Application News

No. S45

High Resolution Scanning Probe Microscopy FM-AFM

Analysis of Phosphate Ester Adsorption Film Formed on Surface of Iron Oxide in Lubricant by SPM-8100FM

R. Fuji, S. Moriguchi

Keywords: Lubricant, additive adsorption film, molecular resolution, evaluation of friction characteristics, cost reduction

Abstract

The SPM-8100FM is capable of analyzing the lubricant-iron oxide interface with molecular resolution from a lubricant sample of only 500 µl. Because the performance of lubricants can be evaluated by a laboratory-scale material test, this instrument is expected to provide a new evaluation technique that substantially reduces costs related to lubricant development.

Liquid lubricants are oils which are used for purposes such as lubrication, cooling, and rust prevention of internal parts of machinery, and consist of a base oil and additives. For example, the component parts in engines operate at high speed, and metal wear and seizure (phenomenon in which cylinders or pistons are damaged) may occur. At this time, the additive contained in the lubricant (engine oil) forms an adsorption film on the metal surfaces, which reduces friction and prevents metal wear by preventing direct metal-to-metal contact. Fig. 1 shows a schematic diagram of the action of the lubricant additives.

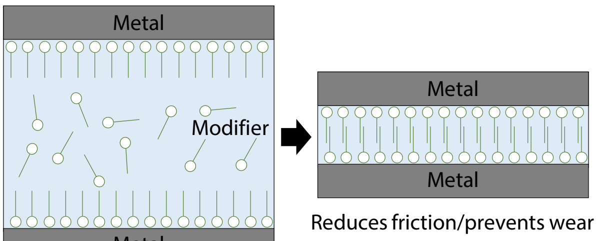

Fig. 1 Schematic Diagram of Action of Lubricant Modifier

Although the additive is the main countermeasure against friction and wear in the sliding parts of engines and other machinery, it is difficult to analyze the adsorption film originating from additives in lubricants, and many questions concerning the film formation process and mechanism of action still remain to be answered. As a result, in actual lubricant development, repeated tests using large-scale devices, such as actual vehicle tests and engine tests, are sometimes conducted to narrow down the candidate types of modifiers and optimum concentration, but the enormous time and cost involved in this kind of testing has become an issue.

Fig. 2 Appearance of Frequency-Modulation Atomic Force Microscope (FM-AFM)

The SPM-8100FM frequency-modulation atomic force microscope (FM-AFM; Fig. 2) is capable of analyzing the lubricant-iron oxide interface with molecular resolution from a lubricant sample of only 500 µl. The SPM-8100FM is expected to provide a new technique that reduces the time and cost related to lubricant development and accelerates lubricant development by making it possible to substitute laboratory-scale material tests for screening in the initial stage of development (Fig. 3).

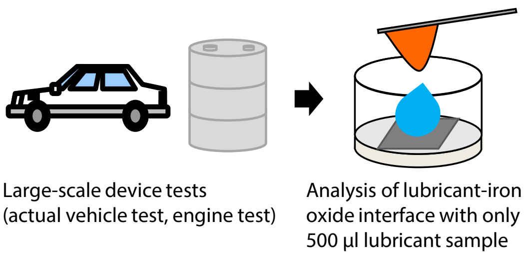

Fig. 3 Expectations for FM-AFM

Iron Oxide and Lubricant Samples

Here, the phosphate ester adsorption film that forms on the surface of iron oxides in a lubricant was analyzed by using an SPM-8100FM.

As the model surface of iron oxide, a film of pure iron (hereinafter, iron oxide substrate) with a thickness of approximately 50 nm was sputtered on a silicon (Si) wafer. An XPS analysis confirmed the existence of an oxide film approximately 2 to 5 nm in thickness on its outermost surface. As the lubricant, PAO4 (poly-α-olefin, a synthetic hydrocarbon base oil with kinematic viscosity of 4 mm^2/s at 100 °C; hereinafter, PAO) was used as the base oil, and a orthophosphoric acid oleyl ester (hereinafter, C18AP) was used as the additive. Fig. 4 shows the molecular structure formulas of the base oil and additive. The analysis was carried out with only PAO (without addition of C18AP), and lubricants in which C18AP was added at concentrations of 0.2 ppm, 2 ppm, 20 ppm, and 200 ppm.

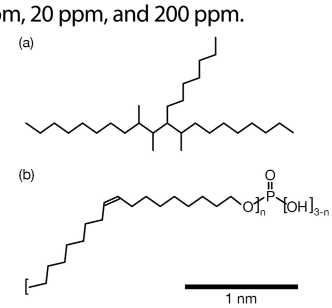

Fig. 4 Molecular Structure Formulas of Base Oil and Additive (a) PAO, (b) Orthophosphoric Acid Oleyl Ester (C18AP)

Analysis of Lubricant-Iron Oxide Interface

Fig. 5 shows the Δf mapping images and force curves at the lubricant-iron oxide substrate interface. In the PAO without added C18AP, a layered structure with a layer-to-layer distance of 0.66 nm was observed. From this layer, it is understood that the PAO molecules have formed a layer oriented in parallel and lying flat on the iron oxide film surface. This layer structure becomes indistinct as the concentration of C18AP increases to 0.2 ppm and 2 ppm and then disappears at 20 ppm and 200 ppm. The disappearance of the layer structure suggests that the orientation of the PAO molecules has been disrupted by C18AP, that is, adsorption of C18AP on the iron oxide substrate.

It is inferred that the surface of the iron oxide substrate is gradually covered by an adsorption film as the concentration of C18AP increases. Specifically, the iron oxide substrate is partially covered at 2 ppm and is completely covered at 20 ppm and 200 ppm. Fig. 6 shows the friction coefficients of the steel-lubricant-steel interfaces measured using a pendulum-type friction tester. The deeply-interesting point in this test is the large decrease in the friction coefficient with PAO containing 20 ppm of added C18AP. Δf mapping confirmed that the surface of the iron oxide substrate was completely covered with a C18AP adsorption layer in PAO with C18AP concentrations higher than 20 ppm. Although the dynamic environment under a sliding condition and the static condition of surface analysis are different, these experimental results are an example demonstrating that the friction characteristics of sliding surfaces can be evaluated by analyzing the lubricant-iron oxide interface by FM-AFM.

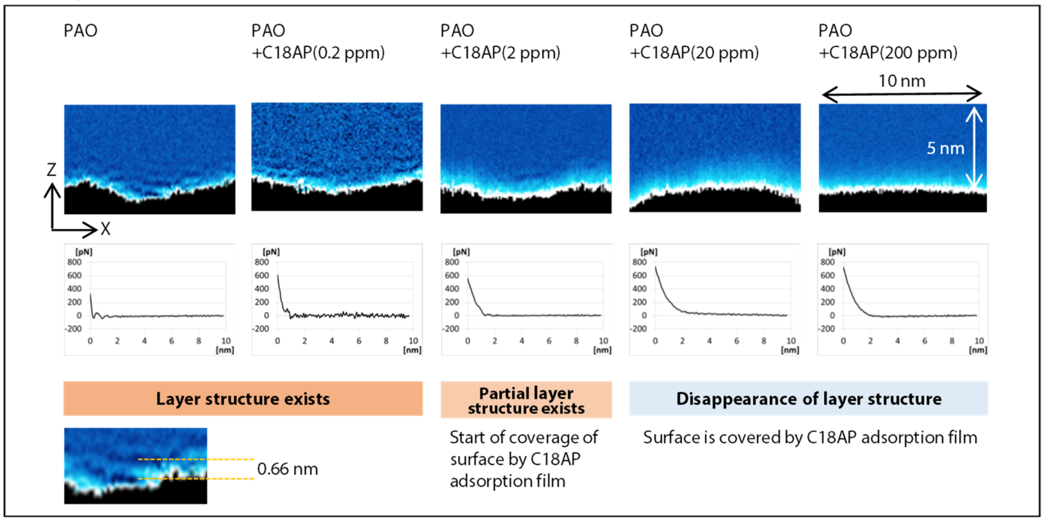

Fig. 5 Δ*f* Mapping Images and Force Curves of Lubricant-Iron Oxide Substrate Interface
(a) PAO, (b) PAO+C18AP (0.2 ppm), (c) PAO+C18AP (2 ppm), (d) PAO+C18AP (20 ppm), (e) PAO+C18AP (200 ppm)

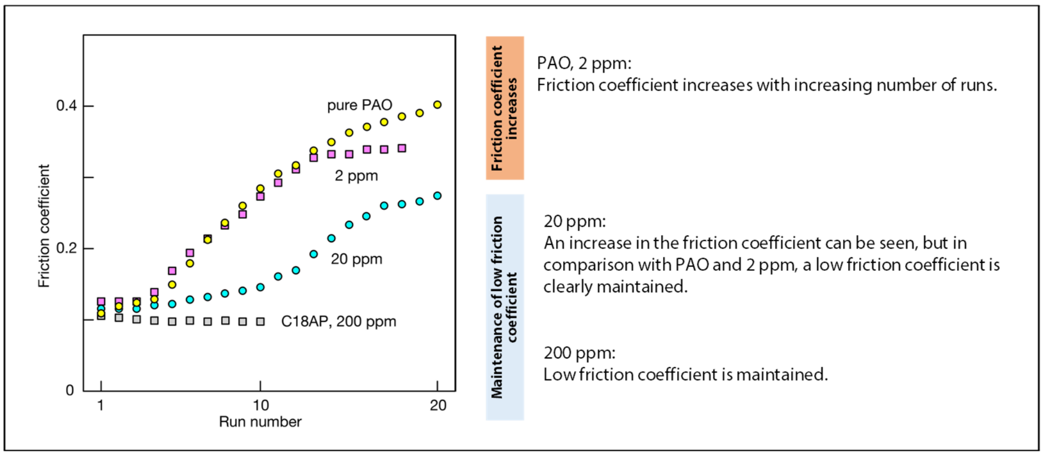

Fig. 6 Friction Coefficients of Steel-Lubricant-Steel Interface Measured Using Pendulum-Type Friction Tester for Friction Coefficient Measurement

Reference
S. MORIGUCHI, T. TSUJIMOTO, A. SASAHARA, R. KOKAWA, H. ONISHI: Nanometer-Scale Distribution of a Lubricant Modifier on Iron Films: A Frequency-Modulation Atomic Force Microscopy Study Combined with Friction Test 4, 17 17593-17599 (2019)

Samples were provided by the following persons:
Sputtered iron oxide substrate samples: Prof. Tomoko Hirayama, Doshisha University
Lubricant: Teppei Tsujimoto, JXTG Nippon Oil & Energy Corporation

First Edition: Mar. 2020

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