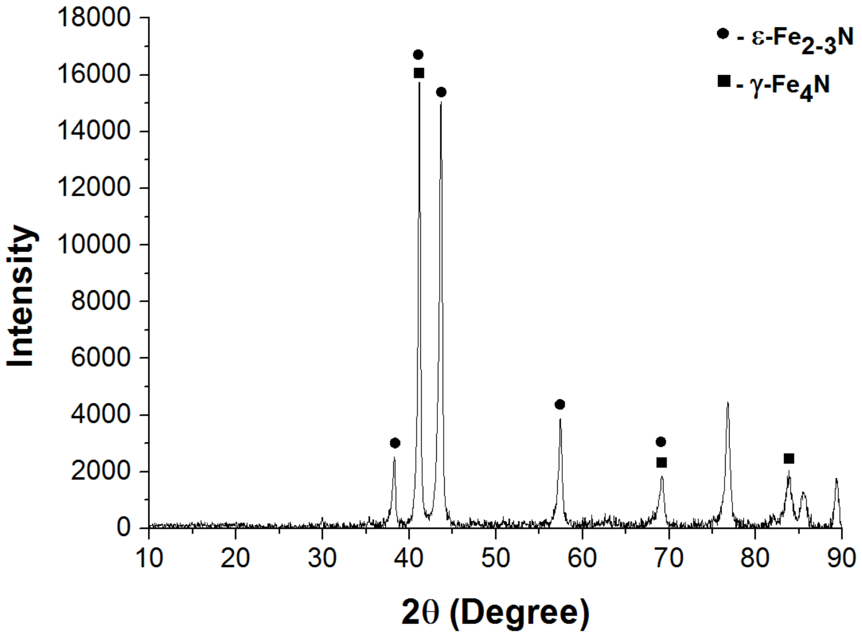


Figure 4. X-ray diffraction pattern of an Iso pin sample.

Figure 4 shows the X-ray diffraction (XRD) scan across the cross-section of the Isonite samples, with the most dominate phases in the compound layer being identified as ε-$Fe_{2-3}N$ and γ'-Fe_4N. The microstructure of the sample matched that expected with samples treated by liquid nitriding as described in the literature [4].

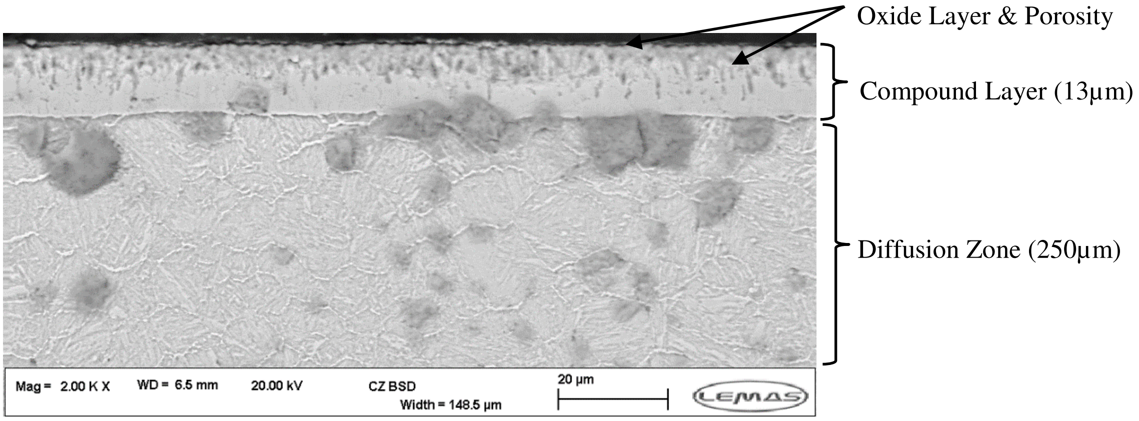


Figure 5. SEM image profile through the cross-section of a QPQ pin sample.

The SEM image of a cross-section of the QPQ treated pin sample (Figure 5) was similar to the Isonite samples; three distinctive layers are detected. A compound (13 µm) and diffusion (250 µm) zone are present as with the Isonite sample however on the very top surface a thin black oxide layer of ~0.5 µm thickness has been formed.

XRD scans (Figure 6) across the QPQ pin sample showed that the oxide layer was primarily composed of Fe_3O_4, whereas the compound layer was predominantly composed of ε-$Fe_{2-3}N$ with traces of γ'-Fe_4N.

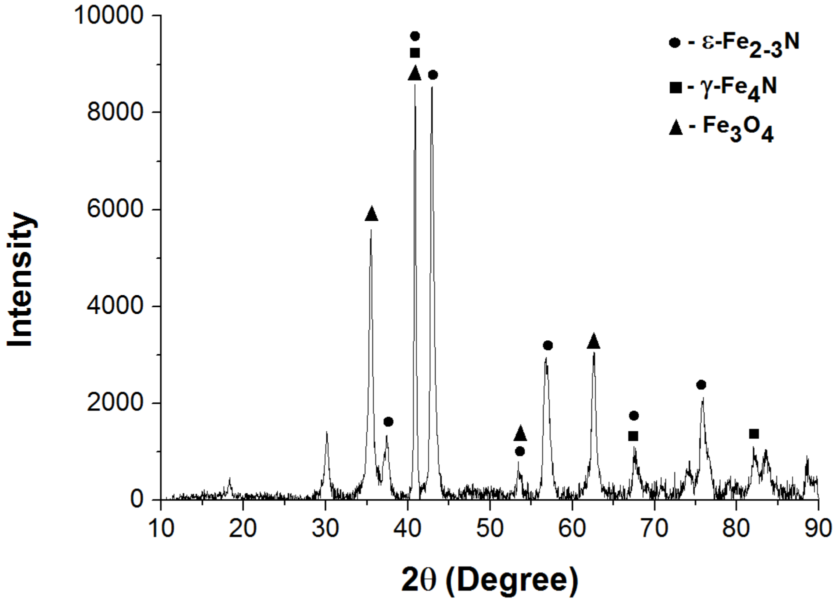


Figure 6. X-ray diffraction pattern of a QPQ pin sample.

The cross-section of the SN sample (Figure 7) showed the presence of a FeS layer (~0.5 µm) and a smaller compound layer (8 µm) in comparison to the previous samples. XRD (Figure 8) showed the presence of FeS, ε-$Fe_{2\text{-}3}N$ and γ'-Fe_4N. The sulphur activated nitrocarburising process stabilises the formation of the ε-phase within the compound layer [16].

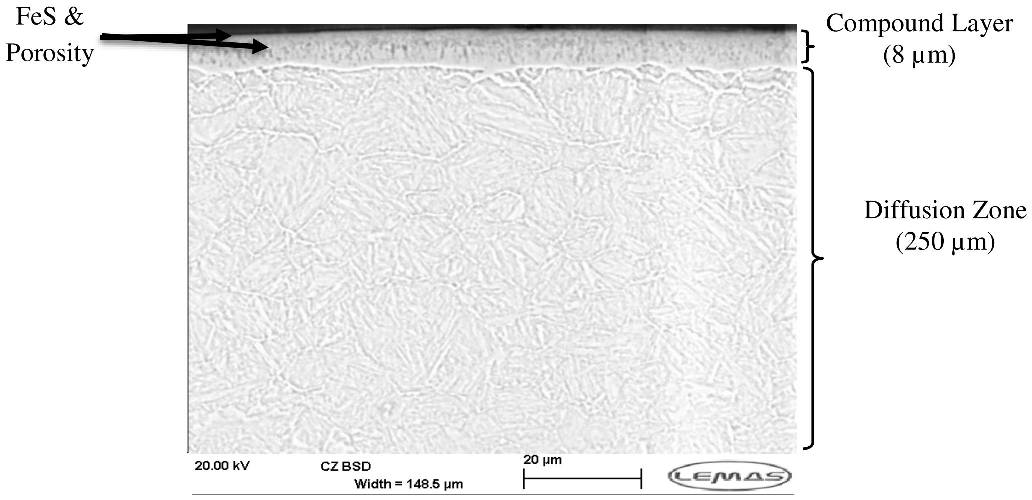


Figure 7. SEM image profile through the cross-section of a SN pin sample.

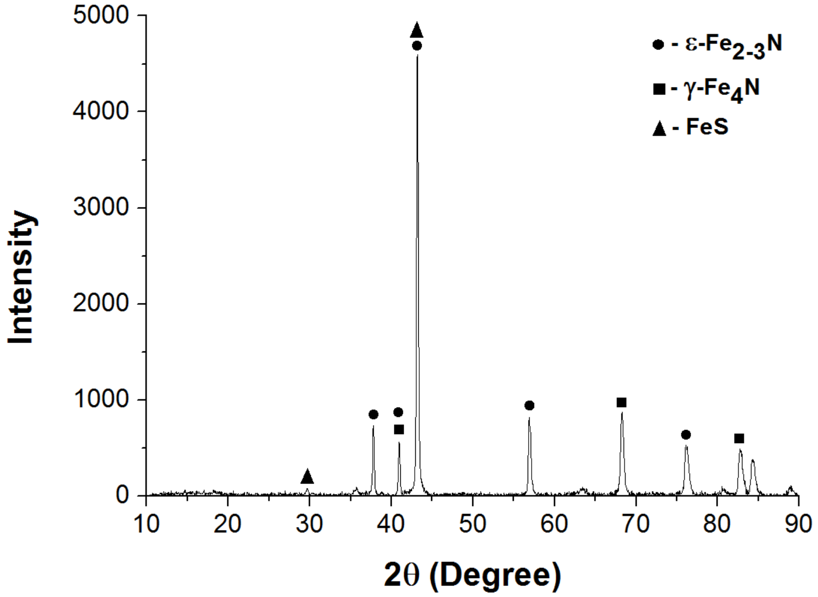


Figure 8. X-ray diffraction pattern of a SN pin sample.

3.2 Friction evaluation

Figure 9 highlights the typical change in friction performance over time observed with the three nitride sample variants during the complete duration of the test. Similar friction trends are observed with all samples types with an initial running-in period until friction reaches a steady state value. Almost identical trends were observed with the QPQ and Isonite samples. The SN samples showed a consistent lower friction behaviour after running-in in-comparison to the alternatively nitride samples.

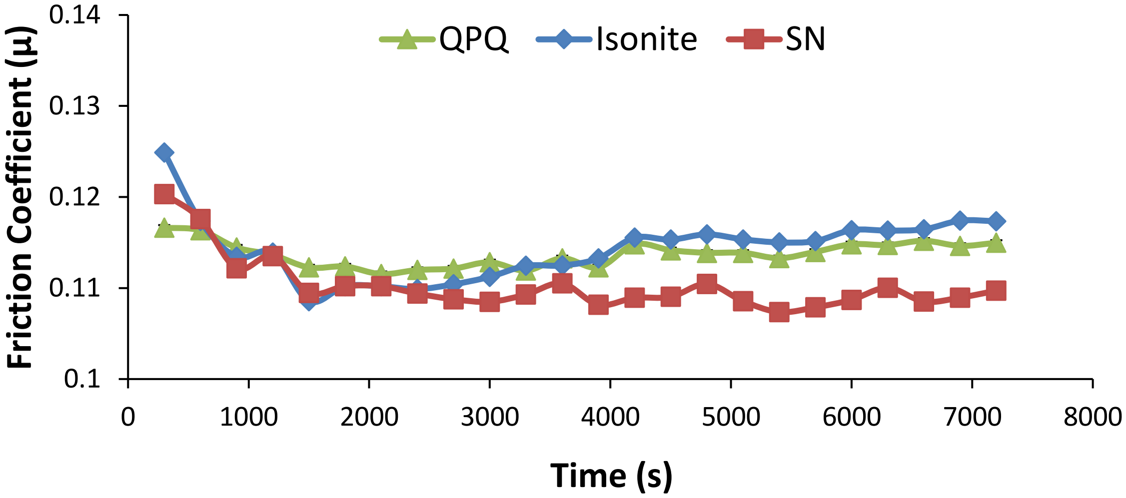


Figure 9. Friction coefficient vs time results over 2 hrs of the three sample variants at a 1.19GPa contact pressure and 25 Hz sliding frequency using fully formulated lubricant at 80°C.

The average friction coefficients for the three sample variants in the stable stage (last 30 min of the test) under various contact pressures and sliding speeds are shown and compared in Figure 10. The general behaviour observed was that the friction response of the QPQ and Isonite samples at the different testing conditions were almost identical and statistically overlap. The friction coefficients of the SN samples were on an average generally lower than that of the alternative samples. The trends observed were similar to that observed in previous studies, with the lower friction behaviour of the SN samples being attributed to the presence of an FeS layer [3].

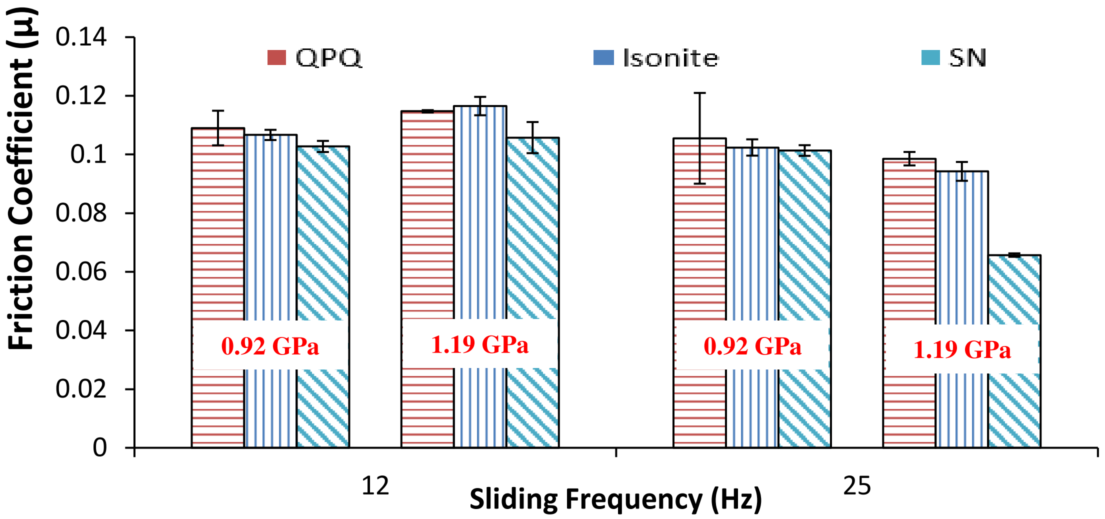
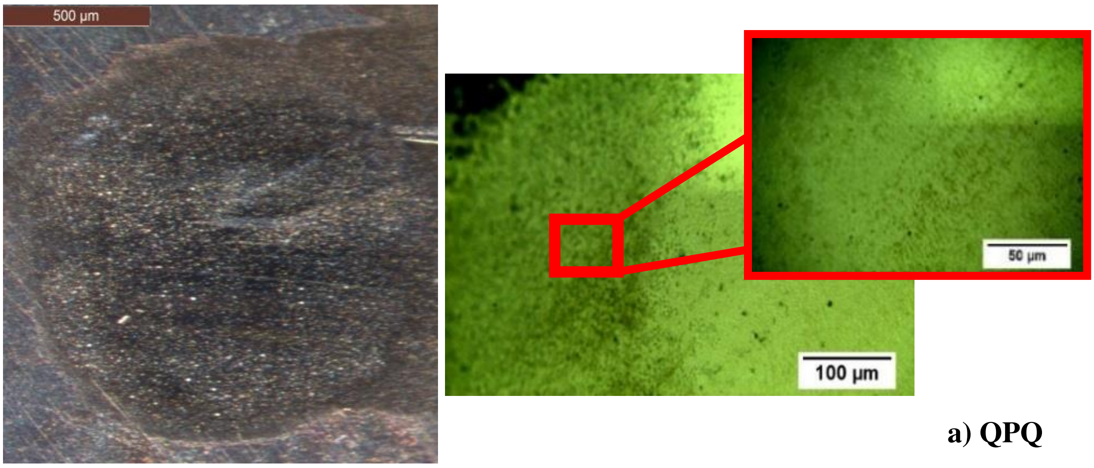


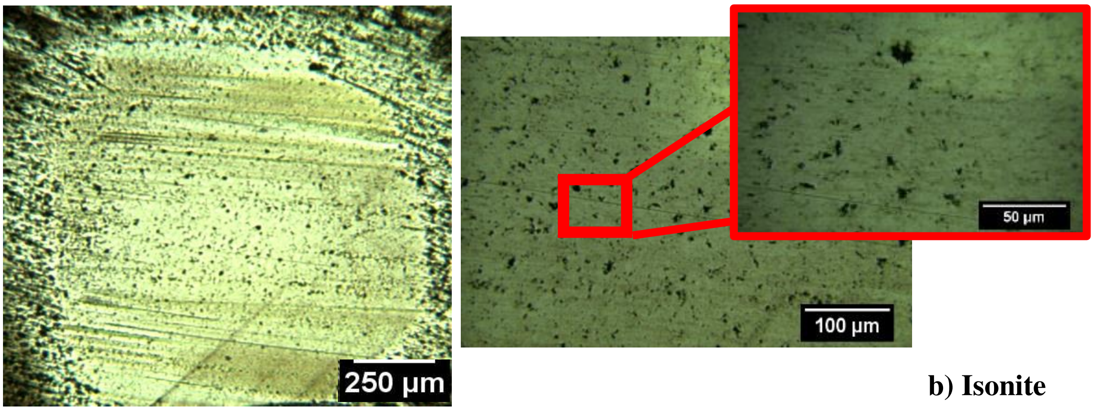
Figure 10. Average friction coefficient results of the last 30 minutes of the experiments with the three sample variants when using two contact pressures (0.92GPa & 1.19GPa) at two sliding frequencies (12Hz & 25Hz) with a fully formulated lubricant at 80°C.

3.3 Wear results

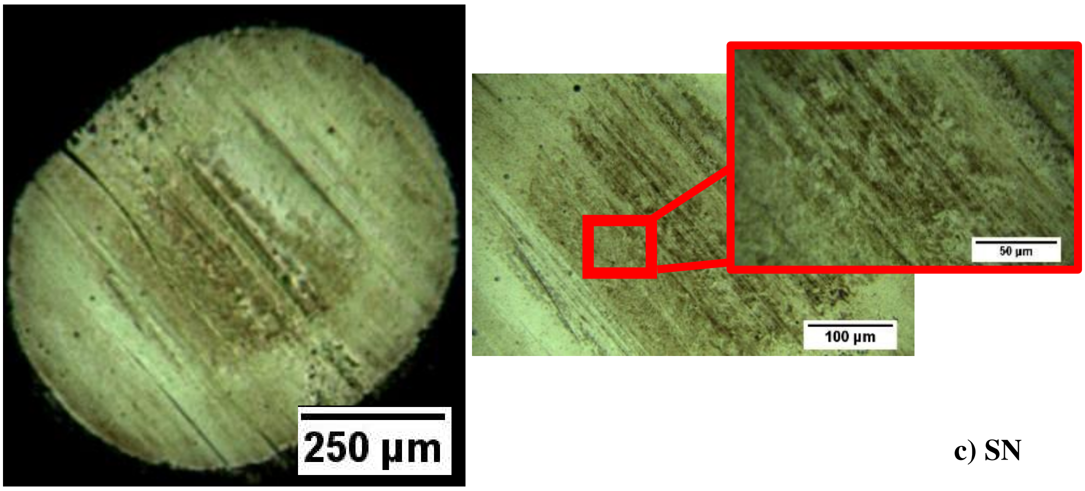
Using an optical microscope the worn surfaces of the different samples (Figure 11) were analysed. With the QPQ and Isonite pins (Figure 11(a) & Figure 11(b)) a smooth surface is exposed. With the Sursulf (SN) samples (Figure 11(c)) the presence of a thick tribofilm can be observed.



a) QPQ



b) Isonite



c) SN

Figure 11. Optical images of the wear scar regions of the different treated pin samples when a 1.19 GPa contact pressure was applied at 12 Hz.

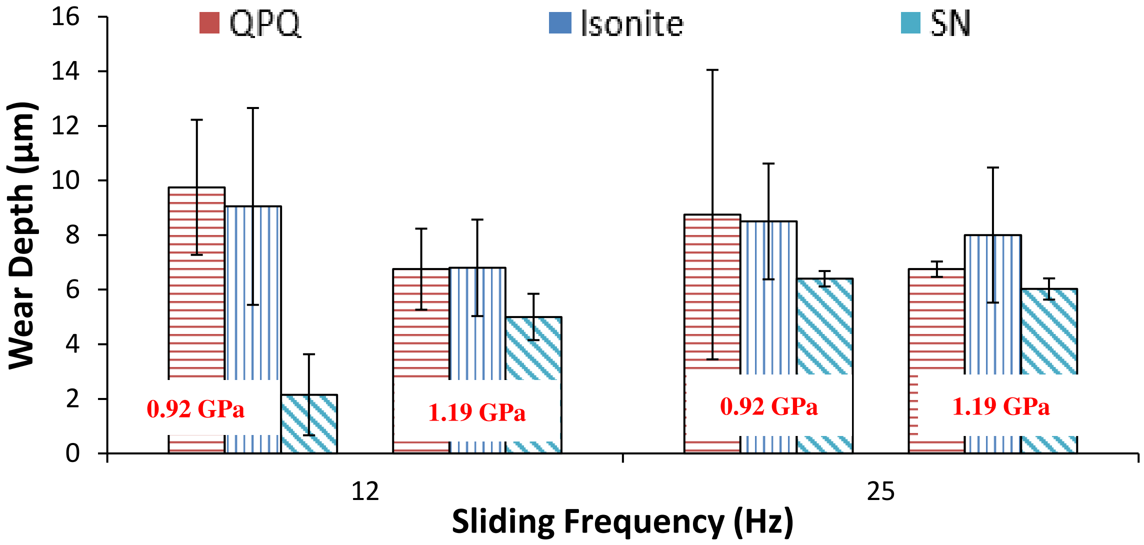


Figure 12. Wear depths of the three types of pins when contact pressures 0.92 & 1.19 GPa are applied at a 12Hz & 25Hz sliding frequencies using fully formulated lubricant at 80°C.

The depth profile measurements using Talysurf (Figure 12) showed that wear did not penetrate past the compound layer (QPQ & Iso = 13 µm and SN = 9 µm) for all the samples. The average wear depths for the QPQ and Isonite samples are almost identical and had statistical overlap. The SN samples on average showed lower wear depths compared to the alternative samples.

With the friction and wear response of the QPQ and Isonite samples being almost identical this suggested that the impact of the Fe_3O_4 layer present with the QPQ samples has minimal impact on friction and wear behaviour. HEF Durferrit state that the presence of the black oxide layer is primarily for cosmetic and corrosion protection purposes [7].

3.4 SEM-EDX Analysis

SEM-EDX was used to analyse the areas inside and outside the worn areas of the different nitride variant pin samples after the tribometer tests using the fully formulated lubricant. The analysis gives an indication whether a tribofilm has been formed on the worn surface and of its chemical composition. It essentially gives a suggestion of the interaction of the surface with the additives within the lubricant.

With the QPQ samples SEM-EDX (Figure 13) a high presence of oxygen is present on the unworn areas of the pin sample, which relates to the presence of a Fe_3O_4 oxide layer. However, within the wear scar a significantly lower oxygen presence is detected most likely due the removal of the oxide layer during testing. Within the wear scar a high concentration of iron and nitrogen is detected relating to the nitride layer exposed under the oxide layer. In comparison a lower presence of sulphur and phosphorous are detected within the wear region, however zinc is not identified. The EDX spectra of the worn area showed the presence of all elements. This indicated the possibility of the formation of a protective tribofilm.

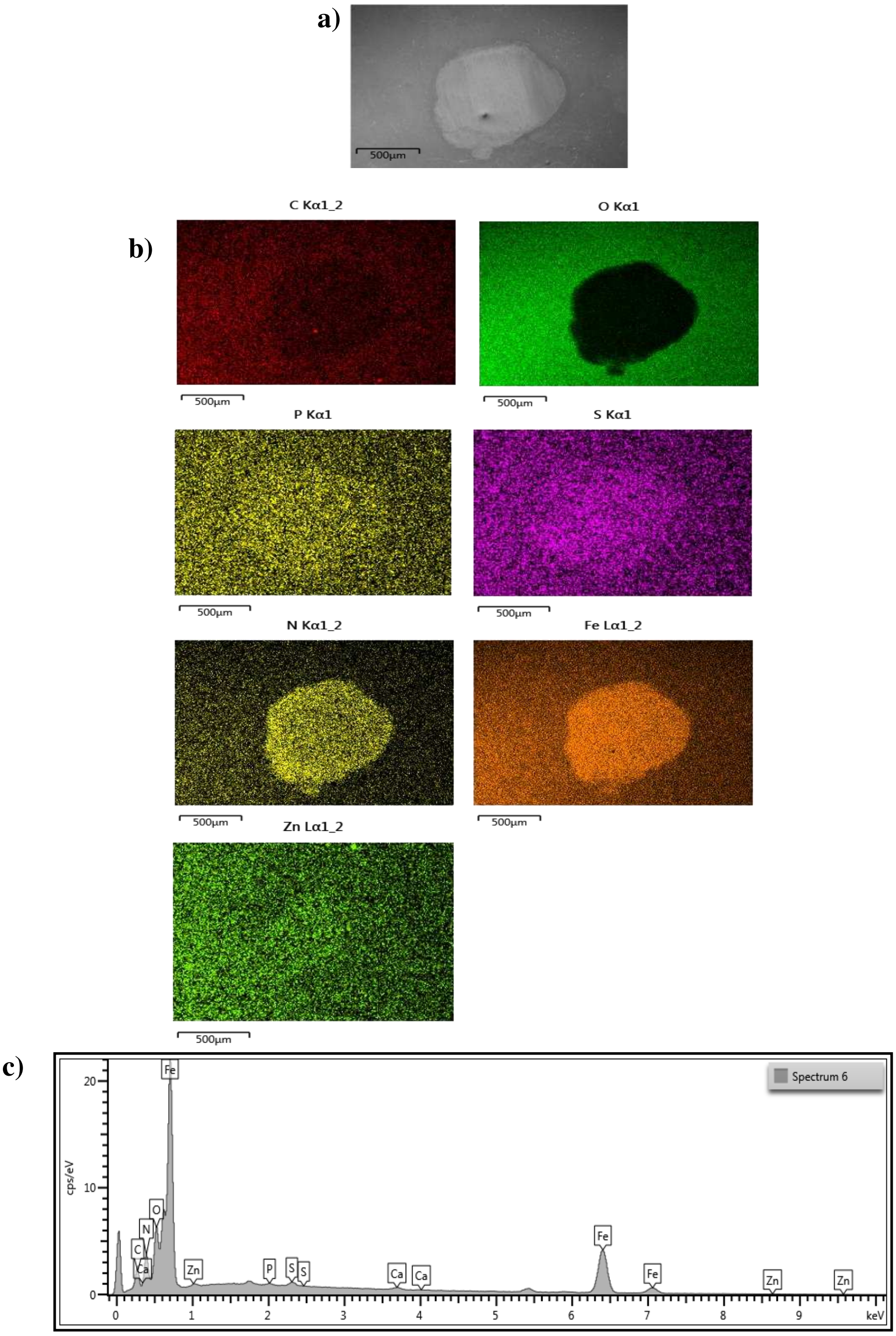


Figure 13. a) SEM image, b) EDX maps and c) spectra of the unworn and worn surface of the QPQ pin samples at 1.19GPa contact pressure and 12Hz sliding speed.

In comparison to the QPQ sample, with the Isonite samples SEM-EDX (Figure 14) showed no real difference of oxygen between inside and outside of the wear scar due to the absence of an oxide layer with this sample. With the absence of an oxide layer there is a high presence of iron and nitrogen mostly likely due to the presence of the compound layer. No real presence of phosphorous, sulphur and zinc from the lubricant additives is detected within the worn area in comparison to the QPQ sample. However the EDX spectrum showed the presence of P, S and Zn within the tribofilm.

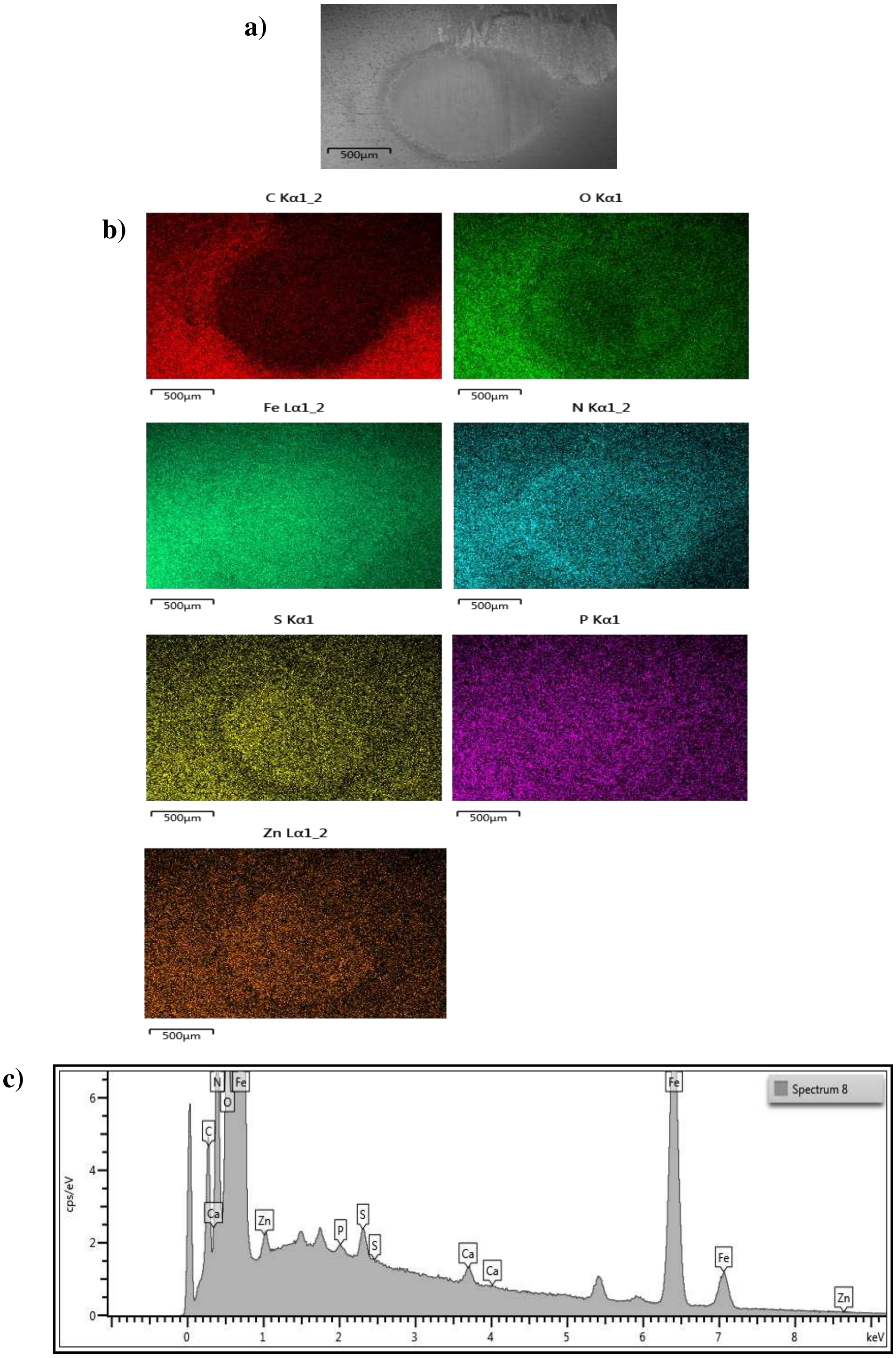


Figure 14. a) SEM image, b) EDX maps and c) spectra of the unworn and worn surfaces of the Isonite pin samples at 1.19GPa contact pressure and 12Hz sliding speed.

With the sulphur nitrided sample EDX (Figure 15) showed a strong presence of iron and sulphur outside the worn area of the pin relating to the presence of a FeS layer after treatment. Within the worn area a higher presence of iron and sulphur is detected possibly indicating the formation and presence of FeS within the contact areas, similar to that observed by Yue *et al* [3] and Liu *et al* [17]. Interestingly also present in the worn area is phosphorous and zinc indicating a protective phosphate tribofilm is also present within the wear area. The presence of nitrogen is detected on the edges of the wear scar however it is absent within it, possibly due to the high presence of iron, sulphur and phosphorous within the area. The EDX spectra shows the presence of all elements within the wear scar.

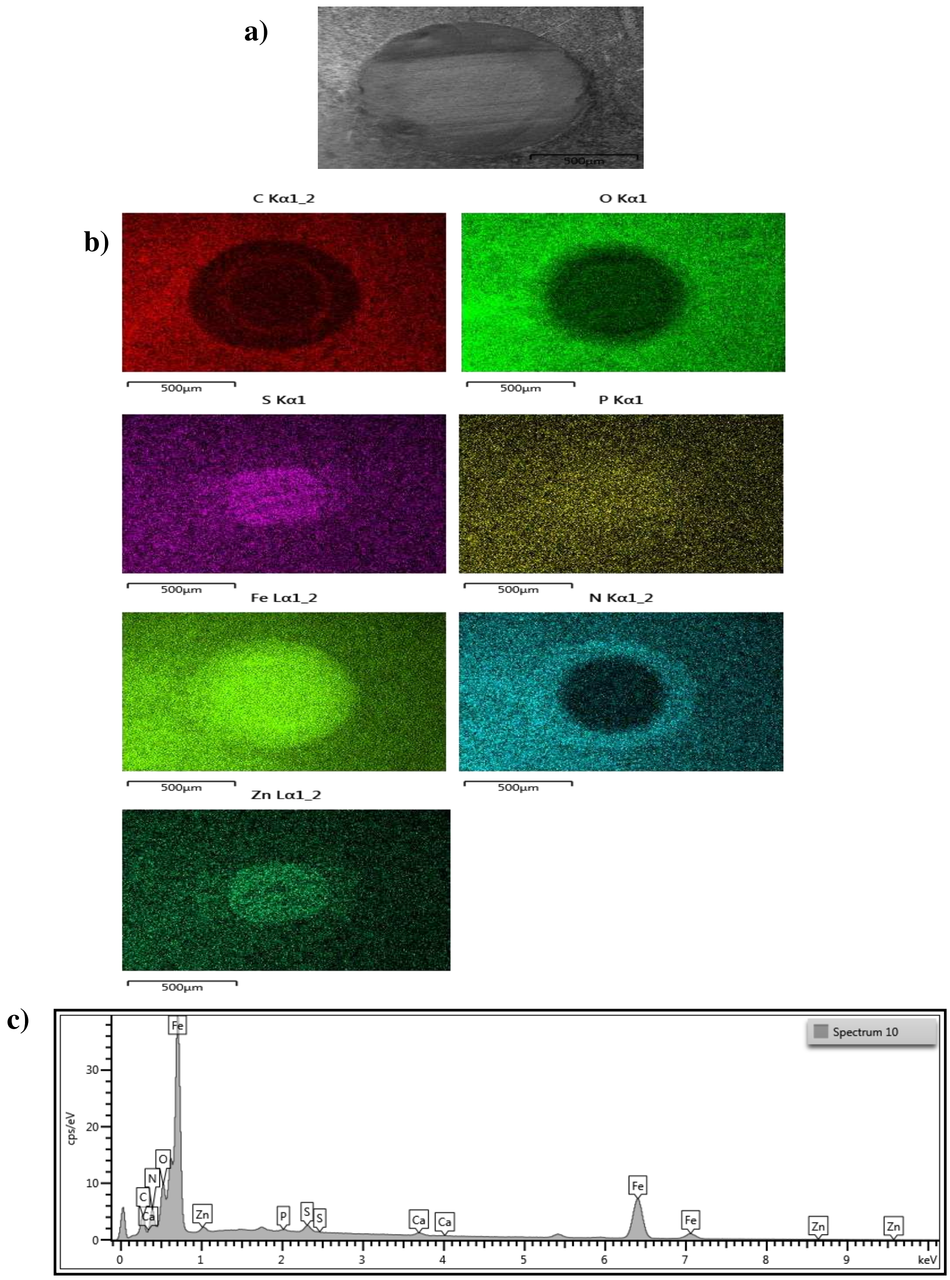


Figure 15. a) SEM image, b) EDX maps and c) spectra of the unworn and worn surface of the sulphur nitrided pin samples at 1.19 GPa contact pressure and 12Hz sliding speed.

3.5 EPMA Analysis

EPMA was utilised to verify and support the findings from SEM-EDX. Elemental maps (Figure 16) were taken at the centre of the wear scars of the three nitride sample variants, allowing comparison of the concentration of elements across the samples. When comparing the QPQ (Figure 16(a)) and Isonite (Figure 16(b)) samples a higher presence of P, S and Ca were detected across the worn surface of the QPQ samples. This supported the EDX results (section 3.4) and indicated the formation of a patchy but thicker tribofilm on the QPQ sample surface. However higher concentrations of Zn were identified with the Isonite samples indicating the possible presence of a tribofilm.

In comparison to the other samples, the SN pins (Figure 16(c)) showed a higher concentration of P, S, Ca and Zn across the surface. The EPMA maps indicated the presence of a thicker tribofilm with a greater surface coverage in comparison to the QPQ samples, similar to that observed with EDX (Figure 15(b)).

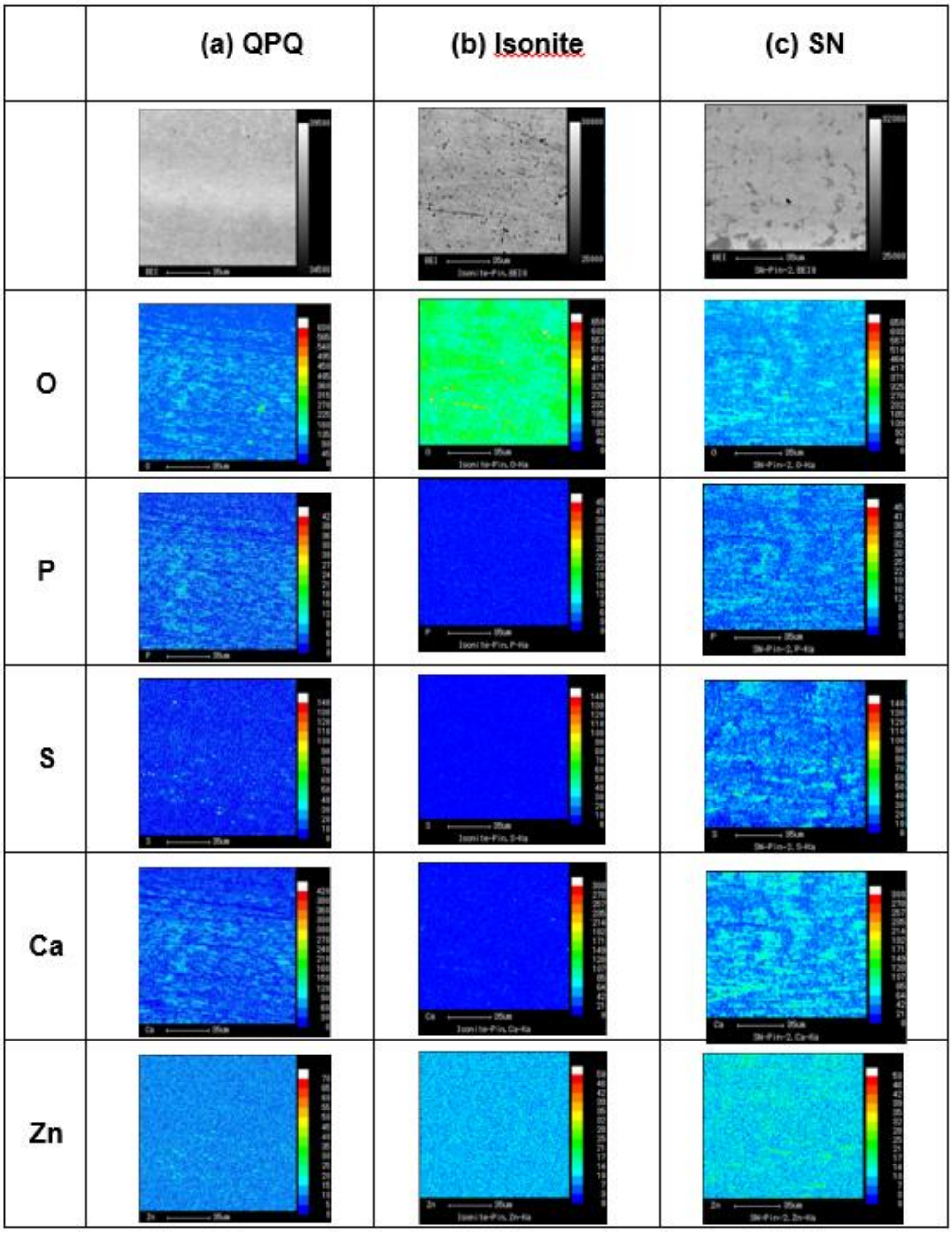


Figure 16. EPMA maps within the wear scars of the nitrided sample variants (a) QPQ (b) Isonite (c) SN.

3.6 XPS analysis of the worn surfaces

To identify the chemical compounds present within the tribofilm and support the findings from SEM-EDX, a more surface sensitive technique - XPS was used. Using XPS to etch through the depth of the tribofilm the results generally showed the formation of a relatively thin tribofilms with the sample variants. Table 3 and Figures 15-17 highlight the key species formed on the worn surface of the different samples when using a fully formulated lubricant. Table 3 shows the species present at an etching depth of 1.34 nm, alongside confirming the presence of a tribofilm with all the additives in this study.

Table 3. General binding energy values for compounds relevant to the tribofilms formed on the worn surfaces of all treated samples [18, 19].

	Element	**B.E / eV** (±1eV)			**Chemical State**		
		QPQ	**Isonite**	**SN**	**QPQ**	**Isonite**	**SN**
Etch Depth 1.33 nm	Fe 2p	710.4	710.1	712.0	Fe_2O_3	Fe_2O_3	FeS
		706.8	-	710.1	FeS_2	-	Fe_2O_3
	N 1s	397.8	397.5	397.1	Nitride	Nitride	Nitride
	P 2p	133.9	133.1	133.2	Phosphate	Phosphate	Phosphate
	Zn 3s	139.9	139.9	139.9	ZnS	ZnS	ZnS
	S 2p	161.7	162.0	161.7	Sulphide	Sulphide	Sulphide

The analysis using XPS (Figures 15-17) allowed the characterisation of the tribofilms formed, to investigate the impact the different layers applied to the top of the nitride surfaces had on chemical state of the tribofilm compared to that formed on the QPQ sample. With wear penetrating the nitride layer for all samples, nitrides (~397.1 eV – N 1s) were detected within each samples tribofilm (Table 3).

With the QPQ samples the key species identified within the tribofilm was the presence of phosphates (~133.9 eV – P 2p) and ZnS/ZnO (~139.9 eV – P 2p) as supported by the SEM-EDX analysis (Figure

13), further indicating the presence of a tribofilm. FeS_2 (706.8 eV – Fe 2p) is detected within the tribofilm (Figure 17(a)) which in high concentrations could impact the friction behaviour of the sample.

With the Isonite samples it was possible to see that with the absence of an oxide layer the species formed within the tribofilm may have been impacted. XPS also detected the formation of a phosphate (~133.1 eV – P 2p) containing tribofilm, which was seen when using SEM-EDX (Figure 14). However in comparison to the QPQ samples iron sulphides were not seen present with XPS.

It was believed that the presence of the (Fe_3O_4) oxide layer led to the formation of FeS_2 which when present in high concentrations can impact friction behaviour. Ito *et al* [20] proposed that with the presence of an iron oxide (Fe_3O_4) layer, above 60°C ZDDP molecules present in the lubricant would decompose creating free zinc ions. These free ions would adsorb on to the iron oxide surface, forming a zinc-rich, sulphur-free adsorption layer ($ZnFe_2O_4$) that can grow without modifying the crystal structure of the surface. During testing, the sliding between two surfaces causes mechanical mixing to occur allowing Zn^{2+} and Fe^{2+} ions to exchange cations. Free iron ions are able to react with sulphur from the DDP^- forming iron sulphides and FeS_2 [20].

The XPS analysis supports the EPMA findings that there was no real presence of iron sulphides within the tribofilm of the Isonite samples, supporting the theory that the oxide layer presence was responsible for the compound's formation. With the FeS_2 absence within the tribofilm of the Isonite samples demonstrated that the compounds presence made minimal impact as the QPQ and Isonite samples friction behaviours were almost identical. This may be due to the thin tribofilm formed which would limit the concentration of key compounds present within it. The study indicates that the Fe_3O_4 layer acts as a source of nascent iron which impacted the formation of a tribofilm. The interaction of the nascent iron and phosphorous present within the lubricant additive would encourage the formation of a protective layer.

With the SN samples which has the presence of a FeS lubricating layer on the nitriding layer, FeS is detected with XPS (~712.1 eV – Fe 2p), Figure 19(a), and this is supported with EDX scans which detected the strong presence of iron and sulphur within the wear scar (Figure 15). The presence of phosphates (~133.2 eV – P 2p) are also detected within the tribofilm indicating the formation of a protective layer, supporting the SEM-EDX analysis (Figure 15) showing the presence of phosphorous in the wear scar.

Yue *et al* [21] using base oil and Wang *et al* [10] in dry conditions observed similar friction, wear and tribochemical trends in their respective studies in-comparison to this paper. The sulphur nitrided samples demonstrated lower friction and wear response (Figure 10 & Figure 12) than the QPQ and Isonite alternatives. This was due to the presence of a FeS layer on the top surface of the pins as identified before (Figure 8) and after (Figure 19) testing. FeS is softer than the metal surface, acting as a solid lubricant which allows easy slip due to its layered structure and would contain wear to its thickness, leading to lower friction and wear [22]. It is also believed that even when the FeS layer was worn away to a certain extent, it could be decomposed under high friction heat and contact stress to produce S ions. It is believed that these ions alongside the sulphur from the additives present from the lubricant would react with Fe atoms from the substrate to continuously form a protective FeS layer over a certain period [3, 21].

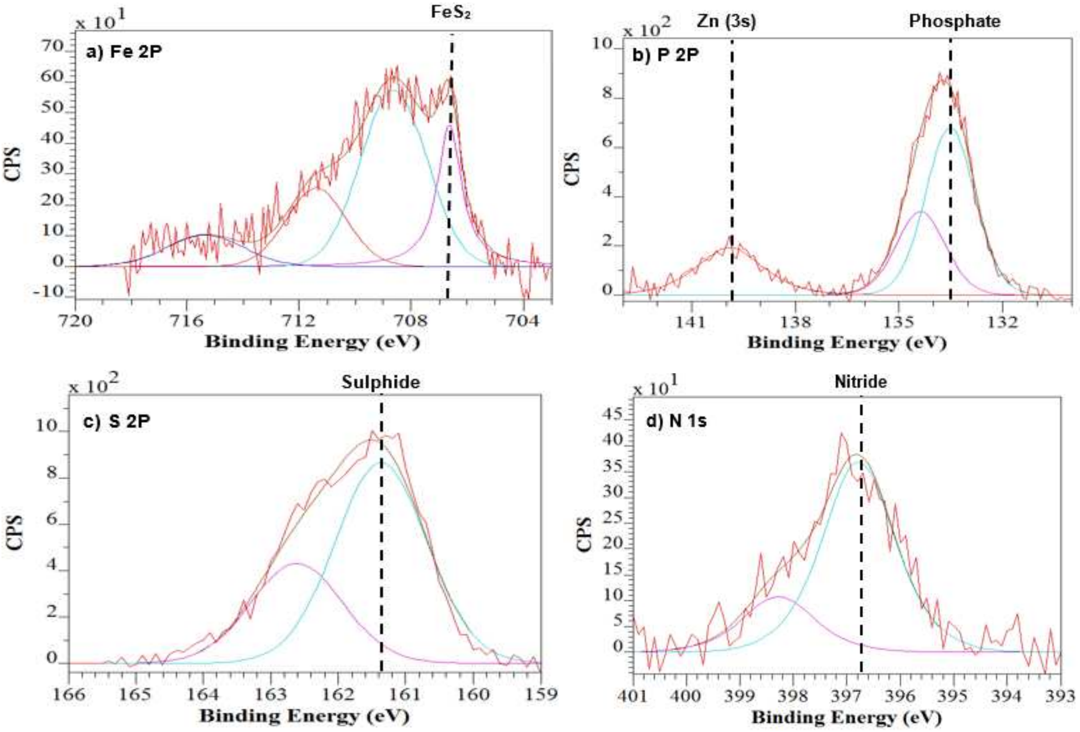


Figure 17. XPS Fe 2p, P 2p, S 2p and N 1s spectra of the tribofilms formed on the QPQ treated samples at an applied contact pressure 1.19 GPa and 1.34 nm etching depth.

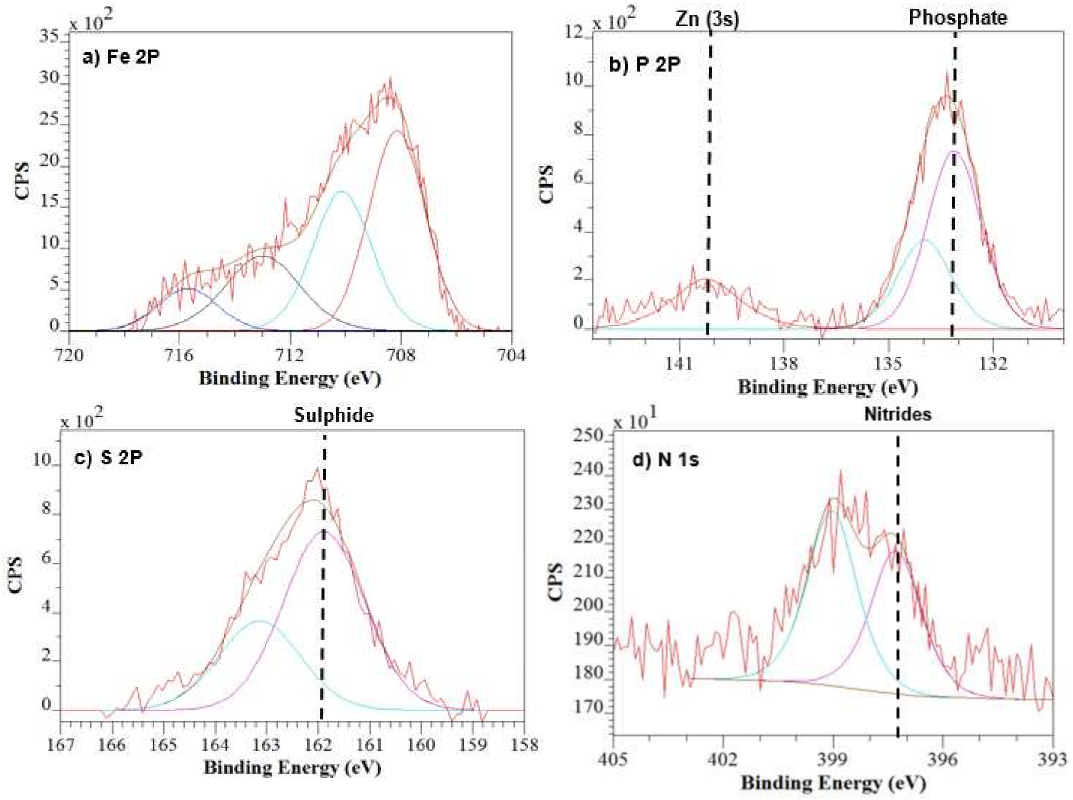


Figure 18. XPS Fe 2p, P 2p, S 2p and N 1s spectra of the tribofilms formed on the Isonite treated samples at an applied contact pressure 1.19 GPa and 1.34 nm etching depth.

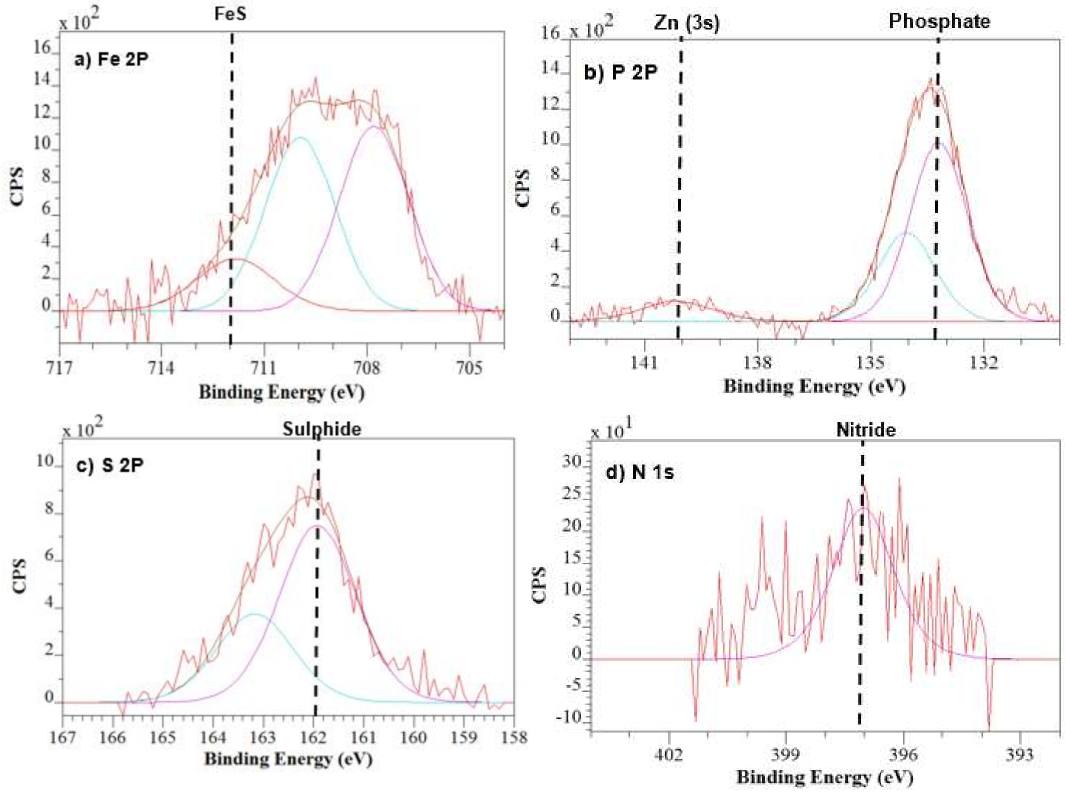


Figure 19. XPS Fe 2p, P 2p, S 2p and N 1s spectra of the tribofilms formed on the SN treated samples at an applied contact pressure 1.19 GPa and 1.34 nm etching depth.

4. Conclusions

The influence of different ferrous layers deposited on nitride surfaces on the tribological and tribochemical properties was investigated. It was shown that the layer composition could influence friction behaviour and tribofilm formation.

- This study determined that the presence of a thin (~0.5 µm) oxide layer on QPQ samples had no influence on friction and wear behaviour in-comparison to Isonite samples where a oxide layer was absent.
- In terms of tribochemical formation the absence of Fe_3O_4 with the Isonite samples limited the presence of iron sulphide formed within the tribofilm, which could have influenced tribological behaviour.
- Results indicated that the FeS_2 detected within the tribofilms or Fe_3O_4 layer of the QPQ samples made no impact on friction or wear behaviour, most likely due to low quantities.
- The presence of a FeS layer after sulphur-nitriding greatly improved friction and wear behaviour as it not only acted as a protective lubricating layer, but it could also potentially regenerate itself due to chemical interactions with sulphur compounds from additives in the lubricant.
- The inclusion of continuously protective FeS layer combined with a hard nitride surface has the potential to further improve component durability in comparison to traditional QPQ and Isonite treatments.

5. References

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Figure captions

- Figure 1. Salt bath nitriding heat treatment process stages for Isonite and QPQ variants [7].
- Figure 2. Comparison of the hardness through the Iso, QPQ and SN pin sample cross-sections and the surface finishes.
- Figure 3. SEM image profile through the cross-section of an Iso pin sample.
- Figure 4. X-ray diffraction pattern of an Iso pin sample.
- Figure 5. SEM image profile through the cross-section of a QPQ pin sample.
- Figure 6. X-ray diffraction pattern of a QPQ pin sample.
- Figure 7. SEM image profile through the cross-section of a SN pin sample.
- Figure 8. X-ray diffraction pattern of a SN pin sample.
- Figure 9. Friction coefficient vs time results over 2 hrs of the three sample variants at a 1.19GPa contact pressure and 25 Hz sliding frequency using fully formulated lubricant at 80°C.
- Figure 10. Average friction coefficient results of the last 30 minutes of the experiments with the three sample variants when using two contact pressures (0.92GPa & 1.19GPa) at two sliding frequencies (12Hz & 25Hz) with a fully formulated lubricant at 80°C.
- Figure 11. Optical images of the wear scar regions of the different treated pin samples when a 1.19 GPa contact pressure was applied at 12 Hz.
- Figure 12. Wear depths of the three types of pins when contact pressures 0.92 & 1.19 GPa are applied at a 12Hz & 25Hz sliding frequencies using fully formulated lubricant at 80°C.
- Figure 13. a) SEM image, b) EDX maps and c) spectra of the unworn and worn surface of the QPQ pin samples at 1.19GPa contact pressure and 12Hz sliding speed.
- Figure 3-12. a) SEM image, b) EDX maps and c) spectra of the unworn and worn surfaces of the Isonite pin samples at 1.19GPa contact pressure and 12Hz sliding speed.
- Figure 13. a) SEM image, b) EDX maps and c) spectra of the unworn and worn surface of the sulphur nitrided pin samples at 1.19 GPa contact pressure and 12Hz sliding speed.
- Figure 14. EPMA maps within the wear scars of the nitrided sample variants (a) QPQ (b) Isonite (c) SN.

- Figure 15. XPS Fe 2p, P 2p, S 2p and N 1s spectra of the tribofilms formed on the QPQ treated samples at an applied contact pressure 1.19 GPa and 1.34 nm etching depth.
- Figure 16. XPS Fe 2p, P 2p, S 2p and N 1s spectra of the tribofilms formed on the Isonite treated samples at an applied contact pressure 1.19 GPa and 1.34 nm etching depth.
- Figure 17. XPS Fe 2p, P 2p, S 2p and N 1s spectra of the tribofilms formed on the SN treated samples at an applied contact pressure 1.19 GPa and 1.34 nm etching depth.

Table captions

- Table 1. Summary of the layers present with the different nitride variant treatments.
- Table 2. TE77 test conditions.
- Table 3. General binding energy values for compounds relevant to the tribofilms formed on the worn surfaces of all treated samples [18, 19].