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Thickness and density of adsorbed additive layer on metal surface in lubricant by neutron reflectometry

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ABSTRACT

The thickness and density of the adsorbed additive layer on a metal surface in lubricant were directly measured by neutron reflectometry. First, two kinds of metal surfaces, iron and copper, on ultra-flat silicon blocks were prepared by physical vapor deposition. After that, each target surface was analyzed by neutron reflectometry in air, in base oil and in base oil with an additive. Poly-alpha-olefin was used as the base oil, while deuterated acetic acid was used as an additive. Fitting operation based on Parratt's theory showed that the thicknesses of the adsorbed layers on the iron and copper surfaces were quite thin, only 2.0 nm. The friction coefficients of the metal surfaces measured by a ball-on-disk tribometer decreased considerably when the acetic acid was added to the base oil. It was concluded that the additive adsorbed layers on the metal surfaces considerably affected friction properties despite being only several nanometers thick.

1. Introduction

Boundary lubrication is one of the most interesting topics in the field of tribology, and the recent development of physical and chemical analyzers has been created a need for better understanding of the behavior of boundary lubrication films [1–10]. Boundary lubrication films are classically divided into two principal categories; one is adsorbed layers due to physical or chemical bonding to a surface and the other is chemical reaction films, called 'tribofilm', formed in a friction process. The former is formed by natural adsorption of oiliness additives, while the latter is formed due to chemical reaction between extreme-pressure additives in lubricants and metal surfaces. A better understanding of both behaviors is quite important and has been necessary in the field of tribology. However, analysis of the former is more difficult than that for the latter in general because the adsorbed additive layer is only nanometers thick, and should be *in-situ* analyzed in lubricant to prevent it from drying. Therefore, there has been still larger room for discussion in the former.

A model illustration proposed by Hardy is the most well known model of a boundary lubrication layer consisting of adsorbed oiliness additives [11,12]. In the model, active groups in the additives, such as hydroxyl or carboxyl groups, adsorb to the metal surface, and hydrocarbon chains in the additives stand vertically on the surface and support the load. Many classical reports confirmed that the adsorptive performance of an additive to the surface greatly affects the friction coefficient of surface [13–15]. However, quantitative analysis for the physical and chemical properties of adsorbed layers had not been done until recent years because of its substantial difficulty.

In the past two decades, to better understand the behavior of adsorbed additives under boundary lubrication, several model studies using self-assembled monolayers (SAMs) standing on surfaces have been done [16–20]. The results are interesting and show unique features of the boundary lubrication films. In response to this gain of momentum, the need has become greater and greater for clarification of the physical and chemical properties of actual boundary lubrication films that consist of adsorbed oiliness additives in lubricants for machines [21–23].

We have used neutron reflectometry to analyze the physical properties, the thickness and density, of adsorbed additive layers to surfaces in lubricant. Neutron reflectometry is a neutron-scattering method and is suitable for analysis of vertical structure at the target surface or interface. In the study, thickness and

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density of naturally-formed adsorbed additive layers on metal surfaces were measured using a neutron reflectometer 'SUIREN'. In addition, the effect of additive layers on tribological properties is discussed on the basis of a comparison of friction test data at the metal surface.

2. Neutron reflectometry

The reasons we focused on the neutron beam for analysis are:

- Neutrons can go deeply into the inner regions of common materials because neutrons physically interact not with electrons but with atomic nuclei. Thus, using the beam, direct observation at the interface between the metal surface and lubricant can be easily realized.
- Neutrons can detect even light atoms such as hydrogen or carbon, in contrast to x-rays, making the neutron beam suitable for studies on lubricants composed of hydrocarbons.
- Labeled molecules by deuterium substitution are clearly distinguished from non-deuterated molecules by neutrons.
- Neutron energy is comparatively weak compared to x-rays or other beams, and thus a non-destructive analysis for the target can be realized.

Reflectometry is a scattering method and is a way to get angstrom-level information on the vertical structure, such as distribution of density and thickness, through the reflectivity of the target surface (or interface) [24–26]. The neutron reflectometer we used is 'SUIREN', which is an angle dispersive reflectometer, operating at JRR-3M in the Japan Atomic Energy Agency (JAEA) [27]. The schematic illustration of SUIREN is shown in Fig. 1. The wave length of the beam in SUIREN is constant at 3.93 Å. We can obtain the reflectivity profile from the target interface through θ (incident angle)–2θ (scattered angle) scanning.

3. Samples

Two kinds of metal surfaces, iron and copper, on ultra-flat silicon blocks were prepared by coating physical vapor deposition. The pressure in chamber was less than 10^{-3} Pa during the deposition and the voltage for electron gun we set was 8 kV. The rate for deposition was kept to be slow, less than 5 Å/sec, to achieve ultrasmooth surface. The source materials for the deposition were pure iron (> 99.9%) and pure copper (> 99.9%) (purchased from the Nilaco Corp.). The size of the silicon blocks was 50 × 50 × t10 mm (purchased from Yamanaka Semiconductor Co., Ltd.) and its original surface roughness was 0.2 nm in *Ra*, measured by atomic force microscopy (AFM). Table 1 lists the specifications of the coating surface: coating thickness and roughness measured by AFM.

The lubricants consisted of a base oil and additives that adsorb to the surface and enable low friction and high durability. We selected poly-alpha-olefin (PAO32, offered from Idemitsu Kosan Co., Ltd.) as the base oil and deuterated acetic acid (> 99 atom%-deuterated, purchased from Sigma-Aldrich Co., Lld.) as a sample of an oiliness additive for the study, because PAO is one of the most widely used base oils in machinery and acetic acid is a typical acid with carboxyl radicals, which have been reported to preferentially adsorb to the metal surface, though they are not used as additive in real machines because of their strong acidity. The reason for deuteration of acetic acid was for clearly distinguishing the acid from PAO by neutrons. Table 2 lists their specifications: structural formula, density, and theoretically-calculated neutron scattering length density *Nb*.

4. Analysis by neutron reflectimetry

4.1. Procedure for analysis

The sample holder with the sample on a setting stage in optical alignment is illustrated in Fig. 2. As shown in the figure, the sample surface was arranged in the vertical setting. The neutron beam cut by two upstream slits entered the target surface through the silicon block, and its reflected beam on the surface was detected by a neutron counter through a slit. In the low-angle range ($0.2 \leq \theta \leq 0.45^{\circ}$), the widths of slits 1 and 2 were set to 0.224 and 0.064 mm, respectively, and in the high-angle range ($0.45 \leq \theta \leq 0.9^{\circ}$),

Table 1
Specifications of metal surfaces for neutron reflectivity study.

	Fe	Cu
Base material	Silicon block	Silicon block
Thickness	About 70 nm	About 70 nm
Base roughness *Ra*	0.2 nm	0.2 nm
Coating surface roughness *Ra*	0.6 nm	0.7 nm
Nb (Theoretical)	8.02e-6 $Å^{-2}$	6.42e-6 $Å^{-2}$

Table 2
Specifications of lubricants for the study.

	Base oil	Additive
Material	PAO32	*d*-acetic acid
Structural formula	$C_{10}H_{21}-(C_{10}H_{20})_n-H$	CD_3COOD
Density at 25°C	0.826 g/cm^3	1.119 g/cm^3
Nb (Theoretical)	−3.7e-7 $Å^{-2}$	5.4e-6 $Å^{-2}$

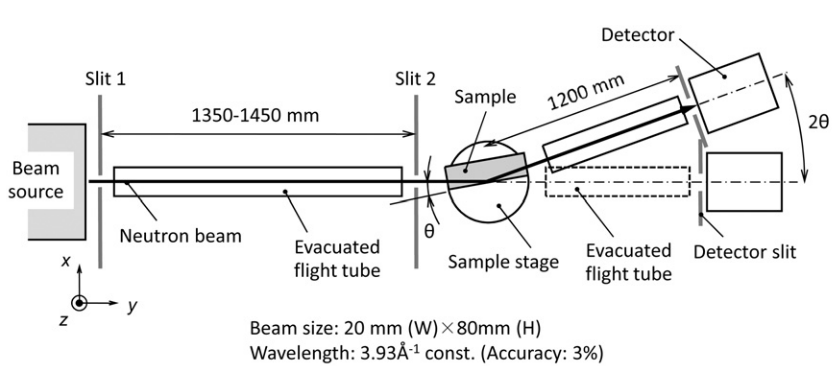

Fig. 1. Beam optics of the neutron reflectometer SUIREN, an angle dispersive reflectometer, operating at JRR-3M in the Japan Atomic Energy Agency.