Friction fade-out at DLC film slid by ZrO_2 pins under heavy applied load

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1. Introduction

A clean hydrogen energy is expected as a promising future energy due to its high energy efficiency and small impact on the environment, and the hydrogen technology is considered one of the key technologies in the 21st century. In order to build hydrogen infrastructures taking into account the requirement of low energy cost, it is necessary to construct low-friction tribology systems against the high reduction power of hydrogen. On the other hand, tribological characteristics of diamond-like carbon (DLC) have been widely studied aiming various applications since DLC generally exhibits low friction, high wear resistance, high hardness and chemical inertness [1], and many reports focused on the ultra-low friction characteristics of DLC with large amount of hydrogen contents or tested under hydrogen environments [2,3,4]. In addition, recent studies are clarifying that an effect of tribochemistry is very important on lubricity of DLC films in hydrogen environment [5], and the formation of tribofilm by chemical reaction is particularly important for making the superlubricity come true [6].

We have reported [7, 8] that the friction coefficient reduced to the friction-tester noise-level of 0.0001 when diamond-like carbon (DLC) plate was slid by ZrO_2 pin under H_2 gas environment and we termed this behavior as friction fade-out (FFO). It was also reported that the tribofilm formation on ZrO_2 surface during run-in process played a very important role for the onset of FFO, and that FFO was stabilized and kept longer time when alcohol vapor was mixed into H_2 gas.

In this report, in addition to the FFO behavior, mechanical and chemical characteristics of tribofilm formed on ZrO_2 surface before and after the onset of FFO is reviewed, and the mechanism of FFO is discussed

2. Friction fade-out

Friction tests were conducted using four ceramic pins slid on DLC surface under H_2 gas condition, then only ZrO_2 pin showed very small friction coefficient of the order of 0.0001 (Fig.1), which was the noise level of the friction tester we used [7].

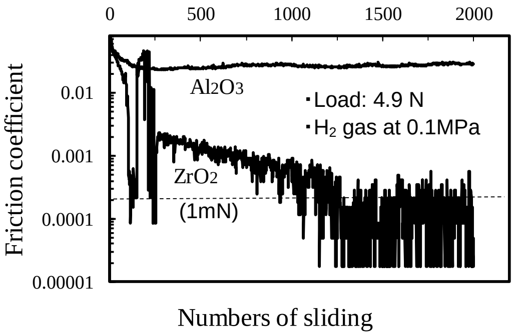

Fig. 1. Friction fade-out at DLC films slid by ZrO_2 pins under H_2 gas environment [7]. (Sliding velocity at 8.0 mm in reciprocating motion with one slid of 4.0 mm).

However, we encountered two problems at this point. The first problem was the instability of FFO, i.e. the friction coefficient frequently varied between 0.0001 and 0.01 even though the sliding and environmental conditions did not change. After many experiments, we found that FFO stability could be achieved by adding alcohol vapors to the H_2 gas during the run-in stage (Fig. 2) [8]. The second problem was that FFO occurred in the H_2 gas environment. It is known that H_2 gas is hazardous by nature because of its potential for explosion and a wide range of flammability limit in air, i.e. from 4.1% to 74%. Therefore, the researchers and workers are reluctant to use H_2 gas in laboratories or industries. We supplied many types of H_2 gas mixtures to the testing area in an attempt to reduce the H_2 content in the gas mixtures. We recently found that FFO occurs in an N_2–H_2 gas mixture in which H_2 content is less than 1.0%, i.e. below the flammability limits of H_2 [9].

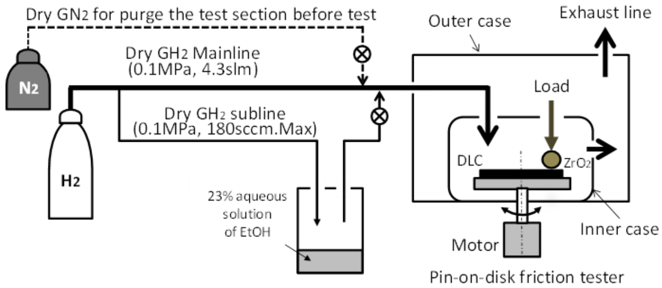

Fig. 2. Friction test under alcohol-vapored H_2 gas environment [8]

It was also found that FFO depended on the applied load [7], i.e., FFO appeared at a heavy load but disappeared at a light load as shown in Fig. 3.

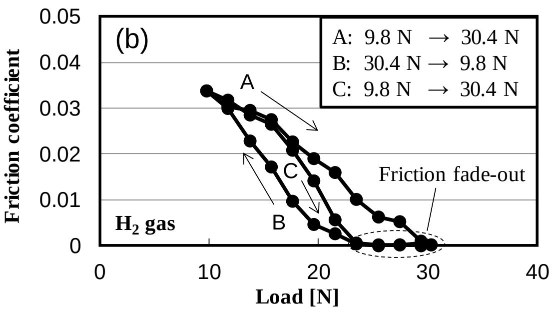

Fig. 3. Load dependency of FFO [7]

3. Characteristics of tribofilm formed on ZrO_2 pin

We observed and measured the tribofilm formed on ZrO_2 pin after FFO occurrence by optical microscope, SEM, nano-indentation tester, surface profile meter, XPS, RAMAN and TOF-SIMS and discussed that the ZrO_2 catalytic reaction plays a very important role for the onset of FFO. Fig. 4 is the surface profile of tribofilm measured by Scanning White Light Interferometer (SWLI, New View 7300, ZYGO INC.) [8], showing that the tribofilm was surrounded by peripheral bumps, and Fig. 5 is the SEM observation at the center of the tribofilm, showing that many blisters and crimps were observed but less sliding marks were observed. These observations suggested that the real contact area was significantly small.

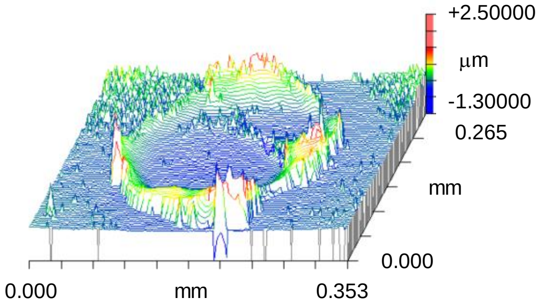

Fig. 4. Tribofilm profile after FFO measured by SWLI [8]

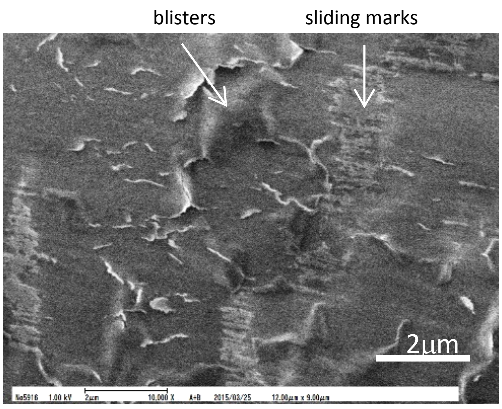

Fig. 5. Tribofilm surface after FFO measured by SEM [8].

It was also found that the tribofilm involved short-chain hydrocarbons and hydrogen atoms coming from dehydrated alcohol molecules [10], in addition to the aromatic series ($C_6H_5^+$ and $C_7H_7^+$), condensed-ring ($C_9H_7^+$) and benzoic acid ($C_7H_5O^-$) as shown in Fig. 6, which were also detected from the wear tracks of DLC surface, and that soft and semi-insulating polymer-like materials were attached on the tribofilm and grew with sliding [9]. These observations and measurements suggest the generation of hydrocarbon gases by ZrO_2 catalytic reaction.

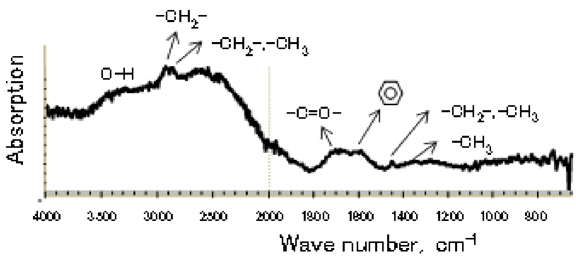

Fig. 6. FT-IR signals from tribofilm [10].

4. Conclusions

It is reported that the friction reduced down to a noise level of the friction tester (friction fade-out), corresponding to the friction coefficient of about 0.0001, when DLC plate was slid by ZrO_2 pin at a heavy applied load of 30N or 60N under an alcohol-vapored H_2 gas. Several observations and measurements are focused on the tribofilm formed on ZrO_2 surface during run-in stage. It is shown that the tribofilm after FFO occurrence is surrounded by peripheral bumps, has many blisters and crimps but less sliding marks, and that a polymer-like materials are attached on the tribofilm. These observations and measurements suggest the hydrocarbon-gas lubrication evolved at the ZrO_2 surface by a catalytic reaction.

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