Tribology International 93 (2016) 660–665

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

# Clarification of relationship between friction coefficient and transformed layer of CNx coating by in-situ spectroscopic analysis

Hidenori Nishimura [a,*], Noritsugu Umehara [a], Hiroyuki Kousaka [a], Takayuki Tokoroyama [b]

[a] Department of Mechanical Science and Engineering, Nagoya University Furo-cho, Chikusa-ku, Nagoya-shi, Aichi 464–8603, Japan
[b] Graduate School of Engineering and Resource Science, Akita University 1-1 Tegatagakuen-cho, Akita-shi, Akita 010–8502, Japan

ARTICLE INFO

*Article history:*
Received 27 August 2014
Received in revised form
20 November 2014
Accepted 10 December 2014
Available online 19 December 2014

*Keywords:*
CNx coating
Transformed layer
In-situ observation
Reflectance spectrometer

ABSTRACT

Carbon Nitride (CNx) coating shows ultra low friction coefficient ($\mu < 0.01$) in dry Nitrogen gas because of existing low sharing strength layer (transformed layer) on bulk CNx coating. In order to use ultra low friction phenomena for industry field, we should establish the friction model of CNx with transformed layer. As a friction model of CNx with transformed layer, we try to use the Halling's friction model that is for developed for thin solid lubrication with roughness. For the friction model, we need to know the thickness and hardness of transformed layer of CNx. In this study, we introduce in-situ measurement methods of thickness and hardness of transformed layer with a reflect spectroscopy during sliding test. And we show the possibility to explain the friction coefficient with the Halling's friction model after in-situ measurement of important parameters with a reflectance spectroscopy during sliding test. As a result, we could estimate the thickness and hardness of transformed layer by using reflectance spectroscopy. And it was confirmed that the estimated friction coefficient followed observed friction coefficient when we supposed that transformed layer is thin solid lubrication layer in Halling's friction model.



## 1. Introduction

Carbon Nitride (CNx) coating is promising tribology material that has possibility to be harder than Diamond if CNx coating have $\beta$-$C_3N_4$ structure [1]. Such hard coating can provide high wear resistant. And CNx coatings were also reported as ultra low friction materials in specific environments [2],[3]. 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]. Also they reported the importance of the generation of graphite-like transformed layer for ultra low friction in dry nitrogen after the XPS (X-ray Photo Spectroscopy) analysis of sliding scar [4]. Tokoroyama et al. also reported that a low shearing strength layer was generated by the elimination of Nitrogen atoms and transformation occurred at the topmost layer of CNx during sliding in dry Nitrogen after AES (Auger Electron Spectroscopy) and XPS analysis [5]. As a mentioned above, it was found that transformed layer could govern friction property of CNx. However it is not clear how transformed layer reduces friction coefficient of CNx. For practical usage, in order to use these ultra low friction phenomena for industry fields, we should establish the friction model involved in the effect of transformed layer on friction. As a thin solid lubricant film friction model, Halling proposed a friction model for sliding friction with thin solid lubricant and roughness [6]. When we consider the friction model with a transformed layer, transformed layer can be considered as a thin solid lubricant film. Our group has already reported that the thickness of transformed layer affected friction coefficient by measuring thickness of transformed layer with reflectance spectroscopy after friction test when Diamond-like Carbon (DLC) coating slid with SUJ2 ball in PAO (Poly Alpha Olefin) oil [7]. In order to establish friction model of DLC coating with a transformed layer, we supposed that transformed layer was solid lubrication coating, and applied Halling's thin solid lubricant film friction model to the explanation of the friction properties of DLC in PAO oil. As a result, we reported that the ratio of thickness of transformed layer (t) to effective surface roughness (Rms⁎) which estimated both surface roughness of DLC coating and that of mating material affected friction coefficient, and friction coefficient decreased when t/Rms⁎ is above certain value. This result showed the possibility that Halling's friction model can be used as friction model of carbonaceous hard coating with soft transformed layer.

In order to clarify the friction mechanism of CNx coating and propose a estimating model of friction for industrial field, we need

* Corresponding author.
*E-mail address:* nishimura@ume.mech.nagoya-u.ac.jp (H. Nishimura).

http://dx.doi.org/10.1016/j.triboint.2014.12.015
0301-679X/

to validate the effectiveness of Halling's friction model which defines transformed layer as solid lubrication layer for CNx coating. When we calculate friction from the Halling's friction model, we should know some parameters as thickness and hardness of transformed layer of CNx as a thin solid film. However these parameters should vary during friction test. Therefore we need to measure both parameters as thickness and hardness of transformed layer in-situ.

In this article, we will introduce in-situ measurement methods of thickness and hardness of transformed layer with a reflect spectroscopy during sliding test. And we will show the possibility to explain the friction coefficient with the Halling's friction model after in-situ measurement of important parameters with a reflectance spectroscopy during sliding test.

## 2. Estimating method for the thickness of transformed layer of CNx coating from optical properties

### *2.1. Principle of estimating method for thickness of transformed layer of CNx coating from optical properties*

Thickness of transformed layer of CNx can be estimated from reflectance R. Reflectance R means the ratio of the reflected to incident light intensity. When a thin layer is deposited on a substrate, relationship between thickness of thin layer and optical constants is characterized by Eq. (1)–(4).

$$R=\left|\frac{r_{01}+r_{12}\exp(-i2\beta)}{1+r_{01}r_{12}\exp(-i2\beta)}\right|^2 \tag{1}$$

$$\beta=\frac{2\pi dN_1}{\lambda} \tag{2}$$

$$r_{ij}=\frac{N_i-N_j}{N_i+N_j} \tag{3}$$

$$N=n-ik \tag{4}$$

where $d$ is thickness of thin layer, $\lambda$ is wavelength of light, $n$ is refractive index, $k$ is extinction coefficient, $N_1$ is complex refractive index of thin layer and $N_0$ is complex refractive index of air. From these equations, we can measure thickness of CNx coating by using optical constants[8].

### *2.2. Validation of thickness of transformed layer by reflectance spectroscopy*

In this part, we validates the thickness of transformed layer by reflectance spectroscopy by comparing the thickness measured by EELS (Electron Energy Loss Spectroscopy) analysis.

CNx coatings are deposited by IBAD (Ion Beam Assisted Deposition) method on Si(100) substrate. The thickness of CNx coating is 100 nm. In this study, we define structural changed layer on bulk CNx coating compared to bulk CNx coating as transformed layer, and CNx coatings are slid against $Si_3N_4$ ball in dry Nitrogen to generate transformed layer. We conduct friction test that the load is 0.1 N, rotating speed is 400 rpm.

Next, we use reflectance spectrometer FE-3000 made by Otsuka electric Co. Ltd. to measure thickness of transformed layer of CNx coating. Reflectance spectrometer shines white light to a specimen, gets the reflectance and measure optical constants of specimen. Reflectance R is expressed by Eq. (5).

$$R=\frac{I_{ref}}{I_{int}} \tag{5}$$

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

In this study, range of wavelength of incident light is 300 nm to 800 nm, and measurement area is a circle of diameter about 10 μm. After the thickness of transformed layer was measured by reflectance spectroscopy, the thickness was measured by EELS (Electron Energy Loss Spectroscopy) analysis.

Fig. 1 shows results of thickness of transformed layer by reflectance spectroscopy and EELS analysis. The thickness by reflectance spectroscopy was 11.7 nm and that by EELS was 11.0 nm. From this result, we could estimate the thickness of transformed layer by reflectance spectroscopy within a tolerance of 6.0 %.

## 3. Estimating method for hardness of transformed layer of CNx coating from optical constants

### *3.1. Principle of estimating method for hardness of transformed layer of CNx coating from optical constants*

J. Robertson reported that halves-three power of hardness of hydrogenated DLC coating was lineally correlated to fraction of C–C $sp^3$ bonds [9]. From this report, it is expected that we can estimate hardness of CNx coating from fraction of C–C $sp^3$ bonds of CNx coating. In this time, when we suppose that optical constants of CNx coating consist of optical constants of C–C $sp^2$ bonds, C–C $sp^3$ bonds and C–N bonds to calculate fraction of C–C $sp^3$ bonds from optical constants of CNx coating, relationship between optical constants of CNx coating and fraction of C–C $sp^3$ bonds is expressed by Eqs. (6) and (7)[10].

$$0=f_{C-Csp^2}\frac{\varepsilon_{C-Csp^2}-\varepsilon}{\varepsilon_{C-Csp^2}+2\varepsilon}+f_{C-Csp^3}\frac{\varepsilon_{C-Csp^3}-\varepsilon}{\varepsilon_{C-Csp^3}+2\varepsilon}+f_{C-N}\frac{\varepsilon_{C-N}-\varepsilon}{\varepsilon_{C-N}+2\varepsilon} \tag{6}$$

$$1=f_{C-Csp^2}+f_{C-Csp^3}+f_{C-N} \tag{7}$$

where $f_{C-Csp^2}$,$f_{C-Csp^3}$,$f_{C-N}$ are volume fraction of C–C $sp^2$ bonds, C–C $sp^3$ bonds and C–N bonds and $\varepsilon_{C-Csp^2}$, $\varepsilon_{C-Csp^3}$, $\varepsilon_{C-N}$ are complex dielectric constant of C–C $sp^2$ bonds, C–C $sp^3$ bonds and C–N bonds respectively.

From Eqs. (6) and (7), we can estimate fraction of CNx coating from optical constants of CNx coating. Finally, relationship between halves-three power of hardness of CNx coating and fraction of C–C $sp^3$ bonds is expressed by Eq. (8) [9].

$$H^{(2/3)}=a\times f_{C-Csp^3}+b \tag{8}$$

where H is hardness of CNx coating, a and b are constant. From above, we can estimate hardness of CNx coating from optical constants of CNx coating if we know a,b,$f_{C-C\ sp^3}$.

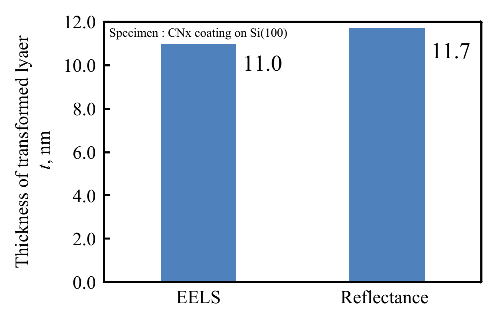


**Fig. 1.** Result of thickness of transformed layer by EELS analysis and reflectance spectroscopy.