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ORIGINAL PAPER

Effect of Adding TiO_2 Nanoparticles to a Lubricant Containing MoDTC on the Tribological Behavior of Steel/Steel Contacts Under Boundary Lubrication Conditions

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Abstract
The tribological performance of lubricants containing TiO_2 nanoparticles and Molybdenum DiThioCarbamate (MoDTC) was investigated using a reciprocating ball-on-flat tribometer in steel–steel contacts. Lubricants containing only MoDTC were used for comparison. The influences of the additive concentration (0.1 wt% and 0.5 wt%) and of the roughness of the counterparts (R_a from 10 to 200 nm) on the performance of the lubricant were studied. Improved friction modification and anti-wear properties were found when TiO_2 nanoparticles were blended with MoDTC compared to MoDTC alone, even at low concentration and with rough surfaces. XPS characterizations and FIB-TEM analyses of tribofilms were performed and suggested that the formation of MoS_2 from MoDTC is favored in the presence of TiO_2 nanoparticles. The results are discussed, taking into account the tribocatalytic properties of TiO_2 nanoparticles.

Keywords TiO_2 nanoparticles · MoDTC · Tribocatalysis · XPS · FIB-TEM

1 Introduction

The use of nanoparticles as lubricant additives has been widely investigated in recent years [1–14]. They are considered as potential substitutes for classical tribological additives. They can easily enter the tribological contact due to their small sizes and rounded morphology (with limited dangling bonds). They are also less sensitive to the environment compared to other molecular additives [15]. Many studies have reported the good friction modification and/or anti-wear properties of nanoparticles when used in dispersion in the lubricant and tested under the boundary lubrication regime [15]. Their lubrication mechanism depends mainly on their composition and morphology. Some of them form a protective film, reducing friction and preventing wear, while additional lubrication mechanisms based on rolling/sliding or exfoliation have been observed with other particles [16].

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Certain studies reported that the tribological performances of nanoparticles can be strongly affected by the roughness of the rubbing surfaces [17]. Tao et al. [18] suggested that nanoparticles could also act as polishers for rough surfaces, making them smoother and reducing the severity of the contact (and therefore reducing friction). Aldana et al. [17] showed that inorganic fullerene (IF) nanoparticles made of metal disulfide (MoS_2/WS_2) were able to fill the asperities/grooves of the rubbed surfaces during the test they carried out. The grooves acted as reservoirs and delivered lubricous nanoparticles/exfoliated flakes throughout the friction test, thus leading to better lubrication.

Carbon-based materials such as nanotubes and nanoparticles, and ceramic oxide nanoparticles such as TiO_2, Al_2O_3, ZnO, and CuO have also been studied for their tribological properties and were found to efficiently reduce friction and wear [4, 5, 9, 11, 19]. Concerning the specific use of TiO_2 nanoparticles, their addition to oil has led to stable friction coefficients due to the formation of protective films on the counterpart surfaces of steel/steel contacts [14]. In addition, it has been shown that TiO_2 nanoparticles exhibit a higher load bearing capacity compared to oil used without TiO_2 nanoparticles [19]. Ali et al. [9] showed that using of TiO_2 nanoparticles in combination with Al_2O_3, with an optimum concentration of 0.25 wt% in base oil, led to significant friction and wear reduction as well as a reduction in friction losses when used in a piston ring-cylinder liner contact.

At present, MoDTC (Molybdenum DiThioCarbamate) is the most widely used friction modifier additive in boundary lubrication conditions [20, 21]. The molecule decomposes to form layered MoS_2 flakes on the rubbed surfaces which reduces the friction between the tribopairs [22]. It was recently shown that the generation of MoS_2 from MoDTC is favored in the presence of TiO_2 APS coatings. No Mo-oxysulfide is formed, contrary to what it is observed with steel/steel contacts [23]. The tribocatalytic activity of the TiO_2 APS coating was the main reason given by the authors to explain this result as it leads to the generation of negatively charged particles at the surface of the rubbed TiO_2 APS coating, thereby reducing the Mo(+V) atoms present in MoDTC molecules into Mo(+IV) (like in MoS_2) [24].

To evaluate whether this tribocatalytic effect also exists in the presence of TiO_2 nanoparticles, blends of TiO_2 nanoparticles with and without MoDTC were tested on reciprocating sliding tribometers under boundary lubrication conditions. Tests were carried out in the presence of smooth and rough steel surfaces to study any additional benefit in using nanoparticles; the influence of the concentration of the two additives on lubricant performance was also studied.

2 Experimental

2.1 Materials and Methods

2.1.1 Materials

2.1.1.1 Tribopairs AISI 52100 steel balls and flats were used as tribopairs sliding over one another in ball-on-flat configuration. "Reference steel" discs were purchased from PCS Instruments, UK. The counterpart balls ($R_a \approx 10$ nm) used were made of reference steel (AISI 52100). To evaluate the effect of roughness parameters on the tribological behavior of steel/steel contacts, steel APS coatings, called "rough steel" in the following, were purchased from Oerlikon Balzers. The Atmospheric Plasma Spray process was used for deposition with micron-sized powders. The roughness parameters of this so-called "rough steel" are extremely high compared to the reference commonly used for cylinder liner applications [25]. Table 1 lists the properties (roughness parameters, hardness and elastic modulus) of the flats used as tribopairs. The average surface roughness, hardness and elastic modulus of the flats were measured by interferometry and a Zwick micro-hardness tester for the reference steel and rough steel flats, respectively.

2.1.1.2 Lubricants The lubricant used was made of a base oil (standard group III mineral oil) blended with MoDTC, with or without the addition of anatase TiO_2 nanoparticles (∅ = 25 nm). The base oil had a viscosity of 0.026 Pa s at 40 °C and 0.008 Pa s at 100 °C. The MoDTC friction modifier additive was provided by total marketing services. TiO_2 anatase nanoparticles (tetragonal crystal system) were purchased from Sigma-Aldrich Inc. Both MoDTC and TiO_2 nanoparticles were added in base oil in two different concentrations (0.5 wt% and 0.1 wt%) and then were blended using magnetic stirrers at 60 °C for 2 h to ensure that the particles are well dispersed. The different blend compositions are reported in Table 2 as are their code names used in the following.

Figure 1 shows the reference blends of **BO_0.5TiO$_2$** (Fig. 1b, white colored) and **BO_0.5MoDTC_0.5TiO$_2$** (Fig. 1a, milky light yellow/green colored). Sedimentation of the nanoparticles at the bottom of the tube is observed for **BO_0.5TiO$_2$** whereas the blend containing the mixture

Table 1 Roughness parameters, hardness and elastic moduli for steel flats

Flat material	R_a (µm)	R_k (µm)	R_{pk} (µm)	R_{vk} (µm)	Hardness (GPa)	Elastic modulus (GPa)
Reference steel	0.01 ± 0.05	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.02	7 ± 1	210
Rough steel	0.19 ± 0.05	0.30 ± 0.05	0.26 ± 0.12	0.49 ± 0.10	5 ± 2	130 ± 30

Table 2 Different blend compositions and code names used in the paper

Blend compositions	Code name
Base oil	**BO**
Base oil + 0.5% wt TiO_2 anatase nanoparticles	**BO_0.5TiO$_2$**
Base oil + 0.5% wt MoDTC	**BO_0.5MoDTC**
Base oil + 0.5% wt MoDTC + 0.5% wt TiO_2 anatase nanoparticles	**BO_0.5MoDTC_0.5TiO$_2$**
Base oil + 0.1% wt MoDTC	**BO_0.1MoDTC**
Base oil + 0.1% wt MoDTC + 0.1% wt TiO_2 anatase nanoparticles	**BO_0.1MoDTC_0.1TiO$_2$**

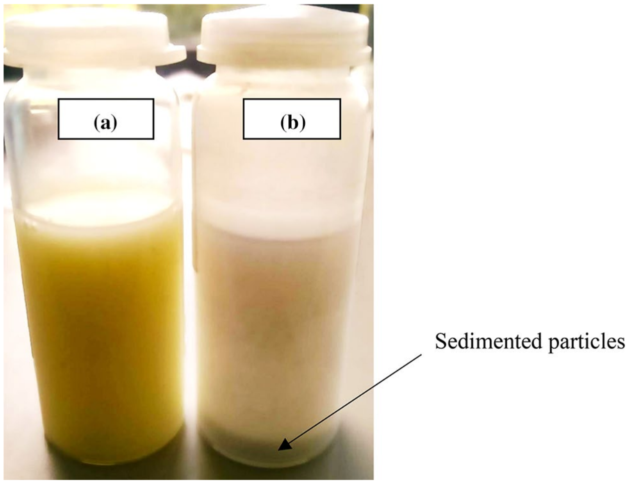

Fig. 1 Optical images of different blends: (**a**) **BO_0.5MoDTC_0.5TiO$_2$** (**b**) **BO_0.5TiO$_2$** (Color figure online)

of TiO_2 anatase nanoparticles and MoDTC shows well-dispersed nanoparticles with no sedimentation even after 6 h. The addition of TiO_2 nanoparticles in base oil containing MoDTC forms a colloidal dispersion. Therefore, the blend did not require any dispersant to keep the nanoparticles dispersed. This is not generally observed with nanoparticles so this type of blend could solve the extremely important issue of nanoparticle dispersion.

2.2 Methods

2.2.1 Characterization of Nanoparticles

The size and the morphology of the TiO_2 anatase nanoparticles were characterized by TEM. The transmission electron microscope used to observe the nanoparticles was a JEOL 2010F operating with an accelerating voltage of 200 kV and equipped with EDS.

2.2.2 Linear Ball-on-Flat Tribotests

Linear reciprocating ball-on-flat tests were carried out with reference steel balls against reference steel flats and rough steel flats. All the tribopairs were cleaned in an ultrasonic bath for 10 min in heptane before testing. The general tribotest conditions used are listed in Table 3. Each test was repeated at least three times. Using Hertzian theory of contact mechanics, normal loads were calculated for different tribopairs, taking into account the elastic moduli of all the tribopair materials. Therefore, a normal load of 6 N was used for the reference steel/reference steel contact and 9 N for the reference steel/rough steel contact. The lubricant was placed in an oil bath created by fixing a glass surrounding the sample holder only in the case of MoDTC. However, when nanoparticles were present in the lubricant, the lubricant was inserted differently. As the nanoparticles sedimented easily, a single drop of the lubricant was used in the contact to ensure that it remained in the contact for the complete duration of the test. In addition, to ensure that the tests were carried out in boundary or mixed lubrication conditions, a lambda ratio was calculated to ensure boundary lubrication conditions [26].

Table 3 Tribotest conditions

Normal Load	6 N—reference steel/reference steel, 9 N—reference steel/rough steel
Temperature	100 °C
Frequency and stroke length	5 Hz and 5 mm
Maximum Hertzian contact pressure	700 MPa
Average Hertzian contact pressure	480 MPa
Test duration	3600 s, 18,000 cycles
Ball material	AISI 52100 Steel (reference steel)
Flat material	AISI 52100 Steel (reference steel), Steel APS (rough steel)

2.2.3 Wear Scar Analysis

Wear scar analysis was carried out using optical microscopy on both the counterparts. Wear scar diameters obtained on the ball as well as on the flat were compared with the respective Hertzian diameters to estimate the wear. The percentage of wear above the Hertzian diameter was calculated to compare the wear for different flat materials. White light interferometry was used to measure the roughness inside and outside the wear scars.

2.2.4 Surface Characterization of the Tribofilms

The tribofilm on the reference steel and rough steel flats was analyzed by XPS (X-ray Photoelectron Spectroscopy). The XPS equipment used was an ULVAC—PHI Versaprobe Spectrometer equipped with a monochromatized Al Kα X-ray source (1486.6 eV). The calibration of binding energy was done using Au $4f_{7/2}$ and Au $4f_{5/2}$ with known binding energies at 87.7 eV and 84 eV, respectively, following the calibration procedure provided by the manufacturer. A charge compensation system was used to compensate the charging effect. Additional charge correction was done by fixing the C 1*s* peak (C–C bond) at 284.8 eV. High-resolution spectra were obtained with a range of 20 eV and a pass energy of 23.5 eV for all the elements present in the tribofilm. All the peaks were fitted and analyzed using PHI Multipack software.

The morphology and the composition of the tribofilms formed on the reference steel and rough steel flats were investigated using TEM. FIB lamellas were prepared at Manutech-USD from a micron-sized part of the tribofilm. To mark the region where the focused ion beam (FIB) cut had to be made, an area was identified using SEM which showed the highest intensity of the elements desired in the tribofilm. To prepare the FIB lamella, a Pt layer was deposited as a protective layer and then Ga^+ ions were used for nanomachining. The subsequent thinning was carried out to make the lamella thin enough to be observed by TEM.

The microscope used to observe the FIB lamellas of the tribofilms was a FEI Titan Environmental Transmission Electron Microscope (ETEM), operating at 300 kV accelerating voltage. This ETEM is a Cs corrected instrument. The EDS data were recorded with an EDS detector manufactured by Oxford Instruments. Carbon contaminations were minimized by operating the ETEM in a high vacuum with an active cold-trap. Before each observation, a beam-shower was performed (magnification was reduced and the beam was used to illuminate the sample).

3 Results

3.1 Characterization of TiO_2 Nanoparticles

TEM micrographs in Fig. 2 show the morphology of the TiO_2 nanoparticles. The shape of the particles is ellipsoidal with hexagonal patches on the surface. They are also found to be nanocrystalline. The size of the TiO_2 nanoparticles is in the range of 25–50 nm. Some aggregates can also be seen (Fig. 2 left side).

3.2 Tribological Behavior of Reference Steel/Reference Steel Contact Lubricated with TiO_2 Nanoparticles

Friction trends for reference steel/reference steel contacts when lubricated with **BO**, **BO_0.5MoDTC**, **BO_0.5TiO$_2$** and **BO_0.5MoDTC_0.5TiO$_2$** are shown in Fig. 3.

The lubricant **BO_0.5TiO$_2$** shows a similar friction coefficient compared to **BO** alone ($\mu = 0.12$). The TiO_2 nanoparticles improved the friction modifier properties of the lubricant. The steady-state friction coefficient obtained for the reference steel/steel contact when lubricated with **BO_0.5MoDTC** was around 0.052. However, for **BO_0.5MoDTC_0.5TiO$_2$**, the friction coefficient decreased gradually and stabilized at the end of the test at around 0.039. This suggests that the addition of TiO_2 nanoparticles to the blend made of base oil and MoDTC had a positive effect on friction reduction in a reference steel/reference steel contact. The comparison of the average steady-state friction coefficient for various lubricants is shown in the

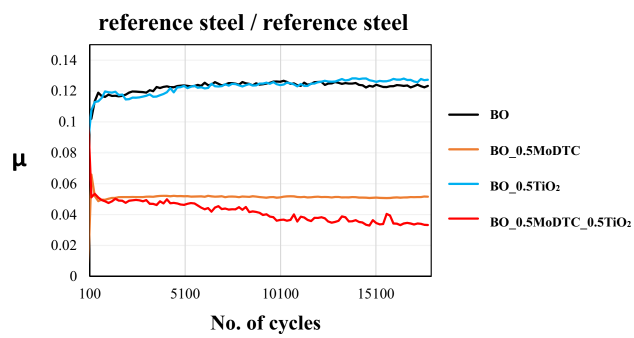

Fig. 3 Comparison of friction coefficients for the reference steel/reference steel contact with **BO**, **BO_0.5MoDTC**, **BO_0.5TiO$_2$**, **BO_0.5MoDTC** and **_0.5TiO$_2$**

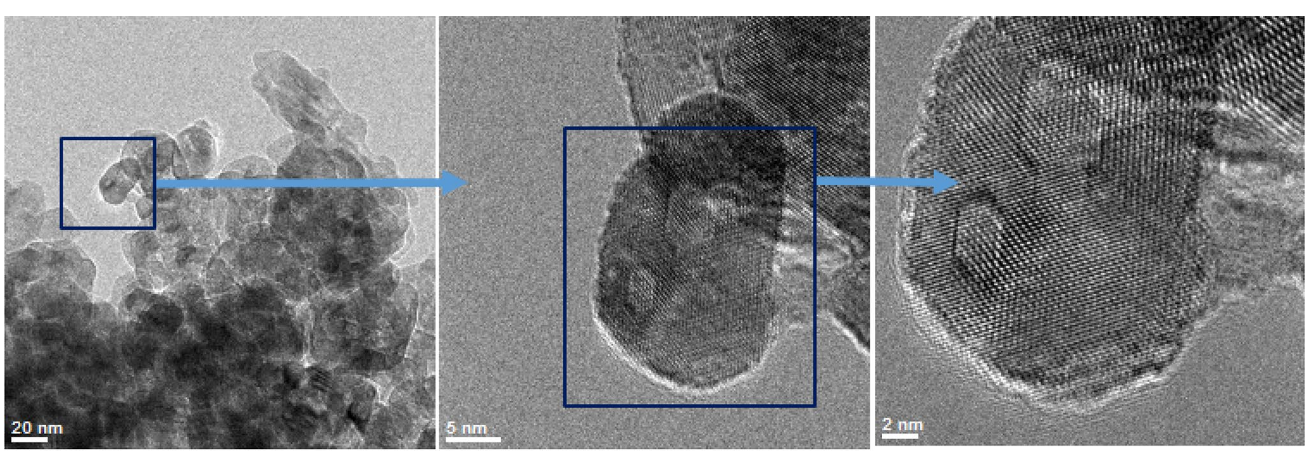

Fig. 2 TEM micrographs of TiO_2 nanoparticles

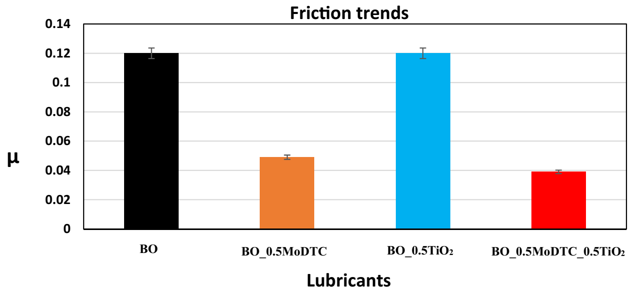

Fig. 4 Average steady-state friction coefficients (± standard deviation) for reference steel/reference steel contact when lubricated with **BO**, **BO_0.5MoDTC**, **BO_0.5TiO$_2$**, and **BO_0.5MoDTC_0.5TiO$_2$**

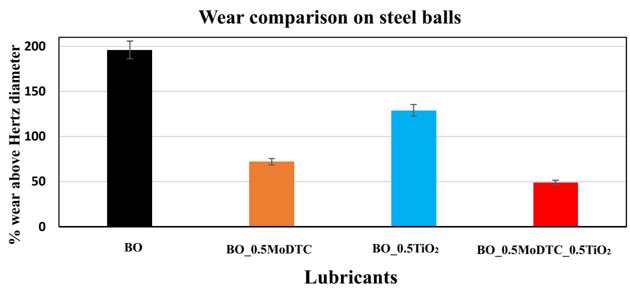

Fig. 5 Percentage of wear above the Hertz diameter (± standard deviation) on the steel ball for the reference steel/reference steel contact when lubricated with **BO**, **BO_0.5MoDTC**, **BO_0.5TiO$_2$** and **BO_0.5MoDTC_0.5TiO$_2$**. The Hertz diameter for the used test conditions is 125 µm

histogram in Fig. 4. The error (± standard deviation) shows the repeatability of the different friction tests.

The comparison of average wear for the reference steel/reference steel contact is shown in Fig. 5. The percentage of wear above the Hertzian diameter of steel balls (125 µm for the used test conditions) is compared for **BO**, **BO_0.5MoDTC**, **BO_0.5TiO$_2$**, and **BO_0.5MoDTC_0.5 TiO$_2$**.

The addition of 0.5 wt% of TiO_2 nanoparticles to base oil mixed with MoDTC (**BO_0.5MoDTC_0.5TiO$_2$**) reduced the wear compared to **BO_0.5MoDTC** and **BO_0.5TiO$_2$**. Significant wear reduction was also observed when TiO_2 nanoparticles were added to the base oil (**BO_0.5TiO$_2$**). As expected, the tests with base oil only (**BO**) showed the highest wear.

3.3 Surface Analysis of the Tribofilms

3.3.1 XPS Analysis on the Reference Steel Flats

XPS analyses were carried out to investigate the differences in tribological behavior observed in the reference steel/reference steel contacts. The high-resolution Mo3*d* and S2*p* XPS spectra inside the tribofilm on the reference steel flats lubricated with **BO_0.5MoDTC** and **BO_0.5MoDTC_0.5TiO$_2$** are shown in Fig. 6.

As can be seen, the high-resolution Mo3*d* peak is divided into three different contributions—MoS_2 (Binding energy = 229.0 ± 0.2 eV), MoS_xO_y (Binding Energy = 229.7 ± 0.2 eV) and MoO_3 (B.E = 232 ± 0.2 eV). The Mo3*d* peak is fitted with various possibilities and that with the lowest chi square value is used for the analysis. The error for the binding energies is 0.5 eV. Fitting is done using the binding energy values assigned to the different contributions in the literature for sulfide, sulfates, oxysulfide (thin films) and Mo oxide [22]. In addition, the FWHM (Full-Width Half Max) values for all the contributions are close to each other and the same for the doublet peaks of different Molybdenum contributions. The S2*s* part in the Mo3*d* peak is also fitted taking into account the binding energy fitted for the sulfide contribution in the S2*p* peak.

It was found that the tribochemistry observed was different for each lubricant, which was in agreement with the friction behavior obtained. Previously, it was shown that the presence of oxy-sulfides in the tribofilms induces a slightly higher friction coefficient than when pure MoS_2 is found [22]. Therefore, for the contact lubricated with **BO_0.5MoDTC**, the presence of Mo-oxysulfide explained the higher friction coefficient of 0.052 compared to the case when nanoparticles were added in the lubricant. For the contact lubricated with **BO_0.5MoDTC_0.5TiO$_2$**, only MoS_2 and MoO_3 were formed inside the tribofilm with no oxysulfides, which was in agreement with the friction behavior. The steady-state friction coefficient decreased until it reached the value of 0.039 at the end of the test. The S2*p* peaks showed sulfide and sulfate contributions when the contact was lubricated with **BO_0.5MoDTC**. However, only the contribution of sulfide was observed when the contact was lubricated with **BO_0.5MoDTC_0.5TiO$_2$**. The contribution of sulfate observed at 168 eV in the S2*p* peak in the case of BO_0.5MoDTC was much lower in S2*s* compared to the Mo3*d* contributions and so did not affect the overall fit of the Mo3*d* peak. A very similar friction coefficient and tribochemistry were observed in the case of the steel ball / TiO_2 APS flat contact under similar conditions [23].

3.3.2 FIB-TEM Analysis on the Steel Ball and Steel Flat

To confirm the presence and investigate the morphology of MoS_2 flakes and TiO_2 nanoparticles present in the tribofilm, FIB-TEM was carried out on a small region of the tribofilm on the reference steel flat when lubricated with **BO_0.5MoDTC_0.5TiO$_2$**. In the TEM images shown in Fig. 7a, it is clear that MoS_2 flakes are formed in layers and are intermixed with TiO_2 nanoparticles. TiO_2 nanoparticles can be clearly observed due to different atomic

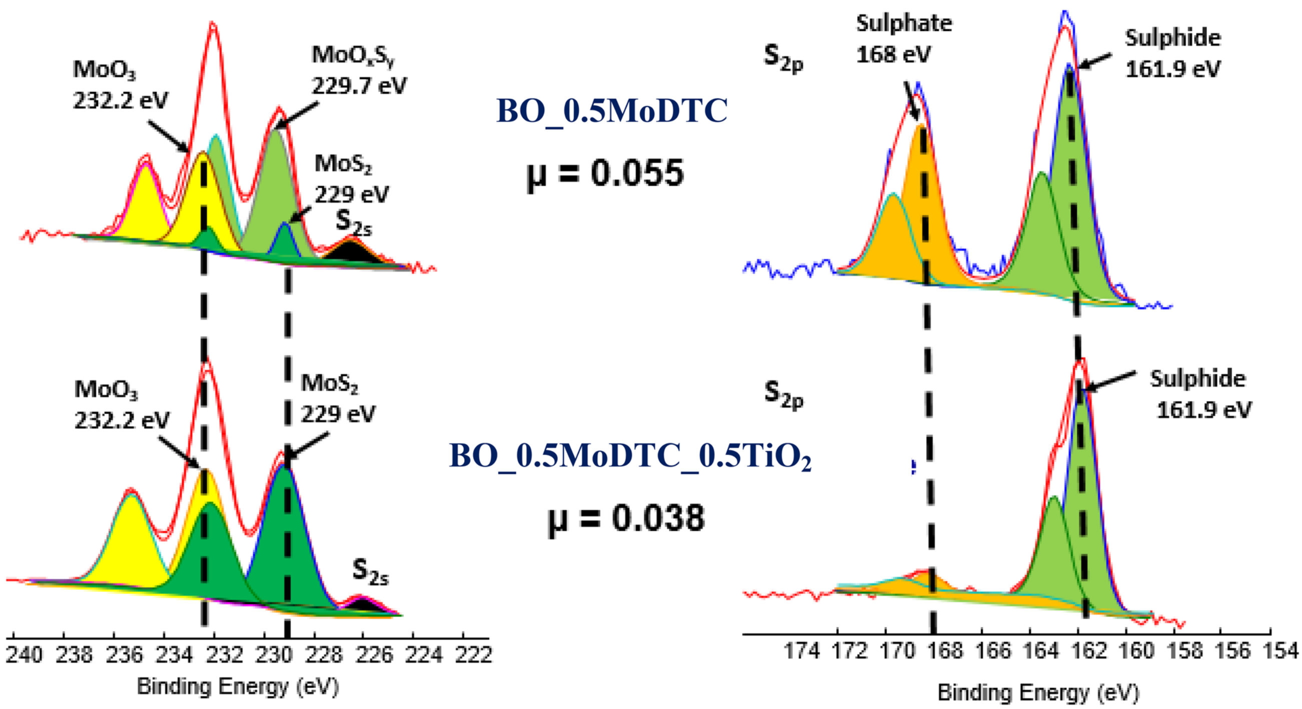

Fig. 6 High-resolution XPS spectra for reference steel flats lubricated with **BO_0.5MoDTC** and **BO_0.5MoDTC_0.5TiO$_2$** in contact against reference steel balls

arrangements (hexagonal), morphologies and shapes (circular or ellipsoidal) compared to MoS_2. The tribofilm (about 50–60 nm thick) is made of two to five layers of MoS_2 flakes and TiO_2 anatase nanoparticles. It is thicker than the tribofilm obtained with **BO_0.5MoDTC** on TiO_2 APS coating. The magnified images in Fig. 7a show MoS_2 flakes and TiO_2 nanoparticles which are clearly distinguishable. This is in agreement with the XPS results that show the formation of MoS_2 in the tribofilm.

To confirm the presence of MoS_2 and TiO_2 nanoparticles in the tribofilm, EDS mapping was carried out on the steel ball (Fig. 8a, b). Maps were recorded from the rectangular area inside the image shown in Fig. 8a. This area includes a small part of the substrate (steel) and tribofilm (MoS_2 flakes and TiO_2 nanoparticles).

From the individual elemental maps, it can be observed that Ti (orange) and O (green) are both present in the form of circular patches along with MoS_2 in the tribofilm zone. This suggests that the MoS_2 flakes and TiO_2 nanoparticles are both present in the tribofilm. The top part of the FIB cross-section is the Pt protection layer which can be observed in Fig. 8b. A substrate consisting of Fe and O can be seen at the top of the elemental mapping image. These elemental maps confirm that a thick tribofilm composed of layers of MoS_2 and TiO_2 nanoparticles is formed on the steel ball.

3.4 Effect of Changing Concentrations of TiO_2 Nanoparticles and MoDTC on the Tribological Behavior of the Reference Steel/Reference Steel Contact

Considering the better friction results obtained with **BO_0.5MoDTC_0.5TiO$_2$**, concentrations of TiO_2 nanoparticles and MoDTC in base oil were reduced from 0.5 to 0.1 wt%. Similar test conditions were used.

The comparison of friction results for reference steel/reference steel for various concentrations of both TiO_2 nanoparticles and MoDTC (0.1 wt% and 0.1 wt% versus 0.5 wt% and 0.5 wt%, respectively) is shown in Fig. 9. When the concentrations of MoDTC and TiO_2 nanoparticles are lowered from 0.5 to 0.1 wt%, an induction time before reaching low friction is observed. However, this induction time is reduced in the presence of TiO_2 nanoparticles and MoDTC (**BO_0.1MoDTC_0.1TiO$_2$**) compared to **BO_0.1MoDTC**. The steady-state friction coefficient is still low even when 0.1 wt% MoDTC and 0.1 wt% TiO_2 nanoparticles are used in the base oil (**BO_0.1MoDTC_0.1TiO$_2$**).

3.5 Effect of Roughness on Tribological Behavior

Aldana et al. [17] observed that rough materials showed better friction coefficients when lubricated with nanoparticles

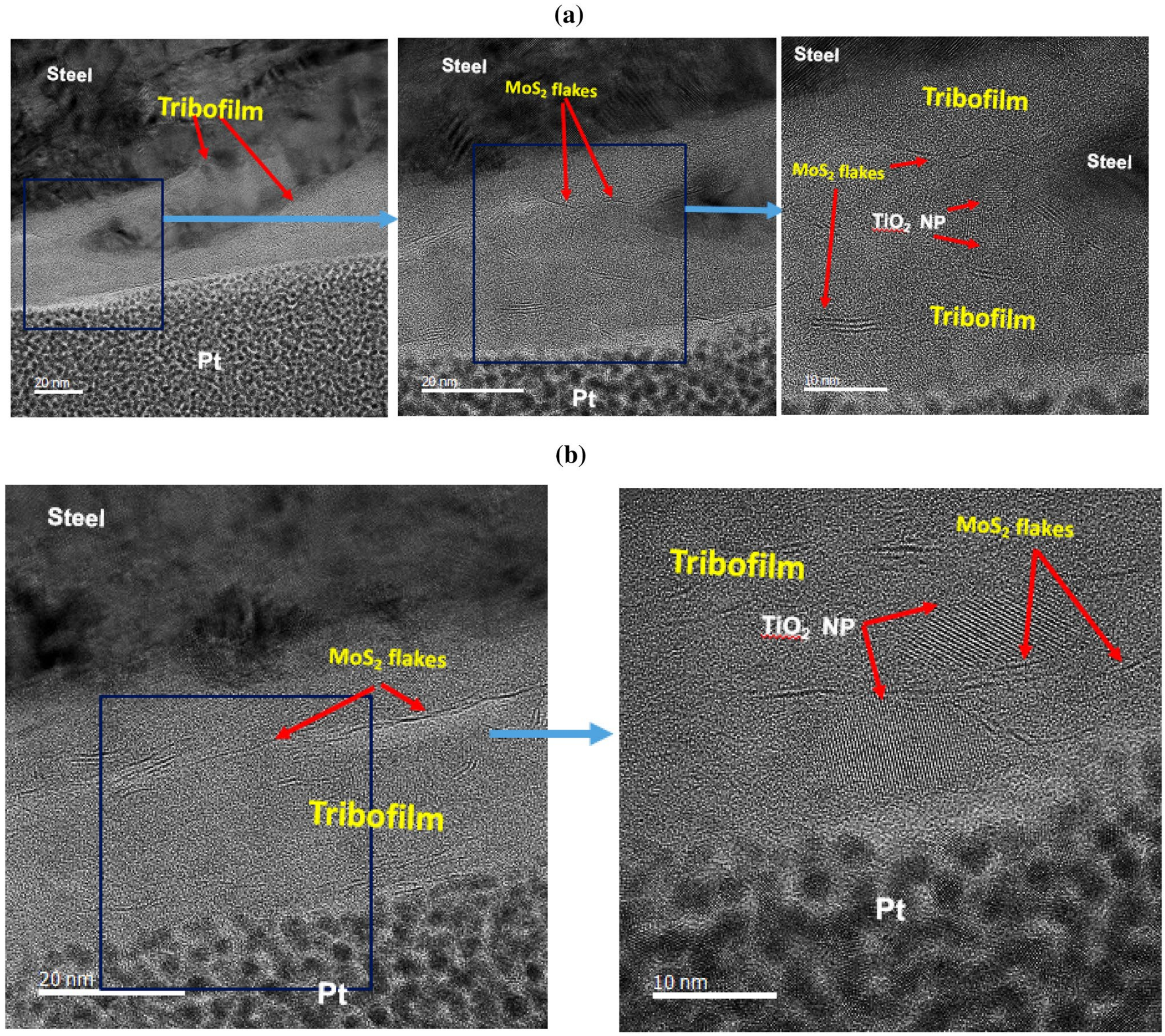

Fig. 7 **a** TEM micrographs of the FIB lamella from the tribofilm on the reference steel flat; **b** Magnified TEM images showing MoS_2 flakes and TiO_2 anatase nanoparticles on the steel ball

as the roughness grooves help to store nanoparticles. Therefore, to study the effect of roughness using the blend of **BO_0.5MoDTC_0.5TiO₂**, rough steel APS coating was used instead of a reference steel flat. The average roughness parameter ($R_{a\ rough\ steel}=0.19$ µm) was much higher than that of the reference steel flat ($R_{a\ ref.}=0.01$ µm). Therefore, the lambda ratio was lower for the reference steel/rough steel contact compared to the reference steel/reference steel contact.

Friction curves with and without the addition of various concentrations of MoDTC and TiO_2 nanoparticles are shown in Fig. 10. Regarding the results discussed before, the steady-state friction coefficient obtained was 0.039 for reference steel/reference steel contact when lubricated with **BO_0.5MoDTC_0.5TiO₂**. However, the steady-state friction coefficient was found to be much lower ($\mu=0.031$) for the reference steel/rough steel contact when lubricated with the same lubricant. Similarly, when the concentration of MoDTC and TiO_2 nanoparticles was reduced to 0.1 wt%, lower steady-state friction coefficient was observed in the reference steel/rough steel contact compared to the reference steel/reference steel contact and no induction time was observed.

To understand the differences in terms of friction behavior, XPS analysis was carried out on the tribofilm formed in the reference steel/rough steel contact with the **BO_0.5MoDTC_0.5TiO₂** lubricant (cf. Fig. 11). It was found that the tribochemistry was similar to that observed

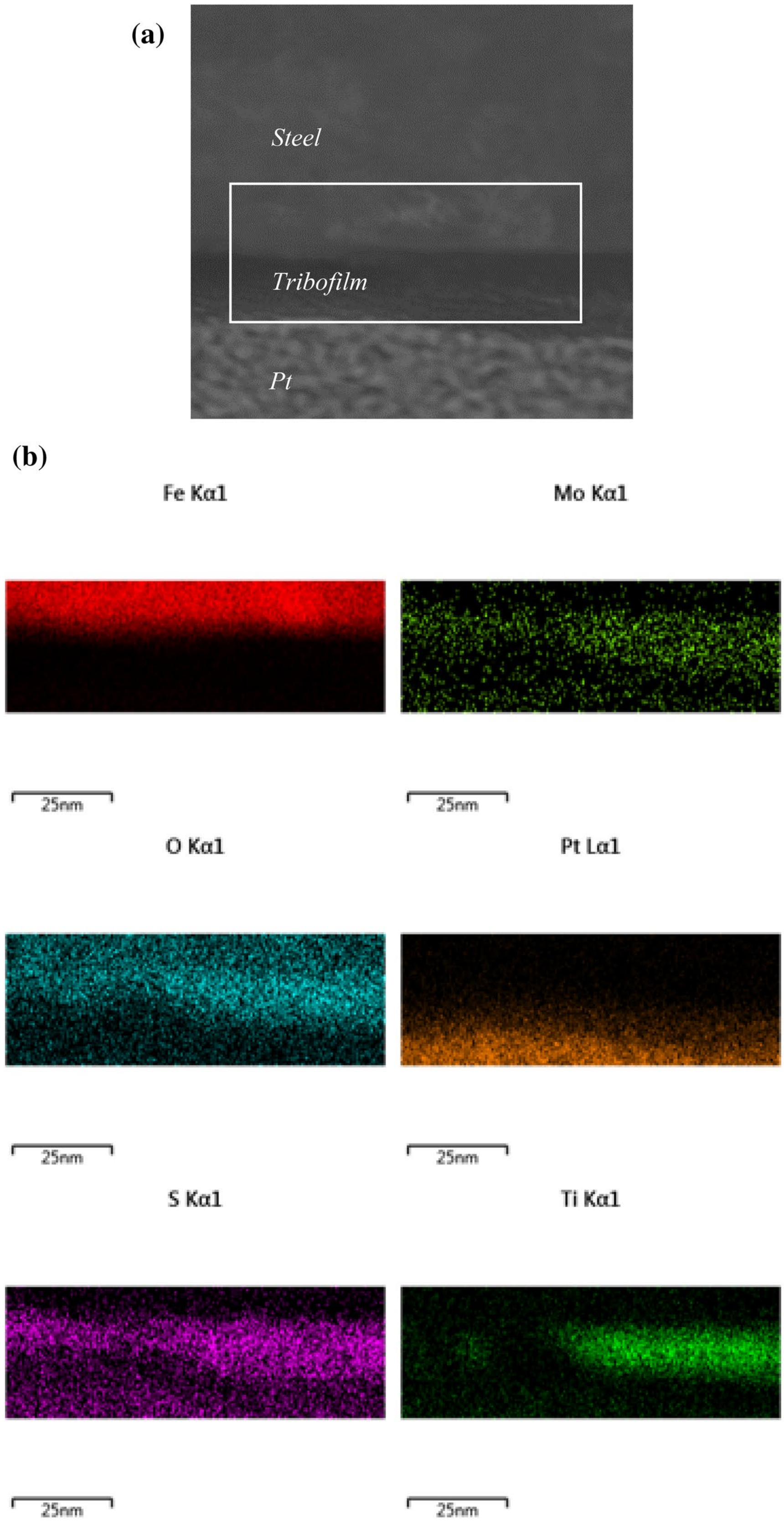

Fig. 8 **a** TEM-EDS image for maps on the steel ball; **b** TEM-EDS maps for the image shown in (**a**) (Color figure online)

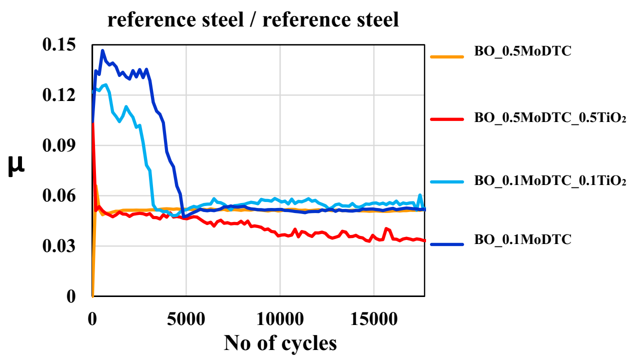

Fig. 9 Friction behaviors for reference steel/reference steel contacts when lubricated with **BO_0.5MoDTC**, **BO_0.5MoDTC_0.5TiO$_2$**, **BO_0.1MoDTC**, and **BO_0.1MoDTC_0.1TiO$_2$**

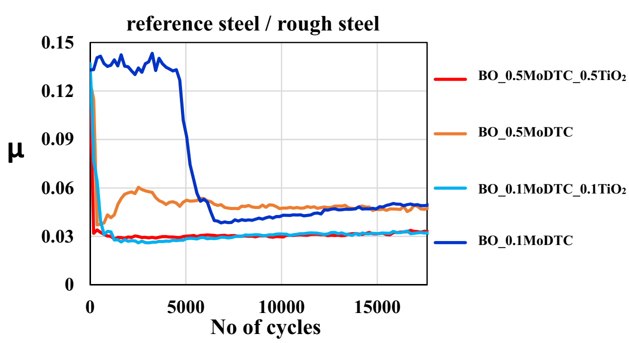

Fig. 10 Friction behavior for the reference steel/rough steel contact lubricated with **BO_0.5MoDTC**, **BO_0.5MoDTC_0.5TiO$_2$**, **BO_0.1MoDTC**, and **BO_0.1MoDTC_0.1TiO$_2$** (Color figure online)

for the reference steel flat with the same lubricant. A strong contribution of MoS_2 was found in the Mo3d peak.

FIB-TEM was carried out in an in-depth investigation of the structure and the composition of the tribofilm formed on the rough steel flat. Figure 12 shows the SEM micrograph of the area where the FIB cut was performed (green line). SEM–EDS was performed to determine the distribution of the elements in the tribofilm. As can be seen MoS_2 flakes as well as TiO_2 nanoparticles are present in this area.

From the TEM images shown in Fig. 13, it is clear that MoS_2 flakes are formed in layers and intermixed with a few TiO_2 nanoparticles which are not clearly visible since they are few in number. TiO_2 nanoparticles (TiO_2 NP) can be distinguished due to their different crystal structure compared to MoS_2.

The blue rectangular area inside the image shown in Fig. 14 was used for EDS maps. This area includes a small part of the substrate (steel), tribofilm (MoS_2 flakes and TiO_2 nanoparticles), Pt protection layer and an open crack.

The individual elemental maps of Ti, O, Fe and Mo clearly show that Ti (green) and O (red) are not only present in circular patches at the beginning of the crack at higher intensity but also in the tribofilm. Mo and S are also present in the tribofilm and inside the crack.

4 Discussion

The most important result obtained in this work was that when TiO_2 nanoparticles were blended with MoDTC in base oil, there was a significant reduction in the steady-state friction coefficient compared to MoDTC alone, even when the concentration of particles and MoDTC was reduced to 0.1 wt%. Further reduction in

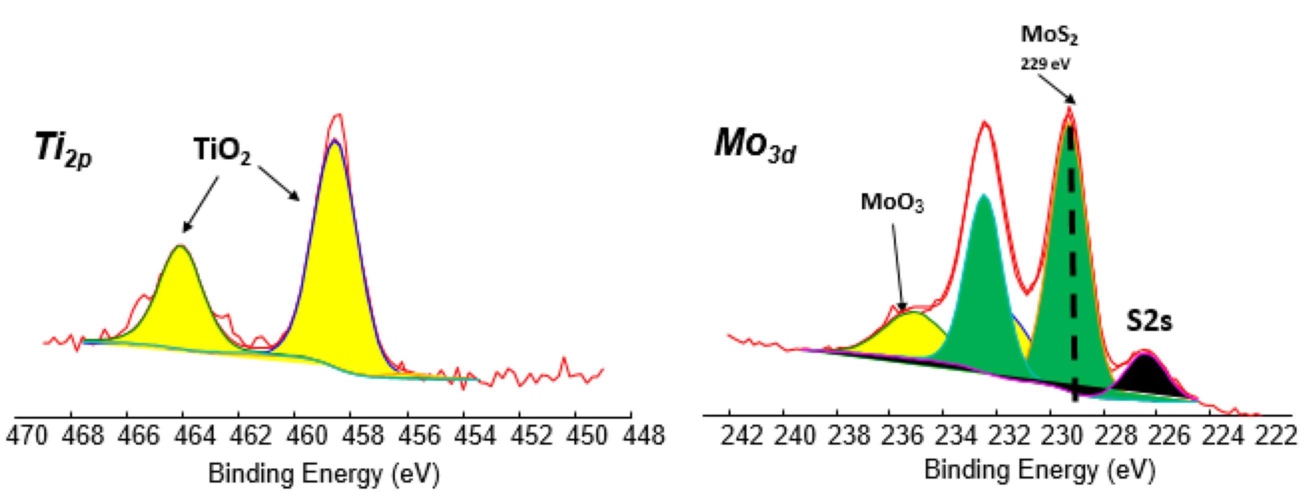

Fig. 11 XPS high-resolution spectra for Ti2*p* and Mo3*d* obtained on the rough steel flat tested against the steel ball with **BO_0.5MoDTC_0.5TiO$_2$**

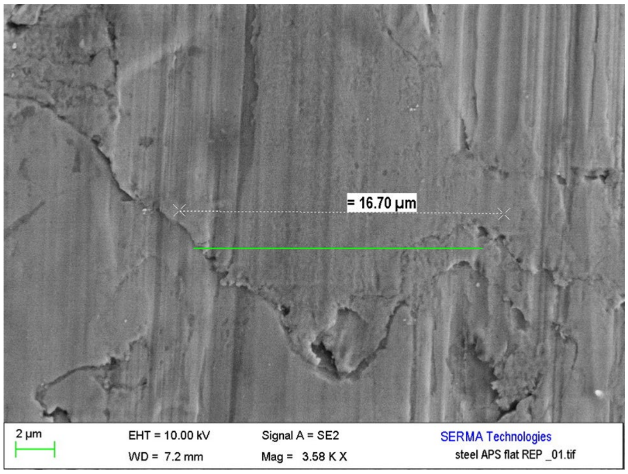

Fig. 12 SEM micrograph of the zone where the FIB cut was carried out on the rough steel flat tested against the steel ball with **BO_0.5MoDTC_0.5TiO$_2$** (Color figure online)

the friction coefficient was observed when the reference steel flat ($R_a \approx 10$ nm) was replaced by a rough steel flat ($R_a \approx 200$ nm). The reasons and mechanisms involved regarding the low friction coefficient obtained when lubrication was provided using the blend of anatase TiO_2 nanoparticles and MoDTC in base oil are discussed in the following.

4.1 Tribochemistry and Morphology of MoS_2

The primary reason for the reduction of the friction coefficient was the formation of a MoS_2 tribofilm without any oxysulfides, which was revealed by surface characterization of the tribofilm using XPS. The various compounds observed inside the tribofilms on the reference steel flat for two different lubricants are summarized in Table 4.

TEM analysis on the FIB lamella showed the formation of MoS_2 flakes throughout the 50–60-nm-thick tribofilm and which were responsible for reducing friction. The tribofilm was composed of layers of MoS_2 flakes and TiO_2 nanoparticles.

Therefore, the friction reduction with BO–MoDTC–TiO_2 blends could be attributed to the presence of MoS_2 flakes without oxysulfides.

4.2 Mechanisms

Similar friction reduction results were obtained in a previous work [24] in which a TiO_2 APS coating was lubricated with MoDTC in base oil. It was shown that the mechanism responsible for such friction reduction was a preferential conversion of MoDTC additive to form MoS_2 and MoO_3 in the presence of TiO_2 due to the tribocatalytic behavior of the TiO_2 APS coating. Similar tribocatalytic behavior to that of a TiO_2 APS coating could be obtained in the presence of TiO_2 nanoparticles and MoDTC, and for the

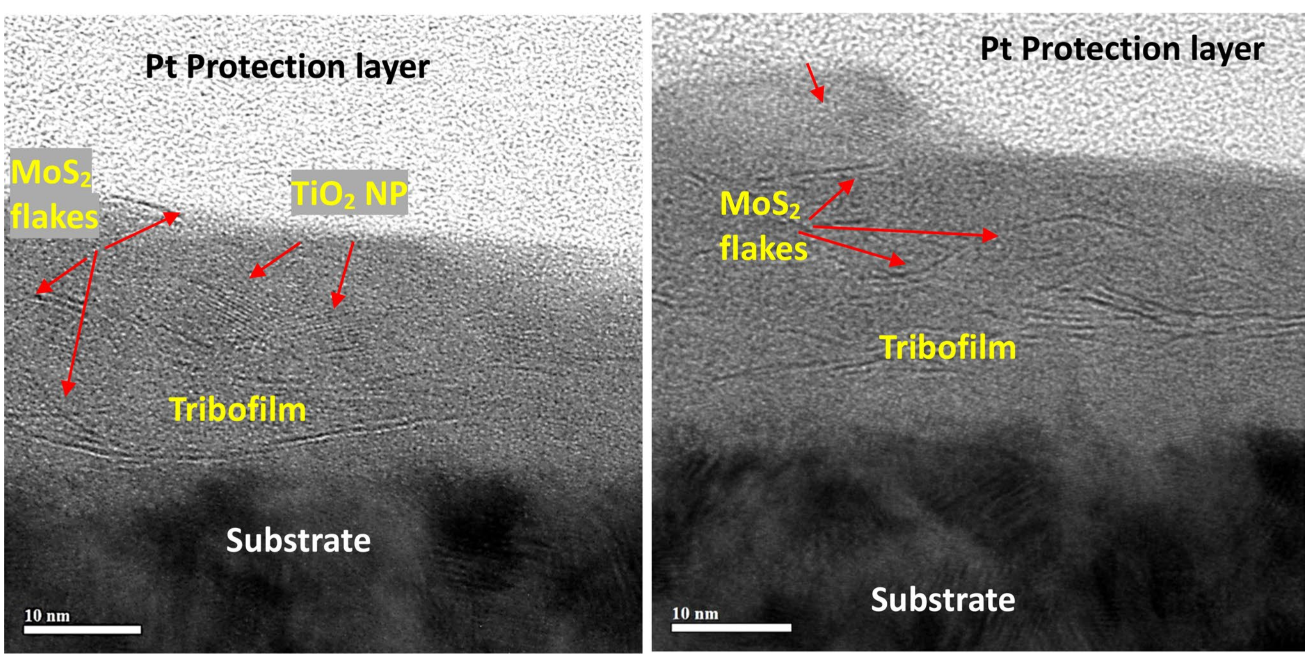

Fig. 13 TEM micrographs of the FIB lamella cut from the tribofilm on the rough steel flat tested against the steel ball with **BO_0.5MoDTC_0.5TiO$_2$**

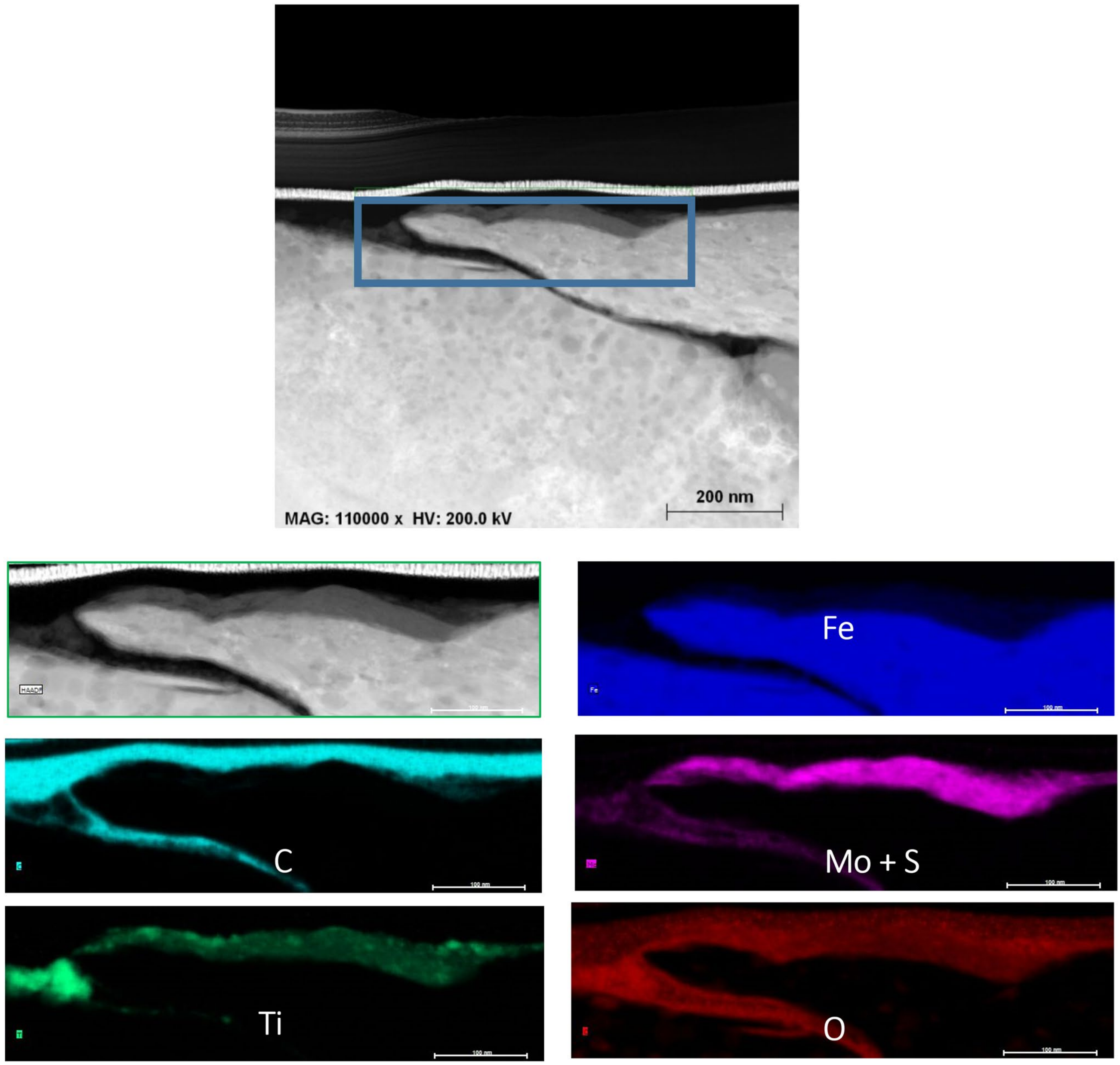

Fig. 14 TEM–EDX image on FIB cut from the tribofilm obtained on the rough steel flat tested against the steel ball with **BO_0.5MoDTC_0.5TiO$_2$** and the corresponding TEM EDX maps

Table 4 List of different compounds formed in the various tribofilms for the steel/steel contacts tested in this work, whatever the roughness

Lubricant	Tribofilm composition
BO_0.5MoDTC	$MoS_2 + MoO_xS_y + MoO_3$, TiO_2, sulphates
BO_0.5MoDTC_0.5TiO$_2$	$MoS_s + MoO_3$, TiO_2, No sulphates

reference steel/reference steel as well as the reference steel/rough steel contacts.

In the case of the reference steel/rough steel contact lubricated with base oil with TiO_2 nanoparticles and MoDTC, the friction coefficient was found to be lower than with the “smoother” reference steel/reference steel contact. The induction time was found to be shorter, which suggests that the decomposition of MoDTC was favored compared to MoDTC alone. This could also be attributed to rough surfaces which lead to more severe contact conditions between asperities, leading to faster conversion of MoDTC into MoS_2.

Previously, in the case of rough contacts, Aldana et al. [27] showed that nanoparticles of WS_2 filled in the roughness grooves and led to a lower friction coefficient. In this case, since the roughness parameters such as R_a, R_{pk} and R_{vk} for rough steel were higher ($R_s = 0.2$ µm, $R_{pk} = 0.22$ µm and $R_{vk} = 0.25$ µm) than those of the reference steel, it could be expected that the 25–40 diameter nanoparticles could easily penetrate the roughness grooves as well as the pores and open cracks present in the coating. These "surface defects" appear to act as reservoirs, delivering TiO_2 nanoparticles and MoDTC throughout the friction test for better lubrication. However, the FIB-TEM cut carried out in the tribofilm on the open crack revealed the latter was partially filled by intermixed TiO_2 nanoparticles and MoS_2 flakes. Therefore, it is difficult to confirm that the considerable reduction of friction in the reference steel/rough steel contact could be due only to the filling of "surface defect reservoirs".

Therefore, the mechanism responsible for the remarkable reduction of friction in the case of the reference steel/rough steel contact could be due to the combined effect of increasing the severity of the contact in the boundary lubrication regime, with the filling of surface defect reservoirs by nanoparticles and the tribocatalytic behavior of TiO_2 nanoparticles in the presence of MoDTC.

5 Conclusion

(1) A stable dispersion was formed by blending 0.5 wt% TiO_2 anatase nanoparticles with 0.5 wt% Molybdenum DiThioCarbamate (MoDTC) in base oil.

(2) The blend containing 0.5 wt% MoDTC and 0.5 wt% TiO_2 nanoparticles showed lower friction reduction capabilities when used in the steel/steel contact compared to blends containing only 0.5 wt% MoDTC. This low-friction behavior obtained in the case of blends containing both TiO_2 nanoparticles and MoDTC was attributed to the formation of long MoS_2 flakes without oxysulfides.

(3) A further reduction of the wear is observed when TiO_2 nanoparticles are added to MoDTC, thus consistent with the low friction observed with the blend containing 0.5 wt% MoDTC and 0.5 wt% TiO_2 nanoparticles.

(4) Reducing the concentration of both TiO_2 nanoparticles and MoDTC from 0.5 to 0.1 wt% in the steel/steel contact still led to a low friction coefficient although an induction time was required.

(5) These results suggest that adding a small amount of TiO_2 nanoparticles to MoDTC in base oil favored the decomposition of MoDTC to form MoS_2 due to the tribocatalytic properties of TiO_2, thereby leading to a lower friction coefficient.

(6) Considerable friction reduction capabilities were obtained when rougher flat samples were used in the presence of a blend containing both MoDTC and TiO_2 nanoparticles. This was attributed to the combined effect of increasing the severity of the contact, filling the "surface defect reservoirs" by nanoparticles and the tribocatalytic behavior of TiO_2 nanoparticles in the presence of MoDTC.

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References

1. Dai, W., Kheireddin, B., Gao, H., Liang, H.: Roles of nanoparticles in oil lubrication. Tribol. Int. **102**, 88–98 (2016)
2. Sahoo, R.R., Biswas, S.K.: Effect of layered MoS_2 nanoparticles on the frictional behavior and microstructure of lubricating greases. Tribol. Lett. **53**, 157–171 (2014)
3. Kogovšek, J., Kalin, M.: Various MoS_2, WS_2 and C based micro- and nanoparticles in boundary lubrication. Tribol. Lett. **53**, 585–597 (2014)
4. Hernández Battez, A., González, R., Viesca, J.L., Fernández, J.E., Díaz Fernández, J.M., Machado, A., Chou, R., Riba, J.: CuO, ZrO_2 and ZnO nanoparticles as antiwear additive in oil lubricants. Wear **265**, 422–428 (2008)
5. Hernández Battez, A., Viesca, J.L., González, R., Blanco, D., Asedegbega, E., Osorio, A.: Friction reduction properties of a CuO nanolubricant used as lubricant for a NiCrBSi coating. Wear **268**, 325–328 (2010)
6. Maharaj, D., Bhushan, B.: Effect of MoS_2 and WS_2 nanotubes on nanofriction and wear reduction in dry and liquid environments. Tribol. Lett. **49**, 323–339 (2013)
7. Rapoport, L., Fleischer, N., Tenne, R.: Applications of WS_2 (MoS_2) inorganic nanotubes and fullerene-like nanoparticles for solid lubrication and for structural nanocomposites. J. Mater. Chem. **15**, 1782–1788 (2005)
8. Wu, Y.Y., Tsui, W.C., Liu, T.C.: Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. Wear **262**, 819–825 (2007)
9. Ali, M.K.A., Xianjun, H., Mai, L., Qingping, C., Turkson, R.F., Bicheng, C.: Improving the tribological characteristics of piston ring assembly in automotive engines using Al_2O_3 and TiO_2 nanomaterials as nano-lubricant additives. Tribol. Int. **103**, 540–554 (2016)
10. Joly-Pottuz, L., Dassenoy, F., Belin, M., Vacher, B., Martin, J.M., Fleischer, N.: Ultralow-friction and wear properties of IF-WS_2 under boundary lubrication. Tribol. Lett. **18**, 477–485 (2005)
11. Joly-Pottuz, L., Vacher, B., Ohmae, N., Martin, J.M., Epicier, T.: Anti-wear and friction reducing mechanisms of carbon nano-onions as lubricant additives. Tribol. Lett. **30**, 69–80 (2008)
12. Tannous, J., Dassenoy, F., Lahouij, I., Le Mogne, T., Vacher, B., Bruhács, A., Tremel, W.: Understanding the tribochemical mechanisms of IF-MoS_2 nanoparticles under boundary lubrication. Tribol. Lett. **41**, 55–64 (2011)

13. Lahouij, I., Dassenoy, F., De Knoop, L., Martin, J.M., Vacher, B.: In Situ TEM observation of the behavior of an individual fullerene-like MoS2 nanoparticle in a dynamic contact. Tribol. Lett. **42**, 133–140 (2011)
14. Ingole, S., Charanpahari, A., Kakade, A., Umare, S.S., Bhatt, D.V., Menghani, J.: Tribological behavior of nano TiO_2 as an additive in base oil. Wear **301**, 776–785 (2013)
15. Dassenoy, F.: Nanoparticles as additives for the developement of high performance and environmentally friendly engine lubricants. Tribology **14**, 237–253 (2019)
16. Wu, H., Qin, L., Dong, G., Hua, M., Yang, S., Zhang, J.: An investigation on the lubrication mechanism of MoS_2 nano sheet in point contact: the manner of particle entering the contact area. Tribol. Int. **107**, 48–55 (2017)
17. Aldana, P.U., Dassenoy, F., Vacher, B., Le Mogne, T., Thiebaut, B.: WS2 nanoparticles anti-wear and friction reducing properties on rough surfaces in the presence of ZDDP additive. Tribology Int. **102**, 213–221 (2016)
18. Tao, X., Jiazheng, Z., Kang, X.: The ball-bearing effect of diamond nanoparticles as an oil additive. J. Phys. D **29**, 2932–2937 (1996)
19. Shenoy, B.S., Binu, K.G., Pai, R., Rao, D.S., Pai, R.S.: Effect of nanoparticles additives on the performance of an externally adjustable fluid film bearing. Tribol. Int. **45**, 38–42 (2012)
20. Grossiord, C., Varlot, K., Martin, J.M., Le Mogne, T., Esnouf, C., Inoue, K.: MoS_2 single sheet lubrication by molybdenum dithiocarbamate. Tribol. Int. **31**, 737–743 (1998)
21. Khaemba, D.N., Neville, A., Morina, A.: New insights on the decomposition mechanism of Molybdenum DialkyldiThioCarbamate (MoDTC): a Raman spectroscopic study. R. Soc. Chem. Adv. **6**, 38637–38646 (2016)
22. De Feo, M., Minfray, C., De Barros Bouchet, M.I., Thiebaut, B., Le Mogne, Th., Vacher, B., Martin, J.M.: Ageing impact on tribological properties of MoDTC-containing base oil. Tribol. Int. **92**, 126–135 (2015)
23. Deshpande, P., Minfray, C., Dassenoy, F., Thiebaut, B., Le Mogne, T., Vacher, B., Jarnias, F.: Tribological behaviour of TiO_2 Atmospheric Plasma Spray (APS) coating under mixed and boundary lubrication conditions in presence of oil containing MoDTC. Tribol. Int. **118**, 273–286 (2018)
24. Deshpande, P., Minfray, C., Dassenoy, F., Le Mogne, T., Jose, D., Cobian, M.: Tribocatalytic behaviour of a TiO_2 atmospheric plasma spray (APS) coating in the presence of the friction modifier MoDTC : a parametric study. R. Soc. Chem. Adv. **8**, 15056–15068 (2018)
25. Ernst, P., Distler, B.: Optimizing the cylinder running surface/piston system of internal combustion engines towards lower emissions. SAE Tech. Pap. **4**, 1–16 (2012)
26. Hamrock, B.J., Dowson, D.: Isothermal elastohydrodynamic lubrication of point contacts: Part 4—Starvation results. ASME J. Lubr. Technol. **99**, 15–23 (1977)
27. Aldana, P.U., Dassenoy, F., Vacher, B., Le Mogne, T., Thiebaut, B.: WS_2 nanoparticles anti-wear and friction reducing properties on rough surfaces in the presence of ZDDP additive. Tribol. Int. **102**, 213–221 (2016)