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Time-of-Flight Secondary Ion Mass Spectroscopy investigation of the chemical rearrangement undergone by MoS_2 under tribological conditions

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ABSTRACT

MoS_2 is a well-known lubricant for vacuum application. However, the role of contamination in achieving low friction and long wear life in industrial applications remains unclear as the literature presents some contradictions. A former study performed in ultrahigh vacuum showed that in a sliding macro contact, the origin of low friction was primarily due to the formation of a 3rd body layer, its trapping and its ability to flow plastically inside the contact. The study showed a homogenisation of the chemical elemental composition of the material and the internal coating contaminants throughout the contact and the 3rd body. To study that homogenisation and to verify if a chemical rearrangement occurred at a molecular level under friction, Time-of-Flight Secondary Ion Mass Spectroscopy analyses are performed. Firstly, they show that the MoS_2 coating made by Physical Vapour Deposition is not a "MoS_2" but is a complex $Mo_xS_yO_z$ structure. Secondly, they show that a chemical rearrangement of the material with the internal contaminants effectively occurs in ultrahigh vacuum and leads to the formation of a unique MoS_xO_y phase. Such a phase shows the beneficial role of reasonable contamination on the tribological behaviour.

1. Introduction

Since its recommendation for vacuum application by Bell & Findlay in 1941 [1], MoS_2 has been widely studied. However, different theories are still discussed on mechanisms inducing low friction including: intrinsic cleavage [2–4], intercrystallite slip [2,5–7] or establishment of a lubricious transfer film [8–12]. The establishment of the transfer film appears to be partly due to particle creation and circulation inside the contact [11,12]. Nonetheless, rearrangement of MoS_2 basal plane parallel to sliding direction often drives conclusion into the intrinsic cleavage theory. It is legitimate to drive such conclusions as studies on superlubricity and superlow friction demonstrated occurrence of such phenomenon on both nanoscale [13] and microscale [14,15] contacts. Studies on amorphous non-contaminated 120 nm thick MoS_2 coating concluded that the superlow friction is attributed to a frictional anisotropy of the basal plane and that the absence of impurities emphasizes superlow friction [14,15]. Such coating was directly tested after deposition without opening vacuum chambers, which is impossible to encounter in an industrial context. Although not actually demonstrated for contacts of a few thousands μm^2 or even mm^2, the intrinsic cleavage theory is the most often encountered in papers. Moreover, coatings used in industry have a thickness usually in the range of [500 nm; 1000 nm]. Above 200 nm, when deposited by Radio Frequency Physical Vapor Deposition (RF PVD) techniques, the coating becomes columnar [16] and more sensitive to contamination due to column porosity [3]. For such industrial columnar coatings, in a mm^2 contact, it appears that the low friction is primarily a matter of 3rd body generation and circulation inside the contact [17]. The velocity accommodation is then linked to equilibrium between plastic deformations of the trapped 3rd body layer and interface sliding between the 3rd body layer and one or both the 1st bodies initially in contact [17]. The reader can also find detailed explanation and description of the 3rd body concept in [18–20].

Another theory is the adsorption mechanism theory as proposed by Finch in 1950 [21], and also reported in [2]. It was rapidly put aside due to the fact that, contrary to graphite, MoS_2 offers low friction under vacuum and high friction under air. This is emphasized by the superlubricity evidence of non-contaminated coatings [14,15]. However, experiments made by Matsumoto and Suzuki [22] showed that small fraction (around 10%) of water increases the wear life of MoS_2 under dry air. Moreover, the most encountered MoS_2 oxide, MoO_3, appears not necessarily detrimental to friction and has some lubrication properties [2,23]. The question of the O contamination role in friction has been raised by Fleischauer and co-workers [24,25]. Thanks to Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) analysis, they showed that an O pollution of the coating could help low friction

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and that a potential $MoS_{(2-x)}O_x$ phase must play a role in the velocity accommodation process of MoS_2 whereas the MoO_3 is more detrimental. The conclusion that contamination is not necessarily detrimental to low friction but can induce it has also been drawn up in a recent study by Colas and co-workers [26]. In that study, two MoS_2 based coatings were tested under four different environments. It resulted in the hypothesis that contamination drives friction and might be helpful. Indeed, both friction and wear of MoS_2 in high vacuum were lower than in ultrahigh vacuum (UHV) thanks to both external (environment) and internal contaminants of the coating. Unfortunately, such affirmation could not be verified for experiments conducted under UHV due to the lack of clear evidence of it. Although MoS_2 underwent a friction induced cleaning (outgassing of coating internal contaminants) detected by conventional mass spectrometry, oxygen still remains inside the track and friction coefficient stays low and stable.

The aim of this paper is to study if chemical changes occur under friction in both 3rd body layer and 1st body film, top surface analyses are conducted with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Such a technique gives access to the molecular nature of the extreme surface. ToF-SIMS analysis has already been conducted in tribological studies on other materials and in different cases: Diamond-like Carbon (DLC) [27–30], zinc dithiophosphate additives [31], and metals [32,33]. Extensively used for decrypting DLC lubrication, it allowed validating the beneficial role of hydrogen (H) in the superlow friction of DLC. As for MoS_2, SIMS [3] and ToF-SIMS [34] studies were only conducted for material characterization, i.e., on MoS_2 which has not underwent friction. In this study, using ToF-SIMS also allows completing the scheme drawn up with AES, XPS and Energy Dispersive X-ray Spectroscopy (EDX) for MoS_2 coating under tribological stress. The former tools bring either chemical binding (XPS, AES), or compositional (XPS, AES, EDX) or structural information (Extended X-ray Absorption Fine Structure (EXAFS), Transmission Electron Microscopy (TEM)) while ToF-SIMS bring molecular information at the extreme surface (information is limited to the first layer(s)). This information will help to determine which chemical reaction occurred inside the contact and will complete the lubrication schemes drawn in former studies.

Hypothetic formation or rearrangement in both the 1st body film and the 3rd body layer during friction in UHV will be studied. The previously supposed interaction with initial coating contamination [17], in particular, will be studied.

ToF-SIMS analysis and extensive EDX analysis are conducted ex situ after interrupted friction tests. Tests are stopped at some key points of the MoS_2 lubrication behaviour which has been deciphered in previous studies [17,26]. After a brief reminder of the tests conditions and measurements, the paper will focus on ToF-SIMS analysis at the different key points. A link with tribological behaviour will be drawn.

2. Experiment

2.1. Friction test

The MoS_2 coating studied here is space qualified and is extensively used in space applications. It is 1 μm thick, with a dense columnar structure and is deposited on AISI440C substrates by RF PVD. The coating is extensively described in previous papers [17,26] and is similar to the coating tested by Fleischauer and co-workers [24] to investigate the oxygen role in its tribological behaviour.

Experiments were conducted in UHV on a fully equipped reciprocating environmental pin-on-plate tribometer. Pin and plate samples are made of AISI440C that was heat treated to obtain a hardness of 58 HRC. The roughness is Ra < 0.1 μm. Only the plate is coated. Fig. 1 represents the contact configuration used and Table 1 summarizes the contact conditions used in this study. Details of the tribometer are described elsewhere [17,35,36]. A glass is mounted above the contact zone to allow partial visualization of the contact zone. A quadrupole mass spectrometer

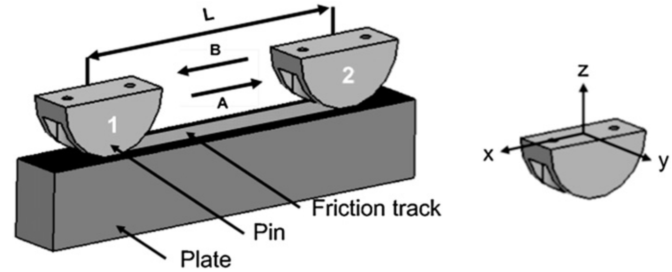

Fig. 1. Specimens: the load is applied in position 1, reciprocating motion A + B can then begin with an amplitude L. After n cycles, the contact is unloaded in position 2.

is also mounted on the chamber to follow gas desorption/adsorption by the contact all along the friction test. Friction forces are measured with piezoelectric force sensors. After the friction tests, samples were removed from the tribometer and underwent ToF-SIMS analysis and both Secondary Electron Microscopy (SEM) and EDX analysis afterwards. The SEM used in this study is a FEI Quanta 600 equipped with an INCA Penta FETx3 EDX probe manufactured by Oxford Instruments. SEM and EDX analyses are conducted at both 5 keV and 10 keV with an emission current of approximately 100 μA.

2.2. ToF-SIMS analysis

ToF-SIMS analyses were conducted on a Physical Electronics TRIFT III ToF-SIMS instrument operated with a pulsed 22 keV Au^+ ion gun (ion current of 2 nA) rastered over a 300 μm × 300 μm area. No charge compensation was required for analysis. Ion dose was kept below the static conditions limit. Data were analysed using the WinCadence software. Mass calibration was performed on hydrocarbon secondary ions. Data were normalized to the total intensity minus hydrogen H^- (because of its critical dependence on slight variations in the experimental settings), fluorine F^- and chlorine Cl^- (because both are ubiquitous contaminants) in negative mode, and to the total intensity minus hydrogen H^+ (same reason as in negative mode), sodium Na^+, silicon Si^+ and potassium K^+ (because the 3 of them are contaminants) in positive mode. Standard deviation calculations were performed from 3 measurements done in each selected zone (centre, outside, extremity … of the track) but in different areas. As shown on Fig. 2, the border region between the inside and the outside of the friction track was also investigated. The depth of the analysis is around a few monolayers.

To compare the coating molecular composition before and after friction to natural MoS_2, a natural MoS_2 powder was analysed. It will also be possible to determine if the coating is returning to natural MoS_2 under friction [7,8] in a molecular point of view. The powder does not undergo friction.

All samples were analysed as received (no pre-sputtering prior to or between measurements). Only plate specimens were studied by both ToF-SIMS and EDX analysis afterwards. Pin specimens were only studied by EDX as their size could not fit the geometry of the sample holder of the ToF-SIMS instrument used in this study. As a significant amount of the trapped 3rd body stays at the track extremity after the opening of the contact (Fig. 2), its analysis was possible without having to analyse the pin which holds the 3rd body layer during friction.

Table 1
Contact conditions used in the study.

Kinematics	Pure sliding Reciprocating: ±15 mm
Temperature	Room temperature
Environment	Ultrahigh vacuum 10^{-6} Pa
$P_{contact}$	1 GPa
$V_{sliding}$	10 mm/s