# Ti 混入による Fe/DLC 摩擦ペアの摩擦特性の改善

Improvement on friction characteristic of Fe/DLC tribopair by Ti-incorporation

名大(学生)\*Jae-Il Kim 名大(正)梅原 徳次 名大(正)野老山 貴之

Jae-Il Kim\*, Noritsugu Umehara\*, Takayuki Tokoroyama\*

\*Nagoya University

#### 1. Introduction

Diamond-like carbon (DLC) has attracted extensive attention as a promising solid lubricant. Based on the sp<sup>2</sup>, sp<sup>3</sup>, hydrogen, and other elements contents, it is divided into four groups, i.e., amorphous carbon (a-C), hydrogenated amorphous carbon (a-C:H), tetrahedral amorphous carbon (ta-C), and elementally doped DLC (DLC:X). Among several types of DLCs, ta-C has been a hotspot in tribological application because of its excellent tribological characteristics derived by high sp<sup>3</sup> fraction, i.e., anti-friction and wear-resistance. Today, as a counterpart against ta-C, iron-and brass-based metals are employed owing to their processibility and economic efficiency. Unfortunately, several researchers have expressed concern over the inferior tribological performance of Fe and Cu sliding against DLC compared to other metals. That's why, measures are required to prevent friction loss caused by mismatched mating materials.

The friction performance of DLC relies on a well-developed carbonous transfer layer. Hence, although numerous methods for promoting a low shearing tribofilm have been developed to prevent CO<sub>2</sub> emissions and global warming, there are technical constraints for a long-lasting transfer layer and efficient friction performance. Tokoroyama et al. [1] reported that UV irradiation on carbon nitride coating changed the amorphous structure to a crystalline graphitic structure on the topmost layer. Kim et al. [2] studied that post-irradiation of O<sub>2</sub> plasma on DLC modified the surface passivation, leading to improving tribological performance. However, these surface modifications through various energy-beam irradiation are not an effective approach for the improvement of friction performance as these methods only bring an initial short-term effect and cannot provide continuous improvement. Murashima et al. [3] developed an in-situ surface treatment using an electric discharge to serve a low frictional interface between Fe and DLC. Sun et al. [4] realized low friction of a-C coating via contact-focusing electron flow. Such approaches are ineffectual in that it uses electrical power to reduce frictional energy and complicates the structure of the tribo-system.

In our previous study, among 3d-transition metals, the high adhesion of Ti to C resulted in the growth of a firmly adhered transferred layer [5]. Wang et al. [6] reported that in the deposition system the reason why Ti interlayer between DLC and Fe could exhibit improved adhesion properties in the first principle perspective. Because the work of separation at the Fe/C interface is comparatively lower than that of the Ti/C and Fe/Ti interfaces, Ti layer serves as an advantageous adhesion layer between C and Fe interface. According to Pauling theory, Ti has the least amount of *d*-character among transition metals, therefore, it is commonly highly reactive and adhesive to other elements.

Herein, we attempted to develop a firmly adhered transfer layer at the Fe/DLC contact interface with the titanium addition in the tribo-system. Ti-overcoated DLCs were fabricated in an effort to enhance the adhesion between Fe and C by transferring Ti to the counterpart material. This revealed the effect of the adhesion properties of Ti on the growth of a robust transfer layer.

## 2. Experimental procedure

High-carbon chromium-bearing steel (SUJ2) disks were utilized as the substrate to fabricate a DLC coating. The surface was ultra-sonically cleaned with benzene and acetone for 15 mins each. For depositions of ta-C and Ti-overcoated DLC (Ti/DLC) coatings, a hybrid coating system was used and comprised of an anode-layer closed-drift linear ion source (LIS), unbalanced magnetron sputter (UBMS), and filtered cathodic vacuum arc (FCVA). The deposition process was carried out in three processes: (1) Ar-plasma etching, (2) Ti-sputtering for the interlayer, (3) ta-C coating, and (4) deposition of Ti-overcoat.

Prior to tribotesting, specimens were cleaned with benzene in an ultrasonic bath. The tribotesting was conducted using a custom-made ball-on-disk type tribometer with the following environments: ambient air; 1 N, normal load; 63 mm/s, sliding speed. The SUJ2 ball (diameter = 8 mm) was employed as the counterpart.

The worn surfaces of the disk and ball were observed using a confocal laser scanning microscopy (Olympus OLS5100, Japan) and a scanning electron microscopy (SEM; JEOL JCM-5700NU, Japan) equipped with an energy-dispersive X-ray spectroscope (EDS; JEOL EX-54175NU). The surface profile was obtained via confocal laser scanning microscopy. EDS analysis was performed at a 5-keV of acceleration voltage to determine the chemical composition of the bulk coating and tribofilm. It obtained the elemental mapping images for minimizing the influence of the sub-layer.

#### 3. Results and discussion

We prepared the various thicknesses of Ti-overcoat (10, 20, 30, 40, and 50 nm). As a result of tribotesting, the CoF of ta-C progressively increased from  $\sim$ 0.17 to  $\sim$ 0.4. In contrast, the CoF of Ti-overcoated DLC sharply decreased by  $\sim$ 0.06 after runningin and gradually increased with the progress of friction (**Fig. 1**).

In order to investigate the low-friction mechanism of Ti/DLC, we conducted a friction test using 30 nm-Ti/DLC according to the friction stages (**Fig. 2**). The friction tests were conducted with 63 mm/s of sliding speed and various rotating radius under ambient air condition. Friction stages were classified into six stages based on the CoF variation. The CoF rose by  $\sim 0.5-0.8$  during runningin, but then, it dropped to  $\sim 0.05-0.06$  with the progress of friction.

The worn surfaces were obtained using a confocal laser scanning microscope (Fig. 3). Figure 8 shows the representative measurement of tribofilm thickness. With the progress of friction, the transfer layer gradually built on the SUJ2 ball. At stage 1, the SUJ2 ball was worn before starting the growth of the transfer layer. After stage 2, the transfer layer gradually grew from an island-like product to a film-like product, then at stage 5, a transfer layer of ~980 nm was formed on the SUJ2 ball. On the Ti/DLC side, at stage 1, tribo-products adhered to Ti/DLC. After stage 1, tribo-products were removed, and Ti-overcoat was gradually worn on DLC. From these, we inferred that CoF decreased with the removal of Ti-overcoat and the growth of the transfer layer.

#### 4. Conclusion

This study addressed the friction characteristics of Ti/DLC sliding against SUJ2. Furthermore, we investigated its low-friction mechanism along with tribofilm characterization. The influences of Ti addition on the friction characteristics of DLC were discussed as follows:

- 1) In Ti/DLC, Ti-overcoat provided low friction for the ta-C/SUJ2 tribopair and grew a well-developed transfer layer on SUJ2. Before forming the carbonous transfer layer, Ti was preferentially transferred to the SUJ2 ball.
- 2) Ti/DLC was a method for developing a carbonous transfer layer on the counterpart. Ti/DLC provided a temporary friction performance improvement. Titanium, its high adhesion properties helped to form a thick and robust tribofilm consisting of carbon on SUJ2 and built-up a low frictional C/C contact interface.

### Reference

- 1) T. Tokoroyama et al.: Influence of UV irradiation in low frictional performance of CN x coatings, Lubr. Sci., 24 (2012) 129–39.
- 2) J.-I. Kim et al.: Improvement of running-in process of tetrahedral amorphous carbon film sliding against Si3N4 under humid air by O2 plasma post-irradiation, Appl. Surf. Sci., 538 (2021) 147957.
- 3) M. Murashima et al.: Development of a new diamond-like carbon surface treatment method with electric discharge for short running-in and friction reduction, Proc. Inst. Mech. Eng. Part J: J. Eng. Tribol., 236 (2021) 1020–30.
- 4) K. Sun et al.: Contact-focusing electron flow induced nanosized graphene sheets formation in amorphous carbon film for fast low-friction, Carbon N. Y., 149 (2019) 45–54.
- 5) J.-I. Kim et al.: Friction characteristics of amorphous carbon coating against various 3d-transition metals, Tribol. Int., 174 (2022) 107690.
- 6) K. Wang et al.: Effects of Ti interlayer on adhesion property of DLC films: A first principle study, Diam. Relat. Mater., 111 (2021) 108188.

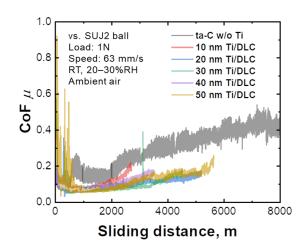


Fig. 1 Friction curves of ta-C and with various the thickness Ti-overcoat.

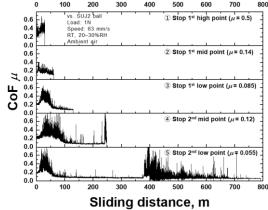


Fig. 2  $\,$  Friction curves with various friction stages for 30 nm  $\,$  Ti/DLC.

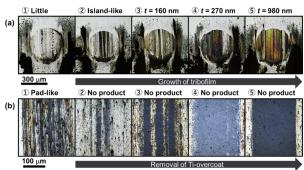


Fig. 3 Optical images of worn surface on (a) SUJ2 and (b) Ti/DLC. 't' means the tribofilm thickness.