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Boundary lubrication: Influence of the size and structure of inorganic fullerene-like MoS_2 nanoparticles on friction and wear reduction

Pierre Rabaso [a,b,c,*], Fabrice Ville [a], Fabrice Dassenoy [b], Moussa Diaby [c], Pavel Afanasiev [d], Jérôme Cavoret [a], Béatrice Vacher [b], Thierry Le Mogne [b]

[a] Université de Lyon, LaMCoS, UMR CNRS 5259, INSA de Lyon, 18–20 Rue des Sciences, F69621 Villeurbanne Cedex, France
[b] Université de Lyon, LTDS, UMR CNRS 5513, Ecole Centrale de Lyon, 36 Avenue Guy de Collongue, F69134 Ecully Cedex, France
[c] PSA Peugeot Citroën Centre Technique de Belchamp, France
[d] Université de Lyon, IRCELYON, UMR CNRS 5256, 2 Avenue Albert Einstein, F69626 Villeurbanne Cedex, France

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ABSTRACT

The use of Inorganic Fullerene-like (IF) nanoparticles in lubricants has proved extremely effective to reduce friction and wear under severe boundary lubrication conditions. It has furthermore been suggested that the synthesis of smaller nanoparticles containing many structural defects would benefit friction and wear reduction, as they would penetrate and exfoliate more easily in the contact, leading to the quick formation of homogeneous tribofilms. In this study, four different types of IF-MoS_2 were synthesized so as to be able to differentiate the influence of both the size and the morphology of the nanoparticles on their tribological behavior. Pure-sliding, reciprocating tribological testing of these four types of nanoparticles revealed their excellent friction-reducing properties in severe boundary lubrication, with splash lubrication taking place for a high number of cycles. High wear reduction was also obtained and confirmed using optical profilometry. Although the nanoparticle structure was found to have an influence on their effectiveness in time, all the nanoparticles tested – regardless of size or crystallinity – were found to achieve the same performances as long as proper oil recirculation took place, ensuring a continuous feeding of the contact in nanoparticles. The formation of MoS_2 tribofilms on the wear surfaces was confirmed using XPS analyses and observed on FIB cross sections, and their nature was discussed in the light of the associated tribological results. As the size and morphology of the IF-MoS_2 did not affect their performance in the range studied, their friction reducing properties were compared to those of bulk h-MoS_2 tested in the same conditions. The benefits of using spherical nanoparticles such as IF-MoS_2 was clearly shown.

1. Introduction

The use of nanoparticles as lubricant additives has been widely explored in recent years, and the advances in synthesis techniques [1–3] have revealed the tribological potential of many different types of nanoparticles. Nanospheres and nanotubes (or nanowires) of different nature have been studied, such as for example carbon nano-onions [4], cobalt-based carbon nanotubes [5], $Mo_6S_3I_6$ nanowires [6] or more recently combinations of iron, copper, and cobalt nanoparticles [7]. Inorganic fullerene-like disulfide nanoparticles, and more specifically IF-MoS_2 and IF-WS_2, have however generated a special interest due to their very low friction and wear reduction properties in severe boundary lubrication regimes [8–11]. Different lubrication mechanisms thought to be associated with these nanoparticles have been described in the literature. First proposed by Cizaire et al. [8] in the case of IF-MoS_2, the exfoliation of IF-WS_2 nanoparticles submitted to high contact pressures into several nanosheets was later observed by Joly-Pottuz et al. [12]. This was confirmed by in situ TEM imaging of IF-MoS_2 nanoparticles under different shear and compression conditions [13,14]. The nanoparticles undergo a rolling process for sliding conditions under low contact pressures, whereas they suffer large deformations and then exfoliation of the outer sheets for higher contact pressures (around 1 GPa). The behavior of IF-WS_2 was found to be quite similar, and the extent of their elastic deformation was successfully observed using HRSEM and used to give an estimation of the compression failure strength of nanoparticles of different sizes and shapes [15]. The three prominent friction mechanisms associated to individual multilayered nanoparticles were then summed up by the same authors and verified experimentally using in situ HRSEM [16], namely (a) rolling for

* Corresponding author at: LaMCoS (INSA Lyon) – LTDS (Ecole Centrale de Lyon) – PSA Peugeot Citroën, INSA Lyon, 18-20, rue des Sciences, 69100 Villeurbanne, France. Tel.: +334 72 43 70 81.
E-mail address: pierre.rabaso@insa-lyon.fr (P. Rabaso).

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low shear rates and relatively low normal stresses (0.96 ± 0.38 GPa), (b) sliding for slightly higher normal stresses and (c) exfoliation for high normal stresses (above 1.2 GPa).

The relationship between this exfoliation process under high contact pressures and the considerable performances of fullerene-like nanoparticles in boundary lubrication regimes was further investigated in [17], where the friction reduction was shown to originate from the adhesion of a tribofilm composed of the resulting hexagonal 2H-MoS_2 nanosheets on the steel surfaces. The crystallinity of the nanoparticles was also shown to be of great influence on their friction reduction capacities, as the presence of many defects will facilitate the exfoliation mechanism, enabling a faster tribofilm formation on the contacting surfaces [18].

According to the literature, and considering the exfoliation mechanism taking place in the boundary lubrication regime, the general agreement today is that the synthesis of smaller fullerene-like nanoparticles will improve friction reduction, by increasing the probability of the nanoparticles passing through the contact. To the author's knowledge, this remains an assumption as no study has yet compared the tribological performances of similar IF-MoS_2 varying only in size. Small nanoparticles however generally show interesting results, such as the poorly crystalline nanoparticles tested in [18] for example, with a diameter comprised between 20 and 50 nm. The larger and less efficient IF-MoS_2 nanoparticles tested in the same operating conditions were however also more crystalline, which makes it difficult to conclude on the influence of nanoparticle size alone. The benefits in reducing the size of IF-WS_2 aggregates has furthermore been shown, either by an effective mixing of the oil before testing [19,20] or by grafting the appropriate dispersants on the nanoparticles [21].

In this study, the tribological behavior of four types of IF-MoS_2 nanoparticles of different sizes and degrees of crystallinity was explored, by comparing their friction and wear reduction capacities under severe boundary lubrication regimes. The results obtained during these tests made it possible to differentiate the influences of nanoparticle size and crystallinity.

2. Experimental

2.1. Tribological tests

All the tribological tests showed in this article were carried out on a PCS Instruments HFRR (High Frequency Reciprocating Rig). The test consists in a pure-sliding reciprocating motion between a diameter 6 mm ball and a flat, with a maximum contact pressure of 1.4 GPa. The test is schematized and the conditions are given on Fig. 1. The contact pressure and the very low surface separation are typical of the severe boundary lubrication met in automotive applications, such as gears or the valve train.

The base oil was the same for all the IF-MoS_2 nanoparticles tested in this study, a blend of PAO 4 and PAO 40, with a viscosity of 9.3 cSt at 100 °C and 54.0 cSt at 40 °C. The materials used were polished AISI 52100 (100Cr6) steel (Ra < 50 nm for the ball and Ra < 20 nm for the flat). All the tests were carried out for an identical mass concentration of IF-MoS_2. This concentration was arbitrarily set to 1 wt% for the purposes of this study, as it relates to many studies already published and was shown to be optimal for similar applications in the literature [8–11,17,18,20]. The oil was thoroughly mixed using a magnetic agitator, and the 2 mL test sample was then placed in the HFRR lower specimen holder immediately before the beginning of the test. The authors deliberately chose not to use an ultrasonic bath for the mixing, so as to obtain a dispersion representative of real-life test conditions. The high number of cycles achieved during the test (144 000) was chosen to provide information on the different nanoparticles' capacity to maintain their tribological performances in time.

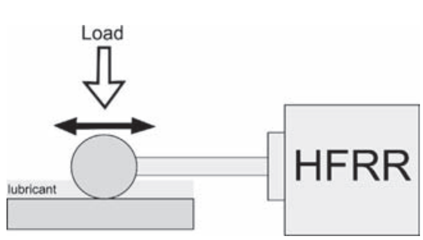
All the HFRR test results presented in this article were repeatable, and a single, typical graph is presented as a result for each test for the sake of clarity.

2.2. Observation and characterization

The topography of the wear scars on the flat counter-surface was obtained using an optical Sensofar PLu neox profilometer, providing information on their depth, volume, length and width. The choice of analyzing the flat surface instead of the ball was made so as to reveal if any plastic deformation took place during the test. The criteria chosen to quantify the wear were the maximum depth of the scar, and the volume of steel lost during the test. This worn volume was obtained by subtracting the plastically deformed matter (total volume above the mean surface) to the volume of the scar (total volume below the mean surface).

A JEOL 2010F operating with 200 kV accelerating voltage was used for the TEM observations of the nanoparticles. To achieve this, a drop of highly diluted IF-MoS_2 in heptane was deposited onto a standard carbon-covered-copper microgrid. In order to fully characterize 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.

Chemical analysis of the tribofilms was performed by XPS. With a probing depth of a few nanometers (5 nm), this technique is the most convenient for surface analysis and wear scar characterization. An Ulvac-PHI Versaprobe II system, with a high power monochromatized Al K_α X-ray source (hv = 1486.68 eV), was used. The X-ray beam was focused in the wear scar and an area of 100 × 100 μm was probed. A survey scan was first recorded in order to identify the chemical elements present in the probed area. Scans were then recorded at some selected peaks in order to get complete information on the chemical composition (chemical bonding) of the tribofilm. The resolution of the XPS was 0.2 eV, and the position of C 1s peak (284.8 eV) was considered as the reference for charge correction. A flood gun was used for charge compensation. The XPS analyses were performed in several areas, in order to verify the repeatability of the results. Multi Pack software was used to analyze the XPS spectra obtained from long scans. Quantitative analyses of the peaks were performed using



Load (N)	10
Maximum hertzian pressure (GPa)	1.4
Stroke length (mm)	1
Frequency (Hz)	10
Cycles	144 000
Oil capacity (mL)	2
IF-MoS_2 concentration (wt%)	1
Temperature (°C)	80

Fig. 1. Schematic of the HFRR and conditions used for the tribological tests.