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Formation of MoS_2 flakes from molybdenum dithiocarbamate-based molecules in a severe lubricated contact: molecular and kinetic approaches

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The objective of this work is to better understand the mechanism of decomposition of the MoDTC molecule leading to the formation of MoS_2 sheets in boundary lubricated steel-steel contacts. To do so, friction tests with different types of MoDTC molecule were carried out. It is demonstrated that the sulfur atoms of the MoDTC ligands participate in the formation of the MoS_2 sheets.
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Keywords (from 3 to 5 max): Friction modifier, MoDTC, MoS_2, Tribochemistry.

1. Introduction

Obtaining low friction coefficients in lubricated contacts running under severe conditions represents a major industrial issue in a global context of energy savings. In the field of thermal engine lubrication, the generation of MoS_2 sheets in a lubricated contact running under boundary lubrication is an effective way of reducing friction losses. This can be done through the use of molybdenum dithiocarbamate (MoDTC), a friction modifier additive used in engine lubricants since the 1970s. The main default of this molecule concerns the low durability of the friction reduction effect due in particular to the ageing of the lubricant in service (temperature, oxidation, etc.).
The scientific objective of this work is to better understand the mechanism of decomposition of the MoDTC molecule leading to the formation of MoS_2 sheets. In a first part, different structures of MoDTC molecules were synthetized and tested to better understand the mechanism of formation of MoS_2 (molecular approach). In a second part (kinetic approach), we have studied more precisely the composition of the tribofilm in the induction period which precedes the achievement of low friction. The idea is to check whether the kinetic of low friction achievement is related to the kinetic of MoS_2 formation.

2. Methods

An experimental approach was used, combining synthesis of molecules, tribological tests and physicochemical and structural characterizations of rubbing surfaces (Raman, XPS and FIB-TEM). The tribological test were carried out with different MoDTC molecules synthetized for the purpose of the project and tested on a reciprocating steel-steel contact working under boundary lubrication conditions. MoDTC-based molecules vary according to their structures by:
- the presence or not of sulfur in the core of the molecule;
- the oxidation state of molybdenum.

2.1. Molecular approach

Results of friction tests with the different MoDTC molecules show that:

- all the Mo-based molecules tested give a coefficient of friction between 0.05 and 0.07. These values are typical of tribofilms containing MoS_2 and are significantly lower than for base oil alone (0.133 ± 0.006);
- MoDTC molecules with sulfur only in thiocarbamate ligands (not in the core of the molecule) allow the formation of MoS_2 and the achievement of low friction.

2.2. Kinetic approach

The analysis of the tribofilms obtained at different number of cycles for MoDTC [A] (Mo+VI and sulfur only in the ligand), shows that:

- as shown in Figure 1, MoS_2 sheets are detected in the tribofilm obtained after 250 cycles, during the induction period and before the achievement of low friction;
- the only presence of MoS_2 sheets is not sufficient to explain the low friction behavior. A specific organization of these sheets at the top of the tribofilm, aligned in the direction of friction, seems necessary. However, a minimum amount of properly organized MoS_2 sheets in the contact should probably be required to achieve low friction.

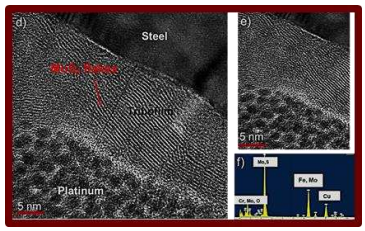

Figure 1: FIB-TEM images of tribofilm (flat) obtained under boundary lubrication with MoDTC [A] after 250 cycles.

3. References

[1] Al Karboutly et al., "Mo(VI) dithiocarbamate with no pre-existing Mo–S–Mo core as an active lubricant additive," 154, Trib. Int. 2021, 106690.