Mechanism of interactions between MoS_2 nanotubes and conventional oil additives under various contact conditions

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1. Introduction

Nanoparticles in tribology have attracted considerable attention because of their excellent physical and chemical properties. When nanoparticles are dispersed into different base liquids, they will greatly enhance their thermal conductivity and tribological performance. The use of transition metal dichalcogenides nanoparticles in oils is an emerging concept in lubrication, to enhance tribological properties of lubricants, such as load-carrying capacity, anti-wear, and friction-reducing properties between moving mechanical components [1]. However, modern industrial elements require additionally other properties such as oxidation and corrosion protection or sludge control to provide a comprehensive protection against degradation. As a consequence, the use of conventional additives as extreme pressure (EP) and anti wear (AW) additives are typically adopted to improve the tribological performance of a liquid lubricants in reducing surface damage under severe conditions [2].

This study aims to characterize the effect of conventional additives, such as AW, EP, detergents and dispersants on MoS_2 nanotubes (NTs) performance under various contact conditions.

The tribological results under reciprocating sliding show synergetic interactions between MoS_2 nanotubes with selected anti-wear and detergents additives, slight synergy with extreme-pressure additives and antagonistic interactions with selected dispersants. On the other, under extreme pressure conditions all selected additives provide synergistic effects with MoS_2 nanotubes. The synergistic and antagonistic mechanisms are investigated using several analytical techniques and discussed in terms of the different tribofilm chemistry.[3].

2. Experimental

2.1. Materials & Lubricants

The test specimens used for SRV® and Brugger tribological tests were AISI 52100 steel. Balls and discs for SRV® tests have hardness of 850 HV10 and roughness Ra = 0.05 µm. The test specimens used for Brugger tribological tests were friction ring (Ø=25 mm) with hardness of 60 HRC and roughness Ra < 0.8 µm and a test cylinder (Ø=8 mm) with hardness of 65 HRC and roughness Ra < 0.2 µm. Specimens used for Mini-Traction Machine (MTM) tests were made of AISI 52100 steel (PCS instruments, London, UK). The initial disc and ball roughness was Ra = 0.01 µm, and their diameters were 46 mm and 19.05 mm, respectively.

The base oil used in this study was PAO 4 having a viscosity of 24.6 mm^2/s at 40 °C. The zinc dialkyl dithiophosphate ZDDP used as AW additive had a primary alkyl structure, with 99% purity. Sulphurized olefin polysulphide (40% of sulphur content) was used as the EP additive. Succinimide dispersant was based on long chained hydrocarbon amines with 2000 molecular weight and overbased Ca- sulfonate was used as detergent. The nanotubes (NTs) investigated in this study were synthesized from $Mo_8S_2I_8$ nanowires by the procedure reported in [4]. The diameter of the NTs is in a range 100–150 nm (Fig. 1a and b), while their length is up to 3 µm. The walls of the NTs are approx. 10 nm thick and form dome terminations. The base oil, additives and NTs used in this study were blended into following mixtures shown in Table 1, applying an ultrasonic processor VC 505 Sonics & Materials.

Table 1 Overview of the mixtures MoS_2 nanotubes with selected oil additives

Blend Designation	MoS_2 NTs	Additive
PAO	-	-
PAO+NTs	5%	-
PAO+AW	-	2% ZDDP
PAO+AW+NTs	5%	2% ZDDP
PAO+EP	-	2% EP
PAO+EP+NTs	5%	2% EP
PAO+disp	-	5% Dispersant
PAO + disp +NTs	5%	5% Dispersant
PAO+det	-	5% Detergent
PAO+det+NTs	5%	5% Detergent

2.2. Tribological test set up

SRV® reciprocating sliding tribotests

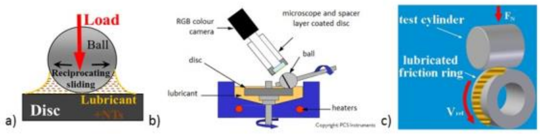
The ball-on-disc tests were performed using a SRV® tribometer (Optimol Instruments Prüftechnik GmbH, Germany), where a 10 mm diameter steel ball was loaded and reciprocated against a stationary steel disc under boundary lubricated, pure sliding condition (Fig. 1a). The oscillation frequency was 10 Hz and the stroke 1.5 mm. All tests parameters are listed in Fig. 1d.

Mini-Traction Machine (MTM) tribotests

MTM creates a mixed rolling/sliding contact between an independently driven ball and disc. The disc was immersed in a lubricant bath, and the ball was loaded against the face of the disc (Fig. 1b) with normal load of 35 N, which corresponds to mean Hertzian contact pressure of 0.7GPa. In order to evaluate the tribofilm with MTM, the effect of running-in was performed at following steps:

- An initial Stribeck curve was taken at room temperature (20 °C), with the mean contact velocity decreasing from 3.2 to 0.002 m/s (transition from hydrodynamic to boundary lubrication regime) and with SRR (Slide to Roll Ratio) 50%.
- Running-in: a long-duration 2 hours test at a constant mean velocity of 0.05 m/s.
- Final Stribeck test under the same conditions as those employed initially.

The MTM was equipped with an optical interferometry module for imaging an additive derived film on the surface. The tests parameters are summarised in Fig. 1d.



d)

	SRV® test	MTM test	Brugger-test
Stroke	1.5 mm	46 mm	78.5 mm
Speed	0.04 m/s	0.05 m/s	1.25 m/s
Normal Load	25 N	35 N	400 N
Mean contact pressure	0.9 GPa	0.7 GPa	1.4 GPa
Temperature	40°C	20°C	20°C
Test duration	2 hours	2 hours	30 sec

Fig. 1 Schematic of the experimental set-up a) SRV, b) MTM, c) Brugger d) summary of the testing parameters.

Brugger tribotests

The Brugger-test is a standardized method for determining the lubrication ability of additivated oils. The Brugger test is known to promote reaction of active additives, but it is less sensitive to the adsorptive agents. According to the Norm: DIN 51347-1 and 2, the Brugger-test creates a wear scar under friction conditions in the contact zone between a friction ring (Ø = 25 mm) and a test cylinder (Ø = 18 mm) (Fig. 1c). The tests parameters are summarised in Fig. 1d.

2.3. Surface Analysis

The tested specimens were rinsed in petroleum ether after the tribological tests. Afterwards, the wear tracks were examined by using a series of surface characterisation instruments including optical interferometer, scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDX) and Focus Ion Beam (FIB).

Surface topography of the tested samples was evaluated using a Leica DCM 3D – combining interferometric and confocal microscopy (Leica, Japan). Surface roughness was measured before and after the tests according to ISO 4287. The Leica Map Premium 0.2.0190 software was used for wear volume analysis, normalised into wear coefficients (K) according to Archard's equation:

$$K = \frac{V}{F \times S} \qquad (1)$$

where, V is the remove wear volume (m^3), F is the normal load (N), and S is the sliding distance (m).

Scanning electron microscopy micrographs were obtained using a ZEISS SIGMA HD VP device. It is equipped with a Schottky field emission gun (FEG) for optimal spatial resolution. The instrument can be used in high vacuum mode (HV), and in variable pressure low-vacuum mode (VP). The microscope is equipped with a TEAM OCTANE PLUS Version. 4.3 from EDAX Energy Dispersive X-ray (EDX) system for chemical analysis. The spectra were collected at 10 and 20 keV and the acquisition time was 60 s.

Focus Ion Beam cuts were performed using FIB QUANTA 200 3D from FEI. The accelerating voltage for FIB was 30 kV, the currents used for milling were 7 nA; 0.5 nA; 0.1 nA, and the current used for imaging was 10 pA. The final size of the FIB cut was 10 µm deep and 30 µm width. Prior to the ion milling process, Pt-protective layer was deposited on top of the surface using a current of 0.3 nA, which resulted in a thickness of 1.5 µm.

3. Results

3.1. Friction performance

In order to better understand the effect of additives on the tribological performance of nanotubes, reciprocating sliding (SRV) and mixed rolling/sliding (MTM) tests were carried out using the prepared lubricant mixtures. The SRV results are presented in a form of frictional scan as a function of time (Fig. 2). It is important to note that the error bars presented on the frictional curves represent the average of three repetitions.

An initial Stribeck curves presented in Fig. 3 represents MTM tests results. The Stribeck curves for each test set-up were acquired thrice (the scatter was always below 10%), and representative measurements are presented in the diagrams.

As expected and reported previously by many researches [3][5][6], the lowest coefficient of friction (COF) of 0.05 was reached for the base oil mixed only with NTs (Fig. 2a and Fig. 3a) for both tests configurations.

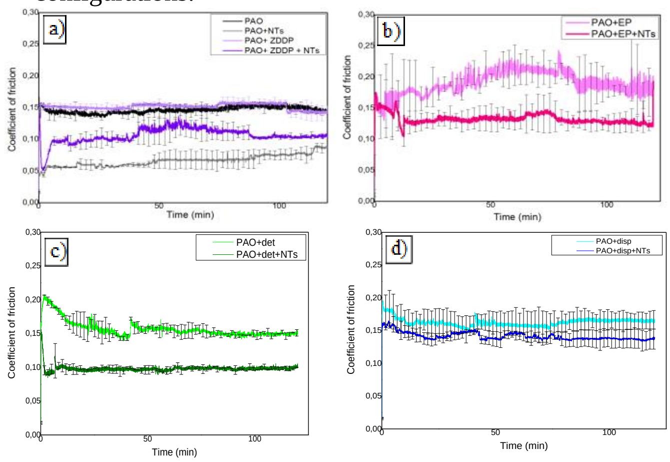


Fig. 2. SRV tests results represented with friction curve including error bars distribution over the curve for following groups of additives a) reference PAO oil, PAO + NTs, PAO+ AW and PAO+AW+NTs; b) PAO+EP and PAO+EP+NTs; c) PAO+det and PAO+det+NTs; d) PAO+disp and PAO+disp+NTs.

The presence of AW additive does not influence the base oil performance in terms of friction, while the addition of NTs to this blend reduces the COF down. In SRV tests the presence of EP additives results in a worse performance, when compared to PAO, as shown in Fig, 2b and the addition of NTs to this blend was able to improve and stabilize the CoF to a value of 0.11. However in MTM tests EP reduces friction compare to PAO, and the addition of NTs to this blend causing huge decrease of CoF, with the largest effect at the lowest sliding velocities in the boundary lubrication regime. The reason for the poor performance of PAO+EP could be the too mild conditions achieved in the SRV tribocontact, insufficient to activate the additive. On other hand EP additive is not expected to reduce COF, only protect the surface from wear.

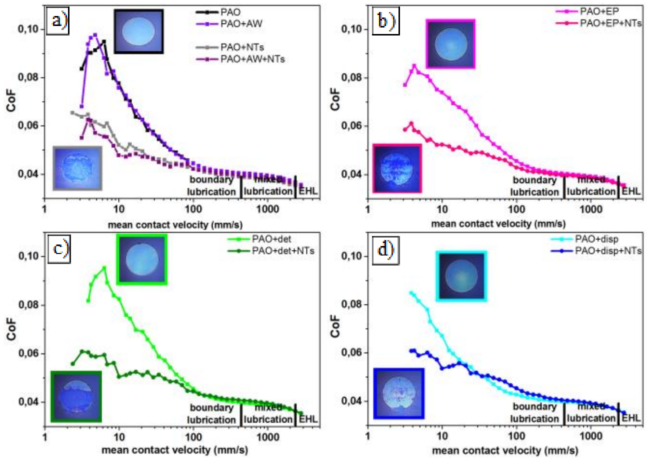


Fig. 3. MTM tests results represented with initial Stribeck curves and optical images of additive film after initial Stribeck tests for following groups of additives a) reference PAO oil, PAO + NTs, PAO+ AW and PAO+AW+NTs; b) PAO+EP and PAO+EP+NTs; c) PAO+det and PAO+det+NTs; d) PAO+disp and PAO+disp+NTs.

Fig. 2c and Fig. 3c show slightly higher COF for base oil additivated with detergent. Nonetheless, NTs fulfilled their function as friction modifier and in both tests configurations their addition to the blend resulted in a reduction of the COF. For SRV tests the worst performance of NTs was observed for the mixture of NTs accompanied with dispersant. As shown in Fig. 2d, only a scant improvement can be achieved compared to PAO+disp blend. This antagonistic interaction between dispersant and MoS_2 nanoparticles was also reported by Rabaso et al in [7]. Nonetheless in MTM tests this antagonistic effect was not observed (Fig. 3d), the addition of NTs to the blend of PAO+disp decreased CoF in similar manner compare to NTs alone in PAO. It can be summarized for MTM tests presented in Fig. 3a-d that the addition of NTs no matter if to the base oil or additivated oil cause great improve of CoF with the largest effect at the lowest sliding velocities in the boundary lubrication regime. In the elastohydrodynamic lubrication (EHL) regime the nanotubes had no effect in the contact. The optical images taken after initial Stribeck tests at Fig. 3a-d shows clearly that the additive derived film is presented only for surfaces lubricated with blends containing NTs.

The third experimental setup to evaluate the synergistic effects between nanotubes and conventional additives under extreme pressure conditions was the Brugger tribotest. The results in terms of load-carrying capacity (LCC) are shown as column graphs in Fig. 4. The color bars denote the value of the load carrying capacity and these are extended by error bars shown in red color. Clearly, the reproducibility of the experiments was good, especially for low load-carrying capacities. The Brugger tests reveal a clear improvement of the load-carrying capacity for all lubricants containing NTs, independently from the additive present in the fluid similar like MTM test results. The only exception was for extreme pressure additives. The addition of EP additives to PAO improves the LCC of the lubricant. However, the further addition of NTs is not able to significantly outperform the mixture PAO+EP. Under the presence of dispersant and detergent, NTs are very effective, even the results show a slightly higher standard deviation. As in the reciprocating sliding tests, also in case of the Brugger tests the exclusive use of NTs in the base oil (without further additives) leads to the best performance, highest load-carrying capacity and minimum wear.

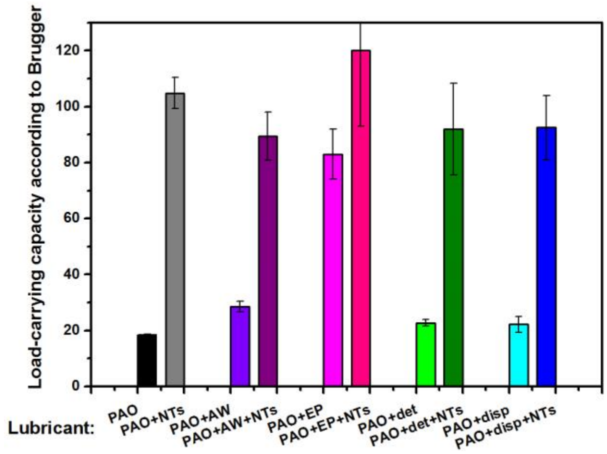


Fig. 4. Load carrying capacity results of Brugger tests for lubricants with additives and nanotubes.

3.2. Wear behaviour

The frictional surfaces after reciprocating sliding and Brugger tests were analyzed with Leica 3D interferometric and confocal microscopy. Based on these data, the removed wear volume was measured in order to calculate the Archard wear coefficient for each tribotest performed. The summary of all Archard wear coefficients for reciprocating sliding and Brugger test is shown in Fig. 5.

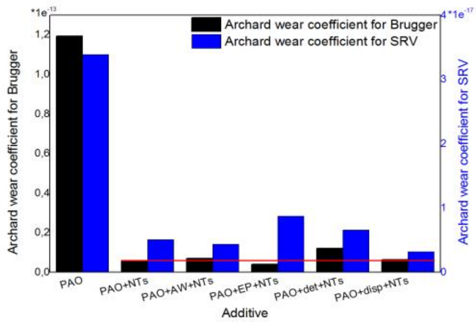


Fig. 5. Archard's wear coefficient calculated for wear tracks on Brugger cylinders and SRV discs.

The wear coefficient in the reference tests performed with PAO is the highest. The addition of NTs in the base oil reduces wear by at least 80% in the SRV and over 90 % in the Brugger tests. However further addition of conventional additives does not improve the results in such a large amount anymore. It is also remarkable that under reciprocating sliding, even the addition of additives to the lubricant mixture containing base oil with nanotubes is not able to maintain the reduced value of the coefficient of friction, in terms of wear, all these mixtures provide a significant improve.

3.3. Role of contact conditions on tribofilm formation

The frictional disc and cylinder surfaces after all tribological tests were analyzed using SEM/EDX in order to reveal the interaction mechanisms under the tested conditions between NTs and additives. The results are shown in Fig. 6. SRV and Brugger test specimens were ultrasonically cleaned after the tests. MTM specimens after the tests were only rinsed with petroleum ether. By observing the SEM morphologies of all the wear tracks it is obvious that most of NTs on the surfaces are left after MTM tribological test (middle column in Fig. 6), followed with EDX. This is due to the fact that those specimens were not ultrasonically cleaned after the test. Nevertheless on SRV and Brugger specimens SEM images and the EDX analysis confirmed the presence of thin (not visible) tribofilm. On SRV specimens EDX shows clear presence of Mo/S peak clearly visible at the surface, obviously deriving from exfoliated MoS_2 nanotubes. On the Brugger cylinders dark zones or spots were visible on the wear tracks. EDX proved that those dark fields are rich in Molybdenum, while in the bright surface around the wear track the concentration of this element is rather poor. Although very small spots rich in Mo and S were found on SRV and Brugger specimens scattered across the surface, these were sufficient to achieve a very low CoF and high load carrying capacity according to SRV and Brugger test results.

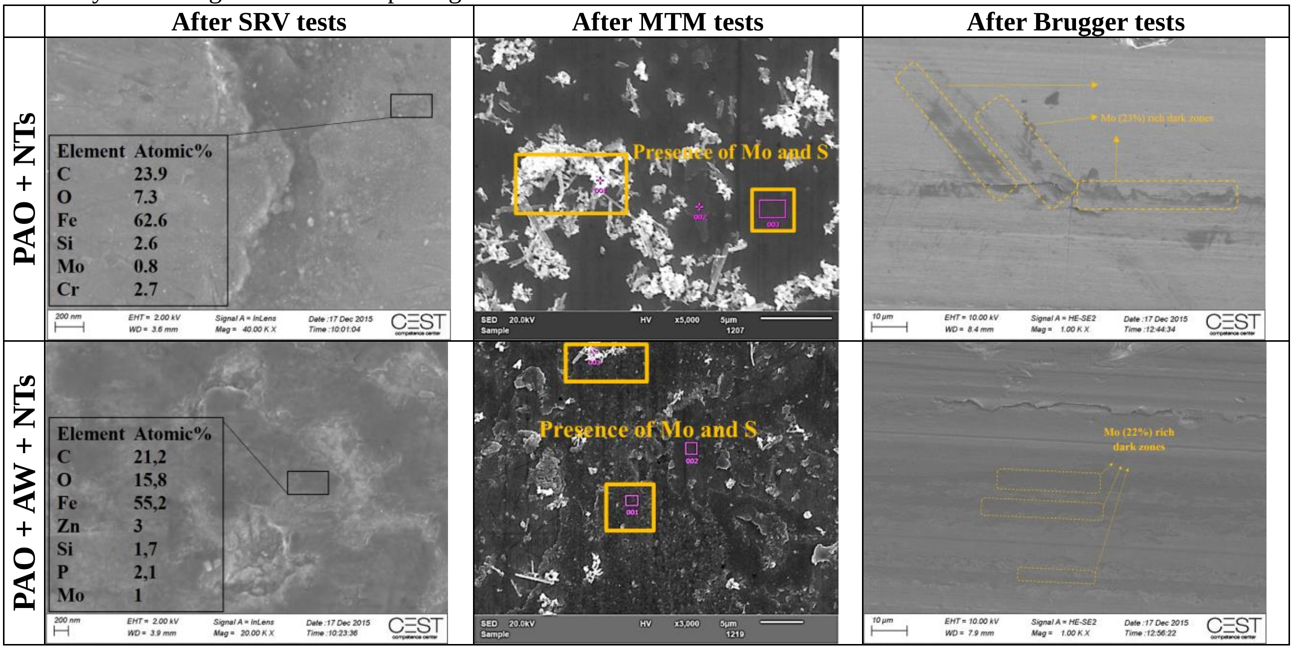


Fig. 6. SEM and EDX analysis of SRV, MTM and Brugger wear marks for PAO + NTs in the first row and PAO+AW+NTs in the second row.

In order to analyse in detail the tribofilm formed by AW and NTs after SRV test shown previously in Fig. 6, the surface was further analysed on SEM/EDX by making a transversal cut using FIB. The cross section of ZDDP/NTs film formed on steel surface after SRV test lubricated with PAO+AW+NTs is illustrated in Fig. 7. The analysis with EDX on tribofilm area confirms the presence of Zn and Mo shown in table in Fig. 7. These results indicate that although the NTs derived layer is not visible by SEM greatest portion of tribofilm consist of ZDDP tribolayer, while MoS_2-derived products are found to be trapped and/or exfoliated within the bulk layer of the tribofilm. Similar tribofilm formation has been reported earlier by Tomala et al. [2], [3] on a steel surface with no presence of ZDDP additive but only NTs and PAO. This can be explained by progressive oxide/ZDDP film formation followed by gradual exfoliation and transfer of molecular sheets onto the asperities of the reciprocating surfaces and it is with agreement with the literature [8]. This explains the presence of small amounts of molybdenum or sulphur in the ZDDP layer.

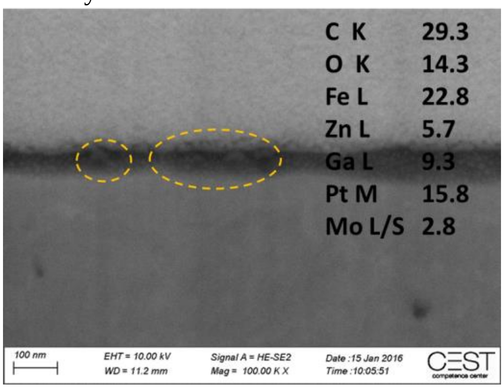


Fig. 7. FIB-SEM micrograph and EDX analysis performed on worn area of SRV disc after the tests lubricated with PAO+AW+NTs.

4. Discussion and Conclusions

The aim of this work was to characterize tribological performance of MoS_2 nanotubes (NTs) in the presence of conventional additives. The group of anti-wear additives (AW) was represented by ZDDP (zinc dialkyl dithiophosphate), extreme-pressure additives (EP) by active sulphurized olefin 40%S, dispersants (disp) by succinimide and detergents (det) by overbased Ca-sulfonate. The presented results reveal synergistic and antagonistic effects in terms of friction, load carrying capacity, wear and tribofilm formation between NTs depending on the accompanying additive.

A comparison of friction curves for NTs additivated and non-additivated lubricants shows the following highlights. In pure PAO, NTs are able to reduce the coefficient of friction by more than 50% compared to reference PAO oil. Only in SRV test all tested groups of additives diminish the effectiveness of NTs when they are present in the lubricant compare to PAO+NTs. Although the NTs accompanied with additives showed different influence on CoF, in terms of wear the Archard wear coefficient in SRV tests was very similar in all mixtures containing NT.

The tribological performance of NTs combined with additives can be explained in terms of tribofilm formation based on the results obtained with SEM-EDX, FIB-SEM-EDX. The frictional surfaces after SRV tests showed under SEM-EDX the presence of a thin (not visible) Mo-containing tribofilm at the surface, obviously deriving from MoS_2 nanotubes. The synergistic effect between NTs and ZDDP could also be highlighted within the present work. A FIB cross section and subsequent EDX chemical analysis of the tribofilm formed by PAO+AW+NTs on steel surface showed the presence of thin round like structures (10-20 nm) embedded in the ZDDP tribofilm (40-80 nm). These results can directly be compared to those obtained in the literature, in a more detail crystallographic analysis using TEM cross sections, as it was presented [2], [9]. In all cases, the synergy between NTs and ZDDP was found to be related to the exfoliation of transition metal dichalcogenide nanoparticles on top of a well-formed ZDDP tribofilm.

The synergy between MoS_2 nanotubes (NTs) and the selected additives was investigated also under rolling contact and severe contact conditions using a Brugger test setup. Similar in all testing configurations best performing lubricant was PAO + NTs compared to reference PAO oil. Presence of additives in MTM and Brugger tests configuration slightly diminish the effectiveness of NTs, but to a much lesser extent compare to SRV frictional results. In MTM and Brugger setup dissimilar to SRV test, the NTs in the presence of dispersant are the same effective as in presence of detergent and AW additive, additionally the response of PAO+EP blend is very strong. The reason for the improvement in MTM friction and Brugger load carrying capacity could be disclosed based on the analyses of the wear scars. Surfaces after the MTM and Brugger tribotests analysed using SEM-EDX clearly showed visible zones rich in molybdenum and sulphur, indicating the local presence of MoS_2.

5. Acknowledgements

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