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ORIGINAL PAPER

Understanding the Tribochemical Mechanisms of IF-MoS_2 Nanoparticles Under Boundary Lubrication

Johny Tannous · Fabrice Dassenoy · Imène Lahouij · Thierry Le Mogne · Béatrice Vacher · Andrew Bruhács · Wolfgang Tremel

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Abstract Inorganic fullerene-(IF)-like nanoparticles made of metal dichalcogenides (IF-MoS_2, IF-WS_2) have been known to be effective as anti-wear and friction modifier additives under boundary lubrication. The lubrication mechanism of these nanoparticles has been widely investigated in the past and it is now admitted that their lubrication properties are attributed to a gradual exfoliation of the external sheets of the particles during the friction process leading to their transfer onto the asperities of the reciprocating surfaces. However, the chemical interaction between these molecular sheets and the rubbing surfaces has so far never been investigated in detail. In this study, the tribochemistry of the IF nanoparticles was carefully investigated. A series of friction test experiments on different rubbing surfaces (Steel, Alumina, Diamond-Like Carbon) were performed with IF-MoS_2 nanoparticles. High-resolution transmission electron microscopy, scanning electron microscopy, Auger electron spectroscopy, and X-ray photoelectron spectroscopy were used to characterize the tribostressed areas on rubbing surfaces. A tribofilm composed of hexagonal 2H-MoS_2 nanosheets was only observed on the steel surface. This transfer film was found to be incorporated into an iron oxide layer. A tribochemical reaction between the 2H-MoS_2 nanolayers and the iron/iron oxide has been proposed as an explanation for the adhesion of this tribofilm. The tribochemical mechanism of the IF-MoS_2 nanoparticles is discussed in this article.

Keywords IF-MoS_2 nanoparticles · Solid lubricant · FM/AW additives · Boundary lubrication · Tribochemistry · XPS/AES · HRTEM

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1 Introduction

Over the past few years, inorganic fullerene-like (IF) nanoparticles of metal dichalcogenide MX_2 (M = Mo, W, etc.; X = S, Se), materials with structures closely related to nested carbon fullerenes and nanotubes, have been synthesized [1, 2]. Due to their low surface energy, high chemical stability, nanometric size, spherical shape, and weak intermolecular bonding, their use as lubricant additives was suggested [3]. Their efficacy for tribological applications was demonstrated in many papers [4–7]. It was shown that the addition of small amounts of IF-MoS_2 or IF-WS_2 into a lubricating oil greatly improve the tribological properties of the lubricant. Most of these tests were performed in the boundary lubrication regime and with steel rubbing surfaces. The lubrication mechanism of these IF-nanoparticles was widely investigated [5–7]. Joly-Pottuz et al. [6] showed that the lubricating properties of the IF nanoparticles are attributed to a gradual exfoliation of the external sheets of the particles during the friction process leading to their transfer onto the asperities of the reciprocating surfaces and a shearing of the basal planes. A tribofilm made of these MoS_2/WS_2 sheets was observed on the rubbing surfaces and

characterized by Raman spectroscopy. The layered structure of the MoS_2 composed of tribofilm was demonstrated. Recently, Tenne and co-workers [7] suggested that an additional rolling process for well-crystallized and round-shaped particles could enhance the lubricating properties of the IF nanoparticles. A recent trend in the synthesis of the fullerenes is to prepare faulted and strained IF nanostructures to facilitate their exfoliation in the tribological contact and thus to optimize the tribological properties of the lubricant [8]. Recently, some metal-doped fullerenes were also prepared [9, 10]. The strain resulting from the metal defects in the lattice might lead to interesting tribological effects.

The exfoliation of the fullerenes under compression and shear stress, and the formation of a tribofilm comprising sheets of MoS_2/WS_2 on the steel rubbing surfaces are at the origin of the good lubricating properties of these nanoparticles. However, some questions remain. How do the MS_2 sheets interact with surfaces? Do these MS_2 sheets interact preferably with rubbing surfaces of a certain chemical composition? The chemical interaction between these molecular sheets and the rubbing surfaces has so far never been precisely investigated. The tribofilm/surface products have also never been clearly identified and the reaction mechanisms between MS_2 sheets and steel surfaces are still largely unknown.

This study helps shed light on the mechanisms of interaction between the tribofilm and the rubbing surfaces. Accessing and characterizing the compositions of the tribofilm as well as the interface between the tribofilm and the substrate are key points. To answer these questions, a set of experimental techniques was used. IF-MoS_2 nanoparticles were tested under boundary lubrication on different rubbing surfaces: steel, DLC, and alumina. After each friction test, worn areas were characterized by surface analysis (AES, XPS, and EDX) and were visualized by electronic microscopy (HRTEM and SEM). Correlations between tribological properties and the chemical and structural nature of tribofilms were found, thereby improving our understanding of the behavior of IF-MoS_2 in the boundary lubrication regime.

2 Experimental

2.1 Synthesis

IF-MoS_2 nanoparticles were synthesized in a customized metal organic chemical vapor deposition (MOCVD) reactor described by Etzkorn et al. [11, 12]. The $Mo(CO)_6$ precursor (ABCR 98%) was placed in a porcelain boat within the quartz reactor setup, heated and carried via argon flow along with the H_2S gas (GHC Gerling, Holz & Co. 99.5% 2.5) to the hot central core of the apparatus [8]. The central receptor around which the gaseous precursors combine and react was heated inductively; hence, the set point of 650 °C was achieved in 20 min with initial heating rates of 100 °C/min. Upon commencing the heating procedure, the flow rate was reduced to 200 mL/min. The H_2S gas flow was monitored separately using a bubble counter (5 bubbles/s) and the exhaust was bubbled through sodium hydroxide solution to moderate the release of noxious gases into the atmosphere. After maintaining the reaction temperature for 90–120 min, the cooling sequence (room temp.) was initiated by simply switching off all heating units and leaving the argon flow at 200 mL/min. IF-MoS_2 product was acquired from the inner deposition quartz cylinder under normal atmosphere.

The induction furnace Hüttinger TIG 5/300 was equipped with a Eurotherm 2704 programmable temperature regulator. Krohne flow meters ensure customization possibilities and reproducibility of reaction conditions.

The typical size distribution of the IF-MoS_2 nanoparticles is between 20 and 60 nm (the median size is $\sim$30 nm) and the morphology determined in HRTEM studies (see Fig. 1) is of spherical IF-type with concentric nested layers showing considerable amounts of point defects and grain boundaries, hereby proving their nearly amorphous character.

2.2 Friction Test

IF-MoS_2 nanoparticles were tested in a lubricated condition using a pin-on-flat tribometer [13]. Fullerenes were dispersed using an ultrasonic bath at 1 wt% in synthetic base oil, a polyalphaolefin (PAO). Tribological tests were carried out in ambient air and at ambient temperature, with a sliding velocity of 2.5 mm/s, and a contact pressure of 1.12 GPa on three different pin and flat surfaces (steel, ta-DLC, alumina). The normal load applied on the pin was adjusted to conserve the same contact pressure whatever the surfaces. Steel materials were made of polished AISI 52100 ($R_a = 25$ nm). The ta-C DLC coating was applied to the polished carburized steel disk and the hardened steel pin to a thickness of 0.5 μm from a graphite target by arc-ion plating, a physical vapor deposition (PVD) process, and did not contain hydrogen. The alumina samples (Sapphire) were provided by the RSA le Rebis-France. Sapphire has a mono-crystalline structure, a high hardness (9 Mohs) and melting point, a very good thermal conductivity, and thermal shock resistance.

2.3 Analytical Tools

The following facilities permit characterization of the surface chemistry in the contact area which yields results

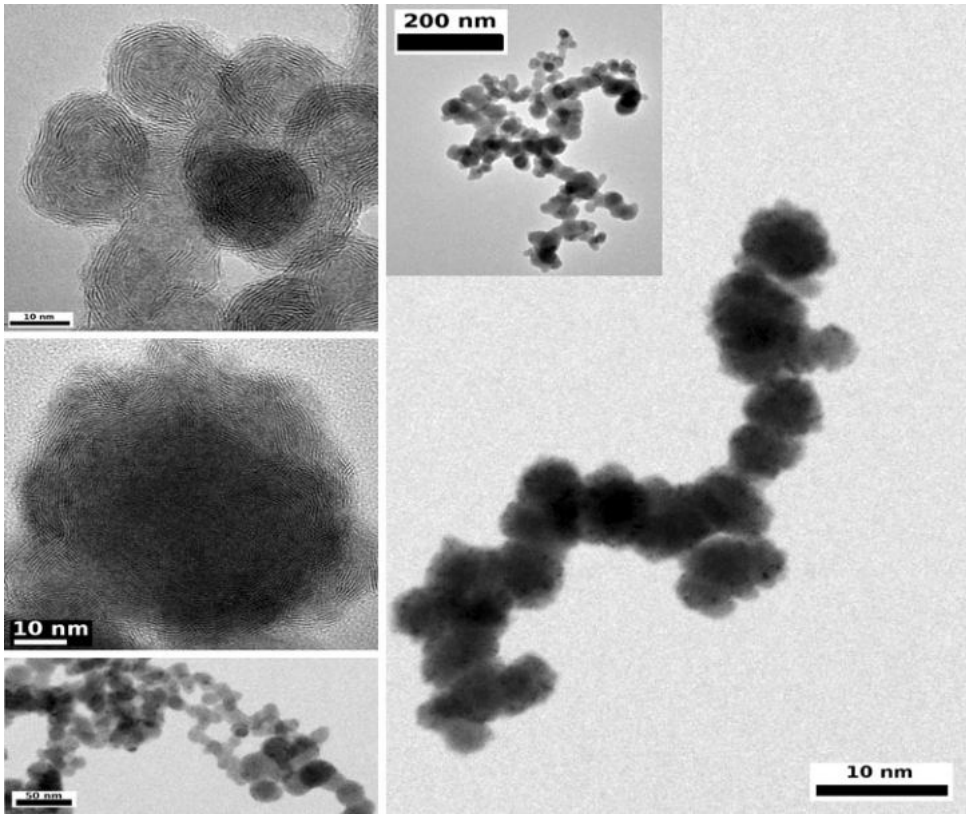

Fig. 1 HRTEM images of IF-MoS_2 nanoparticles

that can be specifically compared to the observed tribological behavior.

XPS and AES analyses and AES depth profiling were carried out on the worn surfaces. For the AES, the electron beam energy is 5 keV (FEG1000-Thermoelectron) and allows a lateral resolution of 0.5 μm. Etching was performed with argon ions (2 keV). For the XPS, a monochromatized AlKα X-ray source was used in a Thermoelectron 220I electron spectrometer. The spectrometer was calibrated with Au $4f_{7/2}$ at 84.0 eV. The charging effect was corrected by fixing the C1s peak (adventitious carbon) at 284.8 eV. The photopeaks were fitted after removing a Shirley background.

TEM samples were prepared by the FIB technique. A transversal cut was performed on the worn surface to obtain a 100-nm thick cross section. Platinum and tungsten layers were previously deposited on the worn track to preserve the surface from nanomachining by Ga+ ion beam. The TEM observations were performed on a JEOL 2010F operating with 200 kV accelerating voltage equipped with Energy Dispersive Spectroscopy (EDS).

The SEM observations were performed on a TESCAN VEGA 5136XM equipped with EDS for compositional analysis.

3 Results

3.1 Tribological Results

Figure 2 shows the friction behavior of IF-MoS_2 nanoparticles on steel, DLC, and alumina surfaces. Even if the behavior of the base oil itself depends on the nature of the surface, the lubricating properties of the fullerenes can only be observed for tests performed on steel. Compared to the base oil, the reduction of the friction coefficient can amount up to 70%, then remaining at a steady value of 0.03. For the two other surfaces, DLC and alumina, no effect of the fullerenes on the friction properties of the dispersion was observed. The friction coefficient is relatively stable with or without the presence of IF-MoS_2 ($\mu \sim 0.04$ on DLC and $\mu \sim 0.06$ on alumina). In optical observations no visible trace of wear was detected on the three surfaces. Figure 3 shows the wear scars on the pin after the test performed on the steel flat for (a) pure PAO and (b) PAO + 1 wt% IF-MoS_2. The wear scar diameter (94 μm) is strongly reduced in the presence of IF-MoS_2 in comparison to the base oil and is very close to the calculated Hertz diameter (92 μm). The presence of a tribofilm is nevertheless very difficult to observe optically.

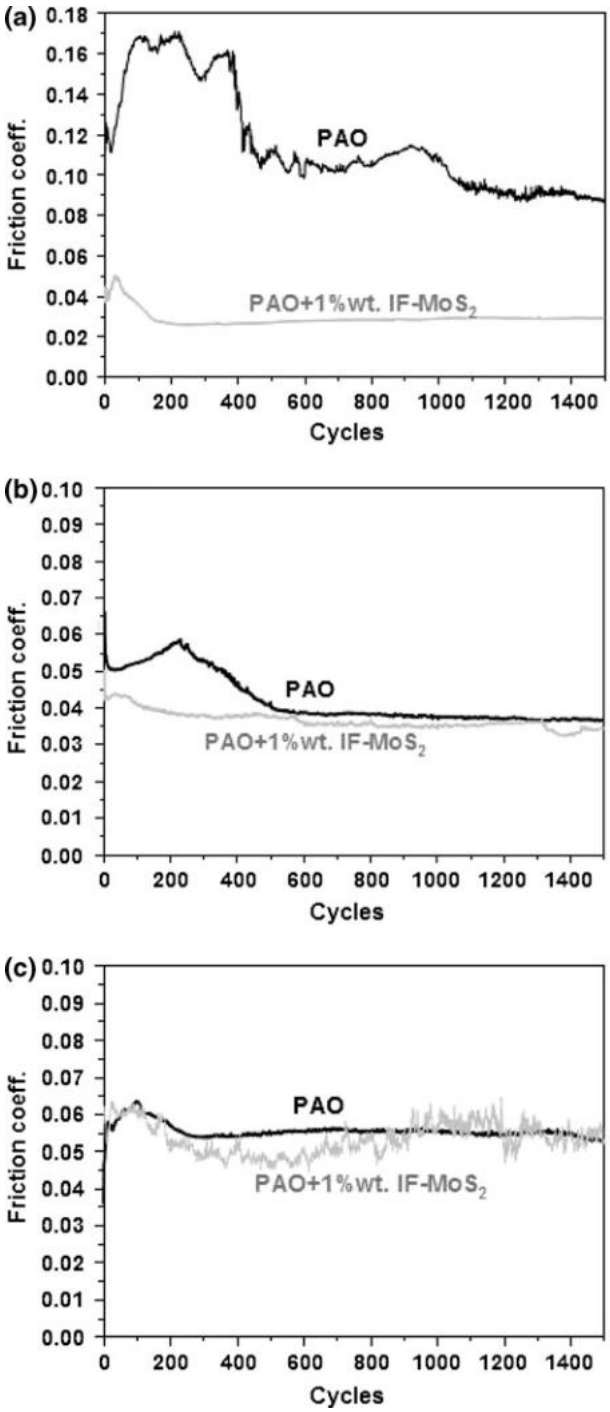

Fig. 2 Evolution of the friction coefficient in a lubricated test for PAO oil and PAO + 1 wt% IF-MoS_2 on **a** steel surface, **b** DLC coating, and **c** alumina surface

3.2 Surface Analysis of the Rubbing Surfaces

3.2.1 Steel

A cross section was performed on the steel worn surface and was thinned by a focused ion beam (FIB). Figure 4 shows the TEM image of the FIB cross section preparation of the steel worn surface. The presence of a 5–10-nm thick tribofilm between the platinum protection layer and the steel substrate is evident. At a higher magnification, TEM images show the presence of nanosheets incorporated into the 4-nm native iron oxide layer. This is confirmed by EDS analysis performed in the tribofilm area. It reveals that the nanosheets which constitute the tribofilm are mainly composed of MoS_2 (see Table 1) mixed with some iron oxide species. The presence of small quantities of sulfur in the iron oxide layer (EDS analysis performed in the iron oxide area) could be related either to the presence of few sheets of MoS_2 layers in this area or to the formation of iron sulfide species [14].

These first observations are in agreement with the lubrication mechanism of the fullerenes proposed in the literature, e.g., a gradual exfoliation and a transfer of molecular sheets onto the asperities of the reciprocating surfaces. This lubrication mechanism has already been observed with IF-MoS_2 by Cizaire [5]. The ultra-low friction is related to the effect of MoS_2 lamellar structure sheets, which are present in the tribofilm. Similar behavior was also observed with IF-WS_2 nanoparticles by Joly-Pottuz et al. [6]. Depth AES profiles were performed to confirm the incorporation of 2H-MoS_2 nanosheets into the iron oxide layer. Figure 5 shows the relative intensity evolution versus etching time inside the worn surface. Mo and S atoms, in the 2H-MoS_2 nanosheets disappear concomitantly with the oxygen of the iron oxide. This is consistent with what was suggested from TEM analysis, i.e., an incorporation of the 2H-MoS_2 sheets into the iron oxide layer. However, these results do not help in determining the chemical interaction between these molecular sheets and the rubbing surfaces. Using XPS analysis inside the worn surfaces, more insights about the interaction between 2H-MoS_2 and steel were gained. Figure 6 compares the Mo3d and S2p XPS spectrum between the IF-MoS_2 nanoparticles and the tribofilm. Molybdenum and sulfur are found in different chemical environments in the nanoparticles and in the tribofilm. Regarding the XPS spectra recorded on the IF-MoS_2 nanoparticles, the sulfur $S2p_{3/2}$ is composed of a main peak at 162 eV corresponding to S–Mo bond of IF-MoS_2 particles. Two small contributions of sulfur at 163 and 169 eV can be attributed to S–S and S–O bonds. The presence of S–S bond could be related to the free sulfur remaining from the synthesis processes. The small contribution at 169 eV is attributed to a soft oxidation of the nanoparticles on the extreme surface. Molybdenum ($Mo3d_{5/2}$ at 228.8 eV) corresponds to Mo–S bond of IF-MoS_2. The comparison between $S2p_{3/2}$ and $Mo3d_{5/2}$ spectra recorded on IF-MoS_2 particles and inside the tribofilm indicates that the main peak of sulfur ($S2p_{3/2}$ at 162 eV) is shifted to low binding energy ($S2p_{3/2}$

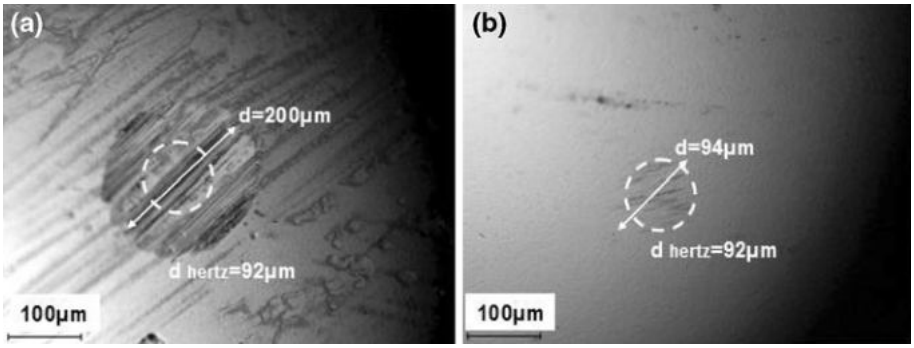

Fig. 3 Optical microscopy of steel pin wear scar for **a** PAO and **b** PAO + 1 wt% IF-MoS_2

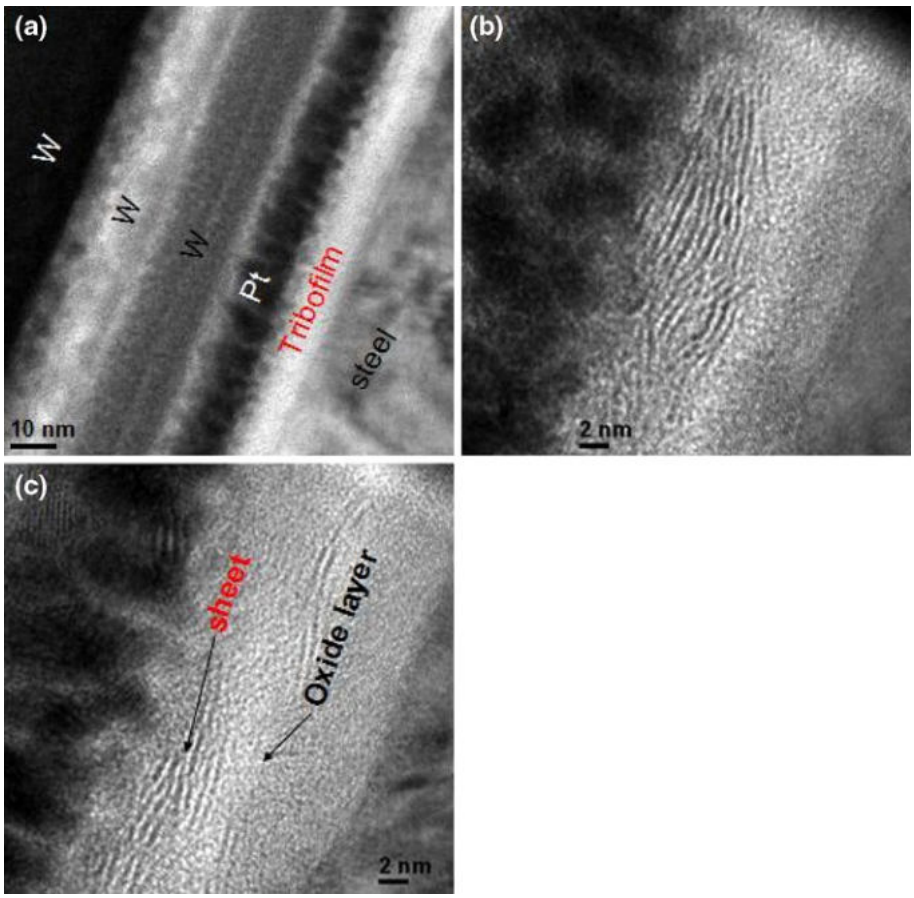

Fig. 4 TEM observations of a FIB cross section preparation of steel worn surface at different magnifications **a** general view and **b**, **c** at high magnifications

Table 1 EDS elements quantification of nanosheets and iron oxide layers

EDS Analysis		
Element	Nanosheets area (%)	Iron oxide layer (%)
Mo	21	7
S	32	11
O	37	47
Fe	10	35
Cr	0	1
Total	100	100

at 161.7 eV) on the spectrum recorded of the tribofilm. This peak is related to the presence of MoS_2 inside the tribofilm. The shift of 0.3 eV could be explained by the presence of small quantities of iron sulfide species in the tribofilm formed either from the free sulfur remaining from the synthesis process and/or from the chemical reaction between the S atoms of the sheets of MoS_2 coming from the exfoliation process of the fullerenes and the Fe atoms. The binding energy of iron sulfide species ($FeS/Fe_{1-x}S$) is between 161 and 162 eV [14]. Moreover, two important contributions at high binding energy ($S2p_{3/2}$ at 166.8 and 168.4 eV) can be attributed to sulfur atoms binding to oxygen. Also, in the Mo3d spectrum recorded from the

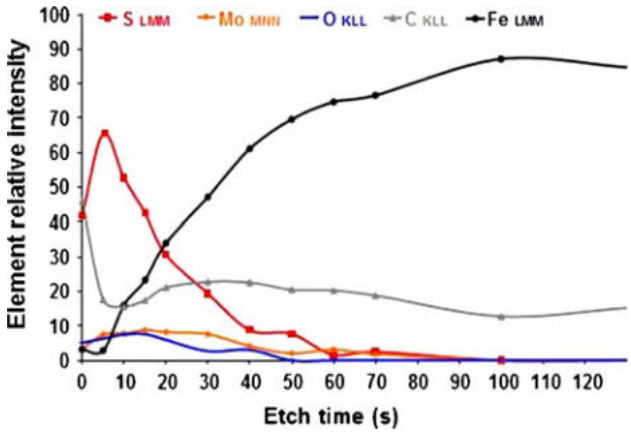

Fig. 5 Depth AES profile inside the steel worn track

tribofilm, molybdenum exists in two different chemical environments, the first position at 228 eV corresponding to Mo–S and the other peak at high binding energy corresponding to Mo–O.

3.2.2 DLC

A depth AES profile was carried out on the DLC worn surface lubricated by IF-MoS_2 (Fig. 7). Studies on the rubbing on DLC coatings are of interest because these coatings are inert materials. As expected, only carbon is detected on the worn surface proving that the 2H-MoS_2 does not adhere to the DLC coating. These results are in agreement with the friction test results obtained on DLC coating where it was shown that the presence of the IFs in the oil does not decrease the friction (Fig. 2b). The friction coefficient with PAO + 1 wt% IF-MoS_2 is equivalent to friction with PAO only.

3.2.3 Alumina

Similar results were obtained with alumina. No improvement of the lubricating properties was observed when adding IF-MoS_2 to the PAO (Fig. 2c). SEM images performed after the test (Fig. 8) show that IF-MoS_2 particles were expelled from the contact during the test. Agglomerates of IF-MoS_2 nanoparticles were detected only on the edge of the wear track. The corresponding EDS spectra are displayed in Fig. 9. The spectrum recorded on the border of the track clearly shows the presence of Mo and S elements (Fig. 9a), whereas the spectrum recorded inside the wear track shows the absence of Mo and S elements (Fig. 9b).

From the results presented here it can be inferred that all materials cannot be precursors of adherence reactions involving IF-MoS_2 and the surface.

4 Discussion

Previous studies of the lubrication mechanisms involving IF-MoS_2 nanoparticles reported that pressure and shear stress trigger the exfoliation of the IF-nanostructures in a tribological contact, leading to a lamellar lubrication mechanism. However, the interaction between the exfoliated sheets and the rubbing surfaces has not been precisely investigated in the literature so far. In this study, we have shown that the effectiveness of the fullerenes was strongly dependent on the nature of the rubbing surfaces. While exceptional results can be obtained with steel surfaces, no effect is observed with other pairs of materials like DLC or alumina.

In the case of the steel-on-steel friction test, a tribofilm composed of 2H-MoS_2 nanosheets was observed. Its analysis highlighted the presence of S–O and Mo–O bond,

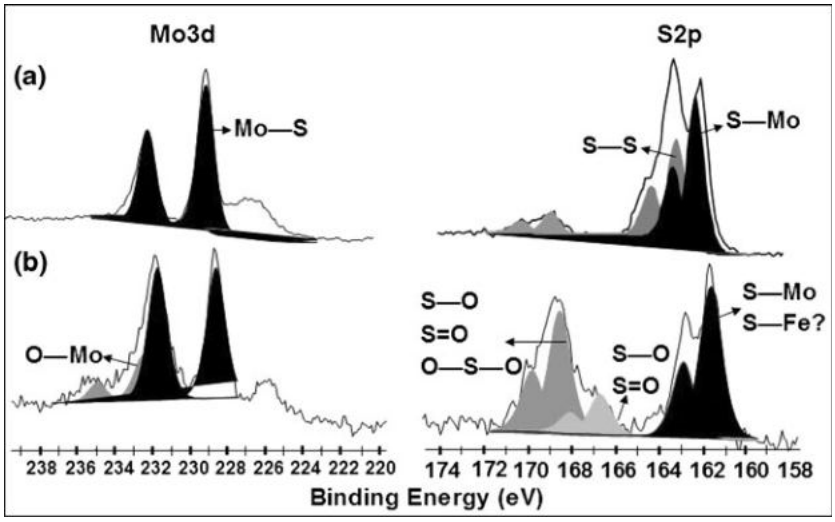

Fig. 6 Mo3d and S2p XPS spectrum of **a** IF-MoS_2 and **b** tribofilm

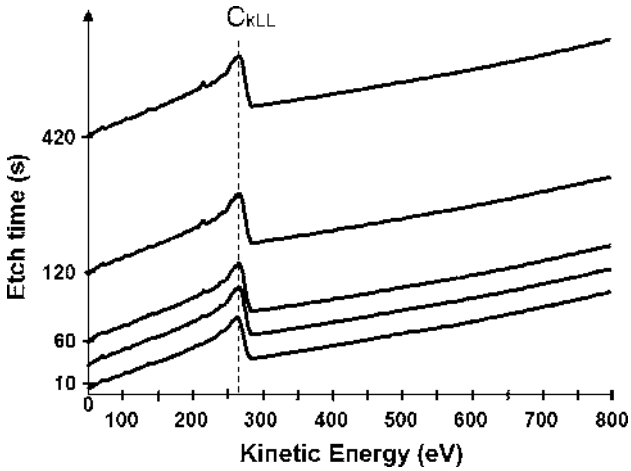

Fig. 7 Depth AES profile inside the DLC wear track

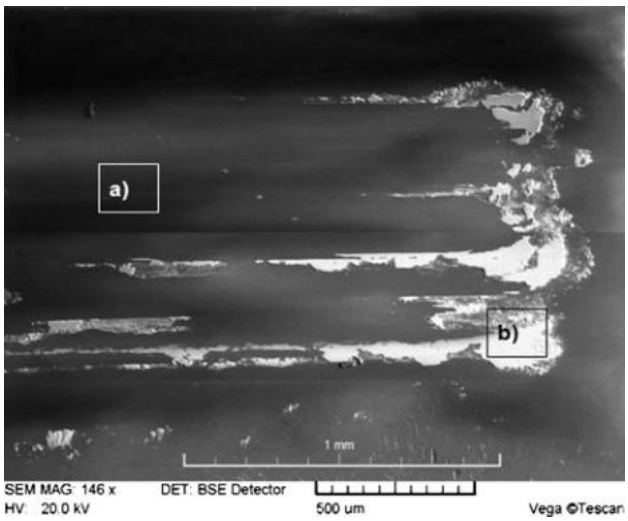

Fig. 8 SEM image of the alumina wear track. EDS area analyses **a** inside the wear track and **b** on the edge of the wear track

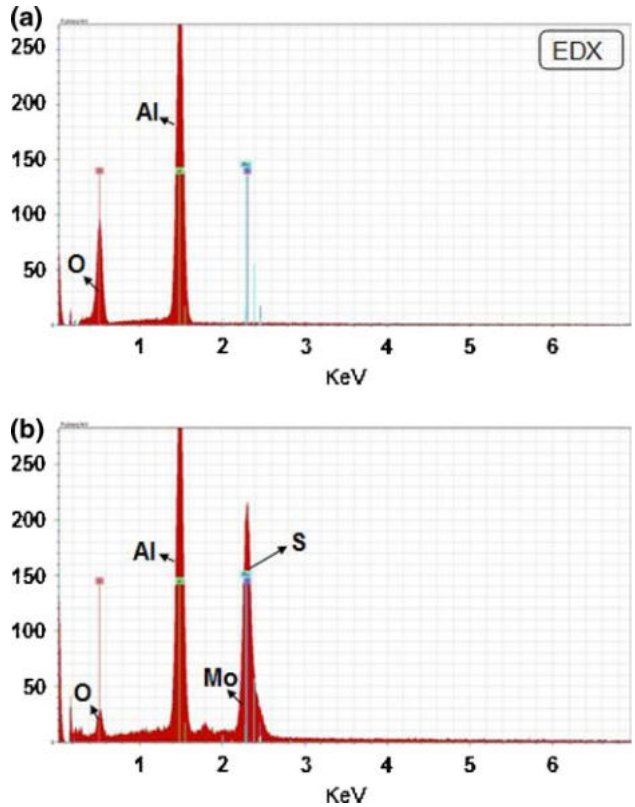

Fig. 9 EDS spectrum recorded **a** inside the wear track and **b** on the border of the wear track

but also the presence of a Fe–S bond. The origin of the sulfur and the oxygen atoms can be discussed. Sulfur atoms could originate either from free sulfur remaining from the synthesis process or from the reactive MoS_2 layers. The oxygen atoms could come either from the native iron oxide layer of the steel or from the air leading to an oxidation of the tribofilm.

From these observations two hypotheses can be made to explain the adhesion of the tribofilm. The first one is that the 2H-MoS_2 layers could be bonded to the iron oxide layer by M–O and S–O bonds as proposed in Fig. 10a. In such a model, the iron oxide layer would play an important role in the lubrication mechanism of IF-MoS_2 on steel surfaces. Its presence would be essential for the adhesion of the MoS_2 layers coming from the exfoliation of the IF-MoS_2 on the steel rubbing surfaces. This nevertheless supposes that (i) the iron oxide layer would be resistant enough to not be exfoliated during the first cycles of the friction test and (ii) a fast reaction between the exfoliated sheets of MoS_2 and the surfaces. If we consider this hypothesis, then the fact that no reaction occurs between alumina and the MoS_2 nanosheets could be explained by a higher energy bonding between Al and O than between Fe and O based on Pearson hardness [15]. Thus, a reaction between sulfur, molybdenum, and the oxygen from Al_2O_3 is chemically less reasonable, whereas it is still possible with the oxygen atoms of the iron oxide species. Our choice of Al_2O_3 for this study was motivated by its very high chemical stability in comparison to iron oxide species.

The oxidation phenomenon may also provide an important role in the sense that it could provide a "soft" oxide-like MoO_3 which also could serve to tether the nanoparticles or nanosheets to the steel surface.

The role of the iron oxide in the tribological performance of additives (molecules or nanoparticles) was also reported elsewhere. Joly-Pottuz et al. [16] reported that maghemite (γ-Fe_2O_3) was formed during friction tests performed with dispersions of carbon onions in PAO while this oxide was not detected in presence of pure base oil. These tests were also performed with steel rubbing surfaces. The reason for the presence of this oxide and its role

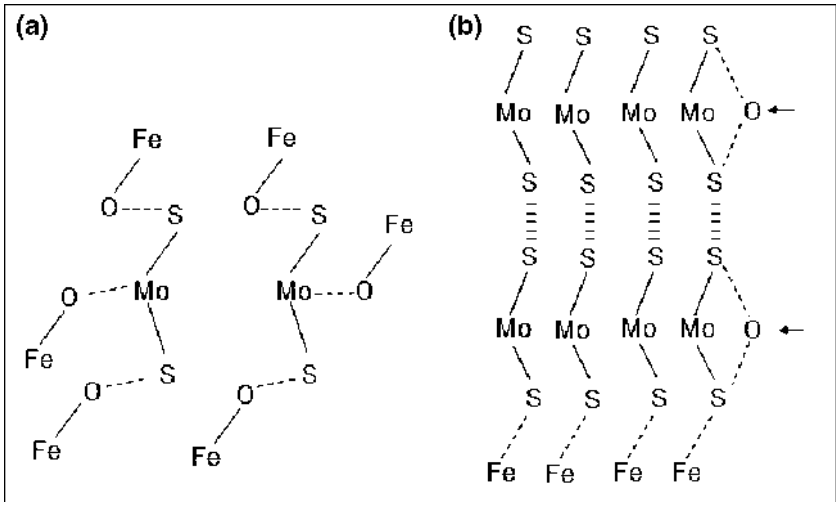

Fig. 10 Possible chemical interaction of 2H-MoS_2 with: **a** iron oxide layer and **b** iron metal atom

on the lubricating properties of the carbon onions is still unknown. Iron oxide also plays an important role in the anti-wear properties of the zinc dialkyl dithiophosphate (ZDDP). This compound is known to confer excellent anti-wear properties in the presence of steel surfaces. Its lubrication mechanism is extremely complex and still unknown. However, it was shown that under pressure and shear stress the compound forms a ~100-nm thick tribofilm on the steel rubbing surfaces which is composed of Zn polyphosphate chains [17]. Among various different models explaining the anti-wear properties of the ZDDP tribofilm, one of the most prominent ones was given by Martin [18]. Based on a chemical hardness approach [15], the author(s) suggest(s) a reaction between the zinc polyphosphate (coming for the precursory film) with the iron oxide coming from the steel surfaces. This reaction would induce a depolymerization of the polyphosphate chains close to the steel surface leading to a layered film formation composed of mixed Zn/Fe polyphosphate with a phosphate chain gradient prediction.

The second hypothesis which could be made to explain the presence of Mo–O and S–O bonds is an oxidation of the tribofilm after the friction test, under air (Fig. 10b). In this case, the adhesion of the tribofilm to the substrate could be the result of a chemical reaction between the Fe metal atoms and the sulfur atoms of the MoS_2 nanosheets. This could be consistent with the observed shift of the sulfur photopeak to lower energy close to the iron sulfide species. In this case, the iron oxide layer (~4 nm) would be removed during the first cycles of the friction test and the reaction between the layers of MoS_2 and the Fe metal atoms could occur. Interfacial and surface reactions between stoichiometric single crystals of molybdenite and iron were studied by Zabinski and Tatarchuk [19, 20] as a function of iron overlayer thickness and annealing temperature. At room temperature, iron was deposited as a relatively contiguous film on the basal plane of molybdenite. Annealing in UHV caused a transfer of the sulfur from the molybdenite basal plane to the iron surface. Annealing above 923 K caused the adsorbed sulfur to desorb or transfer back to the molybdenite and permitted some iron to migrate within the MoS_2 crystal structure forming subsurface layers of $FeMo_2S_4$. Annealing to 1123 K did not increase the fraction of $FeMo_2S_4$ suggesting that a limited number of defects in the molybdenite crystal provided pathways for the diffusion and reaction of iron. A correlation with results obtained in this study can be made since the IF-MoS_2 nanoparticles investigated in this study are of spherical IF-type with concentric layers showing considerable amounts of point defects (Fig. 11).

At this stage it is still extremely difficult to favor one mechanism over the other and to make a conclusion concerning the precise role of the iron oxide layer in the mechanism of adhesion of the tribofilm on the surface. It was shown in this study that a chemical reaction between the exfoliated sheets of MoS_2 could occur either via the native iron oxide layer or via the metal atoms. The origin of the oxygen atoms involved in the S–O and Mo–O bond must be identified clearly to be able to favor one of the two hypotheses. Further experiments are already planned to further proceed in the understanding of the mechanisms of adhesion of the tribofilm comprising layers of MoS_2 and the steel surface. Nevertheless, the IF produced nanoparticles differ in their sizes, number of layers, and crystallinity and they simply provide a different mix of the different tribological mechanisms, and not one or the either.

Concerning the efficiency of the fullerene nanoparticles, it also depends on some of their intrinsic characteristics like (i) their size and their degree of agglomeration: small and well-dispersed particles can more easily enter the contact area, (ii) their structure: the exfoliation kinetics of

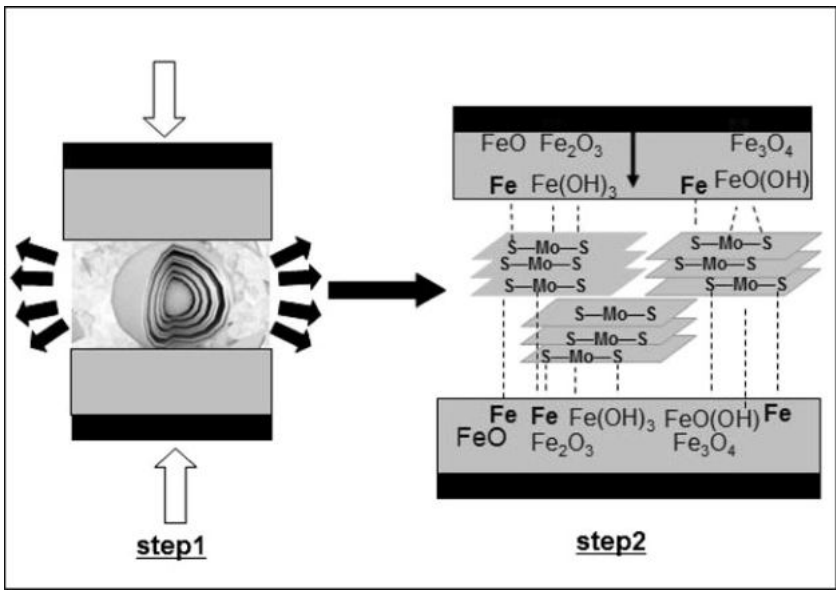

Fig. 11 Possible tribochemical mechanism of IF-MoS2 nanoparticles on steel surfaces

surface layers depends on the crystal defects and the strains in the structure of the nanoparticles [8]. However, it was recently shown [7] that for perfectly crystallized and spherical particles, a rolling process of the particles in the contact can also occur, enhancing the lubrication process nevertheless dominated by the exfoliation process. In [21], Tenne et al. suggested that IFs with a large number of layers (and therefore with higher mechanical resistance) could be considered to behave as genuine nano-ball bearing precluding gradual deformation and exfoliation giving rise to a very low friction coefficient [22].

In a future study, the same series of experiments that we carried out in the present study (e.g., with the three same couples of materials) will be performed with highly crystalline spherical particles. In this way, the contribution of the rolling in the friction reduction for these particles could be highlighted. Supposing that such nanoparticles can roll in the contact area, a decrease of the friction coefficient could be obtained even using DLC or alumina for performing the tribo tests. As it was shown in this study that the adhesion of the 2H-MoS_2 sheets could occur only in presence of certain surfaces the contribution of the exfoliation process in the friction reduction would then become negligible.

5 Conclusion

In this study, we focussed on the interaction between the 2H-MoS_2 nanosheets resulting from the exfoliation of IF-MoS_2 nanoparticles during the friction test as well as on the rubbing surfaces. Three different pairs of materials were investigated (steel on steel, DLC on DLC, and alumina on alumina). A tribofilm composed of 2H-MoS_2 layers was only observed on steel surfaces. It was found that these MoS_2 sheets were not only incorporated in the native iron oxide layer present at the outer surface of the steel but also a reaction occured between MoS_2 and the iron atoms/iron oxide species. S–O, Mo–O, and Fe–S bonds were identified by XPS. In the presence of non-reactive surfaces, no tribofilm was observed. In this case, the IFs did not contribute to friction reduction.

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