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IF-MoS_2 based lubricants: Influence of size, shape and crystal structure

Imène Lahouij, Béatrice Vacher, Jean-Michel Martin, Fabrice Dassenoy *

LTDS-ECL, 36 Avenue Guy de Collongue, 69134 Ecully, France

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ABSTRACT

In this work, we have studied the influence of the crystal structure of IF-MoS_2 nanoparticles on the lubricating properties of the fullerenes added to a synthetic base oil. In steel contacts, we highlight the better lubricating properties of poorly crystallised IF-MoS_2 nanoparticles, with many defects, compared to those of perfectly crystallised spherical particles. We explain the good lubricating properties of poorly crystallised particles by their higher ability to exfoliate and to form rapidly a tribofilm made of h-MoS_2 sheets on the surfaces compared to the perfectly crystallised particles.

1. Introduction

Inorganic fullerene-like (IF) nanoparticles continue to garner widespread interest in tribology applications, such as friction modifiers and anti-wear additives in liquid lubricants [1–4] and as solid lubricants [5–7]. Their efficiency for tribological application when they are dispersed in oil is related to their lubrication mechanism which depends on experimental conditions and intrinsic properties of the nanoparticles.

The lubrication mechanisms of (IF-MoS_2, IF-WS_2) nanoparticles used as additives in oil have been investigated in different experimental conditions. For example, Rapoport et al. [8] showed that in mixed lubrication conditions, the lubrication mechanisms of IF-WS_2 depends on the thickness of the lubricant film. When the film thickness is close to the size of the IF nanoparticles the shape of the nanoparticles is preserved and sliding/rolling of the IF at the interface is thought to be the most dominant mechanism. When the film thickness is lesser than the size of the nanoparticles, deformation and destruction of IF lead to the formation of a transferred IF film on the contact surface (third body theory). In the same way, the lubrication performance of (IF-MoS_2, IF-WS_2) fullerenes was investigated in boundary lubrication conditions [2,3,9]. Joly-Pottuz et al. [3] tested IF-WS_2 nanoparticles as additives in oil under boundary lubrication regime. The authors highlighted several mechanisms to explain the interesting friction reducing and antiwear properties of these nanoparticles, such as fullerenes delamination, formation of tribofilm made of WS_2 sheets on the surfaces, superlubricity of the sheets. A possible rolling/ sliding effect of the particles was also proposed but could not be evidenced. Cizaire et al. [2] gave evidence of a similar lubrication mechanism for the IF-MoS_2 nanoparticles. More recently, from experiments performed on MoS_2 nanotubes, Kalin et al. [10] proposed four possible sub-mechanisms for the adhesion of thin MoS_2 nano-sheets on the surface: (i) the exfoliation of nano-sheets from the individual nanotubes under shear stress; (ii) the exfoliation of MoS_2 sheets from the already deformed and compacted aggregates; (iii) the deformation and smearing of the nanotubes at the surface and (iv) the breaking or tearing apart of the nanotubes. However, these proposed sub-mechanisms are difficult to prove.

Since their discovery by Tenne et al. in 1992 [11], synthesis processes were improved and new fullerenes were developed giving then a variety of layered inorganic compounds [4,12–14] with different intrinsic characteristics (morphology, shape, structure, crystal structure etc.). For example, Rosentsveig et al. [15] modified the synthesis process developed in 1992 by Tenne et al. [11] to produce new perfectly spherical and crystallised IF-MoS_2 nanoparticles presenting a larger number of shells and leaving almost no empty core in the centre of the nanoparticles. It was shown that these particles have superior lubricating properties compared to other IF-MoS_2 nanoparticles prepared by the first original approach.

In the same way, Tannous et al. [4] investigated the lubricating properties and tribochemical mechanisms of new IF-MoS_2 prepared by the MOCVD method. This synthesis route leads to smaller and poorly crystallised particles (containing many defects) compared to those prepared by gas phase reaction. The authors showed that the performance of these IF-MoS_2 nanoparticles surpassed all previously examined IF materials, most likely for the reason that they contain many crystal defects, some of

* Corresponding author. Fax: +33 478 433 383.
E-mail address: fabrice.dassenoy@ec-lyon.fr (F. Dassenoy).

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them being even amorphous. This could contribute to the fast exfoliation of the IF nanoparticles. The same authors [9] investigated the influence of the nature of the rubbing surfaces (steel, DLC, alumina) on the lubricating properties of these "poorly crystallised" particles. It was shown that the formation of a tribofilm made of exfoliated MoS_2 sheets was only observed in presence of steel and that in presence of inert surfaces, no frictional benefit was obtained with this type of IF-MoS_2 nanoparticles, compared to the base oil.

These differences of properties between the "well spherical and crystallised" particles and the "poorly crystallised" particles raise questions of the influence of the intrinsic characteristics of the nanoparticles on their lubricating performance.

The goal of this present work is to go further in the investigation of the lubricating properties and the antiwear performance of these two different types of MoS_2 nanoparticles (namely "perfectly crystallised" and "poorly crystallised" particles). The particles were tested in the same conditions c.a. in dispersion in oil and in boundary lubrication regime. A detailed *post mortem* characterisation on wear debris and tribofilms was performed in order to clearly identify the lubrication mechanism of each of these two systems and to rely their action mode to the structural characteristic of the particles.

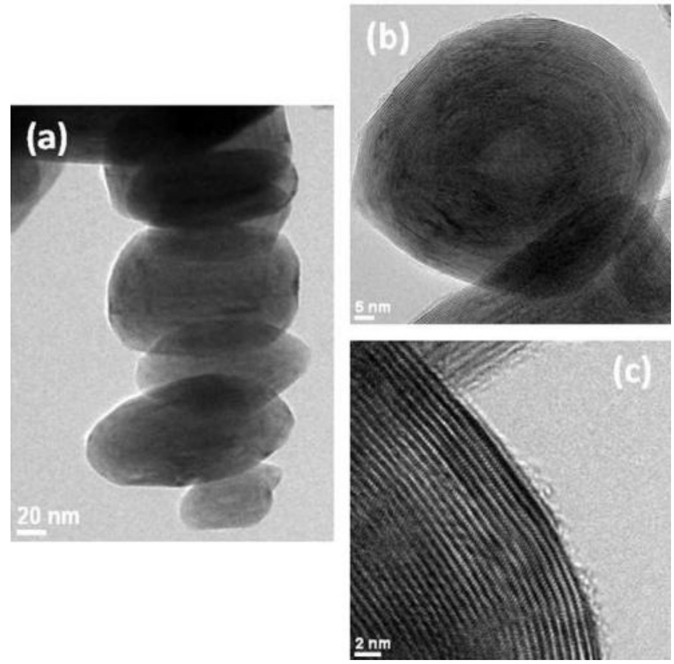

Fig. 1. HRTEM images of perfectly crystallised IF-MoS_2.

2. Experimental

2.1. Synthesis

Two types of MoS_2 nanoparticles synthesised by two different methods were tested in the present work.

Perfectly crystalline and round shape IF-MoS_2 nanoparticles were synthetised in Prof. Tenne laboratory at the Weizmann Institute of Science, in Rehovot, Israel, by reacting MoO_3 vapour with H_2S in a reducing atmosphere using a quartz made reactor [15]. This synthesis method was recently improved using a new quartz reactor designed to permit evaporation of large amounts of MoO_3 powder. The temperature of the evaporation zone in lower part of the reactor was 750 °C and 840 °C in the upper part where much of the sulfidization reaction takes place. The present design of the reactor limits the reaction time to 2 h due to pressure build-up. The IF-MoS_2 nanoparticles thus produced were then further annealed in H_2S atmosphere for 20 h at 840 °C in order to complete the reaction and transform the oxide core into closed MoS_2 layers leaving almost no empty core in the centre of the particle.

Poorly crystallised IF-MoS_2 nanoparticles, with many defects, were synthetised in a customised metal organic chemical vapour deposition (MOCVD) reactor described by Etzkorn et al. [16,17]. $Mo(CO)_6$ precursor was placed into a quartz reactor setup along with H_2S gas under argon reverse flow. The details of the synthesis process of these nanoparticles are described in [4].

HRTEM micrographs (Figs. 1 and 2) reveal the differences of structure, size and crystallinity between the two types of fullerenes prepared using the two distinct synthesis processes: the crystalline IF-MoS_2 has a perfectly structure without any defect and a high crystalline order presenting more than 30 closed shells (Fig. 1), while the IF-MoS_2 nanoparticles prepared by MOCVD (called "poorly crystallised particles" is this paper) appear sintered together (Fig. 2a and b) and show (Fig. 2c and d) some extreme irregular shape and considerable amounts of point defects, hereby proving their nearly amorphous character. The typical size of the "poorly crystallised" IF-MoS_2 nanoparticles is between 20 and 50 nm, appreciably smaller than the crystalline IF-MoS_2 having a mean diameter of about 80 nm.

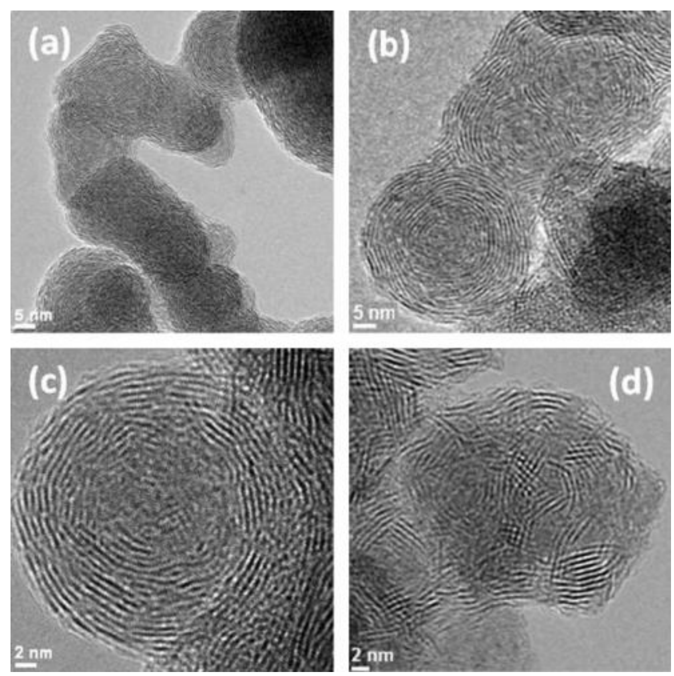

Fig. 2. HRTEM images of poorly crystallised IF-MoS_2.

2.2. Tribological tests

IF-MoS_2 nanoparticles were tested in lubricated conditions using a reciprocating pin-on-flat tribometer [18], materials made of polished AISI 52100 steel (Ra=40 nm). Fullerenes were dispersed using an ultrasonic bath at 1 wt% in synthetic base oil, a polyalphaolefin (PAO6). Tribological tests were carried out at ambient temperature (300 K), with sliding velocity of 3 mm/s, a stroke length of 3 mm, and contact pressure of 1.12 GPa. Friction experiments were run during 60 min, corresponding to 2000 cycles. Additional shorter friction tests were performed (100 cycles) in order to observe the evolution of the formation of the tribofilm all along the friction test.

2.3. Analytical tools

TEM observations were performed on a JEOL 2010F operating with 200 KV accelerating voltage equipped with Energy Dispersive Spectroscopy (EDS).

The characterisation before friction of the nanoparticles was made by depositing a drop of highly diluted nanoparticle dispersions in Heptane onto a standard carbon-covered-copper micro. After friction, the wear particles were collected by gently depressing a grid directly in the wear scar on the pin to be sure to have only nanoparticles which were in the contact area. The grid is then immersed in pure heptane in order to eliminate residual oil.

In order to fully characterise the tribofilm formed on the flat, TEM samples were prepared using 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.

Raman spectra were recorded in back scattering configuration using a Labram HR 800 microspectrometer. Excitation wavelength of 514.5 nm was produced by an argon laser source. A density filter, reducing the incident power close to 50 μW, was used to ovoid heating effect of spectra. The instrumental resolution was 1 cm^{-1} for the 1800 grooves/mm grating. The calibration was performed with silicon semiconductor at 520.7 cm^{-1}.

XPS analyses were carried out on the worn surfaces. A monochromatized AlK_{α} 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 photo peaks were fitted after removing a Shirley background.

The topography of worn scars was obtained using a common optical microscope and a FEI XL 30 ESEM FEG operating in vacuum and with an accelerating voltage of 10 kV.

3. Results

3.1. Tribology

Fig. 3 shows the average friction coefficient measured during friction tests performed with PAO6 base oil, PAO6+1 wt% of "well crystallised" $IF-MoS_2$ particles and PAO6+1 wt% of "poorly crystallised" $IF-MoS_2$. Whatever the type of MoS_2 particles, results show that the addition of 1 wt% of nanoparticles in the base oil contributes to a significant reduction of the friction coefficient compared to the pure base oil alone. The evolutions of friction coefficients as a function of the number of cycles are reported in Fig. 4. In presence of well "crystallised particles", the friction coefficient starts with a value of 0.07 at the beginning of the test and then decreases progressively with the cycle number to stabilise at 0.04 after 1000 cycles. With "poorly crystallised particles", the friction coefficient is quite stable all the friction test long, starting at 0.035 and reaching 0.03 at the end of the test.

Shorter friction tests (100 cycles) were then performed with the two systems (not shown in this paper). Wear scars were observed and compared to those obtained after 2000 cycles of friction test.

Fig. 5 shows the optical microscopy observations of the ball wear scars after each friction test. The wear scar diameters

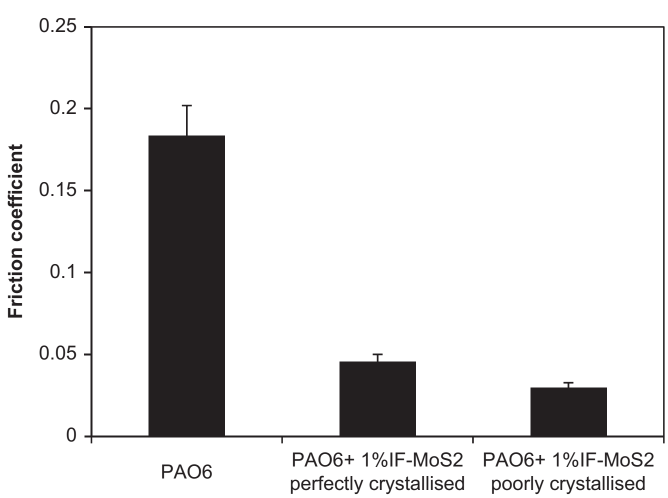

Fig. 3. Friction coefficient of PAO6, PAO6+1 wt% of perfectly crystallised $IF-MoS_2$ and PAO6+1 wt% of poorly crystallised $IF-MoS_2$.

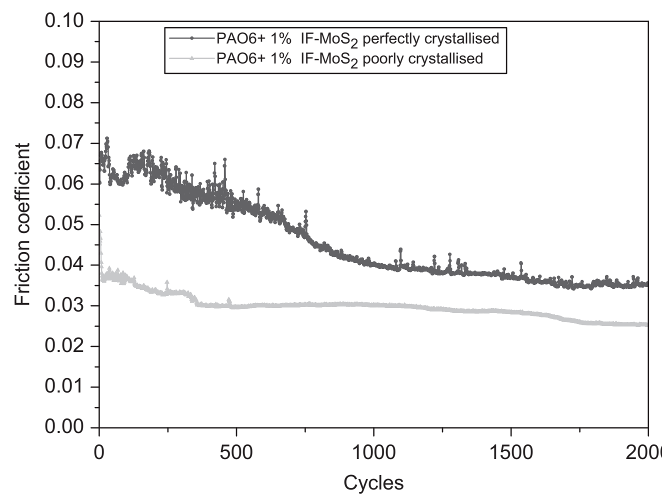

Fig. 4. Evolution of the friction coefficient for a friction test performed on steel surfaces with PAO6+1 wt% of perfectly crystallised $IF-MoS_2$ and PAO6+1 wt% of poorly crystallised $IF-MoS_2$.

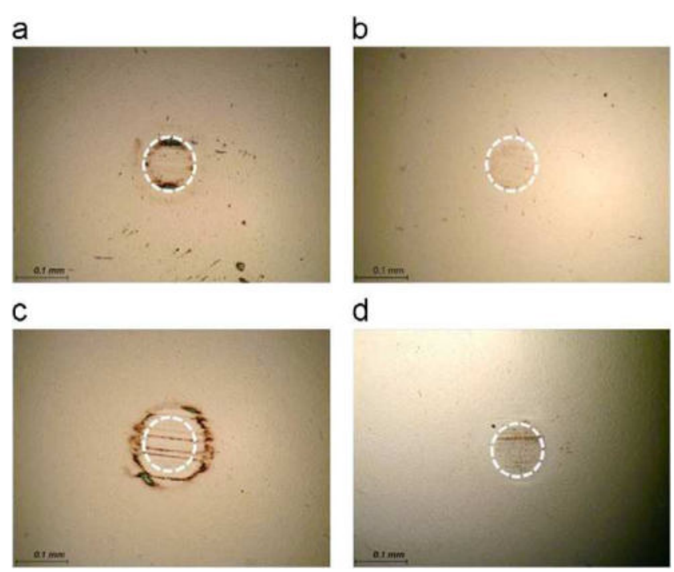

Fig. 5. Wear tracks on pin observed for: (a) perfectly crystallised $IF-MoS_2$ nanoparticles after 100 cycles, (b) perfectly crystallised $IF-MoS_2$ after 2000 cycles, (c) poorly crystallised $IF-MoS_2$ after 100 cycles and (d) poorly crystallised $IF-MoS_2$ after 2000 cycles.

measured on the ball and the flat are listed in Table 1 and compared with the calculated Hertz diameter. Whatever the type of IF-MoS_2, wear scar diameters are smaller than those measured with the base oil alone. However, after 2000 cycles, the anti-wear properties of the "poorly crystallised particles" seem to be better than those of the "well crystallised ones". For the lubricant containing 1 wt% of "poorly crystallised" IF-MoS_2, the two antagonist surfaces are totally preserved against wear (Fig. 5c and d) all the friction test long. The wear scar diameter remains stable and is extremely low, close to the calculated Hertz diameter (92 μm). With the "well crystallised particles", the reduction of wear on the steel surfaces is less important. It is still close to the Hertz diameter after 100 cycles (Fig. 5a) but increases to 165 μm after 2000 cycles (Fig. 5b).

3.2. Characterisation after friction

3.2.1. SEM experiments

Figs. 6 and 7 show SEM images of the topography of the worn surface at the end of the friction tests (2000 cycles) performed with the two types of IF-MoS_2 particles. The rubbed surfaces obtained with the "crystallised particles" appear much more scratched (Fig. 6) than the rubbed surfaces obtained with the "poorly crystallised" particles (Fig. 7). Moreover, the depth of the scratches is higher with the crystallised particles. Small agglomerates are also observed in the wear track (Fig. 6b). Chemical analysis performed by EDX in the wear track (not shown here) confirms the presence of IF-MoS_2 particles/aggregates. With the "poorly crystallised" particles few intact IF-MoS_2 nanoparticles/agglomerates has been detected.

3.2.2. Raman spectroscopy

Raman spectroscopy was carried out on ~10 different areas on each wear track. These spectra were compared with those obtained from pristine nanoparticles (well and poorly crystallised IF-MoS_2 particles) and the lamellar h-MoS_2 structure.

Fig. 8 shows Raman spectra recorded from different areas of the rubbed surface after a friction test (2000 cycles) performed with the "poorly crystallised" particles. Whatever the probed areas, the spectra appear very similar in terms of peak position and intensity. This reveals the homogeneity of the tribofilm which seems to be mainly composed of lamellar h-MoS_2 nano-sheets. The positions of the two peaks are consistent with those of the lamellar h-MoS_2 structure.

Table 1
Wear scar diameters on pins and flats measured after friction tests of 100 and 2000 cycles for the dispersion of 1 wt% in PAO6 of perfectly crystallised and poorly crystallised IF-MoS_2.

Lubricant	PAO6	PAO6+1 wt% of perfectly crystallised IF-MoS_2		PAO6+1 wt% of poorly crystallised IF-MoS_2	
Number of cycle	2000	100	2000	100	2000
Hertz diameter (μm)	92	92		92	
Pin wear scare diameter (μm)	240	100	165	92	100
Flat wear scare diameter (μm)	230	95	130	92	98

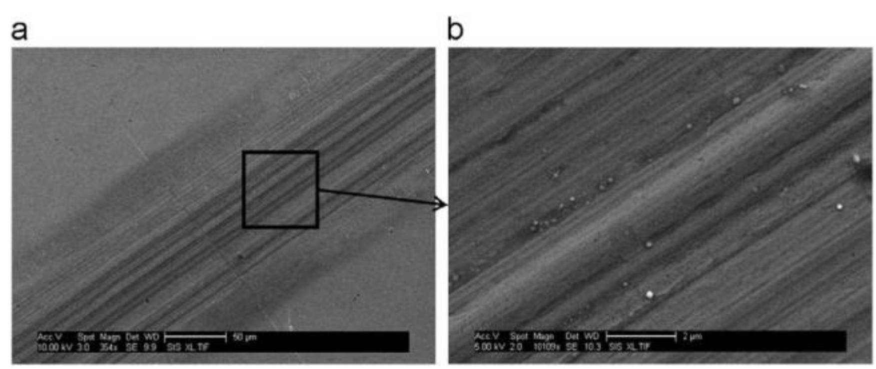

Fig. 6. SEM micrographs of wear tracks on flat lubricated with the PAO6 base oil containing 1 wt% perfectly crystallised IF-MoS_2: (a) overview of the wear track and (b) detail of the centre of the wear track.

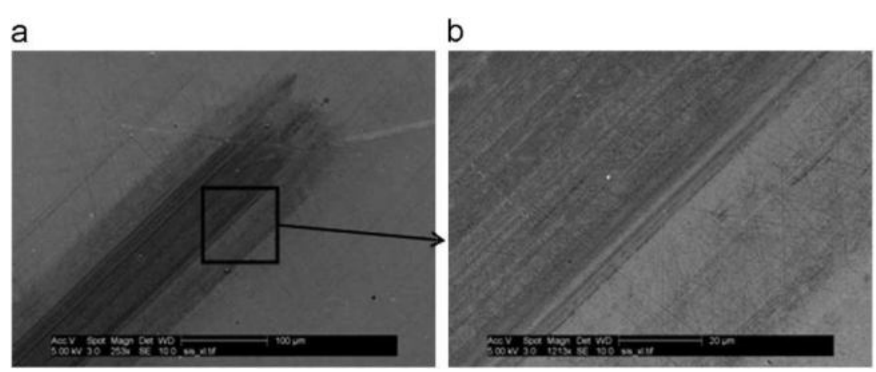

Fig. 7. SEM micrographs of wear tracks on flat lubricated with the PAO6 base oil containing 1% poorly crystallised IF-MoS_2: (a) overview of the wear track and (b) detail of the centre of the wear track.

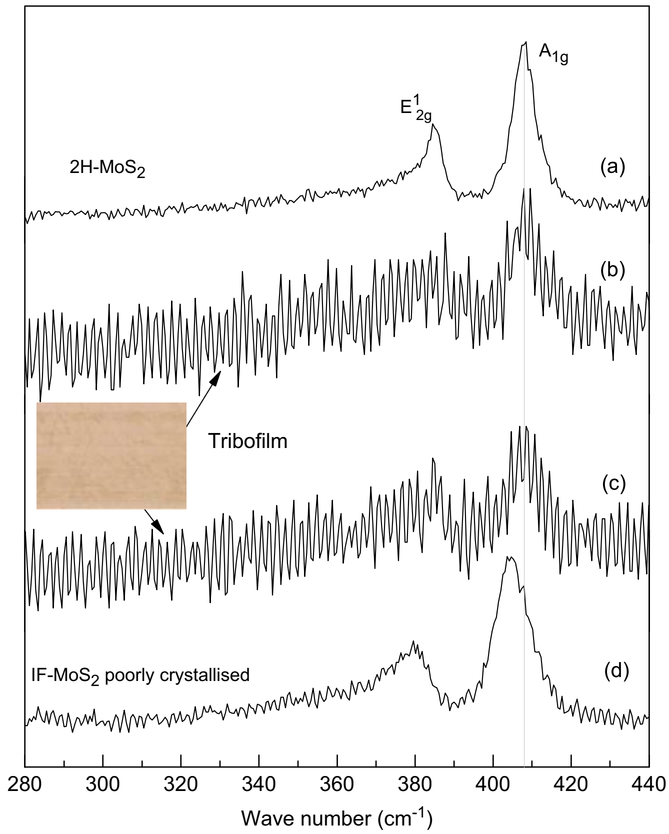

Fig. 8. Comparison of Raman spectra obtained for: (a) 2 h-MoS_2, (b) and (c) tribofilm, (d) poorly crystallised IF-MoS_2.

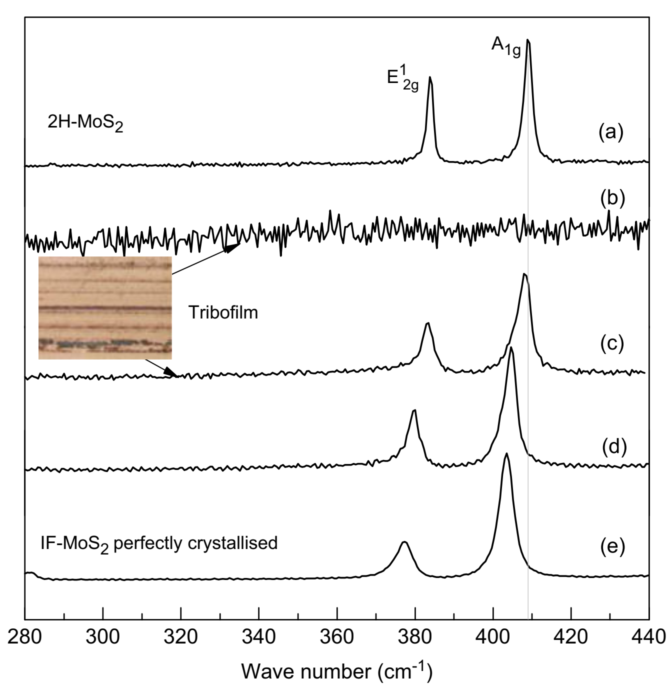

Fig. 9. Comparison of Raman spectra obtained for: (a) 2 h-MoS_2, (b), (c), (d) tribofilm obtained at 2000 cycles and (e) perfectly crystallised IF-MoS_2.

Raman spectra (Fig. 9) recorded from the wear track after a friction test (2000 cycles) performed with the "well crystallised particles" indicate that the tribofilm is much more inhomogeneous than the tribofilm obtained with the "poorly crystallised" particles. Some spectra appear well resolved (Fig. 9c and d) while others (Fig. 9b) indicate the absence of any material in the wear track. The peak positions of the spectrum (Fig. 9d) are consistent with those obtained from the raw particles (Fig. 9e). This confirms the presence of intact particles embedded in the tribofilm and is consistent with the SEM image of the Fig. 6b. The peak positions of the spectrum (Fig. 9c) are consistent with those of the lamellar structure. This indicates that the tribofilm is discontinuous but also heterogeneous in terms of crystal structure.

3.2.3. XPS

In order to understand the difference of friction and wear behaviours of the two types of MoS_2 nanoparticles in PAO, the chemical speciation of elements on the rubbed surfaces was analysed using XPS. Figs. 10 and 11 show respectively the Mo3d and S2p XPS spectra recorded from the two types of nanoparticles and their corresponding tribofilms obtained after 100 and 2000 cycles of friction. Molybdenum and sulphur are found in different chemical environments in the nanoparticles and in the tribofilms. Concerning the XPS spectra recorded from the two IF-MoS_2 nanoparticles, the molybdenum $Mo3d_{5/2}$ is composed of one peak at 228.8 eV corresponding to Mo-S bond of IF-MoS_2 particles; the sulphur $S2p_{3/2}$ is composed of a main peak at 162.47 eV corresponding to the S-Mo bond in the IF-MoS_2 nanoparticles. For the "poorly crystallised" IF-MoS_2 particles, a small contribution of sulphur at 163.84 eV is observed and can be attributed to S–S bond. The presence of this S–S bond could be related to the free sulphur remaining from the synthesis processes.

XPS spectra recorded on the wear tracks after 100 cycles are very similar for both particles. The additional contribution of molybdenum at 232.1 eV can be attributed to Mo–O bond. Another contribution of sulphur at 169 eV can be attributed to S–O bonds.

The XPS spectra recorded on the wear tracks after 2000 cycles are similar for both types of particles but slightly different from the spectra recorded after the test of 100 cycles. Concerning the molybdenum, an increase of the intensity of the Mo–O bond can be observed with the "highly crystallised particles" between the spectra recorded at 100 and 2000 cycles while no intensity changes are observed for the "poorly" crystallised particles. This could be explained by more oxidation of the tribofilm/particle at the end of the friction test with the crystallised particles.

Concerning the sulphur, for both types of particles a new additional contribution is observed at 168.2 eV, still corresponding to S–O bonds. In summary, the comparison between S2p and Mo3d spectra recorded on tribofilms after 100 cycles and 2000 cycles indicates that the contribution of S–O bond is more pronounced on tribofilm obtained after 2000 cycles than after 100 cycles.

Moreover, the comparison between $S2p_{3/2}$ spectra recorded on two types of IF nanoparticles and inside their corresponding tribofilms after 100 cycles and 2000 cycles indicates that the main peaks of sulphur (162.5 eV) and molybdenum (229.7 eV) are shifted to low binding energy ($S2p_{3/2}$ = 161.6 eV) and ($Mo3d_{5/2}$ = 229 eV) on the spectrum recorded of the tribofilm. The shift of sulphur peak could be explained by the presence of small quantities of iron sulphide species in the tribofilm coming either from the free sulphur 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.

3.2.4. TEM: wear particles and FIB observations of the surface

3.2.4.1. Crystallised particles. TEM analysis of the wear particles collected after the friction tests showed that most of the MoS_2

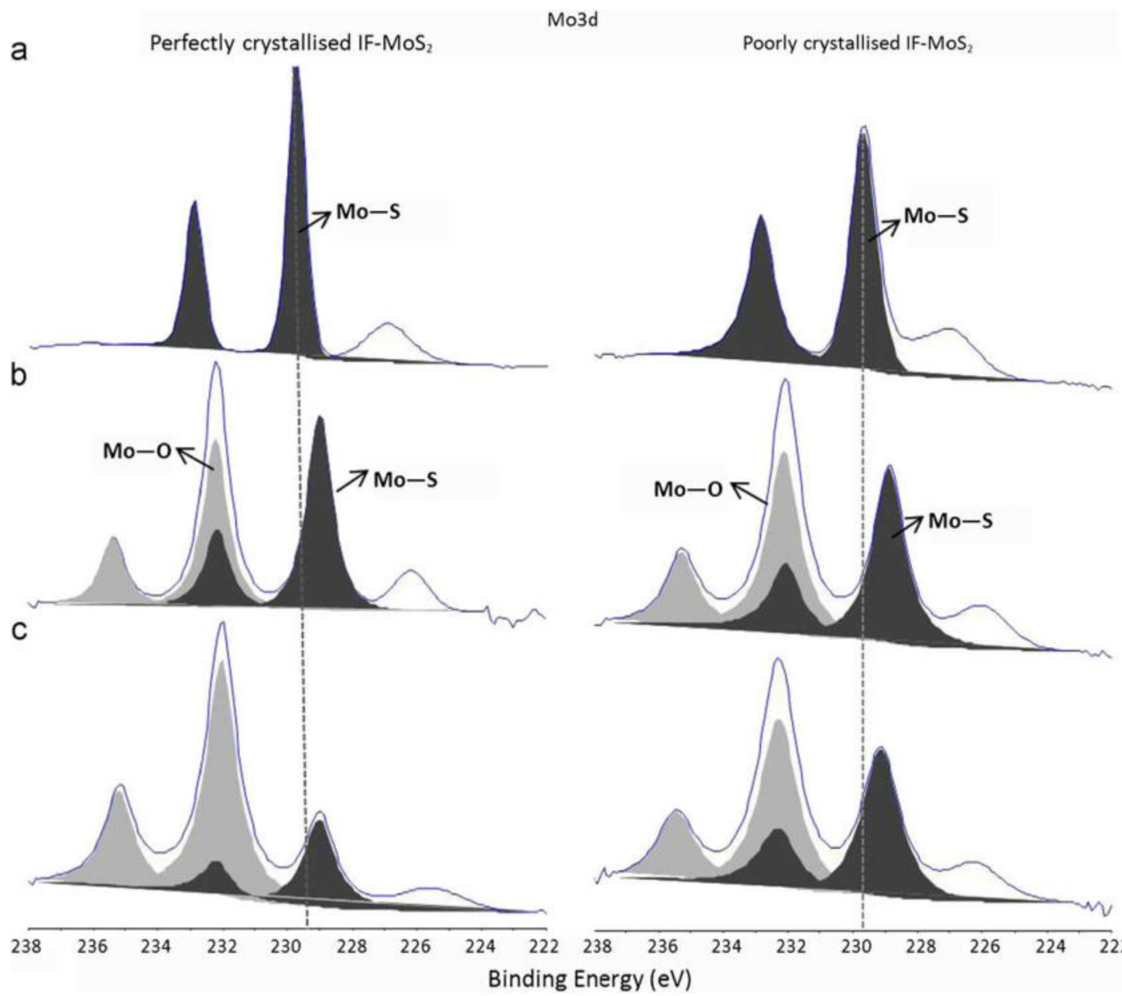

Fig. 10. Comparison of Mo3d XPS spectra between perfectly crystallised and poorly crystallised IF-MoS_2. (a) Powder, (b) tribofilm after 100 cycles and (c) tribofilm after 2000 cycles.

particles remain intact (Fig. 12). The shape of the nanoparticles is generally preserved. Only some MoS_2 sheets can be sometimes observed. These sheets come probably from few MoS_2 particles exfoliated during the friction test. Nevertheless, in most of the damaged nanoparticles only a few external molecular sheets of the IF were exfoliated. The relatively small amount of damaged nanoparticles observed by TEM is consistent with the results obtained by Raman spectroscopy and SEM analysis. TEM observations of the FIB cross section preparation made on the worn steel surface show the presence of a tribofilm (Fig. 13a) the thickness of which is heterogeneous. It varies between 10 and 40 nm depending on the observed areas. This tribofilm is composed of a mixture of: (i) particle fragments (Fig. 13c), (ii) lamellar MoS_2 sheets coming from the exfoliation of some nanoparticles (Fig. 13b) and (iii) intact nanoparticles embedded in the tribofilm (Fig. 13a). It is interesting to notice that very small iron oxide nanoparticles of 5 nm diameter are embedded in the tribofilm as shown in Fig. 13a. Their presence was confirmed by EDS (Fig. 14b). The observation of intact nanoparticles embedded in the tribofilm is consistent with SEM observations. The heterogeneity of the tribofilm was also confirmed by Raman spectroscopy.

3.2.4.2. Poorly crystallised particles. TEM images of the Fig. 15 show that most of the MoS_2 particles are strongly damaged after the friction test in comparison with the crystallised ones. Many MoS_2 sheets can be observed in the wear debris (confirmed by EDS: Fig. 16). TEM observations of the FIB cross section preparation made from the rubbed steel surface indicate the presence of a tribofilm (Fig. 17a) which is thinner than the one obtained with the crystallised particles. It is also much more homogeneous. Its thickness is of about 10 nm and it is mainly composed of exfoliated MoS_2 layers aligned in the sliding direction (Figs. 17b and c).

4. Discussion

Our results clearly show that the lubricating properties of the IF-MoS_2 nanoparticles are strongly dependent on their physical characteristics.

Friction tests performed on steel contact highlight better lubricating performances for ‘‘poorly crystallised’’ nanoparticles. With these particles, the friction coefficient is low and quite stable from the beginning and all the friction test long. At the opposite, with ‘‘well crystallised particles’’, friction decreases slowly and stabilizes at the end of the test at a higher value than with the other particles. The very good lubricating properties of the ‘‘poorly crystallised’’ and defects particles were already highlighted in the past by Tannous et al. [4]. A possible explanation for this finding was the exfoliation of the external layers of the particles under external pressure which is facilitated by the amorphous character of the particles and the presence of defects.

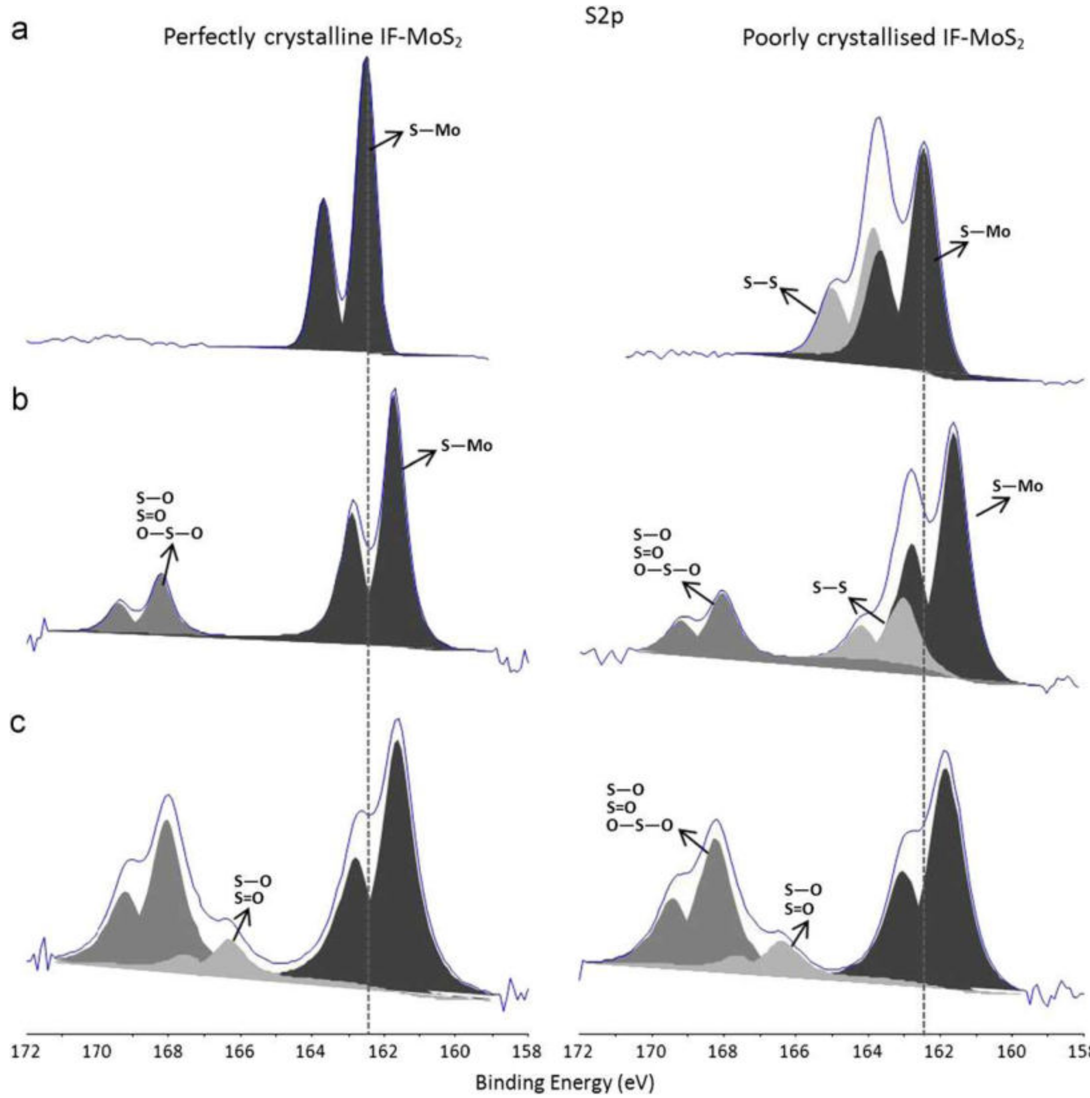

Fig. 11. Comparison of S2p XPS spectra between perfectly crystallised and poorly crystallised IF-MoS_2. (a) Powder, (b) tribofilm after 100 cycles and (c) tribofilm after 2000 cycles.

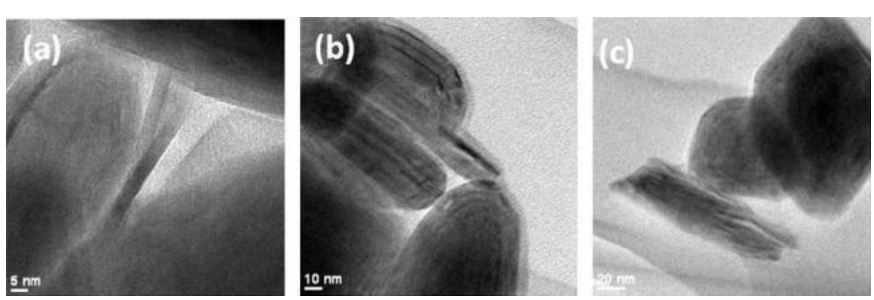

Fig. 12. TEM images of wear particles collected after a friction test (2000 cycles) performed with the perfectly crystallised IF-MoS_2 particles.

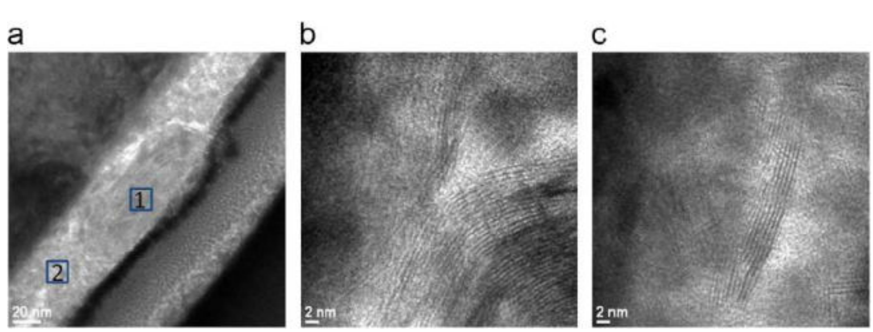

Fig. 13. TEM observations of the FIB cross section prepared from the rubbed flat after a friction test (2000 cycles) performed with the perfectly crystallised IF-MoS_2 particles.

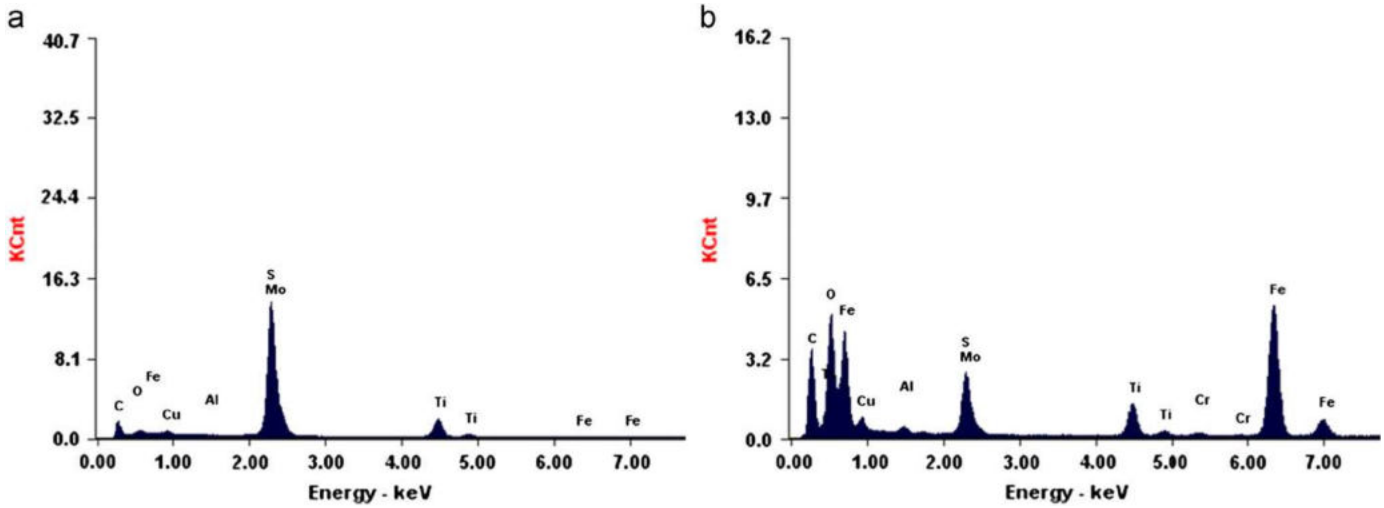

Fig. 14. EDS spectra recorded from the two areas indicated in Fig. 13a. (a) area 1 and (b) area 2.

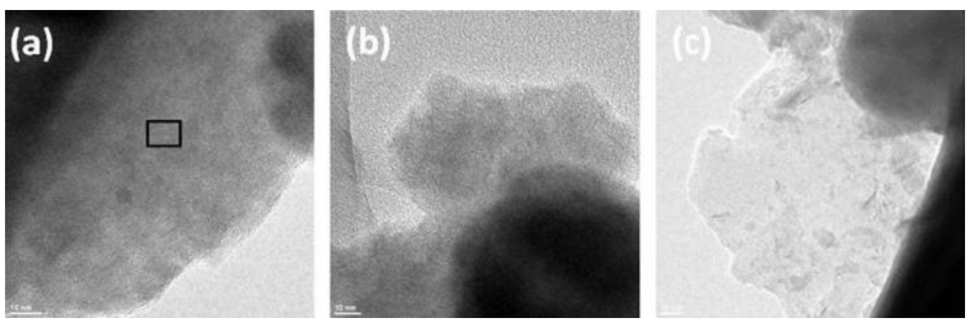

Fig. 15. TEM images of wear particles collected after a friction test (2000 cycles) performed with the poorly crystallised IF-MoS_2 particles.

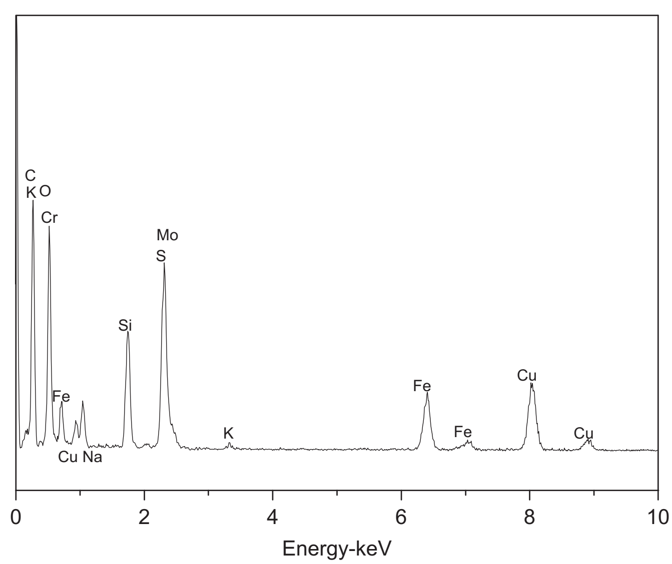

Fig. 16. EDX spectrum recorded from the area indicated in Fig. 15a.

Rosentsveig et al. [15] investigated in the past the lubricating properties of the "well crystallised MoS_2 particles". Different contact pressures were applied (0.83, 1.12 and 1.42 GPa). Surprisingly, at 0.83 GPa no important frictional benefit could be obtained compared to the base oil. At higher pressure (1.12 and 1.42 GPa), less friction for well crystallised particles was observed. Nevertheless their friction curves were similar to those that we obtained in the present work: a slow and progressive decrease of the friction coefficient during the test. The authors ascribed this unusual behaviour to the crystalline perfection and the large number (>30) of closed layers of the nanoparticles. The authors suggested then that even if exfoliation and third body transfer of molecular sheets onto the asperities is a prevalent mechanism for the improved tribological behaviour of IF nanoparticles, the rolling friction could also play some role for the well crystallised particles. It was then suggested that the perfect particles could be considered to behave as genuine nano-ball bearings, at least temporarily, until they gradually deform and start to exfoliate giving rise to very low friction coefficient. However in their work, no *post mortem* characterisation were made on the worn surfaces and wear debris, and the anti-wear properties of the well crystallised particles were not really discussed. We have shown in our study the absence after 100 cycles of wear on the rubbed surfaces and the presence of a tribofilm (XPS analysis). After 2000 cycles the wear is much more pronounced (165 μm) compared to that observed after 100 cycles, or the wear observed with the "poorly crystallised" particles after 2000 cycles. This indicates that with the "crystallised particles", the wear process begins after 100 cycles. It corresponds to the decrease of the friction coefficient which could simply be due to an increase of the contact area. It can be suggested from these observations that as far as the particles remain in the contact they contribute to lubricate the system by a mechanism mainly based on the exfoliation of the nanoparticles. However, based on *post*

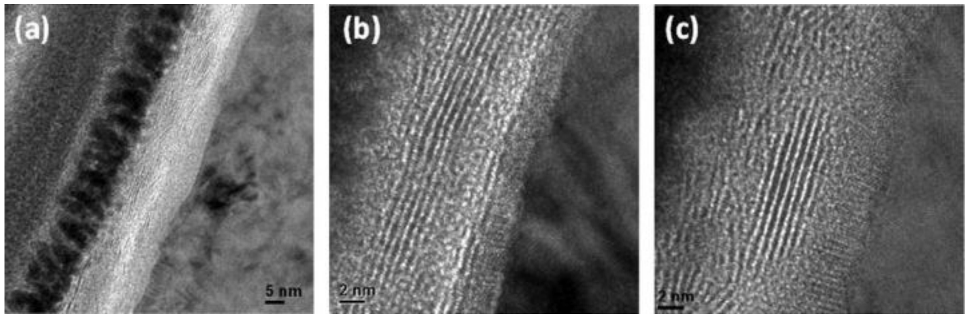

Fig. 17. TEM observations of the FIB cross section prepared from the rubbed flat after a friction test (2000 cycles) performed with the poorly crystallised IF-MoS_2 particles.

mortem analyses, the pure exfoliation process cannot be advanced anymore to explain the decrease of the friction coefficient observed after 100 cycles. The increase of the wear scar diameter and the presence of a very heterogeneous tribofilm at the end of the test (which does not cover the whole surface area) let suppose us that the particles are progressively ejected from the contact and/or cannot penetrate anymore in the contact zone (due to their size and/or their agglomeration). It has been observed on Fig. 5b, after the friction test performed with the ''crystallised particles'', the presence of a brown crown on the pin all around the wear scar which suggests an agglomeration of particles (the largest) all around the contact zone. This could lead to a poor particles supply for the tribological contact. This phenomenon can be enhanced with well spherical and crystallised particles. Due to their good mechanical resistance they do not deform easily under the effect of the gradual increase of the pressure near the contact zone. Recently some authors [19,20] investigated in real time the deformation and degradation behaviour of the same ''well crystallised'' IF-MoS_2 nanoparticles under compression and shear stress using a high-resolution transmission electron microscope equipped with a nanoindentation holder. The authors showed that the ability of the particle to exfoliate was strongly dependent on their physical properties. Thus, it was shown that well crystallised and round shape nanoparticles were much more difficult to exfoliate than ''poorly crystallised'' particles. It was found that under 1–1.5 GPa uniaxial pressure, the shape of single ''well crystallized'' IF-MoS_2 nanoparticles was preserved and that only external layers were exfoliated [20]. Lahouij et al. (to be published) performed the same type of experiments on ''poorly crystallised'' MoS_2 nanoparticles containing many defects.. A much lower pressure resistance was observed. The particles are completely crushed and exfoliated for a contact pressure of less than 0.5 GPa, much lower than for the ''well crystallised'' particles. The behaviours under compression of these two types of particles are consistent with the results obtained in the present work.

5. Conclusion

In this work the role of the intrinsic properties of IF-MoS_2 nanoparticles on their lubricating properties was investigated. In a lubrication test in presence of steel surfaces, it was shown that the IF-MoS_2 nanoparticles containing many defects were much easier exfoliated than the perfect structures. The ability of the particles to exfoliate is directly related to the fast formation of a tribofilm made of MoS_2 nano-sheets that protects the surface against wear and contributes to reduce friction. The exfoliation of perfect MoS_2 particles is more difficult and consequently there is a progressive decrease of the friction coefficient in the friction test.

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