2017

Tungsten and molybdenum containing coatings and their interaction with oil in tribocontacts

Endreport for the Austrian Marshall Plan Foundation

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Outline

In many tribological systems friction and wear are accompanied by tribochemical reactions of the surface material, forming mostly oxidic products. In contacts that contain the elements S and W or Mo the reaction can also lead to the formation of MoS_2 or WS_2. Those two compounds are well known for their low coefficient of friction and are commonly applied as solid lubricants. Several publications have tried to combine the superior properties of those sulfides with the benefits of liquid lubrication. A direct in situ formation of a low friction tribofilm in a contact could reduce the friction and wear drastically at very little expense and offers an elegant alternative to introducing the solid lubricants as nanoparticles.

My work studies W and Mo containing coatings, their properties and their interaction with oil, doped with extreme pressure (EP) additives. The additives we used for this study consist of around 40 % sulphur in form of sulphurized olefin polysulphide. First tribological investigations of W-based coatings showed an anticipated drop of friction if EP additives are added to the base oil. Despite our expectation a reduction of friction was even noticed if no EP additive was applied, and due to the lack of S no sulfides could have formed. A recent paper [1] of Prof. Erdemir et al. in the highly esteemed journal nature describes the formation of a low friction carbon-based tribofilm on Cu-doped coatings. This tribofilm has a graphite-like structure and originates from a catalytic reaction of the lubricant.

My research in the United States focused on the distinction between a carbon based graphite like tribofilm and the in situ generation of MoS_2 or WS_2 tribofilms, what parameters influence them and if there is a competition with the formation of graphite like tribofilms. We investigate the favorable reaction pathway for the generation of MoS_2 and WS_2 and tested if coatings could be applied to aid and fine tune any tribochemical reaction.

Problem definition

As the reports of V. Totolin et al. [11] already described the tribochemical formation of TMD on WC-functionalized hammer peened surfaces, we started our research with tungsten carbide based coatings. To advance our research into the tribochemical reaction we tested tungsten carbide coated steel samples in a SRV oscillation module at varying loads (10 – 50 N), with different lubricant composition (0 % to 5 % EP additive) against a 100Cr6 steel ball counterbody. To assess the tribological properties, the coefficient of friction (COF) was calculated. To illustrate the further argumentation three exemplary measurements (0 %, 1.5 % and 5 % EP additive) at a load of 10 N are plotted in Figure 1 and show the development of the COF with progressing test time. First results indicate that it is possible to reduce the COF in comparison to the 0 % EP additive reference. However, the measurements for higher EP additive concentrations indicate that too high concentrations of the sulfur source are self-defeating and result in much higher friction levels. We suspect this to be the result of accelerated consumption and degradation of the coating. The optimum concentration will be investigated in further tests.

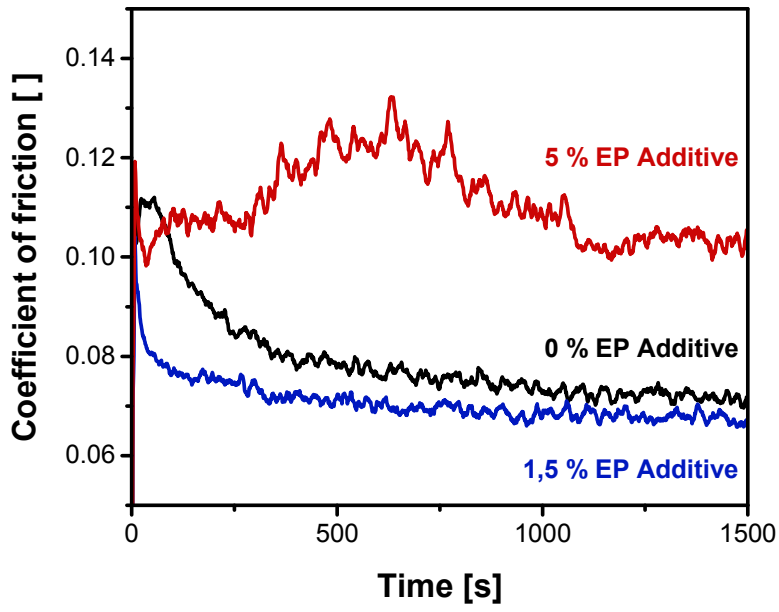

Figure 1: Evolution of the COF of a lubricated tungsten carbide coating against 100Cr6 steel ball contact at 10 N and the influence of the lubricants EP additive level.

Both EP additive containing systems appear to start at elevated friction levels until a low friction tribofilm is formed after a short lag time, reducing the friction considerably for low EP Additive concentrations. In

case of higher EP additive concentration this formation is displaced by detrimental conditions after only a few seconds.

In case of the reference 0 % EP additive base oil we were expecting stable conditions and a more or less constant COF between 0.10 and 0.12. Those expectations clearly haven't been met and a deeper understanding of what happened and why there appears to form a low friction tribofilm without the presence of Mo or W. This unexpected effect could probably be explained by the formation of a low friction carbon based tribofilm. A carbon based type of tribofilm has been recently described at Argonne National Laboratory (ANL) by Prof. Erdemir et al. in their publication [1] in nature. The low friction tribofilm was reported to form catalytically on copper doped molybdenum nitride coatings with the lubricant, a simple PAO 10 base oil, acting as a carbon source. In our case further investigations will have to be made in effort to clear up if this type of tribolayer has formed and if there is any superposition of the formation of a carbon and TMD based tribofilms. We will need to investigate whether there are any interactions between those two lubricating effects in order to be able to accurately distinguish between those two effects and to attribute the appropriate reduction of the COF to the formation of TMD reliably. To be able to differentiate if the reduction of the COF is caused by the formation of a TMD tribofilm or by graphitoid carbon will be essential to understand the tribochemical reaction between EP additives and W or Mo based coatings.

A main necessity was to find the right analytical methods to clearly prove the existence of the in-situ formation of TMD tribofilms. As most promising potential analytical method, Raman Spectrometry was a important focus of this work, since it offers good information about the structure of carbon-based tribofilms and MoS_2 as well as WS_2 do not display any interference with oxide signals that could render any results inconclusive.

Once we are sure that we can keep apart the TMD in-situ formation from any interfering effects like the in-situ generation of carbon-based tribofilms it allows us to further study the reaction pathways a possible in-situ formation chooses by comparing different systems.

Concept of the in-situ formation of MoS_2 and WS_2:

The reduction of friction in combination with lower wear rates is a major goal in order to reduce energy consumption and simultaneously extend the lifetime of industrial components. Most of the commonly used extreme-pressure (EP) and anti-wear (AW) additives are able to successfully meet these demands in lubricated contacts. However, the increasing use of thin films, for enhancing properties of the bulk materials, poses a serious challenge for conventional additives since they were designed to operate in the presence of ferrous surfaces. The development of oil additives specifically tailored to interact with coated surfaces seems currently unviable, as in most applications, only a few of the components lubricated by the same oil are coated.

In recent years, solid lubricants such as transition metal dichalcogenides (TMD) have attracted attention in form of nanoparticle additives for conventional oil-based lubricants. Due to their easy shear plane very low friction can be achieved, but those nanoparticle additives entail several disadvantages, including the need to compose a stable dispersion. An in-situ formation of said lubricating compounds via a tribochemical reaction path between a coating and conventional S containing extreme pressure (EP) additives could prove to be much more advantageous.

In this work, although the Mo-based system is studied as well an emphasis has been placed on WS_2 due to its higher load-bearing capabilities and wider range of application. So far there have been 5 approaches reported in literature [2]:

1. Initial amorphous WS_2 coatings: Crystalline WS_2 coatings are very soft, deformable and lead to a high contact area and wear. Therefore, in order to overcome those problems the coatings can be deposited in an amorphous structure, that is more durable and harder [3]. In a shear deformation of the tribocontacts the unordered coating experiences a long range order that eventually leads to the formation of crystalline structures.
2. Harder alloyed coatings containing W and S: This approach again deals with the problems due to the low hardness of crystalline WS_2. In order to achieve a hard coating, the sputtered WS_2 film is doped with additional elements like C, N, Cr, Ti [3]. In the

tribocontact the surface region of the thin film again is getting rearranged and a removal of the doping elements leads to a WS_2 based tribofilm staying behind.

3. Incorporating WS_2 into a metallic matrix: Solid lubricant nanoparticles are incorporated in a metallic coating like electrolytic nickel coatings [4]. During wear those particles are exposed and their fragments form a lubricating and wear protective tribofilm. A relatively related method, and therefore mentioned in this context, is the application of WS_2 nanoparticles dispersed in oil.
4. Tungsten-DLC and S-containing lubricant: WS_2 tribofilms with astonishing drops in friction have been reported for systems that contain W-DLC coated parts and are operated in lubricated conditions in the presence of S [5,6]. This approach also includes the reports of v. Totolin et al. who reported the formation of WS_2 in linear oscillating reciprocal tribotests on steel samples that contained WC particles that had been imbedded by hammer peening, lubricated with a sulfur containing oil [11].
5. Metallic tungsten reacts with a hard counterface containing S, like metastable S-doped titanium carbide coatings.

In order to evaluate the potential of this in-situ TMD formation and to assess the synergy between protective hard coatings, conventional EP additives and the formed tribofilms, linear unidirectional sliding ball on disk tests (point contact) have been studied. A schematic of the general setup of our tribotests is displayed in Figure 2. The investigations were carried out on sputter deposited W- and Mo-based carbide and nitride coatings on 52100 steel as well as some tests were performed on uncoated metallic bulk materials. In most cases, the counter body was a Si_3N_4-ball, although a few tests also were done with a 52100 steel ball. The contacts were lubricated with a PAO 8 base oil, doped with 0 % to 5 %

of a sulphurized olefin polysulphide EP additive (Lubrizol LZ 5340 MW). This additive has a high S content of about 40%.

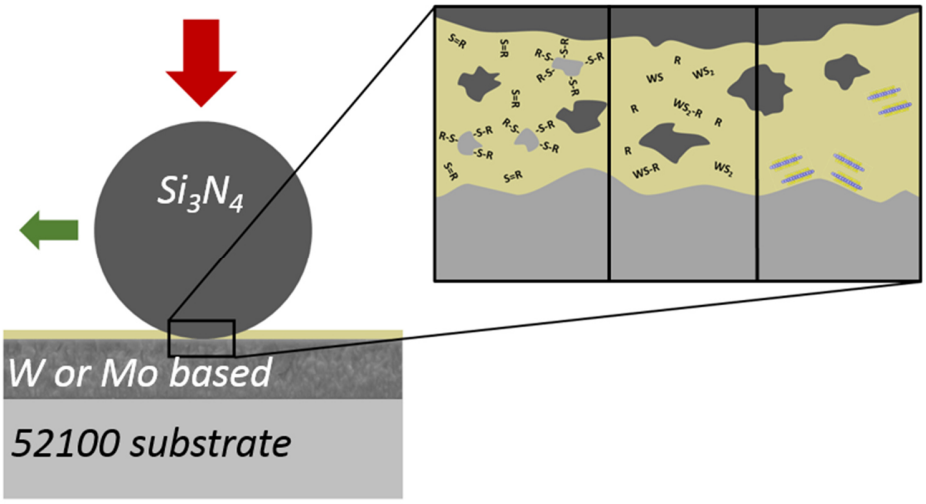

Figure 2: Concept of a in-situ formation of MoS_2 or WS_2 in a unidirectional ball od disk sliding contact with a suggested three stage tribochemical reaction.

Other research groups have reported that the main trigger for an in-situ formation is the contact pressure. In this case most of the tests were carried out with a load of 2 N, resulting in a contact pressure of approximately 0.9 GPa. The sample speed was kept at a constant 0.1 ms^{-1}.

We envision the in-situ formation, as portrayed in the schematics, as a tribochemical reaction that can be divided into three segments. The first step is the interaction of the EP-additive with the contact surface, as well as with wear debris. The Si_3N_4-ball has been chosen because of its chemical inertness and low interactions with the oil itself. Most papers, addressing the in-situ formation of MoS_2 or WS_2 also reported that the presence of Fe is needed to facilitate the tribochemical reaction [8-10]. Applying a Fe free system allows us not only to exclude any analytical interferences from iron sulfides but also tests the hypothesis that Fe might have a catalytic effect.

After the initial interaction of surface and lubricant, the tribochemical reaction that is mainly dominated by high pressure and shear forces in the contact results in the formation of WS_2 molecules and fragments in an isolated or a unoriented state. Only in a third step, the amorphous WS_2 reaction products are reassembled under pressure and shear in the contact to form crystalline structures that display the typical shear planes of WS_2 and allow for the low friction regime. This formation of crystalline WS_2 has already been reported by J. Martin et al. [7] for amorphous WS_2 coatings that form crystalline tribofilms in-situ.

On the analysis of graphite-like C, MoS_2 or WS_2 tribofilms

First of all, we have to distinguish between analytical methods that simply yield a chemical composition of elements and those that also include information about their bonding states and respectively their molecules and structures. The chemical composition of a sample can be determined quite easily with a wide array of methods like X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDX) and many others. But when it comes to gathering information about the exact structure and chemical bonding states in samples we often encounter many additional challenges due to limited methods, sample volume and interferences.

In the case of our tribofilms the sample volume is an extremely limiting factor, since the film might only be a few nm or several atom layers thick and the interacting volume is extremely low. As a result, many conventional methods for structural analysis like XRD are not applicable anymore. The investigation of tribofilms requires methods that are especially surface sensitive like XPS, Secondary Ion Mass Spectronomy (SIMS) or Raman Spectroscopy.

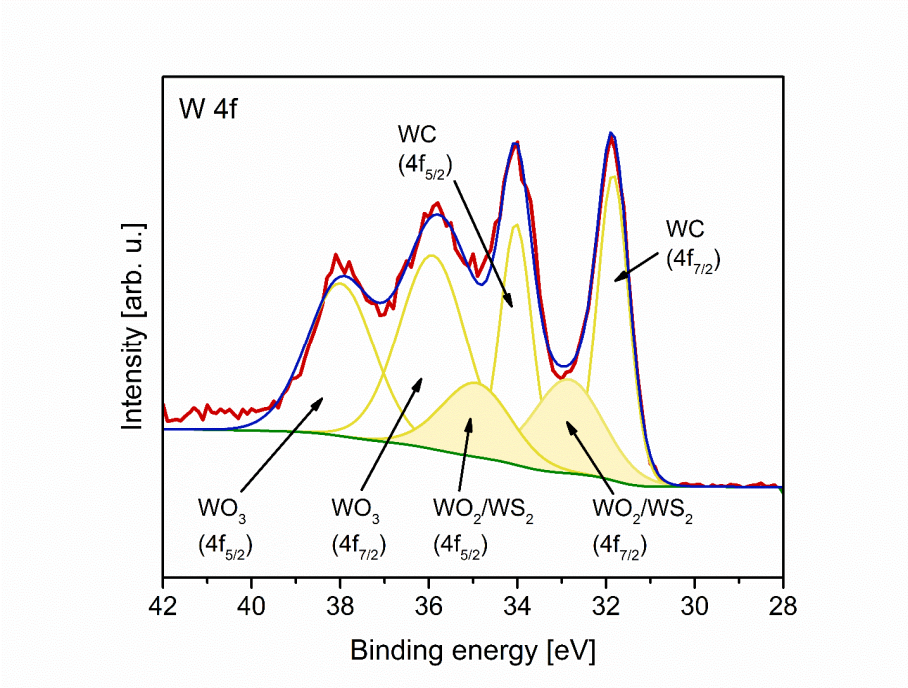

Figure 3: The W4f XPS scan of a tribocontact after the in-situ generation of WS_2, demonstrating the difficulty of overlapping singnals with WO_2.

If we look at the spectrum of a weartrack obtained by XPS we can see that the peaks of WO_3 ,WO_2, WC and WS_2 are highly overlapping. To interpret the measurement correctly a curve fitting process needs to

be applied with high precision. XPS can give us some information about the bonds in the tribofilm, but standing alone it is not sufficient evidence for the in-situ formation of WS_2 or MoS_2 .

Another very surface sensitive method is SIMS, which is based on mass spectronomy. Particles are sputtered from the surface by impacting molecular clusters and are analysed according to their mass in a time-of-flight analyzer. While the mass difference between O- and S- can be resolved, due to the technical achievable resolution and the vast number of isotopes of S, O and especially W, it is not possible to distinguish between for instant a WS^- ion and a WO_2^-.

The first secondary ion mass spectrometer was built by Herzog and Viehböck during the late 1940s at the Vienna University, paving the way for a method of trace analysis and imaging, that SIMS is today. With a detection limit below 1 ppm for all elements SIMS is a very sensitive method that can either be used for simple trace analysis or imaging of the distribution of elements, but also for investigations of depth profiles. In case of the investigation of tribofilms this wide range of measuring modes is a significant benefit. The idea behind SIMS is very straight forward: the sample is subjected to primary ion bombardment from a ion source under high vacuum conditions, instigating the emission of secondary ions and neutrals from the sample material. Since the composition of the secondary ions is proportionate to the sample composition analyzation of the secondary ions in a detection unit with methods of mass spectroscopy e.g. time of flight mass spectroscopy TOF-MS delivers mostly qualitative composition information. Because the sputter yield and rate varies for different elements and is predicated on crystallographic orientation, densities and matrix effects, quantitative information can only be obtained in comparison to very expensive standards that accurately portray the sample's habit.

It has been shown, that higher sensitivities can be achieved if the primary ions are able to react with the sample material. Therefore O^{2+} ions are used to bombard electropositive elements and Cs^+ ions for secondary ion generation of electronegative elements. To generate O^{2+} ions oxygen is submitted to a glow-discharge that is sustained by a magnetron and a electron beam from a tungsten cathode in a so called duoplasmatron. Some of the oxygen molecules are ionized and accelerated towards and throughout a charged grid generating an ion beam. Since Cs melts around 28,5 °C its ions are produced in a liquid metal ion source. A pointed needle within a capillary, that is connected to a molten metal reservoir, is placed close to an extractor with a potential of 10-30 keV. As a result of the capillary action molten Cs is transported towards the needles tip and forms a covering thin film around it. As the acceleration potential is applied to the extractor the thin molten film forms a small crest at the tip (Taylor cone) and the Cs^+ ions are generated in a small fraction of the volume above it and accelerated towards the sample. While a measurement that focuses on tungsten alone would yield better results by sputtering in positive mode, in

order to gain the best results for the distribution of O and S the measurements of the tribofilm are performed in negative mode with Cs^+ ions

To allow for element distribution images to be captured spatial resolved measurements are required, hence the generated ion beam is passed through a focusing and a raster unit, similar to the concept of SEM. If the bombarding ion beam exceeds a dose of 1011 mm^{-2} ions, the surface can be assumed as not intact and a sputter equilibrium is attained at a depth greater than the mean implantation depth. Aside from the generation of secondary ions the sputtering process leads to a variety of alterations in the sample material. Due to the different sputter yields of components enrichment and depletion of some elements can occur. As a result of the enrichment of elements with lower sputter rates, due to their rising mass fraction in the impact zone their contribution to secondary ions increases until the composition of the sample is the same as the composition of the emitted secondary ion cloud. Every sputter process is accompanied by the transfer of impulse on sample material and thereby atomic mixing of the surface regions, that limits the reachable depth resolution. But an even bigger influence on depth resolution is crater bottom roughening induced by variations of sputter coefficients depending on the crystallographic orientation of anisotropic compounds. In order to keep a tribofilm intact the measurements are performed at very mild conditions and the sputtering of the surface is kept at the minimal necessary level. The SIMS setup also includes an adjoining flood gun, which is a cathode, providing the target surface with low energy electrons for compensation of charging effects.

The TOF-MS was developed as a common analyzing unit for application in SIMS. Secondary ions are extracted from the proximity of the sample and accelerated to a given potential, hence all ions possess the same kinetic energy. Before they strike a detector they are enabled to travel along a drift path of the length L allowing for their separation according to:

$$(m*L^2)/(2*t^2)=q*U^0$$

with m being the ion mass, t the time of flight, q the ions charge and U_0 the acceleration potential. Lighter ions travel at higher speeds as heavier ones and as a result the time of flight allows for the calculation of the mass to charge ratio and further mass analysis. To obtain accurate time measurements for travelling ions a well defined "start line" is needed which can be achieved by using a pulsed primary gun. For the generation of discrete packages of ions and the measurement of their time of flight a sophisticated pulsing, counting and timing system with accuracies below one tenth of a nanosecond is required.

For the detection of incoming secondary ions electron multipliers are used up to their saturation intensity of $2*10^6$ s^{-1} ions. Exceeding intensities are measured with a very fine adjusted Faraday cup whose output at the transition to the electron multiplier is identical allowing for continuous measurements at the switch.

As mentioned above, SIMS allows for the gathering of depth profiles with restricted depth resolution due to the surface roughness, atomic mixing and the crater bottom roughening. The gathered TOF-MS data is evaluated in dependence of the sputter time. Subsequent surface analysis using a profilometer allows for association of sputter times with depth values under careful consideration of changing sputter coefficients in different parts or layers of the sample. The primary gun is adjusted for analysis and therefore limited in reachable depth because only 0,1 % of the work cycle is dedicated to ion bombardment. Dual beam techniques make use of a anticyclical secondary gun that without applying a extraction and acceleration voltage for TOF-MS enables sputtering during the analyzing time without interference. As the two guns are not coupled independent adjustment of the secondary gun allows for optimization of intensity, energy, angle and diameter for material removal. A side effect to the intermission of the extraction process is a enhancement of the flood guns efficiency.

In other analytical systems information about the WS_2 content could be gained (with XPS or SIMS) simply by measuring reference spots and comparing the WO_2/WO_3 ratios and attributing the difference to WS_2. But a tribochemical reaction is very complex and yields a quite broad spectrum of chemical components including nonstoichiometric oxides, rendering any conclusion rather useless.

The only technique that is surface-sensitive enough and does not suffer from interference in this problem definition is Raman microscopy. For this work we used a Renishaw inVia Raman Spectrometer and a 633 nm helium-neon-laser. Due to the Raman-effect electromagnetic radiation is scattered inelasticly, exchanging energy with the molecule and exciting a rovibronic state. A spectral analysis of the scattered radiation will therefore not only contain the initial wavelength of the laser, but will also show different wavelengths that are directly linked to the molecules rovibronic states.

The formation of a carbon tribofilm:

The in-situ formation of graphite like carbon tribofilms has first been reported by A. Erdemir et al. from Argonne National Laboratory. Polyolefin chains are broken down and reassembled to form graphite-like carbon structures. The main analytical method to determine whether this type of tribal film has formed is Raman spectroscopy, showing clear peaks for the D and G band [1]. The tribofilm is produced in the presence of copper as a catalyst in and vanadium nitride coating.

In the case of our tribotests on tungsten carbide coatings the potential carbon-based tribofilm could originate from two possibilities: The carbon film could have formed in a similar way as described by A. Erdemir et al. in a catalytic reaction on the coating surface. The other possibility is that a carbon tribofilm could be a result of residual carbon deposits, that could have been introduced by the sputtering process. Excess carbon from the co-sputtering of the graphite cathode could have resulted in the inclusions of amorphous carbon in the coating. In a tribochemical reaction it is plausible, that these carbon deposits could have re-structure to form graphite-like structures.

To rule out the possibility of residual carbon in the coatings, the coatings have been investigated with Raman spectroscopy in top-view and cross-section. All WC-based coatings do not show any of the peaks that could be linked to residual carbon from the sputtering process. Further, Elastic recoil detection analysis (ERDA) was applied to investigate the carbon content of the coatings and showed, that the C-content in the coatings was sub-stoichiometric. This means that if a carbon film had formed, it would most likely be the result of an in-situ formation. While the current reports focus on the catalytic contribution of copper dopants in the coating, it has been suspected that several transition metal nitrides could act as a catalyst opening up the possibility of a carbon-film formation on our coatings.

To revise the tests of our pre-study, we performed ball on disk lubricated unidirectional sliding tests. The 52100 steel flat was coated with a WC-based thin film and the tests vs. a steel ball as well as an inert Si_3N_4-ball were lubricated with PAO 8 base oil doped with 0 % to 5 % EP-additive. Tests were performed with a load of 2N and a sample speed of 0.1 ms^{-1} at room temperature and 100 °C each.

The results in Figure 4 demonstrate at first sight, that the coefficient of friction is very unstable and that the reproducibility is very limited. While with the ceramic ball the friction at elevated temperatures was higher in all tests, the elevated temperatures in combination with a steel ball and EP-additive lead to slightly lower friction and a more stable run. This is most likely due to the formation of iron sulfides. Investigations of all wear tracks with Raman spectroscopy did not yield any formation of a carbon based or transition metal chalcogenide based tribofilm. Investigations into the reason for the unstable behavior of the tests led to the conclusion that the surface roughness of the coating is too high due to the formation of droplet-like particles and other coating imperfections. These hard asperities act similar to grinding paper or a file and result in an extremely high-abrasive wear regime.

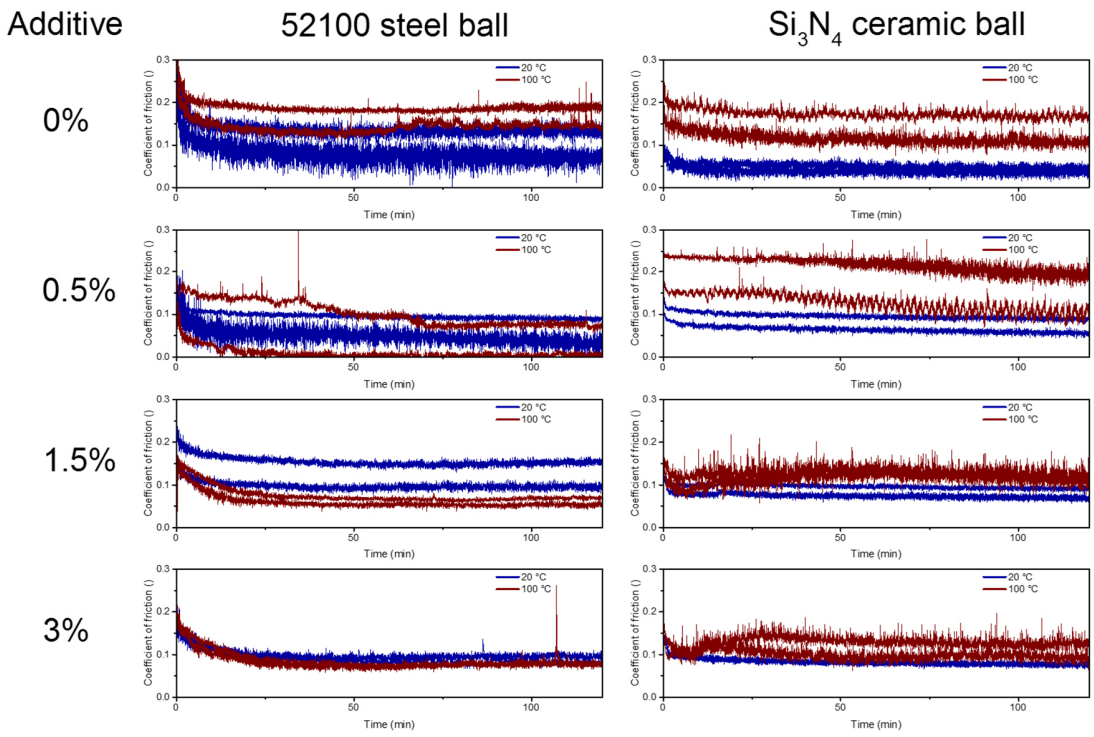

Figure 4: The coefficient of friction of a Si_3N_4-and steel ball, resepectively vs. a tungsten carbide flat demonstrating very unstable tribological behavior. The temperature plays a clear role in the behavior of the coefficient of friction.

Due to the abrasive wear the point contact is ground down to a circular wear scar in just a few cycles. This reduces the contact pressure and hence makes an in-situ formation less likely, while the coefficient of friction seems to decrease due to the bigger contact area and the slightly higher influence of

hydrodynamic friction. This can in particular be demonstrated by one measurement whith the 52100 steel ball and 0.5 % EP-additive at 100 °C that slips into hydrodynamic lubrication almost completely, resulting in a extremely low coefficient of friction below 0.01.

In an attempt to eliminate the influences of the surface roughness we polished the coatings with a 1 µm diamond suspension and retested them. Although the surface was very smooth now, the tests again displayed very instable runs, a high coefficient of friction and high abrasive wear. Microscopy and SEM images revealed, that the coating is suffering from cracks and that small sections are breaking off, acting as highly abrasive hard particles. The reason for this lies in the adverse materials combination. Tungsten carbide is a very hard and brittle material that on top of these properties themselves is under high compressive stress due to the PVD deposition process. Although the martensitic steel substrate is considered to be hard, it still enables microscopic elastic deformation of the surface, that the brittle tungsten carbide can not cope with. This leads to the formation of cracks and the generation of the abrasive particles.

To conduct further research on WC-coatings harder substrates will need to be applied in order to completely eliminate these side effects and to determine, whether WC can facilitate an in-situ formation of WS_2. Furthermore it is important to identify the most favorable reaction pathway, influences, the necessary conditions and if the rate of formation can be high enough to allow for sufficient lubrication and wear protection.

The in situ formation of MoS_2:

As a first step, it was important to uncover under which conditions an in-situ formation can occur and which reaction pathway is the most favorable. We started our investigations with a metallic molybdenum flat due to its higher reactivity as well as weaker metallic bonds and performed lubricated ball on disk tests with a Si_3N_4-ball. The Si_3N_4-ball was chosen because of its high hardness and incapability to react with the oil or EP-Additive. In order to offer a point of reference for all future friction measurements, reference tests with a 52100 steel ball vs. a 52100 steel flat were performed with all additive concentrations, always resulting in a coefficient of friction around 0,12 ± 0,01.

The tests were performed under a load of 2 N, resulting in a contact pressure of 0.9 GPa with pure PAO 8 base oil or with 5 % EP-additivated oil. The results of the tribotest in Figure 5 show that for the pure PAO 8 the friction is higher than the overlaid 52100 vs. 52100 reference. The test generally show a very unstable behavior and leads to a high amount of abrasive wear on the ball.

In contrast, the use of 5 % EP-additivated oil in ambient air shows a first initial phase, which is linked to the generation of a sufficient amount of a tribofilm, leading to a stable low friction regime. This low friction regime is also characterized by an extremely low wear that is not measureable with conventional profilometers.

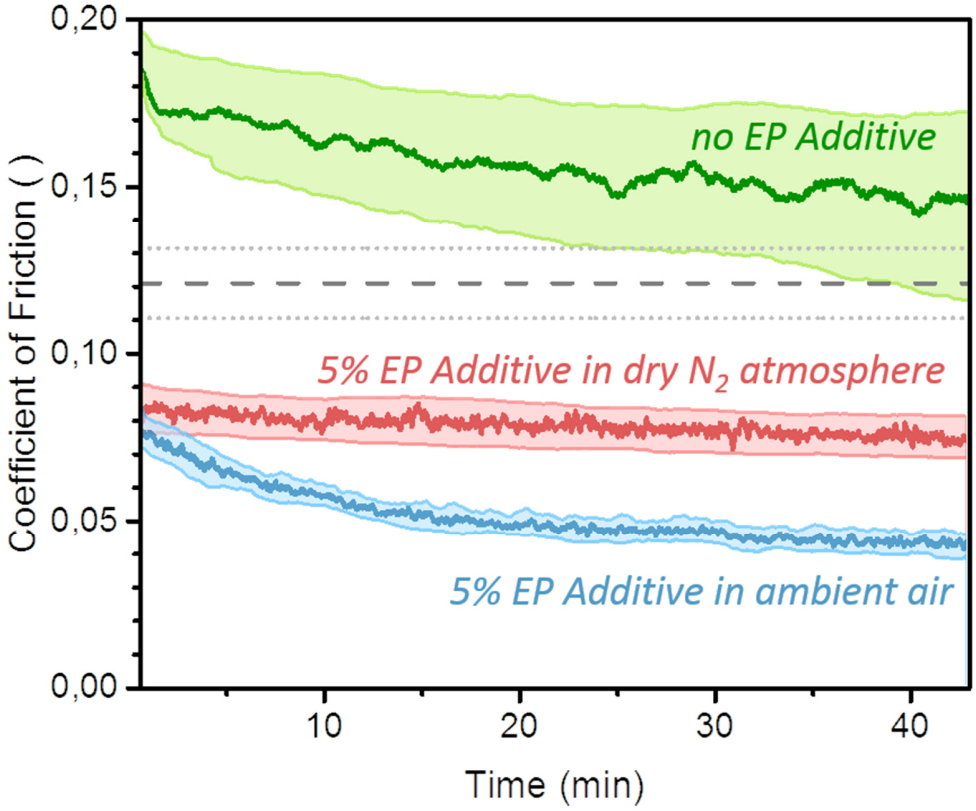

Figure 5: A Si_3N_4-ball vs. a Mo flat demonstrates a clear drop in friction in presence of the S-containing additive. Tests in dry N_2-atmosphere highlight the importance of the presence of oxygen in the contact.

Investigations of the wear track on the flat and the wear debris, located around the ball, with Raman microscopy in Figure 6 show very pronounced MoS_2 peaks. Thus, confirming that lubrication with the EP-additivated oil led to the in-situ formation of MoS_2 in the tribocontact. In general the tribofilm has a tendency to attach rather to the ball than to the flat and any collections of debris are primarily found around the wear scar of the ball. On the flat they are only noticable if high amounts of debris is available. Further XPS analysis contribute that the tribofilm consists of 5.5 at.-% S from sulfides. Surprisingly, the amount of O from Molybdenum oxides in the contact drops from 35 at.-% in tests without the EP-Additive to 14 at.-% with the EP-Additive. This led us to the hypothesis that the in-situ generation predominantly happens via an initial oxidation of Mo and a subsequent reaction with the additive to form MoS_2.

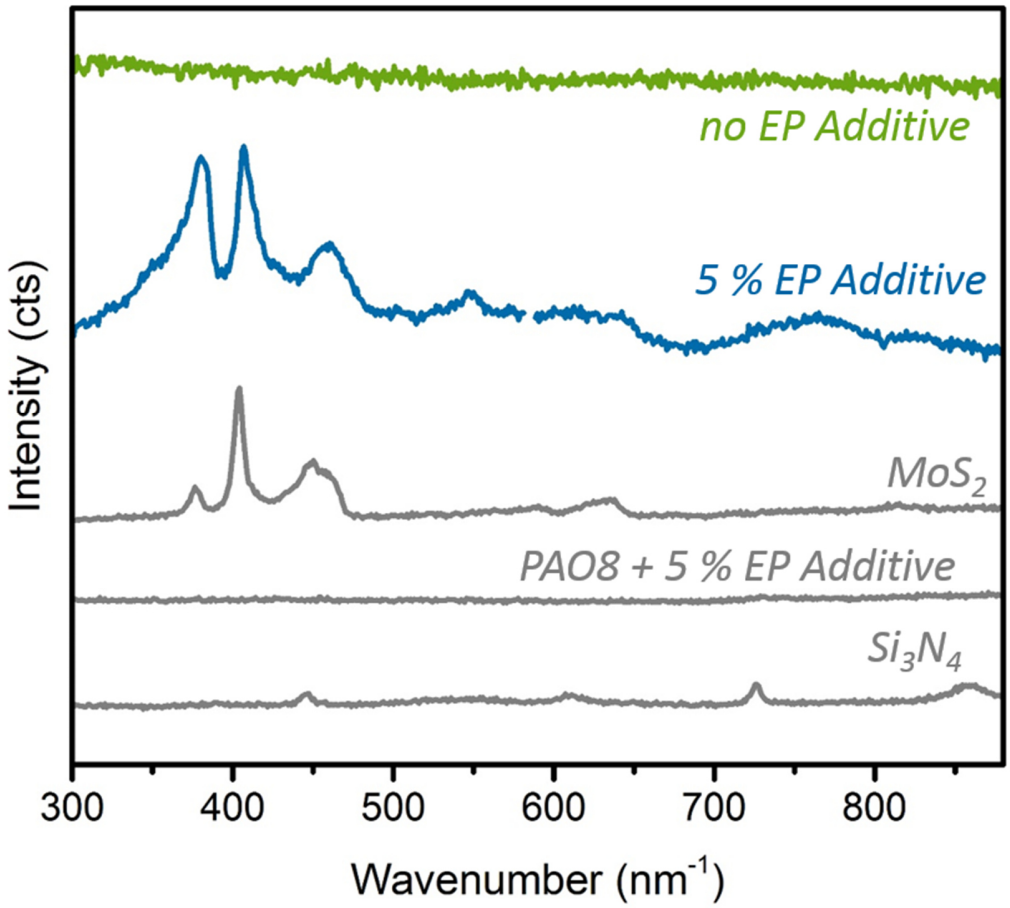

Figure 6: Raman spectra of the wear scars on Mo flats indicate that the EP additive leads to low friction due to the in-situ formation of MoS_2 in the contact.

To verify, tests with Ep-Additive were repeated in a dry N_2-atmosphere. The resulting coefficient of friction starts at the same level as in ambient air but is less stable and does not demonstrate the initial reaction phase including any further reduction of friction. Since the Mo surface passivates very easily and already contains molybdenum oxides before starting the test, a formation of small amounts of MoS_2 cannot be prevented. Although other superimposed reaction paths can as well result in the formation of sulfides, the clearly elevated coefficient of friction in dry N_2-atmosphere demonstrates that the oxide-route is the most favorable and dominant pathway for the in-situ formation of MoS_2.

The in situ formation of WS_2:

Since we were already able to demonstrate that MoS_2 can form in-situ in a tribochemical reaction between a Mo-sample and the EP-Additive in an oil, the next step was to investigate if tungsten behaves in a similar way. If we conduct the same tribotests as before, this time in Figure 7 with a tungsten flat, we can again notice a reduction of friction by introducing the EP-additive in comparison to the not additivated, PAO 8 lubricated, tests. The level of the reduction of the coefficient of friction in relation to the additive concentration plateaus at 1,5 % EP-additive and in comparison to the 52100 vs. 52100 reference the friction is much higher than we would expect it from a WS_2-lubricated contact. Raman measurements, in Figure 8, and XPS investigations in the wear track confirm that there was no in-situ formation of WS_2. Interestingly, the XPS investigations also revealed that the amount of tungsten oxides in the tribocontact, with 1 at.-% O, is significantly lower than in the Mo-tests.

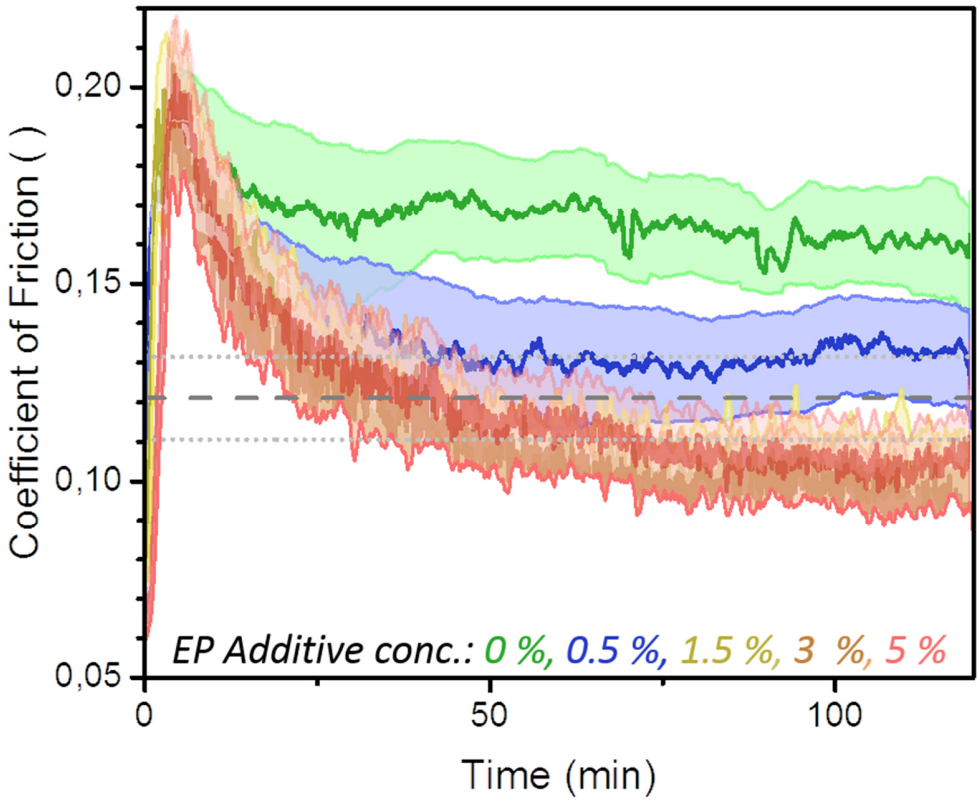

Figure 7: The coefficient of friction on metallic W is reduced by adding a EP-additive, but does not display the low friction we would expect of a WS_2 lubricated contact.

To test if the in-situ formation of WS_2 on W was stifled by the strong W – W bonds and therefore the lack of oxides, we annealed a tungsten flat at 600°C in ambient air to induce a thermally grown oxide scale on the surface. A repetition of the tribotests with the annealed samples yielded a completely different behavior of the coefficient of friction in dependence of the EP-additive concentration. While in Figure 9: there is only a slight difference in the coefficient of friction when small concentrations of 0.5 % EP additive are added, higher concentrations lead to much more pronounced differences. Especially at 3 % EP-additive and higher a clear drop of the coefficient of friction sets in after a short initial reaction period, forming a sufficient tribofilm. This initial reaction can also be recognized in the highlighted area (I) of the 1.5 % EP-additive concentration curve. While the onset of a tribochemical reaction leads to a slow initial reduction of friction, the S-delivery is too low to sustain a continues reaction and the system regresses to a high friction regime.

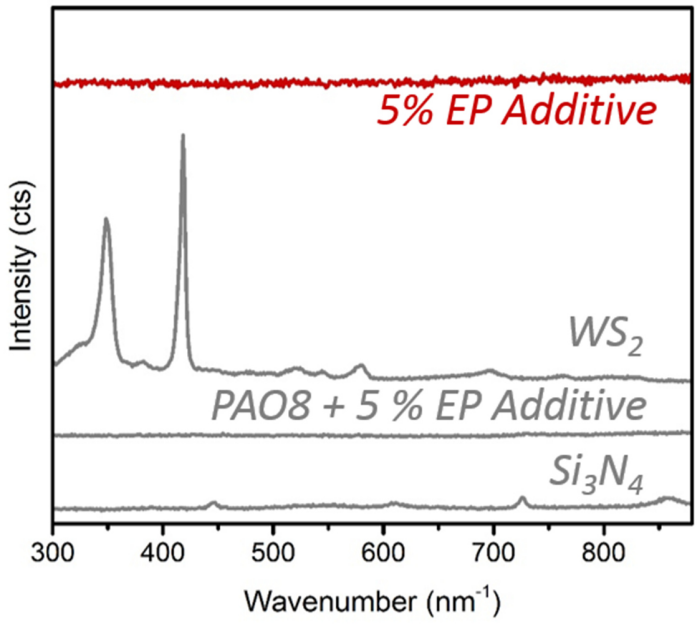

Figure 8: Raman spectroscopy supports the absence of in-situ formed WS_2.

Concentrations of around 3 % EP-additive are enough to stabilize a continues reaction and as a result the coefficient stays at the low levels we would expect from a WS_2 lubricated system. In addition to the reduction of the coefficient of friction, the test is stabilized and yields a very smooth and reproducible run of the coefficient of friction. Tests at 5 % EP-additive concentration resulted in a steep incline of the coefficient of friction towards the end of the tests, highlighted in area (II), which is the result of the breakthrough to the metallic W interface and a depletion of oxides to sustain the reaction. The metallic

W surface again does not oxidize easily and interrupts the in-situ formation of WS_2as soon as all oxides are consumed, leading to a relapse to a high friction and high wear regime.

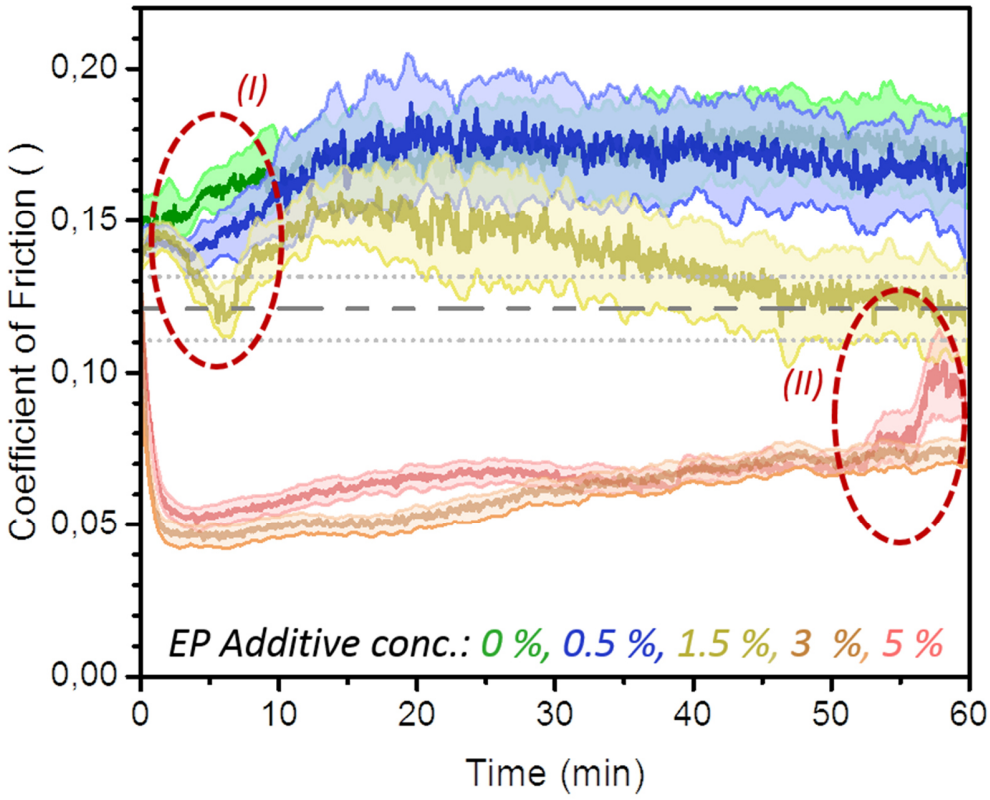

Figure 9: At high enough EP-additive concentrations a tribochemical reaction is induced, leading to a low friction regime which is clearly dependent on the availability of oxides.

Raman Microscopy of the wear tracks and wear debris reveals no detectible WS_2 until the low friction concentration of 3 % EP-additive, at which point the WS_2 peaks in Figure 10: appear as a slight shoulder in the blurry signals of the oxide scale. In case of 5 % EP-additive the WS_2 peaks are very pronounced and easily distinguishable from the oxide peak. The peak positions fit very well to reference measurements and leave no doubt that WS_2 has formed.

The divergent behavior of the metallic W-flat and the oxidized samples demonstrates the clear dependence of the in-situ formation of WS_2 on the availability of tungsten oxide. Therefore, it highlights that for the tribochemichal reaction to form WS_2, equivalent to MoS_2, a reaction pathway via oxide intermediates is the most favorable. The tests also highlight that a lower boundary exists between 1.5 % and 3 % EP-additive at which the concentration is not sufficient to sustain the reaction. At the same time

the tests with high EP-additive concentration also disclose that due to the limited oxidation of the sample and a depletion of oxide reservoirs a upper boundary exists as well. This limits the applicability on both sides and requires a balance between the S-addition and the oxide generation to be a viable application.

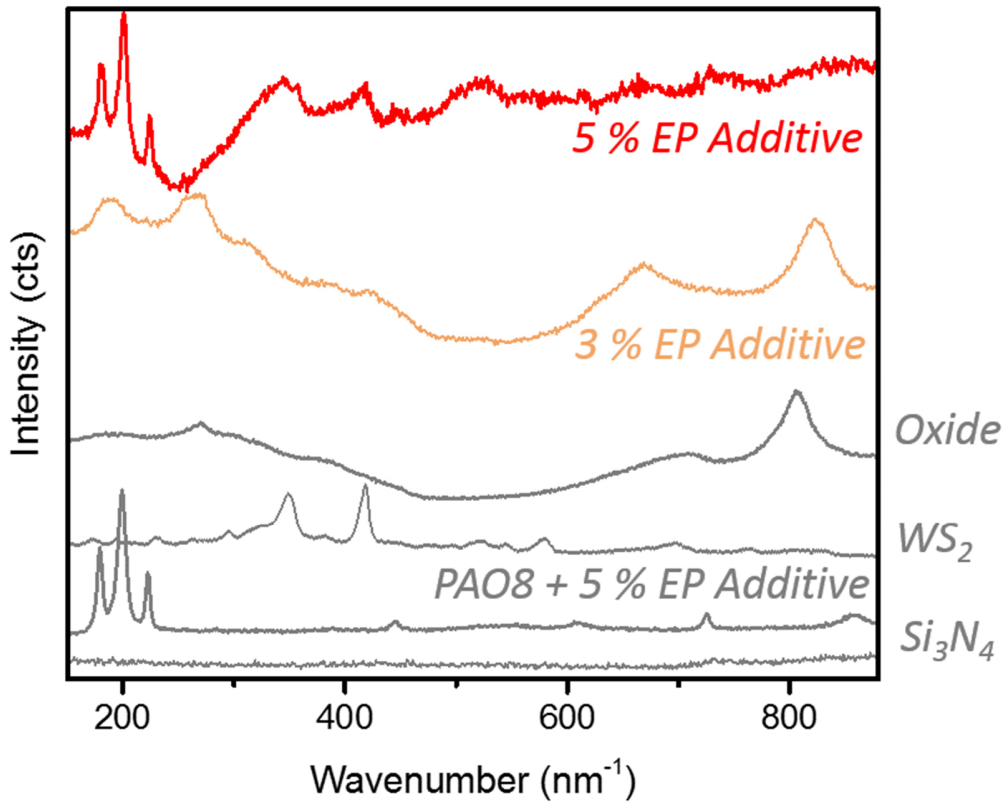

Figure 10: Due to the availability of oxides a WS_2 based tribofilm can form, as shown by Raman spectroscopy and lubricate the contact.

In terms of wear, all tests that display a higher or similar coefficient of friction in relation to the 52100 steel vs. 52100 steel reference also demonstrate high abrasive wear. Tests performed on metallic tungsten showed imbedding of particles into the counter face and micro plowing leads to the formation of very jagged ridges in the wear track. The presence of the oxide scale on the annealed surface leads to a lower initial coefficient of friction than on the metallic surface, but with low EP-additive concentrations, the oxide is worn away within a first stage of the test and the resulting metallic W-surface with the consequent high friction regime again led to high abrasive friction.

The far-ranging influence of a sufficient in-situ formation of WS_2 can be clearly seen if we compare the counter faces of a unadditized Si_3N_4-ball vs. oxidized W-flat test with the same test that has been doped with 3 % EP-additive in Figure 11. The highly abrasive wear regime from before is reduced to a slight polishing of the surface which is not measureable with the applied methods. SEM and EDX investigations show, an intact oxide scale in the wear track that has no significant deformations or wear marks. Protruding sections have been slightly worn while small voids in the oxide surface have been filed with debris from the tribofilm. The in-situ formation of MoS_2 or WS_2 does not only lead to a very efficient and elegant way to improve the friction of lubricated contacts that contain S, it also demonstrates a high wear protection capability, that could be highly significant for any future applications.

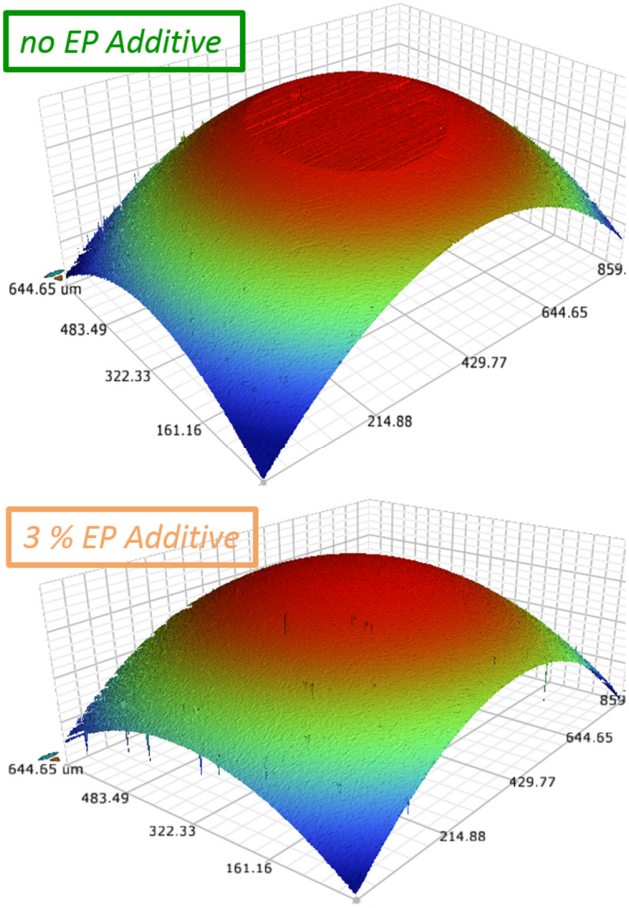

Figure 11: The addition of an EP additive to in-situ form WS_2 in presence of tungsten oxides poses an enormous potential in wear protection.

The in situ formation of WS_2 on tungsten nitride based coatings:

Since the in-situ formation of WS_2 as well as MoS_2 has been linked to the necessary oxidation of the sample material our next investigations focused on, if we can influence the oxidation of the surface by applying a tungsten nitride coating instead of the thermally grown oxide scale. The main trigger to induce an in-situ formation is the contact pressure, while the reaction temperature only plays a limited role. Therefore, the behavior of the tribofilm under loads that are higher than required for its generation is of great interest as well.

The multi-phase coating has been deposited by high power impulse magnetron sputtering (HIPIMS) of a W-target in a mixed Ar/N_2 atmosphere in a CemeCon deposition system. The total deposition pressure was kept at 0.4 Pa and the gas ratio was regulated to 130 sccm/55 sccm, respectively. The coatings where deposited with a power density of 9 W/cm^2 on polished martensitic 52100 steel substrates under low temperatures, reaching a peak temperature of 340°C.

The ball on disk tests of the coatings where performed at three different loads: 2 N, 5 N, 10 N with an EP-additive concentration of 0 % and 5 % each. The tests revealed that in case of the tungsten nitride coating the coefficient of friction is considerably lower if the additive is present compared to the undoped PAO 8. In general the tribotests of the tungsten nitride coatings without additives lead to very unstable conditions and a fluctuating coefficient of friction. Figure 12 shows the very low coefficient of friction close to 0.04 in case of the 2N tests with 5 % EP-additive, but also establishes that the coefficient of friction is significantly higher with increased loads. This leads us to draw the conclusion that the in-situ generated WS_2 based tribofilm is not very stable under load and that at loads already lower than 5 N the tribofilm is worn away and removed from the contact. The blackish debris is afterwards deposited mainly on the ball, but also on both sides next to the weartrack, as can be seen in Figure 13. The wear on the hard coating itself is minimal and limited to a slight change of the surface texture. But even under higher loads the coefficients of friction of the additized tests are considerably lower than those without the EP-additive. The in-situ formation of WS_2 seems to be still functional, but due to the wear on the tribofilm it cannot sustain a low friction regime.

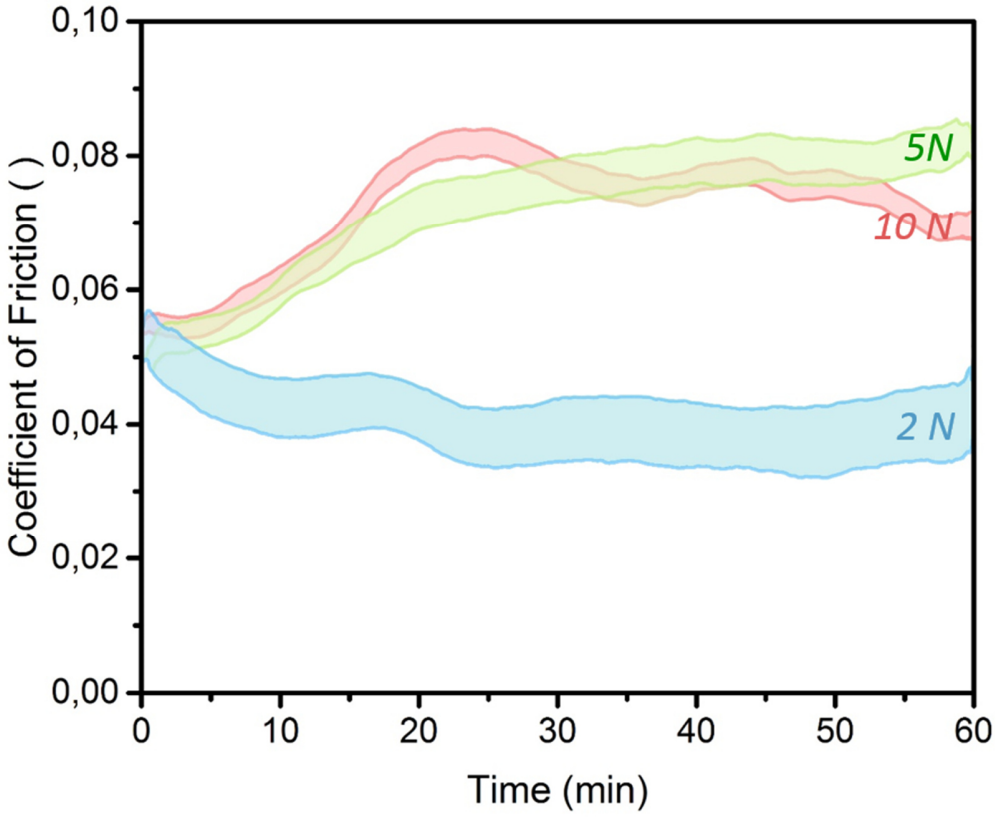

Figure 12: The in-situ formation also occurs on tungsten nitride coatings although the load bearing capability is limited.

If we investigate the wear tracks and debris with Raman spectroscopy we again in case of the higher loaded tests detect the characteristic peaks of WS_2, this time clearly standing out from any underground. In the wear track of the 2 N loaded test, no WS_2 is detectable with Raman spectroscopy, but this does not necessarily mean that the in-situ formation did not happen. Since at higher loads the WS_2 tribofilm is worn away and deposited around the contact, the system is forced to generate more and more WS_2. While, under lower load the tribofilm stays intact and reproduces WS_2 only at much lower rates. Therefore, the amount of WS_2 in the contact is kept to a minimum level, that even with surface sensitive Raman Spectroscopy and XPS is located lower than the detection limit.

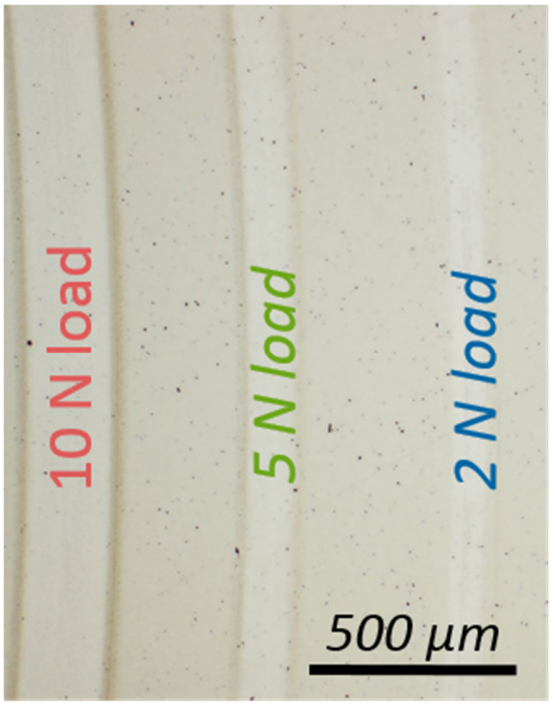

Figure 13: Debris is deposited on the sides of the wear track that does not show any significant wear.

Further investigations of the wear track with SIMS paint a very similar picture. Although we can not detect the WS_2 directly, since it's fragment peaks are overlaid by the corresponding tungsten oxide peaks, it is possible to clearly distinguish in Figure 15 that the debris next to the wear track is very high in S-components and has almost no oxides, consolidating the in-situ formation even further. The S-mapping of the SIMS measurements also uncovers an elevated level of S in the middle of the wear track. It represents the in-situ generation area of the tribofilm, WS_2 is formed in the center of the contact where the contact pressure is the highest. Worn away tribofilm afterwards collects in small coating imperfections or gathers as debris on the sides of the wear track.

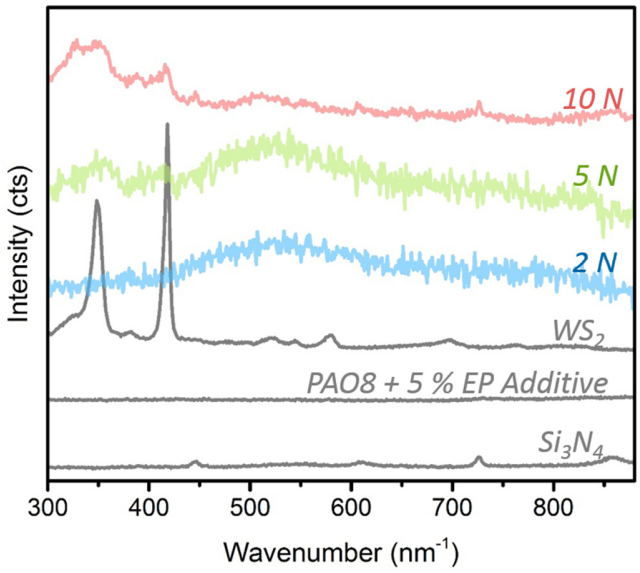

Figure 14: The WS_2 containing Tribofilmis worn away under higher loads, leading to the continues reproduction of bigger amounts os WS_2 debris and therefore easier detection by Raman spectroscopy.

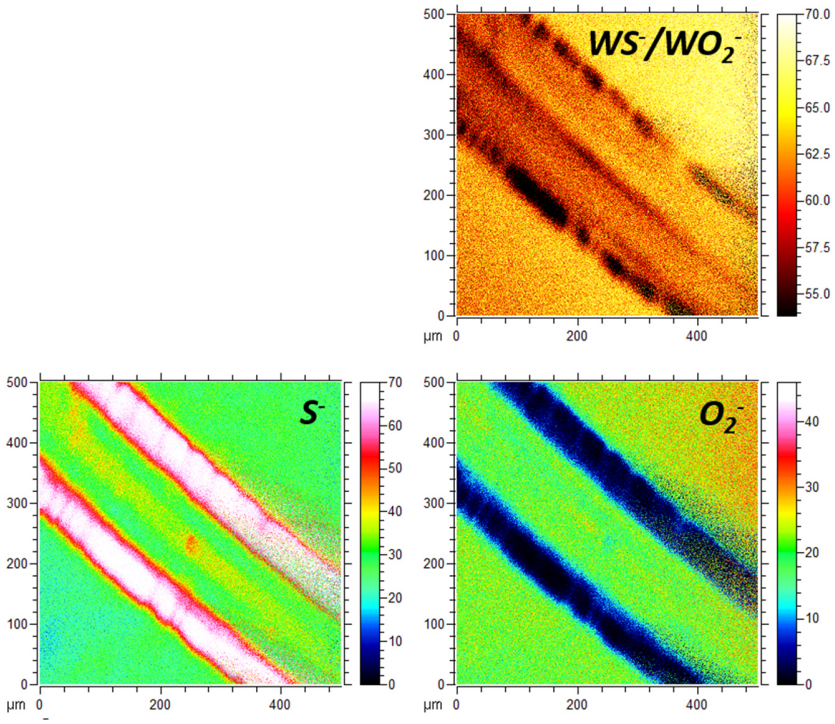

Figure 15: SIMS measurements of the wear track show clear evidence of the accumulation of a sulfide-basend oxygen-depletet debris. It also highlights th in-situ formation zone in the middle of the weartrack.

In previous tests higher friction was always clearly linked to higher wear of the ball, so we also expected the wear on the ball to increase with higher loads due to the worn away tribofilm. Without the EP-additive the system again displays high abrasive wear on the ball that increases with the load. Surprisingly, in Figure 16 we can see that if we introduce the EP-additive to the test, the wear drops to a non measureable slight polishing of the ball surface. This effect is independent of the load in the investigated range. Although we might wear away the lubricating WS_2 tribofilm resulting in higher friction, its reproduction on the coating is fast enough to offer effective wear protection.
XPS investigations of the coating wear track reveal that in contrast to metallic W the bonds within the coating can be broken up and oxidation can occur, leading to around 35 at.-% O from metal oxides in the wear track, that serve as a precursor for the further in-situ formation of the WS_2.

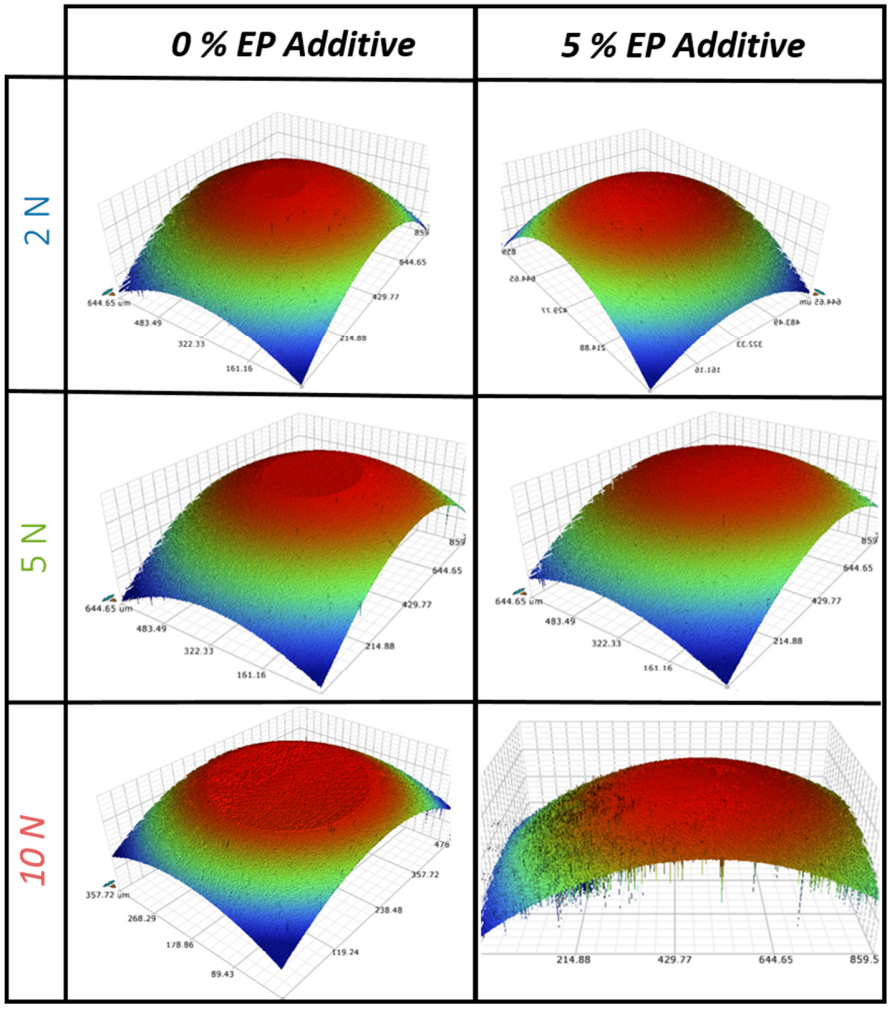

Figure 16: Even under higher loads that wear away the tribofilm the wear protection of the in-situ formation of WS_2 still is operational.

Conclusion:

The research fellowship at Argonne National Laboratory has been a full success and by far exceeded the expectations! It was possible to learn the necessary new techniques, to gather all relevant reference information and to apply and train them under the guidance of the Argonne National Laboratory Team. Most importantly we were able in a cooperation of Argonne National Laboratory, Technische Universität Wien and AC^{2}T research GmbH to determine an analytical strategy that will for the future allow us to clearly identify and investigate the MoS_2 or WS_2 containing tribofilms. The key to a successful identification is Raman spectroscopy, which can be substantiated by other methods that would not suffice on their own, like EDX, XPS, SIMS and Electron Microscopy.

Although catalytic capabilities of transition metal nitrides to form graphite like carbon structures in-situ are suspected by many researchers. In case of the investigated tungsten nitride and tungsten carbide coating no in-situ formation of transition metal sulfides took place. For ball on disk tests tungsten carbide coatings are no applicable due to their brittle behavior and tendency to initiate and support a highly abrasive regime. Future investigations will need to be carried out on different substrates and in conditions that allow the coating to stay intact. Further investigations into the coating itself will also be needed in order to produce more durable thin films that are less prone to cracking and severe coating failure.

The in-situ formation of MoS_2 and WS_2 in a tribochemical reaction with S containing oil has been clearly proven beyond any doubt. It is clearly linked to the induction of a low friction regime and demonstrates truly remarkable wear protection capabilities.

One of the most important achievements during the research fellowship, and a big milestone to my dissertation, was the uncovering of the predominant reaction pathway for the in-situ formation of the tribofilms! Although minor alternative routes are not out of the question, ball on disk tests on metallic Mo revealed that the metal first oxidizes and in a second step reacts with the S from the additive to form the solid lubricant MoS_2. This reaction pathway via the formation of oxides has also been identified for W-based samples. Although in case of metallic W the W-W bonds are too strong to be broken under the applied conditions and with the resulting very low level of oxidation no in-situ formation of WS_2 is possible. But if we aid the oxidation of tungsten by annealing the samples in ambient air before testing we experience a clear in-situ formation of WS_2 from the oxides. The generation of this low friction tribofilm is a very fragile system, that has two strongly limiting influences: On the one hand the S-delivery system, on the other the Oxide reproduction. If the system is starved from S or the source is

simply depleted the low friction tribofilm cannot be formed or reproduced, leading to the collapse of the low friction regime. This is also influenced by the contact pressure the tribofilm experiences. At higher loads it is worn away, increasing the need for reproduction and thereby boosting the consumption of the S source. At the same time oxide is consumed at higher rates as well, which in case of Mo is not a problem since the oxidation rates are high enough to reproduce the reactant. But in case of tungsten, where an artificial support for the oxidation was needed, an elevated consumption of oxide by higher loads or excessive introduction of S leads inevitable to a collapse of the low friction regime. The in-situ formation of MoS_2 and WS_2 is a very delicate and precarious combination of different tribochemical reactions. To achieve a sustainable in-situ formation of a low friction low wear tribofilm, all contributing factors have to be balanced and well tuned. However, if successful, the potential for reduction of friction and wear is astonishing!

This also highlights the huge potential of coatings for this lubrication concept. It has been shown that although the formation of a graphite-like carbon film does not occur the chemical bonds in the coating do allow for a sufficient level of oxidation in a tribocontact. Hence, in the next step a tribochemical reaction with the additive can sustain the in-situ formation of a WS_2 tribofilm on the coating! The combination of the hard coating and the low friction and wear tribofilm shows enormous potential for future applications in wear protection, as even overloading of the tribofilm does (in the observed range) not lead to wear worth mentioning.

One of the most important feature of coatings, aside from high hardness and good mechanically properties, is that we can influence their bonding structure. By introducing dopants or defects it is possible to weaken and strengthen their bonds and therefore we can fine tune the coating to achieve a best possible synergy between the coating and the lubricant.

Many research groups have reported that the in-situ formation of WS_2 only occurred in presence of iron, suggesting that it might have a catalytic effect. Our research clearly states, that no iron is needed in the contact. Although tungsten nitride coatings might possess properties that have been suspected of catalyzing some tribochemical reactions, the results of the annealed W-flats demonstrate that no catalysts are necessary. The reaction simply relies on the presence of a S-source and tungsten oxide.

Aside from describing the reaction pathway this work also highlights the enormous potential use for wear protection and lubrication in technical applications. Due to the use of S and entailing environmental goals, it might not be the best candidate for combustion systems but many other applications rely on the presence of S and could benefit greatly from in-situ lubricating coatings!

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