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Atomic force microscopy and tribology study of the adsorption of alcohols on diamond-like carbon coatings and steel

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ABSTRACT

Polar molecules are known to affect the friction and wear of steel contacts via adsorption onto the surface, which represents one of the fundamental boundary-lubrication mechanisms. Since the basic chemical and physical effects of polar molecules on diamond-like carbon (DLC) coatings have been investigated only very rarely, it is important to find out whether such molecules have a similar effect on DLC coatings as they do on steel. In our study the adsorption of hexadecanol in various concentrations (2–20 mmol/l) on DLC was studied under static conditions using an atomic force microscope (AFM). The amount of surface coverage, the size and the density of the adsorbed islands of alcohol molecules were analyzed. Tribological tests were also performed to correlate the wear and friction behaviours with the adsorption of molecules on the surface. In this case, steel surfaces served as a reference. The AFM was successfully used to analyze the adsorption ability of polar molecules onto the DLC surfaces and a good correlation between the AFM results and the tribological behaviour of the DLC and the steel was found. We confirmed that alcohols can adsorb physically and chemically onto the DLC surfaces and are, therefore, potential boundary-lubrication agents for the DLC coatings. The adsorption of alcohol onto the DLC surfaces reduces the wear of the coatings, but it is less effective in reducing the friction because of the already inherently low-friction properties of DLC. Tentative adsorption mechanisms that include the environmental species effect, the temperature effect and the tribological rubbing effect are proposed for DLC and steel surfaces.

1. Introduction

Diamond-like carbon (DLC) coatings are well known for their excellent low-friction, wear-resistance and anti-adhesion properties [1,2]. Today, they are widely used in various mechanical systems, including highly loaded and lubricated applications [3]. Because both the friction and wear behaviours crucially depend on the lubrication film, investigating such lubricant films is an important issue for understanding and improving the lubrication of DLC coatings. However, knowledge of the basic mechanisms of oil lubrication and the function of the oils and additives is still scarce. It is known, for example, that most carbon films are chemically very stable and, therefore, generally inert towards external species under static conditions. However, under dynamic sliding conditions, DLC surfaces may interact with counter faces and with the gaseous molecules in their surroundings [4]. It was shown in [5] that hydrogen, either atmospheric or unbounded to the carbon that is present in the coating, reacts with DLC surfaces, passivates the surface dangling bonds, and thus results in low friction due to the weak van der Waals forces between the hydrocarbon topcoats (H-termination). On the other hand, studies of DLC contacts in water [6] showed that the DLC reacts tribochemically with water to form CH and COH groups on the surface. It was suggested that hydrophilic hydroxyl groups on the surface (OH-termination) play an important role in reducing the friction and wear of DLC coatings. The hydroxyl groups of opposing surfaces tend to interact via hydrogen bonds, which cause higher friction than in the case of only H-terminated surfaces; however, it is still preferable to strong covalent bonding due to the interaction of non-passivated (σ or π) dangling bonds [4].

Several studies have already proposed the interactions of DLC coatings with oils and additives [7–13]. In [12], where GMO was used as an additive, the authors suggest that the formation of an OH-terminated carbon surface, formed by the tribochemical reaction of alcohol function groups with the friction-activated carbon atoms, results in low-friction properties for the ta-C surfaces. In another study with glycerol [13] the authors support the hydroxylation of the friction surfaces due to a tribochemical reaction with the alcohol groups. Furthermore, hydroxylated species on the surface enable the adsorption of alcohols present in the lubricant via hydrogen bonding and thus their intercalation in the contact. They also suggest that the tribodegradation of glycerol molecules appears under the combined effects of pressure and sheer, thereby generating aldehydes or organic acids and water. Such tribodegradation is detrimental in steel-on-steel contacts, because of the corrosive

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effects, while in the case of ta-C surfaces, the formation of water could be an advantage. Tribochemical reactions with DLC surfaces were also confirmed in cases where relatively complex extreme-pressure additives, like ZnDDP and MoDTC [7–9], were used. It was proposed that the disruption of the H-terminated DLC surface due to wear causes additive species to interact with the dangling bonds on the surface, forming low-shear MoS_2 sheets on the surface. On the other hand, the base oils also influence the performance of the DLC coatings significantly through physical and chemical effects [14–16]. Moreover, there is evidence for an improvement of wear performance due to polar-based adsorption as the amount of saturation and the polarity of the base oil increases [17].

In spite of a better understanding of the different effects and the performance of DLC in the presence of various additives and other chemical species, a systematic investigation of different, fundamental, active groups, such as simple alcohols, is still necessary. The chemical adsorption of polar groups is one of the fundamental boundary-lubrication mechanisms that affect both the friction and wear on steel surfaces. Accordingly, it is relevant to investigate whether such molecules have a similar effect on DLC coatings, which is the focus of this work. It was thus our intention to study the adsorption of polar molecules, such as alcohols, on DLC coatings. In order to determine their chemical interactions without any interference from mechanical and tribological effects, it is important to perform experiments under controlled static conditions on the nanoscale. In this work we have focused on the interactions of DLC with hexadecanol mixed in hexadecane, which served as a model hydrocarbon fluid, similar to the typical oils. An atomic force microscope (AFM) was used to detect the remaining adsorbed molecules on the DLC and steel surfaces after their exposure to various concentrations of hexadecanol solutions. The surface coverage with islands of adsorbed molecules, their number and their size were correlated with the hexadecanol concentrations and are discussed. Tribological tests using boundary-lubricated conditions were also performed to correlate the wear and friction behaviours with the results obtained using the AFM.

2. Experimental

2.1. Materials

The materials used in this work were steel discs of 24-mm diameter, made from AISI 52100/DIN 100Cr6 steel, having a hardness of 850 HV, measured with a microhardness tester (Leitz Miniload, Wild Leitz GmbH, Germany). The discs were polished to an average surface roughness of 3–4 nm for the AFM analyses and to 30–40 nm for the tribological tests. A very low surface roughness in the case of the AFM analyses was necessary in order to observe the adsorbed species on the surface. The balls used in the tribological tests were standard bearing balls. The surface roughness was measured using a CP-II AFM (Veeco, USA). Half of the steel discs were additionally coated with two interlayers, i.e., a Ti adhesion interlayer and a hydrogenated amorphous diamond-like carbon layer containing Si and O (a-C:H:Si:O), and finally with a single layer of hydrogenated amorphous diamond-like carbon (a-C:H, 30% H) coating, having a thickness of 1.5 μm. A hybrid PVD/PACVD process was employed for the deposition of the coating and both interlayers (Sulzer Sorevi SAS, Limoges, France). The composition of the coating layer is presented schematically in Fig. 1. The coating deposition had a minor effect on the surface roughness of the samples. The final surface roughnesses R_a for the uncoated and coated samples are presented in Table 1.

The alcohol selected for the adsorption analyses in this work was hexadecanol (Merck KGaA, Darmstadt, Germany): a straight-chain hydrocarbon with 16 carbon atoms and a hydroxyl (OH) end group.

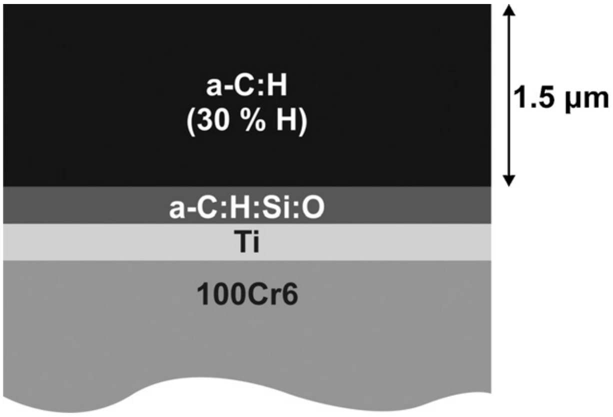

Fig. 1. Schematic cross-section of coated 100Cr6 steel samples.

For the AFM analyses, the hexadecanol was introduced into the hexadecane (Merck KGaA, Darmstadt, Germany) in various concentrations from 2 to 20 mmol/l, which corresponds to concentrations of up to 0.63 wt. %. However, for the tribological tests the hexadecanol was mixed into a poly-alpha olephin PAO6 base oil (Neste Oil, Espoo, Finland) with a kinematic viscosity of 30 mm^2/s at 40 °C, again with concentrations from 2 to 20 mmol/l. Tribotests were also made with pure PAO6 oil in order to serve as a reference.

2.2. AFM analysis

The mixtures of hexadecanol in hexadecane were spread on the surfaces in drops of equal size. One set of mixtures was left on the surfaces for 10 min at room temperature (25 °C) and the other for 20 min at 80 °C so as to allow the adsorption of the hexadecanol molecules onto the surfaces. In both cases the samples were cleaned afterwards in an ultrasonic bath full of ethanol for 1 min to remove the unbound species. After the cleaning, the samples were analyzed using the AFM in contact mode at constant load, which was found to be a suitable technique for the imaging of adsorbed layers in our previous research. The scans were typically made at 50 μm × 50 μm. The analyses were made using ProScan 1.8 Data Acquisition image-analysing software, associated with the AFM. About 15–20 topographic images were collected from different locations on a single sample to ensure statistically representative results. These topographic images were used to determine the average surface coverage with the remaining adsorbed molecules, which appeared in groups in the shape of small islands scattered across a relatively flat surface, as presented in Fig. 2. The average spot size and the spot density (number of spots per unit area) were also calculated. The sign A in Fig. 2 denotes the area of the whole scanned surface, while A_i denotes the projected surface area

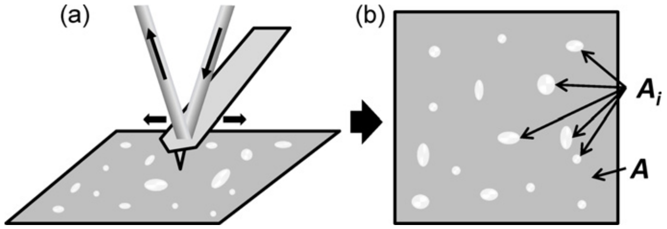

Fig. 2. Schematic representation of (a) the AFM and (b) an image of the surface, where the adsorbed molecules appear in the shape of small bright spots. The sign A denotes the area of the whole scanned surface, while A_i denotes the projected surface area of a single adsorption spot.