A SURFACE ANALYTICAL STUDY OF THE EFFECTS OF WATER AND OXYGEN ON TRIBOLOGICAL BEHAVIOR OF DLC FILMS

* Argonne National Laboratory, Energy Technology Division, Tribology Section, Argonne IL
** Materials Science Department, Auburn University, Auburn AL

ABSTRACT

In this study, we explored the effects of water and oxygen molecules on friction and wear of diamond-like carbon (DLC) films. Specifically, using Raman and x-ray photoelectron spectroscopies we attempted to analyze the near surface chemistry and microstructure of sliding contact surfaces and correlated these findings with changes in friction and wear of DLC films. Tribological tests were run in a ball-on-disk machine under 2 to 5 N loads and in dry and moist nitrogen and oxygen environments. Based on the tribological and surface analytical findings, a mechanistic explanation is provided for the high friction and wear of DLC in dry and humid oxygen environments.

INTRODUCTION

Diamond-like carbon (DLC) films have attracted a great deal of attention in recent years for a wide range of tribological applications, such as seals, bearings, magnetic hard disc drives, and many other moving mechanical assemblies. These films have the potential to reduce friction under both dry and lubricated sliding conditions. Currently, numerous deposition processes can reliably produce DLC films on a wide range of substrate materials. Test conditions and the surrounding environments can significantly affect the friction and wear behavior of these films. Accordingly, modeling of the friction and wear mechanisms of DLC films must take into consideration the effects of environmental factors. Depending on the type of DLC films, the presence or absence of oxygen and humidity in the test chamber may increase or decrease the friction and the wear coefficients of DLC films. For example, hydrogenated DLC seems to work the best in inert or dry test environments, while hydrogen-free DLC films work better in moist test environments [1].

There are a few hypotheses for the explanation of friction and wear behavior of DLC films. One of them is based on wear-induced graphitization of the sliding surfaces of DLC, where graphitized tribo layers control the friction and wear of these films [2]. For the superlow friction and wear of highly hydrogenated DLC films in inert environments, it has been proposed that the effective screening of sliding surfaces of DLC by hydrogen increases their chemical inertness and thus leads to superlow friction [3,4]. In moist or oxygenated test environments, DLC surfaces may interact with water molecules and oxygen in a special manner, and such interactions may lead to marked increases in friction and wear of DLC films [1,2].

In this study we focused our attention on the surface analytical characterization of sliding DLC surfaces in dry and humid nitrogen and oxygen environments. The results of this study may shed light into the complex nature of the tribochemical interactions that take place between sliding DLC surfaces in the presence of oxygen and water.

EXPERIMENTAL

DLC films tested in this study were deposited by capacitively coupled plasma enhanced chemical vapor deposition (CVD) at 13.56 MHz r.f.. Hydrogen (75%) and methane (25%) are used as gas during the deposition, the details of the deposition protocol are described elsewhere [4]. The films were deposited on 25mm x 25 mm size p-type Si(100) wafers and 9.5-mm diameter flattened 440C balls. The friction and wear of these films were evaluated using a CSEM ball-on-disc tribometer at room temperature. Ball-on-disc tests were performed in dry oxygen and nitrogen environments as well as humid (30% relative humidity) oxygen and nitrogen environments. The contact load was 2 N, and the track diameter was 20 mm. The rotational speed was 120 rpm during all tests.

The chemical compositions and/or states of worn surfaces of DLC films were analyzed on a PH-5400 X-ray photoelectron spectrometer (XPS) operated with Mg-K irradiation at a pass energy of 35.75 eV. The structure of worn and unworn disc and ball surfaces were characterized by Raman spectroscopy using 632.8 nm HeNe laser excitation.
RESULTS

The test results confirmed that the presence of oxygen in the test chamber is highly detrimental to the friction and wear behavior of the type of DLC films used in this study (see Figure 1). The friction coefficient of a DLC-coated steel ball against DLC-coated Si wafer in dry nitrogen is less than 0.01. In wet nitrogen, the friction coefficient was steady and around 0.03 during the test. In dry oxygen, the friction coefficient was about 0.05, while in wet oxygen it was steadily increased up to 0.15.

![Figure 1. Friction coefficients of DLC films in different environments.](image1.png)

Raman spectroscopy has suggested that some structural changes had occurred in and around the sliding contact areas of DLC on ball and flat surfaces. In particular, the wear debris particles produced during sliding tests in dry and wet oxygen environments exhibited somewhat more graphitic signature (Figure 2). A shift to positive binding energies was observed in x-ray photoelectron spectroscopy spectrum in the presence of oxygen and/or the humidity in test environment. C=O and C-O type bonding were present at higher energies. As a result, XPS indicated significant amounts of chemical interactions between the oxygen and carbon atoms on sliding surfaces (Figure 3). Specifically, C=O and C-O type bonding were detected along with significant amounts of sp² bonded carbon atoms.

![Figure 2. Raman spectra of wear debris and as received DLC coating.](image2.png)

CONCLUSIONS

The results of this study have further confirmed that the friction behavior of hydrogenated DLC films is very sensitive to environmental moisture and oxygen. Surface studies have shown a higher degree of structural order on rubbing surfaces after tests in oxygen, while XPS suggested that high levels of carbon-oxygen bonding are present on these surfaces and perhaps responsible for the higher friction coefficients shown in Fig. 1.

REFERENCES


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