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Performance of nanolubricants containing MoS_2 nanotubes during form tapping of zinc-coated automotive components

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ABSTRACT

The paper presents the first use of nanolubricants containing MoS_2 nanotubes for form tapping of zinc-coated steel. MoS_2 nanotubes are known for their superb low frictional, anti-wear and extreme pressure properties and have shown a promising performance as nanolubricant additive in many machining and forming applications. However their interfacial interaction with zinc-coated components commonly used in automotive applications and their synergisms and antagonisms with currently used additives in forming oils are two crucial aspects that have not been addressed so far. The assessment of these synergies is of uttermost importance for developing future nanofluid minimum quantity lubrication formulations, since despite their extraordinary performance, MoS_2 nanotubes are not able to fulfil all the roles expected from a forming oil. To this end, this paper aims to investigate the performance of MoS_2-based nanolubricants in combination with representative forming oil additives. The threads are perform using a form tapping unit with customized data acquisition on zinc-coated steel, as a representative part in automotive applications. The performance of the nanolubricants is thoroughly investigated using advanced analytic methods with the aim of revealing the underlying interface interaction mechanisms for the observed torque behaviour and resulting thread morphology and sub-surface hardness. The results show that MoS_2 nanotubes are able to interact and form a tribofilm in Zn coated surfaces that leads to a superb friction performance. In combination with oil additives, MoS_2 based nanolubricants have a particularly positive synergy with extreme pressure additives in terms of friction reduction, sub-surface hardening and thread morphology. On contrary, the lowest synergy is achieved in the presence of dispersants, leading to higher torques during form tapping and higher sub-surface hardness in the formed threads.

1. Introduction

In many industrial processes, the manufacture of internal threads on metal holes is required in order to use screws as fasteners. Threads can be manufactured by cutting or by forming. In form tapping, the thread is formed on the hole by imparting severe plastic deformation. Form tapping is a manufacturing process that is becoming increasingly interesting in industry, since it has several advantages when compared to thread cutting. The severity of the process is smaller when compared to cutting operations due to the lower velocities and temperatures involved. For this reason, tool lifetime and process reliability are higher, which together with the lack of chip formation, make the process attractive for manufacturing, particularly in automotive [1,2]. Despite the industrial relevance of form tapping, the number of scientific works devoted to provide a profound understanding on the process are rather scarce, in particular when compared to other machining and manufacturing processes such as grinding or milling [3]. Due to the severe contact conditions at the interface between tapper and thread, the process requires the use of fully formulated oils in order to lubricate and cool the contact zone. Fromentin et al. presented a study on lubrication during form tapping with particular emphasis on the role of lubricant additives [1]. The work used fully formulated lubricants and emulsions for investigating the additive interaction during forma tapping of C70 carbon steel. The authors found that sulphur containing additives are reacting with the steel surface during forming highlighting the importance of their molecular structure and thermal behaviour. In fact, the contact conditions found during tapping are so demanding that tapping tests has been proposed as standard method for evaluating cutting fluids [4].

Within this context, new regulations limiting or forbidding the use

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of certain compounds in lubricants and coolants are boosting the research into the development of more environmentally acceptable formulations. In a review paper, Bartz highlighted that these formulations should reduce or totally avoid the use of heavy metals, such as zinc, chlorines, boron and silicones [5]. Another current trend is the reduction of lubricant and coolant used in machining and forming processes, a concept that is called minimum quantity lubrication (MQL). According to Boothroyd and Knight, MQL consists in feeding to the machining point the lubricant in fine droplets at a rate ranging 10–100 ml/h [6]. By these means, small droplets of atomized lubricant are brought to the contact using a transport medium, such as air. The ultimate goal is to drastically reduce the use of fluids during manufacturing in order to foresee a future of fluid-free lubricants.

A possible way to achieve these targets is by using nanofluids, which are fluids with a small percentage of nanomaterials used as inorganic lubricant additives [7]. The combination of nanofluids with MQL is called nanofluid minimum quantity lubrication (NMQL) and has showed recently a great potential for enhancing cooling and for increasing the maximum undeformed equivalent chip thickness during grinding [8,9]. Among the promising nanoparticles to be applied in prospective forming and machining processes, transition metal dichalcogenide (TMD) nanoparticles have evidenced an excellent performance for lubricating steels and coatings in a variety of different contact conditions [10–14]. Transition metal dichalcogenides are layered materials formed by a transition metal (W or Mo) with two chalcogen atoms (S or Se). Due to their layered structure with covalent bounds and weak van der Waals interaction between layers, these compounds provide superb friction reduction properties [15]. Since the first synthesis of WS_2 nanoparticles in 1992 [16], the use of these transition metal dichalcogenide nanomaterials as oil additives for reducing friction has gathered a substantial interest, which has boosted over the past years.

The lubricating mechanism of TMD nanoparticles was the subject of long debate. Joly-Pottuz et al. proved that the superb frictional properties of TMD nanoparticles are due to a gradual exfoliation of TMD sheets during the surface interaction [17]. Kalin et al. showed that the used of MoS_2 multi-wall nanotubes reduces friction and wear in sliding contacts operating in boundary lubrication 2 and up to 9 fold, respectively [12]. The mechanism for friction and wear reduction was again attributed to exfoliation and deformation of the nanotubes. More recently, Niste and Ratoi showed using several TMD nanoparticle chemistries and morphologies that under severe contact conditions of temperature and/or pressure, the TMD nanoparticles react with iron substrates producing a tribofilm containing iron sulphides and oxides, besides transition metal oxides and dichalcogenides [18].

Initially, the research on TMD nanoparticles was focused on their lubricating mechanisms when used in nanofluids as lubricant additives. However, their interaction with other lubricant additives started gathering attention much more recently, despite being crucial for their use in fully formulated products for machining and forming applications. The reason is that whereas TMD nanoparticles have superb friction reduction properties, they cannot fulfil all roles required for a lubricant additive, such as corrosion or sludge control. Previous work has revealed the synergy between TMD nanoparticles and ZDDP tribofilms [19–21]. The reason for this synergy is the exfoliation of TMD nanoparticles on top of well-formed ZDDP tribofilms. On contrary, antagonistic effects between dispersants and TMD have been reported [22,23]. In general, it has been noticed that the synergy or antagonism of MoS_2 nanotubes based nanofluids depends on the accompanying additive and contact conditions [23].

Future lubricants for NMQL applications require a deep understanding of the interaction between nanoparticles, other co-additives in the nanofluids and workpiece surface. TMD nanoparticles are known for their superb low frictional, anti-wear and extreme pressure properties and have shown a promising performance in machining processes. However, these investigations have focussed mainly on grinding [7,24,25], while their potential use in form tapping remains unknown. Further, there is a lack of knowledge on the interaction between TMD nanoparticles and zinc-coated parts, despite their enormous industrial relevance in automotive industry. Hence, the aim of the present work is to investigate the potential of MoS_2 nanotubes in nanofluids for form tapping operations. To this end, several nanofluids were prepared and investigated using a tapping machine, with special emphasis on understanding the interaction between MoS_2 nanotubes and other conventional lubricant additives with zinc coatings in terms of torque reduction and resulting thread morphology. The ultimate goal is to understand their synergistic and antagonistic effects in order to develop future formulations of greener lubricants for NMQL applications.

2. Experimental

2.1. Nanolubricant mixtures

The reference nanolubricant was prepared by mixing MoS_2 nanotubes in poly-alpha-olefin 4 (PAO) base oil in order to study the performance of MoS_2 nanotubes in form tapping operations. The reason for selecting MoS_2 nanotubes is due to their superb friction and wear performance shown in previous studies under different contact conditions [23]. The MoS_2 nanotubes were synthesized from $Mo_8S_2I_8$ nanowires at 1073 K in a reactive gas composed of 98 vol% Ar, 1 vol% of H_2S and 1 vol% of H_2 for 1 h according [26]. The pristine MoS_2 nanotubes had a hedgehog self-assembly [13] that can be easily dispersed in polar media using ultrasound. The MoS_2 nanotubes had a diameter of 100 to 150 nm and a length of up to 3 μm (Fig. 1). The walls of the nanotubes are approx. 10 nm thick and form dome terminations. The X-ray diffraction spectrum revealed a pure MoS_2 compound, which can be assigned to 2H polytype of MoS_2 (JCPDS-77-1716).The base oil selected for the nanolubricant mixtures was poly-alpha-olefin (PAO) 4 with a viscosity of 17.9 and 4.0 mm^2/s at 40 and 100 °C, respectively. The low viscosity was selected in order to achieve more demanding conditions during form tapping and highlight the role of the nanotubes.

Further mixtures containing MoS_2 nanotubes and conventional oil additives were prepared for investigating the synergistic and antagonistic effects of the nanotubes (NT) with each individual additive or in combination. The lubricants mixtures used are summarized in Table 1. The concentrations were selected according to previous works performed under reciprocating sliding and extreme pressure conditions [23]. The additives were selected as follows in order to include the most representative chemistry for each group of additives.

- Anti wear (AW): Zinc dialkyl dithiophosphate (ZDDP) with a primary alkyl structure and 99% purity (Lukoil Lubricants Europe, Austria)
- Extreme Pressure (EP): Sulfurized olefin polysulfide with 40% sulfur content (Lukoil Lubricants Europe, Austria)
- Dispersant (Disp): Succinimide based on long chained hydrocarbon amines with 2000 molecular weight (Lubrizol, USA)

The dynamic viscosity was measured at 40 °C using a Physica Modular Rheometer Series (MCR) 101 parallel-plate system (Anton Paar, Austria) with a shear rate of 100 (1/s). Wettability was measured using a goniometer with a Hamilton Microliter syringe 500 μL A 5 μl drop was placed on the surface of a workpiece sample and its contact angle was obtained by image processing.

As reference, a fully formulated oil typically used for form tapping was selected in order to put the obtained results in perspective. The kinematic viscosity of the fully formulated oil was measured to be 77.4 and 7.5 mm^2/s at 40 and 100 °C, respectively. This corresponds to a dynamic viscosity of 69.9 mPa·s. The viscosity was thus significantly higher than the selected PAO base oil, giving it an advantage against the PAO-based nanolubricants. The elemental composition of the oil was measured using inductive couple plasma (ICP) and is shown in

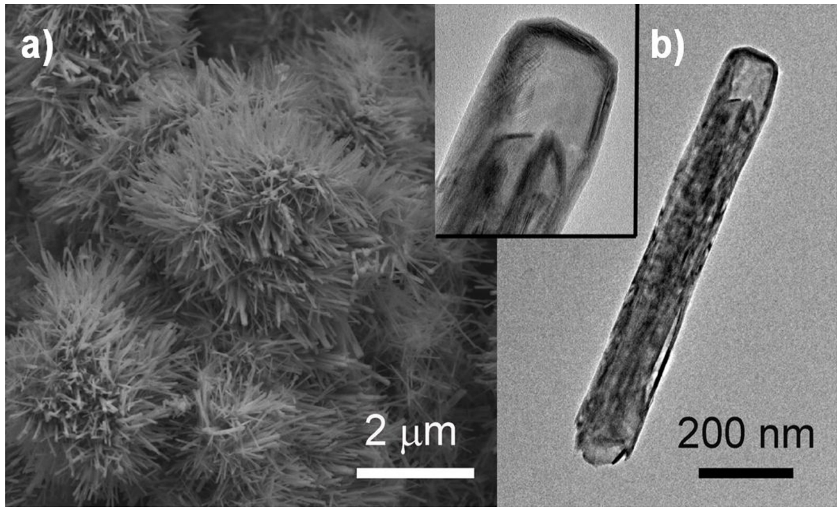


Fig. 1. MoS_2 nanotubes used for the nanolubricant mixtures. SEM image (a) and TEM image (b).

Table 2. As expected, the most abundant element is S, due to its presence in EP and AW compounds. S along with Ca is also found, probably due to the presence of overbased calcium sulfonate, typically used as detergent. P is found in AW additives. The oil is boron and lead free and has a negligible content of Zn.

2.2. Form tapping

The threads were done using a form tapping unit Pronic M400 (Pronic, France) with customized data acquisition in order to monitor the tapping force and torque during the forming process (Fig. 2a). A torque transducer (HBM, Germany) and a bending beam for measuring the forces in axial direction were integrated at the base of the experimental set up, where the workpiece was fixed throughout the form tapping experiment. The material selected for the threads was zinc coated (hot-dip galvanized) HX 260 LAD Z100 MB steel (Fig. 2b) with a thickness of 2.5 mm and a nominal chemical composition as given in Table 3. This material is widely spread in automotive industry and is selected as a representative for form tapping operations.

The form tapping tool was a M12 × 1.5 6HX tap made of high speed steel (Fig. 2c) with a fine martensitic microstructure with dispersed carbides. Before each test, the tap was ultrasonically cleaned 5 min in toluene and 5 min in petroleum ether (HPLC grade).

The nanolubricants were homogenised prior to the test using an ultrasonic processor VC 505 Sonics & Materials. Inc, which is designed for small volume applications (250 μl – 1 l). The ultrasonic vibrations at the probe tip were set to 20% amplitude for 8 min, while the pulse was on for 2 s followed by 2 s pulse off. Subsequently, a drop of nanolubricant mixture (0.5 ml) was applied to the tap before initiating the test. A total of 6 threads were performed for each nanolubricant mixture in order to ensure statistical reproducibility. The formed M12 threads were formed using a rotational speed of 610 rpm, had a height of 27 mm and a slope of 1.5 mm.

2.3. Surface and tribochemical analyses

The quality of the formed threads was analysed using a light microscope Zeiss Axio Imager.M2m (Carl Zeiss, Germany) equipped with a Jenoptic PogRes SpeedXT Core 5 Camera (Jenoptik, Germany). To this end, the threads were wet cut using a rotating saw and embedded in resin. Afterwards the samples were ground and polished, and etched with Nital in order to reveal the microstructure. The 3D morphology of selected samples was investigated using an InfiniteFocus Alicona G5 device (Alicona, Austria).

Microhardness was measured on thread cross-sections using a Future Tech FM-700 microhardness tester (Future-Tech Corp., Japan) with a Vickers diamond tip. The microhardness tester was used to determine the Vickers hardness HV0.01 in thread cross-sections. Prior to the measurements, the thread cross-sections were embedded in epoxy resin and subsequently ground and polished.

Insight about the interaction between the MoS_2 nanotubes and the thread surface during forming was gained using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy with a JEOL JSM 65000F (Jeol, Japan) operated at an acceleration voltage of 20 kV. In this case, in order to avoid damage of the thread surface and chemical contamination, the threads were carefully saw under dry

Table 1
Overview of the lubricants and nanolubricants used in the present study along with their measured dynamic viscosity and contact angle.

Lubricant/Nanolubricant	Denotation	MoS_2 nanotubes (NT)	Anti wear (AW)	Dispersant (Disp)	Extreme pressure (EP)	Dynamic viscosity in mPa·s (40 °C)	Contact angle in ° (Room temperature)
PAO	PAO	–	–	–	–	33.3 ± 0.3	20.8 ± 1.3
PAO + 5%MoS_2	NT	5 wt.%	–	–	–	45.6 ± 2.5	24.0 ± 1.1
PAO + 2%AW	AW	–	2 wt.%	–	–	37.2 ± 0.1	24.2 ± 1.1
PAO + 5%MoS_2 + 2% AW	NT + AW	5 wt.%	2 wt.%	–	–	43.4 ± 0.4	19.1 ± 1.4
PAO + 5% Disp	Disp	–	–	5 wt.%	–	34.7 ± 0.3	19.6 ± 1.1
PAO + 5% MoS_2 + 5% Disp	NT + Disp	5 wt.%	–	5 wt.%	–	38.2 ± 0.2	20.3 ± 1.2
PAO + 2% EP	EP	–	–	–	2 wt.%	29.8 ± 0.3	18.9 ± 0.9
PAO + 5%MoS_2 + 2% EP	NT + EP	5 wt.%	–	–	2 wt.%	39.1 ± 0.2	25.5 ± 0.7
PAO + 5%MoS_2 + 2% AW + 5% Disp	NT + AW + Disp	5 wt.%	2 wt.%	5 wt.%	–	31.8 ± 0.3	25.6 ± 1.2
PAO + 5%MoS_2 + 2% AW + 5% Disp + 2% EP	NT + AW + Disp + EP	5 wt.%	2 wt.%	5 wt.%	2 wt.%	29.6 ± 0.2	25.7 ± 1.0

Table 2
Elemental composition of the fully formulated oil used as reference, as measured using inductive coupled plasma.

Element	Al	B	Ca	Fe	K	Mg	Mn	Na	P	Pb	S	Si	Zn
Concentration in ppM	4	< 1	1640	2	1	8	1	< 10	634	< 10	9310	12	1

conditions and afterwards ultrasonically rinsed 5 min with toluene and 5 min with petroleum ether (HPLC grade).

The chemical composition of the tribofilms was determined using a XPS Thermo Fisher Scientific Theta Probe (East Grinstead, UK), equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) and an Ar^+ ion gun. Prior to the XPS analysis, the tested samples were ultrasonically cleaned in HPLC grade petroleum ether for 10 min. The measurements were performed at a base pressure of 2×10^{-9} mbar. The analysed spot size diameter was 100 µm, and the pass energies used were 200 eV for the survey spectra and 50 eV for the high resolution spectra, respectively. The XPS spectra were acquired after 10 s of fine sputtering which was conducted in order to remove any possible hydrocarbon contamination. All the high resolution spectra were referenced to the adventitious carbon (C 1 s binding energy of 284.8 eV). Afterwards, the spectra were processed by a software (Thermo Fisher Scientific Avantage Data System, East Grinstead, United Kingdom), using Gaussian-Lorentzian peak fitting.

3. Results and discussion

3.1. Influence of nanofluids on torque

Exemplary torque measurements as function of time are shown in Fig. 3 for the threads formed using pure PAO base oil, PAO base oil containing MoS_2 nanotubes (PAO + NT) and the fully formulated reference forming oil. During the form tapping process, the torque initially rises during tap entrance until the so-called formation torque value is reached. After this point, the torque rate of increase diminishes and reaches a maximum torque value. The, part of the torque curve that lies between the formation torque and the maximum torque value is referred to as friction torque, since its behaviour is mainly determined by the lubricating behaviour of the forming oil. Eventually, during the friction torque, the torque can reach a steady-state value. The formation of a steady-state value is determined by the lubricant performance. A lack of steady-state is attributed to the loss of lubricity of the lubricant due to a temperature increase [1].

In our case, it can be observed that after tap entrance, the torque steadily rises during friction torque, indicating a poor performance for the additive-free pure PAO base oil. On contrary, the rate of increase of

Table 3
Chemical composition of the zinc coated steel used for the form tapping experiments.

Element	C	Si	Mn	P	S	Al	Ti	Nb	Fe
Mass %	0.038	0.019	0.23	0.008	0.005	0.038	0.001	0.001	bal.

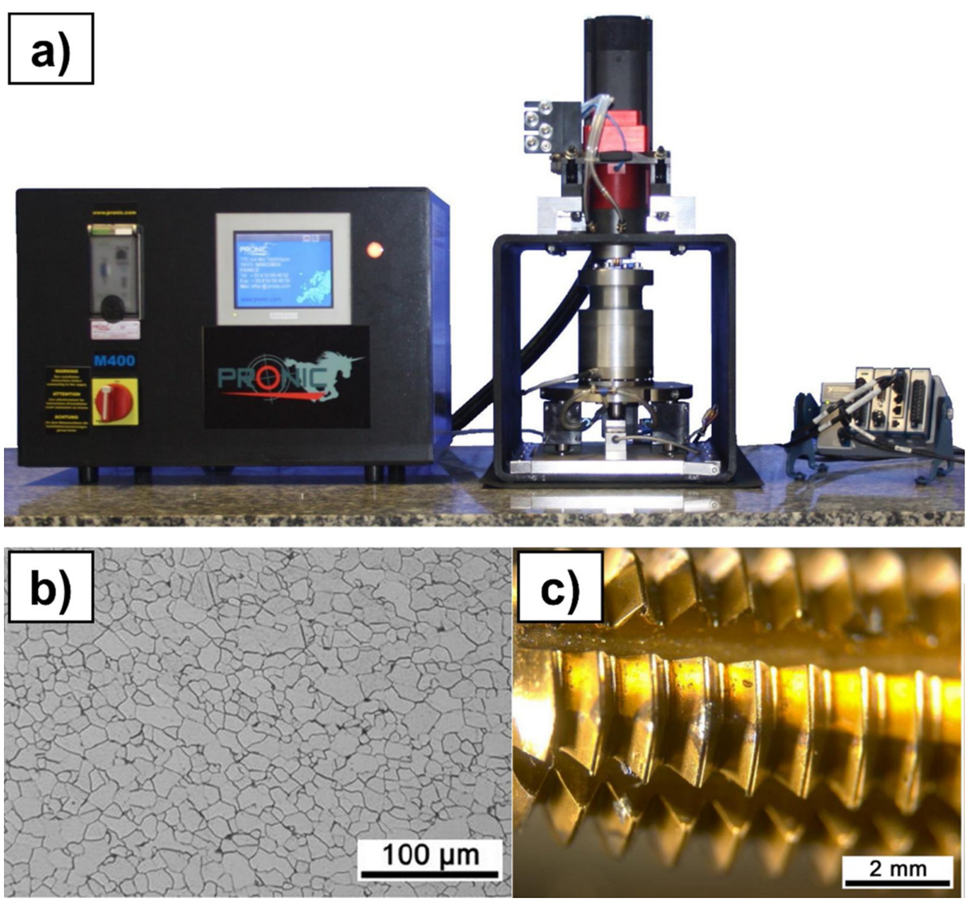


Fig. 2. Overview of the form tapping unit (a). Microstructure of the zinc coated steel used for the form tapping experiments (b). Detail of the TiN coated M12 × 1.5 6HX tap (c). Figures adapted from [27].

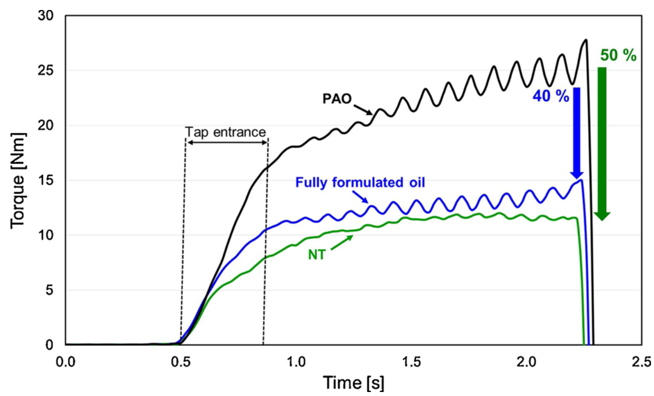


Fig. 3. Torque as a function of time during tap entry for the threads formed using PAO, NT and reference fully formulated oil.

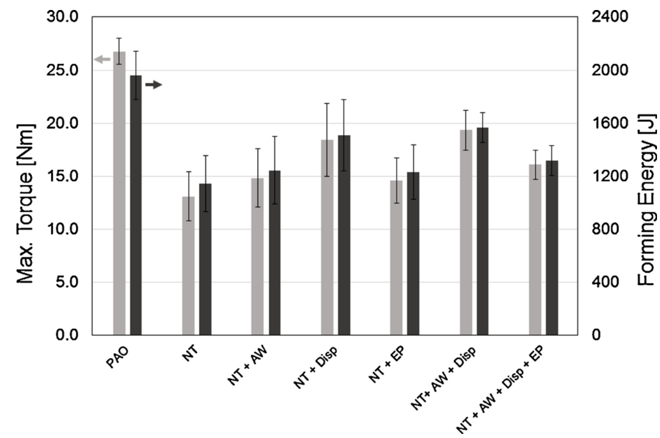


Fig. 5. Maximum torque and forming energy obtained during form tapping using nanolubricants containing MoS_2 nanotubes.

the torque for the threads formed using NT and the fully formulated oil is much smaller, almost leading to a steady-state value. The maximum torque reduction for the fully formulated oil and the NT is approximately 40 and 50%, respectively.

In all cases the maximum torque is measured at the end of tap entry. After tap entry, the torque decreases and switches sign during tap exit. Hereinafter, the results obtained for each nanolubricant are specified as the average maximum torque of 6 experiments.

Fig. 4 shows the maximum torque measured during tapping for all lubricant mixtures containing a single additive. The pure PAO base oil and the fully formulated product are used as reference. The results show that the highest maximum torque value is measured when using the additive-free PAO 4 oil, as expected, due to its low viscosity and lack of additives. The presence either of succinimide dispersant or ZDDP antiwear additive leads somewhat to a negligible improvement of the maximum torque value formation. On contrary, the use of sulfurized olefin polysulfide EP additive leads to a maximum torque reduction of 25%. EP additives are surface active and react forming sulphide compounds that prevent metal to metal contact and, consequently, adhesion [28,29]. The most dramatic reduction is achieved when adding the MoS_2 nanotubes to the PAO base oil. In this case, the maximum torque reduction achieved is of 50%. It has been previously reported that TMD nanoparticles are not only able to reduce friction in reciprocating sliding contacts, but also under extreme pressure conditions by the formation of protective complex iron sulphide and molybdenum disulphide tribofilms [23,30]. The use of a fully formulated oil leads to a maximum torque increase of 18%, despite having a much higher

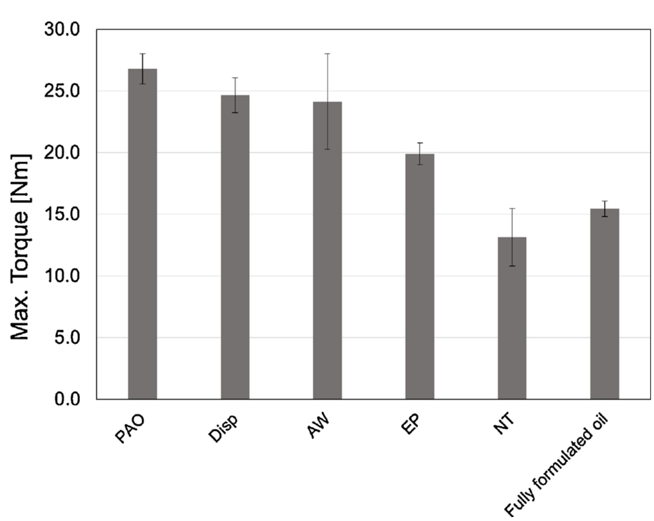


Fig. 4. Maximum torque for the different lubricant mixtures containing a single additive.

viscosity than the base oil used for the mixture containing nanotubes. However, the results have a lower scattering, probably related to the higher inhomogeneity of the lubricant mixture containing the MoS_2 nanotubes.

The beneficial effects of MoS_2 nanotubes in terms of torque reduction strongly depends on synergistic and antagonistic effects with the other lubricants additives present in the mixture. Fig. 5 shows the maximum torque measured during tapping for lubricant mixtures containing MoS_2 nanotubes and NT accompanied with the selected conventional additives. The results shows that the addition of either EP or AW additive into nanolubricants containing MoS_2 NTs leads to a slightly increase of the maximum torque of 11 and 13%, respectively, while the addition of dispersants leads to a severe increase of 40%. In this case, the maximum torque value measured is still significantly lower when compared to pure PAO or PAO with dispersants (Fig. 4). A similar maximum torque value can be measured with the further addition of AW to this mixture (NT + Disp + AW). The lowest torque values when adding succinimide dispersant to the nanolubricant mixture were achieved in combination with EP additive (NT + AW + Disp + EP). In this case, the maximum torque value is 40% lower compared to PAO 4 but 23% higher compared to the lubricant mixture containing exclusively base oil and nanotubes. The measured maximum torque has a value very close to the one obtained using a fully formulated product with a much higher viscosity of the base oil.

An analogous result can be obtained in terms of forming energy (Fig. 5). To this end, the area below the torque M is multiplied by the rotational speed ω in rad/s and integrated over the forming time t_0 to t according to

$$E = \int_{t_0}^{t} M(t) \cdot \omega \cdot dt \tag{1}$$

3.2. Microhardness of the threads

The microhardness as measured at the root of the threads is shown in Fig. 6 for all investigated nanofluids. The results (average of two depth profiles) show that all threads reach the bulk hardness of around 280 HV 0.01 at a distance between 50 to 80 μm below the surface. At the immediate vicinity of the surface (20 μm) the highest hardening at the thread root occurs when forming using pure PAO 4 base oil, as expected, where the hardness rises over 400 HV 0.01. The addition of either AW additive or dispersants leads to a slightly lower hardness of 370. Afterwards, at hardness values ranging from 330 to 340 HV 0.01 the other two nanofluid mixtures containing AW can be found, namely the MoS_2 with AW and dispersants and the same mixture with the addition of EP. The hardness value reached at the thread with these mixtures containing several additives is very similar to the one obtained

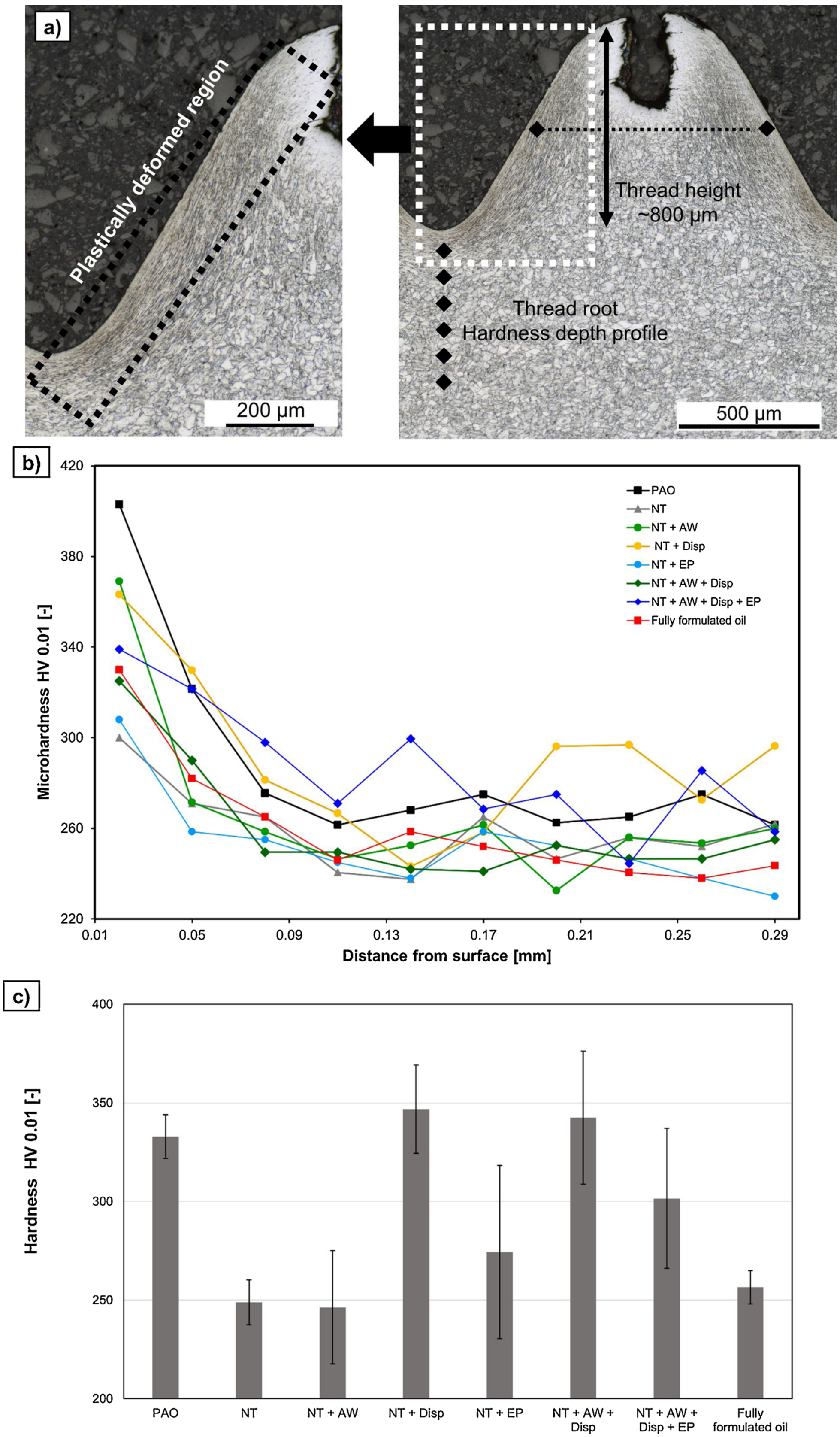


Fig. 6. Microhardness measurements on thread cross-sections. (a) Light microscopy image of a thread cross-section schematically showing the location of the indents. The microstructure near the thread shows grain refinement as consequence of severe plastic deformation. (b) Microhardness HV 0.01 measured at the thread root as a function of distance to surface for all investigated nanofluids. (c) Microhardness HV 0.01 measured on the thread edges at half thread height.

when using the fully formulated reference oil. Finally, the remaining three nanofluids (MoS_2 nanotubes and NT + EP) are found to impart a hardening on the thread that leads to a Vickers microhardness of HV 0.01 of around 300.

The microhardness depth profiles at the thread root revealed that the main differences in surface hardness caused by the different nanolubricants occurs in the immediate surface vicinity. This is in accordance with the depth of the severe plastically deformed zone observed in the microcopy image (Fig. 6a). In order to verify these results with a higher statistics, additional microhardness analyses were performed on the flanges of the split crests (Fig. 6). In this case, the results show the average of 10 individual measurements. The microhardness values show a similar trend with the ones measure at the root of the thread. The highest values (around 340 HV 0.01) are obtained for the pure base oil (PAO), NT + Disp and NT + AW + Disp, showing that the presence of dispersants lead to a significant larger deformations as a consequence of the higher friction. A significant drop in microhardness in the presence of dispersants can be only achieved when adding EP. The lowest values are achieved when using NT alone or only either with EP or with AW. In all these cases, the microhardness values are similar to those measured when using the fully formulated oil.

3.3. Morphology of the threads

In the previous section, the impact of all lubricant mixtures on torque during form tapping was thoroughly addressed. In this section the resulting thread morphology as a function of the used nanofluid will be presented. To this end, the section will focus exclusively on the nanofluids, since the lubricant mixtures containing exclusively PAO base oil with one type of additive were merely used as reference for a better understanding of the interaction between additives and MoS_2 nanotubes. The pure base oil (PAO) and the fully formulated oil will be included as references.

The morphology of the thread cross-section as seen on an optical microscope is shown in Fig. 7. Fig. 7a shows the thread formed using additive-free base oil. The top of the thread shows the characteristic split crest, as previously reported. The split crests are often asymmetric, probably due to the high shear stresses present at the contact interface as a consequence of the lack of additives. When adding the MoS_2 nanotubes, the split crest is much more symmetric even though its area is much larger (Fig. 7b). The addition of either AW additive or dispersants to the nanolubricant results in a similar morphology, as the one observed for pure PAO (Fig. 7c and d), showing asymmetric split crests. In contrast, the addition of EP to the NT leads to a similar split crest as the one obtained with NT alone, but slightly more closed. When simultaneously using AW and dispersants, the split crest is closer but again highly asymmetric, thus indicating a correlation between high friction at the interface and split crest asymmetry. A significant morphological improvement is observed by the addition of EP to the latter. In this case, the split crest is highly symmetric and much more closed. Finally, the morphology of the thread obtained using a fully formulated product results in the presence of a small and closed split crest.

The light microscopy images provide an initial insight into the thread morphology. However, the images provide local and 2D information. In order to obtain a more detail overview of the morphology, selected samples were investigated using 3D microscopy. The results partly reproduce the observations done using light microscopy but provide further details (Fig. 8).

The threads obtained using PAO base oil show an irregular morphology, as observed in the 2D cross-sections. Contrary to the 2D images, the threads obtained using NT show that some of the split crests are almost or even fully closed, which leads to the presence of some cracks on the split crests and debris. A further improvement in the morphology is achieved when using NT + EP. In this case, most of the split crests are closed and the morphology of the thread seems to be more symmetric and homogeneous, without visible cracks. The use of NT + AW + Disp + EP leads to the formation of split crests that are slightly more open, with a morphology closely resembling the one obtained using the fully formulated product. However, the latter seems to be slightly more homogeneous, despite having minimally larger split crests. The depth of the split crest for every nanolubricant is summarized in Table 4.

3.4. Surface analyses

The surface morphology of the threads is further analysed using scanning electron microscopy (Fig. 9). The threads formed using pure PAO base oil show a surface, characterised by the presence of cracks on the deformed metal partly closing the split crests (Fig. 9a). These cracks indicate that the lubrication performance of the base oil was very poor leading to massive shear forces at the contact interface between the forming tool and the thread. When using the nanofluid containing MoS_2 nanotubes (Fig. 9b), the tips of the split crest are found to be closer, with the presence of cracks due to deformation on the tip of the split crest. Some fully closed split crests could be identify (Fig. 10a). Energy dispersive x-ray analyses (EDX) indicate the presence of Mo on some spots of the split crest (values ranging between 0.3–3.0 at.%), suggesting the formation of a MoS_2 containing tribofilm. The addition of AW additive to the nanolubricant mixture results in a similar morphology as the one reported for pure base oil, being the main difference that the split crests are more uniform and have a more homogenous size, despite the presence of cracks (Fig. 9c). EDX analyses are able to detect Mo, but the content is clearly lower when compared to the mixture containing only MoS_2 nanotubes (up to 1.5 at.%). A very similar surface morphology is achieved when adding dispersants to the nanolubricant mixture (Fig. 9d). The major difference is that in this case the Mo signal is also rather weak, with a concentration of typically up to 1.5 at.%. However in some spots very large concentrations of Mo could be measured (10 at.%). Images at higher magnification of these spots reveal the presence of MoS_2 nanotubes and debris forming clusters.

When adding EP instead of AW, the slit crests also have a very homogeneous shape but with a lower presence of cracks. The presence of Mo in the thread surface was also evidenced with a value of typically around 1.5 at.% in some spots. In localized spots, again large Mo concentrations were measured. These spots showed the presence of MoS_2 nanotubes and debris forming clusters (Fig. 10b), as previously observed in the case of NT + Disp. Note that in both cases, the threads were thoroughly cleaned in ultrasonic bath with toluene and petroleum ether (5 min each).

The more complex nanolubricant containing AW and dispersants has a similar split crest morphology as the nanolubricant containing only ZDDP, with an asymmetric split crest containing cracks. In this case, Mo could not be detected on the surface. The further addition of EP leads to improved results in terms of thread symmetry and number of cracks. Finally, the reference fully-formulated oil also shows the presence of cracks at higher magnifications, even though they seem to be shorter and less present, having a certain similarity with the threads formed using the nanolubricant containing MoS_2 with dispersants and EP.

3.5. Surface interaction mechanisms

The XPS results from the survey scans show that the NT mixture is the only one containing both Mo and S as the main elements related to the MoS_2 tribofilm formation inside the threads (Table 5). It should be noted that this mixture clearly outperformed the others in terms of reduced thread torque as shown in Fig. 4.

The high resolution XPS scans performed inside the threads confirm the findings presented in Table 5. The Mo 3d core level spectra showing the presence of a well-defined doublet (corresponding to $3d_{5/2}$ and $3d_{3/2}$ contributions) are obvious in case of the NT mixture (Fig. 11, top). On

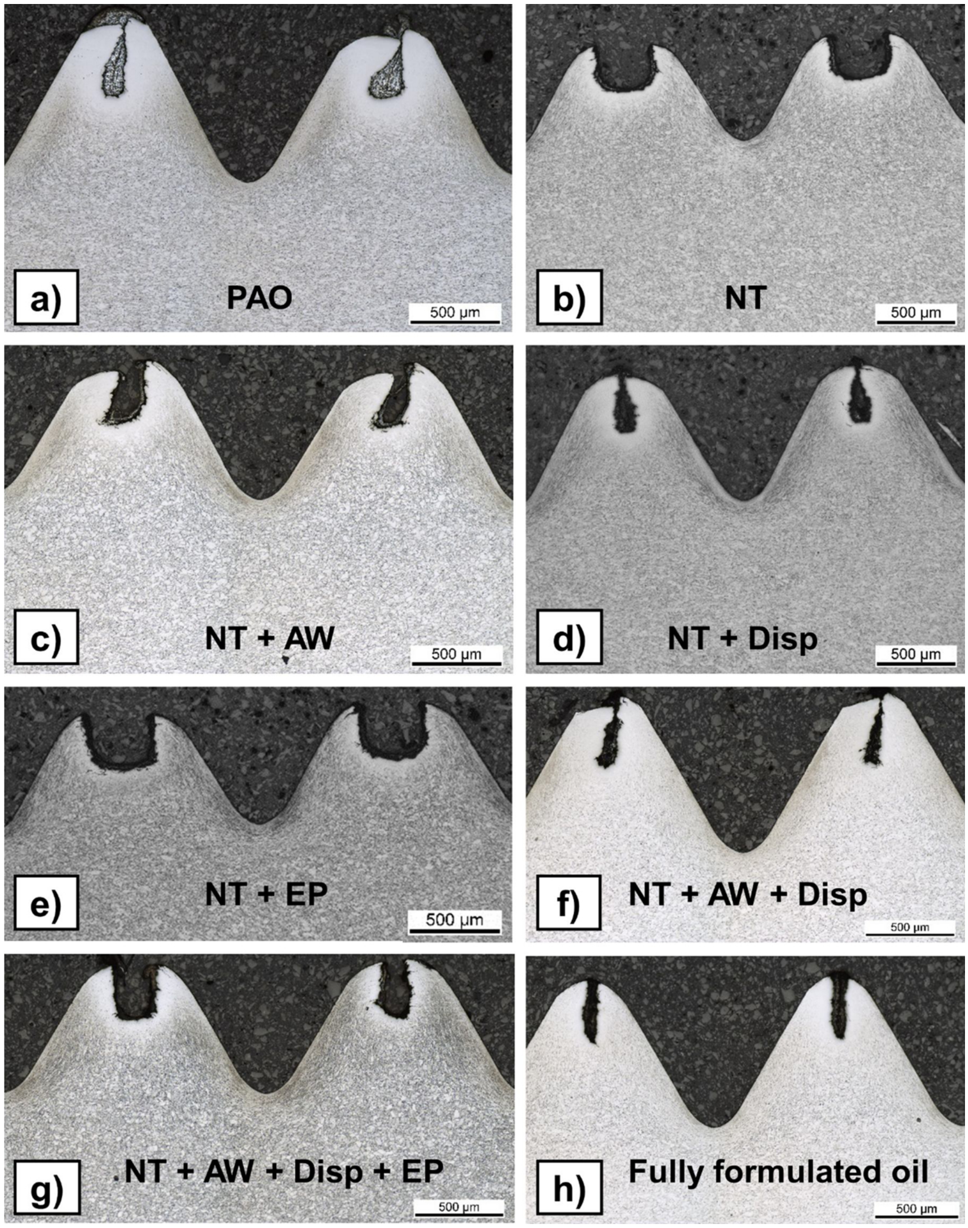


Fig. 7. Cross-section of the threads as seen using light microscopy. (a) PAO, (b) NT, (c) NT + AW, (d) NT + Disp, (e) NT + EP, (f) NT + AW + Disp, (g) NT + AW + Disp + EP, (h) fully formulated oil.

the other hand, no obvious Mo 3d could be detected for any of the other mixtures, but rather S 2 s core level spectra which were more pronounced in case of the fully formulated oil, NT + AW + Disp + EP mixture, and to some extent, in case of the NT mixture. The S 2 s core level spectra are indicative for the sulfide-based tribofilms (mostly ZnS) formed inside the threads [31]. The S 2p core level spectra (Fig. 11, bottom) show the presence of a main S $2p_{3/2}$ peak which is related to the presence of the sulfide-based tribofilms inside the threads. It should be noted that the Mo 3d and S 2p core level spectra were almost inexistent in case of the NT + AW, NT + Disp and NT + EP mixtures, indicating that under these testing conditions, the NT were not successful in interacting with the metal surfaces to form tribofilms. It is suggested that both additives (AW & EP) and the dispersant might have played a role in partly inhibiting the tribofilm formation, as previously reported in several works [22].

The peak fitting for the high resolution XPS scans performed on the threads lubricated with the NT mixture are displayed in Fig. 12. In case of the Mo 3d core level spectrum (Fig. 12, top) a doublet constrained by Mo $3d_{5/2}$ – Mo $3d_{3/2}$ with a spin orbit separation of ˜ 3.1 eV could be observed, and the following chemical species could be ascribed according to previous findings: ZnS (226.1 eV), MoS_2 (228.1 eV and 231.3 eV), MoO_2 (229.8 eV and 232.9 eV) and MoO_3 (232.3 eV and 235.4 eV) [31,32]. Regarding the S 2p core level spectrum, each chemical specie is fit with the S $2p_{3/2}$ and S $2p_{1/2}$ doublet and could be ascribed as follows: MoS_2 (161.5 eV and 162.7 eV) and SO_4 (167.9 eV and 169.3 eV). The presence of MoS_2 inside the threads generated using the NT mixture is therefore confirmed by means of XPS analysis.

4. Discussion

4.1. Interfacial interaction mechanism between MoS_2 nanotubes and zinc coated steel

The present work has investigated the potential of using transition metal dichalcogenide nanoparticles for forming operations. As an illustrative example, the form tapping process was selected for being

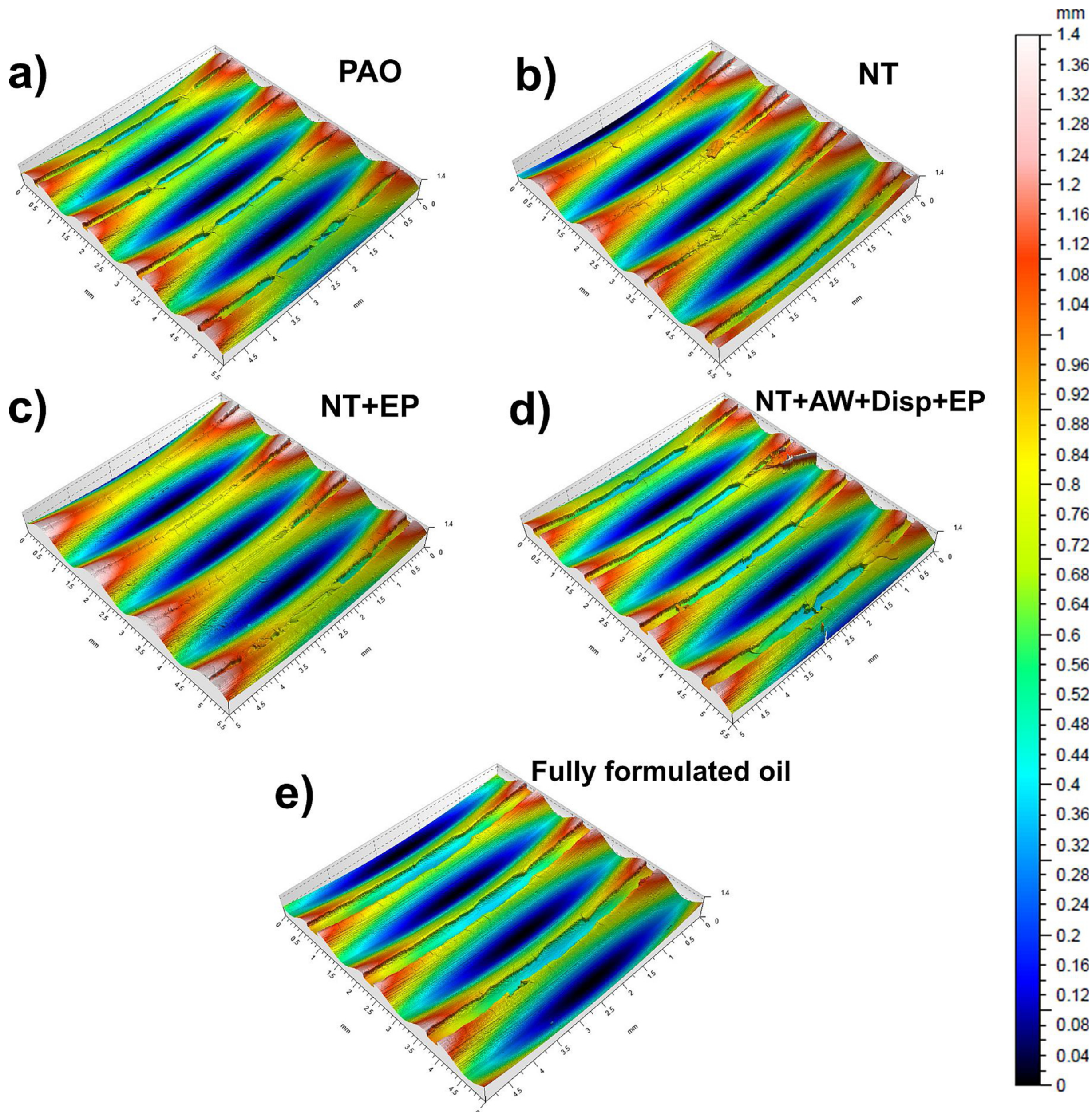
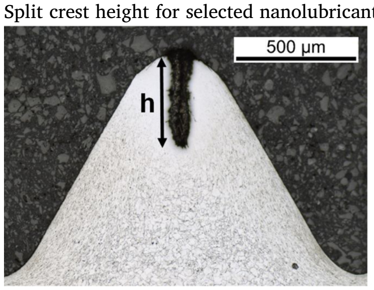


Fig. 8. Topography images of the threads formed using: (a) PAO, (b) NT, (c) NT + EP, (d) NT + AW + Disp + EP, (e) fully formulated oil.

Table 4
Split crest height for selected nanolubricants measured using 3D topography.



Nanolubricant	Split crest height *h* (mm)
PAO	0.27 ± 0.02
NT	0.31 ± 0.02
NT+EP	0.32 ± 0.01
NT+AW+Disp+EP	0.28 ± 0.02
Fully formulated oil	0.30 ± 0.01

representative of a forming process with highly demanding contact conditions. The form tapping process has received little attention in the literature, when compared to other machining processes such as milling or grinding. Further, the work focused on the use of zinc coated surfaces, which are highly relevant in automotive applications, but the performance of transition metal dichalcogenide containing nanofluids on such coatings has not being addressed so far to the best of our knowledge.

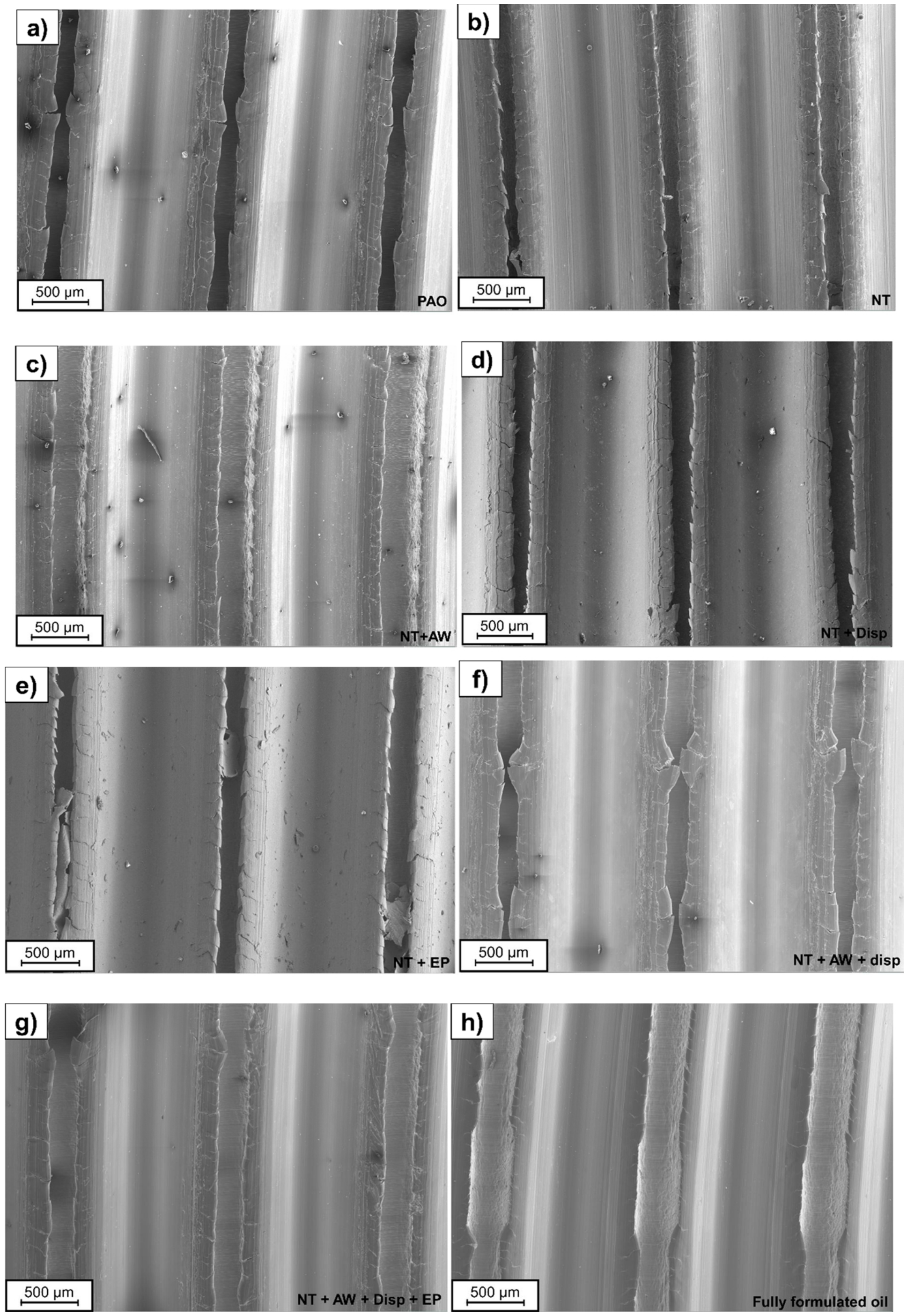


Fig. 9. SEM images of the threads. (a) PAO, (b) PAO + NT, (c) PAO + NT + AW, (d) PAO + NT + Disp, (e) PAO + NT + EP, (f) PAO + NT + AW + disp, (g) PAO + NT + AW + disp + EP, (h) reference fully formulated product.

The results obtained show that MoS_2 nanotubes are excellent friction modifiers and have a superb performance in terms of torque reduction during tapping. This results in the lowest sub-surface hardening of the thread, as shown on the surface microhardness and microhardness depth profile. The reason for friction reduction is attributed to the formation of MoS_2 tribofilm on the thread surface, as evidenced using XPS. The friction reduction mechanism between MoS_2 nanoparticles and steel surfaces was the subject of an intensive debate in the past. However, since the pioneering work of Joly-Pottuz [17] and the subsequent experimental evidence of Lahouij using in situ TEM experiments [33], there is a consensus that the dominant mechanism for friction reduction relies on exfoliation of MoS_2 nanosheets from the nanoparticles and adhesion of the exfoliated MoS_2 to the counterbody. The exfoliated sheets contain a few atomic monolayers of MoS_2. MoS_2 has a lamellar hexagonal structure characterised by tight covalent bonds within a lamella, and weak Van der Waals interaction between lamellas that allow easy shearing. The presence of a MoS_2 in the high resolution Mo3d XPS spectrum indicates that the formation of a MoS_2 tribofilm on zinc coated surfaces is feasible and is the mechanism leading to the observed friction reduction and the subsequent lower sub-surface hardening. The high resolution S2p spectrum also indicates the formation of ZnS during the form tapping process. This observation seems plausible when comparing to some previous studies using transition metal dichalcogenide nanoparticles under extreme pressure

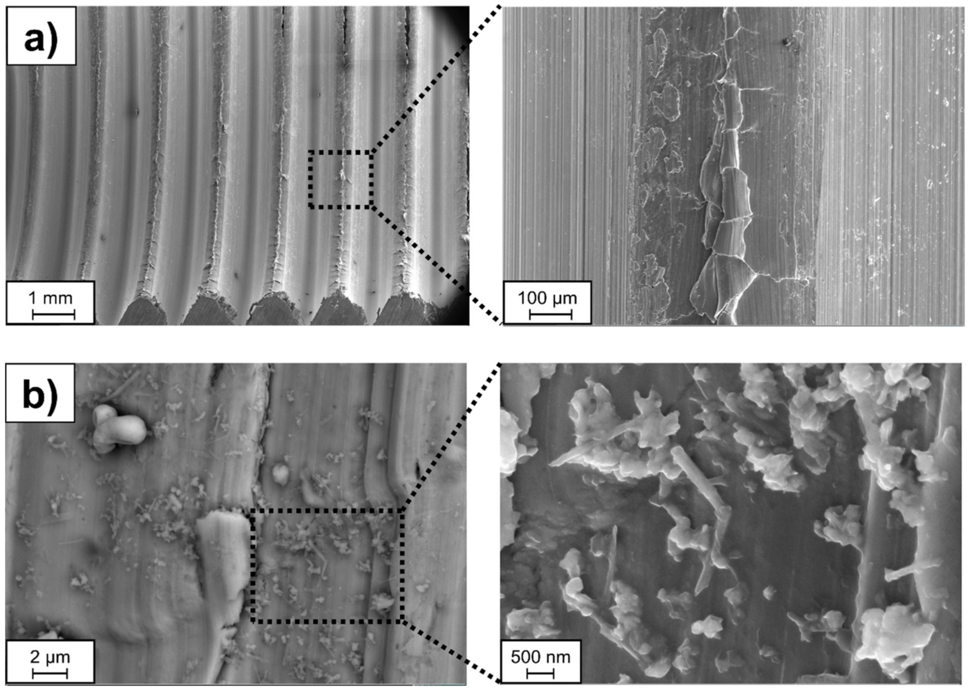


Fig. 10. Overview of a thread formed using NT and detailed of a fully closed split crest (a). Cluster of MoS_2 nanotubes and nanotubes debris found in the thread formed using NT + EP (b).

conditions in uncoated steel. In those previous works it was observed that the tribofilm formed under extreme contact pressures does not only contain exfoliated TMD nanoplatelets but also the presence of FeS_x, $FeSO_x$ compounds and MO_x (with M either Mo or W), both indicating a reaction between the MS_2 nanoparticles and the Fe substrate [14,30]. In our case, since the threads were hot-dip galvanized Zn coated steel, the presence of the coating leads to a tribochemical reaction with the nanotubes and formation of ZnS accompanied by MoO_x.

Some nanofluids are known to improve their performance in forming and machining operations due to an increase of the heat conductivity caused by the presence of nanoparticles in the fluid. However, in the present work, the contribution of heat conductivity is not expected to play a dominant role in the performance of the nanofluids investigated. As discussed by [24] in the context of MoS_2 and carbon nanotubes-based (CNT) nanofluids, the main role of MoS_2 nanoparticles in nanofluids is to improve their lubrication performance. On contrary, other nanoparticles chemistries, such as CNT, are known to enhance the heat conductivity of the nanofluid. The coefficient of thermal conductivity of carbon multi wall nanotubes is 3000 W/ m K in contrast to 138 W/ m K of MoS_2 nanoparticles [25]. Hence, the torque reduction mechanism that leads to lower surface hardening seems to be mainly due to an exfoliation mechanism of the MoS_2 nanotubes and subsequent adhesion of the MoS_2 platelets on top of Zn-coated steel, combined with a tribochemical reaction that leads to the formation of ZnS. The contact angle measurements also show no correlation between wettability of the nanolubricants and their performance during form tapping.

4.2. Interfacial interaction of MoS_2 nanotubes in the presence of oil additives

The performance of MoS_2-containing nanofluids in machining and forming operations has been previously investigated by some authors but the interaction of TMD nanoparticles with lubricant additives during forming has been overlooked so far. However, this interaction is crucial since nanoparticles alone cannot fulfil all the expected functions of a lubricant and need to be dispersed in stable solutions. To this end, we formulated the nanofluids by mixing the selected MoS_2 nanotubes individually with commonly used lubricant additives.

A viable use of nanolubricants in forming and machining operations requires the readily availability of stable dispersions. Otherwise, the addition of nanoparticles to a base lubricant generally results in a progressive sedimentation of the nanoparticles to the bottom of the mixture container. Dispersants play a crucial role in order to achieve stable dispersions. However, their interaction with MoS_2 nanoparticles has posed serious concerns so far. According to the available literature, the presence of succinimide dispersants led to antagonistic effects with TMD nanoparticles under reciprocating sliding in steel surfaces [22]. The reason was attributed to the lack of tribofilm formation. TMD

Table 5
Relative surface atomic concentrations of elements found inside the threads.

Element	Concentration (atomic %)						
	Fully formulated oil	NT + AW + Disp + EP	NT	NT + AW + Disp	NT + AW	NT + Disp	NT + EP
S 2p	3.0	6.2	5.4	2.1	4.4	2.4	2.8
Mo 3d	–	–	1.7	–	–	–	–
C 1 s	29.6	34.8	26.7	44.1	54.6	80.5	80.9
O 1 s	27.1	24.0	33.5	29.2	21.9	9.7	8.6
Zn 2p	40.4	35.0	32.7	21.0	19.2	6.4	6.7
N 1 s	–	–	–	3.6	–	–	–
Fe 2p	–	–	–	–	–	1.0	1.0

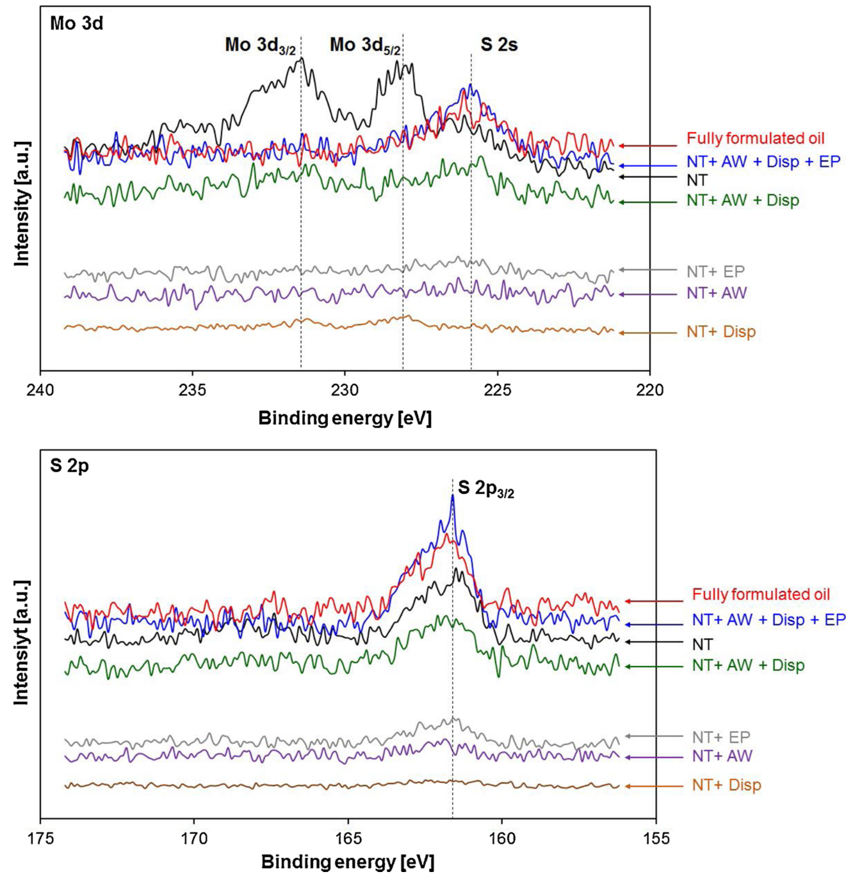


Fig. 11. High resolution XPS spectra of Mo 3d (top) and S 2p (bottom) acquired from all the tested threads.

nanoparticles were able to become trapped in the contact and could exfoliate. However, the presence of succinimide prevented the adhesion of exfoliated platelets to the counterbody and the subsequent low friction. On contrary, other authors reported a similar antagonistic effect but they found the presence of a tribofilm containing mainly transition metal oxides [23]. Under extreme pressure conditions, the interaction between TMD nanoparticles and succinimide results in the tribochemical formation of sulphide compounds that prevent metal to metal contact and increase the load carrying capacity of the nanolubricant [23].

In our study, the performance of MoS_2 nanotubes (NT) is in general impaired in the presence of dispersants but the performance loss is significantly less dramatic when compared to reciprocating sliding contacts. In form tapping, we noted that despite the torque rise observed, the maximum torque is still far lower when compared to the use of dispersants alone (without nanotubes), thus indicating the interaction of the NT with the surface despite the presence of dispersants. The confirmation of this interaction was evidenced by the Mo signal measured on the threads using SEM/EDX and by the clusters of nanotubes found in the thread. Note that the threads were ultrasonically cleaned in solvents after the tests and before the surface analyses, so that the results indicate the formation of a low friction tribofilm containing Mo and can not be attributed to the presence of non-reacted remnants of the nanolubricant. Combined with the results of XPS that indicate the presence of sulphide compounds for some of the nanolubricants containing dispersants, it points out that in forming operations the local contact conditions are severe enough to lead to a tribochemical reaction of the MoS_2 nanotubes with the Zn coating. Such tribochemical reaction was observed by the authors in “naked” steel surfaces in the context of extreme pressure experiments and were able to significantly improve the load carrying capacity of the nanolubricant [21].

In case of the anti wear additive, ZDDP, the available literature has highlighted the synergy between ZDDP tribofilms and TMD nanoparticles in reciprocating sliding contacts [19,20]. The reason was attributed to the exfoliation of TMD nanoplatelets on top of ZDDP tribofilms, as evidenced using transmission electron microscopy [20]. Also a good synergy was found under EP conditions [23]. In form tapping, the performance in terms of torque reduction seems to be present, even though the maximum torque values measured are higher than when using NT alone. Remarkable is the fact that the thread morphology when using AW additive is not symmetric and homogeneous, and particularly important, in the additional presence of succinimide dispersants, the torque values are high. The reason for this lack of synergy between MoS_2 nanotubes and ZDDP during our form tapping experiments is attributed to the lack of formation of a ZDDP tribofilm. It is known that ZDDP requires a number of cycles for building a protective tribofilm [34–36]. Also ZDDP tribofilm formation is supported by temperature [37]. Therefore, ZDDP is particularly suitable for additive in engine oils that operate at around 100 °C under reciprocating sliding. In our experiments, since six threads were formed for each lubricant, the conditions were not favourable for tribofilm formation.

The best synergy between NT and lubricant additives during form tapping seems to be given by the sulphur-containing EP, which is an additive already widely spread used in forming oils. As reported in literature, under reciprocating sliding conditions the surface competition between NT and EP leads to a poor friction performance. However, under EP conditions, their combined performance is superb [23]. The reason is that whereas NT partly react with the substrate to build sulphides and MO_3 (with M being Mo or W) [14,23,30], the presence of the S containing additive allows the in situ re-sulfurization of the tribofilm, thus improving the NT performance. In this case, even lower torque values can be achieved in the presence of dispersants as well, supporting our observations that, besides exfoliation, tribochemical

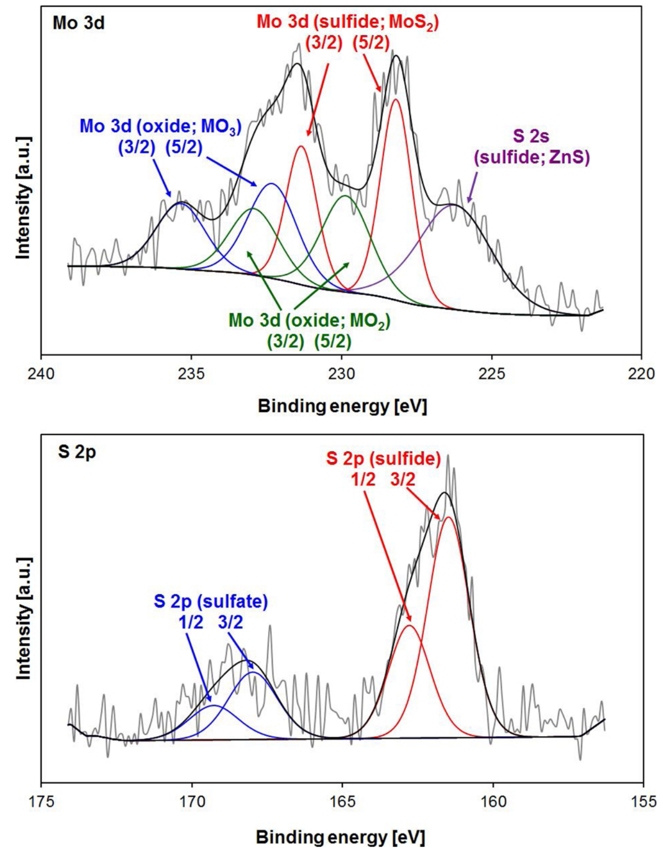


Fig. 12. High resolution XPS spectra of Mo 3d (top) and S 2p (bottom) acquired from the thread lubricated with NT mixture (best performer in terms of torque).

reactions play a fundamental role during form tapping. A similar re-sulfurization process has been recently observed on nanolubricants containing MoO_3 nanotubes on the presence of S-containing additives [38].

4.3. Outlook

To sum up, it can be stated that MoS_2 nanotubes are a promising lubricant additives for forming and machining applications due to their excellent performance in extreme-pressure conditions. This could be exploited for developing novel and greener forming oils formulations with lower base oil viscosity and may open the door for the future use of nanoemulsions in applications that still require straight oils nowadays and for their use in nanofluid minimum quantity lubrication set ups. However, special care should be set when using the NT in fully formulated products since antagonistic effects can hamper their superb friction and wear performance.

As mentioned, form tapping has been proposed as reference test for cutting fluids, thus being particularly relevant [4]. This means that the results presented can provide an initial insight for other forming processes that operate under similar contact conditions.

For prospective studies, the key point seems to lie in finding a suitable balance between dispersant concentration and mixture stability. Previous works have identified that sulfurized olefin polysulfide is already able to provide a certain dispersibility of MoS_2 NT [23], even though the long term stability of the mixture was not address. This could help to balance in a more favorable way the use of succinimide. Also in terms of thread morphology the performance of NT + EP is satisfactory, since the formation of sulfides at the contact interface of the zinc-coated steel prevents metal to metal contact and adhesion.

5. Conclusions

This work has investigated the feasibility of using MoS_2 nanotubes in form tapping of zinc-coated automotive parts by studying their performance alone and in combination with lubricant additives typically found in fully formulated forming oils.

The results show that MoS_2 nanotubes are able to form a tribofilm on zinc coated steel surfaces that results in torque reduction and the lowest sub-surface hardening. The surface analyses point out that the tribofilm formation mechanism is by exfoliation along with the tribochemical formation of ZnS. The presence of oil additives in the nanofluid leads always to a poorer performance in terms of friction.

The lowest synergy was obtained with succinimide dispersants, even though the MoS_2 nanotubes were still be able to partly reduce the torque. The torque reduction could be attributed to a tribochemical reaction between nanoparticles and the zinc coating.

In combination with anti wear additive, the nanotubes were found to perform well in terms of torque reduction but the morphology of the threads show asymmetry of the split crests and crack formation. The formation of a protective anti wear tribofilm requires the continuous sliding over a surface for a certain number of cycles, which did not occur during our experiments.

Sulfurized olefin polysulfide extreme pressure additive has a very good synergy with MoS_2 nanotubes in form tapping. While the torque measured during tapping is only slightly larger than when using nanotubes alone, the thread morphology becomes symmetric and with lower cracks. Sulfurized olefin has a good performance even in the presence of anti wear additive and dispersants. Since sulfurized olefin is currently widely spread in forming oils, their synergistic effect with nanotubes makes them suitable candidates for being used in prospective formulations.

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