Evaluating surface corrosion of copper surface in metallic soap formation by neutron reflectometry

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Fatty acid is one of the lubricant additives widely used, and it adsorb on metal surfaces to form a molecular film. Adsorption of fatty acid by weak forces such as van der Waals forces is classified as physisorption, while adsorption by chemical bonds between metals and carboxylic acids is classified as chemisorption. The transition from physisorption to chemisorption takes place within a few hours. Fatty acids also form metal complexes, which transform into metallic soap films when the metal is exposed to high temperatures or for long term in lubricating oil contain fatty acid. Although forming metallic soap is a reaction involving corrosion of the metal surface, it shows lower friction coefficient than normal adsorbed molecular films.

The purpose of this study is to evaluate the change over time of the amount of corrosion on metal surfaces during the formation of metallic soaps. This analysis is important for setting the fatty acid concentration and temperature conditions for good lubrication by metallic soaps. The feasibility of the measurement was assessed using MINE, a neutron reflectometer.

A substrate of approximately 300 Å Cu deposited on a mirror-polished Si block of 50 mm × 50 mm in size and 10 mm thick was used for the measurements. The substrate was immersed in a lubricant containing 10 mM palmitic acid (PA: $C_{15}H_{31}COOH$) dissolved in hexadecane (HD: $C_{16}H_{34}$) and the neutron reflectivity measurements were carried out continuously over a long period. Deuterated additives are generally used when analyzing the thickness and density of the adsorption film formed on metal surfaces by additives. Since neither HD nor PA used in this study are deuterated, the scattering length density (SLD) values are almost the same value (SLD ~ 0). The structure of the adsorption film cannot therefore be analyzed, but the thickness change by corrosion of the Cu film (SLD~6×10^{-6} Å^{-2}) can be analyzed. In the present study, the time evolution of corrosion of Cu thin films was analyzed by measuring the neutron reflectance over a long period of several days in a room temperature environment.

Figure 1 shows the neutron reflectivity profiles immediately after immersion in HD or lubricant oil and after 10 days, respectively. It should be noted that even the immediate immersion measurement is the result of an analysis after about five hours of immersion, as it takes long time to complete a measurement after the substrate has been set up. Since HD is a non-polar solvent and does not corrode Cu, the profiles are very similar between the initial and after 10 days later. When immersed in lubricants containing PA, the profile changed compared to that of in HD. However, no changes occurred immediately and after 10 days, indicating that the corrosion of Cu was already complete 5 hours after immersion and that subsequent changes were small. A fitting analysis to the profiles revealed the thickness of the corroded copper surface was 7 Å.

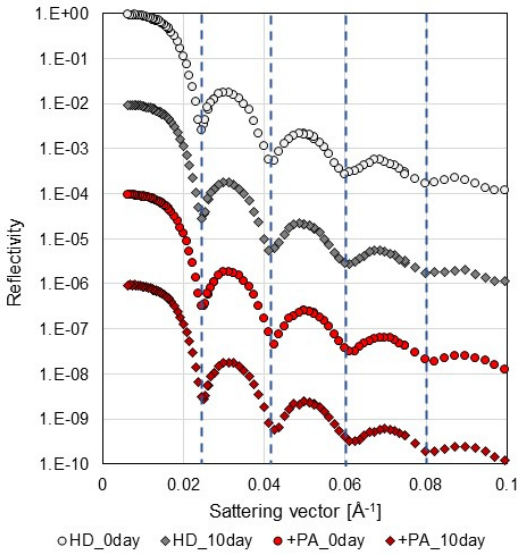

Fig. 1. Neutron reflectivity profiles in base oil HD and lubricant (+PA) measured by MINE.