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Modeling effects of gas adsorption and removal on friction during sliding along diamond-like carbon films

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Abstract

In this paper, the physical and tribochemical processes that occur in a sliding contact between two diamond-like-carbon (DLC)-coated counterparts are discussed. The applicability of some of the most cited of the adsorption kinetics equations for modeling the gas adsorption process when environment molecules form bonds to the surface are examined. The process modeling is also discussed when part of the adsorbate is removed due to rubbing the surface by a slider. A direct connection between a kind of molecular friction and gradual wear is established. The models are compared with some recent experimental results. The present computer simulations of the adsorption and mechanical desorption of oxygen help to explain how microscopic processes, such as the breaking and forming of interatomic bonds, may affect macroscopic phenomena such as friction. In particular, it is shown that the initial roughness of the DLC surface may have a considerable influence on the probability of breaking bonds during mechanical removal of adsorbate and on the process of the gradual tribochemical wear of DLC films.

PACS: 81.40 Pq; 81.65 Mq; 68.35 Gy
Keywords: Friction; Adsorption; DLC films

1. Introduction

Amorphous carbon (*a*-C) films are widely used as protective overcoats in various industries. In particular, protective *a*-C coatings are used in the computer industry when a coating of several nanometers thick is placed over the recording head and the magnetic alloy of a computer hard disk. Amorphous carbon is a disordered three-dimensional material where the sp^2 and sp^3 hybridizations are both randomly present. There could also be some sp^1 hybridization in the films. Because *a*-C has no exact geometric configuration, the following characteristics of *a*-C samples are commonly used: (i) the density of a sample, (ii) the sp^3/sp^2 ratio, and (iii) the hydrogen concentration. Amorphous hydrogenated carbon coatings are denoted as *a*-C:H. If the density and sp^3/sp^2 ratio are high and the hydrogen concentration is low (up to 30%), then *a*-C:H coatings are called hydrogenated diamond-like carbon (DLC:H) coatings. Otherwise, they are soft *a*-C:H films. The ratio between the carbon atoms in these hybridizations depends on deposition conditions and other factors. Quite often during deposition of diamond-like carbon (DLC) films, some metals, for example, tungsten, are added. The properties of DLC:H films include high wear resistance, high hardness, and low friction coefficients.

It was established that the friction and wear properties of carbon-based coatings are dependent on the atmospheric conditions, the structure of the films, and surface chemistry (see, e.g., Refs. [1–4]). However, various kinds of carbon-based coatings, i.e., graphite, diamond, *a*-C, hydrogen-free DLC, and DLC:H, may demonstrate drastically different tribochemical and frictional properties under various environmental conditions [4–7]. In particular, adding oxygen to the experimental environment reduces friction of graphite [6,7], while friction of DLC:H films increases [2].

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In this paper, environmental effects on the friction of DLC coatings and their modeling are under consideration. It is known that understanding the physical and tribochemical processes that occur in a sliding contact is a question of particular interest for tribology [8]. The applicability of the Elovich equation and the linear adsorption kinetics equation for modeling the gas adsorption process when environment molecules form bonds to the surface are examined. Also discussed is the modeling of friction and gradual wear when some part of the adsorbate is removed due to rubbing the surface by a slider. In particular, the models are compared with some recent experimental results on friction between two DLC-coated counterparts [1]. The DLC coatings used in the above experiments were prepared by low temperature, plasma-assisted chemical vapor deposition in a hydrogen, and hydrocarbon-rich environment. The procedure of preparation of the coatings is described by Erdemir et al. [9]. These DLC coatings demonstrate the superlow friction behavior; that is, the friction coefficients were observed below 0.01 in vacuum or in dry nitrogen. However, as mentioned, the friction increases by exposure to oxygen.

The presented numerical simulations of the adsorption and mechanical desorption of oxygen during sliding along a DLC surface are helping to explain how microscopic processes, such as the breaking and forming of interatomic bonds, may affect macroscopic phenomena such as friction. As part of the analysis, it is shown that the initial roughness of the DLC surface may have a considerable influence on the probability of breaking bonds during mechanical removal of adsorbate and on the process of the gradual tribochemical wear of DLC films.

2. Preliminaries

It is known (see, e.g., Refs. [10,11]) that surfaces exposed to ambient air possess adsorbed layers of hydrocarbons and other small molecules or atoms. The thickness of the layers is usually just a few angstroms. The substance that adsorbs and desorbs is referred to as the adsorbate and the substance to which the adsorbate adsorbs is called the substrate. There are two types of adsorption to a surface, namely, chemisorption, when chemical bonds between the adsorbate and the substrate are formatted, and physisorption, that involves van der Waals interactions such as dispersion forces or a dipolar interaction. Inasmuch as the latter interactions are very weak, physisorbed molecules can be easily desorbed, for example, by raising the temperature (thermal desorption) or by mechanically breaking the interacting forces between the adsorbate and substrate.

It was found (see, e.g., Refs. [2–4]) that dry sliding interaction between a slider and a coated surface leads to various chemical and physical transformations in DLC coatings. For example, under action of various factors, in particular, due to transient short-life high-temperature field and shear stress, the sp^3 phase of DLC films can be transformed to graphite-like sp^2 carbon. This is the so-called graphitization of DLC films that was observed under contact loading by various authors (see, e.g., Refs. [12,13]). The micro-Raman studies by Ronkainen et al. [14] showed clear graphite formation for the *a*-C:H film, whereas the graphite formation on the hydrogen-free tetrahedral amorphous carbon film was not so evident. Dry sliding in the presence of oxygen can also cause a reaction between the oxygen and carbon atoms of the coatings. A possible explanation for this reaction is the dissociation of a physically adsorbed oxygen molecule into two oxygen atoms. Hence, the oxygen molecule O_2 can first become physically adsorbed and then undergo a dissociation into two oxygen atoms due to activation of the sliding interface. This leads to chemisorbed O atoms. This scenario agrees with a previous discussion of a similar process [15]. The paper does not concentrate on details of DLC structure and such details of the process as the possible chemical reactions of the coating and gases. The objective is to study the influence of adsorption and the removal of the adsorbate on friction between two DLC-coated counterparts to give an opportunity for the qualitative study of adsorbate removal as a possible mechanism for gradual degradation (tribochemical wear) of DLC:H coatings.

The fractional coverage of adsorbate θ can be defined as (see, e.g., Ref. [16])

$$\theta = \frac{N_c}{N}$$

where N_c is the number of surface sites occupied by adsorbate, and N is the total number of substrate adsorption sites. Evidently, $0 \le \theta \le 1$. It is known that the adsorption reaction is kinetically controlled. There are various equations of adsorption kinetics (see, e.g., Ref. [17]). One of the most cited of the adsorption kinetics equations is the Elovich (or Roginsky–Zeldovich) equation [18], which is used to describe the adsorption process of chemical reactions involving chemical adsorption of gasses on solid surfaces without desorption of products:

$$\frac{d\theta}{dt} = Be^{-\alpha\theta}. \tag{1}$$

Here, α and B are constants during any one experiment, and θ is the fractional part (the relative amount) of solute adsorbed at time t. The constant B can be regarded as the initial rate inasmuch as $(d\theta/dt)$ tends to B as θ tends to zero.

To describe the kinetics of gas adsorption in studies of friction between a ball- and carbon-based coatings during repeated passes of the ball over the same regions of a surface, Zaïdi et al. [7] and Heimberg et al. [1] considered a particular integral of Eq. (1) when the initial time $t_0=0$ and $\theta(0)=0$

$$\theta(t_p) = \frac{1}{\alpha}\ln(1 + B\alpha t_p) \tag{2}$$

where t_p is the period of the cycle. This formula gives the value of θ after one period if there was no adsorbate at the