FM-AFM Investigation into the Molecules Adsorption State on Steel Surface in Oiliness Additive Solution

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Molecular adsorption film plays an important role in friction reduction. *In-situ* measurements with high-resolution analysis techniques are strongly desired to reveal the detailed structure of such adsorption film. FM-AFM (Frequency Modulation AFM) enables an observation in liquid with quite higher sensitivity comparing with conventional AFM techniques. In this study, the adsorption film structures of oiliness additives on steel surface were investigated by liquid cell FM-AFM in order to understand the friction mechanism contributed by the adsorption film. The results suggest that non-polar base oil molecules exist with parallel orientation at the outermost surface of stearic acid adsorption film.

Keywords: Oiliness additives, Nano tribology, Adsorption film

1. Introduction

Adsorption film of oiliness additives, which thickness is only several nanometers, prevents direct contact of sliding materials and leads to friction reduction in boundary lubrication. To understand the detail of adsorption film, FM-AFM (Frequency Modulation Atomic Force Microscope) has been applied [1]. FM-AFM can detect force with much higher sensitivity than conventional AFM and enables to detect the solvation structure forming above adsorption film. There are some reports about the FM-AFM measurements on smooth surfaces such as sputtered metal film on silicon wafer [1]. However, the measurement on the surface of steel which is actually used in industry has not been achieved. In this study, the adsorption film structure of oiliness additives on steel substrate was investigated by FM-AFM.

2. Methods and materials

In FM-AFM measurement, the cantilever is constantly oscillated at its resonance frequency by self-excited oscillation on the control system. When the cantilever approaches to the area where molecules densely exist, the repulsive force between the cantilever and molecules leads to higher shift of the resonance frequency of the cantilever. By detecting this frequency shift with scanning along the substrate, the density distribution of molecules can be visualised in Z-X plane. In this study, Z-X images (height and scanning direction) are obtained by FM-AFM (SPM-8000, SHIMADZU, Japan).
We examined the adsorption film of a solution (stearic acid 0.1 mass% in hexadecane) on AISI 52100 substrate. To distinguish the hexadecane and stearic acid, we also used methyl-terminated SAM (Self-Assembled Monolayer) to mimic the surface of stearic acid film, and compared adsorption behavior of hexadecane, stearic acid and oleic acid onto well-ordered methyl surface.

3. Results and Discussion

Figure 1 shows a Z-X image of AISI 52100 in the solution of hexadecane and stearic acid. Two layers of repulsive force were observed. The lower layer is attributed to the surface of adsorption film of stearic acid. The thickness of upper layer is 0.56 nm which corresponds to the width of hexadecane and stearic acid. Figure 2 shows Z-X image of SAM in three liquids: (a) hexadecane and solutions of (b) hexadecane and stearic acid and (c) hexadecane and oleic acid. In each solution, two layers of repulsive force were observed and the width of the upper layer was ~ 0.6 nm. If the oleic acid exists on SAM surface, the thickness would become thicker because of its bent structure. It is therefore hypothesized that hexadecane molecules exist parallel to the plane of the methyl groups due to interaction between non-polar groups. These results suggest the importance of the role of non-polar base oil molecules for friction behavior in the boundary lubrication.

4. References

[1] S. Moriguchi et al, Nanometer-Scale Distribution of a Lubricant Modifier on Iron Films: A Frequency-Modulation Atomic Force Microscopy Study Combined with a Friction Test, ACS OMEGA, 4, 17, 2019, 17593-17599.

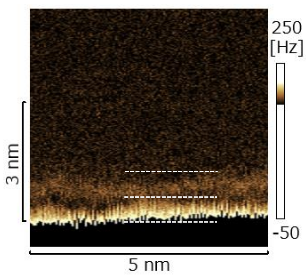

Figure 1: Z-X image of AISI 52100 in stearic acid solution

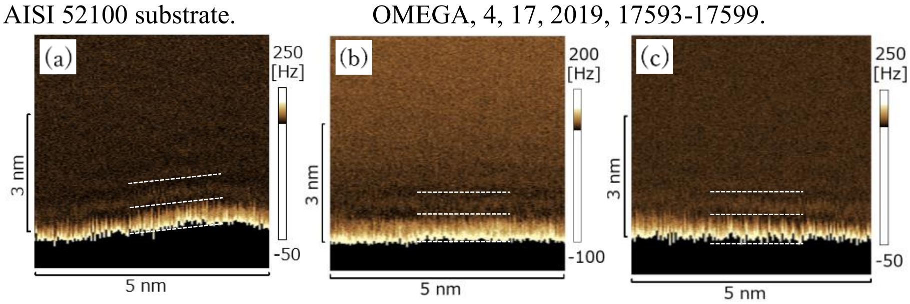

Figure 2: Z-X image of SAM
((a) hexadecane (b) hexadecane with stearic acid (b) hexadecane with oleic acid)