

Direct observation of adsorbed additive layer at solid-liquid interface by frequency-modulation atomic force microscopy

K. Fujino¹, R. Kawamura¹, T. Matsuoka¹, T. Hirayama^{1,2,*}, H. Onishi³

¹) Faculty of Science and Engineering, Doshisha University, 1-3 Miyakodani, Tatara, Kyotanabe, Kyoto 610-0394, Japan.

²) JST Presto, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

³) Faculty of Science, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan.

*Corresponding author: thirayam@mail.doshisha.ac.jp

Keywords: Frequency-modulation atomic force spectroscopy; adsorbed layer; solid-liquid interface

ABSTRACT – Although an adsorbed additive layer is known to reduce friction, the layer structure on a metal surface is still unclear. In particular, there have been no studies that succeeded in obtaining cross-sectional images of an adsorbed layer in lubricant. This study used frequency modulation atomic force microscopy (FM-AFM) to obtain *in-situ* images. Hexadecane and palmitic acid were used as a model base oil and a typical oil additive, respectively, and a copper-coated silicon wafer was used as the target surface. A clear cross-sectional image of the solid-liquid interface was obtained. It showed that the additive layer was initially monolayer. Then, as the concentration of palmitic acid was increased, the additive layer grew into a multilayer.

1. INTRODUCTION

Reducing friction at sliding surfaces is one of the best ways to reduce friction loss and to extend the life of machine components. While it is well known that an additive in a base oil forms a boundary layer on a metal surface, the structure of the boundary layer is still unclear because there have been no studies that have succeeded in obtaining cross-sectional images of an adsorbed additive layer. We have obtained *in-situ* cross-sectional images of an adsorbed additive layer on a metal surface by using a frequency modulation atomic force microscope (FM-AFM).

2. EXPERIMENT

Fig. 1 shows a schematic diagram of the FM-AFM. A small cantilever was installed in the AFM for scanning the surface of the *xy*- and *xz*-planes to obtain images of the boundary layer. The cantilever was excited at the resonance frequency during measurement. If the sharp tip of the cantilever probe scanned in an area where the liquid density was higher or lower than the bulk liquid, the resonance frequency slightly shifted. Mapping of the amount of shift created, in principle, images showing the density map at the solid-liquid interface, as shown in Fig. 2. The FM-AFM we used was a commercially available AFM (Shimadzu, SPM9600) modified with a low-noise optical deflection scheme.

Hexadecane (C₁₆H₃₄) and palmitic acid (C₁₅H₁₃COOH) were used as a model base oil and a typical oil additive, respectively. Hexadecane molecules are non-polar while palmitic acid molecules have a

carboxylic radical. A copper-coated silicon wafer was used as a target surface.

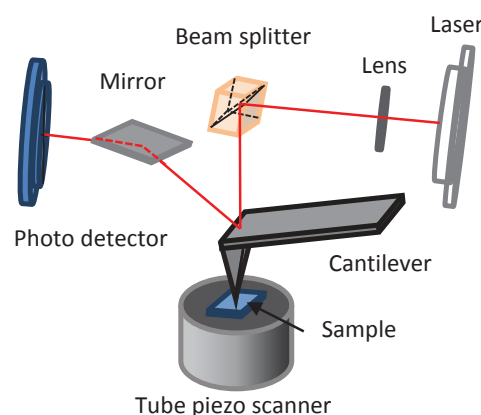


Figure 1 Schematic diagram of FM-AFM.

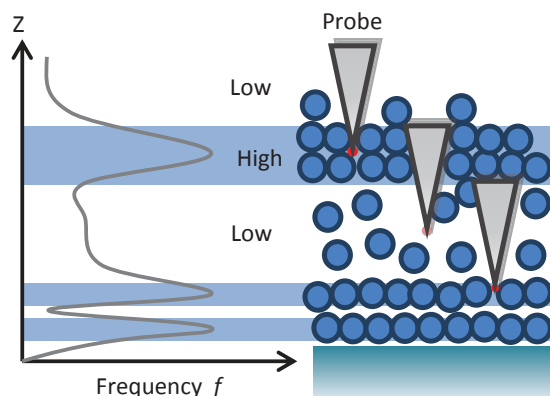


Figure 2 Operation principle of FM-AFM detecting density profiles at solid-liquid interface on *xz*-plane.

3. RESULTS AND DISCUSSION

To check the performance of the FM-AFM, we prepared a KCl solution dropped on a mica surface. The cross-sectional image we obtained is shown in Fig. 3. The white area corresponds to a relatively higher force area, where we expect the density is higher (but still under discussion [1,2]). Clear hydration layers are clearly evident at the solid-liquid interface. The layer pitch was only 0.25 nm, which matches the size of water molecules.

An example cross-sectional image of the adsorbed additive layer is shown in Fig. 4. The concentration of palmitic acid was 0.01 mass%. The white area is apparently the adsorbed layer, and its thickness was about 5 nm. (This white area was not observed when only hexadecane was used.) This layer was monolayer or two-layers thick at the most because the molecular length of palmitic acid is about 2.4 nm.

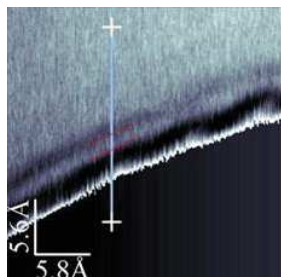


Figure 3 Cross-sectional image at mica-KCl water interface.

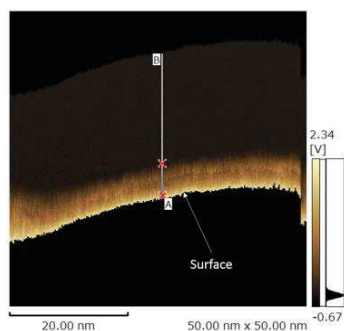


Figure 4 Cross-sectional image of adsorbed additive layer on copper-coated surface.

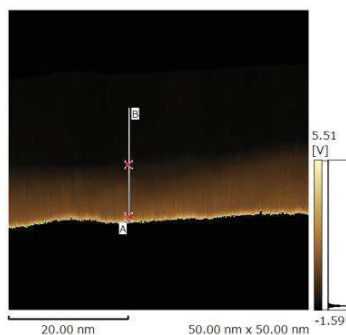


Figure 5 Cross-sectional image of adsorbed additive layer with additive concentration of 0.03 mass%.

Fig. 5 shows a cross-sectional image of an adsorbed additive layer with an additive concentration of 0.03 mass%. The white area, i.e., the adsorbed layer, was thicker than that shown in Fig. 4. The thickness was

about 8.7 nm, meaning that the layer was multilayer, three–four layers at least.

Fig. 6 shows cross-sectional images of an adsorbed additive layer with an additive concentration of 0.3 mass% showing the difference in image with a change in the pushing force of the cantilever. When a lower pushing force was used, the left image was obtained. When the pushing force was increased, the right image was obtained, and the white area became much thicker. The cantilever moved in the vertical direction when scanning the xz -plane and was programmed to return to the upper direction when the detecting force of the cantilever exceeded the limit of the pushing force. This means that a much thicker layer existed on the surface when the additive concentration was 0.3 mass%, and the tip of the cantilever could not reach the copper surface even when the pushing force was increased.

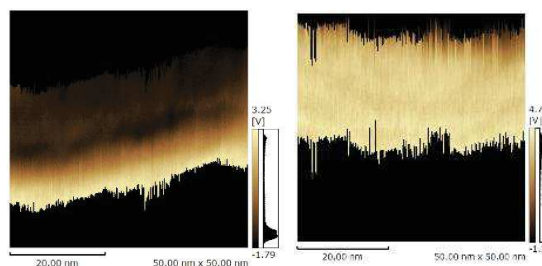


Figure 6 Cross-sectional images of adsorbed additive layer with additive concentration of 0.03 mass% showing difference in image with change in pushing force (left: lower pushing force, right: higher pushing force).

4. CONCLUSION

We used an FM-AFM with a small cantilever to obtain cross-sectional images of an adsorbed additive layer, a boundary layer, formed by palmitic acid in hexadecane. The additive layer was initially monolayer, and it became multilayer when the additive concentration was increased.

5. ACKNOWLEDGMENTS

This study was supported by Canon Foundation, a Japan Society for the Promotion of Science KAKENHI grant (no. 25289025) and JST PRESTO.

6. REFERENCES

- [1] M. Watkins and B. Reischl, *J. Chem. Phys.*, 138 (2013) 154703.
- [2] K. Amano, K. Suzuki, T. Fukuma, O. Takahashi and H. Onishi, *J. Chem. Phys.*, 139 (2013) 224710.