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Chemical analysis of boundary lubrication film formed on metal nitride coatings with ethanol by means of TOF-SIMS

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ABSTRACT

Tribochemistry of metal nitride coatings in the presence of alcohol was investigated by using a stable isotopic tracer. The tribological properties were evaluated by a ball-on-disk type tribo-tester with steel ball and metal nitride coated disk under reciprocating motion. It was found that the friction coefficient of CrN was approximately 60% lower than that of TiN. On the other hand, TiN afforded lower wear than CrN. Considerable amount of deposit was observed on TiN. The rubbed surfaces were chemically analyzed by means of time-of-flight secondary ion mass spectroscopy (TOF-SIMS). In order to eliminate the undesirable fragment ions originated from organic contaminations in TOF-SIMS analysis, pentadeuterioethanol was used as an isotopic tracer. It was found that CrN reacted with alcohol to provide chromium ethoxide as boundary film. On the other hand, transferred Fe ion from the ball was the major contents on rubbed surfaces of TiN coatings.

1. Introduction

Surface reaction products formed during lubrication tests affect tribological properties in boundary lubrication. Since the amount of the products is expected to be very small, the most sensitive techniques have been applied to detect the products. A radioactive-tracer technique is one of the sensitive methods to detect the components of boundary films and wear debris. For example, quite small wear-rate of engine piston rings has been measured [1] and also wear of UHMWPE hip-joint liners has been detected in vitro [2] by using radioactive tracers. Tribochemical reaction mechanism has also been investigated using radioactive compounds of additives such as ^{14}C and ^{35}S for an oiliness agent [3] and EP additives [4], respectively. Stable isotopes instead of radioactive tracers can be applied for the investigation of tribochemical reactions using mass spectroscopy. We have reported tribochemical decomposition of benzene on nascent nickel surfaces using deuterated benzene (C_6D_6) [5], and tribochemical decomposition of formic acid using deuterated formic acid (DCOOD) [6]. Recently, TOF-SIMS has been employed for the investigation of tribochemistry, and it is powerful to detect lubricant components and tribochemical reaction products because of its high sensitivity and high mass resolution.

In order to realize a reduction in the usage of petroleum resources, ethanol generated from biomass resources has recently received attention as a new energy source, especially for the usage of fuels for automobile engines. The engine system involves such sliding components as a fuel injection plunger and a piston ring, which are subjected to sliding under the fuel substance. TiN and CrN are candidate tribo-coatings utilized for the engine components to reduce friction and wear. It is well known that the friction and wear of hard coatings composed of metal nitrides are often dramatically improved by water [7,8] or alcohol [9,10]. The importance of tribochemistry was pointed out in this literature. Since less study has been conducted on the tribochemical reaction between TiN and CrN with ethanol, we aimed to clarify the reaction scheme by means of TOF-SIMS method in this paper. To this end, we used C_2D_5OH (referred as ethanol-d_5) instead of C_2H_5OH as lubricant fluid in order to eliminate the organic contaminations which can be detected undesirably by TOF-SIMS. The utility of stable isotopic tracers in studying tribochemistry had been reported in our previous reports [11,12].

2. Experimental details

TiN and CrN are synthesized on a steel disk of 20 mm in diameter and 5 mm thick by means of an arc ion plating method. The thickness of both films is 3 μm. The hardness of TiN is 2300 kg/mm^2 and that of CrN is 1800 kg/mm^2.

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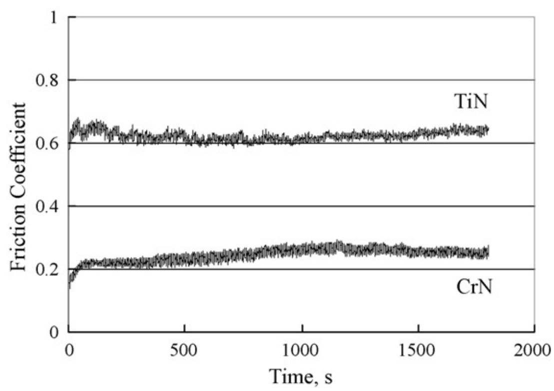

Fig. 1. Effect of materials on friction coefficient obtained in ethanol-d_5 (load: 3.92 N, sliding speed: 10 mm/s).

In the friction experiments, reciprocated sliding was made on the coated disk against a 10 mm diameter stainless steel (SUS 304) ball, using a ball-on-disk type tribo-tester. During sliding, a small amount of ethanol-d_5 was supplied into sliding interface using a micro-dispenser, so that a meniscus of the fluid was always formed in the sliding contact area. Since the present study aims to clarify the tribochemical reaction at the sliding interface, the typical sliding condition is selected as follows: the applied load is 3.92 N, sliding speed is 10 mm/s.

In order to analyze the chemical structure of boundary lubrication films formed on the rubbed surface, TOF-SIMS (time-of-flight secondary ion mass spectroscopy) was applied, with Ga^+ as primary ion source. Other conditions of measurement were shown in detail in our previous work [11–14]. We analyzed both the rubbed surface (4 positions), the outside (4 positions) and the boundary (1 position) to identify the different chemical species existing on these areas.

3. Results and discussion

3.1. Friction tests

The average friction coefficient of TiN was 0.62, while that of CrN was 0.26 during the period of the sliding time of 10 min (Fig. 1). After the tribo-test, the disk was immersed in ethanol-d_5 in a glass container until it was subjected to a TOF-SIMS analysis.

3.2. Optical micrograph of rubbed surface

Morphology of wear tracks was studied by an optical microscope, as shown in Fig. 2. TiN provided a narrower wear scar width than CrN under these conditions. A clear deposit was found on TiN surfaces, whereas those on CrN were not obvious. It was suggested that the higher friction coefficient of TiN disk was due to the formation of the deposits. Therefore, TOF-SIMS analysis was conducted to understand the chemical structure of the boundary lubrication film on wear tracks.

3.3. TOF-SIMS analyses

In order to analyze the chemical structure of the boundary lubrication film, chemical images and mass spectra were obtained by TOF-SIMS with a high spatial or a high mass resolution. These results are discussed as follows.

3.3.1. Chemical images by TOF-SIMS

CrN disk: the intensity of positive fragment ion at m/z 52 (Cr^+) derived from CrN coating on the rubbed surfaces was lower than outside (Fig. 3a). On the other hand, the intensities of m/z 56 (Fe^+) and 2 (D^+) on the rubbed surface were higher than those outside. These results can be explained by the transfer of iron from ball surface onto CrN coating and the tribochemical reaction of ethanol-d_5, which results in a boundary film.

TiN disk: similar to the result of CrN coating, m/z 48 (Ti^+) and 56 (Fe^+) were found on outside and inside of the wear tracks, respectively (Fig. 3b). However, the intensity of m/z 2 (D^+) was too weak to obtain the chemical image by TOF-SIMS.

3.3.2. TOF-SIMS spectra and relative intensity of the key fragment ions

The chemical image of D^+ ion by TOF-SIMS in Fig. 3 suggests the formation of a D-containing film on the rubbed surface of CrN. Then careful studies of TOF-SIMS spectra were carried out in order to identify the chemical structure of the boundary lubrication film containing deuterium. Among several D-containing fragment ions, we paid attention to the quasi-molecular ion at m/z 50.07 ($C_2D_5O^-$), which can be generated by the migration of hydrogen from C_2D_5OH.

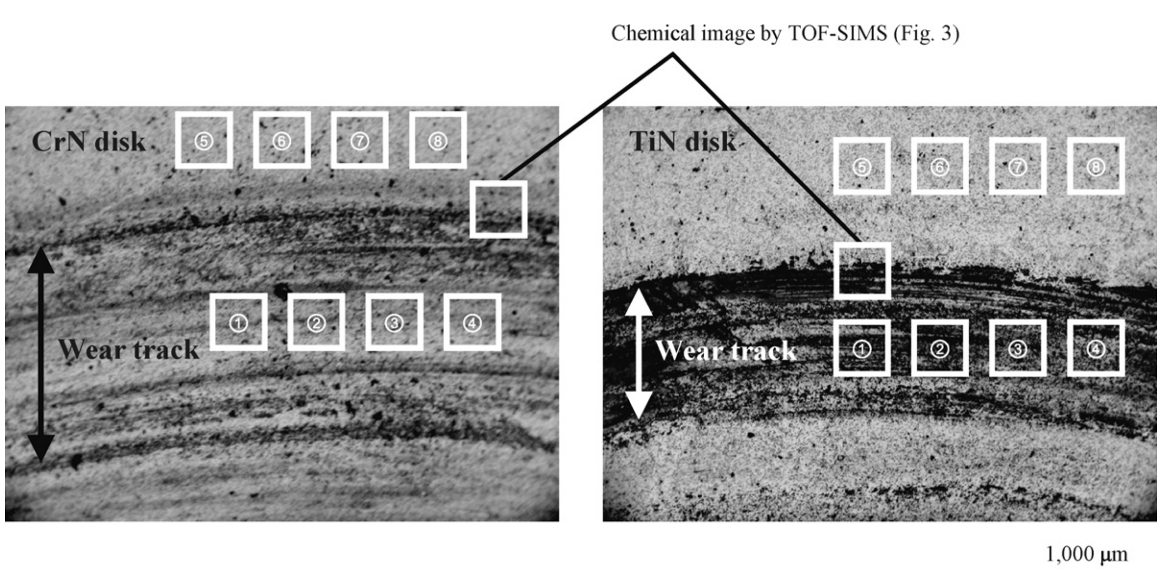

Fig. 2. Optical micrographs of the wear track and the positions at TOF-SIMS analysis.