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Evaluation of the transformed layer of DLC coatings after sliding in oil using spectroscopic reflectometry

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ABSTRACT

Diamond-like carbon (DLC) coatings continue to attract attention for their low friction and high wear resistance. The transferred or transformed layer, which has a high sp^2 carbon content induced by cyclic friction, results in an ultralow friction coefficient in ambient air. However, there are few reports on such layers, especially the transformed layer in oil lubrication, because this transformed layer could be too thin to be measured quantitatively. M. Kano and C. Matta reported the 3 nm thickness of a sp^2 carbon layer using EFTEM study. The spectroscopic reflectometry technique has been applied to measure the thickness of the transformed layer of the DLC's wear scar after friction under oil boundary lubrication. The purpose of this study was to develop a quantitative method for measuring the thickness of the transformed layer in hydrogen-free DLC (ta-DLC) and two types of hydrogenated DLC coatings. Then, we clarified the friction model of these DLC coatings under oil lubrication as the transformed layer was the solid lubricant film. Consequently, we observed that there were optimum ranges of wavelengths and optical models for measuring the transformed layer of the DLC. The optimum wavelength range was 300–500 nm, and the bi-layer model was the best for DLC1, which was the hydrogen-free DLC. For the thicker and un-transmissive coatings, which were hydrogenated DLC coatings, the ranges of wavelengths were 600–800 nm, and the optical model was hypothesized to be a single-layer model. From these optical models, we observed that the thicknesses of the transformed layers of the DLC coatings under oil boundary lubrication were approximately 10–200 nm in the hydrogen-free DLC and 0–200 nm in the hydrogenated DLC. From the analysis of the thickness of the transformed layer and surface roughness, σ^*, of various DLC coatings, we observed that the friction coefficient of the DLC under oil boundary lubrication was determined by the possibility of breaking the transformed layer. This result strongly suggested that the DLC film was a material that realized self-surface modification. We believe that the results of this study could be developed as a guideline for designs of surfaces with DLC coatings.

1. Introduction

Diamond-like carbon (DLC) coatings are well known for their excellent low-friction and wear-resistance properties [1,2]. Currently, these coatings are widely used in various mechanical systems. However, there are no clear systematic guidelines for the use of DLC coatings in lubricated mechanical systems. We believe that this lack of guidelines for the use of DLC coatings is because the mechanism for the low friction of the DLC coating is unclear and because there are few models of DLC friction. Of course, there is a report on the super-lubricity mechanism for the ultralow friction of glycerol-lubricated ta-C coatings [3]. Furthermore, this report demonstrates that the adsorbed molecules from the oil additives play a critical role in obtaining ultralow friction. However, it is not clear what mechanism is valid for oil that does not contain any additives or mineral oil. Additionally, it has been reported that the transformed layer, which is a structure of a DLC surface enriched with sp^2 carbon, could reduce the friction of DLC under dry conditions [4]. However, it is only a qualitative factor, and this transformed layer could not be easily observed under oil lubrication. Therefore, there is a need for quantitative methods to measure the thickness of the transformed layer of DLC under oil lubrication. A model for the friction of DLC under oil boundary lubrication is required to describe how the transformed layer of DLC functions.

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Several methods have been developed for measuring the structure of DLC. For example, typical methods for this purpose include Raman spectroscopy, EELS, NEXAFS, NMR, PBS-ERDA and ESR. However, these methods are complex measurement techniques, and excessive amounts of time and costs are required to measure the DLC. Therefore, reflectance spectroscopy is considered to be a simple, rapid and low-cost method because once the optical model is defined, the thickness of the target film can be easily calculated. Spectroscopic reflectometry is a measurement technique that is based on an interferometric measurement. This method is a new method for quality control of the thickness and quality of DLC. Reflectance spectrometry can measure the optical constant and film thickness of thin films from 1 to 5 nm in thickness based on the spectroscopic analysis of reflected light [5]. Furthermore, this system can measure the thickness with high resolution and accuracy. Therefore, spectroscopic reflectometry is expected to be an effective method for measuring the DLC film.

DLC films are thought to be predominantly amorphous, in which small clusters of microcrystalline structures with sp^3 and sp^2 bonding and an amorphous matrix coexist [6,7]. Therefore, the DLC could change its own structure from sp^3 to sp^2 with mechanochemical reaction under friction. Sanchez-Lopez et al. reported that friction-induced structural transformations of diamond-like carbon affect its friction coefficient under various atmospheres, such as in ambient air (RH 30–40%), dry air (RH -1%), and dry nitrogen (0–1%) [3]. Mabuchi et al. observed that the DLC transformed its rich sp^2 carbon layer after sliding, which is obtained from friction under oil lubrication. They used transmission electron microscopy (TEM) and determined that the thickness of the transformed layer is a few nanometers [8]. This transformed layer has a π^* plasmon peak, which indicates that the transformed layer includes a high content of sp^2 carbon. Therefore, we believe that this transformed layer also had optical properties different than those of the original DLC. Consequently, the transformed layer could affect the friction coefficient of the DLC layer under oil boundary conditions. Therefore, the transformed layer of the DLC coating could be observed using reflective spectroscopy, and its thickness could also be quantitatively measured.

The DLC's transformed layer on the original DLC surface could be considered to be a bi-layer [9]. However, there are no experimental examinations concerning this model because of the lack of quantitative measurement systems for the transformed layer of DLC. Therefore, the purpose of this study was to develop a reflective spectroscopy method to quantitatively measure the transformed layer. We then compared the relationship between the friction coefficient of the DLC and t/σ^* with calculations based on the Halling model. t is the thickness of the transformed layer of the DLC coating after sliding under oil boundary lubrication. σ^* is the deviation of the roughness height. The t/σ^* parameter represents the probability of breaking the transformed layer by surface asperities. This paper is composed of four parts. The first part details our optical model to explain reflectance intensity spectrum of the DLC wear scar after sliding in oil. The second part reports the influence of the oil temperature, contact pressure and sliding distance on the thickness of the transformed layer. In third part, the relationship between the thickness of the transformed layer and friction coefficient is clarified from the viewpoint of the friction model of DLC under oil boundary lubrication. In the final part, we attempt to expand the thin solid lubricants model of Bowden–Tabor [12], Dayson [10] and Halling [11] to explain the friction of DLC under oil boundary lubrication.

2. Experimental method and procedure

2.1. DLC coatings and counter material

We prepared three different types of DLCs, including a hydrogen-free DLC that is named DLC1 and has a hardness of 5000 Hv and a coating thickness of 700 nm. One of the hydrogenated DLCs is named DLC2, and it has a hardness of 1000 Hv and a coating thickness of 4 μm. The other hydrogenated DLC, which is named DLC3, has a hardness of 500 Hv and a coating thickness of 10 μm. The counter material is a disc of S55C bearing steel.

Tests were performed on DLC-coated SUJ2 rollers against a milled steel disc of S55C. SUJ2 steel pins with a surface roughness of Ra 25 ± 5 nm and S55C steel discs, which were polished using several steps to obtain a surface roughness Ra of 25 ± 5 nm, were used as the steel pair. Boundary lubrication friction tests were conducted using a pin-on-disc type tribometer, as shown in Fig. 1. The λ value, which was calculated using EHL (elastohydrodynamic lubrication) theory, was controlled in the range of 0.07–0.1. The DLC-coated pin, which had a diameter of 5 mm and a length of 5 mm, was loaded and rubbed against the DLC-coated or steel disc under pure sliding conditions. The pin was located 6 mm from the center of the disc and fixed to prevent it from rotating. Both the pin and disc were fully immersed in lubricating oil. This lubricating oil was mineral oil, and its kinetic viscosity was 95.2 mm^2/s(40 °C) and 10.8 mm^2/s(100 °C) without any additives. All the samples were washed with benzene and acetone in an ultrasonic bath before and after the friction test to remove contaminants and oil species for surface analysis.

The spectroscopic reflectometry measurement system is a FE3000 made by Otsuka Electronics, and it is shown in Fig. 2. The reflectance spectra were recorded after the samples were washed.

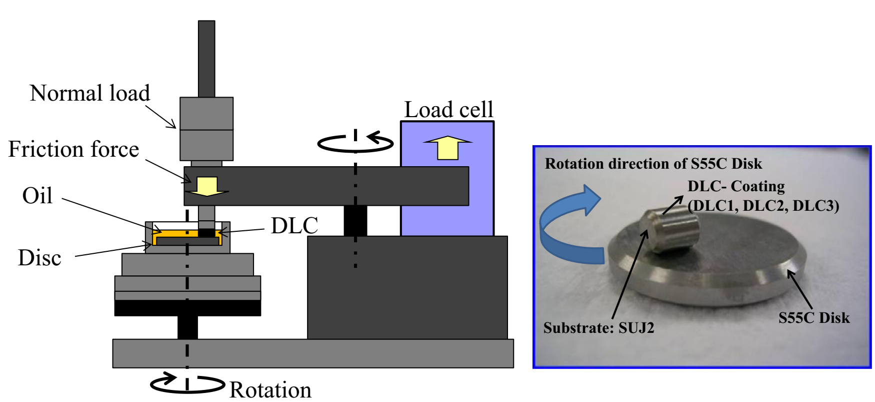

Fig. 1. Schematic illustration of the pin-on-disc type tribometer and a photograph of the pin and disc.