Original Article

Tribological assessment of partially sulfidated molybdenum oxide

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Molybdenum sulfide is widely used as an additive in lubricated systems due to its van der Waals forces and its sliding sheets that produce low friction coefficients. Different morphologies and chemical compositions have been tested with good performance. In all circumstances, the behavior of sulfurized structures in the presence of oxygen remains unwanted. In this work, molybdenum oxide with hexagonal and orthorhombic phases crystalline structures and molybdenum oxide partially sulfidated were tested in boundary-lubrication range. The results show that partially sulfidated molybdenum oxide decreases the coefficient of friction despite the high oxygen content and it remains low during the entire test. The partially sulfidated materials present lower friction coefficients than pure oxides.

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1. Introduction

Energy saving is one of the most studied topics. Nowadays, energy generation, uses and conservation are the main world interest. Tribology focuses on energy conservation, mainly to avoid loss of energy between moving parts, increase the efficiency of mechanical systems and decrease the cost of replacing expensive equipment parts. Materials, such as carbon, composites, metals, oxides, rare earth, sulfur and others have been tested in tribological studies [1]. Most of them report friction or wear reduction with the use of these materials, the best application results are obtained with materials that have weak interplanar van der Waals forces, which facilitates their movement resulting in lower friction coefficients and wear rates. Due to this phenomenon, sulfur materials show better development in friction and wear reduction in tribological tests [1–3].

The mechanism to decrease friction and wear is usually the formation of a tribofilm. Its generation plays an important role in the tribological performance and depends on different parameters such as type of oil, oil flow, additive concentration, additive size, additive morphology, work temperature, environment, load between two solids and displacement speed [1,4,5]. Some authors suggest that the main lubricant mechanism is due to rolling particles at low loads and sliding and breaking off (exfoliation) at high normal stresses [1,3,6,7]. In boundary lubrication, both conditions, sliding and/or exfoliation govern the lubrication process. For the additive selected,
the ability to penetrate between surfaces in contact and remain there is determined by its chemical and physical properties and that will determine the friction coefficient and wear rate.

Molybdenum sulfide is widely used in several technology applications. Different molybdenum sulfide structures have been synthesized and tested in tribology [1] in the form of nanoparticles [8], nanosheets [9,10], nanorods [11], nano-oils [12], fullerene-like [6,13,14], flower-like [15,16], microspheres, nano-balls [17], nano slides [17], nanoribbons [18], nanotubes [3,19,20], nano-onions [7,21], micro-crystalline powder [22] and films [23]. Many of methodologies proposed to synthesize these structures are complicated and difficult to scale up to industrial quantity production, and the yields are usually low. Despite the great efforts made to synthesized controlled morphologies, in the boundary lubrication regime, as mentioned previously, the high stresses usually break off or exfoliate the structures and, as a result, the original morphology is lost and the tribofilms are reported to have a different structure. Some authors report that the tribological performance does not depend on the particle size in the range of nanometers [1,6]. Rabasso et al. reported differences with particles in the micrometer size range where the friction coefficient was increased [6]. Rosentsveig et al. reported the exfoliation of fullerene-like MoS₂ nanoparticles into MoS₂ nanosheets at high contact pressure [21]. Crystallinity, associated with the proper morphology, is important because it provides the chemical structure and the properties to form an effective tribofilm [1,6]. According to these reports, the chemical composition of the additive plays an important role in the boundary lubrication regime where breaking off the molybdenum sulfide particles occurs reducing its original size in order to reduce friction and wear.

Molybdenum sulfide lamellar structures exhibit excellent performance in tribological tests. Many hypotheses have been proposed to explain the molybdenum oxidation process and its relation to van der Waals forces reduction. The crystallinity of a tribofilm is important to obtain effective wear protection. Changing the crystalline structure due to internal processes during the test may decrease the effectiveness of the tribofilm. Partial oxidation difficulties were reported when testing molybdenum sulfide [22]. Oxygen may be present in the oil, metal or environment. Some studies follow the oxidation of molybdenum but not in working conditions [13,22]. Rabasso et al. and Tannous et al. reported the partial oxidation of molybdenum in real time during tribological tests and concluded that there was not any deactivation effect due to the partial molybdenum oxidation. On the contrary, they report possible benefits because oxygen can serve as an anchor between the surface and the tribofilm providing more stability for wear protection [6,13]. Reduction of the amount of molybdenum sulfide between two moving surfaces increases the wear rate and increasing the oxygen content could be beneficial if the interplanar van der Waals forces of the molybdenum sulfide are not affected.

Simple synthesis methodologies to produce controlled molybdenum sulfide morphologies are of industrial interest. The microwave-assisted hydrothermal method produces molybdenum structures with homogeneous morphology and chemical composition. According to a previous report, molybdenum oxide can be synthesized by microwave assisted hydrothermal method [24]. This procedure promotes the formation of controlled morphology and crystalline structures. Thermal treatment and sulfurization processes allow us to change the chemical composition while keeping the selected morphology and crystallinity. The tribological performance of sulfurized and partially oxidized structures with specific morphology and crystallinity shows an important reduction of friction and wear.

In this study, we report the synthesis of stable MoO₃ structures by microwave-assisted hydrothermal method and heat treatments. These materials were partially sulfidated and tested to asset their tribological behavior.

## 2. Experimental

### 2.1. Molybdenum oxide synthesis

Molybdenum oxide with hexagonal rod morphology (MHR) was synthesized by a microwave-assisted hydrothermal method (MAHM). Similar to a previous report by Santos-Beltran et al. [24], 10 mL of 0.3 M ammonium heptamolybdate (NH₄)₆Mo₇O₂₄ 4H₂O aqueous solution were adjusted to a pH of 6 with 2.2 N nitric acid. The solution was kept in a closed flask for 45 min in continuous stirring at 70 °C. Then, 10 mL of the aged solution was mixed with 10 mL of water and 10 mL of the 2.2 N nitric acid and transferred to a Teflon vial. The final solution was introduced to the microwave system (Anton Parr, Multiwave PRO) for 20 min at 200 °C, reaching a pressure of 41 bars. After this, the produced MHR was washed with tri-distilled water and dried for 5 h at 90 °C.

In order to obtain a more stable molybdenum oxide phase, a thermal treatment was performed to MHR. A sample was heated in a muffle for 45 min at 450 °C in a static atmosphere. After this heat treatment, the morphology of the MHR materials changes to hexagonal terraced rods (MHTR) with an orthorhombic crystalline structure.

### 2.2. Molybdenum sulfide synthesis

In order to obtain different molybdenum sulfide structures, MHR and MHTR were sulfurized according to the procedure described by Albiter et al. [25] for similar structures. This sulfidation process performed inside a tubular furnace with 15% H₂/H₂S flow at 500 °C for 4 h with a heating rate of 4 °C/min. The sulfurized MHR and MHTR samples were identified as MHR-S and MHTR-S, respectively.

### 2.3. Tribological tests

Tribological tests were conducted in a commercial pin-on-flat tribometer (NanoVea T1). The contact was formed by a 6 mm diameter AISI 52100 ball loaded against standard AISI 1018 steel plates (50 mm × 25 mm × 3 mm) with a surface roughness of 0.32 μm and Rockwell C hardness 24.6 HRC. In this equipment, a stationary holder secures the ball while the plate is attached to a container connected to a variable-speed electric motor. The contact is completely submerged in the test fluid (Fig. 1). A linear-voltage displacement transducer attached to
the ball holder monitors the friction coefficient and the readings are recorded continuously throughout the test. Tests were carried out at a constant temperature of 27°C and 48% relative humidity. The dead weight of 20 N was used in each test. The bottom container rotates at a sliding speed of 60 mm/min for 1 h, running a total distance of 3.6 m for each test. Under these conditions, the tests were conducted in the boundary lubrication regime.

The lubricants were prepared by adding 0.3% weight of the molybdenum compound (MHR, MHR-S or MHTR-S) to vegetable soy oil and vigorous stirred for 30 min before each test. After the tests, the steel ball and steel plates were removed from the tribometer, washed with isopropanol alcohol, dried with air at room temperature and storage for characterization.

### 2.4. Characterization

All the synthesized molybdenum compound materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD patterns were obtained on a Philips X’Pert MPD Diffractometer, with Cu Kα1 radiation (λ = 1.54056 Å) working at 40 kV and 30 mA current. SEM analyses were acquired with two microscopes, a JEOL JSM-6010LA and a HITACHI SU3500. The HITACHI microscope is equipped with energy dispersive X-ray spectrometer (EDS) detector (Oxford X-Max 50). Both SEM microscopes were operated at 30 kV to acquire image and EDS, respectively. The tracks of the worn plates were examined using both microscopes mentioned above.

### 3. Experimental results and discussion

#### 3.1. Molybdenum oxide characterization

Controlling morphology is crucial in materials synthesis. Microwave-assisted hydrothermal method (MAHM) produces controlled morphologies, sizes, and crystalline structures. Fig. 2 shows SEM images acquired with secondary electrons of an MHR sample. The images show that hexagonal rods with uniform sizes were obtained by this method. In general, all samples have the same morphology; nevertheless, some surface defects on the faces of the hexagonal rods are observed. The images also show that the rods have a rounded-shape termination (Fig. 2b). Statistical analyses of length and diameter of 200 MHR particle measurements are shown in Fig. 3. The rods have average lengths of 11.9 ± 3.2 μm and diameters of 3.8 ± 0.9 μm. These results are similar to those reported by Santos et al. [24]. The MAHM synthesis method is fast and produces more controlled morphologies than the hydrothermal method, which requires a longer time (days) for the reaction to take places and the obtained compounds are not always in pure phase [24]. The obtained yield of MHR structures was above 92%. From these results, we conclude that this method allows us to produce high yields of molybdenum oxide rods with controlled morphology.

Thermal treatments are employed to stabilize materials, change phases, improve or change crystallinity, modify morphologies and/or grow crystals. Fig. 4 shows the SEM images of an MHR sample after thermal treatment (MHTR). The images show rods with the same size as hexagonal rods (MHR) but they present “terraces” formation in the horizontal and longitudinal directions. Statistical analyses of 100 MHTR rods are shown in Fig. 5. It presents a wide distribution of “terraces”, with an average diameter of 1080 ± 744 nm and an average thickness of 46 ± 32 nm. Santos et al. reported an average particle size of 5700 ± 2200 nm and an average thickness of 162 ± 40 nm for samples obtained at similar chemical reaction conditions. They also observed complete delamination of the
original rods after thermal treatment to form long individual sheets [24]. Our images show the formation of terraces with lower size and thickness than those reported by Santos et al. and not completely delaminated. These results confirm that the thermal treatment changes the internal morphology into “terraces”, which may be.

Fig. 3 – Statistical distribution of (a) diameter and (b) length measurements of MHR samples.

Fig. 4 – SEM images of MHR rods after thermal treatment at (a) low and (b) high magnification.

Fig. 5 – Statistical analyses and distribution of (a) thickness and (b) length measurements of MHTR samples.

Fig. 6 shows the XRD patterns of molybdenum oxide rods of the MHR and MHTR samples. According to these results, both patterns show different crystalline structures. The XRD pattern of the MHR sample shows the presence of a MoO$_3$ meta-stable hexagonal crystalline phase and no evidence of other crystalline phase was found. This pattern was index
formation of pure phases and specific morphologies depending on the reaction conditions.

3.2. Molybdenum oxide sulfdation process

According to previous reports, molybdenum exhibits great tribological properties in its sulfurized form [3]. Efficient sulfidation depends on the morphology of the sample and sulfidation method. The first step in the sulfidation process is the reduction of MoO$_3$ to MoO$_2$ in a hydrogen atmosphere which occurs between 50 °C and 350 °C. Molybdenum is reduced from Mo$^{6+}$ to Mo$^{4+}$. The second step is the sulfidation process of MoO$_2$ to form MoS$_2$ in H$_2$S atmosphere at an initial temperature of 350 °C [25-27]. The first reaction step of this method is shown in Eq. (1). The complete reaction process is shown in Eq. (2), assuming that all molybdenum is sulfurized. Both materials MHR and MHTR were sulfurized in a tubular furnace at 500 °C with 15% H$_2$/H$_2$S flow during 4 h. SEM images (Fig. 8) show the MHR morphology after the sulfidation process (MHR-S). The images show the formation of small particles on the surface of MoO$_3$ hexagonal rods. From the statistical analysis (Fig. 9), these small particles have an average size of 274.5 ± 108 nm. Fig. 10 shows a SEM image of the material obtained after the sulfidation process of the MHTR sample (MHTR-S). In this case, the morphology due to the thermally treated sample is kept and there is no formation of a small crystal, like in the previous case was observed. From these results, we can conclude that the sulfidation process performed at the same conditions have different results depending on the initial particle morphology and crystalline structure. In the case of the hexagonal MoO$_3$ thermally treated, two phenomena are observed: change of the crystalline phase and the sulfidation process. In the case of the orthorhombic MoO$_3$ takes place only the sulfidation process.

\[
\text{MoO}_3 + \text{H}_2 \rightarrow \text{MoO}_2 + \text{H}_2 \rightarrow \text{MoS}_2 + \text{H}_2\text{O} \quad (1)
\]
MoO$_3$ + $\uparrow$ H$_2$ + $\uparrow$ H$_2$S $\rightarrow$ MoS$_2$ + $\uparrow$ H$_2$O \hfill (2)

The sulfidation process in H$_2$/H$_2$S atmosphere is governed mainly by the diffusion of hydrogen sulfide. The sulfidation starts on the sample surface and continues toward the center of the sample [27]. Bigger samples will present greater difficulty to achieve a complete sulfidation. MHR-S and MHTR-S samples were characterized by XRD and the diffraction patterns are shown in Fig. 11. These results clearly indicate that a complete phase transformation (reaction scheme 2) is not achieved. It is also noticed that a complete reduction occurs after the sulfidation process. Patterns of both samples do not show any signal of the original MoO$_3$ hexagonal or orthorhombic phase. Following the reaction scheme 1, all the MoO$_3$ may reduce to MoO$_2$ but not all MoO$_2$ can be transformed to MoS$_2$. We found a mixture of phases that indicates that our sulfidation process follows the reaction scheme 1. The XRD patterns indexation was performed using the JCPDS 01-074-4517 card with 136 P42/mm spatial group for MoO$_2$ and the JCPDS 006-0097 card with 194 P63/mmc spatial group for MoS$_2$. The MHR-S XRD pattern shows high MoO$_2$ content after the sulfidation process indicated by the strong MoO$_2$ signals detected. Weak MoS$_2$ signals are detected in the pattern, which indicates a slight formation of MoS$_2$ in this sample. On the other hand, the MHTR-S sample XRD pattern shows strong MoS$_2$ signals and weak MoO$_2$ signals. These results suggest that as the sample becomes bigger in size, there are more problems to transform the structures into MoS$_2$ entirely, in accordance with the reaction scheme 2. According to Kumar et al. [27], hydrogen sulfide is more difficult to diffuse than
hydrogen or sulfur. In MoO₃ rods, the reduction process is faster than the sulfidation process; in spite of the high sulfidation time, bigger particles always present poor sulfidation than smaller ones due to diffusional difficulties and, as a result, low molybdenum sulfide conversion is achieved.

Homogeneous distribution of all elements are present in the sample, it is an indication of the control of the reaction parameters during the synthesis. Fig. 12 shows the EDS elemental mapping of the samples after the sulfidation reaction. It is clear that oxygen and sulfur are present in all materials and there is no segregation of these elements. Table 1 shows the average quantification for several analyses obtained from different zones. The results show poor sulfidation of hexagonal molybdenum rods and good sulfidation for hexagonal-terraced molybdenum rods at the same sulfidation process conditions. There is high MoO₃ content (86.1%) for the MHR-S sample while low MoO₂ content (36%) for the MHTR-S sample. These differences in sulfidation yields are due to the diffusional problems in large particles.

### 3.3. Tribological behavior of materials

The tribological properties of all synthesized materials were tested. For this purpose, the particles were dispersed in soy oil; Fig. 13 shows the friction coefficient behavior (COF) for all samples as a function of time. Soy oil without particles exhibits an increase of COF from 0.077 to 0.158 during the first 15 min of the test time. After that time, this value decreases to ~0.140 and remains at this value for the rest of the test time. MHR and MHTR samples show similar behavior as the soy oil alone, they present an increase of the COF from ~0.095 to ~0.125 for the first 35 min and then show steady values at ~0.134 and ~0.133 for the rest of the test time respectively. In the case of the sulfurized sample, MHR-S display an initial increase of the COF from ~0.082 to ~0.138 for the first 15 min and then it decreases to get a final value of ~0.113. The MHTR-S material shows the best performance in comparison to other tested samples. In this case, the COF displays an initial value of ~0.075, which gradually increases to reach a final value of ~0.107 at the end of the test. These COF values clearly show that sulfurized samples exhibit lower values than not-sulfurized ones. The wear protection was measured form the width of the wear scars, it was taken from the SEM images (Fig. 14), and these values are greater for sulfurized materials than for non-sulfurized samples. Table 2 summarizes the average friction coefficient and the width of the wear scars at the end of the test. According to SEM images, all molybdenum structures tested were broken off before to protect against wear (Fig. 14).

**Table 1 – Average sulfidation quantity (at.%).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mo</th>
<th>%O</th>
<th>%S</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHR-S</td>
<td>30.7</td>
<td>60.4</td>
<td>8.9</td>
<td>100</td>
</tr>
<tr>
<td>MHTR-S</td>
<td>30.1</td>
<td>24.9</td>
<td>45.0</td>
<td>100</td>
</tr>
</tbody>
</table>

*Fig. 12 – EDS mapping of (a) MHR-S sample and (b) MHTR-S sample.*

*Fig. 13 – Pin-on-flat tribological test results value evolution.*
Although MHR and MHTR samples exhibit COF values similar to soy oil alone at the end of the test, their performance is different. MHR are bigger than MHTR because MHR rods are one single crystal but MHTR rods are formed with many small joined sheets (Fig. 4) making it easier to delaminate and perform better. Orthorhombic MoO$_3$ have linked octahedral MoO$_6$ that create bilayer sheets stacked in the [0 1 0] direction with lamellar formation trough (0 0 1) plane with weak van der Waals forces [28,29]. This may be the reason why the MHTR material shows better tribological values (Table 2).

Table 2 – Wear and COF of the different materials tested.

<table>
<thead>
<tr>
<th>Material</th>
<th>Wear (µm)</th>
<th>Coefficient of friction (at 60 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOY OIL</td>
<td>239</td>
<td>0.1391</td>
</tr>
<tr>
<td>MHR</td>
<td>178</td>
<td>0.1332</td>
</tr>
<tr>
<td>MHTR</td>
<td>143</td>
<td>0.1347</td>
</tr>
<tr>
<td>MHR-S</td>
<td>164</td>
<td>0.1133</td>
</tr>
<tr>
<td>MHTR-S</td>
<td>165</td>
<td>0.1066</td>
</tr>
</tbody>
</table>

show in Fig. 13 and Table 2 are strong evidence that partially sulfurized molybdenum oxide can improve the tribological behavior of the material. MHTR-S samples have less amount of MoO$_3$ than MHR-S sample. Since the sheet-structure morphology brace off easily, it is evident that MoS$_2$ starts acting from the beginning of the test exhibiting a low COF value, which stabilizes after 15 min. Although all the materials tested, oxides and partially sulfurized oxides, show better tribological behavior than soy oil alone, it is important to notice that the partially sulfurized samples show the best performance regardless of the oxide content, morphology and size. The chemical composition seems to be the key factor to achieve the best tribological values. This found result is in agreement with previously published results [1,6].

4. Conclusion

Pure MoO$_3$ with hexagonal phase and rod morphology was synthesized by microwave-assisted hydrothermal method. Thermal treatment of this material was effective to produce hexagonal terraced rods with orthogonal phase MoO$_3$. These terraces are ~ 1% of the width of the hexagonal rods and 9% of their length, and they are joined together. The sulfidation process of MoO$_3$ produces a mixture of MoO$_2$ and MoS$_2$ phases. Due to the diffusion difficulties, the formation of MoS$_2$ in the MoO$_3$ hexagonal rods was limited to ~13.9% content of the sample. Sulfidation of the MoO$_3$ orthorhombic-terraced rods produces approximately 86.1% of MoS$_2$. The best tribological results were obtained for the sulfurized samples. The sample with the highest MoS$_2$ content showed the lowest coefficient of friction (~0.107). Wear protection does not depend on the oxide content, morphology or size, but strongly depends on the chemical composition of the sample.

Conflicts of interest

The authors declare no conflicts of interest.
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