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Application News

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High Resolution Scanning Probe Microscopy FM-AFM

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

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Abstract

By using the SPM-8100FM, it was possible to evaluate a comparatively hard adsorption film that formed on an iron oxide surface in a lubricant from changes in surface shape, and a flexible adsorption layer, which cannot be captured as shape change, by cross-sectional imaging.

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.

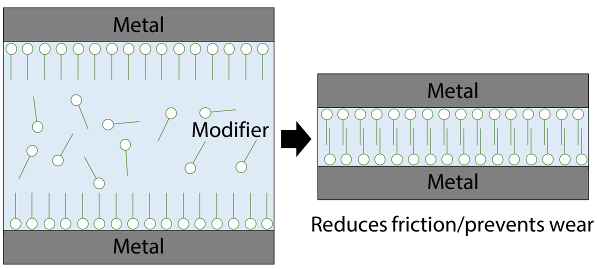


Fig. 1 Schematic Diagram of Action of Lubricant Modifier

Analysis of Adsorption Film Originating from Additive by Frequency-Modulation Atomic Force Microscopy

In analyses of lubricant-metal interfaces by the SPM-8100FM frequency-modulation atomic force microscope, comparatively hard adsorption films that form on a metal surface can be evaluated by the change in surface shape before and after adsorption (Fig. 2). In the case of soft adsorption layers which are too flexible to capture by shape change, the adsorption layer can be evaluated as a liquid structure at the lubricant-metal interface by cross-sectional imaging (Fig. 3)

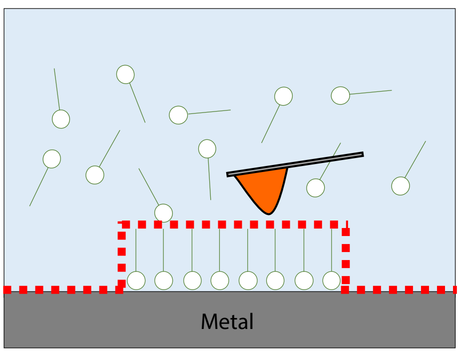


Fig. 2 Observation of Hard (Solid) Adsorption Film

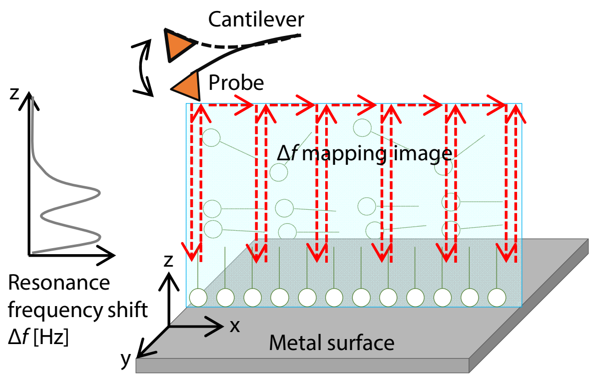


Fig. 3 Observation of Soft (Liquid) Adsorption Film

Iron Oxide and Lubricant Samples

Here, lubricant additive adsorption films formed on the surface of iron oxide in a lubricant were analyzed by using an SPM-8100FM.

The iron oxide model surface used here was a Fe_2O_3(0001) single crystal substrate (hereinafter, denoted as iron oxide substrate). An atomic step was confirmed on this surface (Fig. 4)

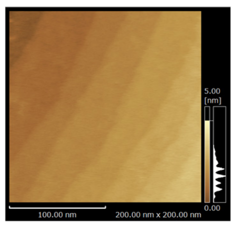


Fig. 4 Image of Surface Shape of Fe_2O_3(0001) Single Crystal Substrate

As the lubricant, PAO4 (poly-α-olefin, a synthetic hydrocarbon base oil with kinematic viscosity of 4 mm²/s at 100 °C; hereinafter, PAO) was used as the base oil, and oleic acid and stearic acid were used as additives. Fig. 5 shows the molecular structure formulas. The analysis was conducted using a lubricant consisting of only PAO and lubricants in which 1 mmol/kg of oleic acid or stearic acid was added to the PAO.

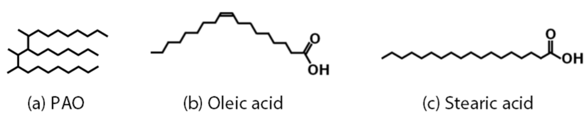


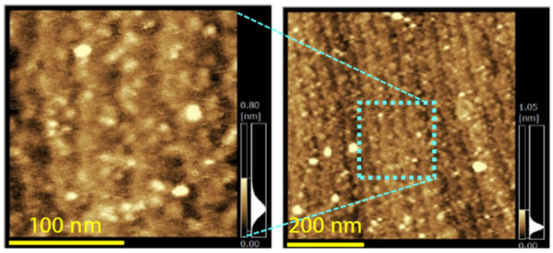
Fig. 5 Molecular Structure Formulas of PAO and Additives (a) PAO, (b) Oleic Acid, (c) Stearic Acid

Evaluation of Comparatively Hard Adsorption Film by Shape Change

Fig. 6 shows topographic images of the surface of the iron oxide substrate observed in the lubricants. As the lubricants used here, (a) is PAO only, (b) is PAO containing oleic acid, and (c) is PAO containing stearic acid. With (a) PAO only, no shape changes due to the quasi-sliding in which the probe scans the sample surface can be seen. In contrast, with (b) and (c), raised areas with a height of sub-nm to several nm can be confirmed. This is considered to be due to the formation of adsorption films originating from the additive under quasi-sliding.

Evaluation of Flexible Adsorption Layer by Liquid Structure

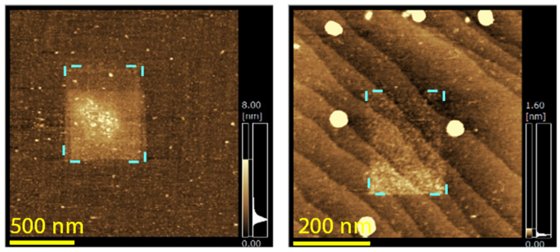
Fig. 7 shows the cross-sectional images at the lubricant-iron oxide substrate interface (upper row) and an illustration of the estimated molecular models of the adsorption layers (bottom row). Here, the lubricants are (a) PAO only, (b) PAO containing oleic acid, and (c) PAO containing stearic acid. With all three lubricants, a structure having a layer-to-layer distance of approximately 0.6 nm formed by the PAO and additive molecules can be seen in the bottom part of the images. In particular, a layer with an intermediate color can be observed at the bottom of the layer structure only with lubricants (b) and (c), which contained a modifier. It is thought that this layer shown in intermediate color represents the resistance force due to the flexible tail part of the additive molecules which have been chemically adsorbed on the surface of the iron oxide substrate.



: the region scanned by probe

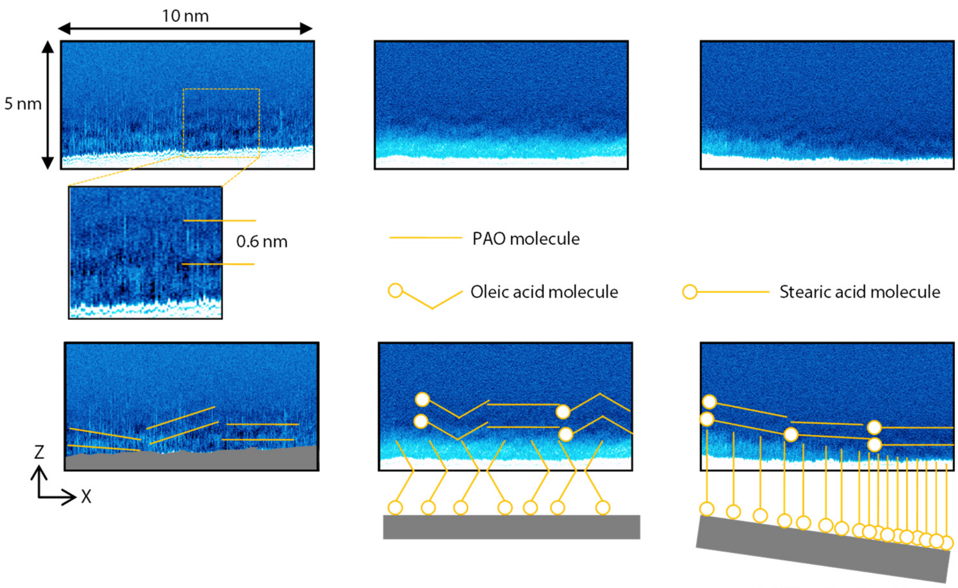
No shape change (formation of adsorption film) due to scanning can be seen in the region where the probe was scanned (range of field of view in topographic image at the left).

(a) PAO



(b) PAO + oleic acid (c) PAO + stearic acid

Fig. 6 Topographic Images of Surface of Iron Oxide Substrate Observed in Lubricants



(a) PAO (b) PAO + oleic acid (c) PAO + stearic acid

Fig. 7 (Top) Z-X Cross-Sectional Images Around Lubricant-Iron Oxide Substrate Interface and (Bottom) Illustrations of Estimated Molecular Models of Adsorption Layers

Samples were provided by the following persons:
Iron oxide substrate samples: Prof. Hiroshi Onishi and Associate Prof. Akira Sasahara, Kobe University
Lubricant: Teppei Tsujimoto, JXTG Nippon Oil & Energy Corporation

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