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Tribological performances of $Mo_6S_3I_6$ nanowires

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Abstract

A new nanowire-like material with the chemical formula $Mo_6S_3I_6$ was studied as an additive in a synthetic base oil, a polyalphaolefin (PAO). This material presents interesting friction reducing properties, friction coefficient reaching a value of 0.04 in boundary lubrication. Transmission and scanning electron microscopy, X-ray diffraction, and Raman spectroscopy were used to characterize nanowires before and after friction. The combination of these techniques gave evidence of MoS_2 formation in contact area during friction test. This structural evolution of nanowires explains their good friction reducing properties.

Keywords: Mo-S-I nanowires; Lubrication; Friction; Tribology; Additives

1. Introduction

Lamellar compounds such as graphite and metal dichalcogenides (MoS_2, WS_2) are widely used both as solid lubricants or as additives to liquid lubricants.[1] These materials are characterized by weak interatomic interactions between their layers (Van der Waals forces), allowing easy, low-strength shearing. The endurance of MoS_2 films depends on the environment: they present excellent friction and wear resistance in vacuum, but poor properties in the presence of oxygen or humidity.[2] These poor properties are attributed to chemical reactions between oxygen and the dangling bonds of the structure, leading to the oxidation of MoS_2 in MoO_3.[3] Due to their spherical and cylindrical shape, closed structures materials (nanoparticles, fullerenes, nanotubes) exhibit no dangling bonds and can also present good tribological properties. These last years, progresses were made in the synthesis of metal dichalcogenides nanotubes.[4] Recently, a new technique of preparation of nanotubes was developed by Mihailovic et al. leading to a new form of nanowire-like material containing molybdenum, sulphur, and iodine with a chemical formula of $Mo_xS_yI_z$.[5] The particularity of these materials is that they are composed of small-diameter nanowires bound in bundles. The advantage of this technique is the possibility to play on the S/Mo ratio and therefore to synthesize material containing less sulphur than MoS_2. The less content of sulphur constitutes an advantage since new European norm will impose very soon lower concentration of sulphur in automotive oil (less than 0.5 wt.%).[6] Thus, nanotubes could be an alternative to replace traditional additives at the origin of some problems of toxicity and pollution.

In this paper, we report first tribological results of $Mo_6S_3I_6$ nanowires used as additive in a synthetic base oil, a polyalphaolefin (PAO), and tested in a regime of boundary lubrication. Structural characterization of nanotubes before and after friction was performed by transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. These techniques are very powerful to observe structural changes induced by the friction process. Thanks to these techniques, the correlation between tribological properties and structural modification can be established.

2. Experimental section

2.1. Synthesis

The experiments were performed on the materials previously described[7] according to a single-step synthesis procedure described in PCT/EP04/001870.

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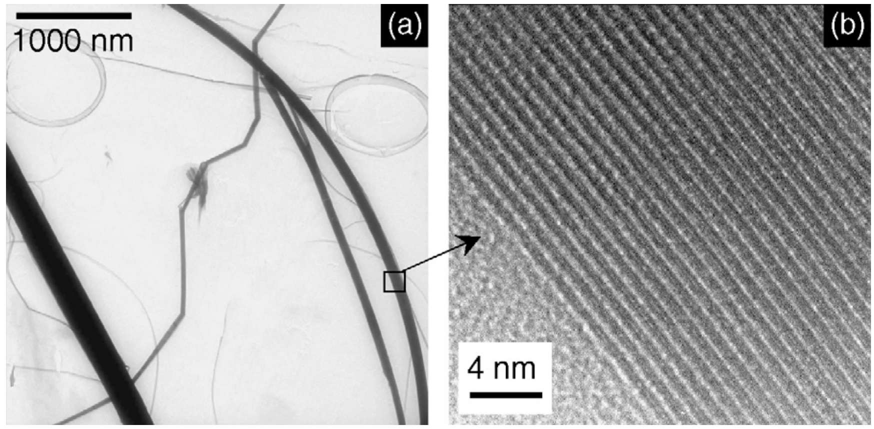

Fig. 1. TEM image of nanowires bundles: (a) general view, (b) view of one bundle.

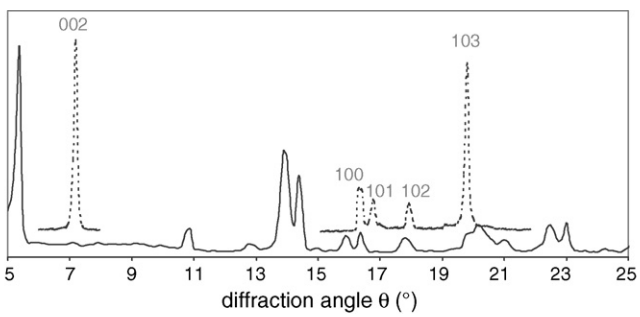

Figure 2. XRD patterns of the pristine material (full line) and pure hexagonal MoS_2 (dotted line).

2.2. *Tribological conditions*

Nanowires were tested in a lubricated contact using a pin-on-flat tribometer,[8] with both surfaces made in AISI 52100 steel. Nanowires were dispersed at various concentrations in PAO by ultrasonic bath. Measurements were performed in ambient air and ambient temperature (25 °C), with a sliding velocity of 2.5 mm/s. Different contact pressure were used to test the influence of the contact pressure on nanowires properties: 0.66, 0.83, 1.12, 1.42 GPa. With these conditions, experiments are performed under boundary lubrication.

3. Characterization before friction

Fig. 1 show a TEM image of the nanowires. They are bound in bundles of different diameters (up to 500 nm) depending on the number of nanowires. One bundle can contain up to a million of nanowires and can be up to 10 μm long. Diameter of one single nanowire is about 1 nm (Fig. 1b). Fig. 2 shows the XRD pattern of the pristine material compared to that of the pure hexagonal MoS_2. Characterization of nanowires by Raman (Fig. 3) indicates the presence of three characteristic peaks at 220, 285 and 320 cm^{-1}.

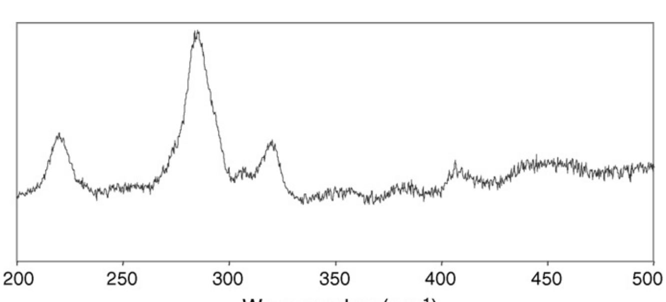

Fig. 3. Raman spectrum of Mo-S-I nanowires.

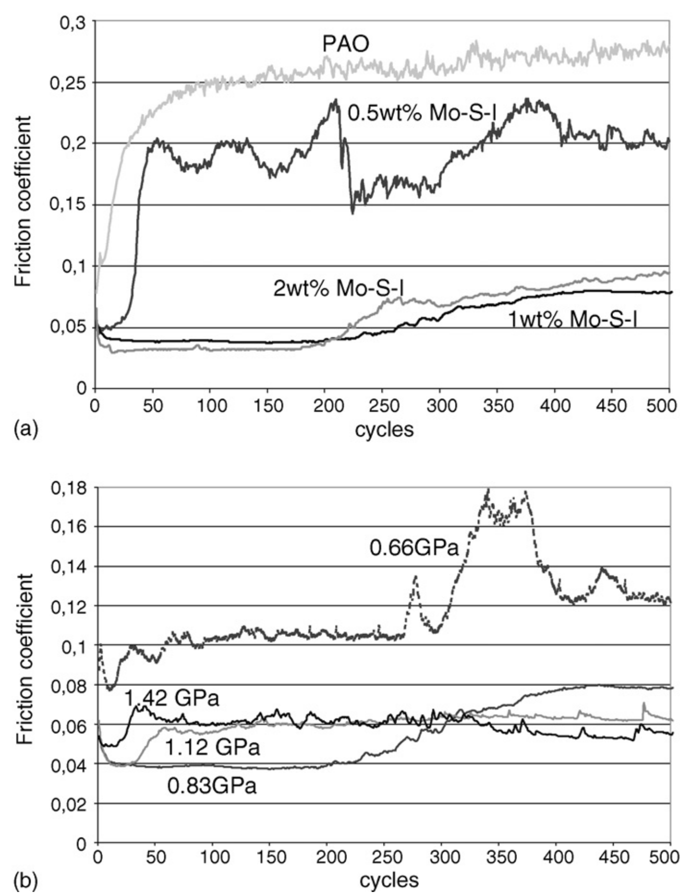

Fig. 4. Evolution of friction coefficient in a lubricated contact: (a) influence of nanowires concentration in PAO – contact pressure of 0.83 GPa, (b) effect of contact pressure for 1 wt.% nanowires in PAO.

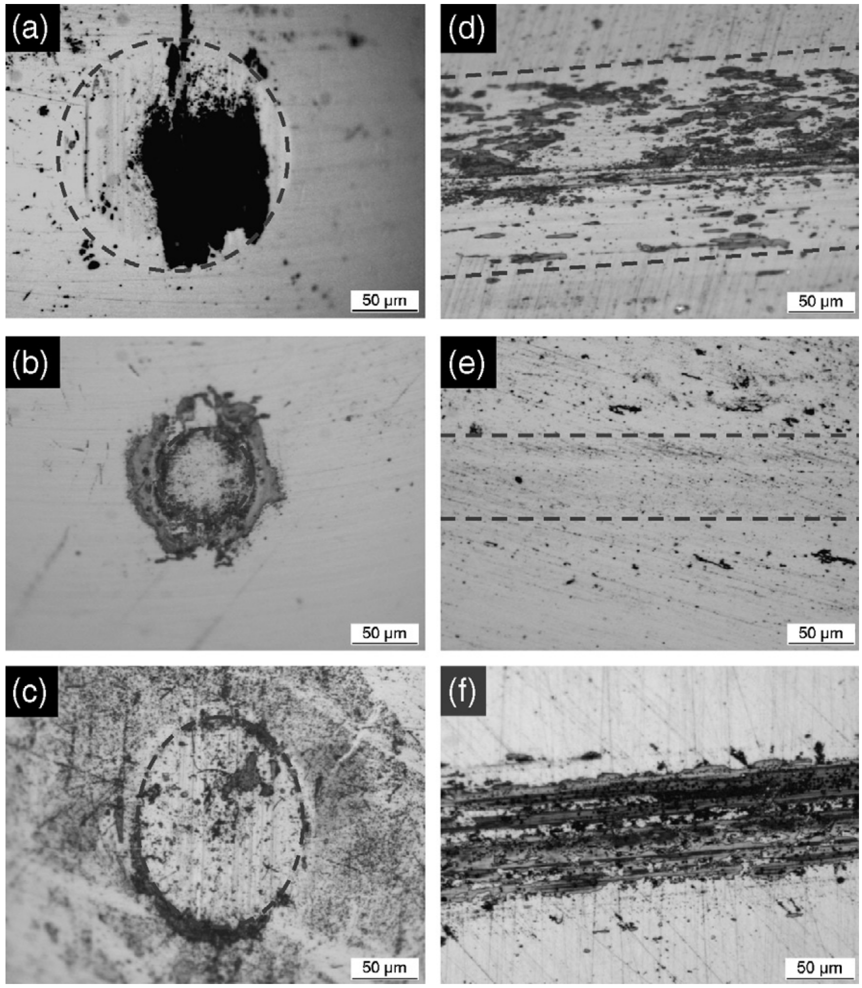

Fig. 5. Wear tracks on pin for: (a) PAO, (b) PAO + 1 wt.% nanowires after 200 cycles, (c) PAO+1 wt.% nanowires after 500 cycles – Wear tracks on flat for: (d) PAO, (e) PAO+1 wt.% nanowires after 200 cycles, (f) PAO + 1 wt.% nanowires after 500 cycles.

4. Tribological results

The effect of nanowires concentration on tribological properties was studied using a contact pressure of 0.83 GPa. Fig. 4a shows the evolution of friction coefficient with cycles number for different lubricants: PAO, PAO with 0.5, 1 and 2 wt.% of nanowires. Addition of 1 wt.% of nanowires is already sufficient to strongly decrease the friction coefficient. For this test, two steps can be distinguished. Up to 200 cycles, the friction coefficient is very low (∼0.04) and fairly stable. Then it progressively increases and stabilizes at 0.08. The same evolution is observed for 2 wt.%.

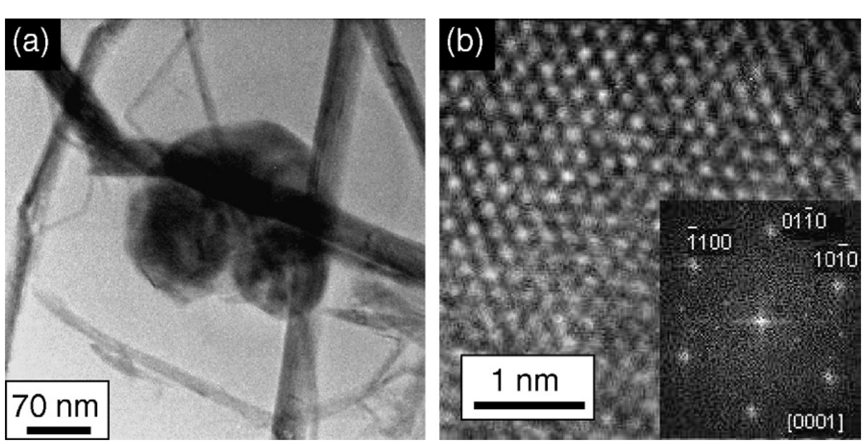

Fig. 6. (a) TEM image of MoS_2 sheets observed in wear particles, (b) HRTEM image of one sheet and its corresponding Fourier transform.

In order to understand this evolution, an experiment was stopped after 200 cycles. Wear scars observed on the flat after 200 cycles are different from those observed after 500 cycles (Fig. 5e and f). After 200 cycles, the width of the scar is 65 μm indicating a low wear. At the opposite, wear on the flat after 500 cycles is important. Wear on pin is also more important after 500 cycles (Fig. 5b and c). A comparison with the wear tracks obtained with pure PAO (Fig. 5a and d) indicates a diminution of wear both on the pin and flat when nanowires are added (Fig. 5c and f).

Effect of contact pressure was also studied. Fig. 4b shows that a minimal contact pressure of 0.83 GPa must be applied on nanowires to decrease the friction coefficient. For higher pressures (1.12 and 1.42 GPa), the evolution of the friction coefficient is similar than with 0.83 GPa. For each pressure, friction is very low at the beginning of the test and then increases and stabilizes at a higher value. The main difference comes from the length of the first stage. The shorter it is, the higher the pressure. This study seems to prove that a structural modification of the nanowires is necessary to enhance their tribological properties.

4.1. Characterization after friction

Fig. 6b shows a HRTEM image of a spherical wear particle observed among nanowires (Fig. 6a) together with its corresponding diffractogram. The structure of this particle was clearly identified as a hexagonal structure.

XRD pattern recorded from wear particles is different from that obtained from the pristine material (Fig. 7a and b). Additional peaks can be observed. Their angle positions are in perfect agreement with those of the hexagonal structure of MoS_2. This pattern indicates clearly the coexistence of two phases/structures: that of the nanowires (see spectrum b)) and the hexagonal structure of MoS_2.

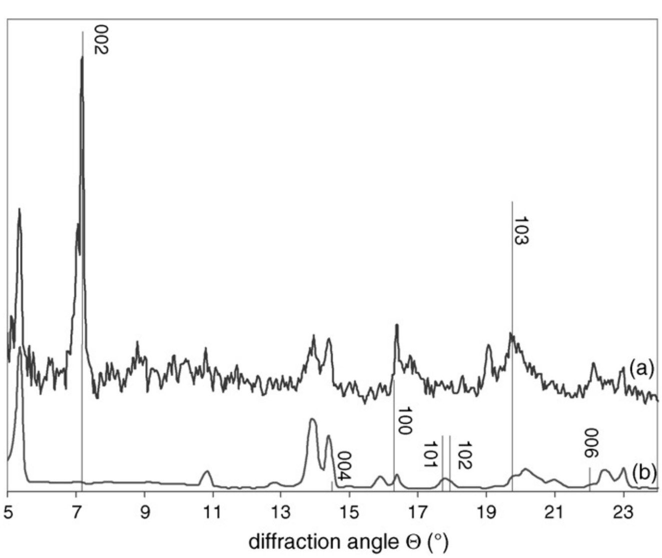

Fig. 7. XRD patterns of: (a) wear particles collected after friction and (b) nanowires. Values of pure hexagonal MoS_2 peaks given by the JCPDS 77-1716 are indicated.

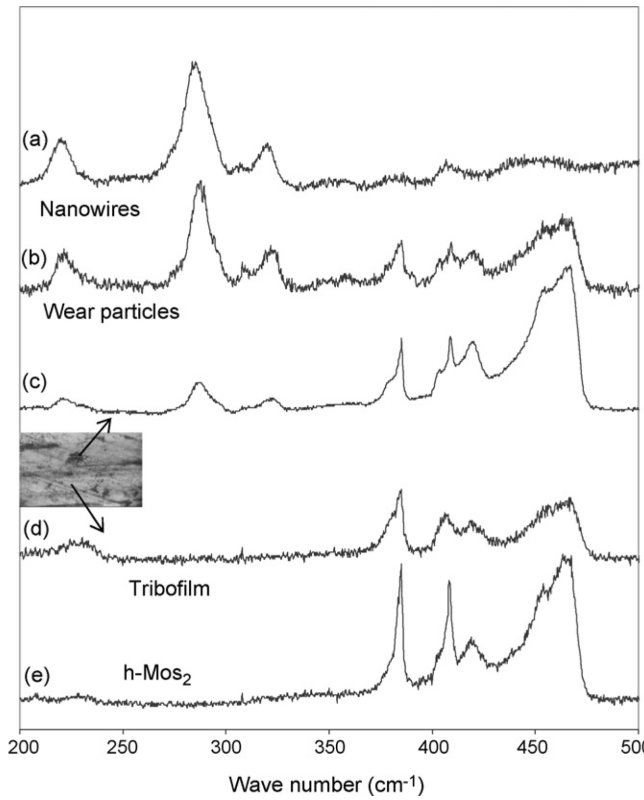

Fig. 8. Comparison of Raman spectra obtained for: (a) nanowires, (b) wear particles, (c) heap inside wear scar, (d) tribofilm and (e) h-MoS_2.

Raman spectroscopy was carried out both from wear particles (Fig. 8b) and on different parts of the wear track. These spectra were compared with those obtained from initial nanowires (a) and pure hexagonal MoS_2 (e). The spectrum recorded from the tribofilm is similar to that of the h-MoS_2. Wear particles contain both nanowires and h-MoS_2 materials.

5. Conclusion

Tribological tests have shown that $Mo_6S_3I_6$ nanowires present good friction reducing properties. Addition of only 1 wt.% of this material to a PAO base oil is sufficient to strongly decrease the friction coefficient in a lubricated standard pin-on-flat test. By correlating the results obtained from several techniques of characterization (TEM, Raman spectroscopy, XRD), it has been proved that these properties are due to a structural modification of the nanowires leading to the formation of MoS_2 sheets in the contact area.

One of the main advantages of these Mo-S-I nanowires is that they improve friction coefficient at the same level than h-MoS_2 while containing much less sulphur than h-MoS_2. Moreover, it has been shown in this study that Mo-S-I nanowires are efficient from the beginning of the test and at room temperature. This is of special interest for automotive lubrication especially for the cold starting which is a critical phase for the engine. These Mo-S-I nanowires could therefore constitute a good alternative to the traditional polluting additives.

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