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Clarification of effect of transformed layer and oil film on low friction coefficient of CNx coating in PAO oil lubrication by in-situ observation of friction area with reflectance spectroscopy

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ABSTRACT

In order to clarify a low friction mechanism of CNx (Carbon Nitride) coating in PAO (Poly Alpha Olefin) oil lubrication, we measured reflectance spectrum at friction area in-situ by reflectance spectroscopy. And we obtained thicknesses and polarizabilities of oil film and transformed layer formed on bulk CNx coating during friction test by analyzing reflectance spectrum. From results, we concluded that the increments of polarizabilities of transformed layer and oil film had an effect on increasing thickness of oil film, and then the lubricated condition changed from boundary to mixed lubrication. Finally CNx coating showed low friction coefficient in PAO oil lubrication.

1. Introduction

Carbon Nitride (CNx) coating is expected to be harder than diamond if CNx coating has β-C_3N_4 structure [1]. Umehara et al. reported that amorphous CNx coating showed ultra low friction coefficient ($\mu < 0.01$) when CNx coating slid to Si_3N_4 ball in dry nitrogen [2]. Moreover, Ogawa et al. reported that the CNx coating showed low friction coefficient ($\mu < 0.05$) when CNx coating slid to Si_3N_4 ball in PAO (Poly Alpha Olefin) oil lubrication. And they reported that CNx coating showed lower friction coefficient than a hydrogenated DLC (Diamond-like Carbon) coating under boundary lubrication [3]. Therefore it is expected to use CNx coating to mechanical components under boundary lubrication as a new low friction material. But the low friction mechanism of CNx coating under boundary lubrication isn't clarified yet. Since it is necessary to clarify the mechanism to apply CNx coating to industrial components, we focused on the clarification of low friction mechanism of CNx coating in PAO oil under boundary lubrication in this paper.

At first, we need to decide which parameters we should observe for clarifying low friction mechanism of CNx coating under boundary lubrication. Therefore we put together reports about low friction mechanism of CNx coating. Tokoroyama et al. reported that CNx coating showed ultra low friction coefficient in dry nitrogen gas environment. And a low shearing strength layer without nitrogen (Transformed layer) was generated on bulk CNx coating in wear scar by AES (Auger Electron Spectroscopy) analysis after friction test [4]. Nishimura et al. estimated thickness and hardness of the transformed layer from in-situ observation of friction area by reflectance spectroscopy in dry friction. And they suggested that the low friction mechanism of CNx coating followed a friction mechanism which Halling suggested [5,6]. That is to say, they suggested that transformed layer acted as soft thin layer from Halling's report, and thickness and hardness of transformed layer affected friction coefficient [5,6]. From above, it is important for ultra low friction coefficient of CNx coating to exist transformed layer at friction area in dry friction. Similarly, it is reported that the transformed layer is important to show low friction coefficient for a carbonaceous coating in oil lubrication too. Ohara et al. reported that the thickness of transformed layer effected friction coefficient by measuring thickness of transformed layer by reflectance spectroscopy after friction test when DLC coating slid with SUJ2 ball in PAO oil [7]. These reports mean it is important to observe the transformed layer in order to clarify the low friction mechanism. Also Tagami et al. reported that a lubricated condition of CNx coating transited from boundary lubrication to mixed lubrication in PAO oil by using a pendulum style friction tester [8]. From this report, since it is thought that a oiliness of CNx coating increases under boundary lubrication, it is necessary to observe thickness of oil film in order to clarify low friction mechanism of CNx coating [8]. Moreover Ogawa et al. suggested that low friction mechanism of CNx coating in PAO oil was related to an physical adsorption of PAO molecules on surface of CNx coating [3]. From this report, it is important to observe a parameter related to the physical adsorption in-situ. In this paper,

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we observed a polarizability of transformed layer because the polarizability was related to a van der Waals force which controls physical adsorption [9].

Summary, we need to observe four parameters during friction test in order to clarify low friction mechanism of CNx coating in PAO oil under boundary lubrication. One is the thickness of transformed layer, second is the thickness of oil film, third is the polarizability of transformed layer and forth is the polarizability of oil film. But it is very difficult to observe the transformed layer during friction test because it is needed to use destructive method like XPS (X-ray Photoelectron Spectroscopy) and EELS (Electron Energy-Loss Spectroscopy) after friction test in order to observe transformed layer. Whereat, we used in-situ observation method by reflectance spectroscopy in this report. From Nishimura's report, the in-situ observation of friction area by reflectance spectroscopy is a strong method to clarify the low friction mechanism of CNx coating [6]. However nobody suggests the way to observe transformed layer and thickness of oil film by reflectance spectroscopy in PAO oil under boundary lubrication, so we need to construct the way before in-situ friction test. In this study, firstly we suggest the way how to obtain thicknesses and polarizabilities of the transformed layer and oil film by reflectance spectroscopy. Secondly we conduct friction test for CNx coating in PAO oil under boundary lubrication, and obtain their thickness and polarizability in-situ. Finally we verify physical meanings of measured parameters in-situ, and clarify an effect of transformed layer and oil film on low friction coefficient of CNx coating in PAO oil under boundary lubrication.

2. Experimental

2.1. Apparatus

Fig. 1 shows friction tester with reflectance spectrometer FE-3000 made by Otsuka electric Co. Ltd. The reflectance spectrometer shined white light to a specimen, got the reflectance from the specimen. Reflectance R is expressed by Eq. (1).

$$R = \frac{I_{\mathrm{ref}}}{I_{\mathrm{int}}} \tag{1}$$

where I_{ref} and I_{int} are intensity of reflected light and incident light respectively.

In this study, the range of wavelength of incident light was 300–800 nm, and the measurement area was a circle of diameter about 10 μm. We set the reflectance spectroscopy above friction area, and we used sapphire hemisphere as a mating material which could transparent the visible light as a mating material of CNx coating. We conducted friction test under the sliding condition as PAO4 of lubricant oil, 0.1 N of normal load and 400 rpm (83.7 mm/s) of rotation speed of CNx

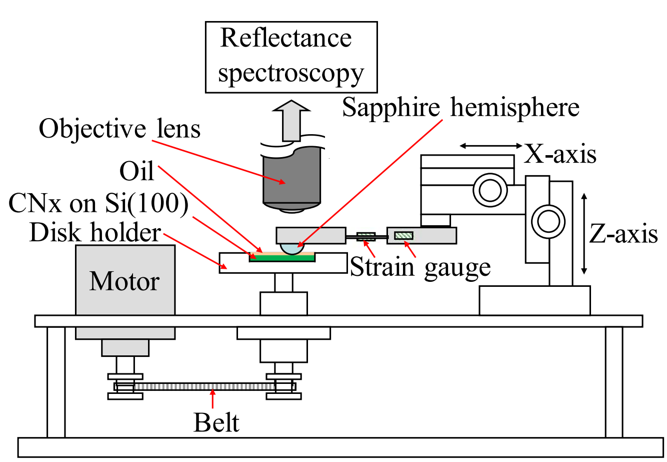

Fig. 1. Schematic of pin-on-disk friction tester with reflectance spectrometer.

coating. And reflectance of CNx coating was measured by reflectance spectrometer every 200 cycles.

2.2. Specimen

CNx coatings were deposited by IBAD (Ion Beam Assisted Deposition) method on Si(100) substrate. The deposition process of CNx coating consisted of two essentials: one was the sputtering deposition of amorphous carbon on the substrate, and the other was an ion-mixing process of the coating by N+ions. Therefore, CNx coatings were produced by a combination of both deposition and mixing processes. N+ ions for the ion-mixing process had the energy of 0.5 KeV and an ion current density of 30 uA/cm^2. The thickness of CNx coating was 300 nm. N/C ratio was 0.015. The surface roughness Ra, Rz and Rp were 9.5 nm, 172.2 nm and 125.2 nm, respectively. Ra was the average variation from mean line of surface roughness curve, Rz was distance from the highest peak to the deepest valley and Rp was the highest peak above the mean line. And the standard deviations of Ra, Rz and Rp were 2.5 nm, 12.0 nm and 8.3 nm, respectively.

The sapphire hemisphere was made by Humanity Co., Ltd. The radius was 4.0 mm, the surface roughness Ra, Rz and Rp were 1.8 nm, 12.5 nm and 6.5 nm, respectively. And the standard deviations of Ra, Rz and Rp were 0.5 nm, 2.5 nm and 1.7 nm, respectively.

3. Preparations of in-situ measurement by reflectance spectroscopy

3.1. Overview

In this part, we suggest methods to measure parameters assumed to be related to low friction coefficient of CNx coating by reflectance spectroscopy. We deal with four parameters should measure by in-situ observation. One is thickness of transformed layer, second is thickness of oil film, third is polarizability of transformed layer and forth is polarizability of oil film. We suggest the relationship between these parameters and reflectance R in turn.

3.2. Relationship among reflectance, thickness of transformed layer and that of oil film

Thickness and optical property of CNx coating can be measured from reflectance R. When a thin layer is deposited on a substrate, relationship between thickness of thin layer and optical constants is characterized by Eq. (2) to Eq. (5).

$$R = \left| \frac{r_{01} + r_{12}\exp(-i2\beta_1) + [r_{01}r_{12} + \exp(-i2\beta_1)]r_{23}\exp(-i2\beta_2)}{1 + r_{01}r_{12}\exp(-i2\beta_1) + [r_{12} + r_{01}\exp(-i2\beta_1)]r_{23}\exp(-i2\beta_2)} \right|^2 \tag{2}$$

$$r_{ij} = \frac{N_i - N_j}{N_i + N_j}\ (i = 0,\ 1,\ 2\ j = 1,\ 2,\ 3) \tag{3}$$

$$\beta_m = \frac{2\pi t_m N_m}{\lambda}\ (m = 1,\ 2) \tag{4}$$

$$N_m = n_m - ik_m \tag{5}$$

where N_0 is complex refractive index of sapphire hemisphere, N_1 is complex refractive index of oil film, N_2 is complex refractive index of transformed layer, N_3 is complex refractive index of bulk CNx coating, t_1 is thickness of oil film, t_2 is thickness of transformed layer, λ is wavelength of light, n is refractive index and k is extinction coefficient. From these equations, we can measure thicknesses of transformed layer and oil film from reflectance R [10].