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Khaemba, DN, Neville, A and Morina, A (2016) New insights on the decomposition mechanism of Molybdenum DialkyldiThioCarbamate (MoDTC): a Raman spectroscopic study. RSC Advances, 6 (45). pp. 38637-38646. ISSN 2046-2069

https://doi.org/10.1039/C6RA00652C

New insights on the decomposition mechanism of Molybdenum DialkyldiThioCarbamate (MoDTC): A Raman spectroscopic study

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Abstract

Molybdenum DialkyldiThioCarbamate (MoDTC) is a friction modifier that has been used in automotive engines for many years. However, its exact decomposition mechanism within tribocontacts is not fully understood. In this study, an attempt has been made towards understanding the mechanism of MoDTC decomposition in steel/steel contacts by employing Raman spectroscopy. Results show that the main MoDTC decomposition products are MoS_2, $FeMoO_4$ and sulphur-rich molybdenum compounds, MoS_x (x>2), in contrast to the previously reported MoS_2 and MoO_3. Formation of these products is dependent on tribological parameters. Raman results from this study indicate that the Mo^{6+} species previously observed in X-ray Photoelectron Spectroscopy (XPS) analysis are probably from $FeMoO_4$ and not MoO_3. This paper presents an alternative reaction pathway for MoDTC decomposition in steel/steel contacts with MoS_x as an intermediate product and MoS_2 as the final product. $FeMoO_4$ is formed from a side reaction of iron oxides with molybdenum compounds at low temperatures and low MoDTC concentrations. Results also show that friction is dependent on the nature of decomposition products at the tribocontact. Knowledge of MoDTC decomposition reaction pathway will enable the friction performance of MoDTC lubricants to be optimized.

1 Introduction

Lubricants play an important role in different engineering systems. In the automotive industry, engine lubricants are key to ensuring the effective performance of internal combustion engines and improving fuel economy as a result. The efficiency of engine lubricants is determined by additives present in the lubricant. Of these additives, friction modifiers and antiwear additives are of particular importance especially for components operating in the boundary lubrication regime. Boundary lubrication refers to the regime where there is no substantial fluid film separating the surfaces. Friction modifiers and antiwear additives perform their various functions by decomposing at the rubbing interface (tribocontact) to form thin films commonly known as tribofilms. A good understanding of additive decomposition in tribological contacts is thus crucial in lubricant development and formulation. Although there are numerous studies on friction and wear performance of various engine lubricant additives, there are still limited studies on additive decomposition pathways and reaction kinetics.

Molybdenum DialkyldiThioCarbamate (MoDTC) has been used as a friction modifier in engine lubricants since early 1970s.[1-3] The friction performance of MoDTC-containing lubricants in steel/steel sliding contacts has been shown to be dependent on contact parameters such as temperature, additive concentration, stroke length, sliding speed and surface roughness.[3-7] Low friction (μ=0.04-0.06) has been observed when tribofilms composed of MoS_2, formed from MoDTC decomposition, are present at the tribocontact while high friction (μ=0.1) has been observed when only iron oxides are formed at the tribocontact.[4] Intermediate friction values (μ=0.06-0.09) have also been observed in certain test conditions. Friction behaviour of MoDTC is intimately related to the chemical species present in the tribocontact, thus, it is important to have a good understanding of the degradation process. It is appreciated that reactions involved in the degradation of MoDTC in tribocontacts cannot simply be considered by simulating the necessary temperature as one would do for thermally-activated reactions. One reason for this is that under purely thermal conditions MoDTC decomposes to form MoS_2 at 300°C [8] while in tribological conditions MoS_2 is formed at 100°C. [9] This indicates that the rubbing motion in tribocontacts contributes to the kinetics and perhaps the mechanism of degradation of MoDTC.

A mechanism for MoDTC decomposition within tribocontacts has already been proposed based on results obtained from X-ray Photoelectron Spectroscopy (XPS) analysis.[10] According to this mechanism, MoDTC decomposes in two stages. In the first stage the thiocarbamate groups dissociate from the MoDTC molecule via the Mo-S bond leaving the $Mo_2S_2O_2$ core. In the second stage, the two thiocarbamate groups combine via the S-S bond forming thiuram disulphide while the $Mo_2S_2O_2$ core decomposes to form MoS_2 and MoO_2. MoO_2 is further oxidized to form MoO_3.

There are few unexplained aspects of the mechanism proposed by Grossiord et al. [10]. Firstly, although MoO_2 and MoO_3 have been suggested as decomposition products based on XPS analysis, the presence of these oxides has not been detected using other analysis techniques such as Raman spectroscopy.[4, 5] XPS analysis is incapable of clearly distinguishing compounds with elements having the same oxidation state due to overlapping peaks. It is probable that Mo^{4+} and Mo^{6+} species detected by XPS are due to formation of other species besides MoO_2 and MoO_3 which have similar oxidation states. Raman spectroscopy, on the other hand, is capable of clearly distinguishing molybdenum species; even those with the same oxidation state. Raman spectroscopy thus provides more accurate characterization than XPS for this specific aspect of tribochemistry. Secondly, the mechanism does not explain what happens to MoDTC in conditions where MoS_2 is not formed or whether other MoDTC decomposition products are formed besides MoS_2. The presence of other decomposition products would explain intermediate friction values observed at certain test conditions.

Understanding the mechanism for MoDTC decomposition within tribocontacts is necessary because; (1) it can be used to predict the friction performance of MoDTC lubricant and will thus be useful in numerical simulation studies (2) it provides guidance to lubrication engineers on lubricant formulation so as to optimize the friction performance of MoDTC (3) it provides a great starting point in the development of future additives with similar decomposition mechanism. To facilitate this, tribotests were conducted using a MoDTC lubricant at varying temperatures, MoDTC concentrations and contact pressures. MoDTC decomposition products formed on the rubbing surfaces after tests were analysed using Raman spectroscopy.

2 Experimental section

2.1 Tribological tests

Tribotests were conducted using a high speed ball-on-disc tribometer under unidirectional sliding conditions. Steel discs used had a thickness of 1 mm and an outer diameter and inner diameter of 42 mm and 25 mm, respectively. The steel ball used had a diameter of 6.5 mm. The ball was fixed while the disc rotated against the fixed ball generating a circular wear scar on the disc. Information on test materials and test conditions is shown in Table 1.

Table 1. Tests conditions used in the tribotests

Test condition	Parameters
Base oil	Group III mineral oil
MoDTC concentration	0.1-0.9 wt%
Temperature	20-100°C
Contact pressure	0.98 - 2.12 GPa
Sliding speed	200 rpm (0.3 m/s), 400 rpm (0.6 m/s)
Test duration	2h
Material	Disc: AISI 1050, Ball: AISI 52100
Hardness	Disc: 60-64 HRC, Ball: 60-67 HRC
Young's Modulus	190-210 GPa (Ball and disc)
Roughness	Disc: R_a=177 nm, Ball: R_a= 10 nm
Lambda ratio (λ)	0.02-0.13 (Boundary lubrication regime)

To study the influence of temperature, tribotests were conducted with 0.5 wt% MoDTC at 200 rpm (0.3 m/s), 2.12 GPa. Tests were conducted at room temperature (20℃), 40℃, 60℃ and 100℃. To study the influence of MoDTC concentration, tribotests were conducted at 400 rpm (0.6 m/s), 1.67 GPa, 60℃ using 0.1 wt%, 0.5 wt% and 0.9 wt% MoDTC. To study the influence of contact pressure, tests were conducted with 0.5 wt% MoDTC at 400 rpm (0.6 m/s), 60℃. Tests were conducted at the following contact pressures; 0.98 GPa, 1.67 GPa, and 2.12 GPa. For repeatability, each test was carried out at least 2 times. There was good friction repeatability (3.2% error) calculated from the average friction values during the last one hour of the tests.

2.2 Wear analysis

Optical images of wear scars generated on the tribopair after tests were obtained using an optical microscope. From these images, ball wear scar diameters (WSD) were determined. Wear from the discs has not been reported in this study since the widths of the wear scars wear similar at different test conditions and the wear depths were too small to be detected by white light interferometry.

2.3 Chemical characterisation of wear scars

Raman spectroscopy analysis was used to determine the chemical composition of the reaction products from the tribochemical reaction. After tests the tribopair samples were rinsed with heptane in an ultrasonic bath for 1 minute before Raman analysis. Although Raman analysis can be carried out on unrinsed samples, the samples in these tests were rinsed so as to obtain a good Raman signal of the MoDTC decomposition products. Unrinsed samples have a layer of lubricant on the surface and when analysed with Raman spectroscopy they show very strong peaks from the mineral base oil. The strong Raman peaks from the mineral base oil make it difficult for the rather weak peaks from MoDTC decomposition products to be observed.

Removing the lubricant from the sample by rinsing in heptane allowed Raman peaks from MoDTC decomposition products to be distinctly observed in the spectra.

Analysis of the wear scars was carried out with Renishaw Invia spectrometer (UK). Raman spectra were obtained with 488 nm wavelength laser at 1 mW laser power and 1s exposure time. Several accumulations were obtained in each spectrum so as to increase the signal-to-noise ratio. At these Raman acquisition parameters, determined in a previous study[11], there is no laser damage to MoDTC tribofilms. All the Raman spectra were analysed using the Renishaw WiRE program for peak position.

3 Results

3.1 Influence of temperature

Figure 1a shows friction coefficient values obtained during tests at different temperatures. For tests conducted at room temperature (20°C), friction was high (μ=0.1) at the beginning of the test and decreased gradually with rubbing time. The friction coefficient at the end of the test was 0.09. In tests carried out at 40°C, there was rapid friction drop to low steady friction values after an induction time of about 10 minutes. The friction coefficient after the friction drop was 0.07. Tests conducted at 60°C and 100°C also showed rapid friction drop to low values (0.05-0.06) after only a short induction time. It was noted that rapid friction drop was only observed when temperatures were increased from 20°C. Figure 1b shows the wear scar diameter (WSD) of wear scars formed on the balls at different temperatures. The WSD was highest at 20°C and decreased to lower values when the temperature was increased. In tests conducted with only the base oil, the WSD was 808 μm. This was almost twice the WSD obtained when MoDTC lubricant was used. These results thus show that MoDTC reduced wear of the steel substrate in agreement with previous studies.[12]

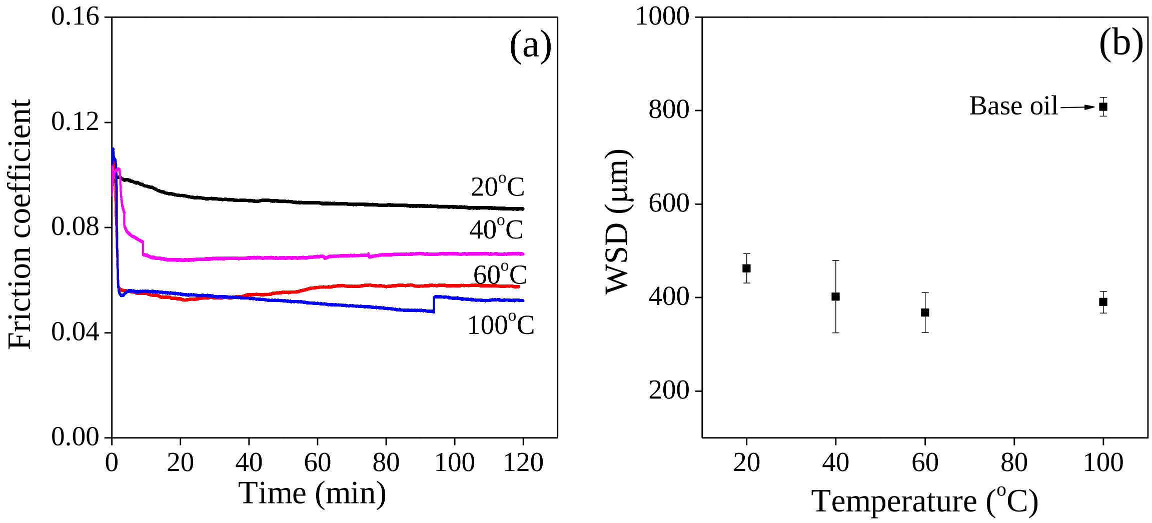

Figure 1. (a) Friction coefficient obtained during tests (b) Ball wear scar diameters (WSD) after tests. Tests were conducted with 0.5 wt% MoDTC at 200 rpm, 2.12 GPa

Figure 2 shows Raman spectra obtained from tribopair wear scars after tests at different temperatures. It should be highlighted that the chemical composition in the wear scars was non-uniform especially for tests conducted at 40°C and 60°C. Consequently, spectra obtained from different regions of the wear scars varied greatly. The spectra shown in Figure 2 only indicate the chemical composition at a given single spot within the wear scars.

Figure 2a shows a typical Raman spectrum obtained from the disc wear scar at 20°C. Spectra obtained from different regions on the tribopair wear scars are shown in Figure S1. In general, spectra obtained from different regions on the tribopair wear scars were very similar indicating spatial uniformity in chemical composition. The spectra had broad peaks at 335 cm^{-1}, 453 cm^{-1} and 925 cm^{-1}. Spectra from the disc wear scar had an additional peak at 670 cm^{-1} which was assigned to the formation of magnetite (Fe_3O_4). [13]

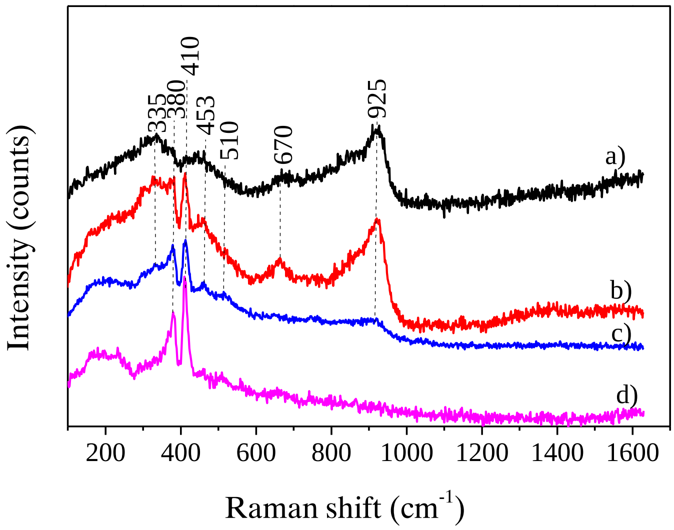

Figure 2. Raman spectra obtained from tribopair wear scars after tests at different temperatures (a) 20℃ (b) 40℃ (c) 60℃ (d) 100℃

In previous Raman studies on the MoDTC additive, there have been no reports of spectra similar to those shown in Figure 2a. This can be due to the fact that no Raman analysis has been carried out on samples generated at 20°C. Most of the previous studies analysed samples generated at higher temperatures and Raman spectra showed MoS_2 peaks at 380 cm^{-1} and 412 cm^{-1}.[5] As will be shown later in this study, samples generated at higher temperatures do indeed have MoS_2 peaks but this was not the case for samples generated at lower temperatures. To the knowledge of the authors, this is the first time Raman peaks at 335 cm^{-1}, 453 cm^{-1} and 925 cm^{-1} have been observed in tests with MoDTC. Observation of these peaks has given a new insight on the mechanism of MoDTC decomposition which is discussed in detail in Section 4.3.

It is possible that MoDTC decomposition did not occur at 20℃ and that the chemical composition of the wear scars was due tests being conducted in base oil. In a previous study by the authors it was observed that in tribotests carried out in base oil the tribopair wear scars were composed of hematite (Fe_2O_3) and magnetite (Fe_3O_4).[11] In Figure 2a, Raman peaks belonging to Fe_2O_3 were not observed; only the peak at 670 cm^{-1} belonging to Fe_3O_4 was observed. Hence, the spectra observed in Figure 2a cannot be attributed to tests being conducted in mineral oil or from the mineral oil itself (Figure S10).The possibility that the spectra observed in Figure 2a were due to adsorbed MoDTC on the substrate was considered and Raman spectrum of MoDTC was investigated. Figure S10 shows the Raman spectrum obtained from the MoDTC additive concentrate. The spectrum of the additive has strong sharp peaks at 971 cm^{-1} and 430 cm^{-1} due to vibration of terminal oxygen atoms ν(Mo=O) and bridging sulphur atoms ν(Mo-S_2-Mo), respectively.[14, 15] Peaks belonging to MoDTC additive were not observed in Figure 2a, indicating that adsorbed MoDTC was not present on the rubbing surfaces. It was therefore concluded that the broad peaks observed at 335 cm^{-1}, 453 cm^{-1} and 925 cm^{-1} in Figure 2a were due to chemical species formed as a result of MoDTC decomposition at the tribocontact.

From previous reports, probable MoDTC decomposition products are MoO_2 [16, 17], MoO_3 [10, 16], MoS_xO_{2-x} [10] and MoS_2 [18]. These chemical species were previously identified using XPS. However, by carefully examining Raman spectra obtained from pure powders of MoS_2, MoO_2 and MoO_3 (Figure S11) and those reported in literature[19-24], it was concluded that MoS_2, MoO_2, MoO_3 and MoS_xO_{2-x} were not present in MoDTC tribofilms generated at 20℃.

Based on reports in literature, the broad peak at 925 cm^{-1} was assigned to Mo=O stretching in $FeMoO_4$.[25-27] This is the first time $FeMoO_4$ is being reported as a product of MoDTC decomposition. Also from reports in literature, the broad peaks at 335 cm^{-1} and 453 cm^{-1} were assigned to the formation of amorphous sulphur-rich molybdenum compounds, MoS_x (x>2), with bridging sulphur atoms (S_2^{2-}). [28-33] Formation of amorphous MoS_x from MoDTC decomposition has not been reported in literature but examples of MoS_x compounds from decomposition of other compounds has been reported. [31, 34-39]

Figure 2b shows a typical spectrum obtained from the disc wear scar after tests at 40°C. Spectra obtained from different regions on the tribopair wear scars varied greatly as can be seen in Figure S2. Spectra obtained from some regions had broad peaks at 335 cm^{-1}, 453 cm^{-1} and 925 cm^{-1}. In some regions, the MoS_2 A_{1g} peak at 410 cm^{-1} was observed emerging from the broad peak at 453 cm^{-1}. In other regions, distinct MoS_2 peaks were observed at 381 cm^{-1} (E^1_{2g} peak) and 414 cm^{-1} (A_{1g} peak). The broad peak at 335 cm^{-1} which became less intense when the E^1_{2g} peak became distinct was attributed to ν(Mo-S) vibration in a structure containing bridging S_2^{2-} ligands.[31] The broad peak at 453 cm^{-1} disappeared when the MoS_2 A_{1g} peak became distinct and less intense peaks were observed at 453 cm^{-1} and 510 cm^{-1}. The peak at 453 cm^{-1} was assigned to ν(Mo-S) vibration while the peak at 510 cm^{-1} was assigned to ν(S-S) vibration of terminal S_2^{2-} ligands.[31] Overall, spectra obtained at 40°C indicated the presence of a mixture of Fe_3O_4, $FeMoO_4$, MoS_2 and MoS_x.

Figure 2c shows a typical Raman spectrum obtained from the disc wear scar after tests at 60°C. Spectra obtained from different regions of the tribopair wear scars are shown in Figure S3. Spectra from the ball wear scar were all very similar to each other and showed MoS_2 peaks. Spectra from the disc wear scar also showed MoS_2 peaks. In addition, peaks were also observed at 670 cm^{-1} (Fe_3O_4) and 925 cm^{-1} ($FeMoO_4$). Overall, wear scars generated at 40°C were observed to have high amounts of MoS_2 and traces amounts of Fe_3O_4 and $FeMoO_4$.

Figure 2d shows a typical Raman spectrum obtained from the disc wear scar after tests at 100°C. The spectrum shows the presence of MoS_2 peaks. Spectra obtained from different regions on the tribopair wear scars (Figure S4) were similar to the spectrum in Figure 2d indicating uniformity in the chemical composition of the wear scars. The broad peak in the 100-250 cm^{-1} region was attributed to stress-induced disorder in MoS_2 crystal structure.[11, 40]

3.2 Influence of MoDTC concentration

Figure 3a shows friction curves during tests at different MoDTC concentrations. The friction coefficient was high (0.10) at the beginning of the test in all tests. In the tests with 0.1 wt% MoDTC, the friction decreased gradually and reached 0.06 at the end of the test. In tests conducted with 0.5 wt% and 0.9 wt% MoDTC, high friction was only observed at the beginning of the test and rapidly dropped to low values (0.06) after a very short induction time. From wear results presented in Figure 3b it was observed that the WSD decreased slightly when MoDTC concentration was increased from 0.1 to 0.5 wt% and then remained low at higher concentrations.

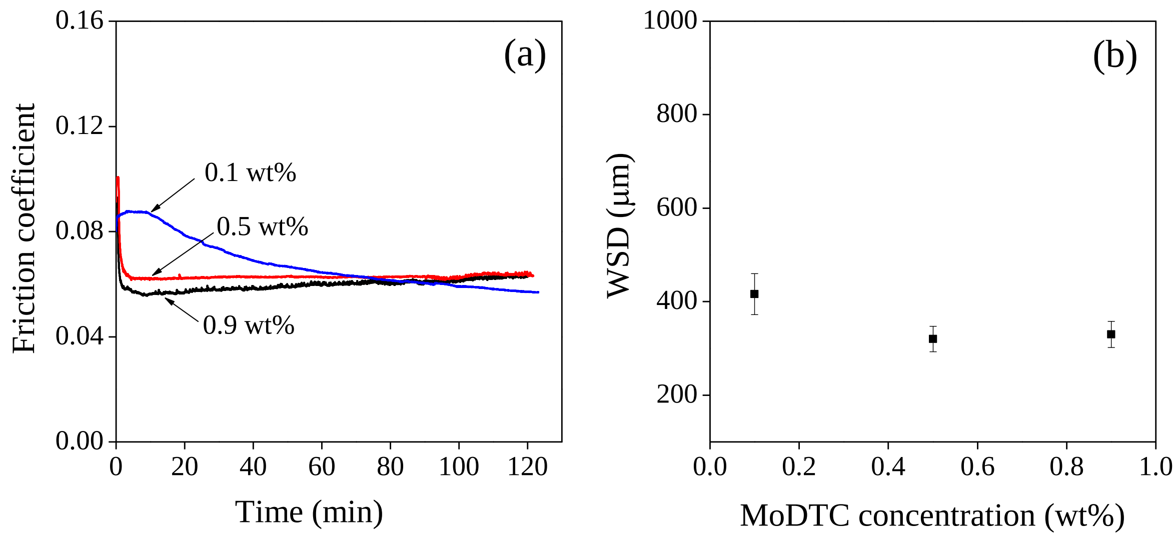

Figure 3. (a) Friction curves during tests (b) Ball wear scar diameters (WSD) after tests. Tests were conducted at varying MoDTC concentration at 60℃, 400 rpm, 1.67 GPa

Figure 4 shows examples of typical spectra obtained from disc wear scars after tests at varying MoDTC concentrations. Figure 4a shows an example of a Raman spectrum obtained from the disc wear scar after tests using 0.1 wt% MoDTC. The spectrum indicates the presence of Fe_3O_4, $FeMoO_4$ and MoS_x within the wear scars. Spectra obtained from different regions of the tribopair wear scars showed a uniform chemical composition (Figure S5). Figure 4b shows a typical Raman spectrum obtained from the disc wear scar after tests with 0.5 wt% MoDTC. Spectra obtained from different regions of the tribopair wear scars (Figure S6) indicate the presence of MoS_2 with traces of $FeMoO_4$ and Fe_3O_4. Figure 4c shows a typical Raman spectrum obtained from the disc wear scar after tests using 0.9 wt% MoDTC. Spectra obtained from different regions on the tribopair wear scars varied from region to region as shown in Figure S7. In some regions, MoS_2 peaks were observed while in other regions peaks attributed from MoS_x, Fe_3O_4, and $FeMoO_4$ were observed.

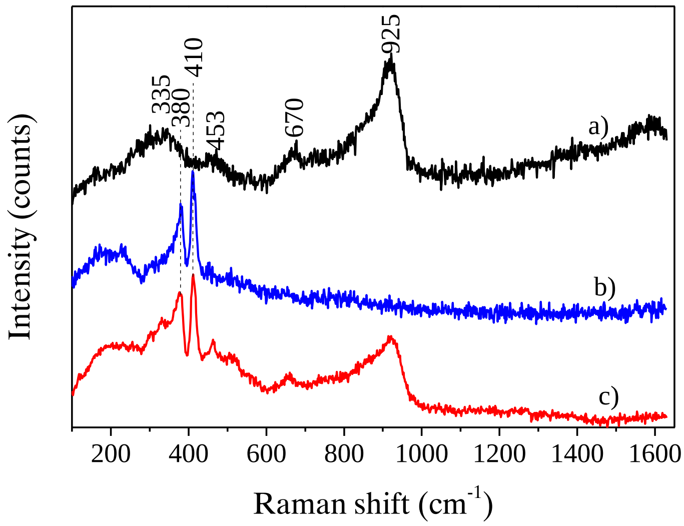

Figure 4. Raman spectra obtained from the disc wear scars after tests at varying MoDTC concentrations (a) 0.1 wt% (b) 0.5 wt% (c) 0.9 wt%

3.3 Influence of contact pressure

Figure 5a shows friction curves observed when tests were conducted at various contact pressures. The friction behaviour was similar at all pressures. There was high friction (μ=0.10) at the beginning of the test followed by rapid drop to low steady friction values (μ=0.07- 0.06) after very short induction time. The WSD increased with increase in contact pressure as expected (Figure 5b).

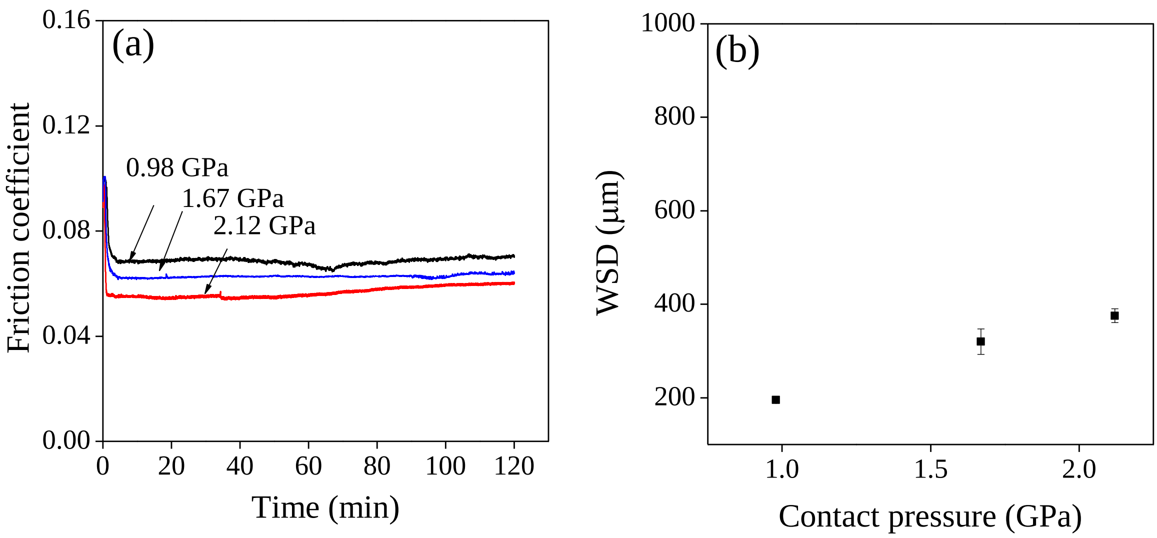

Figure 5. (a) Friction curves during tests (b) Ball wear scar diameters (WSD) after tests. Tests were conducted at varying contact pressures at 0.5 wt% MoDTC, 60℃, 400 rpm.

Figure 6 shows representative Raman spectra obtained from tribopair wear scars after tests at 0.98 GPa and 2.12 GPa. Spectra obtained from different regions within the tribopair wear scars after tests at 0.98 GPa varied from spot to spot, especially on the ball wear scar (Figure S8). The Raman spectrum in Figure 6a shows that the wear scar was composed of a mixture of MoS_2, MoS_x and $FeMoO_4$. A typical Raman spectrum obtained from tribopair wear scars after tests at 1.67 GPa was shown in Figure 4b. Figure 6b shows a typical Raman spectrum obtained from tribopair wear scars after tests at 2.12 GPa. The spectrum indicates that the wear scar was composed of MoS_2. Spectra obtained from different regions of the tribopair wear scar showed the chemical composition was uniform (Figure S9).

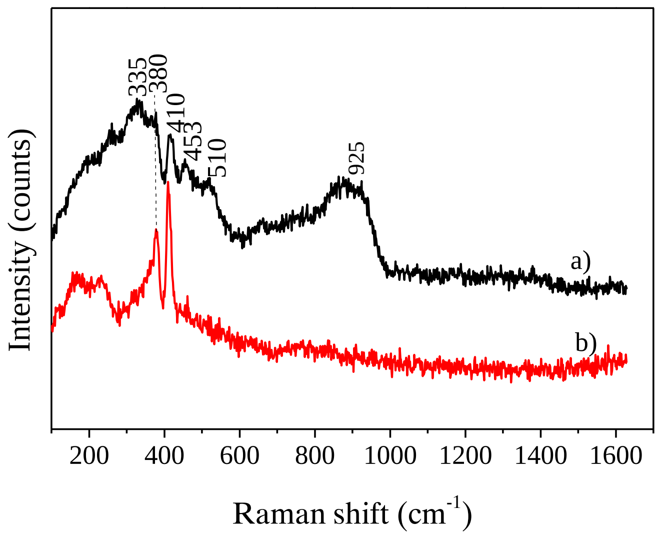

Figure 6. Raman spectra obtained from the tribopair wear scar after tests at (a) 0.98 GPa (b) 2.12 GPa

4 Discussion

4.1 MoS_x and $FeMoO_4$ species

Tribological tests with MoDTC resulted in the formation of MoDTC tribofilms composed of MoS_2, MoS_x and $FeMoO_4$. Although the formation of MoS_2 has been widely reported, the formation of $FeMoO_4$ and MoS_x has not been reported before. Key information about these two compounds is presented below.

MoS_x ($x>2$) compounds are normally formed at lower temperatures than MoS_2 and have been reported to undergo recrystallization at high temperatures to form MoS_2. [31, 39, 41-43] Recrystallization of MoS_x has also been observed under tribological conditions. Lince et al. [44] reported the formation of MoS_2 after tribological tests on MoS_3 coatings. Based on this information, it can be concluded that (1) MoS_x is an intermediate compound in the formation of MoS_2 and (2) the transformation of MoS_x to MoS_2 is dependent on temperature and shear stress.

Singer [45] reported that the formation of molybdenum oxides such as Fe_2MoO_4 and $FeMoO_4$ was possible in a system comprising of Fe, Mo, S and O. The formation of $FeMoO_4$ has been reported when MoS_2 coatings were rubbed with steel counterparts.[46] In literature, it has been reported that $Fe_2(MoO_4)_3$ can be formed from a reaction of molybdenum compounds with Fe_2O_3 at temperatures of about 120ºC. [47] It has also been reported that metal molybdates can be formed at room temperature when mechanically activated (mechanical milling). [48] It is therefore not surprising that $FeMoO_4$ was formed in tests with MoDTC lubricant since Fe, O and Mo were present at the contact. The formation of $FeMoO_4$ in a system comprising of Fe, Mo and O was also confirmed by the authors by heating MoDTC at 100ºC in the presence of Fe_3O_4 (Figure S13). From reports in literature and results obtained in this study it can be deduced that in tribotests with MoDTC lubricant, $FeMoO_4$ was probably formed from a reaction of molybdenum compounds with iron oxides on the steel surface. Also, that the reaction leading to the formation of $FeMoO_4$ was mechanically-activated.

Previous XPS analysis of MoDTC tribofilms showed Mo 3d peaks at 229, 232.3 and 235 eV.[10, 18] From these XPS studies it was concluded that MoDTC tribofilms were composed of MoO_3 due to the presence of Mo $3d_{5/2}$ peak at 232.3 eV. The Mo $3d_{5/2}$ peak for $FeMoO_4$ is at 232.3 eV. [26, 49] Molybdenum in MoO_3 and $FeMoO_4$ have the same oxidation state (+6) therefore from XPS analysis it is impossible to differentiate the two compounds due to overlapping peaks. Raman spectra of MoO_3 [50] and $FeMoO_4$ [25] are completely different and can thus be used to distinguish the two compounds. In this study, Raman peaks belonging to $FeMoO_4$ were observed while those belonging to MoO_3 where not observed at all. It is possible that the Mo (6+) peak observed in MoDTC tribofilms using XPS analysis is probably due to the presence of $FeMoO_4$ and not MoO_3.

4.2 Tribochemical reactions

In tests conducted at 20ºC, it was observed that MoDTC decomposed to form MoS_x and $FeMoO_4$ (Figure 2a). This is an interesting observation as such a reaction would not happen in non-tribological conditions since the temperature is too low to cause thermal decomposition of MoDTC. These results indicate that the tribochemical reaction was not only driven by temperature as is the case for thermally-activated reactions. The presence of shear stress in tribological tests also promoted the decomposition of MoDTC. This conclusion is supported by simulation studies conducted by Onodera et al. [51] where it was reported that decomposition of adsorbed MoDTC occurred only when pressure and sliding were applied. Numerical studies have shown that tribochemical reactions also occur in other molecules when shear stress is applied. [52] It is therefore suggested that the tribochemical reaction of MoDTC is best defined by Eq.1.[53]

$$k_{tribo} = A_o \, exp^{\frac{\sigma V - E_a}{k_B T}} \qquad \text{Eq.1}$$

Where k_{tribo} is the reaction rate constant, A_o the pre-exponential factor, σ the shear stress, V the material constant, E_a the activation energy, T the temperature and k_B the Boltzmann constant. The shear stress component in Eq.1 provides additional energy which enables MoDTC decomposition to occur at low temperatures. The rate of MoDTC decomposition in tribological contacts is therefore dependent on shear stress, temperature as well as MoDTC concentration (Eq.2).

4.3 Newly proposed decomposition mechanism

The mechanism for MoDTC decomposition proposed by Grossiord et al. [10] cannot be used to explain MoDTC decomposition products obtained in 20℃ tests since MoS_2, MoO_2 or MoO_3 were not detected in the wear scars. The previously proposed mechanism suggests the formation of MoO_2 and MoO_3 however these oxides were not detected by Raman spectroscopy in this study. There is therefore a need to propose a decomposition pathway for MoDTC that would accommodate the observations made in this study.

In determining the new reaction pathway, the chemical composition of MoDTC tribofilms formed at various contact parameters was considered. As discussed in Section 4.2, shear stress participates in the decomposition of MoDTC probably through rupturing of bonds. To determine which bonds would be most susceptible to rupturing under shear stress, bond dissociation energies of bonds in MoDTC were obtained from literature. From bond dissociation energies for various bonds in MoDTC (Table S1), the C-S bond has the lowest bond dissociation energy therefore it is the weakest bond and can be easily ruptured under shear stress.[53, 54] Cleavage of C-S bond in dithiocarbamates has been proposed in literature.[55] Figure 7 shows the proposed reaction pathway for MoDTC decomposition initiated by shear stress.

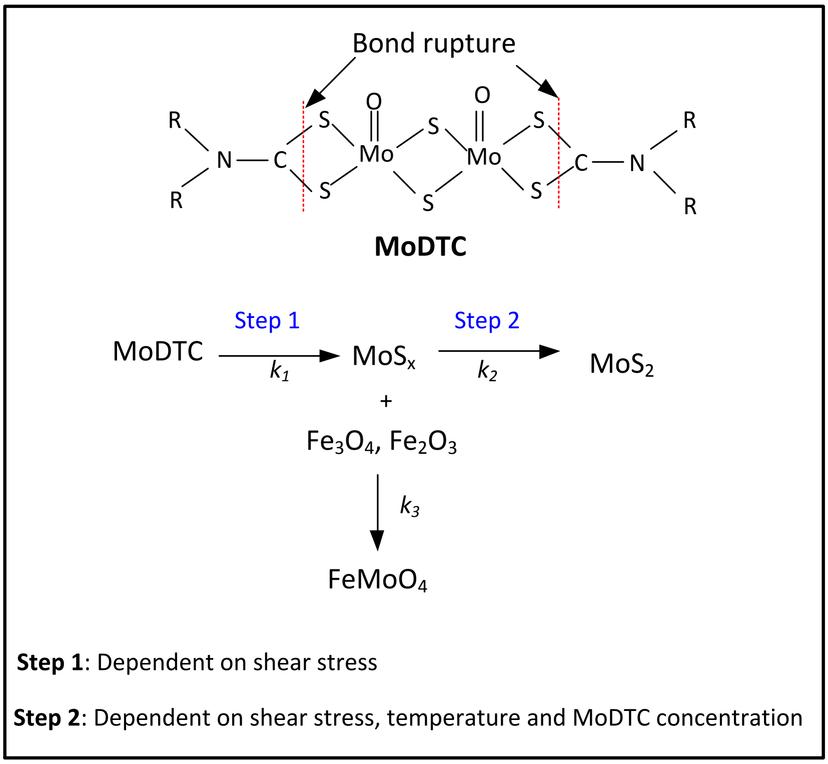

Figure 7. Proposed reaction pathway for decomposition of MoDTC within tribocontacts

The decomposition process occurs as follows.

- MoDTC first adsorbs on the tribopair surfaces.[51]
- In Step 1, shear stress applied on adsorbed MoDTC molecules causes decomposition to occur. The decomposition process begins by rupturing of C-S bonds forming molybdenum intermediate compound which undergoes intramolecular sulphonation forming amorphous MoS_x.
- In Step 2, MoS_x is converted to MoS_2. Since MoS_x is formed at lower temperatures than MoS_2, the activation energy for formation of MoS_x is lower than that for the formation of MoS_2. Therefore, MoS_2 can be formed from MoS_x either through increasing the energy at the contact by increasing temperature or increasing shear stress.
- $FeMoO_4$ is formed from a reaction of iron oxides on the steel surfaces with MoS_x.

The rates of reactions for formation of the various molybdenum species are shown in Eq 2-4. It should be noted that these are simplified expressions as the order of the reactions is currently unknown.

$$r_{MoS_x} = k_1[MoDTC] \qquad \text{Eq.2}$$

$$r_{MoS_2} = k_2[MoS_x] \qquad \text{Eq.3}$$

$$r_{FeMoO_4} = k_3[MoS_x]\,[iron\ oxides] \qquad \text{Eq.4}$$

Although the exact values for reaction rate constants k_1, k_2 and k_3 has not been determined in this study, it is believed that the reaction constants can be described by Eq.1.

Reaction constant k_1 is not dependent on temperature as MoS_x is formed even at 20ºC given that shear stress is applied. Reaction constant k_2 is dependent on both temperature and shear stress since recrystallization of MoS_x is dependent on these two parameters (Section 4.1). Varying the temperature and shear stress will therefore affect k_2 values which will in turn affect the molybdenum sulphide compound formed as follows.

$k_1 \gg k_2$ MoS$_x$

$k_1 > k_2$ MoS$_x$, MoS$_2$

$k_1 \ll k_2$ MoS$_2$

In Figure 2, it was also shown that the amount of MoS_2 increased while the amount of $FeMoO_4$ decreased with increase in temperature. This observation suggests that two competing reactions occur at the tribocontact; (1) oxidation of the surface and (2) formation of MoS_2. Formation of $FeMoO_4$ is dependent on the presence of iron oxides at the tribocontact. Iron oxides are formed as a result of surface oxidation. Oxidation of the steel substrate is favoured when the formation of MoS_2 at the contact is inhibited. On the other hand, rapid formation of MoS_2 at the contact will hinder surface oxidation and the subsequent formation of $FeMoO_4$.

4.4 Effect of temperature and MoDTC concentration

Results presented in Figure 2 showed that the chemical composition of MoDTC tribofilms changed from MoS_x, $FeMoO_4$ to MoS_2 when the temperature was increased from 20ºC to 100ºC. These observations have not been reported elsewhere in literature. In the study by Morina et al. [7] it was reported that MoDTC tribofilms formed at 30ºC had lower amounts of Mo and S than those formed at higher temperatures (100-150ºC). It was also reported in the same study that more Mo oxides (MoO_3) were formed at 30ºC than at higher temperatures.

MoDTC concentration was also found to affect the composition of MoDTC tribofilms in this study (Figure 4). At a low concentration of 0.1 wt%, MoS_x and $FeMoO_4$ were formed while at 0.5 wt%, MoS_2 was formed. MoDTC tribofilms formed at 0.9 wt% were comprised of a mixture of MoS_2, MoS_x and $FeMoO_4$. In a previous study, it was reported that sulphates were formed at low MoDTC concentrations (Mo 100 ppm) while MoS_2 was formed at high concentrations. [9] In another study, it was reported that the amount of MoS_2 increased with MoDTC concentration. [56]

Reports in literature on the influence of temperature and MoDTC concentration on the composition of MoDTC tribofilms are not in complete agreement with findings in this study. This can be due to differences in analysis techniques used in this study and in the previous studies. This is because different techniques have varying capabilities when distinguishing molybdenum compounds.

Temperature and MoDTC concentration affect MoDTC decomposition in the following three ways. (1) Affecting the adsorption of MoDTC on rubbing surfaces (2) determining the nature of products formed (3) affecting the rate of the MoDTC decomposition. Adsorption of additives has been shown to increase with increase in temperature and concentration. [57, 58] At low MoDTC concentrations and low temperatures, there is less MoDTC adsorbed on the surface. Lower MoDTC coverage will promote oxidation of the steel surface while higher MoDTC coverage will hinder oxidation of the steel surface. From the discussion presented in Section 4.3, it can be seen that high temperatures will promote the formation of MoS_2 formed while low temperatures will lead to formation of MoS_x. High temperatures will also lead to rapid formation of MoS_2 (Eq.1). Also, from Eq.2, it can be seen that high MoDTC concentrations will increase the rate of MoS_x formation. These insights on MoDTC adsorption and decomposition can be used to explain the trends observed in this study at varying temperatures and MoDTC concentrations.

Observations made at varying temperatures can be explained as follows. The formation of $FeMoO_4$ at low temperatures is due high surface oxidation due to low MoDTC coverage. The decrease in $FeMoO_4$ amount with increase in temperature is due to a decrease in surface oxidation as formation of MoS_2 on the surface occurs.

Observations made at varying MoDTC concentrations can be explained as follows. At low concentrations, $FeMoO_4$ is formed due to the presence of an oxidised surface as a result of low

MoDTC coverage. At the temperature used (60°C), the formation of MoS_2 was expected. However, MoS_x was formed instead of MoS_2. The formation of MoS_x can be attributed to the slow rate of MoS_x formation due to a lower MoDTC concentration (Eq.2). Consequently, the rate of MoS_x conversion to MoS_2 would be very slow because of low MoS_x concentration (Eq.3). The formation of MoS_2 would therefore require a longer time than the duration used in the test (2h). Increasing MoDTC concentration from 0.1 wt% to 0.5 wt% resulted in the formation of MoS_2 as expected. This could be because the formation of MoS_x was faster. Increasing the concentration further to 0.9 wt% MoDTC resulted in a mixture of MoS_x and MoS_2 which was unexpected. This observation can be due to the rate of MoS_x formation being too high to balance the rate of MoS_2 formation. To increase the rate of MoS_2 formation, k_2 values have to be increased. This can be done either by increasing the temperature or the shear stress.

4.5 Relationship between friction and chemical composition of MoDTC tribofilms

As it is well known, friction reduction by MoDTC is due to the formation of tribofilms composed of MoS_2. However, this study has shown that in certain test conditions MoS_x and $FeMoO_4$ can be formed and this affects the friction behaviour. In test conditions where MoS_2 was formed, there was a rapid drop in friction to low values after a short induction time. The mechanism by which MoS_2 reduces friction was reported by Onodera et al. [59] When MoS_x and $FeMoO_4$ were formed, the friction reduction was gradual. Friction reduction was achieved due to the presence of MoS_x as $FeMoO_4$ does not have any friction reducing capabilities. [44] Friction reduction with MoS_x is however less compared to that achieved with MoS_2. In tests where MoS_x, MoS_2 and $FeMoO_4$ were observed at the tribocontact, the friction values were slightly lower than those observed when only MoS_x and $FeMoO_4$ were present at the tribocontact. These results indicate that the chemical composition of MoDTC tribofilms determines the friction observed. Thus the intermediate friction values observed in previous studies[4, 5] can be explained by the presence of MoS_2, MoS_x and $FeMoO_4$ at the tribocontact in varying proportions.

4.6 Effect of contact parameters on wear

It was observed that the ball WSD decreased by about 50% when MoDTC was added to BO. This is in agreement with previous studies. [12, 56] Wear reduction can be attributed to the formation of MoDTC tribofilms. It has been reported that MoDTC tribofilms have a lower hardness (0.4-0.5 GPa) than steel. [60] This means that, the tribofilms can be easily sheared instead of the steel substrate. This way MoDTC tribofilms protect the substrate from wear.

Larger WSD were observed at low temperatures (20ºC) and low concentrations (0.1 wt%). At these conditions, it was also observed that the induction time was longer than that observed at higher temperatures and higher concentrations. The longer induction times indicate that the formation of MoDTC tribofilms was delayed. The absence of MoDTC tribofilms during the long induction period could explain the slightly higher wear observed at low temperatures and low MoDTC concentrations.

5 Conclusions

This study has investigated the influence of temperature, MoDTC concentration and contact pressure on the MoDTC decomposition within tribological contacts. Chemical composition of wear scars after tribological tests was conducted using Raman spectroscopy. Results show that MoDTC decomposition in steel/steel contacts is highly dependent on test conditions. MoDTC decomposes to form MoS_2, $FeMoO_4$ and MoS_x depending on tests conditions. The various MoDTC decomposition products formed within the tribocontact determine the friction performance. Low friction was observed when MoS_2 was formed while high friction values were obtained when MoS_x and $FeMoO_4$ were formed. MoS_x formed at low temperatures was converted to MoS_2 at higher temperatures indicating that MoS_x was an intermediate compound in the formation of MoS_2. Furthermore, it has been shown that ferrous surfaces participate in the decomposition of MoDTC by reacting with the decomposition products to form $FeMoO_4$. Based on Raman analysis results obtained in this study, a new decomposition pathway for MoDTC in tribological contacts has been proposed.

Acknowledgement

This study was funded by the FP7 program through the Marie Curie Initial Training Network (MC-ITN) entitled "ENTICE - Engineering Tribochemistry and Interfaces with a Focus on the Internal Combustion Engine" [290077] and was carried out at University of Leeds, UK.

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